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THESIS

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ALISTAIR J. McLENNAN B.Sc.

Department of Chemistry,
University of Glasgow.

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CYCLOPENTADIENYL PLATINUM COMPLEXES
AND ORGANIC GROUP TRANSFER REACTIONS

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ABSTRACT

cis-[PtX_2(CO)L] (X is Cl or Br, L, is tertiary phosphine or arsine) reacts with TlC_5H_5 stereospecifically to produce the isomer of [PtX(η^1-C_5H_5)(CO)L] with C_5H_5 *trans* to L. The same isomer is produced when $Hg(C_5H_5)_2$ and $Ph_3PAuC_5H_5$ are used as the cyclopentadienylating agents. The second halide can be replaced when excess TlC_5H_5 is used, producing *cis*-[Pt(η^1-C_5H_5)$_2$(CO)L]. The η^1-bonded cyclopentadienyl groups of either mono- or di- substituted compounds can readily exchange in solution with a halide of *cis*-[PtX_2(CO)L] to produce exclusively the same isomers of [PtX(η^1-C_5H_5)(CO)L]. The cyclopentadienyl groups do not transfer as fast as halide ions between the same species, but do so considerably faster than an accompanying CO scrambling process. Substituted aryl complexes of the same geometry, [PtCl(Ar)(CO)L], Ar *trans* to L, behave similarly, exchanging the aryl group for a chloride of *cis*-[$PtCl_2$(CO)L']. Both TlC_5H_5 and $Hg(C_5H_5)_2$ react with [PtCl(C≡CR)(CO)L] (R = Me, Ph), Cl *trans* to L, to produce [Pt(η^1-C_5H_5)(C≡CR)(CO)L], C_5H_5 *trans* to L. The reaction with $Hg(C_5H_5)_2$ does not stop at this point, but continues to produce [PtCl(C_5H_5)(CO)L], C_5H_5 *trans* to L, and some *cis*-[Pt(C≡CR)$_2$(CO)L]. TlC_5H_5 and [PtCl(Ar)(CO)L] similarly produce only one isomer (Ar *trans* to CO) of [Pt(η^1-C_5H_5)(Ar)(CO)L]. The mixed diorganoplatinum complexes [Pt(η^1-C_5H_5)(C≡CR)(CO)L] and [Pt(η^1-C_5H_5)(Ar)(CO)L] react with *cis*-[$PtCl_2$(CO)L'] in chloroform to transfer specifically the organic group *trans* to L (i.e. C_5H_5) to platinum. Cyclopentadienyl from the η^1-bonded complexes, and from [Pt(η^5-C_5H_5)L_2]$^+$ X^- (X = Cl, SO_3CF_3) can also be readily transferred to mercury when treated with $HgCl_2$.

Reactions between $[PtCl(\eta^1\text{-}C_5H_5)(CO)L]$ and either $Hg(C{\equiv}CR)_2$ or $HgPh_2$ are complicated. The reaction with $Hg(C{\equiv}CR)_2$ produces initially both $[Pt(\eta^1\text{-}C_5H_5)(C{\equiv}CR)(CO)L]$, C_5H_5 trans to L, and $[PtCl(C{\equiv}CR)(CO)L]$, Cl trans to L, but finally only cis-$[Pt(C{\equiv}CR)_2(CO)L]$. The reaction with $HgPh_2$ produces a number of species, including $[Pt(\eta^5\text{-}C_5H_5)(COPh)L]$ and cis-$[PtPh_2(CO)L]$. The mixed bis-acetylide complex $[Pt(C{\equiv}CR)(C{\equiv}CR')(CO)L]$, CO cis to L, $C{\equiv}CR'$ trans to L, exchanges $C{\equiv}CR'$ with a Cl from cis-$[PtCl_2(CO)L']$ to produce $[PtCl(C{\equiv}CR)(CO)L]$ and $[PtCl(C{\equiv}CR')(CO)L']$, the isomers with Cl trans to L in each case. The complex also reacts with $[PtCl(Ar)(CO)L]$, Ar trans to CO, to produce $[PtAr(C{\equiv}CR')(CO)L]$, $C{\equiv}CR'$ trans to L, and with $[PtCl(Ar)(CO)L]$, Ar trans to L, to produce the other isomer of the mixed aryl acetylide complex, $[PtAr(C{\equiv}CR')(CO)L]$, with Ar trans to L. An isomerisation route operates for $[Pt(C{\equiv}CR)(C{\equiv}CR')(CO)L]$ in the presence of $[PtCl(C{\equiv}CR)(CO)L]$, Cl trans to L. $HgPh_2$ reacts with cis-$[Pt(C{\equiv}CR)_2(CO)L]$ to produce the complex $[PtPh(C{\equiv}CR)(CO)L]$, Ph trans to L.

$[PtCl(C{\equiv}CR)(CO)L]$, Cl trans to L, reacts with $HgPh_2$ in chloroform to produce $[PtPh(C{\equiv}CR)(CO)L]$, Ph trans to L, which equilibrates in solution with a novel acetylide-bridged dimer $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2L_2]$ when R = Me. The reaction between an equilibrated mixture of $[PtCl(Ph)(CO)L]$, Ph trans to L, and $[Pt_2(COPh)_2(\mu\text{-}Cl)_2L_2]$ with $HgPh_2$ also produces, initially, the acetylide-bridged dimer $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2\text{-}L_2]$ for both R = Me and R = Ph, but this equilibrates with $[PtPh(C{\equiv}CR)(CO)L]$, Ph trans to L, and the equilibrium position for R = Ph lies completely on the side of non-inserted material. The reaction between $[PtCl(Ar)(CO)L]$, Ar trans to L ($Ar = C_6H_4CO_2Me$-p), and $Hg(C{\equiv}CR)_2$ leads directly to $[PtAr(C{\equiv}CR)(CO)L]$, Ar trans to L, without the intermediacy of an acetylide-bridged dimer. TlC_5H_5 reacts with $[PtCl(Ar)(CO)L]$, Ar trans to L, to promote carbonyl insertion and produces $[Pt(\eta^5\text{-}C_5H_5)(COAr)L]$ when Ar = Ph and $C_6H_4CO_2Me$-p, but not with a non-inserting aryl group such as C_6H_4Cl-o, or with the group C_2Cl_3.

The decomposition of $[PtX(C_5H_5)(CO)L]$, C_5H_5 trans to L, in solution leads to the formation of a novel, asymmetrically substituted platinum dimer, which can be prepared in higher yield by the reaction between cis-$[PtX_2(CO)L]$ and two equivalents of TlC_5H_5. The dimer contains a platinum-platinum bond with a bridging carbonyl ligand, and one π-bonded cyclopentadienyl ring. This "Asymmetric Dimer" has been identified as $[L(Cl)\overline{Pt(\mu\text{-}CO)Pt}(\eta^5\text{-}C_5H_5)L]$. One of the phosphines is trans to the metal-metal bond and exhibits a very large two-bond platinum-phosphorus coupling constant, the size of which is remarkably independent of the identity of the phosphine. Reactions of the "Asymmetric Dimer" produce a number of other dimeric platinum complexes. Addition of L' (L' is phosphine or arsine) at low temperature displaces chloride and produces another platinum-platinum bonded dimer, $[L(L')\overline{Pt(\mu\text{-}CO)Pt}(\eta^5\text{-}C_5H_5)L]^+$. The reaction between "Asymmetric Dimer" and $AgSO_3CF_3$ appears to produce a cyclopentadienyl-bridged, platinum-platinum bonded dimer, $[L\overline{Pt(\mu\text{-}CO)(\mu\text{-}C_5H_5)Pt}L]^+$, while a similar complex, $[L\overline{Pt(\mu\text{-}Cl)(\mu\text{-}C_5H_5)Pt}L]$, seems to be formed by loss of CO.

In the presence of alcohols cis-$[PtCl_2(CO)L]$ and two equivalents of TlC_5H_5 produce an unidentified dimeric π-cyclopentadienyl complex which converts slowly to "Asymmetric Dimer" in solution.

Reactions of platinum cyclopentadienyl complexes, $[PtCl(C_5H_5)(CO)L]$, C_5H_5 trans to L, $[Pt(\eta^5-C_5H_5)L_2]^+ X^-$ and $[Pt(\eta^5-C_5H_5)(CO)L]^+ X^-$ with phosphine lead to the production of a remarkable number of trisphosphine complexes, $[PtL_3Y]^{n+}$ (Y = neutral or anionic ligand, L = phosphine, n = 1 or 2). Several of the tris-phosphine complexes are also obtained from the reaction between $[PtClL_3]SO_3CF_3$ and TlC_5H_5, and the possibility of five-coordinate intermediates and of isomerisation of $\eta^1-C_5H_5$ to its vinyl isomer are examined. A trisphosphine solvento complex, $[PtL_3S]^{2+}$, or a four- or five-coordinate complex, $[PtL_3X_n]^{m+}$ ($X = SO_3CF_3, BF_4, PF_6$, n = 1 or 2, m = n-1) is easily obtained by abstraction of Cl from $[PtClL_3]^+$ with a silver salt, and carbonylation of this unidentified species produces $[PtL_3(CO)]^{2+}$. The reaction between the species and TlC_5H_5 produces a different trisphosphine complex to that obtained with $[PtClL_3]^+$, as does the reaction with $HgPh_2$. $[PtClL_3]^+$ and $HgPh_2$ react in chloroform to produce $[PtPhL_3]^+$. Addition of halide to $[PtXL_3]^+$ produces $[PtX_2L_3]$ for X = Br,I.

Attempts to promote carbonyl insertion in cyclopentadienyl platinum complexes appear to be unsuccessful. Addition of phosphine or halide to $[PtCl(C_5H_5)(CO)L]$, C_5H_5 trans to L, produces a large number of complexes, most of which are unidentified, including metal-metal bonded dimers.

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CHAPTER 1

INTRODUCTION

Background to Organotransition Metal Chemistry

Although the subject of organometallic chemistry began with platinum in 1827[1], when Zeise discovered the first organometallic complex ever prepared, $K[PtCl_3(C_2H_4)]$, commonly referred to as Zeise's salt, it was the discovery of diethylzinc by Frankland[2] which initiated the rapidly developing interest in organometallic compounds during the latter half of the nineteenth century. While organometallic chemistry of the main-group metals blossomed, attempts to make stable transition metal alkyls and aryls met with little success. The first transition metal alkyls were prepared in 1907, by Pope and Peachey[3], and again these were platinum compounds, trimethyl platinum complexes $[PtMe_3X]_4$. At about the same time Hofmann and von-Narbutt prepared a platinum complex of dicyclopentadiene in alcohol[4], which was recognised by Chatt <u>et al.</u>[5] as the first example of a platinum (II) alkyl, in which the platinum complex was an alkoxydicyclopentadiene platinum chloride dimer, $[(C_{10}H_{12}OMe)PtCl]_2$. In the same paper they made reference to a simple alkyl, $[PtIMe(PPr^n{}_3)_2]$, prepared by Chatt and Foss.

An upsurge in organometallic chemistry of the transition metals occurred in the 1950's with the discovery of ferrocene[6], the first pure hydrocarbon derivative of iron and the first cyclopentadienyl of a transition metal. Very soon after its discovery, the novel sandwich model for its structure had been proposed[7] and confirmed by X-ray crystallography.[8] Cyclopentadienyl transition metal compounds now have an extensive chemistry, and compounds of virtually every transition element are known.

The next important development was the preparation of an extensive series of alkyl and aryl complexes of palladium[9] in 1958 and platinum[10] in the following year. Since then organoplatinum chemistry has developed rapidly, and now has a very extensive and detailed literature.[11,12]

Organotransition-metal complexes are important in homogeneous catalysis, with at least two dozen major processes in use in industry.[13] Organometallic chemistry has grown more rapidly in scope than the classical divisions in chemistry in the last two decades. A large variety of compounds have now been synthesised, containing π and σ-bonded organic groups and metal-metal bonds.

Structure and Reactivity

The reactivity of transition-metal organometallic compounds is viewed as a kinetic phenomenon, related to the characteristic transition-metal properties of variable oxidation states and coordination numbers.[14,15] The electron density at the metal atom is important as regards the stability of transition-metal complexes. The first attempt at rationalising this was the so-called "18-electron-rule", which required that the central metal in a complex should achieve the formal electron-count of the next noble gas.[16] This 18-electron-rule was empirical, depending only on the observation that the nine outer orbitals of a transition-metal can accommodate 18 electrons, from the metal atom and donated by the ligands. It successfully explained the stability of metal carbonyls, e.g;- $Cr(CO)_6$. It was also applicable to the stability of organometallic compounds, where elaborate electron counting rules have been developed. The success of the 18-electron rule can be explained qualitatively. In a molecular orbital treatment of a complex, there will be nine bonding and non-bonding (or π-bonding) orbitals, derived from the metal ns orbital, three np and five (n-1)d orbitals. Filling all nine orbitals and leaving the antibonding orbitals empty confers greatest stability on the complex. If the nine bonding and non-bonding orbitals are filled, the compound is said to be coordinatively saturated; attack on the metal by a nucleophile would add electrons to an antibonding orbital, and is unfavourable.[13] Thus, ligand substitution processes at 18-electron complexes usually proceed via initial dissociation to an unsaturated (16-electron) species, able to react with the incoming ligand.

Towards the end of the transition series the 18-electron rule breaks down and 16-electron molecules are common for Pd and Pt, while stable 14-electron molecules are common for the coinage metals.[14] This is explained by the increase in nuclear charge causing a decrease in the energies of the metal d-orbitals, which results in increased promotion energies for the nd → (n+1)p electronic transition. Attainment of the full 18-electron configuration is less favourable. A consequence of the lanthanide contraction is that, on descending a group, the changes in the nd → (n+1)p promotion energies do not vary regularly. For the nickel triad the energies increase in the order $Ni < Pt < Pd$, thus the formation of 18-electron species is most difficult for palladium and easiest for nickel.[17]

Tolman[18] has proposed the 16 and 18 electron Rule for the diamagnetic organometallic complexes of Groups IVB–VIII. This has as its basic premise that diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons and that organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons, for example:-

$$\begin{tikzcd}
{[IrH_2(CO)_2\{P(C_6H_{11})_3\}_2]^+} \arrow[r, "-H_2"] & {[Ir(CO)_2\{P(C_6H_{11})_3\}_2]^+} \\
\text{18-electron} & \text{16-electron} \arrow[d, "+P(OMe)_3"] \\
 & {[Ir(CO)_2\{P(C_6H_{11})_3\}_2P(OMe)_3]^+} \\
 & \text{18-electron}
\end{tikzcd}$$

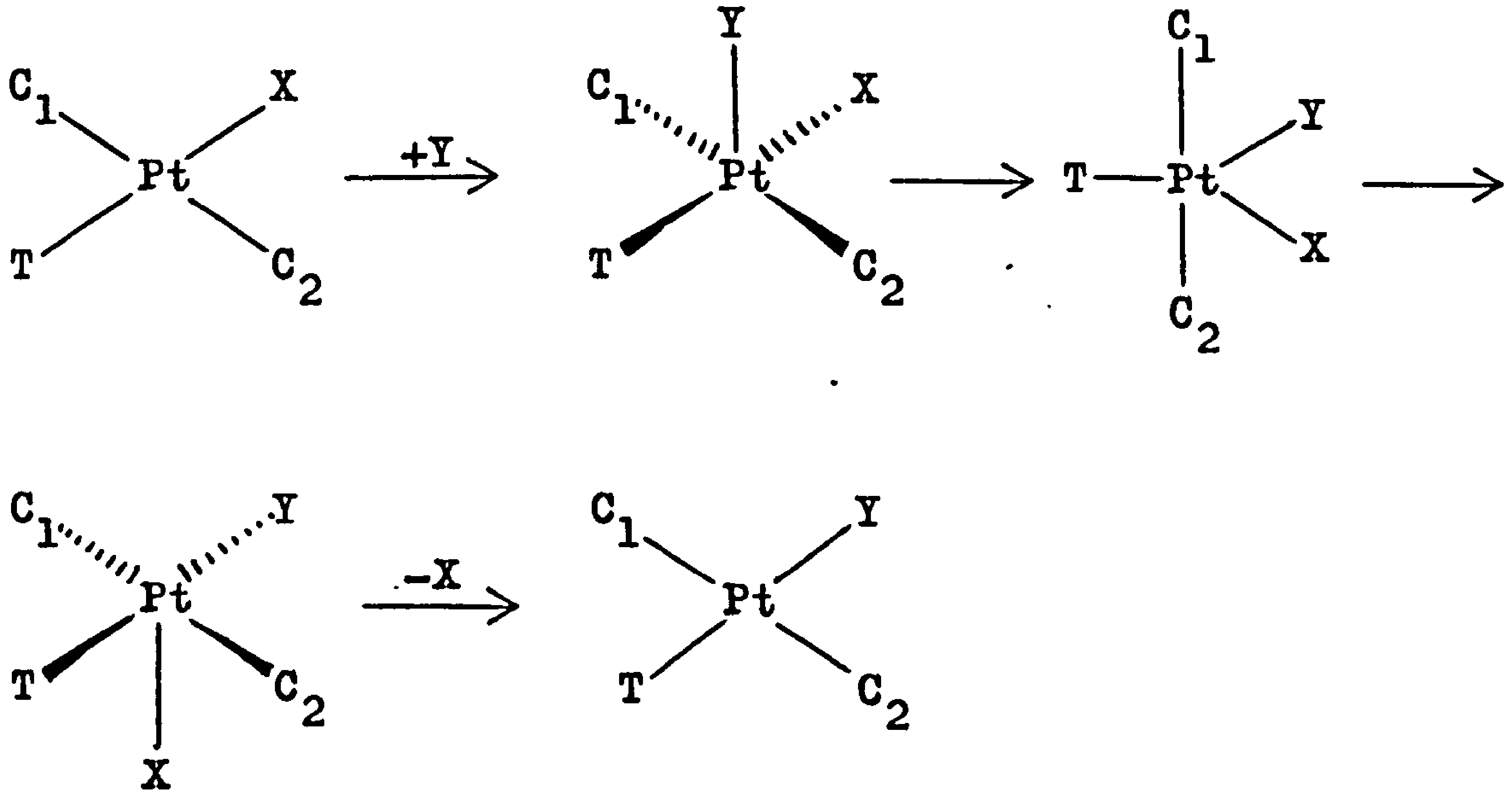
$$\begin{tikzcd}
{\underline{trans}\text{-}[PtRCl(PEt_3)_2]} \arrow[r, "+py"] & {[PtRCl(PEt_3)_2py]} \\
\text{16-electron} & \text{18-electron} \arrow[d, "-Cl^-"] \\
 & {\underline{trans}\text{-}[PtRpy(PEt_3)_2]^+} \\
 & \text{16-electron}
\end{tikzcd}$$

Recently 14-electron species have been proposed as intermediates in some reactions of 16-electron Pt and Pd complexes.[19,20] These have been suggested as intermediates in the uncatalysed isomerisation of <u>cis</u>-$[PtRXL_2]$,[21] in the thermolysis of <u>cis</u>- and <u>trans</u>-$[PdMe_2L_2]$[22] and in carbonyl insertion at $[PtX(R)(CO)L]$.[23] It was proposed that such three-coordinate 14-electron intermediates remain T-shaped (and retain the geometry of the parent square planar complex) and may be described as <u>cis</u>-like or <u>trans</u>-like.

Within the framework of the 16 and 18-electron Rule a number of important reaction pathways are possible.

Nucleophilic Substitution

Substitution reactions of square planar complexes are believed to proceed by an associative mechanism involving a trigonal bipyramidal transition state.[24-26] Such substitutions proceed with retention of geometric configuration.



A second, solvent assisted route can also operate in which X is initially displaced by a solvent molecule which is then subsequently replaced by the incoming nucleophile Y.

This gives a rate law for substitution as follows:-

$$\text{Rate} = (k_s[S] + k_2[Y])\,[\text{complex}].$$

Oxidative Addition

The term "oxidative addition" is used to designate a type of reaction of low-spin transition metal complexes in which oxidation of the metal is accompanied by an increase in the coordination number.[27] In effect, the complex behaves simultaneously as a Lewis acid and Lewis base. The reaction can be written generally as:-

$$L_yM^n + XY \rightarrow L_yM^{n+2}(X)(Y)$$

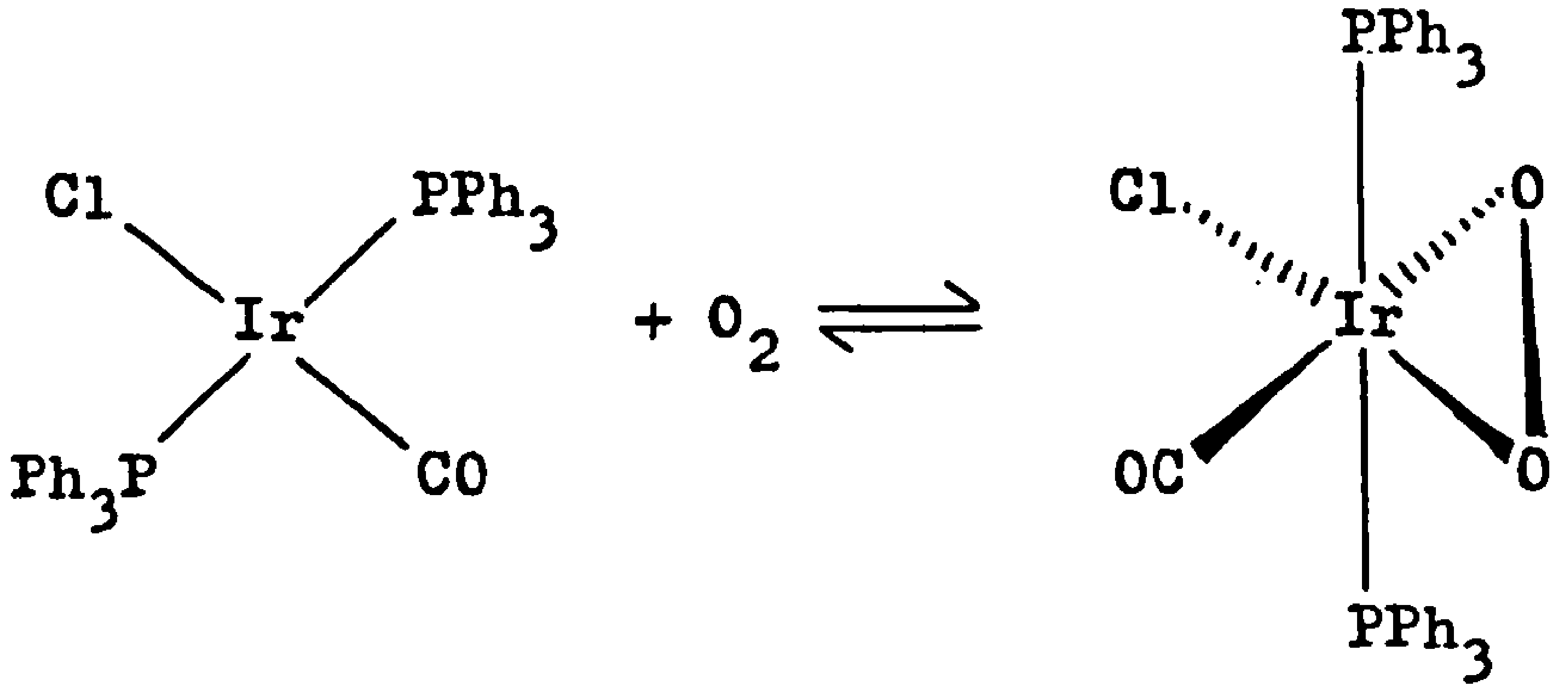
This can be considered as the metal inserting into the X-Y bond.

The reverse reaction can be termed "reductive elimination". For transition metals, the most intensively studied reactions are those of complexes of metals with the d^8 and d^{10} electron configuration, notably $Fe^{\bar{0}}$, $Ru^{\bar{0}}$, $Os^{\bar{0}}$; Rh^{I}, Ir^{I}; $Ni^{\bar{0}}$, $Pd^{\bar{0}}$, $Pt^{\bar{0}}$ and Pd^{II} and Pt^{II},[24] in particular complexes such as $Ir(CO)L_2Y$ and PtL_3 (L = phosphine, Y = halide).[27]

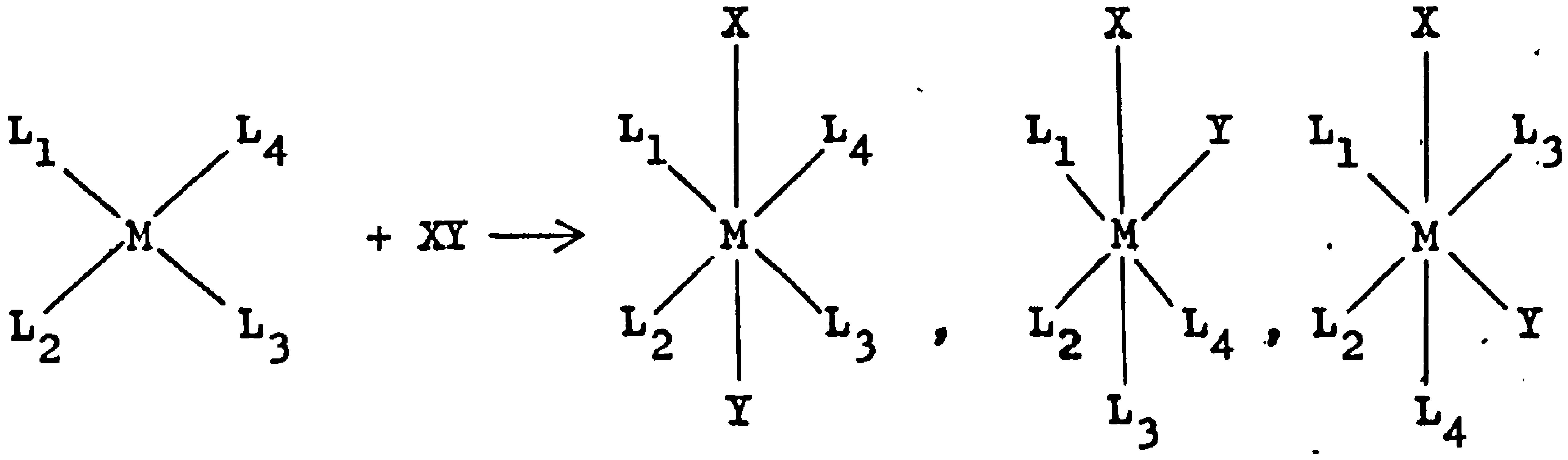
e.g.:- <u>trans</u>- $Ir^{I}Cl(CO)(PPh_3)_2 + HCl \rightleftharpoons Ir^{III}HCl_2(CO)(PPh_3)_2$

The tendency for d^8 complexes to undergo oxidative additions depends markedly on the nature of the central metal ion and the ligands attached to it. In general, the tendency increases down a triad and on passing from right to left within group VIII.[28]

When the XY molecule adds without severance of X from Y the two new bonds to the metal are necessarily in cis-positions,[24] e.g.:-



When X and Y are separated the product may be one or more of several isomers with either cis- or trans-MX and -MY groups.



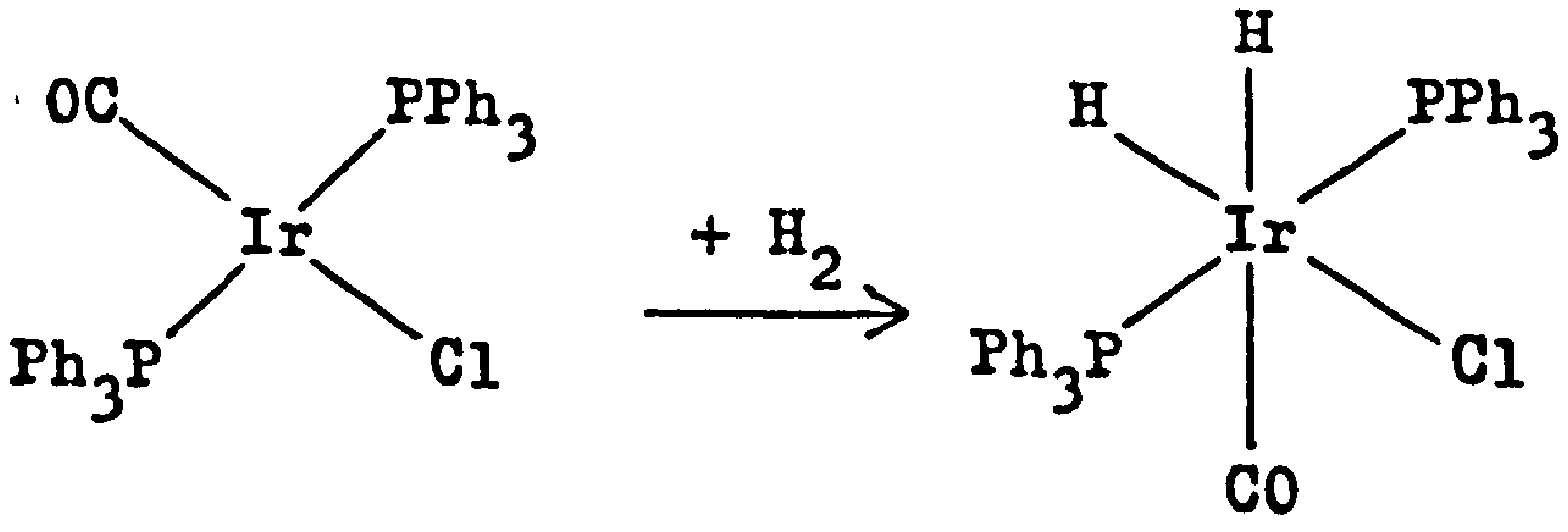
A number of different routes have been proposed for the oxidative addition reaction. These are:-

1) An ionic mechanism involving a 5-coordinate cationic intermediate, especially in polar solvents with ionizable molecules such as HCl.

2) An S_N2 type attack of the metal on alkyl halides, e.g.:- $[C_5H_5\ M(CO)(PPh_3)]$ + MeI (M = Co,Rh,Ir)[29]

3) A one-step concerted addition which initially gives products with the new bonds in cis-positions.[30]

e.g.:-



The *cis*- reductive elimination reaction has been shown to be concerted,[31] viz:-

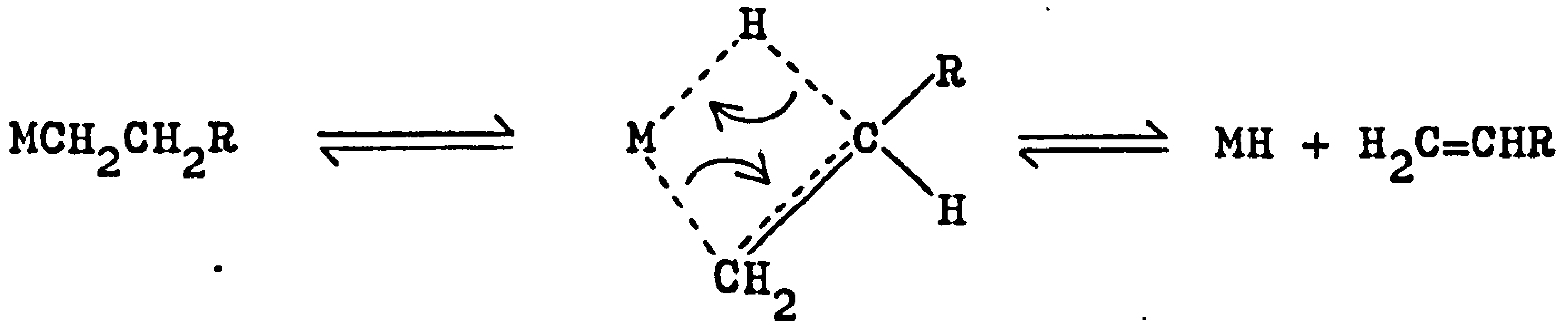
$$[(PhMe_2P)_2PtMe_3I] \rightarrow [(PhMe_2P)_2PtMeI] + C_2H_6$$

The reaction being first order, and isotopic labelling showing that it is intramolecular.

The combination of an oxidative addition reaction, followed by a reductive elimination, provides a versatile route for reactions of transition metal complexes, and is limited to unsaturated, i.e. planar d^8 complexes.[28]

β-Elimination

This is a reaction involving no overall change of co-ordination number or formal oxidation state of the metal. The main requirement is a substituent on the β-carbon which may become bonded directly to the metal, usually a hydrogen atom, and a vacant coordination site on the metal.[32] For simple alkyls it may be represented thus:-



The mechanism was elucidated by deuteriation studies.[33]

$$CH_3CH_2CD_2CH_2CuPBu_3 \longrightarrow DCuPBu_3 + H_2C{=}CDCH_2CH_3$$

The simplest reaction of this type is that in which ethylene is lost from an ethylmetal complex, and such reactions are often reversible.[34,35]

$$\underline{\text{trans}}\text{-}[PtX(C_2H_5)(PEt_3)_2] \underset{\text{pressure}}{\overset{\text{heat}}{\rightleftharpoons}} \underline{\text{trans}}\text{-}[PtHX(PEt_3)_2]+C_2H_4$$

Ethylene may be retained in the coordination sphere of the metal in the β-elimination step,[36]

e.g.:-

$$[C_5H_5Rh(C_2H_5)PMe_3]^+ \rightleftharpoons [C_5H_5RhH(C_2H_4)PMe_3]^+$$

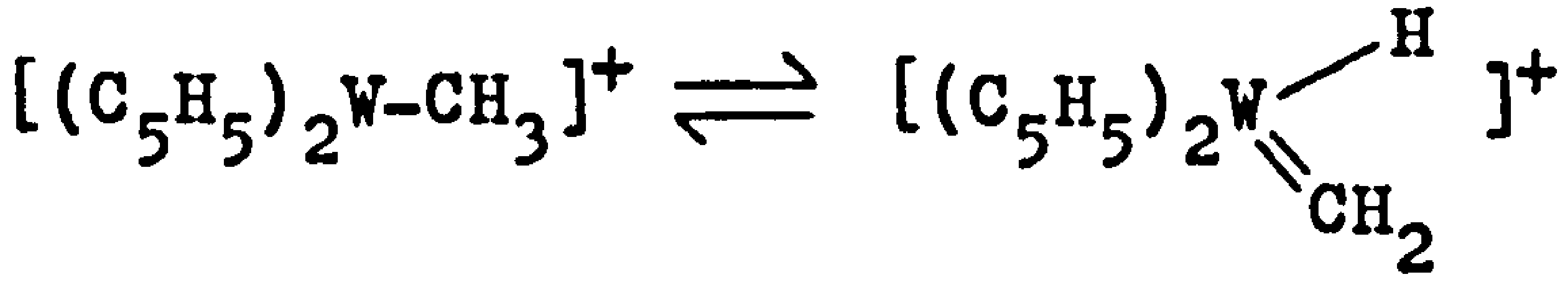
The facility with which β-eliminations can take place often makes it necessary to use organic groups, such as methyl, benzyl and trimethylsilylmethyl, which can not undergo this reaction.

α-Elimination

α-Elimination involves elimination of two fragments, one bonded to the metal and one bonded to the α-carbon of a substituent, (the latter usually being a proton), thus:-

$$R^1MCHR_2 \longrightarrow R^1\text{-}H + M{=}CR_2$$

This may involve hydride transfer to the metal followed by reductive elimination, or it may be a concerted process. α-Elimination is generally less well established than β-elimination throughout the periodic table,[37] but some examples are known, for example:-



$$[(C_5H_5)_2W\text{-}CH_3]^+ \rightleftharpoons [(C_5H_5)_2W(H)(=CH_2)]^+$$

This equilibrium is proposed[38] in the reaction between $[W(\eta^5\text{-}C_5H_5)_2Me(C_2H_4)]^+$ and PMe_2Ph to give $[W(C_5H_5)_2H\text{-}(CH_2PMe_2Ph)]^+$. Recently a mechanism has been suggested for stereospecific Ziegler-Natta catalytic olefin polymerisation involving α-transfer of hydride to titanium.[39]

α-Elimination has sometimes been overlooked because of the facility with which β-eliminations occur. The rearrangement of platinacyclobutanes to platinum alkene complexes has recently been shown to occur by α-elimination[40] rather than β-elimination as had previously been reported.

Binuclear Elimination

Binuclear elimination is a reductive elimination process involving two metal complexes, in which both metal atoms have their coordination numbers and oxidation states reduced by one, and the eliminated species is formed by two fragments, one from each metal centre, e.g.:-[41]

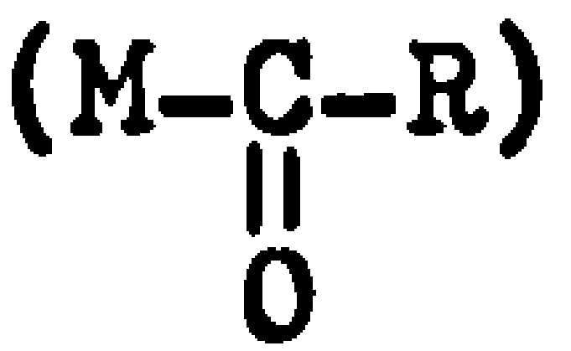
$$2CH_3Au(PPh_3) \rightarrow C_2H_6 + 2Au + 2PPh_3$$

Insertion Reactions

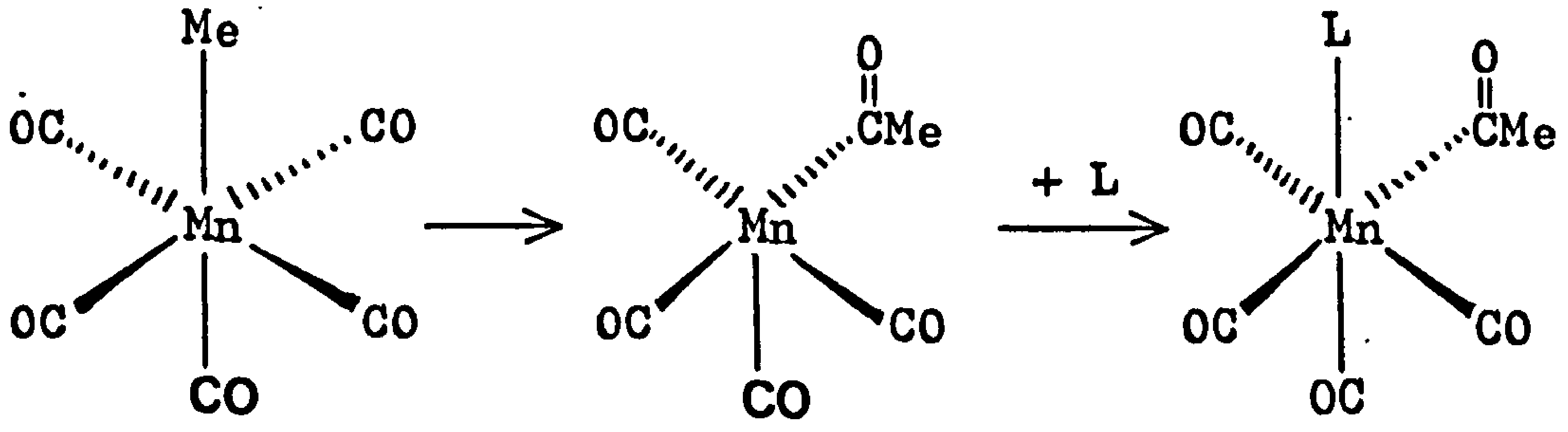
Insertion reactions are common in organometallic chemistry and may be defined as a reaction wherein any atom or group of atoms is inserted between two atoms initially bound together:-

$$L_nM—X + YZ \rightarrow L_nM—(YZ)—X.$$

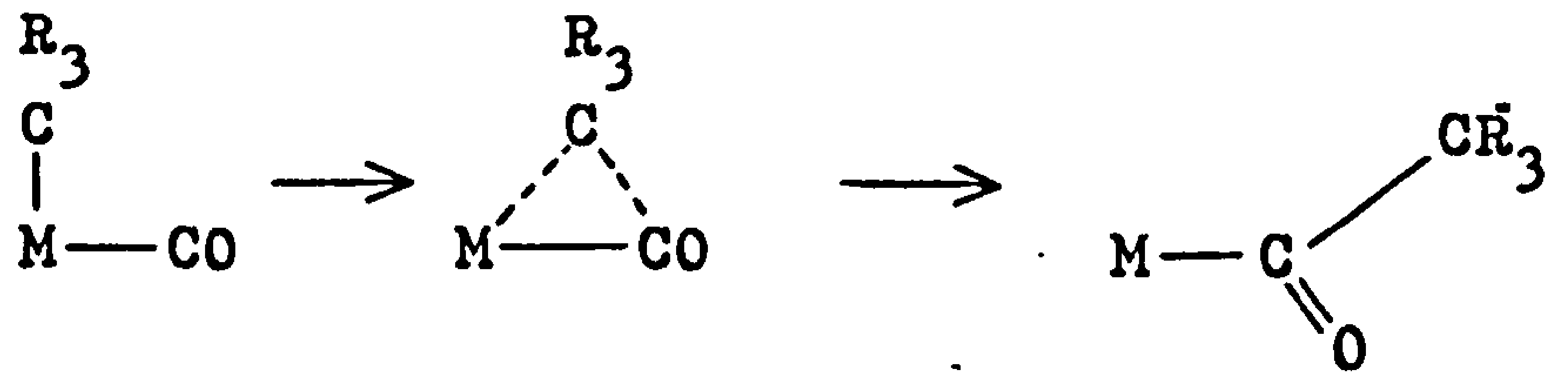
Insertions into metal-hydrogen, metal-carbon, metal-oxygen, metal-nitrogen, metal-halogen and metal-metal bonds are all known. Some of the more common inserting molecules are CO, SO_2, SO_3, CO_2, carbenes, olefins and isonitriles.[42]

The most detailed studies have been made on the "insertion" of CO into metal-carbon bonds. Carbon monoxide insertions are intramolecular and in all cases a 1,1 addition  $(M-\underset{\underset{O}{\|}}{C}-R)$ product rather than a 1,2-addition (M-C-O-R) product is obtained.[42]

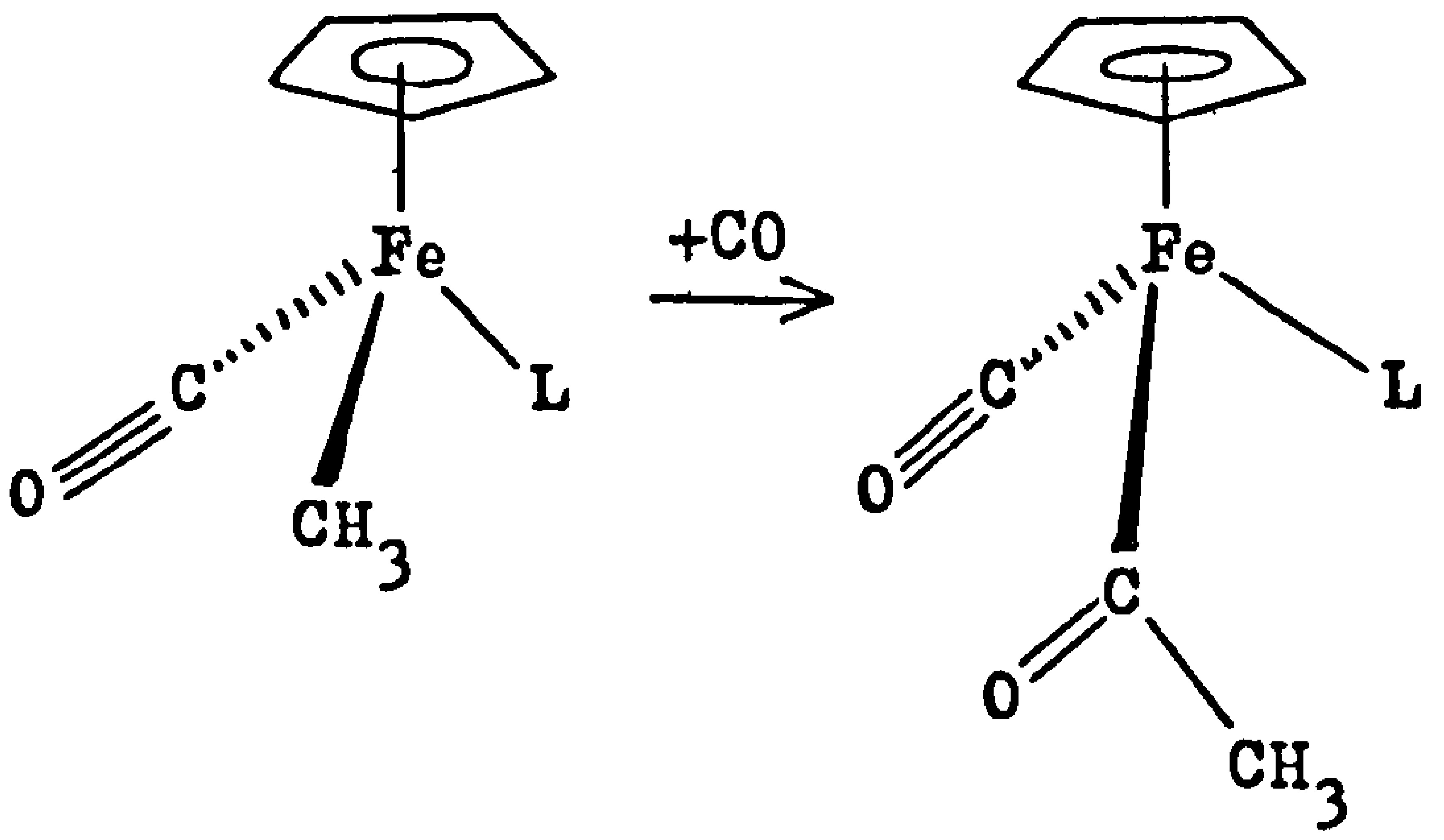
The insertion of carbon-monoxide into a metal-carbon bond was first observed for alkylpentacarbonylmanganese systems.[43] This reaction has been shown, by ^{13}C nmr spectroscopy[44] and molecular orbital studies[45] to involve an alkyl migration to CO, rather than a CO insertion, which proceeds through a square-pyramidal intermediate with a basal acetyl group.



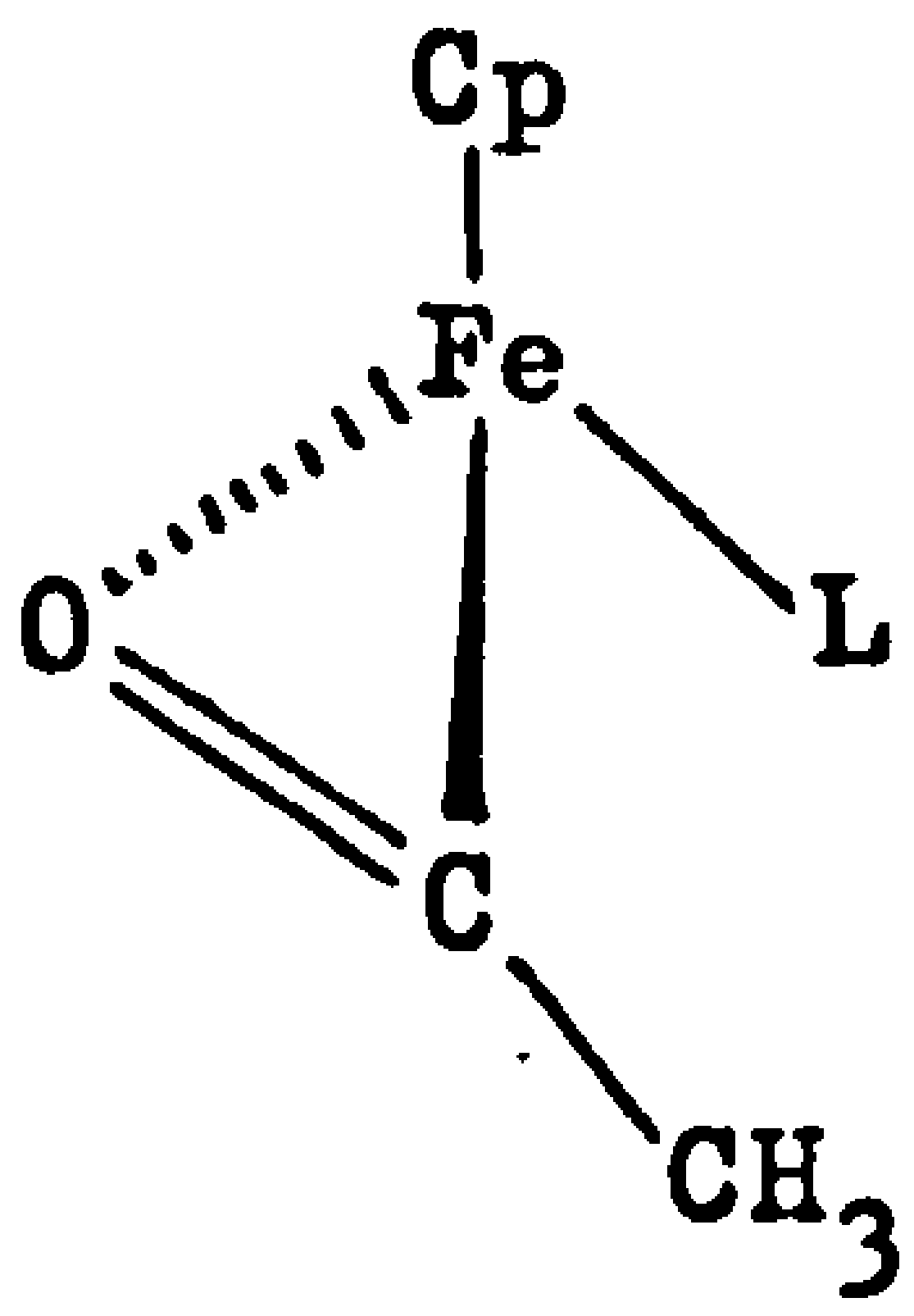
The intimate mechanism can be represented as:-



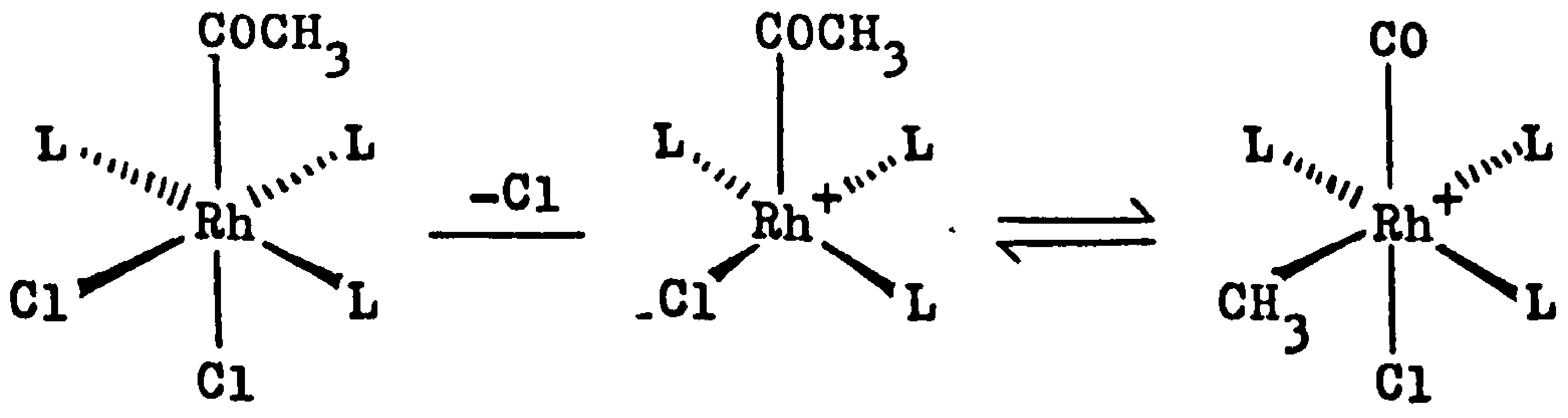
CO insertion has been shown to be an alkyl migration for the Me-Mn system and this was expected to be a general feature of such reactions.[46] However, recently Brunner and Vogt found an example of insertion of CO into a Me-Fe bond which appeared to be a carbonyl insertion, rather than a methyl migration.[47]



In this case, an intermediate η^2-acetyl complex is considered likely.



CO insertion is often reversible and many decarbonylation reactions have been studied, which also involve alkyl migration.[48]



Trans-Effect and Trans-Influence

The trans-effect and trans-influence are sometimes confused in discussions of reactivity of metal complexes.

The trans-effect in square planar substitutions, first recognised by Werner[49] and elaborated on by Chernyaev[50] refers to the effect of a ligand on the lability of a group trans to it. The best definition of the kinetic trans-effect is the following, by Basolo and Pearson:-[51]

"The trans-effect is the effect of a coordinated group upon the rate of substitution reactions of ligands opposite to it."

A series, in order of decreasing trans-effect at square planar complexes, was found to be:-[24,25,51]
CN^-, CO, C_2H_4, NO $>$ PR_3, H^- $>$ $SC(NH_2)_2$, CH_3^- $>$ $C_6H_5^-$, NO_2^- $>$ I^-, SCN^- $>$ Br^- $>$ Cl^- $>$ NH_3, py, $>$ OH^- $>$ H_2O.

Ligands of high trans-effect were those which resulted in the most rapid substitution of the trans-group. The trans-effect is thus solely a kinetic phenomenon, depending on activation energies. Two mechanisms were recognised for the trans-effect. Strong π-accepting groups such as CO and C_2H_4 have a high trans-effect by virtue of their ability to stabilise a 5-coordinate trigonal bipyramidal transition state, by withdrawing metal dπ-electron density into their own empty π or π* orbitals. Strong σ-donor ligands like H^- have a high trans-effect by a strong interaction with a metal p-orbital, weakening and lengthening the bond trans to it in the ground state. This weakening of the trans bond is called the trans-influence, and is a thermodynamic phenomenon. Recent molecular orbital studies have suggested that, for σ-bonding ligands, the ability to act as a donor in the transition state may also be important,[52] but the trans-influence is more important when the two effects do not reinforce each other.

The trans-influence of a ligand has been defined as[53]:- "the extent to which that ligand weakens the bond trans to itself in the equilibrium state of a substrate."

A structural trans-influence series was obtained by X-ray crystallographic studies as follows,[54] in decreasing order of trans-influence:-

R_3Si^-, σ-C, $H^- \geqslant$ carbenes, $PR_3 \geqslant AsR_3 >$ CO, RNC, C=C, Cl^-, $NH_3 >$ O (acac).

The trans-influence of a series of ligands can be determined by X-ray crystallographic measurement of the length of a metal-ligand bond trans to them in a series of analogous compounds. For example, in compounds $[PtX(PEt_3)_3]^+$, the length of the Pt-P bond trans to X varies from 2.239 to 2.335 Å as X varies from F to H.[55] Since X-ray crystallography measures ligand-metal bond lengths directly it takes account of both σ- and π-bonding contributions.

It has been shown in platinum (II) phosphine complexes that the value of $^1J_{PtP}$ is dependent mainly on the Pt-P bond length.[56] The variation of $^1J_{PtP}$ as the ligand trans to phosphine changes has been correlated with the ligands' trans-influences,[53,57,58] and a strong relationship between $^1J_{PtP}$, Pt-P bond length and trans-influence of the ligand trans to phosphine was observed. It was found that the platinum-phosphorus coupling constant depended mainly on the covalency and s-character of the Pt-P bond.

Cis-Effect and *Cis*-Influence

In square-planar complexes, *cis*-groups have only a very small effect on substitutuion rates, and are only important when comparing groups of nearly equal *trans*-effect.[25] In contrast, however, it has recently been recognised that the *cis*-influence may be more important. Molecular orbital studies have indicated that ligands exert a bond-weakening *cis*-influence almost comparable with their *trans*-influence, and suggest that the bond-weakening ability of a σ-bonding ligand is not directed specifically to the *trans*-position.[59] The order of *cis*- and *trans*-influences appeared to be the same. This theoretical result has not been substantiated, and in fact it has been shown experimentally that nmr *cis*- and *trans*-influences are not simply related.

^{13}C nmr studies on a series of complexes [DIARS Pt (CH_3) X] and [DIARS Pt (CH_3) L]$^+$ where X is an anionic ligand and L a neutral ligand showed that there is no correlation between *cis*- and *trans*-influences.[60] The *cis*-influence for a series of ligands was:-

$CO > CH_3CH_2NC > Ph_3As >$ *p*-$MeOC_6H_4CN > Ph_3P > \gamma$-$MeC_5H_4N$

while the *trans* influence in a series of *trans*-methyl-platinum derivatives was:-

$Ph_3P > CO, CH_3CH_2NC > Ph_3As > \gamma$-$MeC_5H_4N >$ *p*-$MeOC_6H_4CN$

The authors suggested that whereas the *trans*-influence is due to σ-orbital rehybridisation, the nmr *cis*-influence may in part be related to a ligand's steric bulk.

X-ray structural studies on a series of compounds *cis*-$[PtCl_2(PEt_3)L]$ have shown that the ligands L exert a *cis*-influence on the Pt-P bond lengths (ca 0.06 Å) which is almost as large as their *trans*-influence on the Pt-Cl (*trans* to L) bond lengths (ca. 0.07 Å).[61,62] However, the steric properties of L were considered to be at most a minor factor and the *cis*-influence is primarily an electronic effect. Strong *cis*-influence ligands tended to be strong π-acids, e.g.:- CO and PF_3, which could compete with PEt_3 for metal atom dπ-electrons. (This assumed that PEt_3 was a weak π-acid). The structural and nmr ($^1J_{PtP}$) *cis*-influences did not correlate well, with $^1J_{PtP}$ reflecting changes only in the s-component of the σ-bond while Pt-P bond lengths reflect overall bond order.

Organoplatinum Complexes

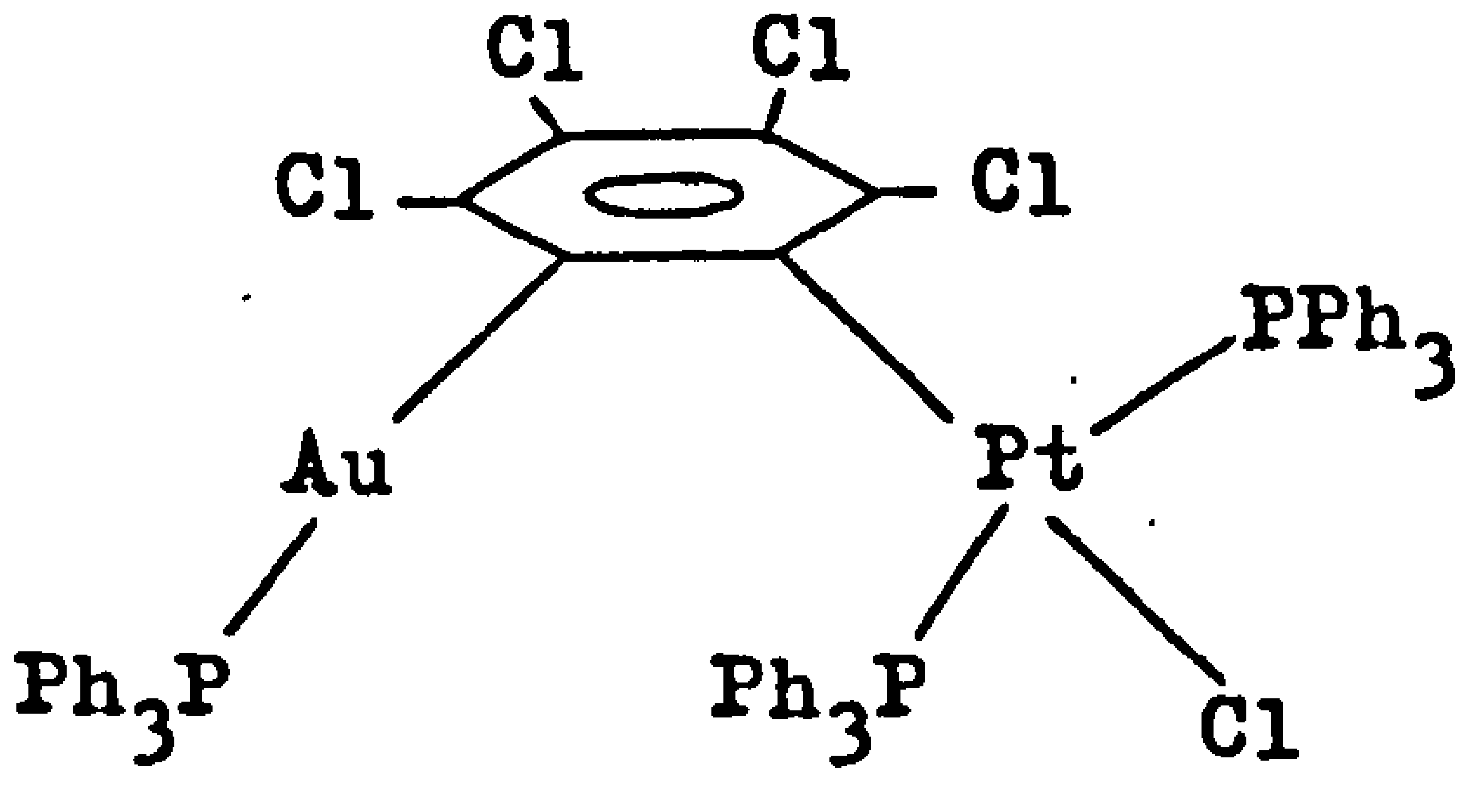
Platinum has a very extensive organometallic chemistry,[63-65] and has been a particularly important element in this field because it forms a wide range of compounds that are kinetically sufficiently inert to enable them to be isolated and characterised. Its most common oxidation states are 0, +2 and +4, and of these, the +2 state is the most important.[11] Complexes of the +1 state have recently become more common, but complexes with platinum in the +3 state are rare. Organometallic complexes of platinum with oxidation states of +5 or +6 are unknown.

Of the organometallic complexes formed by metals, platinum forms carbonyls, isonitriles, olefins and acetylenes in the 0 and +2 states, alkyls, aryls, acetylides, vinyls, ylides and cyclopentadienyls in the +2 and +4 states and allyls in the +2 state.[63]

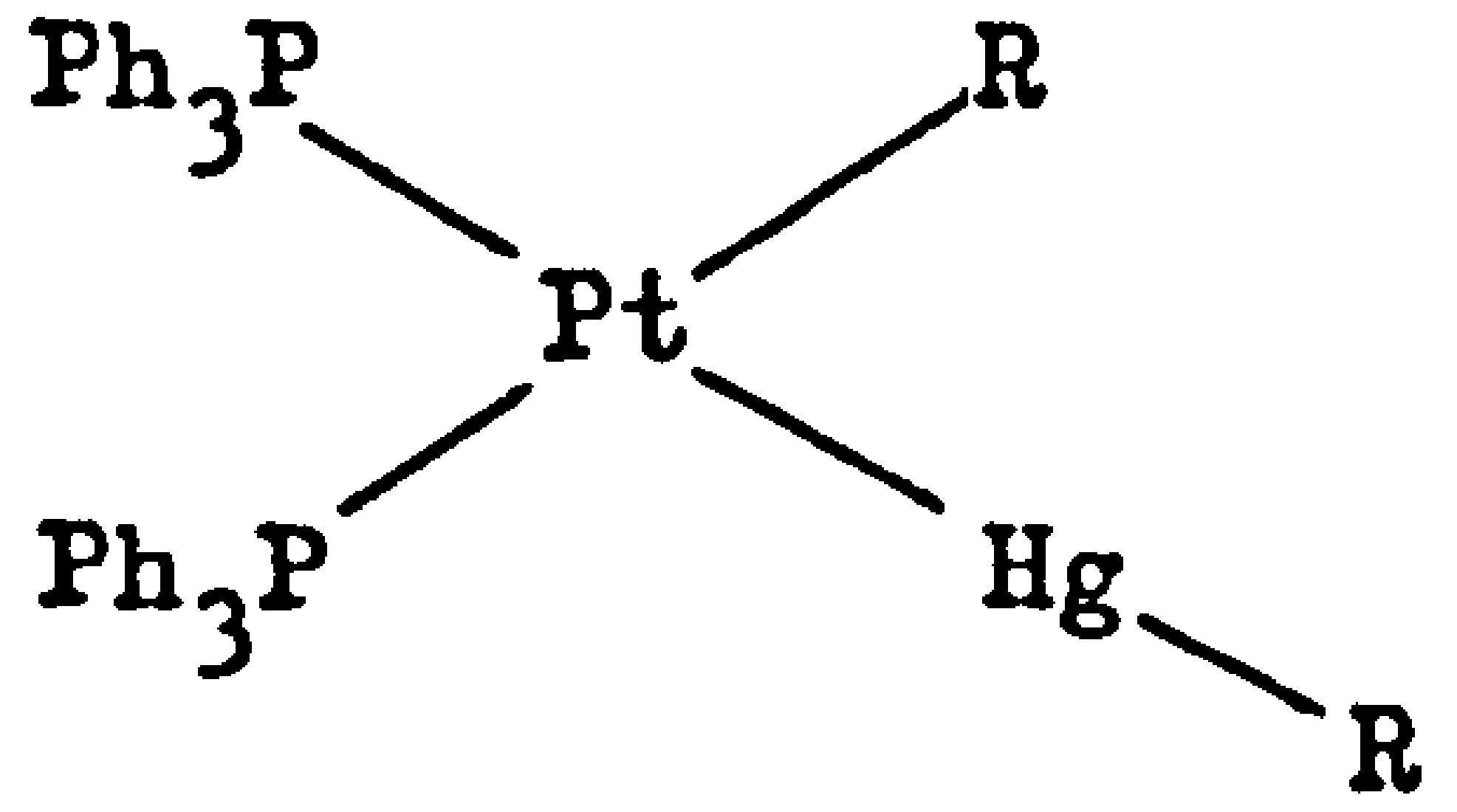
The zero oxidation state platinum complexes are mainly those containing phosphine ligands, either alone as $[Pt(PR_3)_n]$,(n=2,3,4) or with olefins and acetylenes, as $[Pt(PR_3)_2(olefin)]$ and $[Pt(PR_3)_2(acetylene)]$.[66] Zerovalent platinum complexes readily undergo oxidative addition reactions to give platinum (II) species with a wide variety of substrates, for example:- alkyl halides,[67] aryl-chloride bonds[68] and mercury-aryl bonds[69]:-

$$[Pt(C_2H_4)(PPh_3)_2] + CH_2I_2 \rightarrow \underline{cis}\text{-}[Pt(CH_2I)I(PPh_3)_2]$$

$[Pt(PPh_3)_3] + Ph_3PAuC_6Cl_5 \rightarrow$

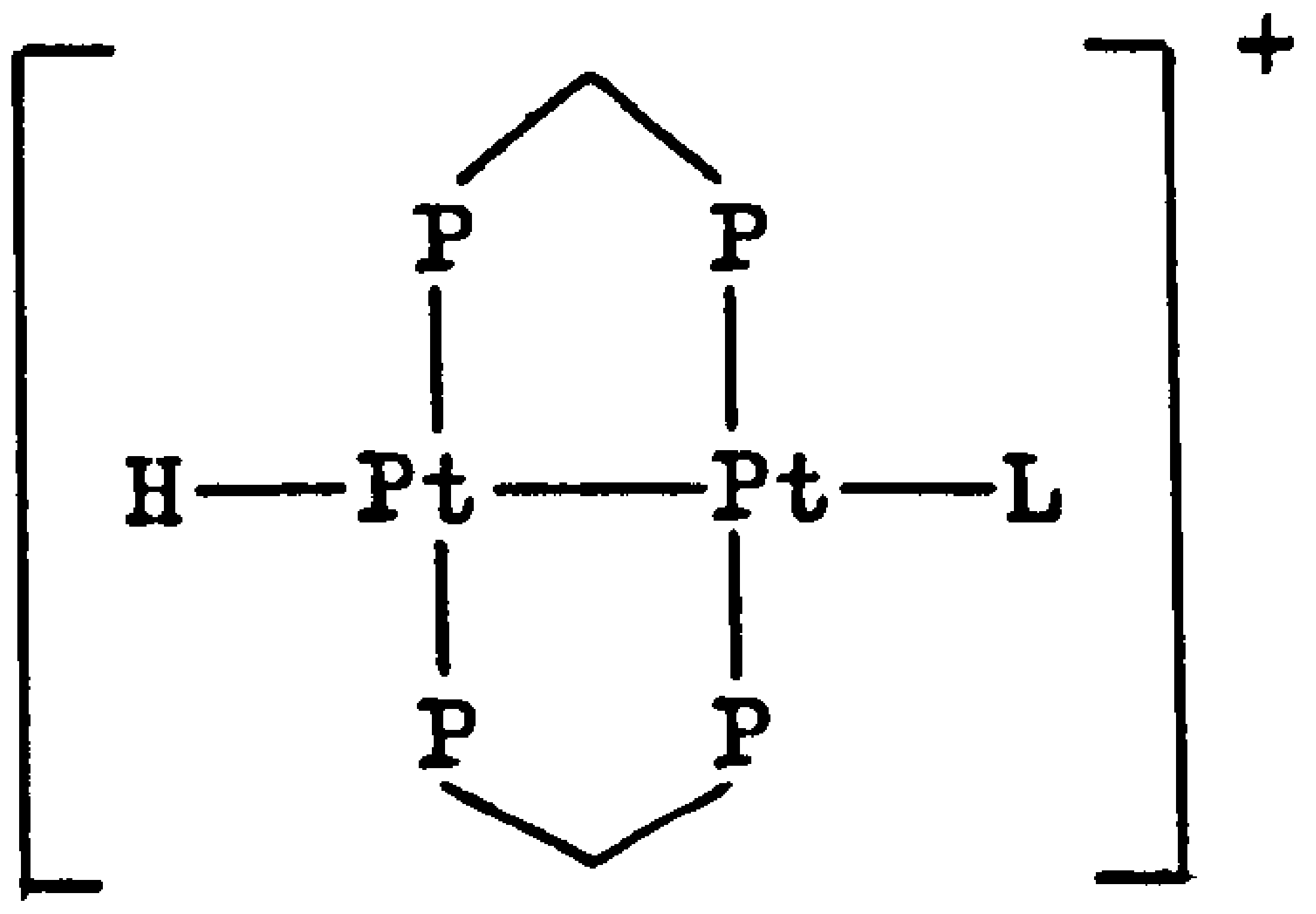


$[Pt(PPh_3)_3] + HgR_2 \rightarrow$

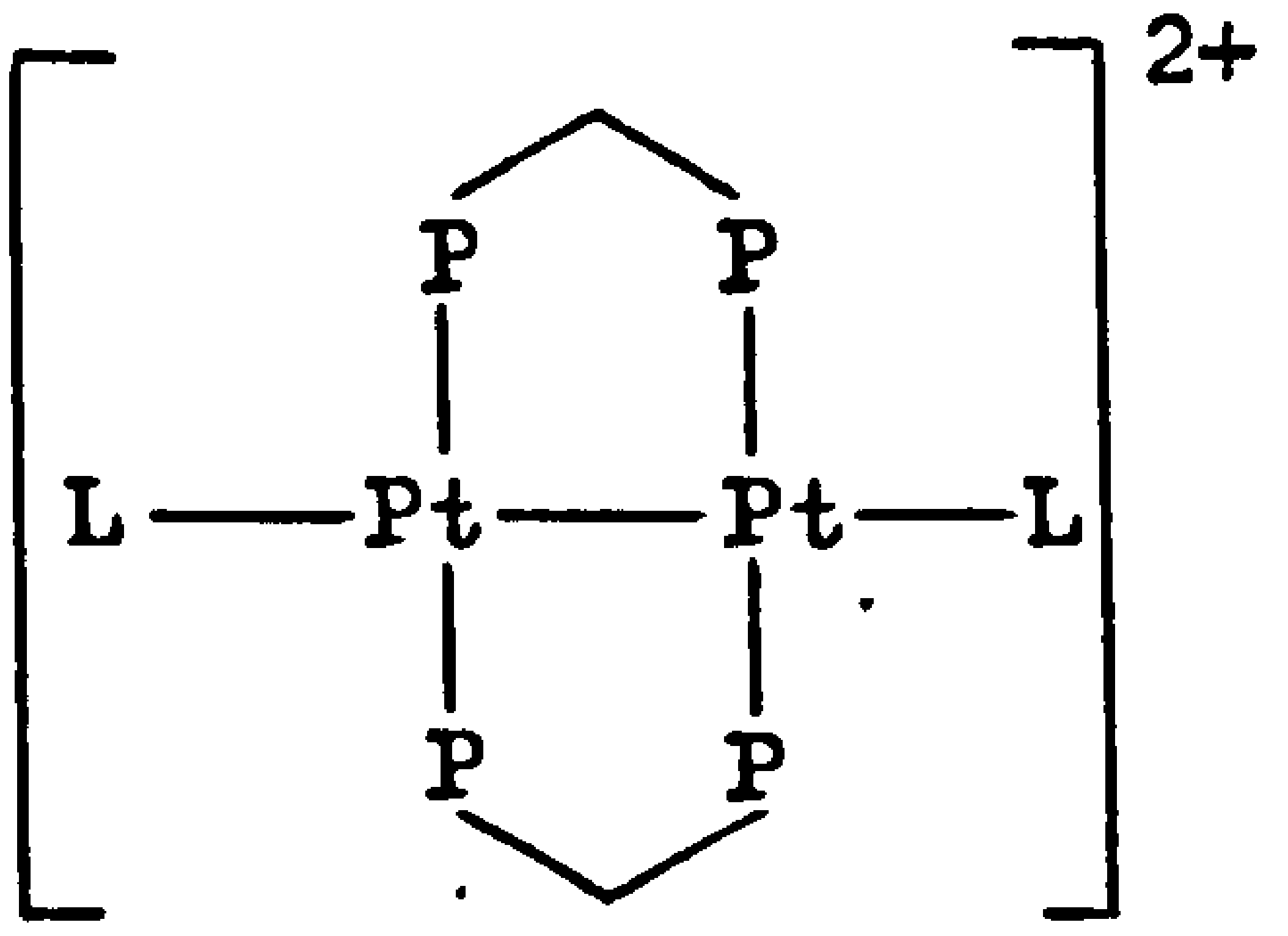


Platinum (O) complexes containing only olefins, $[Pt(olefin)_n]$, have also been described[70] and are useful starting materials in the synthesis of other complexes.

Complexes of the +1 oxidation state are normally dimers with a platinum-platinum bond to allow electron pairing and a diamagnetic complex, for example $[\{(\eta^5\text{-}C_5H_5)(CO)Pt\}_2]$[71] and $[Pt_2X_4(CO)_2]^{2-}$, (X = halogen).[72] Recently an increasing number of platinum (I) dimers with bridging dppm ligands have been reported, so-called "A-frame dimers".[73-75]

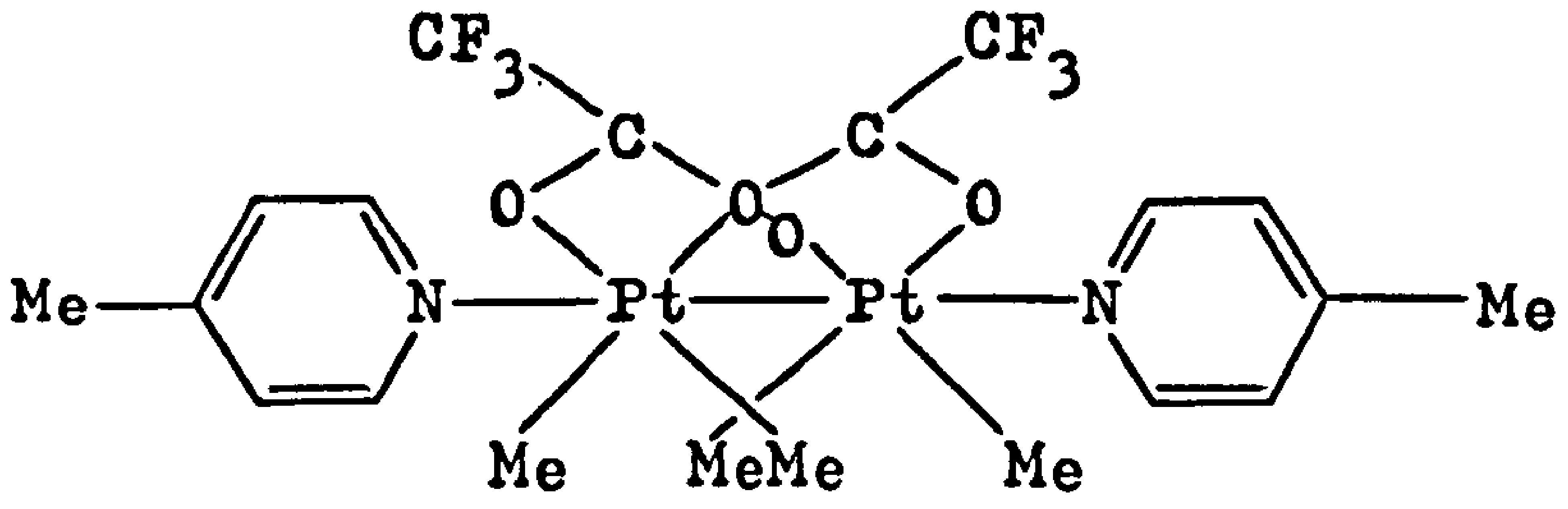


L = phosphine, CO



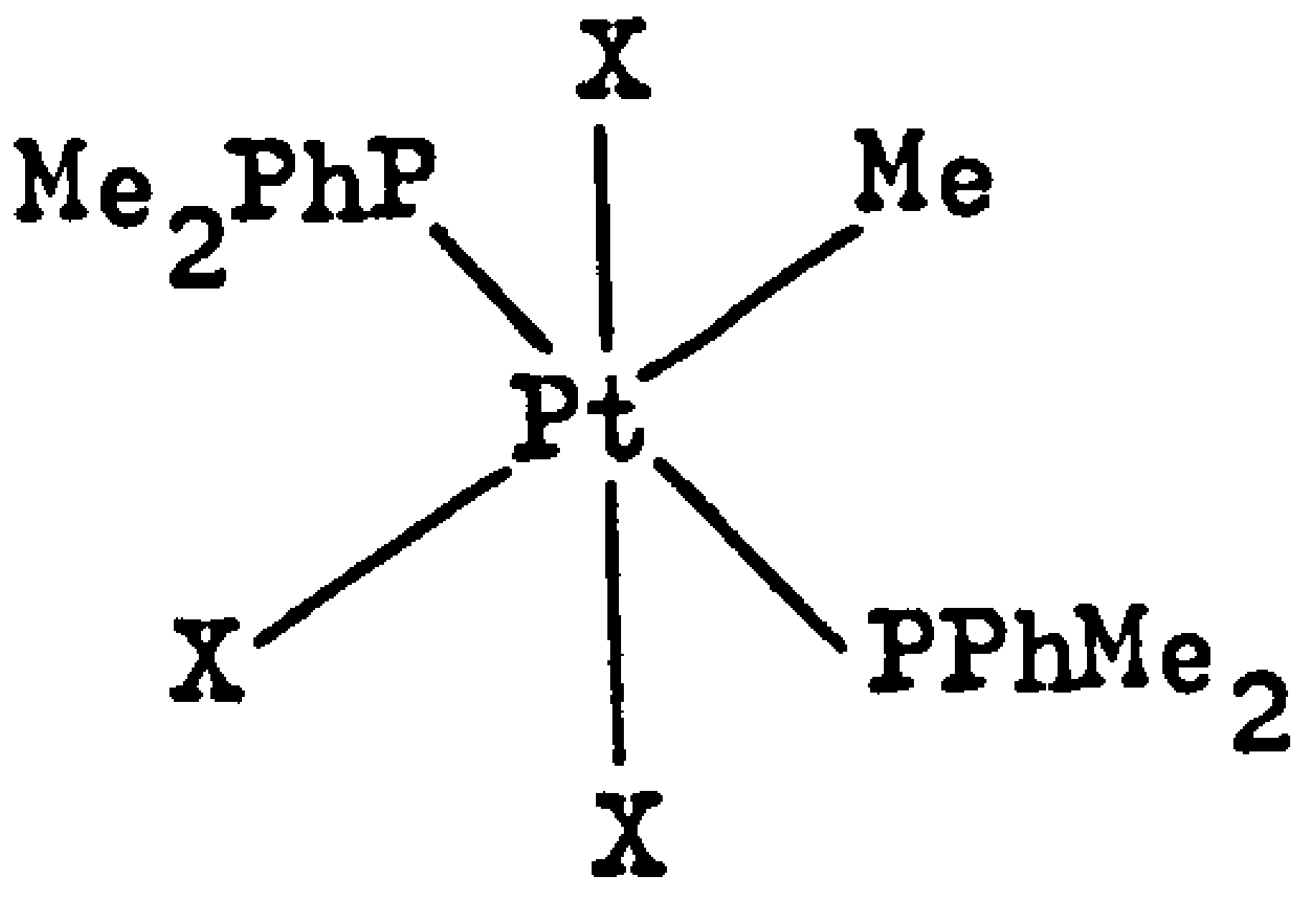
L = phosphine, CO, NH_3, py

There are very few alkyl or aryl platinum (III) complexes known, and these are also dimers such as $[Pt_2(pop)_4(CH_3)I]^{4-}$, (pop = $P_2O_5H_2{}^{2-}$)[76] and complexes of the type $[\{PtL(O_2CR^1)R_2\}_2]$ of which the following is a typical example[77]:-

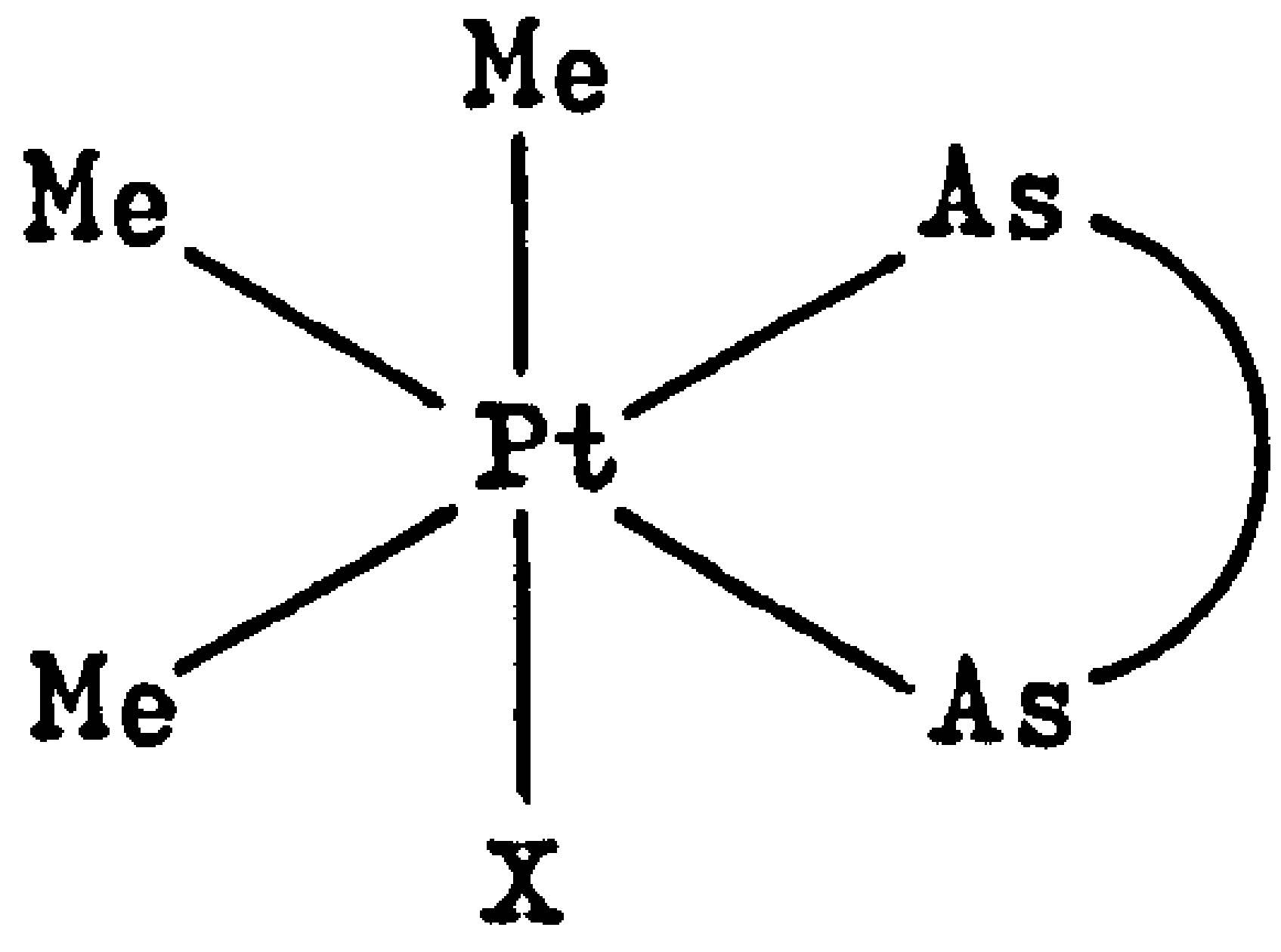


Platinum (IV) alkyls were amongst the earliest platinum organometallics known,[3] and the trimethylplatinum (IV) unit is particularly stable. $[PtMe_3(\eta^5\text{-}C_5H_5)]$ is the only platinum (IV) cyclopentadienyl complex known.[78] Platinum (IV) alkyl and aryl complexes are octahedral, 18-electron molecules and can be prepared from Grignard or lithium reagents, or by oxidative addition of halogen[79] or alkyl halide[80] to platinum (II) complexes.

<u>trans</u>-$[Pt\ X\ Me(PMe_2Ph)_2] + X_2 \rightarrow$

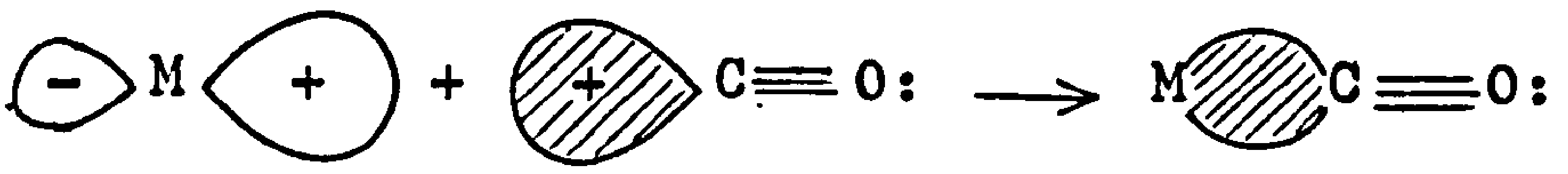


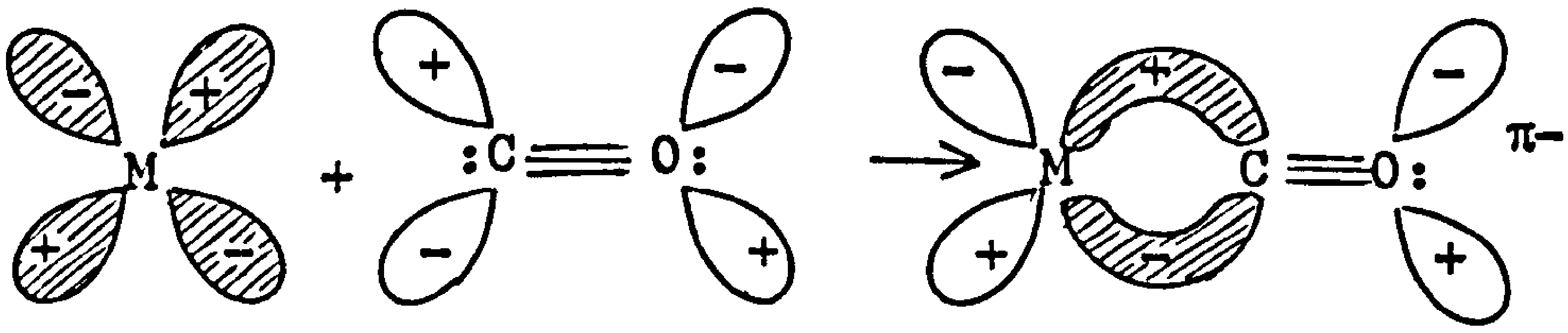
<u>cis</u>-$[PtMe_2(\overset{\frown}{As\ As})] + MeX \rightarrow$



Platinum (II) forms both monomeric and dimeric organometallic complexes, cationic, anionic and neutral, with one or more organic groups per platinum. The complexes are usually 4-coordinate, square-planar 16-electron compounds. Platinum (II) organometallic compounds can be made in a variety of ways, including using Grignard, organolithium, organotin and organomercury reagents and oxidation of platinum (o) species.[11,63] Platinum (II) - carbon σ-bond strengths have been measured for Pt-C_6H_5 and Pt-CPh=CHPh as 264 and 215 kJ mol^{-1} respectively,[81,82] and the platinum-methyl bond has been found to be of comparable strength to the platinum-iodide bond.[83] These values are rather less than the strength of carbon-carbon or carbon-hydrogen bonds, suggesting that the stability of platinum-carbon σ-bonds is not thermodynamic, but kinetic, due to lack of a suitable decomposition pathway.[11]

Platinum-carbonyl bonds also involve σ-bonding, but because of the π-acceptor qualities of CO there is also considerable π-bonding. The two types of interactions are shown below:-





The overlap of a filled sp-hybrid orbital on the carbon atom with a vacant hybrid orbital on the metal, complemented by π-back donation of electron density from filled metal d or dp hybrid orbitals to empty π* (anti-bonding) orbitals on the CO forms a bonding system which is synergic. The presence of electrons in the π* orbitals of CO weakens the C-O bond, reducing the stretching frequency from 2155cm^{-1} in free CO.[11]

The bonding between phosphorus and platinum is considered to be largely a σ-interaction, with little evidence for significant π-bonding.[84] Variations in Pt-P bond lengths can be explained by variations in sp character. The variations of Pt-P bond lengths in the complexes $[Pt(PR_3)_2]$, $[Pt(PR_3)_3]$ and $[Pt(PR_3)_4]$ are explained in terms of changes in formal σ-hybridisation of the metal from sp to sp^2 to sp^3.

Many π-bonded complexes of platinum (II) are also known, with olefins and acetylenes,[85] as well as delocalised aromatic π-systems such as $C_5H_5^-$.[86] The bonding in olefin complexes also consists of σ- and π- contributions. In this case, the olefin donates electron density from its filled π-orbital by a σ-bond to Pt and receives back-donation of electron density from filled orbitals on platinum into the empty π* orbital of the olefin.

CHAPTER 2

CYCLOPENTADIENYL PLATINUM COMPLEXES AND C_5H_5 TRANSFER REACTIONS

INTRODUCTION

Cyclopentadienyl Complexes

A large number of cyclopentadienyl complexes of platinum are now known. Early synthetic methods generally involved the use of NaC_5H_5, and were often low yield processes.[71,78,88,89] A more convenient preparation is via halide displacement by $C_5H_5^-$ from TlC_5H_5[86,90-93] or $Hg(C_5H_5)_2$.[86] The products are η^1-bonded 16-electron molecules, or η^5-bonded 18-electron molecules, depending on the number and type of other ligands present. Interconversion between the two types have been reported.[90,93,86]

$$[\text{PtMe}(\eta^1\text{-C}_5\text{H}_5)\text{cod}] \xrightarrow[\text{-cod}]{\text{L}} [\text{PtMe}(\eta^5\text{-C}_5\text{H}_5)\text{L}]$$

$$\text{L} = \text{CO},\ \text{P(OMe)}_3,\ \text{P(OPh)}_3,\ \text{P(OMe)Ph}_2$$

$$[\overline{\text{Pt}(\text{PBu}^t_2\text{CMe}_2\text{C}}\text{H}_2)(\eta^5\text{-C}_5\text{H}_5)] \xrightarrow{\text{PPh}_3} [\overline{\text{Pt}(\text{PBu}^t_2\text{CMe}_2\text{C}}\text{H}_2)(\eta^1\text{-C}_5\text{H}_5)(\text{PPh}_3)]$$

$$[\text{Pt(Ph)}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)] \xrightarrow{\text{PPh}_3} [\text{Pt(Ph)}(\eta^1\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{PPh}_3)]$$

Cyclopentadienylthallium

Cyclopentadienylthallium is easily prepared by treatment of thallous sulphate in NaOH with cyclopentadiene[94]

$$Tl_2SO_4 + C_5H_6 + NaOH \rightarrow (C_5H_5)Tl + Na_2SO_4 + H_2O.$$

The TlC_5H_5 is purified by vacuum sublimation to yield pale yellow crystals and is stable in air, although it darkens slowly on exposure to light.[95] A major advantage in using TlC_5H_5 is that the byproduct is TlCl, which is insoluble and is easily removed from the system.

The structure and bonding in TlC_5H_5 are thus of interest and much work has been done in this area. In the gas phase, it has a half-sandwich structure, with C_{5v} symmetry,[96] with the thallium atom situated centrally above the cyclopentadienyl ring. The nature of the bonding is still not clear, although covalent bonding is favoured.[97] Crystalline, (polymeric) TlC_5H_5 has been shown to consist of infinite zig-zag chains made up of alternate thallium atoms and cyclopentadienyl rings.[98] The chains are presumed to be held together by interactions between the metal atoms. In isostructural InC_5H_5 the metal-metal distance (3.99Å) is such that metal-metal bonding is possible. The ring-metal distance in the crystal (3.19Å) is considerably larger than that in the vapour.[98] An infrared and laser Raman spectroscopic study of TlC_5H_5 showed that the symmetry in the crystalline state is D_{5h}, indicating that the bonding is predominantly ionic.[99] Covalent bonding was expected to give a symmetry of C_{5v}, as in the vapour.

Dicyclopentadienylmercury

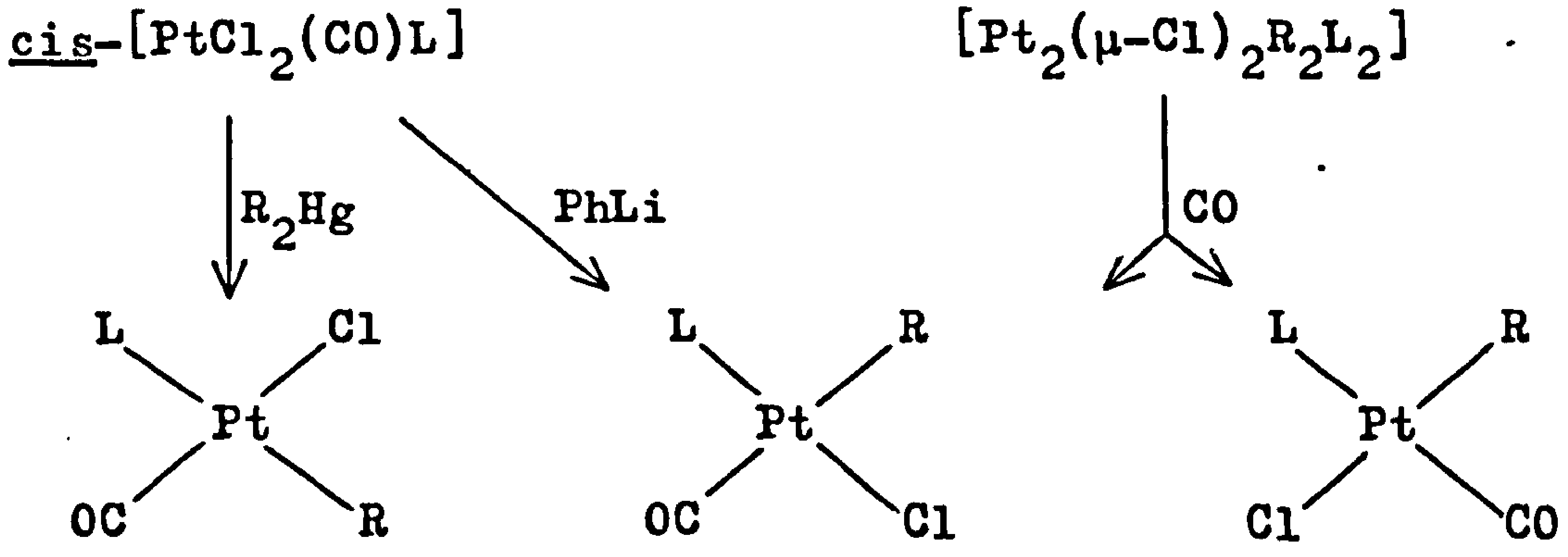
Dicyclopentadienylmercury was the first σ-bonded cyclopentadienylmetal complex reported which has been substantiated.[100] It is a light yellow crystalline solid when pure, but is unstable. On the basis of its infrared spectrum and chemical behaviour, Piper and Wilkinson considered it to have σ-cyclopentadienyl rings, which was later substantiated.[101] The compound was found to be fluxional; thus in the ^1H nmr spectrum at room temperature all of the C_5H_5 protons were found to be equivalent, but at low temperature the expected AA'BB'X type spectrum was obtained.[102] The fluxional rearrangement was postulated to involve 1,2-shifts of the metal round the carbons of the ring.

Dynamic properties of η^1-C_5H_5 rings

It is now well established that fluxional rearrangement of η^1-C_5H_5 complexes involves 1,2-shifts for all systems examined, both of main group and transition metals,[103] e.g;- $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$.[104] This has been established by the consideration of line shapes in the ^1H nmr spectra.[103] The 1,2-shifts may be regarded as degenerate [1,5] sigmatropic rearrangements, since the transition state for the rearrangement of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$ is essentially non-polar.[105] Earlier proposals for the rearrangement to proceed through a dipolar metal-olefin transition state[104] or a partially dissociated polar state[106] were clearly invalidated. Woodward Hoffmann rules for pericyclic reactions can be used in studying the fluxional process in σ-bonded cyclopolyenyl metal complexes. Almost all of the known cases can be explained by [1,5] sigmatropic shifts.[107] The Woodward Hoffmann rules require that an allowed 1,5 migration be suprafacial with retention of configuration at the migrating group, or antarafacial with inversion.[108] Fabian and Labinger have recently shown that the fluxional process in complexes of type $[(\eta^5\text{-}C_5H_5)Fe(CO)L(\eta^1\text{-}C_5H_4R)]$, ($L = P(OPh)_3$, PF_2NMe_2; R=H,Me) is suprafacial migration with retention of configuration of the migrating group.[109]

Isomers of [PtClR(CO)L]

Previous work has shown that a wide variety of organomercurials, R_2Hg (R = alkyl or aryl), react with cis-$[PtCl_2(CO)L]$ (L is a tertiary phosphine or arsine) to produce quantitatively the isomer of [PtClR(CO)L] with L trans to R, isomer (I).[23,110-112] The other two isomers, with CO trans to R, isomer (II), and Cl trans to R, isomer (III), were produced by CO cleavage of the halide-bridged dimers $[Pt_2R_2(\mu\text{-}Cl)_2L_2]$. The reaction between cis-$[PtCl_2(CO)L]$ and phenyl-lithium led to several products including some isomer (II) of [PtClPh(CO)L], but none of the isomer (I), (figure 1).



(I) (II) (III)

figure 1.

Isomers (II) and (III) were shown to interconvert, the equilibrium favouring isomer (II).

The variation in products was rationalised in terms of the different reaction mechanisms. It was suggested[23] that phenyl lithium would be most likely to react by a carbanion attack at platinum to produce a five-coordinate intermediate. The kinetic trans effect[54] of CO would stabilise the intermediate with the entering and leaving groups in the same trigonal plane as itself, thus ensuring loss of the Cl^- trans to it. Diphenyl mercury was expected to react via an electrophilic attack on the mercury bound carbon atom (S_E2) or by an oxidative addition/reductive elimination sequence. The high trans influence[54] of tertiary phosphine would weaken the Pt-Cl bond trans to it, favouring its elimination.

Transfer Reactions

In this chapter, the exchange of a C_5H_5 group between Tl, Hg and Au and Pt has been studied, as well as exchanges between two platinum complexes. In the following chapter, exchange reactions of other organic groups are considered. In view of the popularity in using organomercury[113-117] and organotin reagents[118-122] to prepare organoplatinum compounds, the transfer mechanism has been the subject of much comment.[123] Two routes in particular have been singled out. The first is the S_E2 (cyclic) mechanism,[119,121,123] which involves the simultaneous transfer of the two migrating groups, and is well documented for mercury.[124] The second is consecutive operation of oxidative addition and reductive elimination,[114,123,125-127] which is well known for square-planar d^8 complexes.[27,28] At this point, it will be useful to discuss the two types of mechanisms.

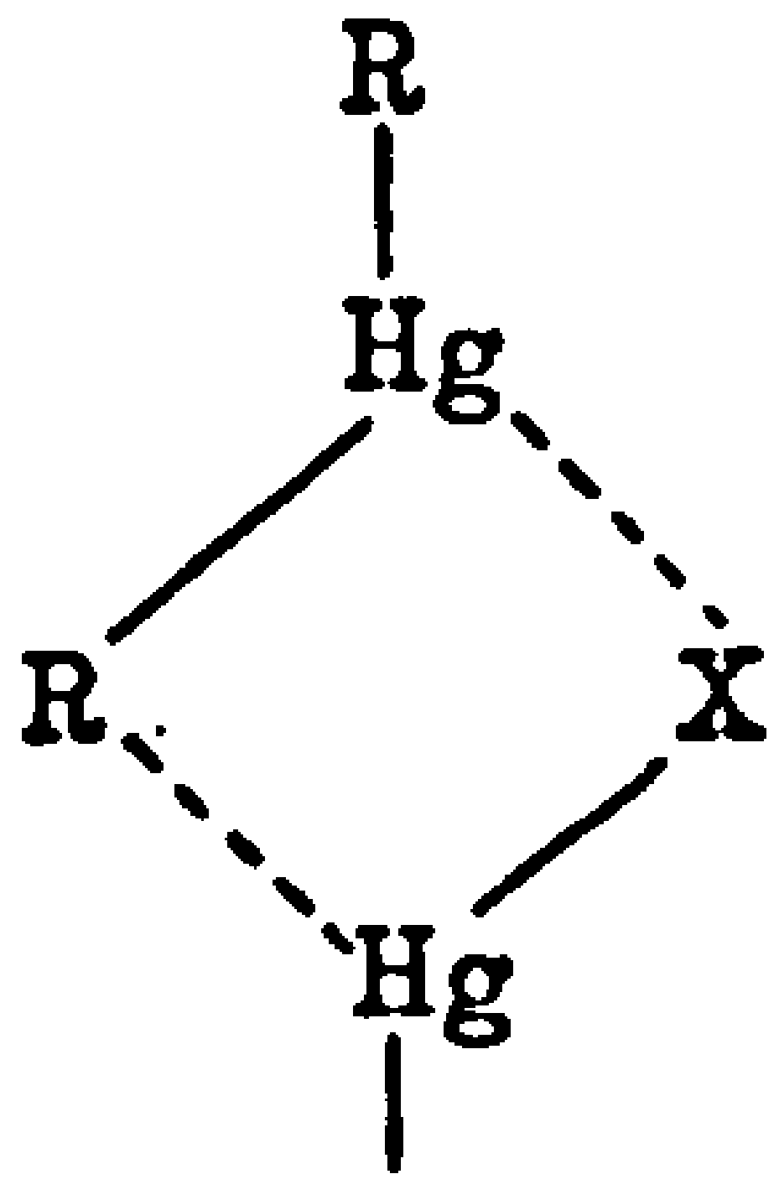
Bimolecular Electrophilic Substitution Mechanisms

The S_E2 (cyclic) mechanism for organic group exchanges developed from the study of mercury systems. The exchange of organogroups between mercury compounds has generally been found to be a bimolecular process.[124]

The S_E2 (cyclic) mechanism involves a simultaneous transfer of the two migrating groups, and a 4-membered cyclic transition state. For example, in the following exchange of an organo group for a halide in the reaction,

$$R_2Hg + HgX_2 \rightleftharpoons 2RHgX$$

the transition state is :-



S_E2 (cyclic)

In this mechanism, as the electrophile (HgX_2) attacks the metal bonded carbon atom, the nucleophilic part (X) coordinates with the metal atom. Nucleophilic coordination with the metal atom can occur simultaneously with, or before, electrophilic attack at the carbon atom, but there is no kinetic difference between these mechanisms, and both may be classed as S_E2 (cyclic)[124].

It has been established experimentally that when an organic group is transferred, e.g.:- in the reaction between cis- and trans- methoxycyclohexylmercurychloride and $HgCl_2$ (^{203}Hg-labelled),[128] the organic group is transferred with retention of configuration. In all cases of bimolecular electrophilic substitution which were studied,[124] the strict retention of configuration at saturated carbon was established. Retention of configuration is predetermined by coordination of the nucleophilic part of the electrophile with the metal atom.

The S_E2 (cyclic) mechanism is not the only possible bimolecular electrophilic substitution mechanism. There are some examples of transfer reactions in mercury chemistry which proceed by an S_E2 (open) mechanism, i.e. where there is no coordination of the nucleophilic part of the electrophile with the metal atom. The S_E2 (open) mechanism can proceed with either retention or inversion of configuration at saturated carbon. No such inversions were found in mercury systems.

In the cleavage of organic groups from tin, Fukuto and Jensen have recently demonstrated some S_E2 (open) reactions which proceed with inversion of configuration.[129] They concluded that a system expected to promote S_E2 (open) inversion would contain the following features; (1) A leaving group which is relatively stable when bearing a positive charge; (2) a leaving group with no low-lying vacant orbitals (hence the reason for using Sn instead of Hg); (3) steric hinderance to front-sided substitution and little hinderance to inversion; (4) a polar solvent.

The three transition states for S_E2 cleavage of $MCR^1R^2R^3$ in the following reaction are shown in figure 2:-

$$Y^{\delta-}\text{———}Z^{\delta+} + R^1R^2R^3CM \rightarrow R^1R^2R^3CZ + MY$$

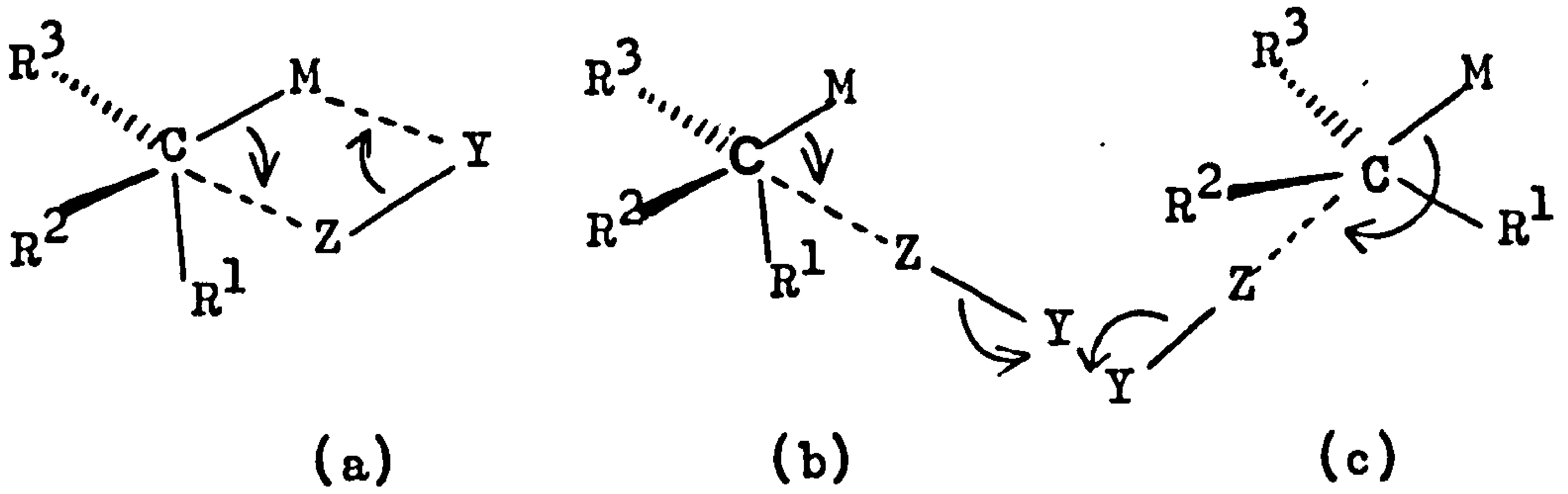


figure 2.

(a) S_E2 (cyclic); retention.
(b) S_E2 (open); retention.
(c) S_E2 (open); inversion.

Oxidative Addition/Reductive Elimination

The possibility of transferring an organic group by an oxidative addition/reductive elimination sequence is well known, when the group is transferred between two transition metals. Oxidative additions are common with Ir^I and Pt^0 complexes. Of particular interest are transfers of organic groups from mercury and tin reagents.

Addition of HgY_2 (Y=Cl, Br, I, OAc, CN, SCN) to Vaska's compound has been reported to produce octahedral Ir^{III} complexes $[(Ph_3P)_2(CO)Cl(Y)Ir(HgY)]$, with an iridium-mercury bond, but the stereochemistry of the addition was not known.[130] A similar study on the addition of $HgCl_2$ to trans- $[(Ph_2MeP)_2Ir(CO)Cl]$ yielded a species with mercury perpendicular to the plane containing the phosphines and CO,[131] (fig. 3).

Similarly $Hg(C{\equiv}CR)_2$ (R=Ph, C_5H_{11}) has been found to add oxidatively to trans-$[Ir(PPh_3)_2(CO)Cl]$ to give a product with mercury in the plane of the phosphine and carbonyl ligands (fig. 4).[132]

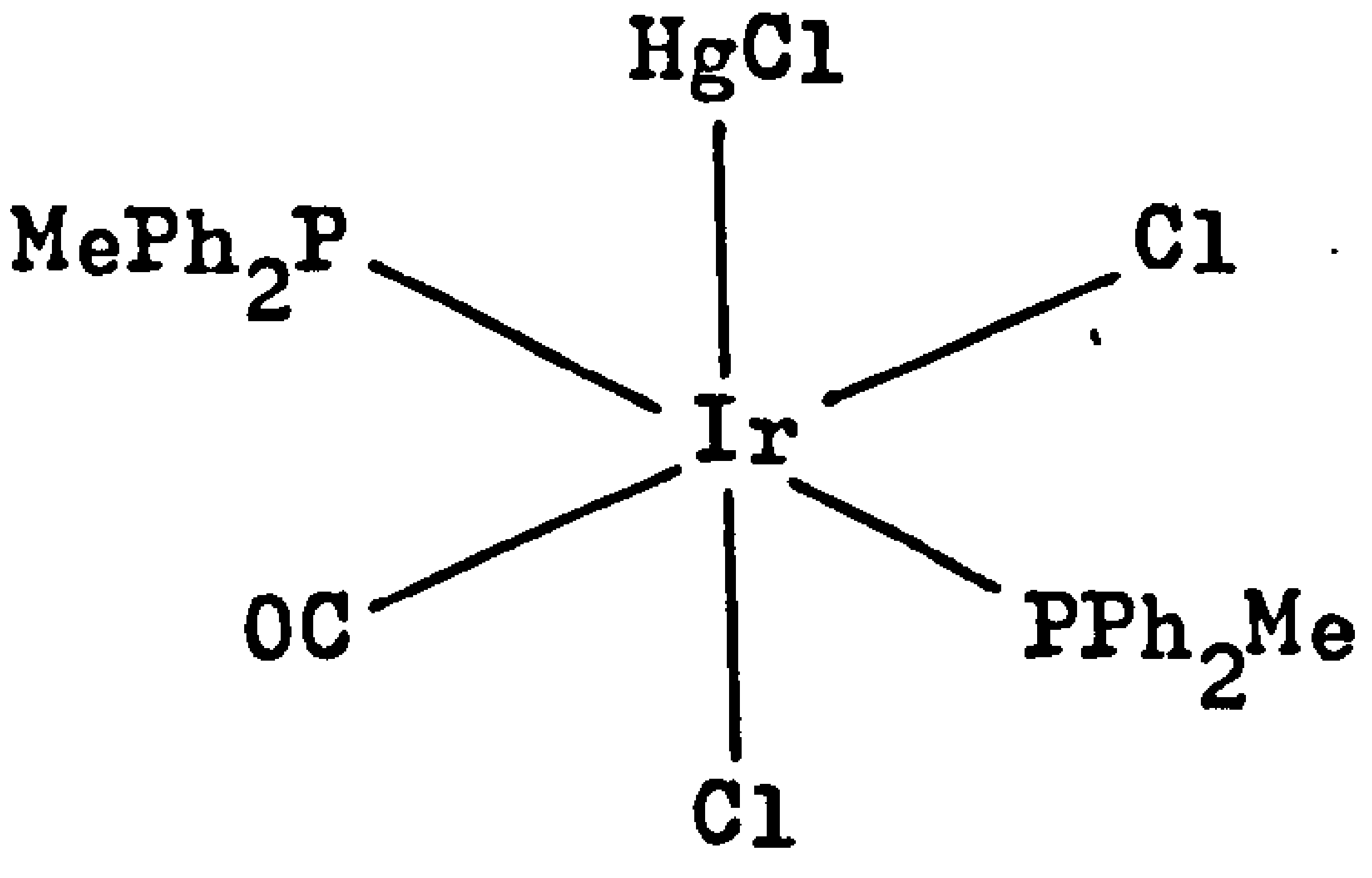


figure 3.

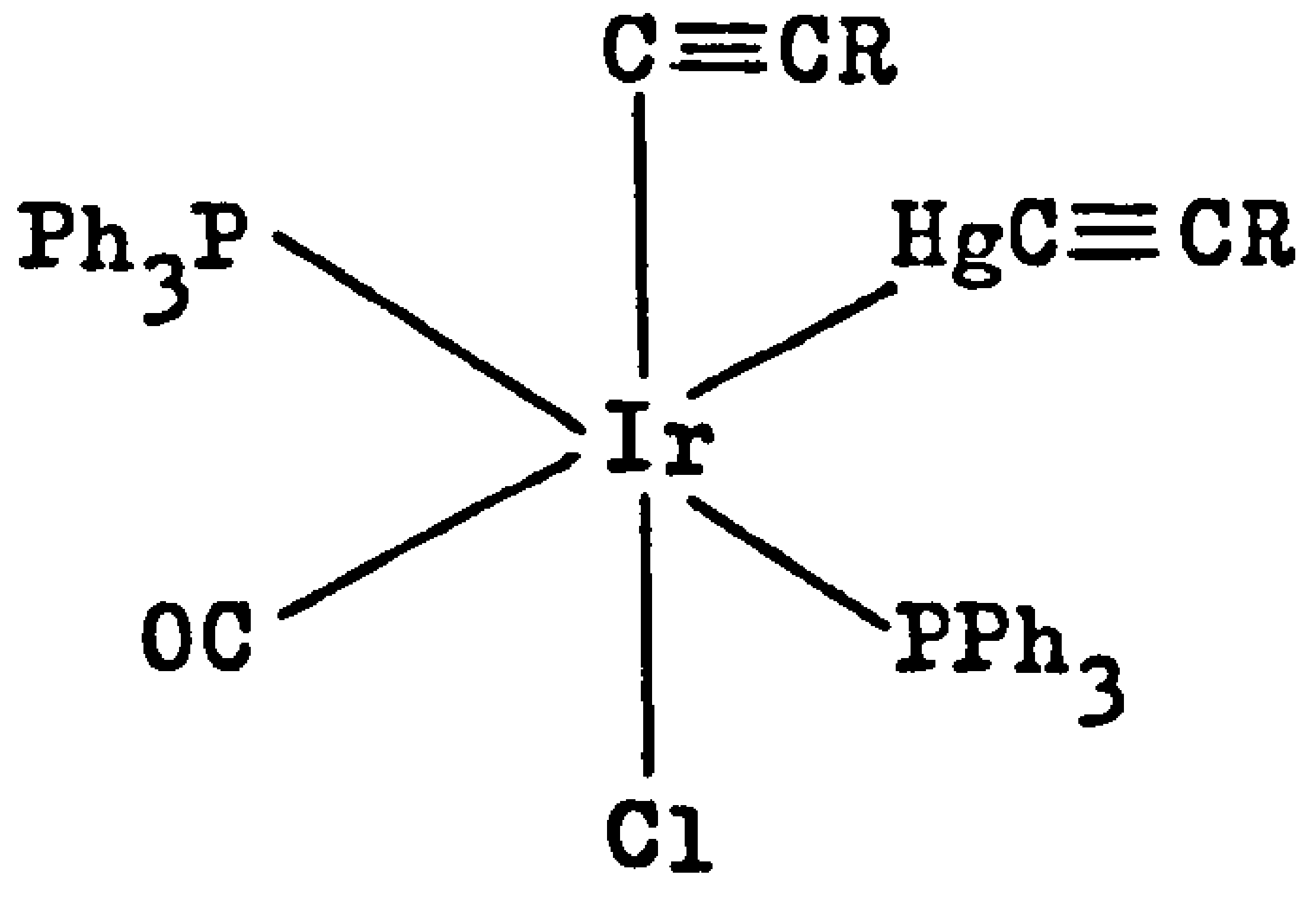


figure 4.

Reactions of platinum (o) compounds with tin reagents have also been reported,[122,133-135] with insertion of platinum into the Sn-C or Sn-Cl bond, depending on the reagent used. $[Pt(C_2H_4)(PPh_3)_2]$ reacts with SnR_3X (R = Ph or Me, X = halide) to give cis-$[PtR(PPh_3)_2(SnR_2X)]$ for example,[134] but with $SnRCl_3$ it gave trans-$[PtCl(SnCl_2R)(PPh_3)_2]$.[135] With mixed methylaryl tin reagents, the platinum inserted into the tin-aryl bond,[134]:-
$[Pt(C_2H_4)(PPh_3)_2] + SnPhMe_2Cl \rightarrow$ cis-$[PtPh(PPh_3)_2(SnMe_2Cl)]$

There are also a number of oxidative addition reactions of platinum (II) known, involving tin reagents, and mercury reagents. The reaction of $[PtMe_2(N-N)]$ (N-N = 2,2'-bipyridine,1,10-phenanthroline) with methyl tin or aryl tin-halogen compounds, SnR_nCl_{4-n} has been reported to proceed via a trans-oxidative addition of the Sn-Cl bond to Pt.[125] (fig. 5) A similar result was obtained with $PbPh_nCl_{4-n}$. The same author later showed that the analogous organogermanium-, organosilicon- and organocarbon-chlorides also oxidatively added to $[PtMe_2(N\text{-}N)]$ with <u>trans</u> addition.[126]

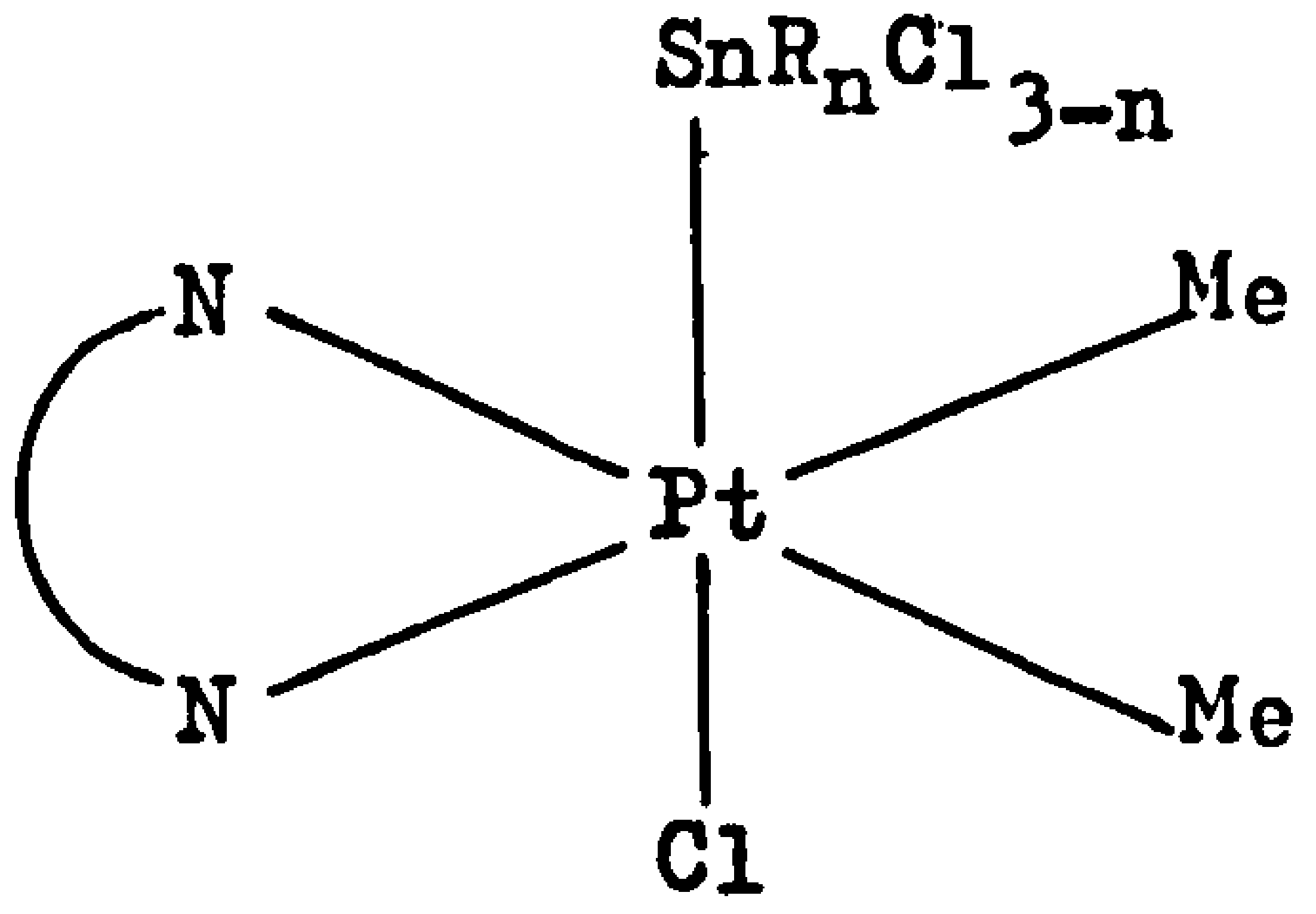
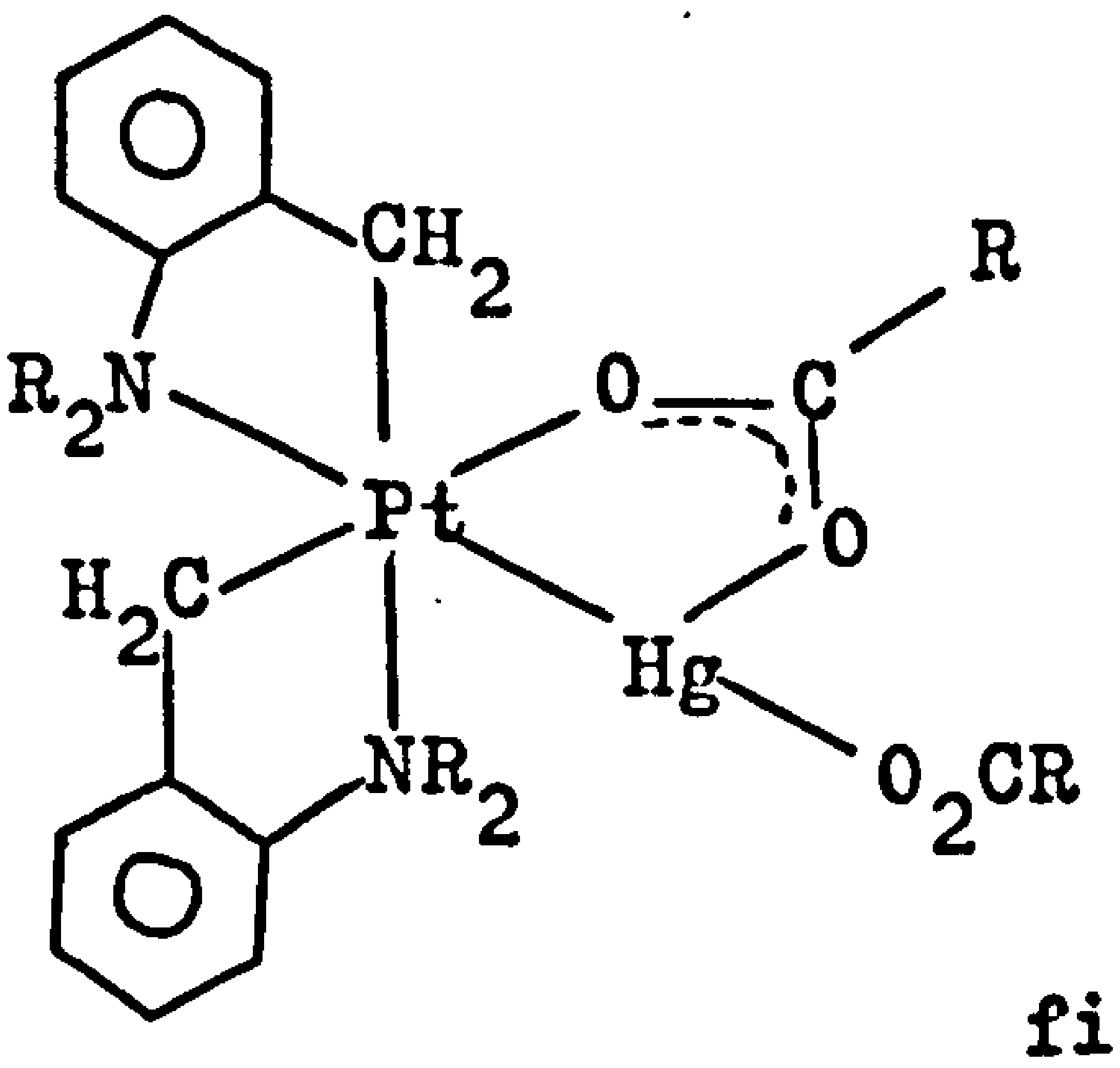


figure 5.

The platinum complex $[PtMe_2(N\text{-}N)]$ is one which has frequently been used in the study of oxidative additions to platinum (II). Recently, MeOH and EtOH have been oxidatively added to produce five coordinate, cationic platinum (IV) compounds, $[PtMe_2(OR)(N\text{-}N)]^{+}$[136].

Mercury carboxylates have been oxidatively added to platinum (II) complexes to produce platinum (IV) complexes with a platinum-mercury bond.[137,138] The mercury carboxylates gave a <u>cis</u>-oxidative addition with mercury in the positions shown, in the platinum (IV) products, (fig. 6)



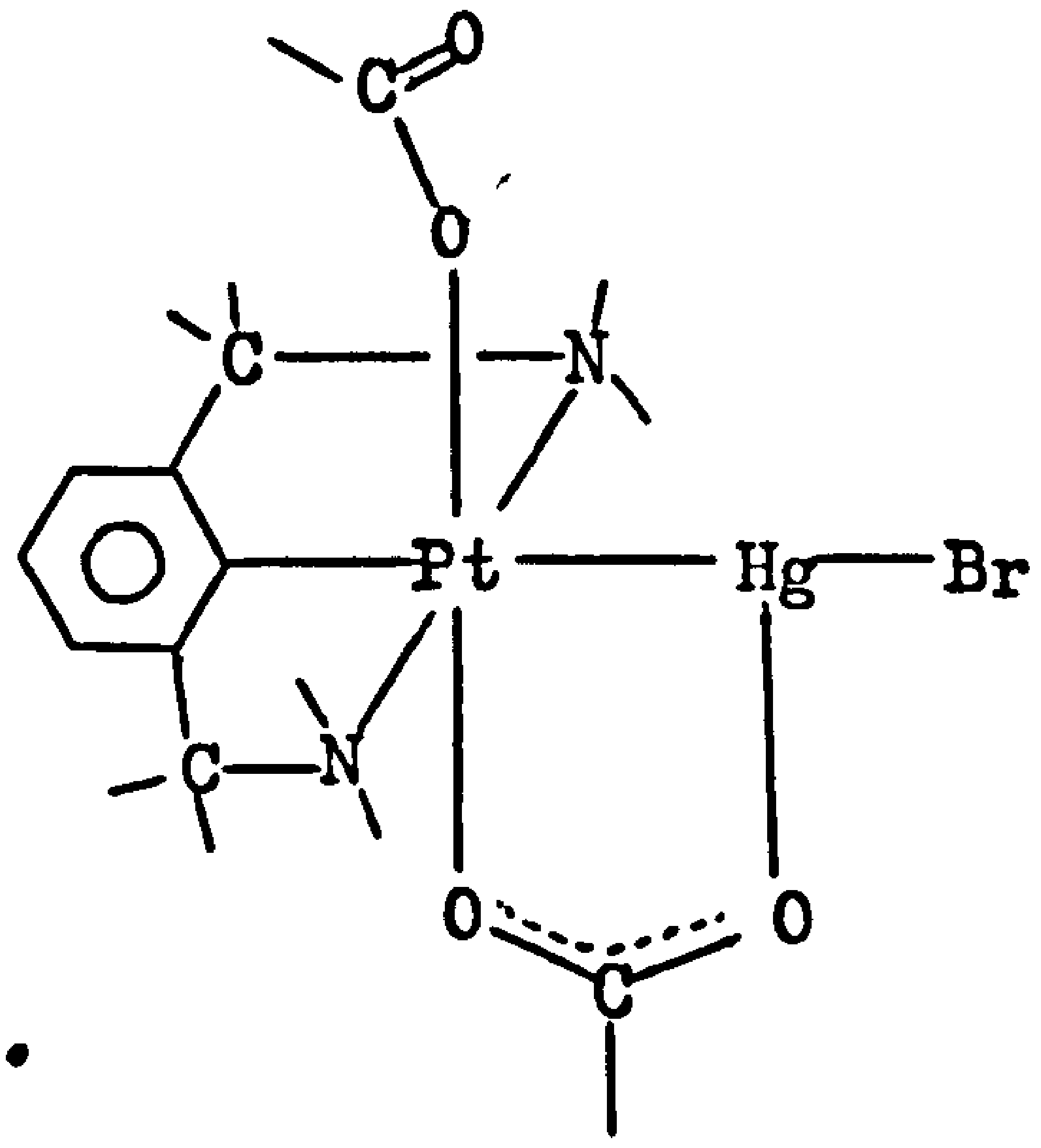


figure 6.

The same authors have also reported complexes with proposed platinum (II) to mercury (II) donor bonds,[138,139] (fig. 7).

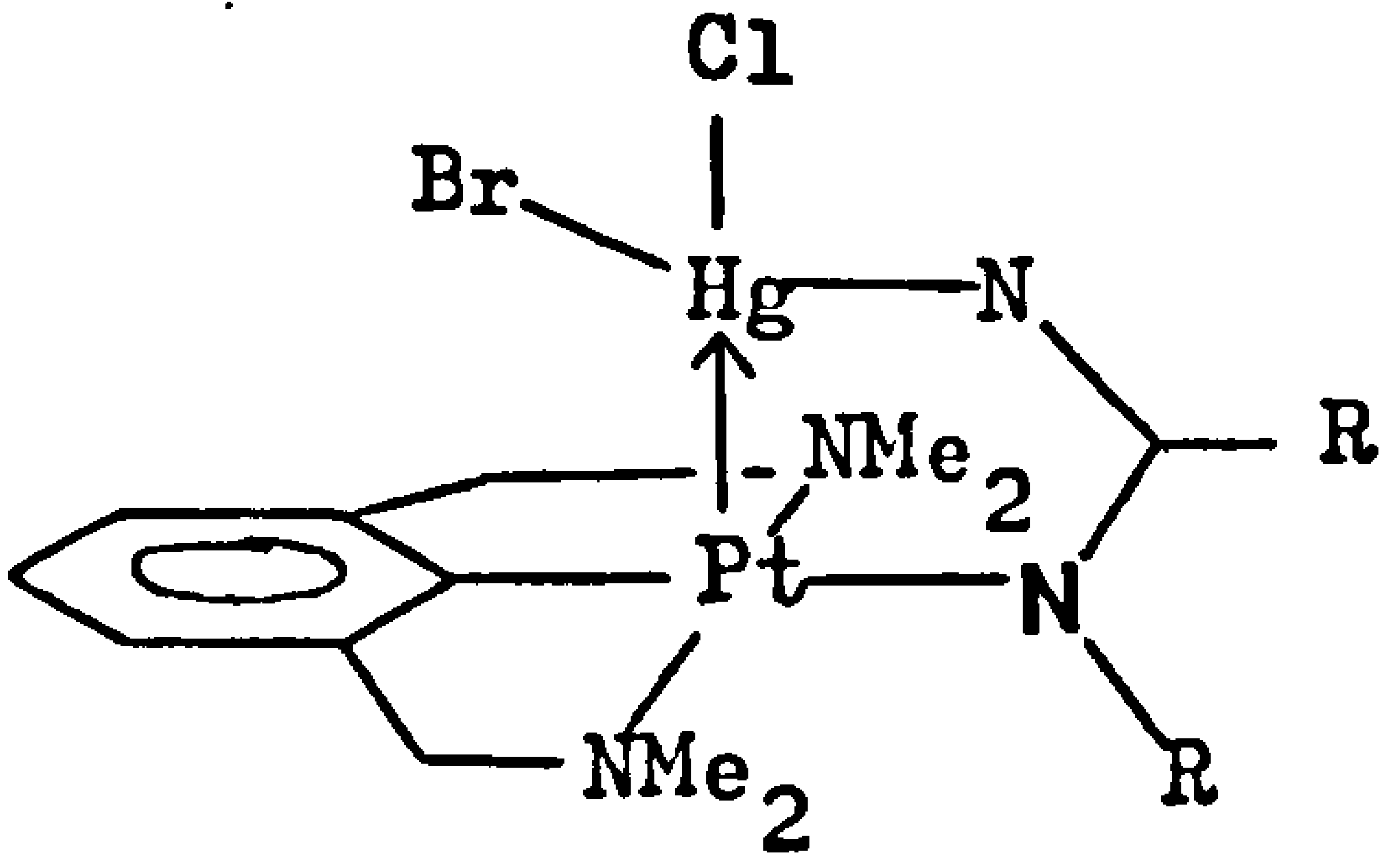


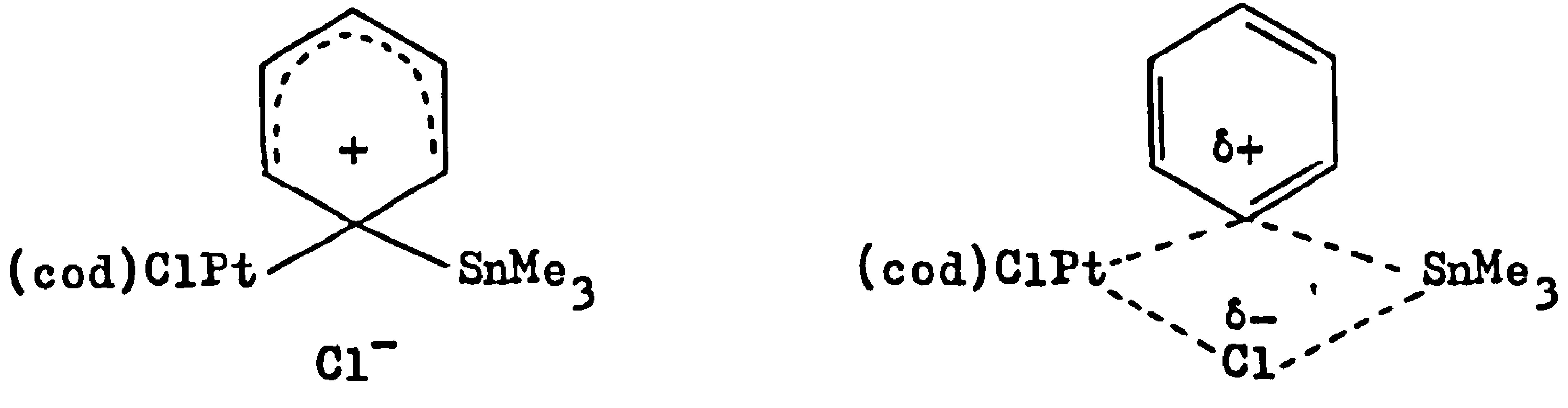
figure 7.

Analogous complexes containing a platinum-silver bond have also been prepared,[140] with the first reported ^{195}Pt- ^{109}Ag coupling constant showing that the two metal atoms are bonded.[141]

Distinction between Transfer Mechanisms

In organo group transfer reactions firm evidence for the type of mechanism operating is scarce. S_E2 (cyclic) mechanisms have been proposed for the reaction of $[Pt(cod)Cl_2]$ and $SnMe_3R$ (R = aryl).[119] A series of substituted aryl groups was studied and it was found that the transfer reaction was facilitated by an electron releasing substituent and retarded by an electron withdrawing substituent, which is consistent with electrophilic aromatic substitution. In oxidative addition of $SnMe_3R$ to $[Pt(C_2H_4)(PPh_3)_2]$, the rate of reaction was increased by electron-withdrawing substituents on the aryl group.[122] Further support for the S_E2 (cyclic) mechanism came from the reactivity of MMe_3R (M = group 4 element) which was found to be $Pb > Sn \gg Ge > Si$. Similarly,

$SnRMe_3$ was shown to react with $[Pt(O_2CCF_3)_2L_2]$ with a related effect on reactivity with changes in the R group, although the authors postulated that this reaction could involve substantial Wheland intermediate character.[121] A Wheland intermediate would be a transition state of type (a) in fig. 8, as opposed to the normal S_E2 (cyclic) transition state (b).[119]



(a) (b)

Figure 8 : (a) Wheland intermediate;
(b) S_E2 (cyclic) intermediate.

<u>cis</u>-$[Pt(C_2H_4)Cl_2L]$ was also proposed to react with $SnRMe_3$ by an S_E2 mechanism, followed by loss of ethylene to give $[Pt_2R_2Cl_2L_2]$.[120] <u>cis</u>-$[PtCl_2(CO)L]$ reacted to produce the insertion product $[Pt_2(COR)_2Cl_2L_2]$ and the authors considered this to be produced by an oxidative addition/reductive elimination sequence. They considered that the Cl <u>trans</u> to CO would be replaced by an S_E2 (cyclic) mechanism to produce [PtClR(CO)L], R <u>trans</u> to CO, because of the greater <u>trans</u> effect of CO.[54] This isomer is incapable of undergoing CO insertion and thus Eaborn <u>et al.</u> concluded that an S_E2 (cyclic) mechanism could not have operated. Whereas the Cl trans to CO would be replaced

in a nucleophilic substitution, it is considered by other authors that the chloride trans to phosphine would be replaced by an S_E2 (cyclic) mechanism due to the greater trans influence of the phosphine.[23] If this is the case, the product, $[Pt_2(COR)_2Cl_2L_2]$ is perfectly consistent with an S_E2 (cyclic) mechanism as [PtClR(CO)L], R trans to L, is the isomer which inserts.

Oxidative addition/reductive elimination sequences have been shown to operate in some reactions of platinum (II) with mercurials where a platinum (IV) intermediate has been isolated. In the $HgCl_2$ cleavage of a methyl group from $[PtMe_2(bipy)]$, a platinum (IV) intermediate was isolated.[127] The authors favoured a cis-oxidative addition resulting in mercury in the plane of the bipy ligand (fig. 9).

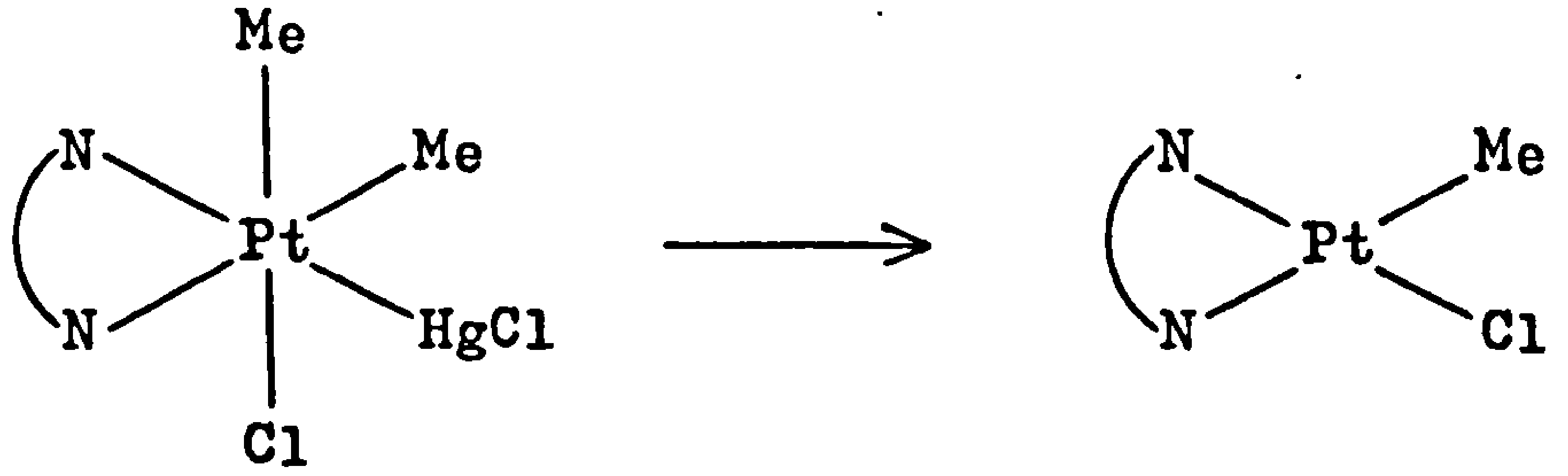
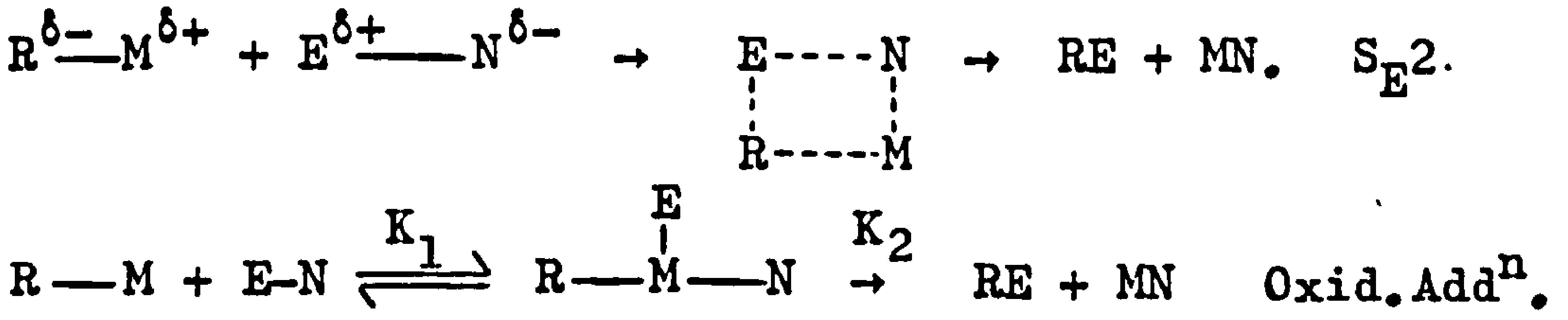


figure 9.

There was a slow reductive elimination on heating to give [PtClMe(bipy)] and MeHgCl.

Similarly, the complex $[PtCl_2(dppm)]$ reacts with two equivalents of $Hg(SiMe_3)_2$ to produce the platinum (IV) complex $[Pt(SiMe_3)_2(HgSiMe_3)_2(dppm)]$, which was isolated and thought to have trans mercury atoms.[114] Slow elimination of Hg and Si_2Me_6 produced $[Pt(SiMe_3)_2(dppm)]$. A similar reaction with Ph_2Hg produced $[PtPh_2(HgPh)_2-(dppm)]$.

In most cases, attempts to differentiate between S_E2 and oxidative addition mechanisms prove ambiguous. The two reactions are as follows:-



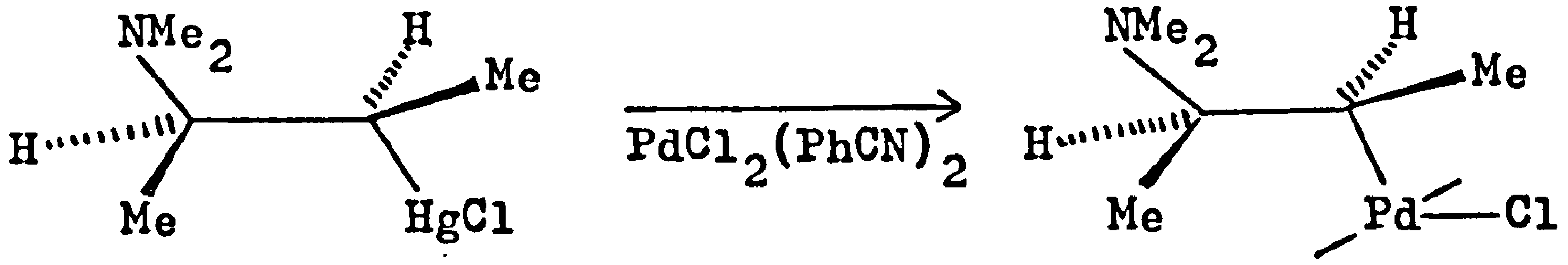
$$R^{\delta-}\!-\!M^{\delta+} + E^{\delta+}\!-\!N^{\delta-} \rightarrow \begin{array}{c} E\text{----}N \\ \vdots \qquad \vdots \\ R\text{----}M \end{array} \rightarrow RE + MN. \quad S_E2.$$

$$R-M + E\text{-}N \overset{K_1}{\rightleftharpoons} R-\overset{\overset{E}{|}}{M}-N \xrightarrow{K_2} RE + MN \quad \text{Oxid.Add}^n.$$

In the oxidative addition mechanism, if $K_1 \gg K_2$ the intermediate adduct is isolable or detectable, but if $K_2 \gg K_1$ this will not be possible. Thus, only if $K_1 \gg K_2$ can oxidative addition mechanisms be proven.[127] In other cases, it will be extremely difficult to distinguish between S_E2 and oxidative addition/reductive elimination (with no intermediate detectable). Oxidative addition followed by reductive elimination can yield the same product as an S_E2 (cyclic) mechanism, and this mechanism has been termed S_E(oxidative).[142]

Puddephatt has attempted to distinguish between S_E2(cyclic) and oxidative addition/reductive elimination reactions by studying mixed aryl methyl complexes of gold and platinum.[123,143] He found that an aryl group was cleaved from [PtMeAr(cod)] and _cis_-$[AuMe_2Ar(PPh_3)]$ but that a methyl group was cleaved from _cis_-$[PtMeAr(PMePh_2)_2]$ by a wide range of electrophiles, including HCl, $HgCl_2$ and platinum complexes. The results were interpreted as aryl cleavage being the result of an S_E2 (cyclic) mechanism and methyl cleavage being the result of an oxidative addition/reductive elimination mechanism. He argued that, since aryl groups are cleaved much more rapidly than alkyl groups in the reactions of R_2Hg and R_4Sn with electrophiles[144,145] the S_E2 (cyclic) mechanism should selectively cleave an aryl group from platinum, or gold. On the basis of photoelectron spectra of the complexes[146] it was suggested that the platinum phosphine complexes undergo oxidative addition and selective cleavage of a methyl group because their HOMO's are a 5d orbital localised on the platinum, and that in the gold and platinum complexes where an aryl group is cleaved, an S_E2 mechanism operates because the HOMO's are σ (Me-Au) or σ (Me-Pt) orbitals. However, these conclusions have been challenged recently.[147] It has been shown that mixed methyl aryl tin reagents will selectively transfer an aryl group to platinum by both S_E2 (cyclic)[119] and oxidative addition[134] mechanisms. In the transfer of organic groups between platinum complexes or gold and platinum complexes, it has been suggested that mechanisms intermediate between the extremes of S_E2 and oxidative addition/reductive elimination could operate.[148] Great care should be taken in assignment of mechanisms. The methyl transfer reactions from platinum and gold complexes to platinum were originally designated as S_E2 (cyclic)[149] before eventually being proposed as oxidative addition/reductive elimination reactions.[123] It is, for example, stated that cleavage of an organic group from [$AuMe_3L$] or [$AuMe_2ArL$] by a platinum complex must be by an S_E2 (cyclic) mechanism because oxidative additions to Au (III) are unknown.[123,149] However, the possibility that the Au complex could oxidatively add to the Pt (II) complex is completely neglected.

Other methods of mechanistic investigation also prove to be ambiguous. The transfer of alkyl from mercury to palladium has been shown to proceed with retention of configuration of the alkyl ligand by the reaction of <u>threo</u>- and <u>erythro</u>- $MeCH(NMe_2)CH(HgCl)Me$ with bisbenzonitrilepalladium chloride.[115]



<u>threo</u> <u>threo</u>

This was interpreted as being consistent with an S_E2(cyclic) or an S_E2 (open) retention reaction. Indeed, retention of configuration at saturated carbon is demanded by the S_E2 (cyclic) mechanism.[124] However, retention of configuration would also occur in a concerted <u>cis</u>-oxidative-addition/reductive-elimination sequence. $HgCl_2$ cleaves the optically active alkyl group from <u>threo</u>-$PhCHDCHDFe(CO)_2$-(η^5-C_5H_5) and <u>trans</u>-(<u>threo</u>-R)—$W(CO)_2(PEt_3)$(η^5-C_5H_5) with retention of configuration by the S_E (oxidative) mechanism,[142] and with inversion from <u>cis</u>-(<u>threo</u>-R)$Mn(CO)_4(PEt_3)$ by an

S_E2 (open) mechanism involving a backside attack by the electrophilic agent on the α-carbon atom.

$$\underline{\text{threo}}\text{-PhCHDCHDFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) + \text{HgCl}_2 \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl} + \underline{\text{threo}}\text{-PhCHDCHDHgCl}$$

$$\underline{\text{cis}}\text{-(}\underline{\text{threo}}\text{-PhCHDCHD)Mn(CO)}_4\text{PEt}_3 + \text{HgCl}_2 \rightarrow \underline{\text{cis}}\text{-Mn(CO)}_4(\text{PEt}_3)\text{Cl} + \underline{\text{erythro}}\text{-PhCHDCHDHgCl}$$

$$\underline{\text{trans}}\text{-(}\underline{\text{threo}}\text{-PhCHDCHD)W(CO)}_2(\text{PEt}_3)(\eta^5\text{-C}_5\text{H}_5) + \text{HgCl}_2 \rightarrow \underline{\text{cis}}\text{-(}\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2(\text{PEt}_3)\text{Cl} + \underline{\text{threo}}\text{-PhCHDCHDHgCl.}$$

This is also rationalised by considering the energy difference between the HOMO (metal carbon σ-bonding character) and the filled non-bonding metal d-orbitals.

Aryl transfer reactions between platinum complexes, $[\text{Pt(cod)R}_2]$ and $[\text{Pt(cod)Cl}_2]$; and $[\text{Pt(cod)R}_2]$ and $[\text{Pt(cod)R}_2{}^1]$ have been reported[119] and the mechanism proposed to be S_E2 (cyclic) on the basis that the ease of transfer of aryl group was consistent with the ease of electrophilic attack on the carbon atom of the aryl-metal bond, but the authors were not totally confident that the product compositions reflected rates of migration rather than positions of equilibria.

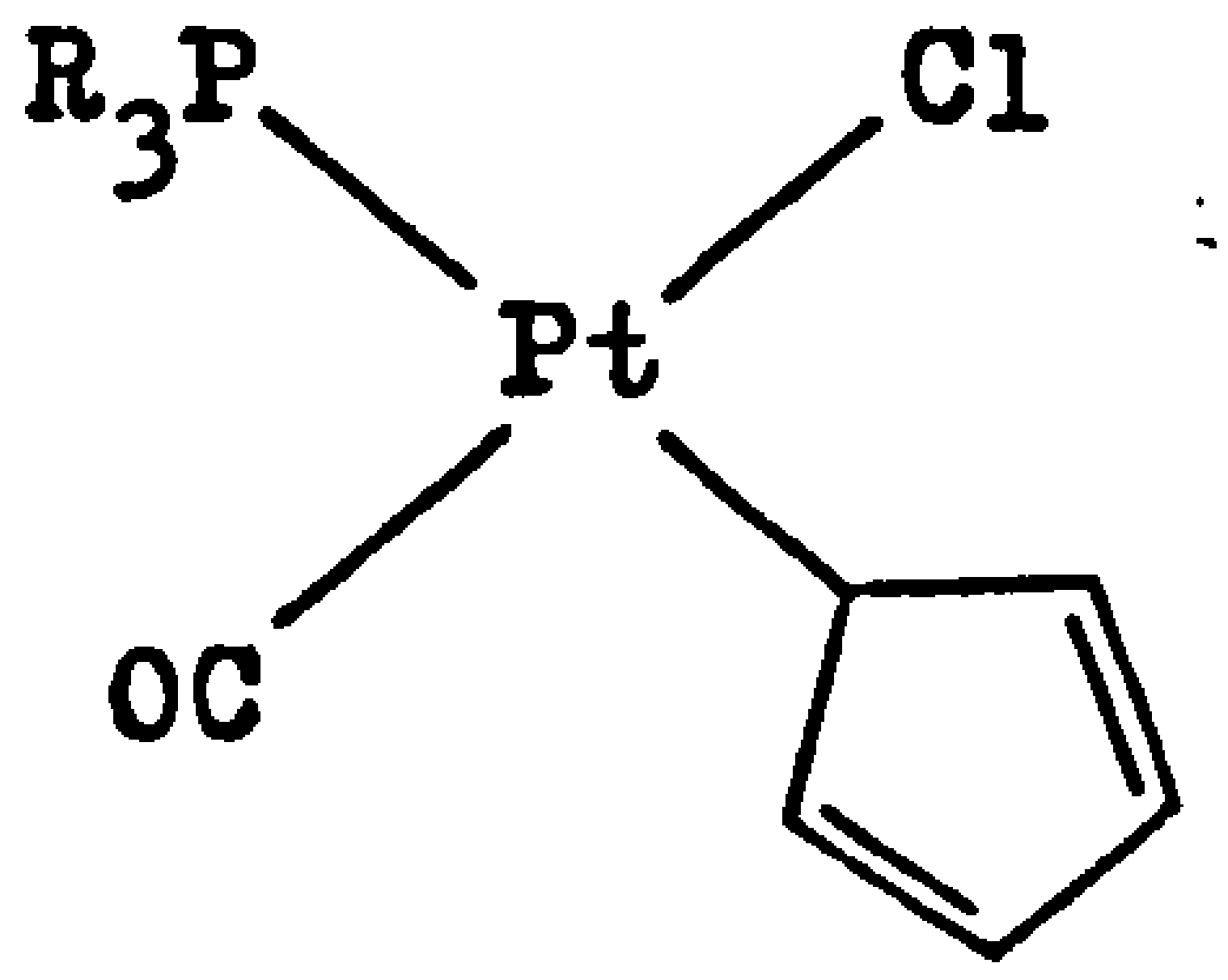
Thus the difficulties encountered in mechanistic interpretation of transfer reactions involving transition metals can be seen.

RESULTS AND DISCUSSION

Preparation of [PtX(C_5H_5)(CO)L] isomer (I)

A suspension of cis-dichlorocarbonyl (triphenyl phosphine)-platinum (II) and cyclopentadienyl thallium in benzene reacted over one hour to yield [PtCl(C_5H_5)(CO)-PPh_3] and insoluble TlCl. The cyclopentadienyl platinum complex was crystallised with difficulty from acetone/pentane mixtures to produce an orange powder. Although in the solid phase the compound appears to be indefinitely stable (samples have survived unchanged in air in diffuse light for more than 6 months), decomposition in solution proceeds over several days at ambient temperatures.

The ^{31}P nmr spectrum of the platinum complex revealed a ^{195}Pt- ^{31}P coupling constant of only 1780 Hz., which is typical of complexes with phosphine trans to an organic group in compounds of this type.[23] The ^1H nmr signals from the cyclopentadienyl group showed averaged proton signals with J_{PtH}=31.0 Hz and J_{PH}=4.4 Hz. This is consistent with a fluxional η^1-cyclopentadienyl trans to phosphine.[86] The compound is therefore assigned the structure (I).



I

A deuteromethylene chloride solution of [PtCl(C_5H_5)-(CO)(PPh_3)] (I) was examined by ^1H nmr spectroscopy at low temperature (see fig. 10). At -90°C the signal for the

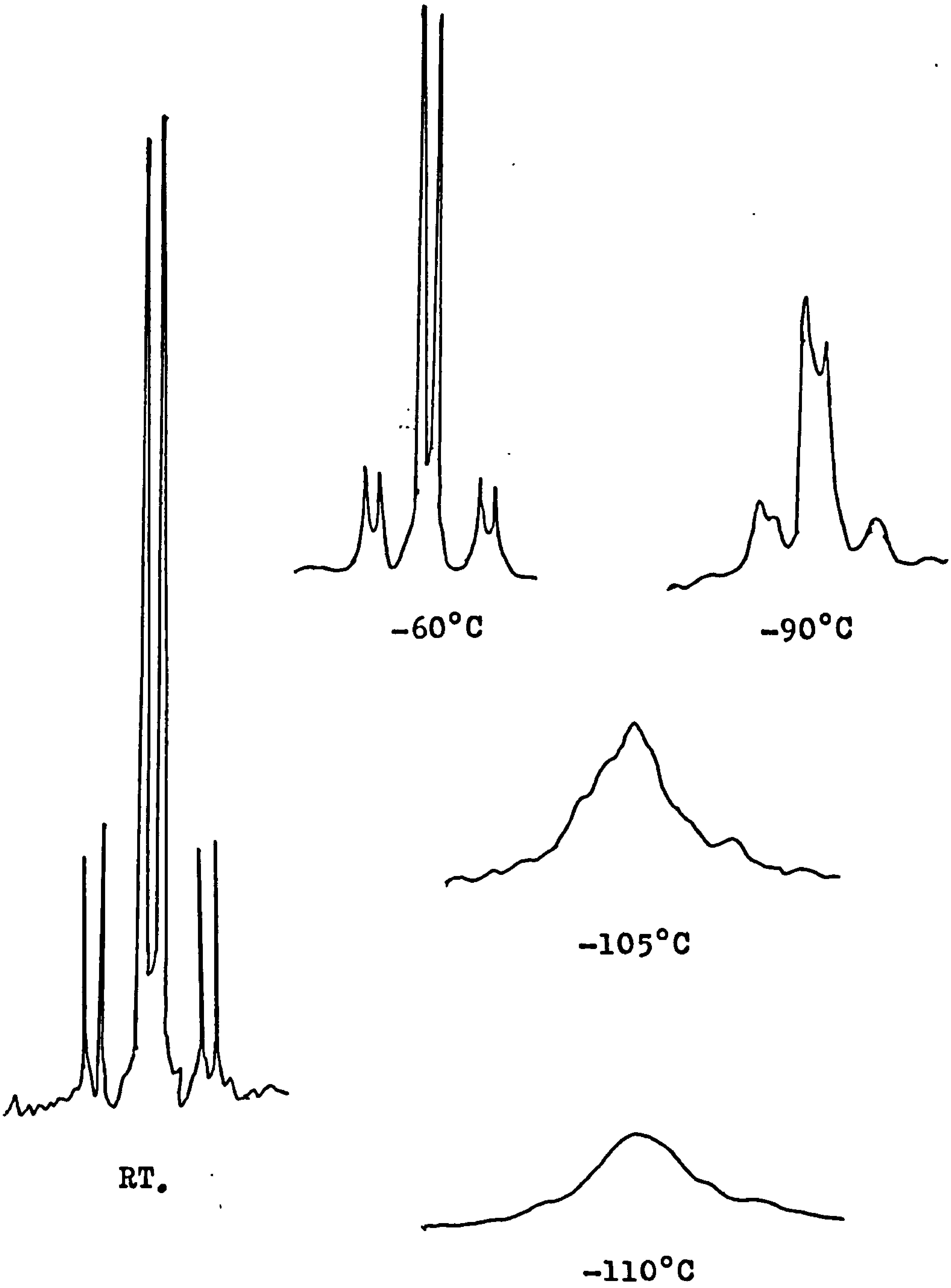


Figure 10

Low-temperature ^1H nmr spectra of C_5H_5 protons of $[PtCl(\eta^1-C_5H_5)(CO)(PPh_3)]$ isomer(I) in CD_2Cl_2.

C_5H_5 protons had begun to broaden, and the $^{31}P - ^1H$ coupling could only be resolved in the main peak, the satellites being broad. At -105°C, neither $^{31}P - ^1H$ nor $^{195}Pt - ^1H$ coupling was resolved, the C_5H_5 resonance being a broad peak. At -110°C the peak was broader and flatter, but the solution froze at lower temperatures, thus the AA'BB'X spectrum for a non-fluxional η^1-cyclopentadienyl group could not be observed. The fluxional process in other η^1-cyclopentadienyl complexes has been shown to be a series of 1,2-shifts, where the metal-carbon bond moves around the ring, and has been termed "ring-whizzing".[102-109]

The complexes cis-$[PtX_2(CO)L]$ (X = Cl; L = PPh_2Me, $PPhMe_2$, PEt_3 or $AsPh_2Me$: X = Br; L = $PPhMe_2$) also reacted with one equivalent of TlC_5H_5 to produce quantitative yields of complexes with structure (I). The same materials were produced when TlC_5H_5 was replaced by $Hg(C_5H_5)_2$ (X = Cl; L = PPh_2Me or $PPhMe_2$) or $[(Ph_3P)Au(C_5H_5)]$ (X = Cl; L = PPh_3), the byproducts in these cases being the soluble C_5H_5HgCl or Ph_3PAuCl.

These compounds (I) appear to be somewhat less stable than their PPh_3 analogue. Although they survive in solution for up to 24 hours, attempted isolation tended to lead to decomposition. $[PtCl(\eta^1-C_5H_5)(CO)(PMe_2Ph)]$ was finally obtained as an impure yellow solid; no attempts were made to isolate the others, and they were examined in solution after TlCl had been removed by filtration. Spectroscopic parameters are listed in tables 1 and 2.

Table 1. ^{1}H nmr of $[PtX(\eta^1-C_5H_5)(CO)L]$ isomer (I) in $CDCl_3$ at 25°C.

L	X	δC_5H_5(ppm)	J_{PH}(Hz)	J_{PtH}(Hz)	δCH_3(ppm)	J_{PH}(Hz)	J_{PtH}(Hz)	$\nu_{(CO)}$(cm^{-1})$^{(a)}$
PPh_3	Cl	+6.21	4.4	31.0	-	-	-	2085
$PMePh_2$	Cl	+6.25	4.5	30.5	+2.25	10.0	20.0	2080
PMe_2Ph	Cl	+6.18	4.5	30.0	+2.00	11.0	22.0	2080
PMe_2Ph	Br	+6.23	4.5	30.0	+2.00	12.0	23.0	2080
PEt_3	Cl	+6.17	4.3	29.0				2075
$AsMePh_2$	Cl	+6.25	-	35.4	+2.09	-	12.9	

(a) 0.02M solutions in $CHCl_3$, path length 0.5mm, NaCl cells.

Table 2. ^{31}P nmr of $[PtX(\eta^1-C_5H_5)(CO)L]$ isomer (I) in $CDCl_3$ at 25°C.

L	X	δP (ppm)	$^1J_{PtP}$(Hz)	$^2J_{CP}$(Hz) (c)
PPh_3	Cl	+18.6	1780	10.0
PPh_3	I	+12.4	1847	
PPh_3 (a)	F	+22.0	1821 (b)	
$PMePh_2$	Cl	+ 6.3	1760	10.5
$PMePh_2$	Br	+ 2.9	1780	
PMe_2Ph	Cl	- 5.0	1733	10.5
PMe_2Ph	Br	- 8.7	1749	9.5
PMe_2Ph (a)	I	-14.3	1804	
PEt_3	Cl	+21.3	1763	

(a) Measured at -60°C.

(b) $^2J_{PF}$ = 28.6 Hz.

(c) In complexes labelled with ^{13}CO.

Mechanism of Formation of $[PtX(C_5H_5)(CO)L]$ isomer (I)

The formation of $[PtCl(C_5H_5)(CO)PR_3]$ isomer (I) with C_5H_5 trans to PR_3 was expected from the reaction of the organomercurial. Numerous organomercury compounds react to produce this geometry.[23,110,112] Nucleophilic attack by anions on cis-$[PtX_2(CO)PR_3]$ usually displaces the halide trans to CO, however,[23] so the isomer with C_5H_5 trans to CO, (II), might have been expected from the reaction of TlC_5H_5. The non-appearance of this isomer is interesting, and might indicate the operation of a non-ionic reaction mode for C_5H_5Tl, an anomalous reaction of $C_5H_5^-$ compared to other carbanions, or a rapid rearrangement of (II) to (I). If isomer (II) (C_5H_5 trans to CO) was the initial product from TlC_5H_5 and cis-$[PtCl_2(CO)PR_3]$ it could be converted rapidly to isomer (I) by intermolecular transfers (which does not occur with aryl complexes.) Isomer (II) converts to (I) only very slowly and by a dissociative route.[23] Neither is any reaction observed between (II) ($R=C{\equiv}CMe$ or $C{\equiv}CPh$) and cis-$[PtCl_2(CO)(PR_3)]$ to produce isomer (I)[150]). Reversible conversion to an η^5-bonded compound is another possibility. Attempts were made to detect intermediates during formation of isomer (I) by nmr spectroscopic investigation at low temperatures, but none were observed. The first detectable products from TlC_5H_5 and $[PtCl_2(CO)PR_3]$ were (I), thus if such isomerisations are part of the preparative routes to (I), they must be faster than the initial formation of the precursor to (I).

Although intermolecular transfers of C_5H_5 between platinum complexes were found to be rapid, none of the investigated exchanges progressed at a sufficiently fast rate that it could not be monitored spectroscopically. The reversible conversion to an η^5-bonded C_5H_5, although possible, should not proceed at such a rate that intermediate η^5-C_5H_5 complexes were undetectable.

Thus, if isomer (I) is formed directly from TlC_5H_5 and <u>cis</u>-$[PtCl_2(CO)L]$, it must mean either that $C_5H_5^-$ reacts differently from other carbanions, or that a non-ionic reaction is occurring. There is no reason why $C_5H_5^-$ should react differently from $C_6H_5^-$, which attacks <u>cis</u>-$[PtCl_2(CO)L]$ to replace the Cl^- <u>trans</u> to CO.[23] Also, a cyclopentadienide carbanion might be expected to undergo H/D exchange with a deuterated solvent[151] and no such exchange was detected in the reactions of TlC_5H_5 with <u>cis</u>-$[PtCl_2(CO)L]$. Nor was any $CHCl_3$ produced when TlC_5H_5 was suspended in $CDCl_3$ for 24 hours.

Although solid TlC_5H_5 is ionic, it is perhaps unreasonable to expect free cyclopentadienide ions in solution. TlC_5H_5 is virtually insoluble in all organic solvents,[96] although it does slowly react in $CHCl_3$ or CCl_4, forming TlCl. Thus the reaction of platinum complex with TlC_5H_5 could be a heterogeneous one, with the <u>cis</u>-$[PtCl_2(CO)L]$ reacting at the surface of the TlC_5H_5. In this case, steric effects of the phosphine ligand may control the approach of the platinum complex to the surface, such that the chloride trans to phosphine is replaced, (fig. 11).

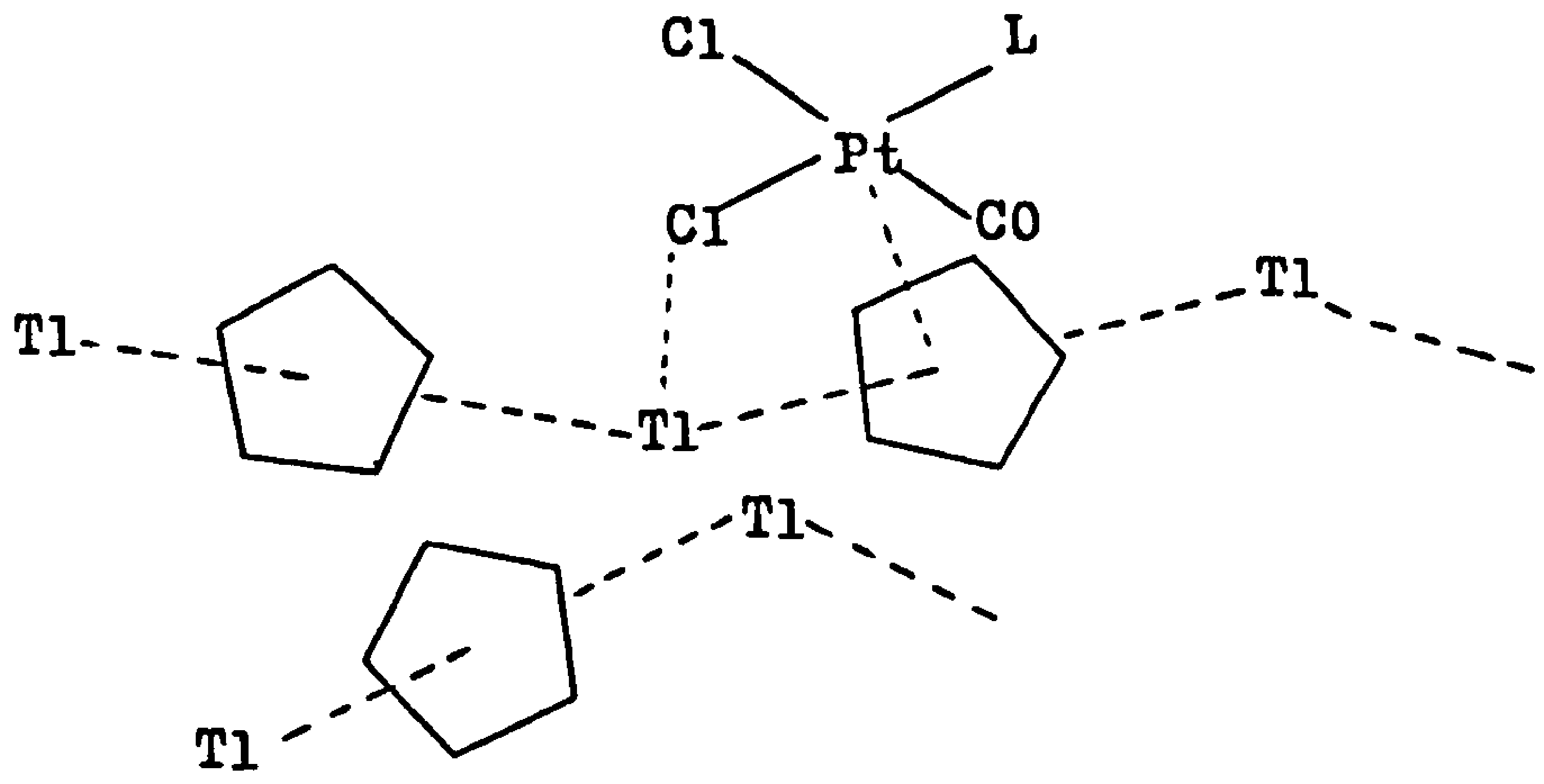
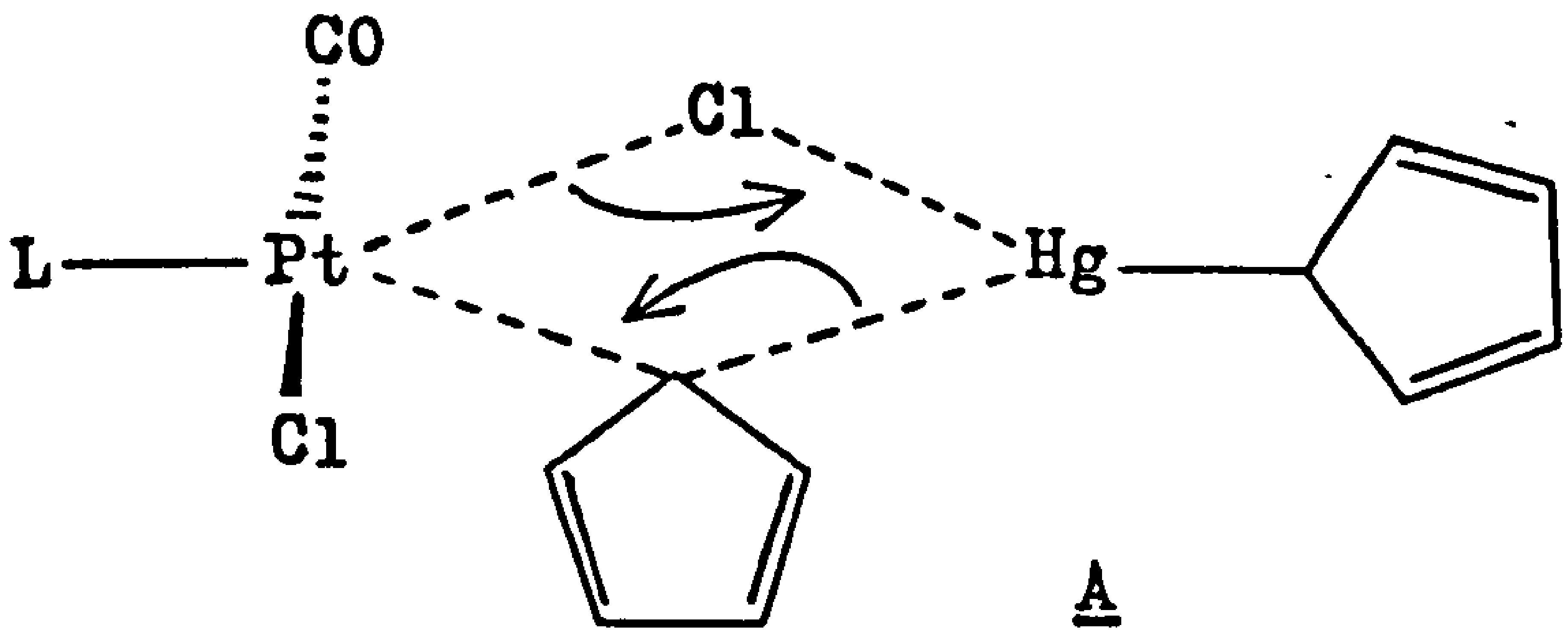


figure 11.

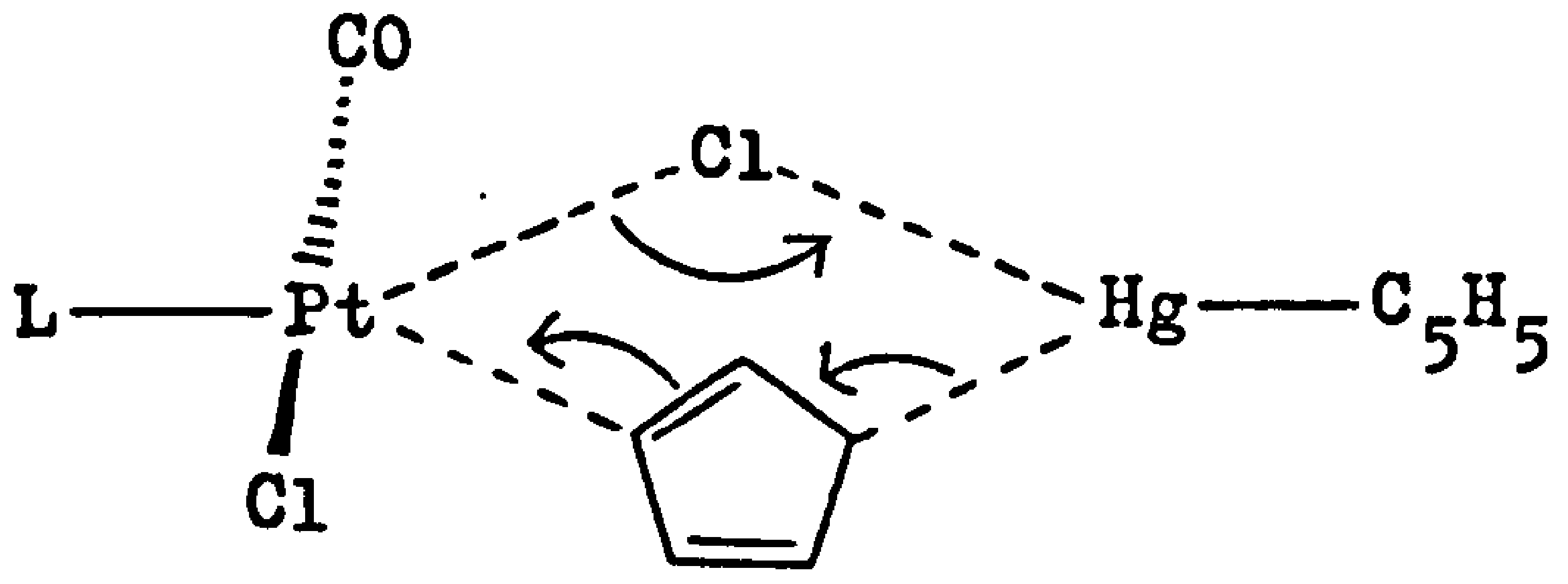
A further possibility is that small molecular fragments of C_5H_5Tl could react with the platinum complex in a similar way to $Hg(C_5H_5)_2$. However, it is not possible to determine which, if any, of these mechanisms is actually operating.

Organomercurials have been postulated to react with platinum complexes via S_E2 (cyclic), mechanisms[23] or oxidative addition/reductive elimination reactions.[114] The reaction of $Hg(C_5H_5)_2$ with cis-$[PtCl_2(CO)L]$ via an S_E2 (cyclic) mechanism would involve a transition state of type A.



A

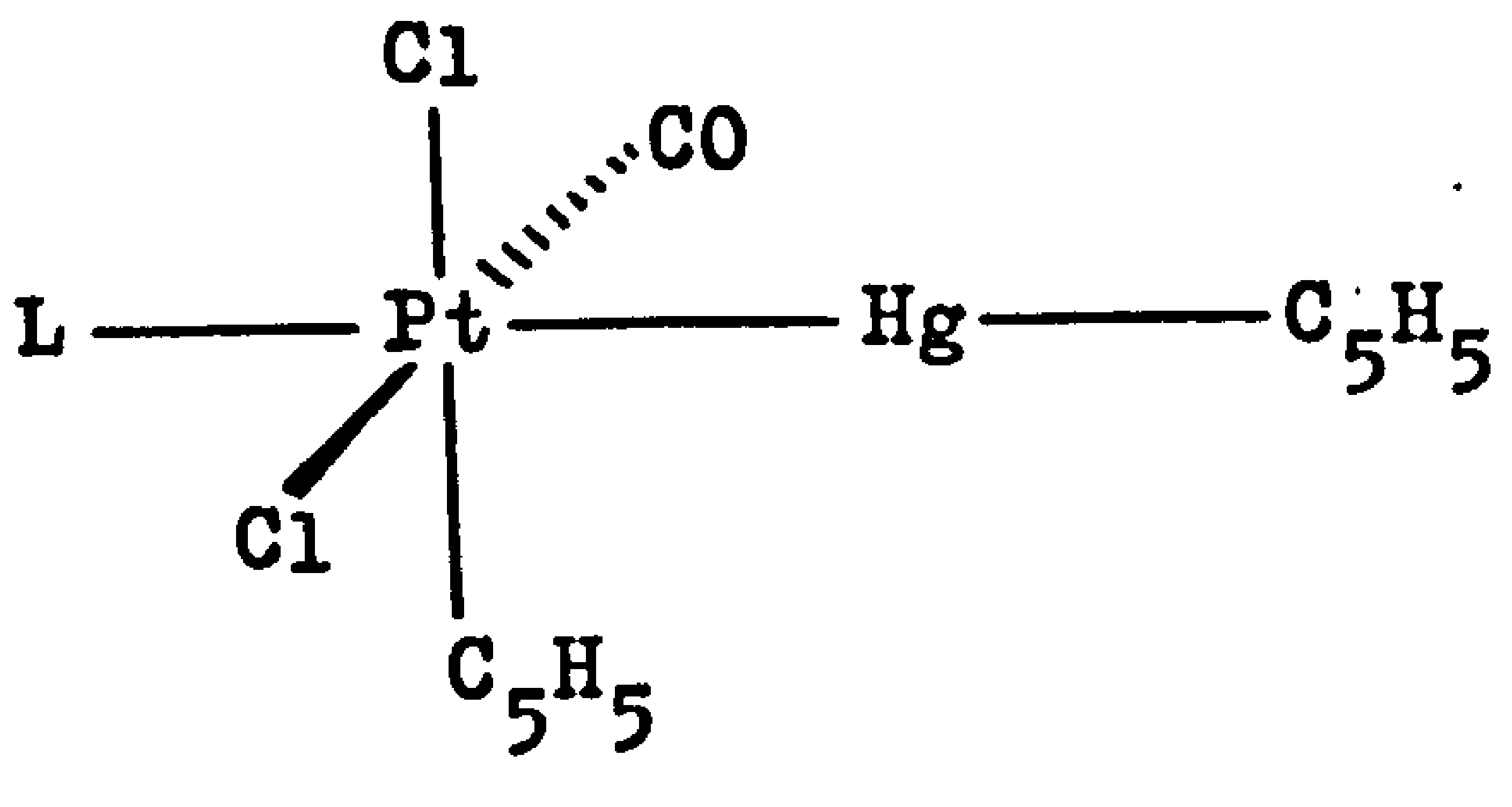
With C_5H_5 a second type of S_E2 (cyclic) mechanism is also possible, utilising the π-system of the C_5H_5 ring, and involving a transition state of type B.



B

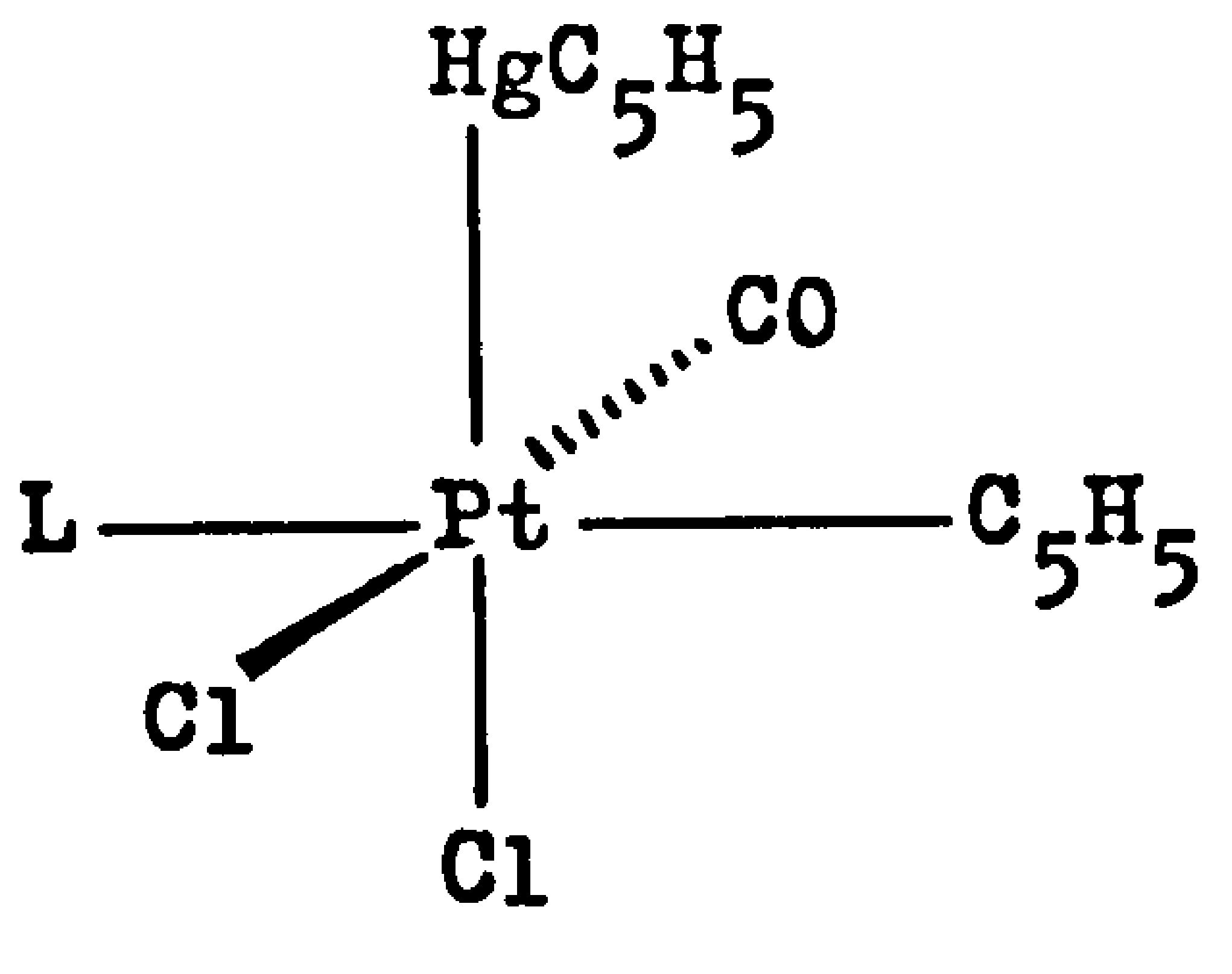
Such a transfer mechanism has been postulated in the exchange of C_5H_5HgCl with $HgCl^{152}$ and appears to operate in the exchange cf η^1-allyl groups.

The reaction could also proceed via oxidative addition/reductive elimination cycles. Concerted cis-oxidative addition with approach of Hg in the plane of the Pt complex and trans to phosphine would give the same product as an S_E2 cyclic mechanism, and the intermediate, C, can be regarded as related to transition state A by a strong Pt–Hg interaction.

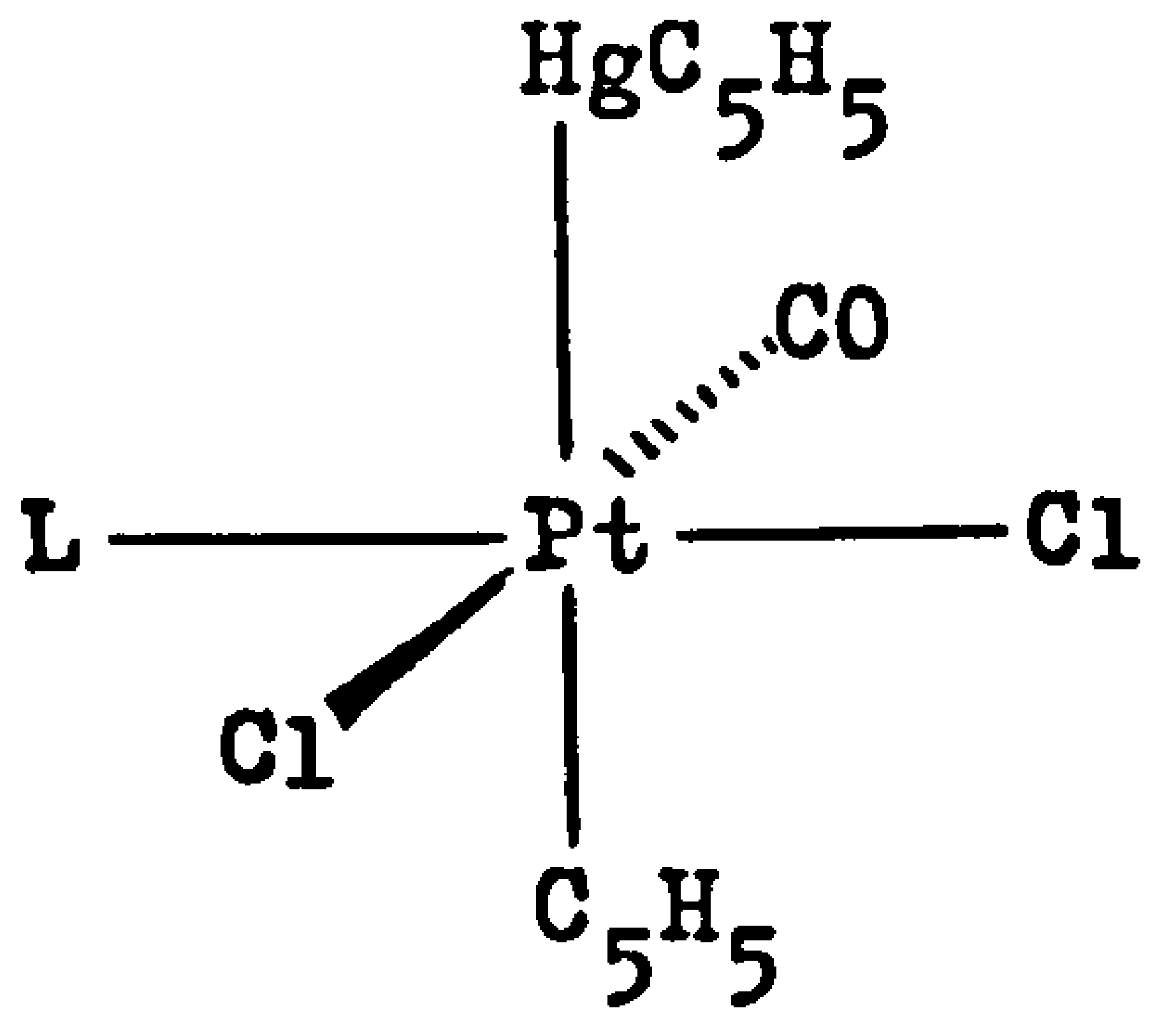


C

A concerted cis-oxidative addition/reductive elimination with an intermediate in which Hg approaches axial to the plane of the complex, is also possible, D.



D



E

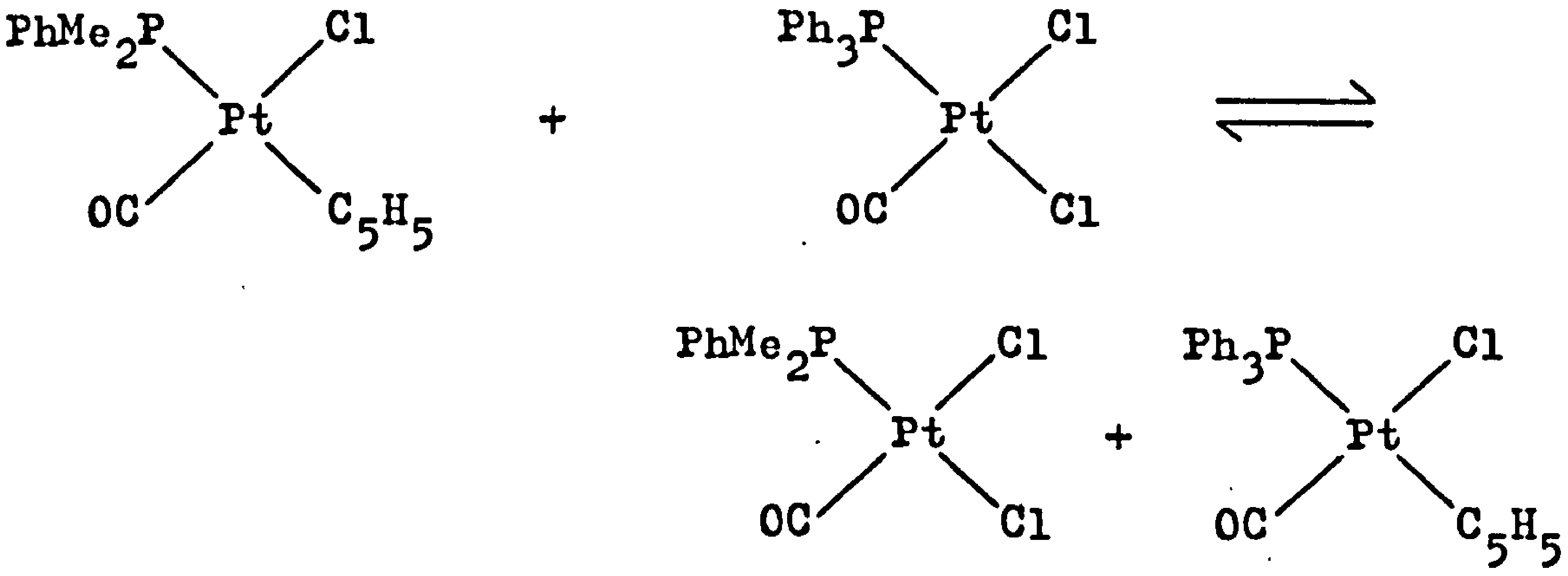
A trans-oxidative addition to produce an intermediate of geometry E would have to be by an ionic route, which is unlikely under the conditions employed. Concerted trans-oxidative additions are not allowed thermal processes on symmetry considerations.[14] Also, cis-reductive elimination of C_5H_5HgCl from E need not necessarily lead to one specific product, as either Cl could be eliminated.

Thus, a choice of three mechanisms remains. S_E2 (cyclic), oxid.add$^{n.}$/red.elim$^{n.}$ with Hg in the plane of CO and phosphine ligands (intermediate C) or Hg perpendicular to the plane of CO and phosphine (intermediate D). In the preparation of analogous aryl platinum complexes, the reaction between $HgAr_2$ and cis-[$PtCl_2(CO)L$] to produce [$PtClAr(CO)L$] (I) was considered to be S_E2 (cyclic),[153] because of the effect of substituents on the aryl group. Electron-withdrawing substituents inhibited the reaction and electron-donating substituents favoured the reaction, which is the situation expected in S_E2 (cyclic) reactions. Only para-substituents were used, to avoid complications due to steric effects.

Thus, the most likely reaction mode for $Hg(C_5H_5)_2$ is S_E2 (cyclic). The gold cyclopentadienyl [$Ph_3PAuC_5H_5$] could react in exactly the same manner as was considered for $Hg(C_5H_5)_2$, i.e. by S_E2 (cyclic) or oxidative addition/ reductive elimination. The same types of intermediates, A, C and D would be involved (with HgC_5H_5 replaced by $AuPPh_3$). The gold complex is also more likely to react by an S_E2(cyclic) mechanism, although there is less evidence against the alternatives.

Transfer of C_5H_5 from Isomer (I) to Platinum and Mercury

When $CDCl_3$ solutions of $[PtCl(\eta^1\text{-}C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) and cis-$[PtCl_2(CO)(PPh_3)]$ were mixed at ambient temperatures, a rapid equilibrium occurred, in less than 30 minutes as shown by ^{31}P nmr investigation.



This, and related systems revealed that, at equilibrium, the C_5H_5 group showed a preference for the less basic phosphine (or that with the smaller trans influence).[110]

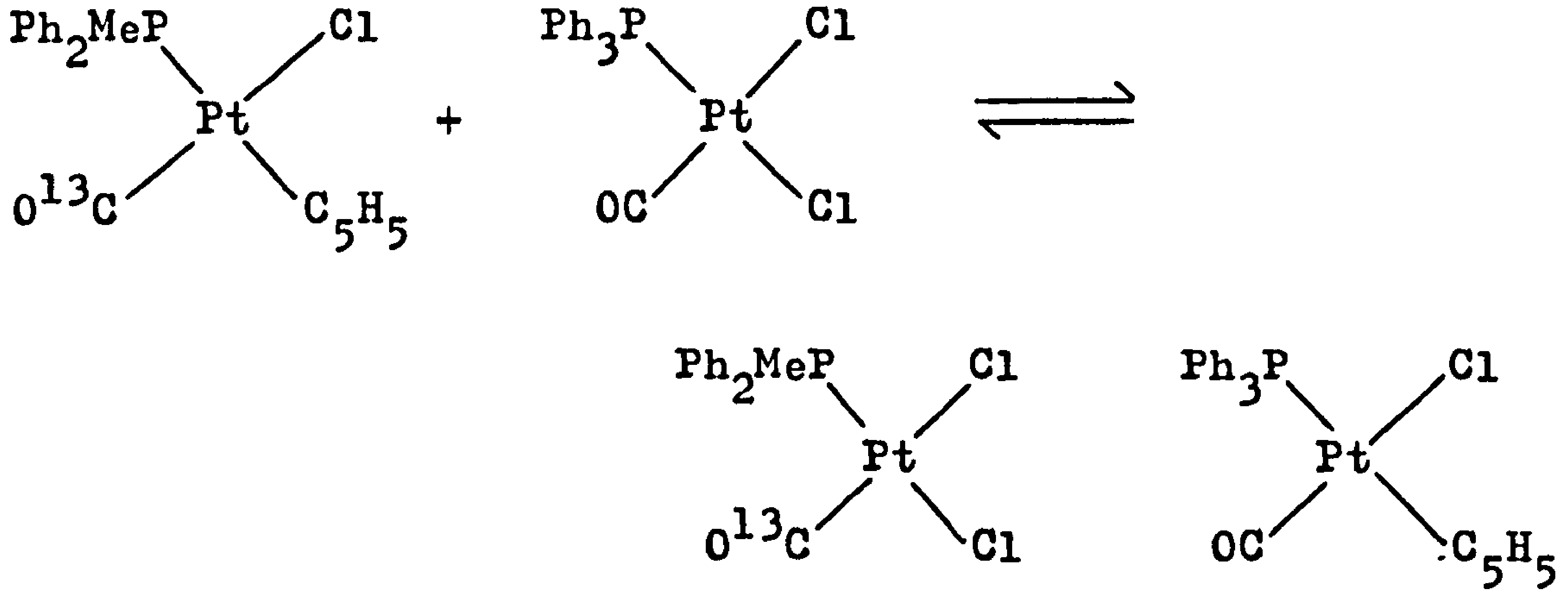
$$[PtCl(C_5H_5)(CO)(PPh_3)] + \textit{cis}\text{-}[PtCl_2(CO)(PMePh_2)] \rightleftharpoons \textit{cis}\text{-}[PtCl_2(CO)(PPh_3)] + [PtCl(C_5H_5)(CO)(PMePh_2)]$$

$$[PtCl(C_5H_5)(CO)(PPh_3)] + \textit{cis}\text{-}[PtCl_2(CO)(PMe_2Ph)] \rightleftharpoons \textit{cis}\text{-}[PtCl_2(CO)(PPh_3)] + [PtCl(C_5H_5)(CO)(PMe_2Ph)]$$

$$[PtCl(C_5H_5)(CO)(PMe_2Ph)] + \textit{cis}\text{-}[PtCl_2(CO)(PEt_3)] \rightleftharpoons \textit{cis}\text{-}[PtCl_2(CO)(PMe_2Ph)] + [PtCl(C_5H_5)(CO)(PEt_3)]$$

Equilibrium constants for the reactions were approximately 0.3, 0.2, and 0.45 respectively, and equilibration was complete in about 30 minutes.

That the migrating groups in these reactions were C_5H_5 and Cl, and not PR_3, was established by using samples labelled with ^{13}CO.



^{31}P nmr spectra easily identified the coupling of ^{13}C to ^{31}P as of cis geometry,[154] and showed that these parts of the molecule retained their integrity in the time of scrambling of C_5H_5 and Cl. Over 24 hours, however, a slower reaction was also observed, leading to scrambling of the CO (or PR_3) groups.

Experiments on compounds with different halides indicated that reactions of the type discussed were accompanied by exchange of halides. Thus, ^{31}P nmr spectroscopic examination of the reaction between $[PtCl(C_5H_5)(CO)PMe_2Ph]$ and cis-$[PtBr_2(CO)(PMe_2Ph)]$ showed that it reached equilibrium in less than 10 minutes, producing $[PtBr(C_5H_5)(CO)(PMe_2Ph)]$ and one isomer of $[PtClBr(CO)(PMe_2Ph)]$ (δ - 8.1 ppm, $^1J_{PtP}$= 2832 Hz: the coupling constant suggests that a halide is <u>trans</u> to PMe_2Ph.[154]). This isomer is presumably thermodynamic, since it is the major product when solutions of <u>cis</u>-$[PtCl_2(CO)(PMe_2Ph)]$ and <u>cis</u>-$[PtBr_2(CO)(PMe_2Ph)]$ are mixed. The other isomer (δ-13.1, $^1J_{PtP}$ = 2841 Hz) is only a minor product. If it were the kinetic product resulting from a single exchange of two halide ions, it would mean the involvement of different specific sites on each Pt. The similarity of Cl and Br makes this unlikely. ^{31}P nmr examination of the reactions between $[PtBr(\eta^1-C_5H_5)(CO)-(PMe_2Ph)]$ and <u>cis</u>-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ revealed that all the materials contained ^{13}CO after only 15 minutes. Since it is unlikely that CO exchange would have progressed this far in such a short time, the scrambling must originate from rapid halide and C_5H_5 migration. Mixing $[PtCl(\eta^1-C_5H_5)(CO)(PMePh_2)]$ and <u>cis</u>-$[PtBr_2(CO)(PMe_2Ph)]$ resulted in rapid (in less than 10 minutes) conversion of half of the cyclopentadienyl complex to its bromide analogue before C_5H_5 had been transferred to any great extent to the other platinum atom. Halide exchange in these systems appears to be two or three times faster than cyclopentadienyl exchange.

These C_5H_5 transfer reactions appear to proceed quite rapidly compared to other organic group-transfers. Exchange reactions of methyl and aryl groups between platinum (II) bis-phosphine complexes have been reported to take anything up to a month for completion, for example.[123] This comparison may be misleading, however, as the nature of the other ligands is thought to exert as big an influence on the transfer rate as the organic groups themselves.[148] No reaction was detected between [PtCl(C_5H_5)(CO)(PMe_2Ph)] and cis-[$PtCl_2L_2$] (L = PMe_2Ph or PPh_3) in 24 hours. Also, where the site trans to phosphine was blocked by another organic group, (C_2Cl_3 was chosen as it is fairly unreactive), in [PtCl(C_2Cl_3)(CO)($PMePh_2$)] isomer (I), no C_5H_5 transfer reaction from [PtCl(C_5H_5)(CO)(PPh_3)] could be detected in 24 hours. This showed that there was no C_5H_5 transfer to the site trans to CO, and no exchange between either organic groups, or phosphines, occurred in this time. This implies that the reactions involved in scrambling the ^{13}CO label in a mixture of [PtCl(C_5H_5)(CO)L] and cis-[$PtCl_2$(CO)L^1] is more likely to involve CO exchange than phosphine exchange.

However, a slow phosphine exchange was observed in the reaction of cis-[$PtMe_2(PEt_3)_2$] with cis-[$PtCl_2(PMe_2Ph)_2$], taking about 30 times as long as the alkyl exchange reaction.[148] In this system, it was also found that the alkyl group had a preference for the more basic phosphine.

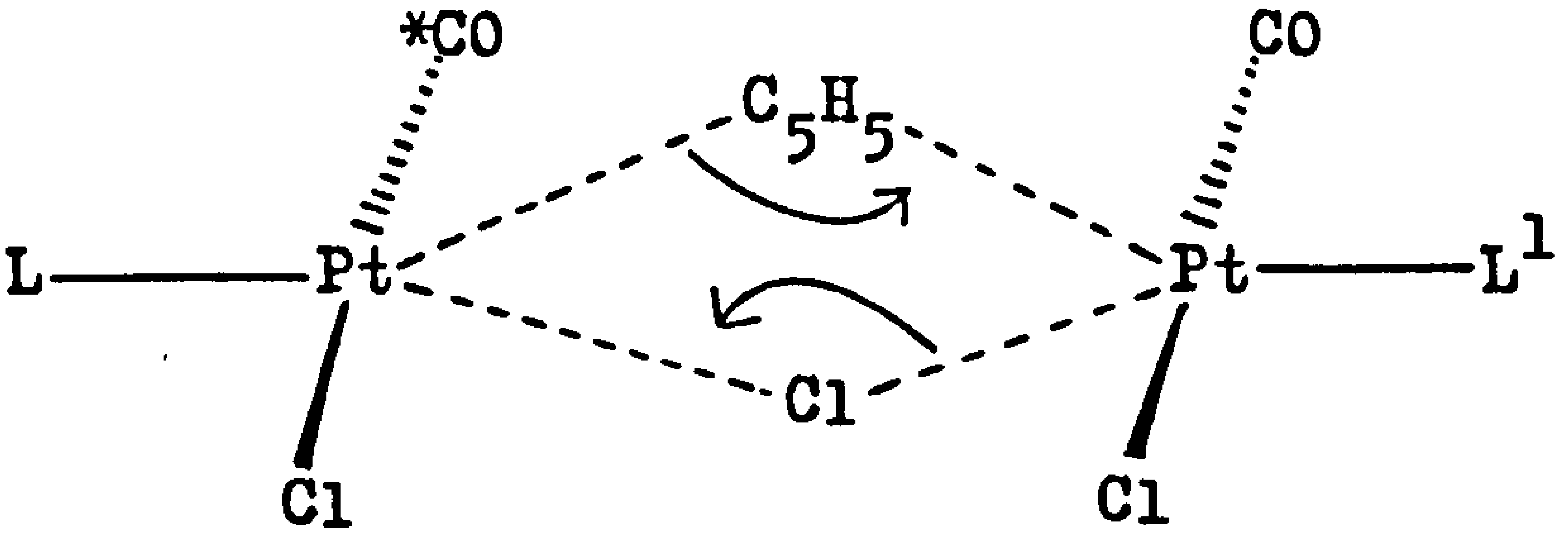
The identity of the organic group also has a profound effect on the rate of transfer. Three analogous aryl platinum compounds, [PtClAr(CO)(PMe_2Ph)] isomers (I), (Ar = $C_6H_4CO_2Me$-p, C_6H_4OMe-o, C_6H_4Cl-o) were studied. These aryl complexes were chosen because they exist in solution largely as isomer (I), whereas many other complexes exist largely as [$Pt_2(\mu\text{-}Cl)_2(COAr)_2L_2$]. (Most organic group isomer (I) type complexes undergo carbonyl insertion and exist in solution as an equilibrium mixture of isomer (I) and acyl or aroyl platinum dimers).[23,110,112]

The aryl group of [PtCl($C_6H_4CO_2Me$-p)(CO)(PMe_2Ph)] isomer (I) was transferred to the platinum of cis-[$PtCl_2$(CO)(PPh_3)] about 3 times more slowly than C_5H_5 was transferred, and equilibration was complete within 2½ hours. The ortho-substituted aryl of [PtCl(C_6H_4OMe-o)(CO)(PMe_2Ph)] showed no substantial movement to the same dichloroplatinum complex until ca 12 hours had elapsed and required about 1 week to reach equilibrium. Interestingly, the exchange of C_6H_4Cl-o for Cl in the reaction between [PtCl(C_6H_4Cl-o)-(^{13}CO)(PMe_2Ph)] and cis-[$PtCl_2$(CO)(PPh_3)], which showed substantial transfer of C_6H_4Cl-o in 12 hours, was not accompanied by $^{12}CO/^{13}CO$ scrambling in this time. Such scrambling would be appreciable in the analogous cyclopentadienyl system. $^{12}CO/^{13}CO$ scrambling had occurred by the time equilibrium was reached, in ca 1 week. This suggests a link between the various transfers. As in the cyclopentadienyl system, the aryl groups showed a preference for the platinum atom with the less basic phosphine.

The C_5H_5 group was also cleaved from isomer (I) by $HgCl_2$:-

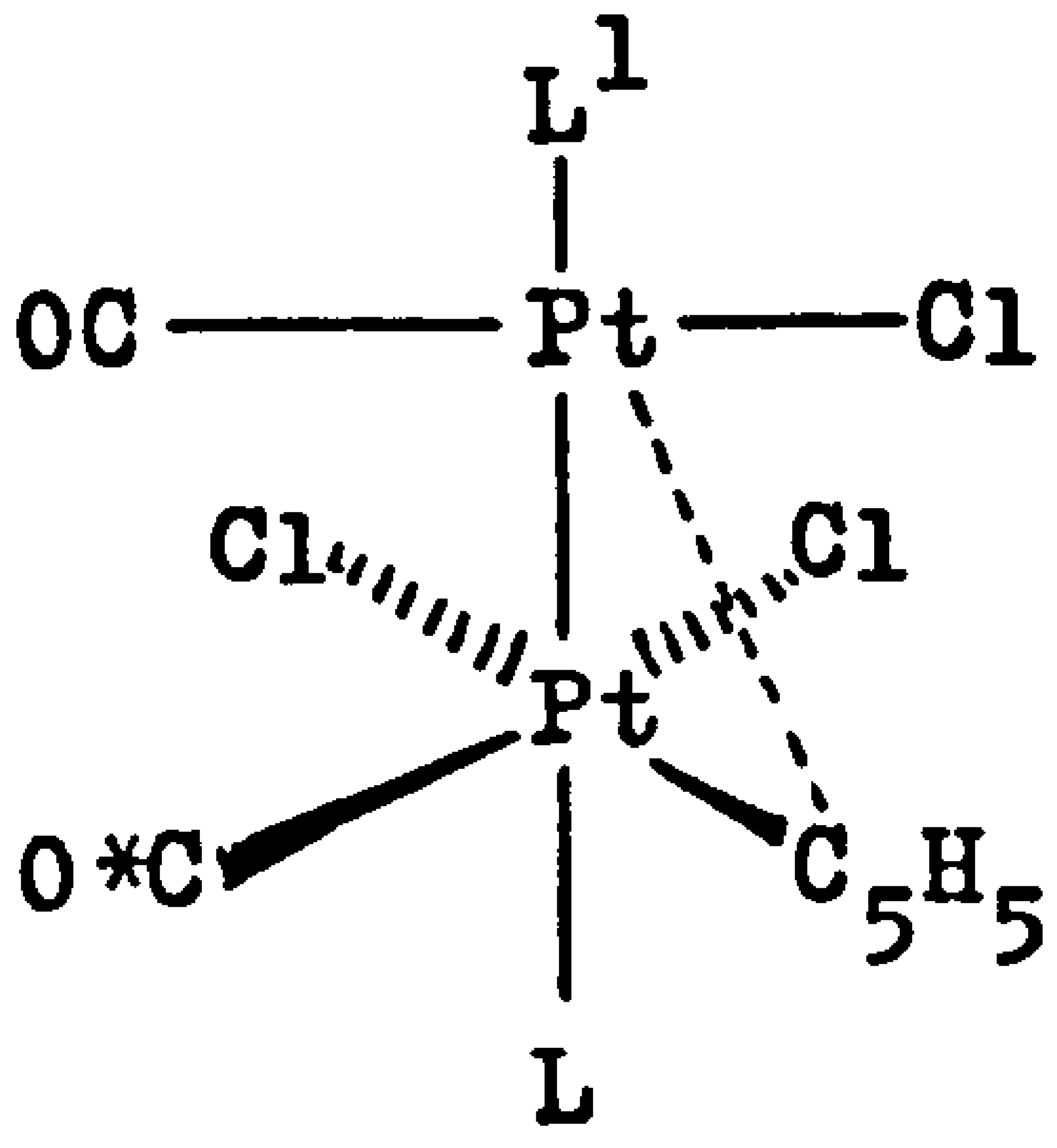
$$I(PMe_2Ph) + HgCl_2 \rightarrow HgCl(C_5H_5) + cis\text{-}[PtCl_2(CO)(PMe_2Ph)]$$

The transfer of C_5H_5 between platinum atoms could also be by either S_E2 (cyclic) or oxidative addition/reductive elimination reactions, and both mechanisms have been proposed for other organic group transfers.[119,123,143,149] In all of the C_5H_5 transfers from (I) to <u>cis</u>-[$PtCl_2(CO)L$], the groups exchanged are <u>trans</u> to phosphine, the expected result of an S_E2 (cyclic) mechanism. The transition state is shown by F.

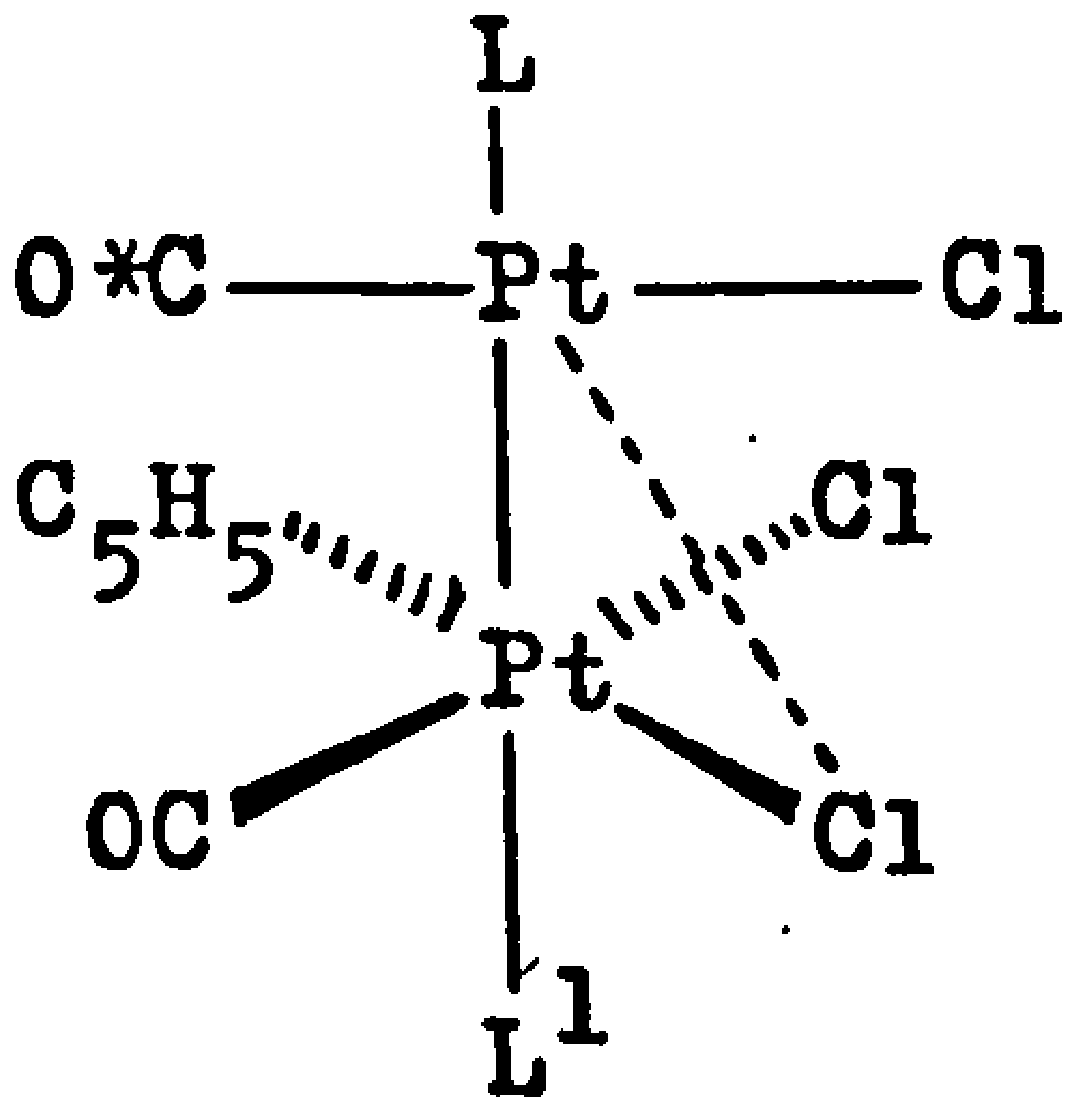


F

Again, there are oxidative addition/reductive elimination routes which could lead to the same product.



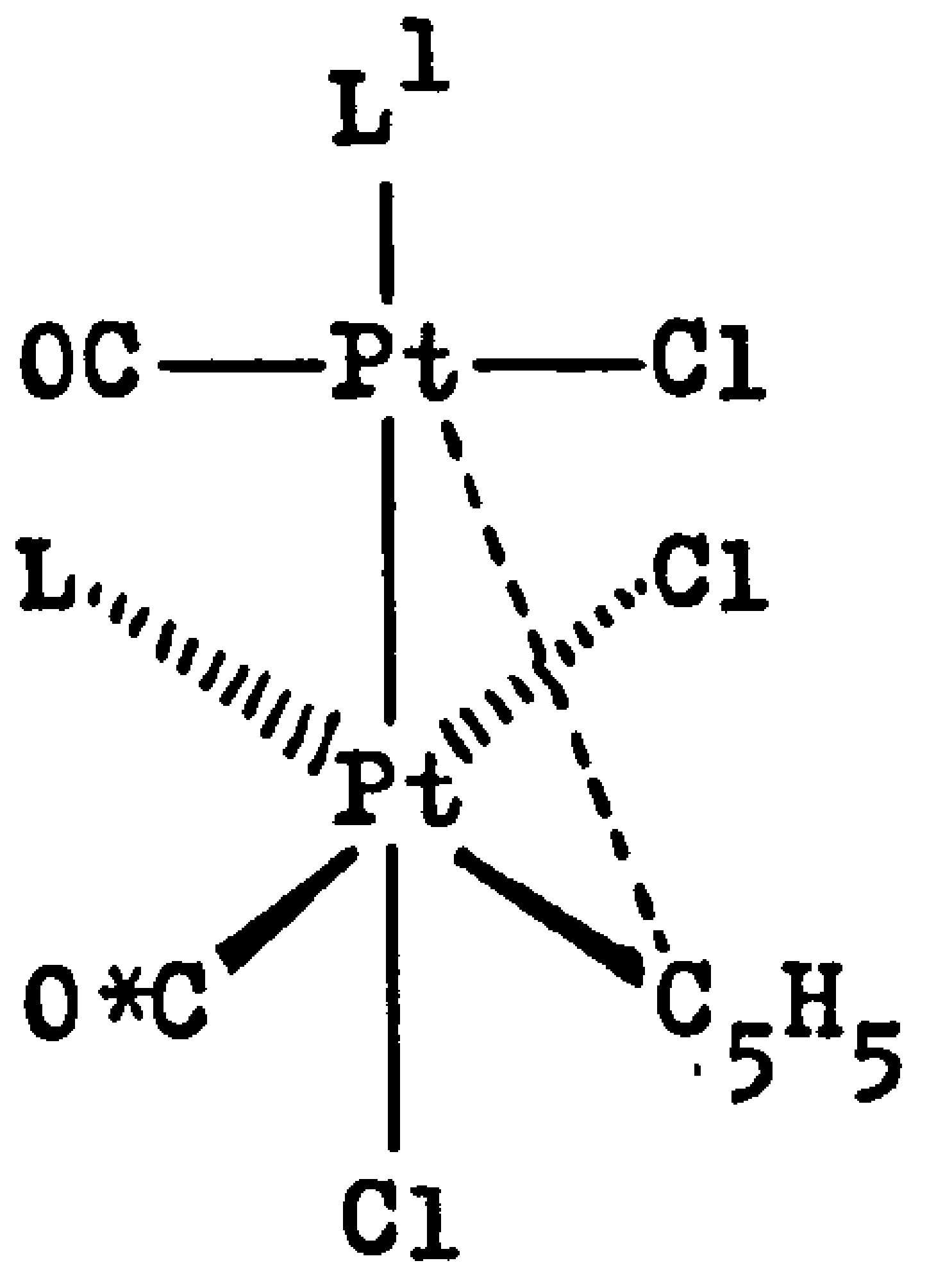
G



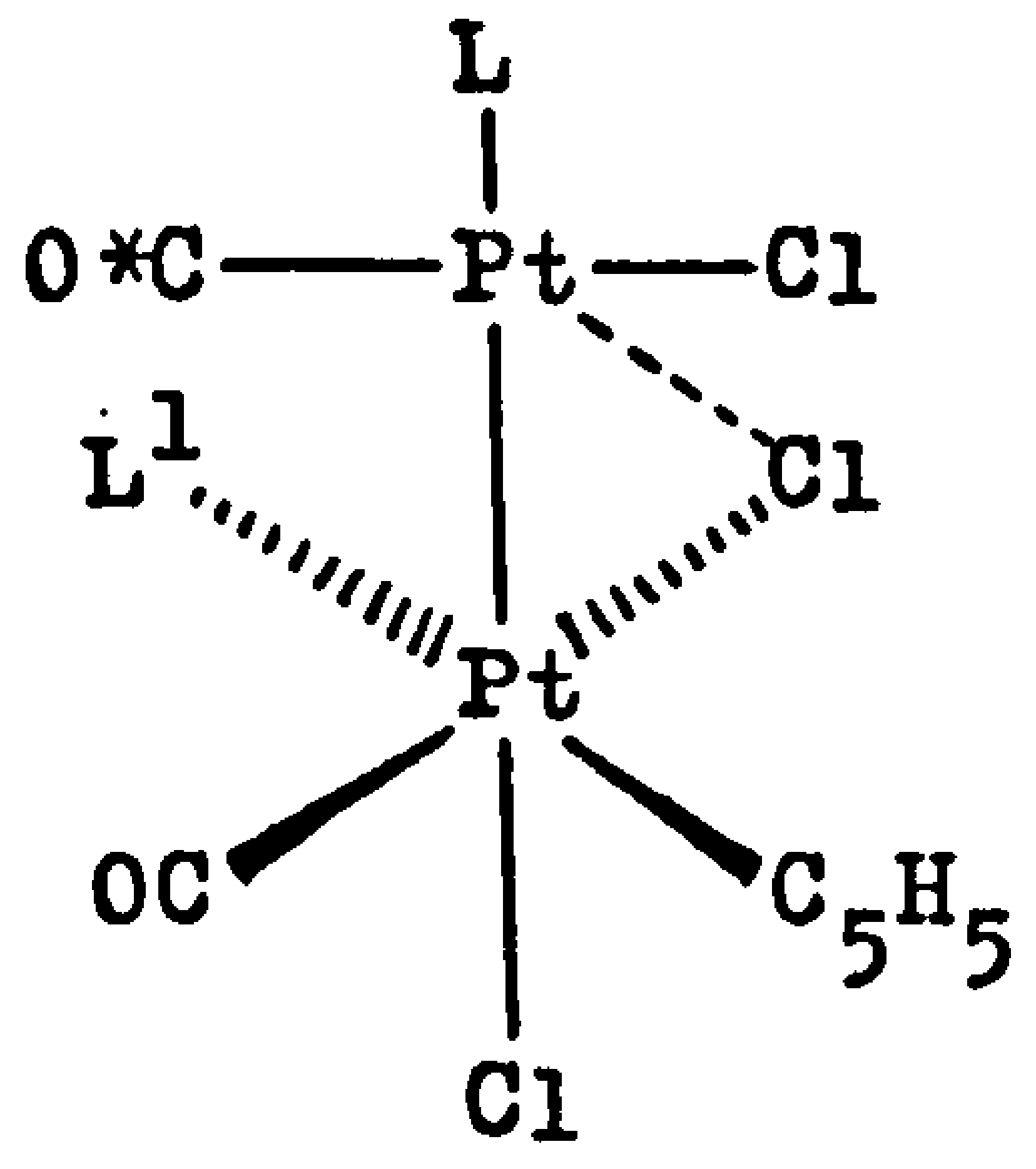
H

G and H represent the two extremes of Pt-Pt bond formation from the transition state, F. Concerted <u>cis</u>-oxidative addition of <u>cis</u>-[$PtCl_2(CO)L^1$] to (I) gives the intermediate G, and addition of Pt-C_5H_5 of (I) to <u>cis</u>-[$PtCl_2(CO)L^1$] gives the intermediate H. That is, the platinum complex acting as the electrophile ends up with its platinum <u>trans</u> to phosphine in the octahedral complex of the other platinum.

These are not the only possible intermediates from oxidative addition/reductive elimination routes.



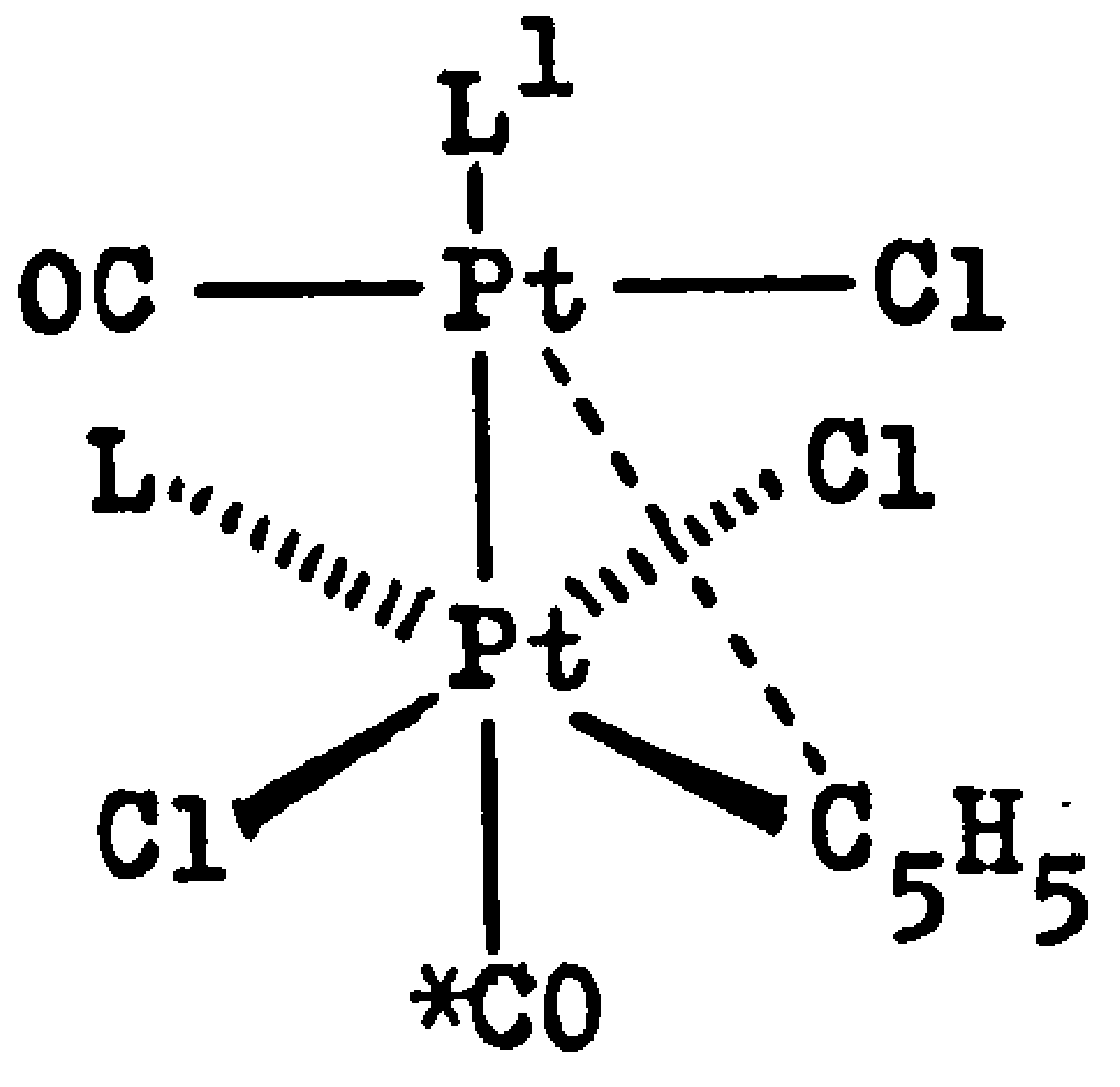
J



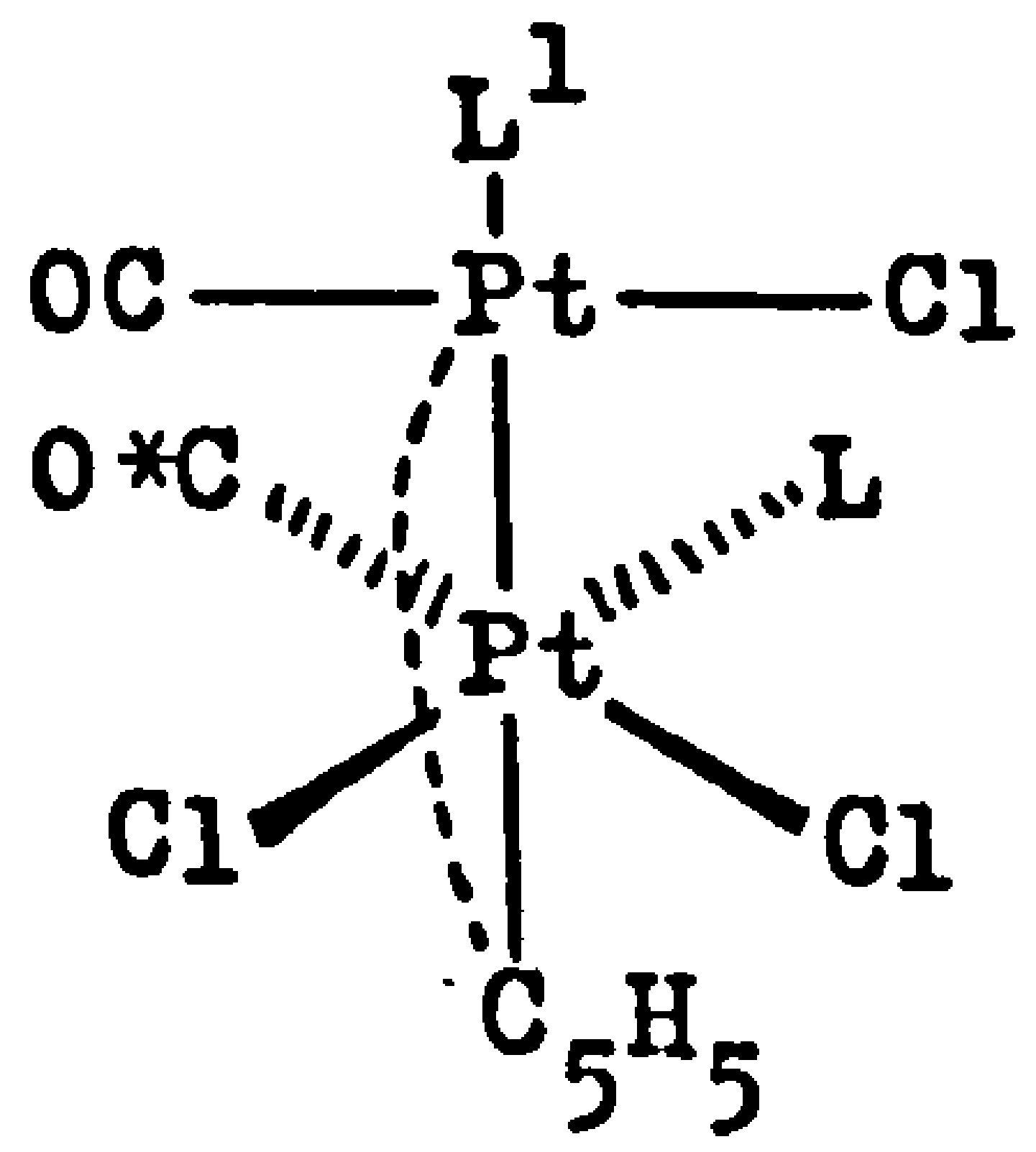
K

<u>cis</u>-oxidative addition of <u>cis</u>-[PtCl$_2$(CO)L^1] to (I) to displace Cl <u>trans</u> to CO gives intermediate J, and addition of (I) to <u>cis</u>-[PtCl$_2$(CO)L^1] displacing Cl <u>trans</u> to L^1 gives intermediate K. That is, the platinum complex acting as the electrophile ends up <u>cis</u> to phosphine and CO in the octahedral coordination around the other platinum.

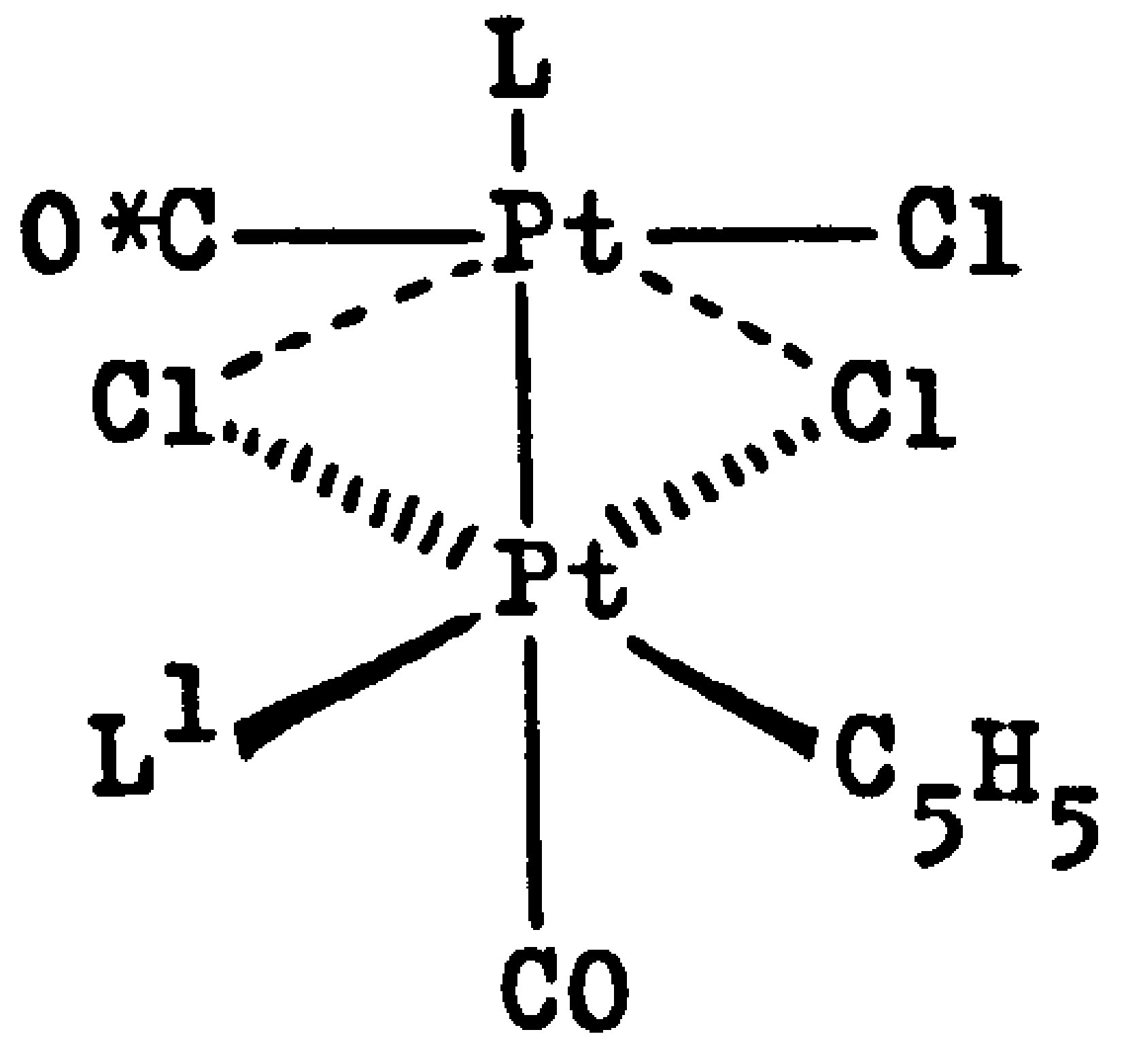
These are the only four intermediates which could lead to the product (by the reductive elimination indicated on each). The other four intermediates attainable by <u>cis</u>-oxidative additions would not yield the desired product on elimination, L,M,N,P.



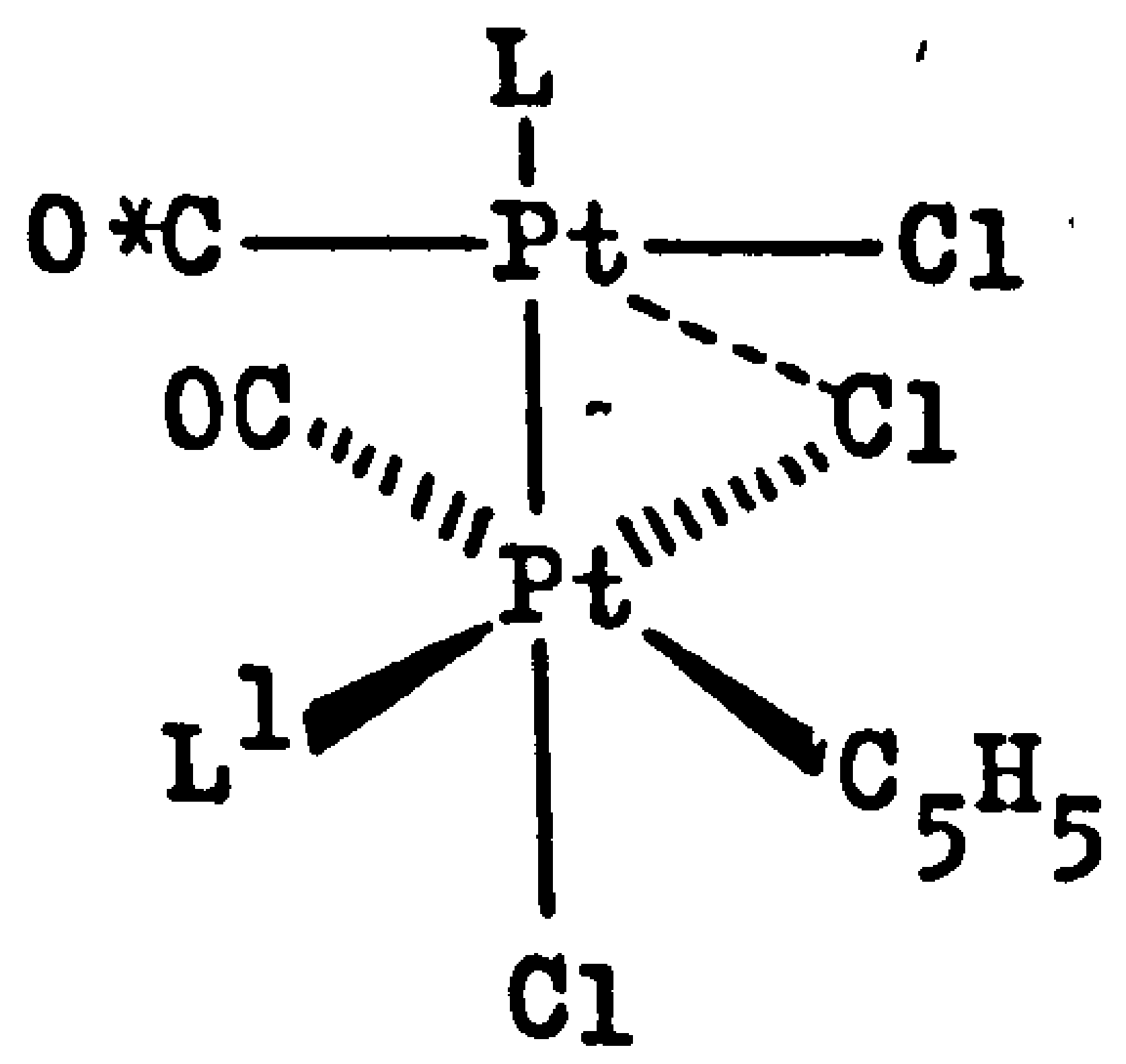
L



M



N



P

L and M would arise from cis-[$PtCl_2(CO)L^1$] acting as the electrophile and oxidatively adding to isomer (I), while N and P would be the result of isomer (I) acting as the electrophile and oxidatively adding to cis-[$PtCl_2(CO)L^1$]. None of these four intermediates would give the correct products on reductive elimination.

cis-reductive elimination of the groups indicated in intermediates L and N would require a twist mechanism to produce the observed products which is symmetry forbidden.[155] Even if such a forbidden elimination were to take place, intermediate N could give a mixture of products. Intermediate M could only lead to the observed products by a trans-reductive elimination, which is also symmetry forbidden as a concerted process.[14] Cis-reductive elimination from P would produce isomer (II) of [$PtCl(C_5H_5)(CO)L$], instead of isomer (I).

Cis-oxidative additions are not the only type known. A trans-oxidative addition of cis-[$PtCl_2(CO)L^1$] to isomer (I) could also give intermediate K for example, but trans-oxidative additions are not allowed as a concerted process,[14] and would have to proceed by an ionic route, which is unlikely under the conditions employed.

In the reaction between cis-[$PtCl_2(CO)L$] and $Hg(C_5H_5)_2$ there were two possible oxidative addition intermediates, since it was clear that the mercurial was the electrophile. However, in the isomer (I) + cis-[$PtCl_2(CO)L^1$] reaction, there were four possible oxidative addition/ reductive elimination intermediates. This is because no decision was made as to which complex (isomer (I) or cis-[$PtCl_2(CO)L^1$])was acting as the electrophile and which was acting as the nucleophile. This depends on the nature of the ligands. As far as the phosphine is concerned, the more basic phosphine (that with a higher trans influence) increases the nucleophilicity of its platinum atom. An organic group also has a higher trans influence than a chloride, and should increase the nucleophilicity of its platinum atom. In isomer (I), however, the phosphine is trans to the organic group, so how the effects balance out is difficult to determine. There may also be steric effects.

Exactly the same transition states and intermediates (J→P) could be drawn for the transfer of an aryl group from [PtCl(Ar)(CO)L] isomer (I) to cis-[$PtCl_2(CO)L^1$], with Ar replacing C_5H_5. The three aryl groups studied, $C_6H_4CO_2Me$-p, C_6H_4OMe-o and C_6H_4Cl-o all transferred to give isomer (I), the $C_6H_4CO_2Me$-p being much faster than the two ortho-substituted aryls, although still slower than the C_5H_5. It was found[153] that in the reaction of $HgAr_2$ with cis-[$PtCl_2(CO)L$] to produce isomer (I), para- and meta-substituted aryls were transferred at a rate that correlated roughly with their Hammett parameters and that electron donating substituents enhanced the reaction, which was consistent with S_E2 (cyclic) reactions. Ortho-substituted aryls were transferred only very slowly and steric reasons were considered to be the important cause, overriding electronic effects of the substituents. It was also found, however, that $HgCl_2$ cleaved C_6H_4Me-o faster than $C_6H_4CO_2Me$-p from a mixture of the isomer (I)'s. This was rationalised in terms of oxidative addition/reductive elimination, since steric hinderance of the ortho group was considered to be less important than in S_E2 (cyclic) reactions. The electron donating Me increased the nucleophilicity of platinum while the electron withdrawing CO_2Me decreased it. The more nucleophilic platinum thus underwent oxidative addition faster.

In the transfer of aryl from isomer (I) to cis-$[PtCl_2(CO)L]$, the ortho substituents retard the reaction, despite being more electron donating than p-MeO_2C, thus apparently conforming to the S_E2 (cyclic) mechanism rather than the oxidative addition/reductive elimination mechanism.

The C_5H_5 transfers are also probably via an S_E2 (cyclic) mechanism, although obviously oxidative addition/reductive elimination cannot be ruled out.

The lack of reaction between $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ and cis-$[PtCl_2(PMe_2Ph)_2]$ may simply reflect the effect of different substituents. cis-$[PtCl_2L_2]$ reacts more slowly with C_5H_5Tl than cis-$[PtCl_2(CO)L]$. However, the lack of a reaction between C_5H_5 isomer (I) and $[PtCl(C_2Cl_3)(CO)$-$(PMePh_2)]$ is interesting. Obviously the two organic groups being trans to phosphine, it might have been expected that some exchange would take place. However, C_2Cl_3 is a very unreactive substituent and $Hg(C_2Cl_3)_2$ only reacts extremely slowly with cis-$[PtCl_2(CO)L]$ to produce (I).[153] This did show, however, that C_5H_5 would not transfer to the site trans to CO when the other site trans to phosphine was occupied. There was no exchange of phosphine between the two isomers (I) which may support the idea that $^{13}CO/^{12}CO$ scrambling, which occurred in both C_5H_5 and C_6H_4Cl-o transfers, was due to an exchange involving carbon monoxide and not phosphines.

The rapid halide exchange (ca. 3 times faster than C_5H_5) is not unexpected. Rapid halide exchanges have been reported for the reaction of $[PdX_2(dpm)]$ and $[PdY_2(dpm)]$ (X,Y = Cl,Br,I),[156] and it was suggested that the mechanism involved formation of halogen bridges between palladium complexes. In reactions of isomer (I), only one mixed halide isomer was observed [PtClBr(CO)L] (CO and L cis), and this same isomer was the major product when cis-$[PtCl_2(CO)L]$ and cis-$[PtBr_2(CO)L]$ were mixed. Since this isomer is the thermodynamic one, rather than the kinetic one, and since it is not possible to assign which halide (Cl or Br) is trans to phosphine, detailed mechanistic information cannot be obtained. It is likely that the halide exchange occurs via halide bridges and that the transition state is analogous to the S_E2 cyclic (fig. 12).

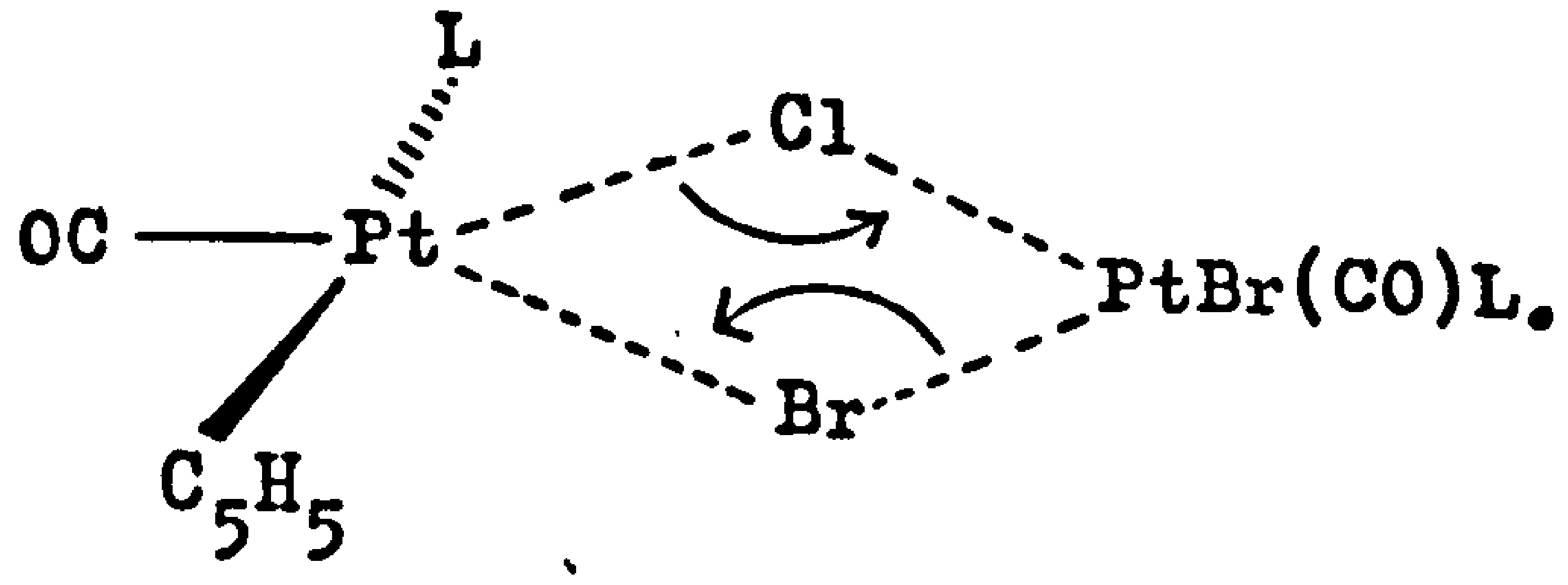
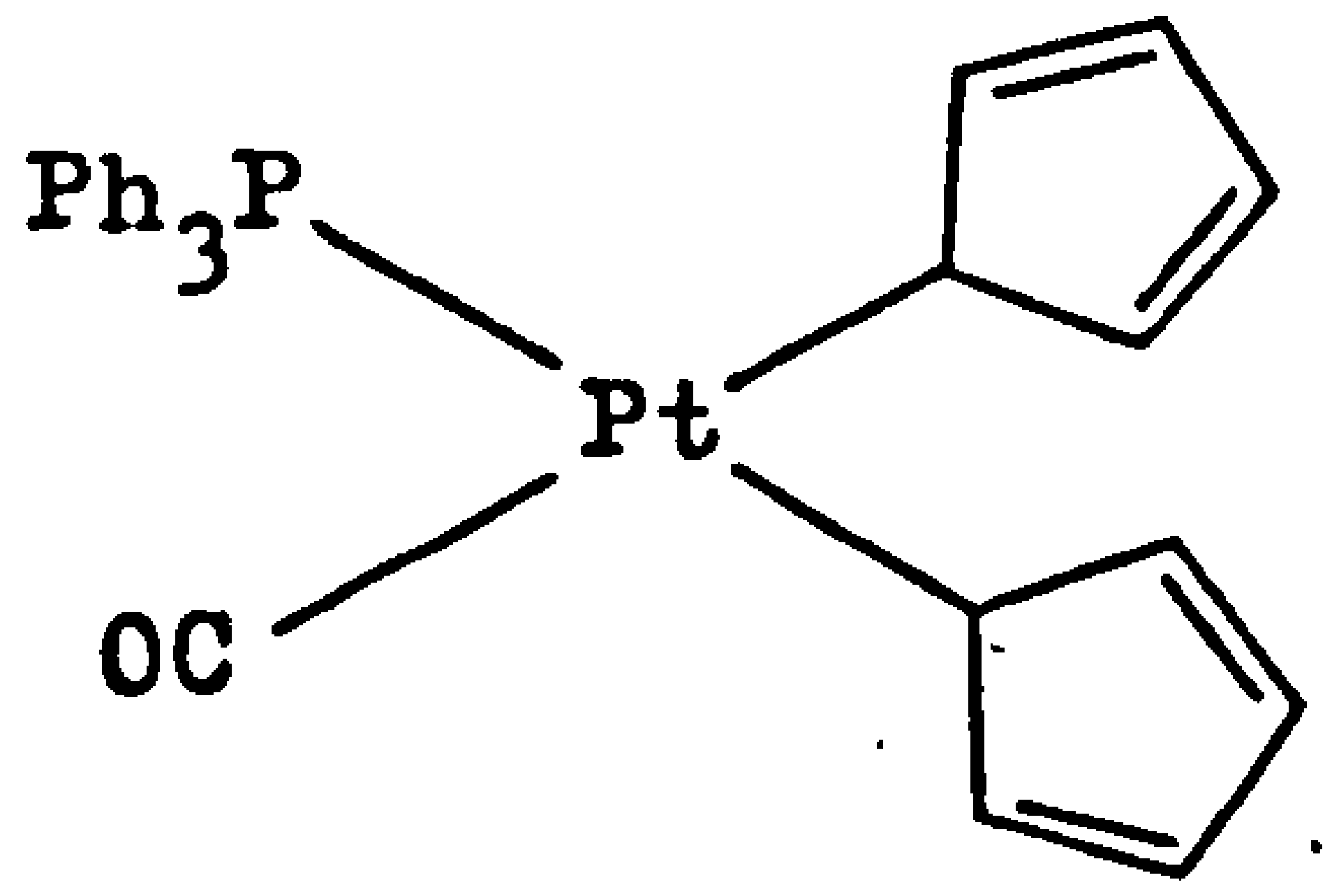


figure 12.

$HgCl_2$ cleaved the C_5H_5 from $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ to regenerate cis-$[PtCl_2(CO)(PMe_2Ph)]$. This could have been via either an S_E2 (cyclic) mechanism or oxidative addition/reductive elimination mechanism. The latter has been suggested for cleavage of an aryl group from aryl isomer (I).[153] The reaction of $HgCl_2$ with a C_5H_5 isomer (I) was much slower than that of a cis-$[PtCl_2(CO)L]$ complex, but no definite mechanistic information can be extracted from this.

Reactions of cis-bis (σ-cyclopentadienyl) platinum Complexes

The reaction of cis-$[PtCl_2(CO)(PPh_3)]$ with excess TlC_5H_5 led to the formation of the bis(cyclopentadienyl) complex, cis-$[Pt(\eta^1-C_5H_5)_2(CO)(PPh_3)]$:-



This decomposed much more readily than the mono-cyclopentadienyls, and could not be isolated. Spectroscopic data are given in table 3 for this bis (σ-cyclopentadienyl) complex and the analogous PPh_2Me and PMe_2Ph complexes. As with compounds (I), bis-cyclopentadienyl complexes of other phosphines appear to be even less stable, and relatively small amounts were obtained in solution before decomposition products became apparent. The reaction to produce $[Pt(C_5H_5)_2(CO)L]$ complexes is unpredictable and non-reproducible, very often further reaction occurs to produce a dimeric platinum species,

Table 3. ^{31}P and ^{1}H nmr of cis-[Pt(η^1-C_5H_5)$_2$(CO)L] at 25°C in $CDCl_3$.

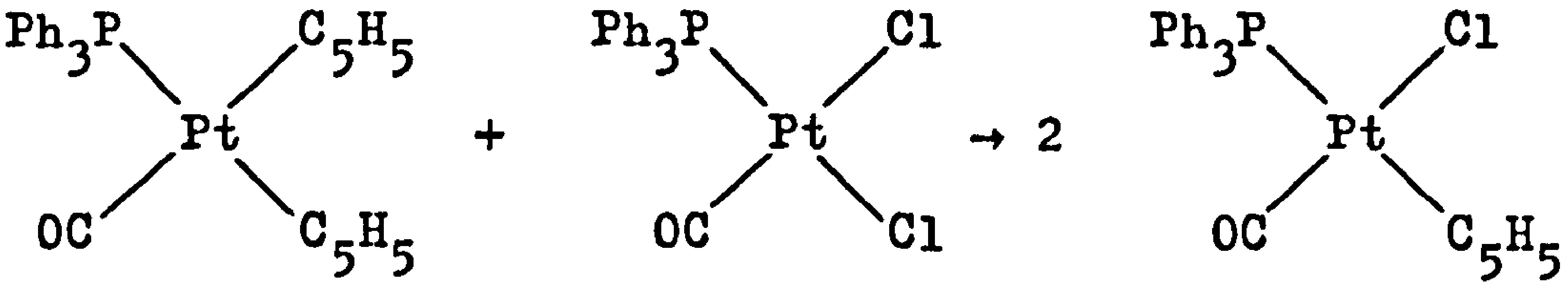
L	δC_5H_5	J_{PH}(Hz)	J_{PtH}(Hz)	δP(ppm)	$^1J_{PtP}$(Hz)
PPh_3(a)	+5.90 +5.45	3.5 5.0	33.0 33.0	+20.0	2127
$PMePh_2$	+5.95 +5.45	3.0 5.0	39.0 32.0	+ 3.0	2107
PMe_2Ph	+5.89(b) +5.41	3.0 4.5	32.0 30.0	- 9.8	2095
PEt_3	+6.02 +5.38	2.9 4.2	32.8 30.6		

(a) IR in $CHCl_3$ (0.02M). ν_{CO} = 2075 cm^{-1}.

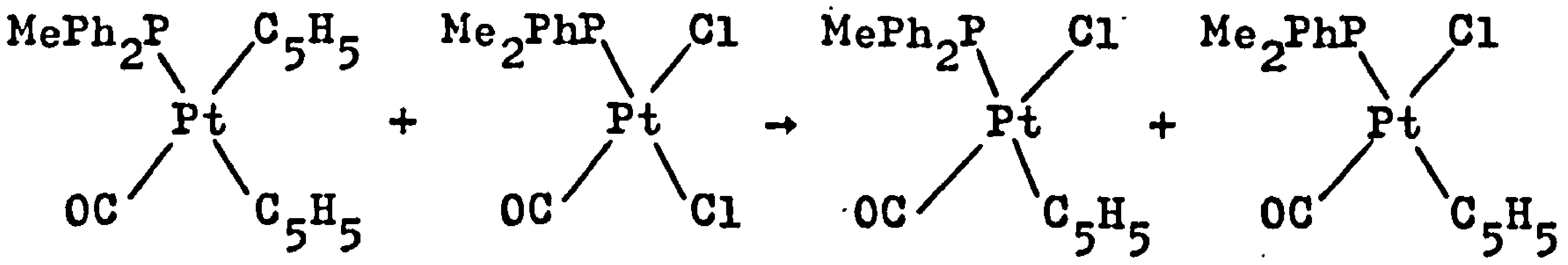
(b) At -60°C.

which will be discussed in a later chapter.

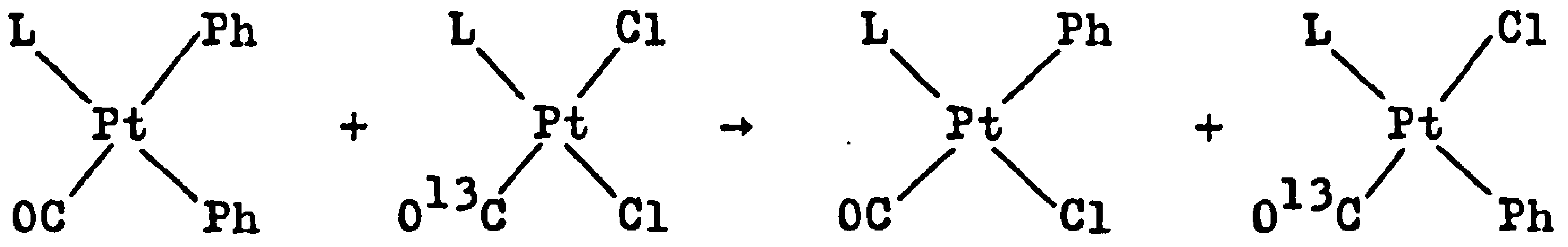
When $CDCl_3$ solutions of cis-$[PtCl_2(CO)(PPh_3)]$ and cis-$[Pt(\eta^1\text{-}C_5H_5)_2(CO)(PPh_3)]$ were mixed at ambient temperatures, a rapid redistribution reaction took place leaving only $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) in solution:-



A similar result was obtained from mixtures of cis-$[Pt(\sigma\text{-}C_5H_5)_2(CO)(PMe_2Ph)]$ and cis-$[PtBr_2(CO)(PMe_2Ph)]$. When complexes of different phosphines were employed, geometry (I) was observed for both products:-

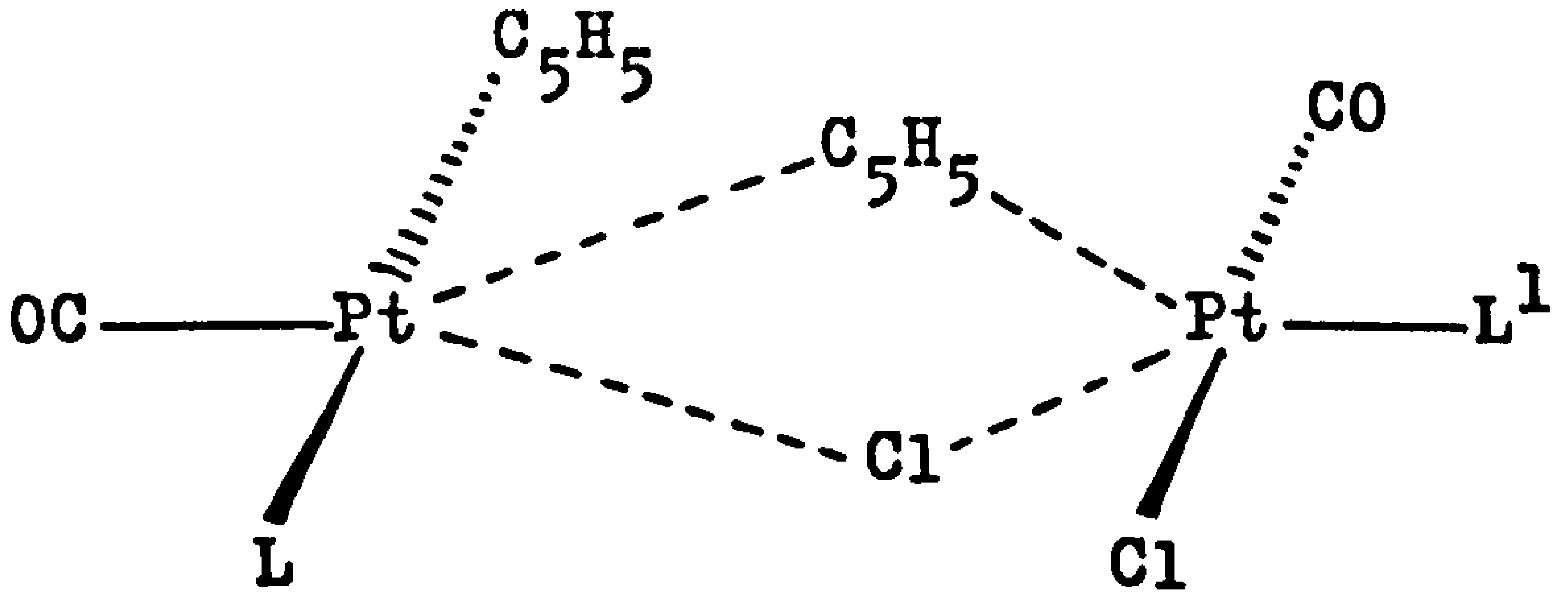


In this case, C_5H_5 has been transferred from a site trans to CO on one platinum to a site trans to phosphine on the other platinum, i.e. the transfer reaction involves different specific sites on platinum. In the case of transfer of C_5H_5 from isomer (I) to cis-$[PtCl_2(CO)L]$, the C_5H_5 was transferred from a site trans to phosphine on one platinum to the same site on the other platinum. Also, with the bisphenyl platinum complex, the transfer of Ph from cis-$[PtPh_2(CO)L]$ to cis-$[PtCl_2(^{13}CO)L]$, involves the same specific sites on each platinum:-



In this reaction, the phenyl trans to phosphine is transferred to the same site on the other platinum to produce a mixture of isomers (I) and (II). This was the expected result of an S_E2 (cyclic) mechanism, although it could not be proven as the reaction could also have proceeded by a number of oxidative addition/reductive elimination routes.[153,157]

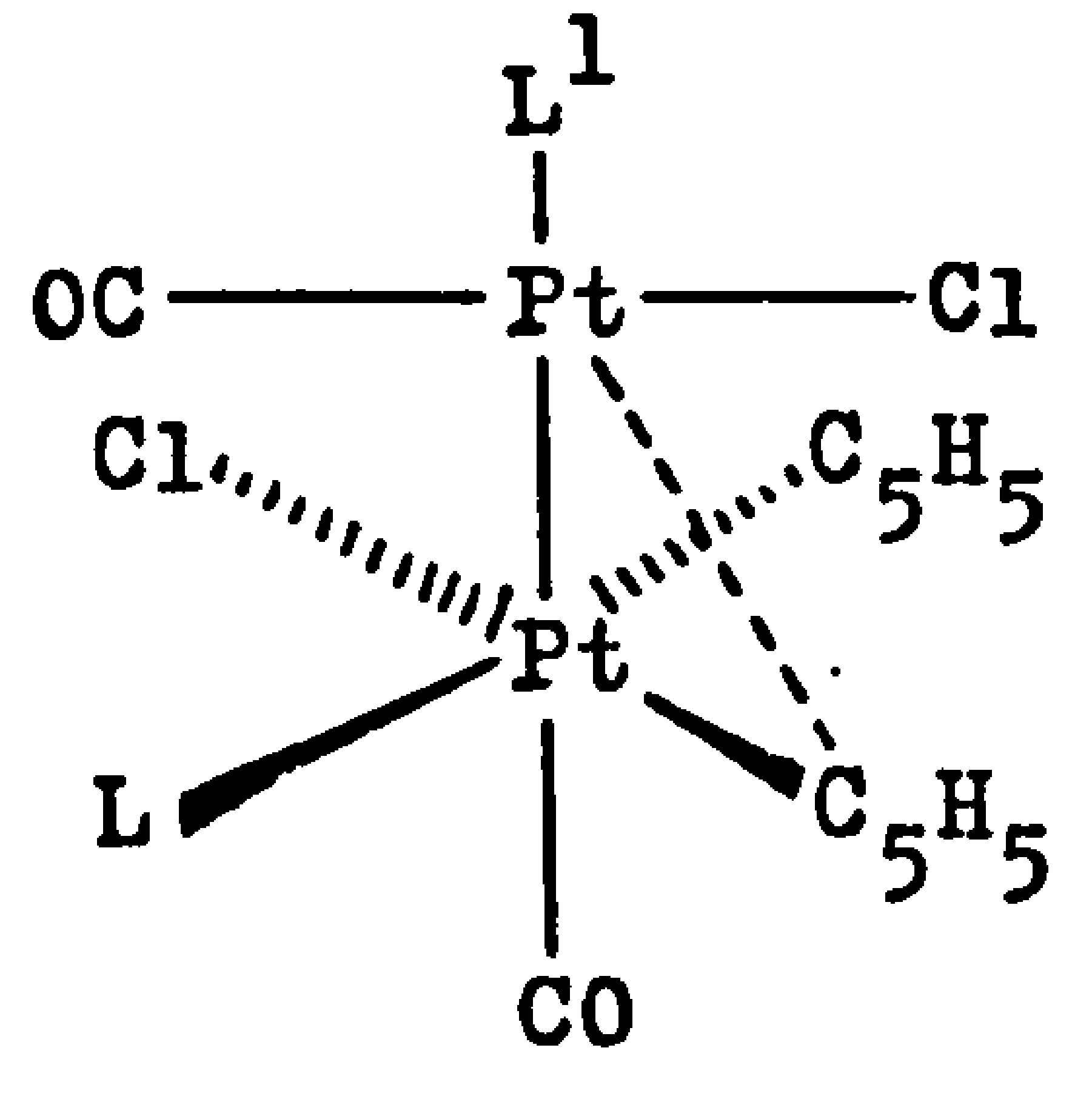
The reaction of cis-[Pt$(C_5H_5)_2$(CO)L] with cis-[PtCl_2-(CO)L^1] did not give the products expected of an S_E2 cyclic mechanism. The C_5H_5 was either transferred from the site trans to CO to the other platinum complex to give two lots of isomer (I), or the cyclopentadienyl trans to phosphine was transferred leaving behind an isomer (II) which underwent rapid isomerisation. Rapid isomerisation of an isomer (II) cannot be disproven, but is not likely. An S_E2 (cyclic) transfer is therefore only possible if it involves different specific sites on each platinum, which again appears unlikely. The transition state is shown in fig. 13.



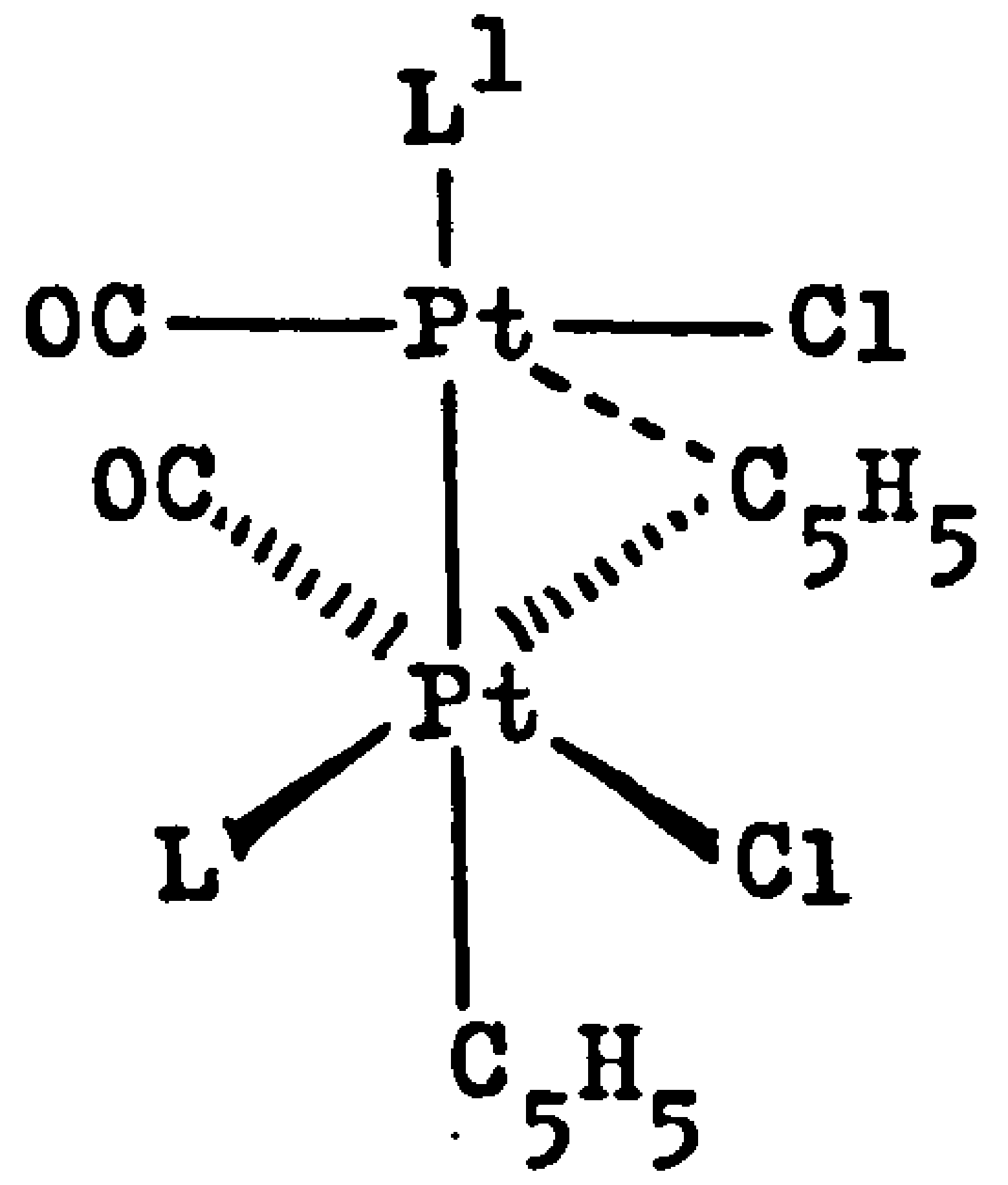
S_E2 (cyclic)

figure 13.

Oxidative addition/reductive elimination routes can explain the products. Assuming that *cis*-[Pt$(C_5H_5)_2$(CO)L], with two C_5H_5 rings (high *trans* influence) will have the more nucleophilic platinum, then *cis*-[PtCl_2(CO)L^1] will act as the electrophile and add oxidatively to it. There will be only two intermediates capable of giving the products observed (and attained by *cis*-oxidative additions). These are R and S.

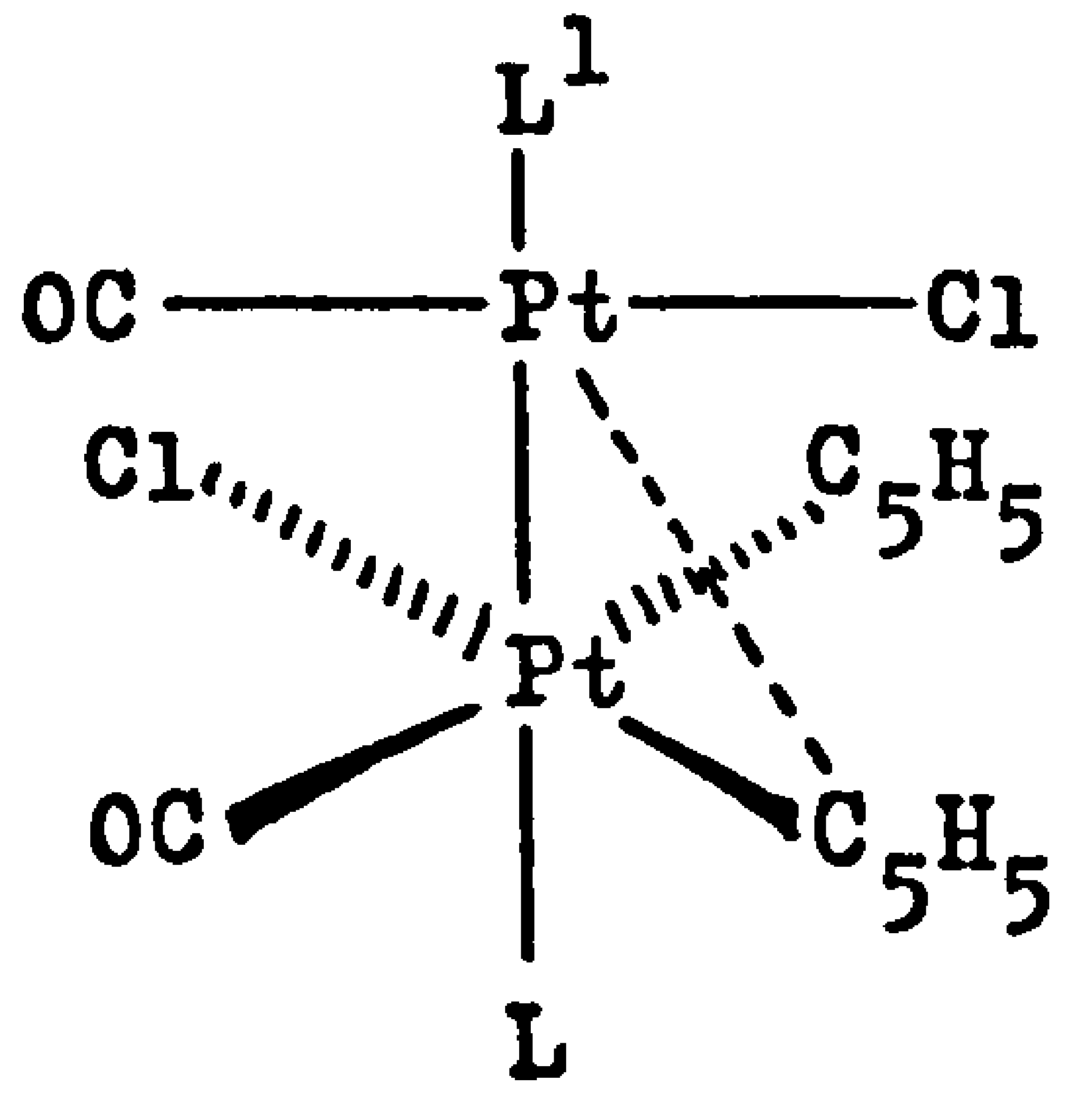


R

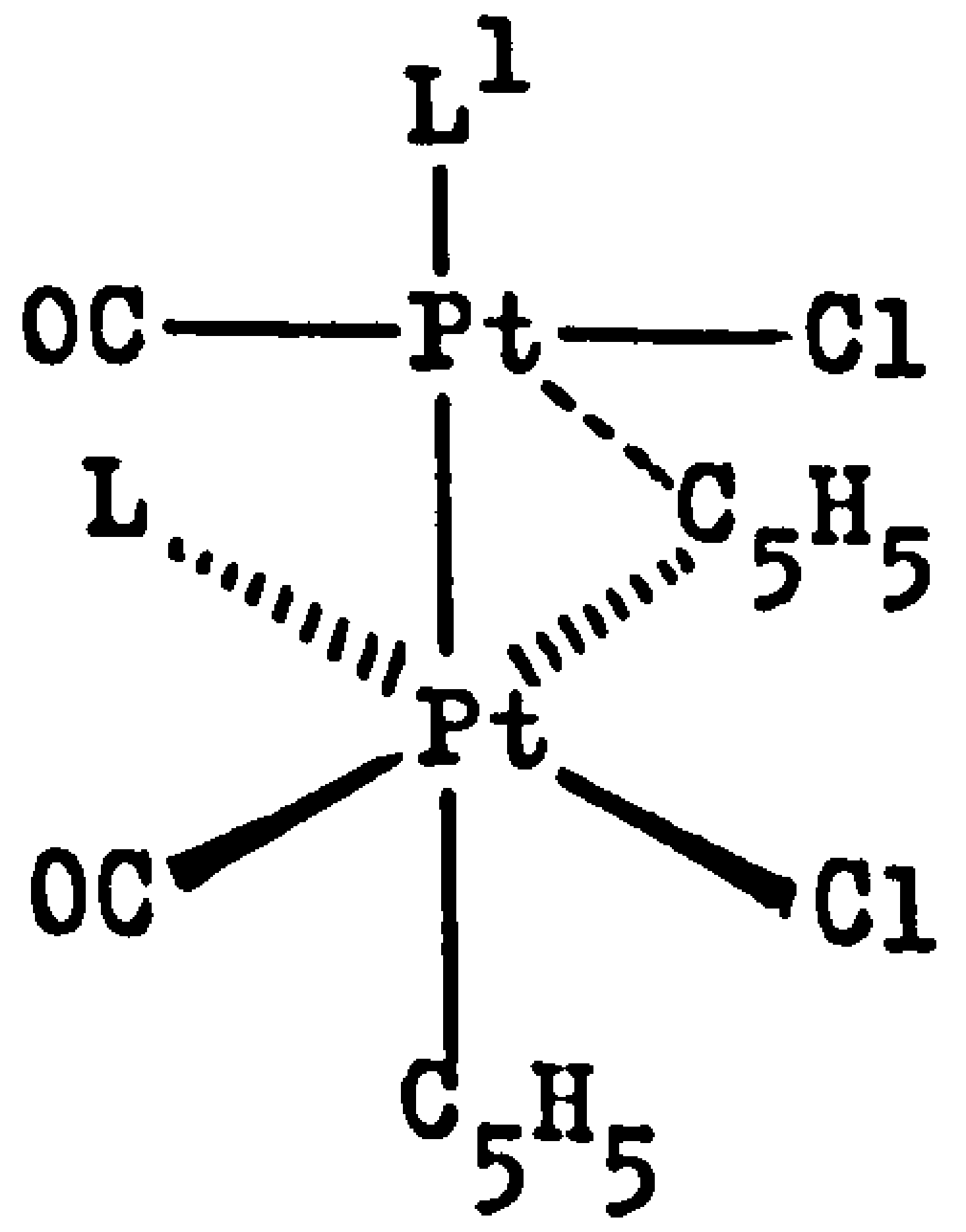


S

Reductive elimination from R and S as indicated gives the observed product. Elimination of the other C_5H_5 requires a symmetry forbidden twist to obtain the observed products.[155] The other two possible intermediates, T and U, give the wrong isomer of [PtCl(C_5H_5)(CO)L], isomer (II), C_5H_5 *trans* to CO. Elimination of the other C_5H_5 from T also requires a symmetry forbidden twist, to give the observed products.



T

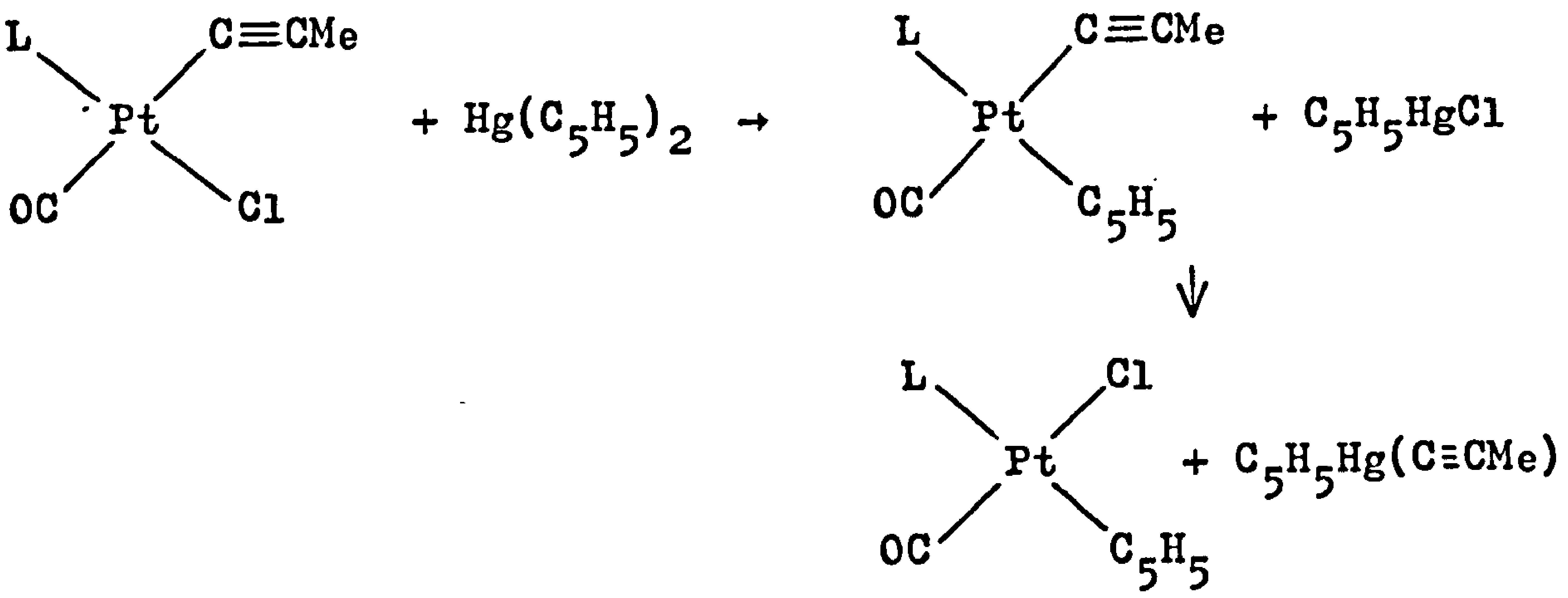


U

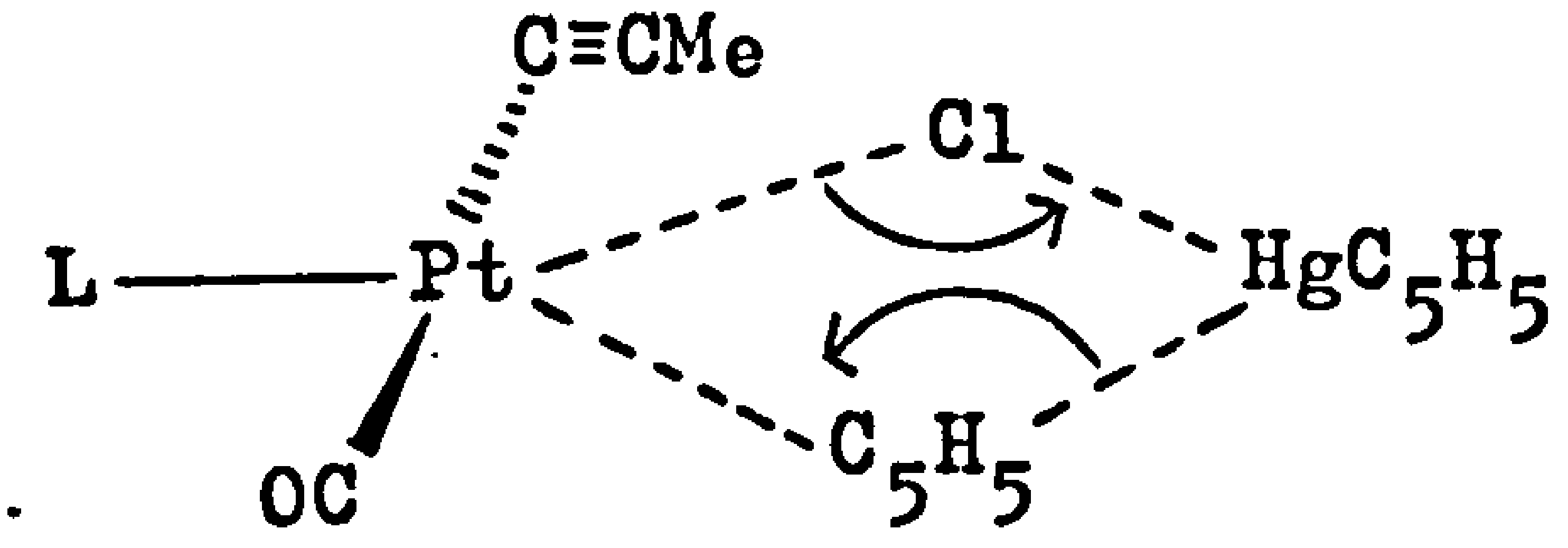
Asymmetrically Substituted Cyclopentadienyl (organo) platinum complexes

To explore these geometrical variations further, some asymmetrically substituted platinum complexes, $[Pt(C_5H_5)-R(CO)L]$ were studied. The reaction between $[PtCl(C{\equiv}CMe)-(CO)(PMePh_2)]$ (Cl trans to L), isomer (II), and TlC_5H_5 proceeds smoothly in $CDCl_3$ to produce $[Pt(\eta^1-C_5H_5)(C{\equiv}CMe)-(CO)(PMePh_2)]$ after 10 minutes at room temperature. Observed by ^{31}P nmr spectroscopy, the complex was indefinitely stable in solution at -60°C, but slowly decomposed at room temperature and no attempt was made to isolate it. Its identity was confirmed by ^1H nmr spectroscopy. The cyclopentadienyl protons at $\delta 6.27$ ppm and $J_{PH} = 4.5Hz$, $J_{PtH} = 35.5Hz$ are typical of a fluxional σ-bonded species trans to tertiary phosphine. The $^5J_{PH}$ coupling of the methyl protons of the ethynyl (3.0Hz) matches values found for such groups cis to $PMePh_2$.

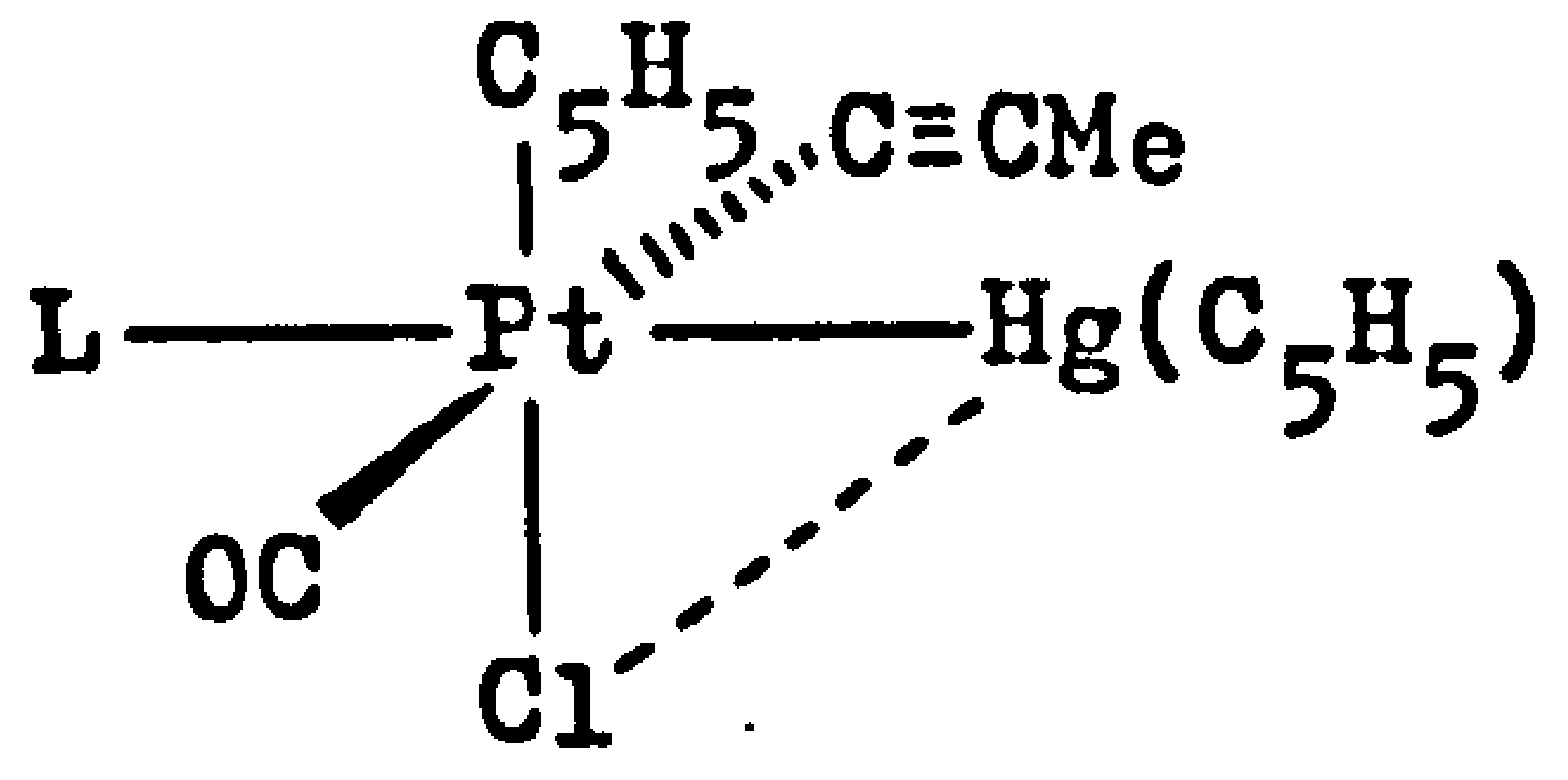
The same compound is produced from the reaction of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) and $Hg(C_5H_5)_2$, but the reaction proceeds further to give $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I) and small amounts of cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$, presumably from subsequent reactions of the organomercuric halide by-product. (This complication appears in several reactions of organomercurials when two or more organic groups are involved).



The formation of [Pt(C_5H_5)(C$\equiv$CMe)(CO)L] can be explained by an S_E2 (cyclic) mechanism, and a transition state such as V seems appropriate.



V

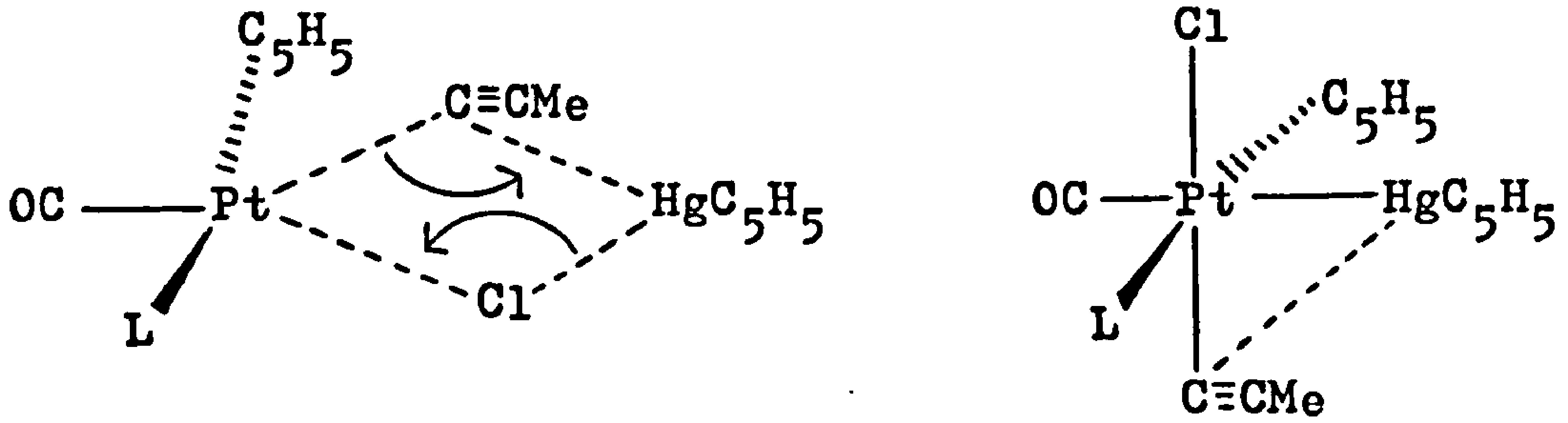


W

In this case, the only cis-oxidative addition/reductive elimination intermediate which could lead to [Pt(C_5H_5)-(C$\equiv$CMe)(CO)L] is the one which is related to S_E2 (cyclic), i.e. intermediate W, by a strong Pt–Hg interaction.

The reaction of [Pt(C_5H_5)(C$\equiv$CMe)(CO)L] with the mercury containing by-product to cleave off C$\equiv$CMe could also be by an S_E2 (cyclic) mechanism, but this would involve the site trans to CO which is perhaps unlikely. A more plausible mechanism would be an oxidative addition/reductive elimination. A cis-oxidative addition/reductive elimination mechanism suffers from the same drawback as the S_E2 cyclic mechanism, in that the only allowed intermediate comes from attack of mercury trans to CO (the extreme of the other S_E2

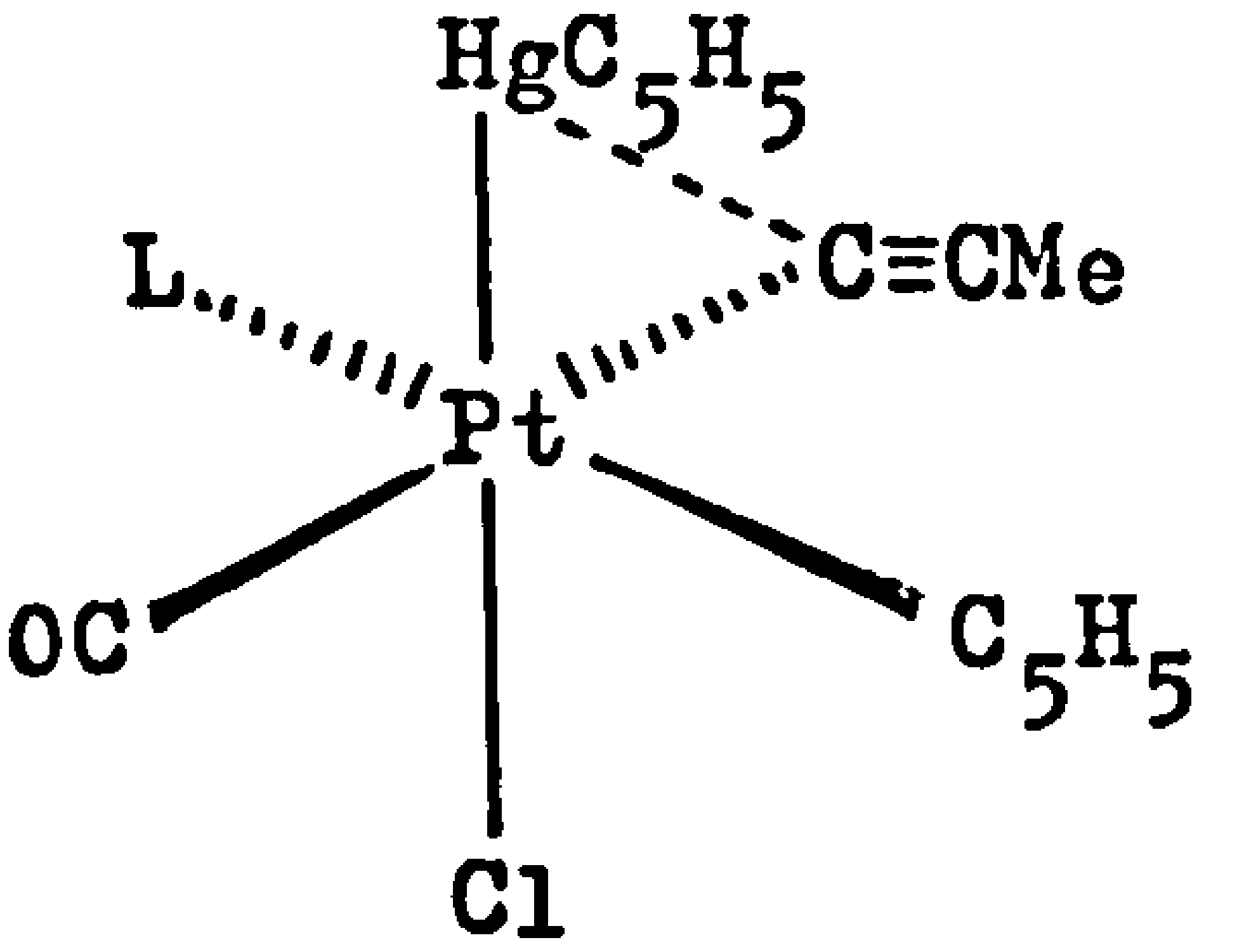
cyclic mechanism with Pt-Hg bonding interaction), fig. 14.



S_E2 (cyclic)

figure 14.

In this case, trans-oxidative addition should not be ruled out, and an intermediate, X, could also lead to the observed product.



X

Although trans-oxidative additions of organomercurials HgR_2 and of platinum complexes are considered unlikely under the conditions employed, a trans-addition of RHgCl or $HgCl_2$ is much more feasible by an ionic route. Nucleophilic attack by platinum at mercury could release Cl^- and lead to trans-oxidative addition. Oxidative addition of CH_3I and CF_3I to trans-$[PtRI(PMe_2Ph)_2]$ and cis-$[PtR_2L_2]$ goes by such a trans-route in chloroform.[158] Also $HgCl_2$ oxidative addition to trans-$[Ir(CO)ClL_2]$ goes by trans-oxidative addition[131] but $Hg(C\equiv CR)_2$ undergoes cis-oxidative addition.[132]

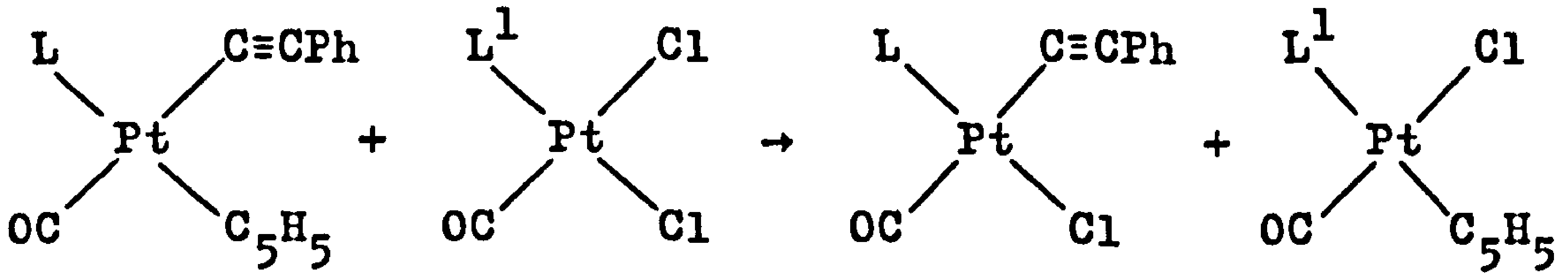
$HgCl_2$ cleaves the cyclopentadienyl group from $[Pt(C_5H_5)(C\equiv CMe)(CO)L]$, (where C_5H_5HgCl apparently cleaved $C\equiv CMe$).

This is perfectly consistent with an S_E2 cyclic mechanism or the analogous extreme _cis_-oxidative-addition/reductive elimination. However, here also a _trans_-oxidative addition/ _cis_-reductive elimination could operate.

There was no reaction between $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ and Ph_3PAuCl, except for normal decomposition of the platinum species, over 24 hours at room temperature. Thus the equilibrium for transfer of the organic groups C_5H_5 and $C{\equiv}CMe$ between Au and Pt must lie to the platinum side.

The chloride of $[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl _trans_ to phosphine) is also cleanly replaced by C_5H_5 on treatment with TlC_5H_5. Spectroscopic parameters for the new platinum complexes are in tables 4 and 5.

Followed by ^{31}P nmr spectroscopy, there was a rapid reaction between $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ and _cis_-$[PtCl_2(CO)(PMePh_2)]$ at room temperature.



In this reaction, the cyclopentadienyl was transferred to produce $[PtCl(C_5H_5)(CO)L^1]$ isomer (I) and leave $[PtCl(C{\equiv}CPh)(CO)L]$ isomer (II). This exchange involves the site _trans_ to phosphine on each platinum, and is consistent with an S_E2 (cyclic) mechanism, with transition state Y. In this example, the bis organo complex will have a more nucleophilic platinum than the bis chloro complex since organic groups are more electron donating than chlorides and PMe_2Ph is more donating than $PMePh_2$. Thus, for oxidative addition,

Table 4. ^{1}H nmr of $[Pt(C_5H_5)R(CO)(PMePh_2)]$ in $CDCl_3$ at 25°C. C_5H_5 trans to $PMePh_2$.

R	δC_5H_5(ppm)	J_{PH}(Hz)	J_{PtH}(Hz)	$\delta PM\underline{e}Ph_2$	J_{PH}(Hz)	J_{PtH}(Hz)
C≡CMe$^{(a)}$	+6.27	4.5	35.5	+2.33	10.5	28.5
C_6H_5	+6.14	4.0	39.5	+1.55	10.5	unresolved

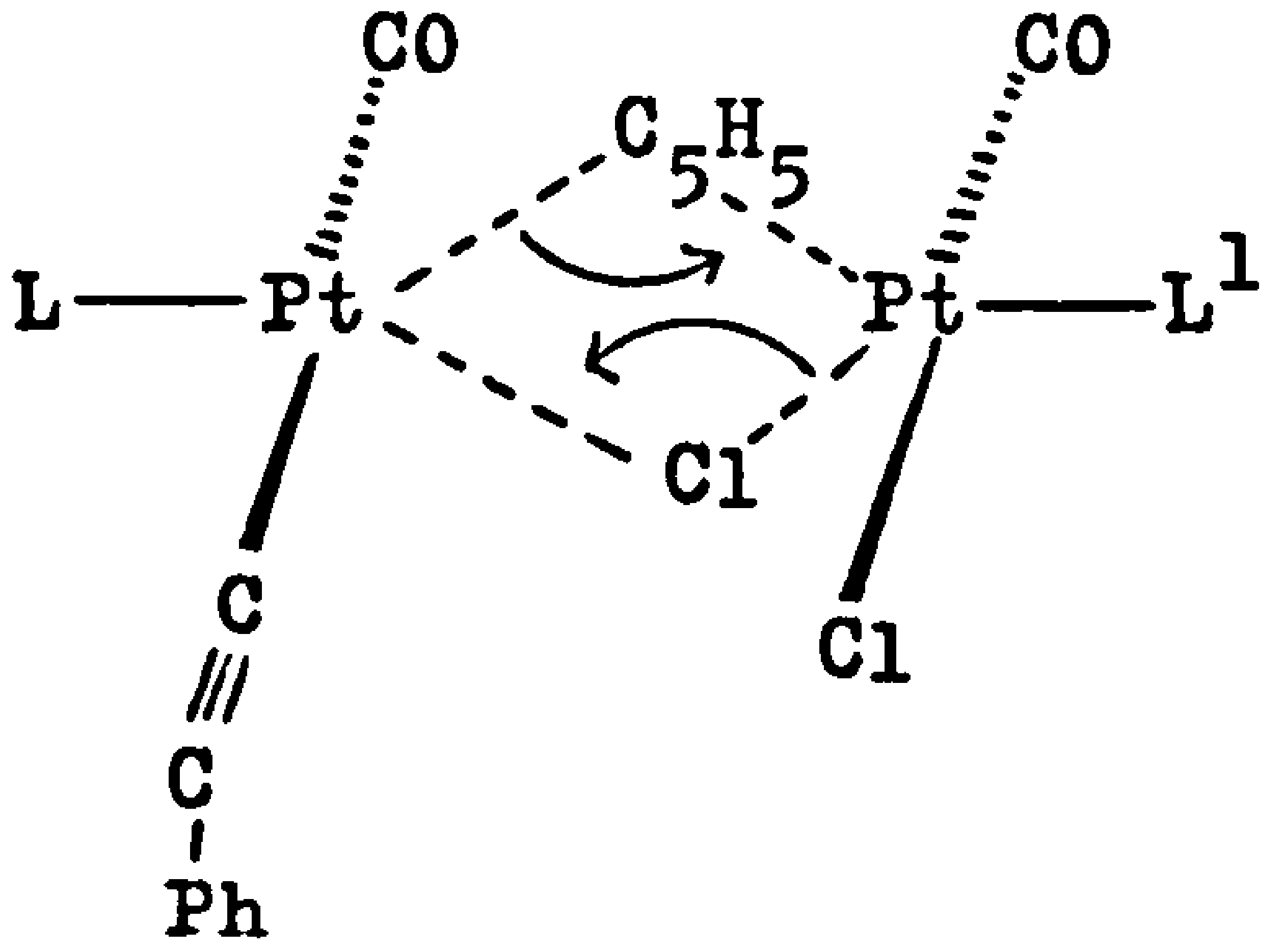
(a) C≡CM̲e δ + 1.91ppm, J_{PH} = 3.0 Hz, J_{PtH} = 16.0 Hz.

Table 5. ^{31}P nmr of $[Pt(C_5H_5)R(CO)(PR_3)]$, C_5H_5 trans to PR_3, in $CDCl_3$ at +25°C.

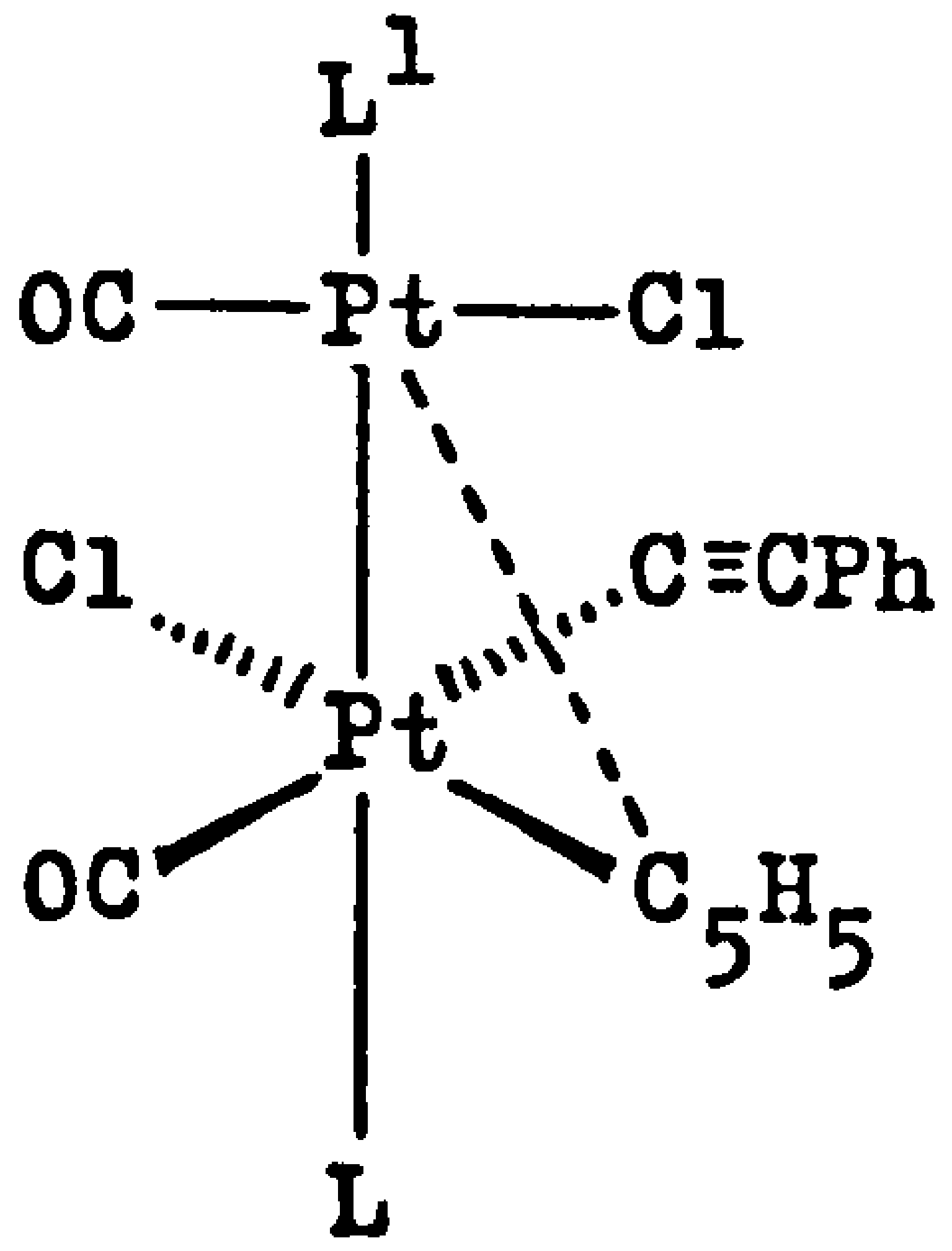
PR_3	R	δP(ppm)	$^1J_{PtP}$(Hz)
$PMePh_2$	$C\equiv CMe$	-2.2	1848
PMe_2Ph	$C\equiv CPh$	-14.4	1799
$PMePh_2$	C_6H_5	0.0	2296
$PMePh_2$(a)	$C_6H_4CO_2Me$-p	-0.7	2272

(a) Recorded at -60°C.

<u>cis</u>-[$PtCl_2(CO)L^1$] will act as the electrophile and there will be only one allowed intermediate, Z, capable of giving the observed products, i.e. the one related to the S_E2 transition state.

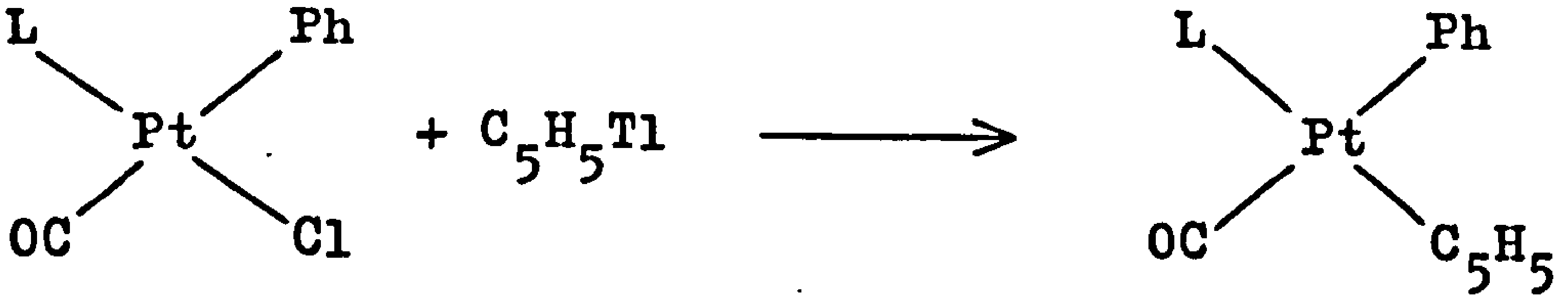


<u>Y</u>



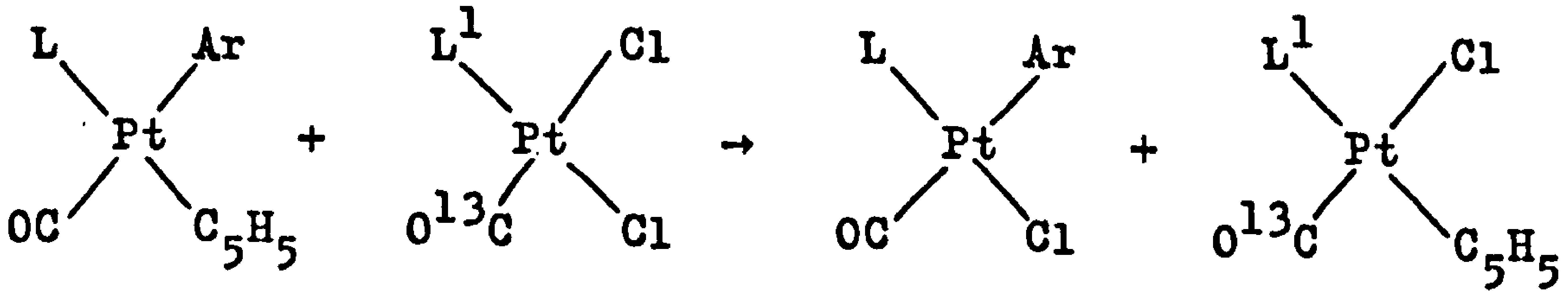
<u>Z</u>

Cyclopentadienylthallium and [$PtClPh(CO)(PMePh_2)$] (Ph <u>trans</u> to CO) also react readily at room temperature, the chloride on platinum being replaced by C_5H_5.



A small amount of <u>cis</u>-[$PtPh_2(CO)(PMePh_2)$] was also evident among the products, however.

The <u>p</u>-carbomethoxyphenyl complex, [$PtCl(C_6H_4CO_2Me$-<u>p</u>)-($CO)(PMePh_2)$] reacts with C_5H_5Tl in a similar manner to afford [$Pt(C_5H_5)(C_6H_4CO_2Me$-<u>p</u>)$(CO)(PMePh_2)$]. This latter material reacts with <u>cis</u>-[$PtCl_2(^{13}CO)(PMe_2Ph)$] at room temperature to transfer the C_5H_5 group.



The use of different phosphines, and ^{13}C-labelled carbon monoxide show unambiguously that once again the sites trans to tertiary phosphine are involved in the transfer. A transition state or oxidative addition intermediate similar to those for the mixed $C\equiv CPh,C_5H_5$ complex, (intermediates Y and Z), again are appropriate.

In both $[Pt(C_5H_5)(C\equiv CR)(CO)L]$ and $[Pt(C_5H_5)(Ar)(CO)L]$ the C_5H_5 is cleaved from trans to phosphine to give C_5H_5 isomer (I) by cis-$[PtCl_2(CO)L^1]$. The reaction is consistent with S_E2 (cyclic) in each case, and seems to be similar to the transfer from C_5H_5 isomer (I) to cis-$[PtCl_2(CO)L^1]$. There is only one possible oxidative addition/reductive elimination route, the route related to S_E2 cyclic by a strong Pt-Hg interaction.

η^5-Cyclopentadienyl Complexes

The reaction of TlC_5H_5 with cis-$[PtCl_2L_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph) produced the η^5-bonded complexes $[Pt(\eta^5-C_5H_5)L_2]Cl$. ^1H nmr parameters were typical of compounds of this type (tables 6 and 7). Replacement of the chlorides by $SO_3CF_3^-$ from $AgSO_3CF_3$ created no change in the nmr parameters, indicating no close association of Cl^- with the cation in $CDCl_3$. Silver salts also abstracted halide from complexes (I) to yield η^5-bonded materials, $[Pt(\eta^5-C_5H_5)(CO)L]SO_3CF_3$ (L = PMe_2Ph, PPh_3).

The complex $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]Cl$ reacts rapidly with $HgCl_2$ by C_5H_5 transfer.

$$[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]Cl + HgCl_2 \rightarrow C_5H_5HgCl + \text{cis-}[PtCl_2(PMe_2Ph)_2]$$

Table 6. ^1H nmr of $[Pt(\eta^5-C_5H_5)L^1L^2]^+ X^-$ in $CDCl_3$ at +25°C.

L^1	L^2	X	δC_5H_5(ppm)	J_{PH}(Hz)	J_{PtH}(Hz)	δCH_3(ppm)	J_{PH}(Hz)	J_{PtH} (Hz)
PPh_3	PPh_3	Cl	+5.39	1.5	11.5	-	-	-
$PMePh_2$	$PMePh_2$	Cl	+5.55	1.5	12.0	+1.95	11.0	34.0
PMe_2Ph	PMe_2Ph	Cl	+6.05	1.5	11.0	+1.95	11.0	39.0
PMe_2Ph	PMe_2Ph	SO_3CF_3	+5.95	1.5	11.0	+1.85	11.0	39.0
PPh_3	CO	SO_3CF_3	+6.00	1.25	13.5	-	-	-
$PMe_2Ph^{(a)}$	CO	SO_3CF_3	+6.15	1.25	13.25	+2.45	12.5	43.5

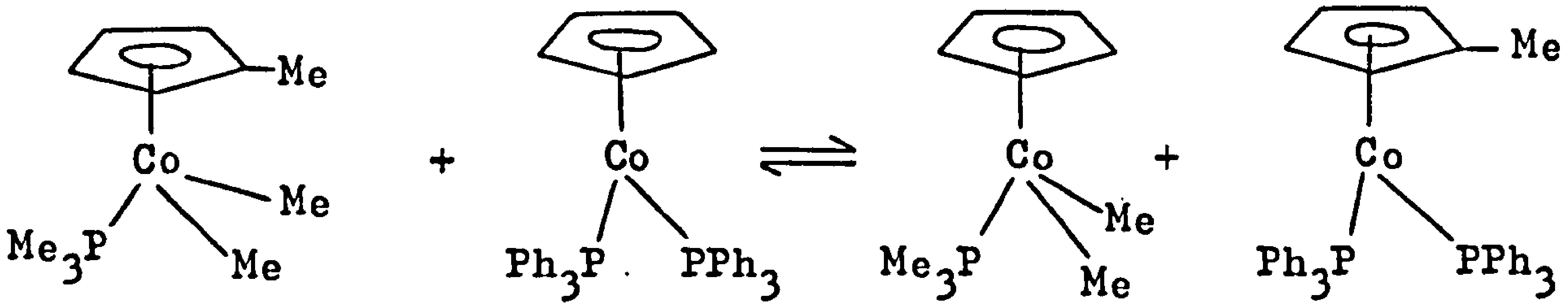
(a) IR in $CHCl_3$ (0.02M) $\nu_{CO} = 2065\ cm^{-1}$.

Table 7. ^{31}P nmr of $[Pt(\eta^5-C_5H_5)L^1L^2]^+ X^-$ in $CDCl_3$ at 25°C.

L^1	L^2	X	δP(ppm)	$^1J_{PtP}$(Hz)
PPh_3	PPh_3	Cl	+ 3.9	4736
$PMePh_2$	$PMePh_2$	Cl	-14.1	4578
PMe_2Ph	PMe_2Ph	Cl	-28.2	4498
PMe_2Ph	PMe_2Ph	SO_3CF_3	-28.3	4504
PEt_3	PEt_3	Cl	+ 4.1	4383
PPh_3	CO	SO_3CF_3	+ 2.3	3972
PMe_2Ph	CO(a)	SO_3CF_3	-25.2	3724

(a) With ^{13}CO, $^2J_{CP}$ = 15.1 Hz.

It is possible that the transfer reaction may be preceded by an $\eta^5 \rightarrow \eta^1$ conversion of C_5H_5. A similar reaction was performed using $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ and $HgCl_2$, and in this case production of <u>cis</u>-$[PtCl_2(PMe_2Ph)_2]$ was much slower. Transfer of $\eta^5-C_5H_5$ between cobalt atoms has been reported.[159]



The reaction is slow, and the mechanism is not known, although the authors considered a bridging transition state to be possible, or an $\eta^5 \rightarrow \eta^3$ rearrangement of the C_5H_5 ring.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solutions on a Varian XL100 spectrometer operating in the Fourier transform mode (^{31}P and ^{1}H) or on a Perkin-Elmer R32 90 MHz continuous-wave spectrometer (^{1}H). Chemical shifts are positive to low field w.r.t. 85% H_3PO_4 (^{31}P) and TMS (^{1}H). All measurements were made at 25°C unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 580 or 257 spectrophotometer as KBr discs or as 0.02 mol dm^{-3} $CHCl_3$ solutions in NaCl cells (0.5mm path length).

Starting materials, TlC_5H_5, $Hg(C_5H_5)_2$, $[Ph_3PAuC_5H_5]$, $Hg(C{\equiv}CR)_2$, $HgAr_2$, cis-$[PtCl_2(PR_3)_2]$, cis-$[PtCl_2(CO)(PR_3)]$ and cis-$[PtCl_2(C_2H_4)(PR_3)]$ were prepared by literature methods.

TlC_5H_5[96]

To Tl_2SO_4 (5.0g, 10mmol.) in 20ml of 4M NaOH solution was added 4ml of freshly distilled cyclopentadiene and the mixture was shaken for 20 minutes. The precipitate was filtered, dried in vacuo and then purified by vacuum sublimation at 80°C/0.1mm, to yield yellow needles of TlC_5H_5.

$Hg(C_5H_5)_2$

TlC_5H_5 (2.1g, 7.6mmol.) was suspended in dry THF (10ml) under a nitrogen atmosphere at 0°C. $HgCl_2$(0.8g, 3mmol) dissolved in THF (15ml) was added dropwise, the reaction was kept at 0°C for 1½ hours. The precipitate was removed by filtration, and washed with 5ml THF. The THF was removed in vacuo, the resulting solid was extracted with dry ether (25ml), which was filtered, then cooled to -40°C. Yellow needles formed and were filtered off to yield $Hg(C_5H_5)_2$ (0.25g, 25%).

$[Ph_3PAuC_5H_5]$[160]

$[Ph_3PAuCl]$ (500mg, 1.0mmol.) was suspended in 20ml of dry ethanol and 5ml of a solution of NaOEt (46.5mg Na, 2.0mmol in 10ml EtOH) was added followed by a solution of freshly distilled C_5H_6 (73.6mg, 1.1mmol.) in 1ml EtOH. The solution was stirred at 0°C for 2 hours. The white precipitate was filtered to give $[Ph_3PAuC_5H_5]$ (316mg, 60%) which was stored in the dark at 5°C.

The organomercurials, $Hg(C\equiv CR)_2$($R = Me,Ph$) and $HgAr_2$ ($Ar = C_6H_4CO_2Me$-p, C_6H_4OMe-o, C_6H_4Cl-o) were prepared by literature methods.[161]

The complexes cis-$[PtCl_2(CO)(PR_3)]$ and $[PtCl_2(C_2H_4)(PR_3)]$ were prepared by bridge-cleavage of $[Pt_2Cl_4(PR_3)_2]$ by CO or C_2H_4. A typical procedure is shown below.

cis-$[PtCl_2(PMe_2Ph)_2]$[162]

K_2PtCl_4 (10.0g, 24 mmol.) was suspended in 80ml H_2O/120 ml ethanol under a nitrogen atmosphere. PMe_2Ph (6.9ml, 48 mmol.) was added and the mixture stirred for 20 hours. The solid was filtered, dried with ether, and recrystallised from CH_2Cl_2 to yield cis-$[PtCl_2(PMe_2Ph)_2]$ (9.8g, 72%).

$[Pt_2Cl_4(PMe_2Ph)_2]$[163]

Cis-$[PtCl_2(PMe_2Ph)_2]$ (6.8g, 12mmol.) was dissolved in 80ml. sym tetrachloroethane at 80°C. $PtCl_2$ (3.3g, 12.3mmol.) was added, the mixture was heated at 120°C for 18 hours under N_2, filtered while hot and reduced in volume. Addition of pentane precipitated a yellow powder, $[Pt_2Cl_4(PMe_2Ph)_2]$ (9.4g, 94%).

Cis-[$PtCl_2(CO)(PMe_2Ph)$]

CO was bubbled through a suspension of [$Pt_2Cl_4(PMe_2Ph)_2$] (4.4g, 5.4mmol.) in benzene (100ml) until a colourless solution and white precipitate was obtained, the solution was reduced in volume, the solid filtered, and recrystallised from benzene to yield *cis*-[$PtCl_2(CO)(PMe_2Ph)$] (4.31g, 93%).

Cyclopentadienyl Platinum Complexes

(a) [$PtX(\eta^1-C_5H_5)(CO)(ER_3)$] isomer (I)

Chloro(cyclopentadienyl)carbonyl(triphenylphosphine) platinum(II)

Cis-dichloro(carbonyl)triphenylphosphine platinum (II) (293mg; 0.53mmol.) and cyclopentadienylthallium (146mg; 0.54mmol.) were stirred together in benzene (5ml) under a nitrogen atmosphere for 1 hour. After removal of TlCl by filtration, the solvent was removed under vacuum leaving an orange semi-solid which was dissolved in acetone (3ml). Addition of pentane (10ml) precipitated the product, [$PtCl(\eta^1-C_5H_5)(CO)(PPh_3)$] as an orange powder, m.pt. 106-108°C, 181mg, 59%. (Found; C, 49.35%; H, 3.5%: Required for $C_{24}H_{20}ClOPPt$; C,49.2%; H, 3.4%.

Chloro(cyclopentadienyl)carbonyl(dimethylphenylphosphine) platinum (II)

Cis-[$PtCl_2(CO)(PMe_2Ph)$] (306mg; 0.71mmol.) and TlC_5H_5 (193mg; 0.72mmol.) were stirred together in benzene (5ml) under a nitrogen atmosphere for 45 minutes. Removal of TlCl and the solvent left a sticky orange semi-solid. Attempts to crystallise the orange material from several solvents led to decomposition and formation of brown or black solids or oils. Finally, the remaining material was dissolved in a minimum of benzene and the product precipitated as a slightly impure yellow powder on addition of pentane, m.pt. 73-79°C, 64mg, 20%. (Found; C, 35.5%; H, 3.0%: Required for $C_{14}H_{16}ClOPPt$; C, 36.4%; H, 3.5%).

No attempts were made to isolate other examples of these monocyclopentadienyls. Solutions were prepared in situ for examination of their reactions. Spectroscopic parameters are listed in tables 1 and 2.

Chloro(cyclopentadienyl)carbonyl(methyldiphenylphosphine) platinum (II)

cis-$[PtCl_2(CO)(PMePh_2)]$ (25.6mgs, 0.052 mmol.) and TlC_5H_5 (15.1mgs, 0.056mmol., 1.08 equiv.) were allowed to react in 0.5ml of $CDCl_3$ under an atmosphere of nitrogen for thirty minutes. The solution was then filtered and ^1H and ^{31}P nmr spectra were recorded, showing it to be $[PtCl(C_5H_5)(CO)(PMePh_2)]$, C_5H_5 trans to phosphine.

Chloro(cyclopentadienyl)carbonyl(triethylphosphine) platinum (II)

cis-$[PtCl_2(CO)(PEt_3)]$ (27.0mgs, 0.066mmol.) and TlC_5H_5 (0.066mmol. 1.01 equiv.) were allowed to react together in $CDCl_3$ (0.5ml) for 30 minutes under a nitrogen atmosphere. The solution was then filtered and ^1H and ^{31}P nmr spectra were recorded, showing the product to be $[PtCl(C_5H_5)(CO)(PEt_3)]$, C_5H_5 trans to phosphine.

Bromo(cyclopentadienyl)carbonyl(dimethylphenylphosphine) platinum (II)

cis-[$PtBr_2(CO)(PMe_2Ph)$] (30.5mgs, 0.059mmol.) and TlC_5H_5 (15.2mgs, 0.056mmol., 0.96 equiv.) were allowed to react in $CDCl_3$ (0.5ml) under a nitrogen atmosphere for 45 minutes, then the solution was filtered and ^1H and ^{31}P nmr spectra showed it to be [$PtBr(\eta^1-C_5H_5)(CO)(PMe_2Ph)$], C_5H_5 trans to phosphine.

Chloro(cyclopentadienyl)(carbonyl)(methyldiphenylarsine) platinum (II)

cis-[$PtCl_2(CO)(AsMePh_2)$] (21.8mgs, 0.040 mmol.) and TlC_5H_5 (10.9mgs, 0.040mmol., 1.0 equiv.) were allowed to react in $CDCl_3$ (0.5ml) under a N_2 atmosphere. After $1^3/4$ hrs. a ^1H nmr spectrum showed that the solution contained mainly [$PtCl(\eta^1-C_5H_5)(CO)(AsMePh_2)$], C_5H_5 trans to arsine.

cis-dichlorocarbonyl(dimethylphenylphosphine) platinum (II) and biscyclopentadienylmercury

cis-[$PtCl_2(CO)(PMe_2Ph)$] (25.2mgs, 0.058 mmol.) was dissolved in $CDCl_3$ (0.4ml) in an nmr tube under a N_2 atmosphere. A solution of $Hg(C_5H_5)_2$ (19.6mgs, 0.059mmol. 1.02 equiv.) in $CDCl_3$ (0.2ml) was added at -60°C. There was no reaction at this temperature, and a reaction occurred only on warming briefly to RT, to produce [$PtCl(CO)(\eta^1-C_5H_5)(PMe_2Ph)$], C_5H_5 trans to phosphine, (identified by its ^{31}P nmr spectrum).

cis-dichlorocarbonyl(methyldiphenylphosphine) platinum (II) and biscyclopentadienyl mercury

cis-[$PtCl_2(CO)(PMePh_2)$] (30.0mgs, 0.061mmol.) and $Hg(C_5H_5)_2$ (20.2mgs, 0.061mmol. 1.0 equiv.) were allowed to react in $CDCl_3$ (0.5ml) at RT, and ^{31}P nmr spectra were recorded, showing the product to be [$PtCl(C_5H_5)(CO)(PMePh_2)$].

cis-dichlorocarbonyl(triphenylphosphine) platinum (II) and cyclopentadienyl(triphenylphosphine) gold (I)

$Ph_3PAuC_5H_5$ (26.1mgs, 0.0498mmol.) was dissolved in $CDCl_3$ (0.3ml) and a solution of cis-[$PtCl_2(CO)(PPh_3)$] (27.6mgs, 0·0498mmol. 1.0 equiv.) in $CDCl_3$ (0.3ml) was added at RT. The reaction was rapid to produce Ph_3PAuCl and [$PtCl(C_5H_5)(CO)(PPh_3)$], C_5H_5 trans to phosphine (identified by ^{31}P nmr).

cis-[$PtCl_2(CO)(PMe_2Ph)$] and C_5H_5Tl at low temperature

cis-[$PtCl_2(CO)(PMe_2Ph)$] (23.1mg, 0.053mmol.) was dissolved in $CDCl_3$ (0.5ml) and then added to TlC_5H_5 (16.1mg, 0.060mmol.) in a N_2-filled nmr tube at -60°C. After 2½ hours at -60°C, ^{31}P nmr showed only a 5% reaction with [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) the only product. On warming to -40°C for 2 hours, there was 30% reaction, but only isomer (I) was detected.

Low temperature ^1H nmr of [$PtCl(C_5H_5)(CO)(PPh_3)$] isomer (I)

[$PtCl(\eta^1-C_5H_5)(CO)(PPh_3)$] isomer (I), (10.2mgs, 0.017 mmol.) was dissolved in CD_2Cl_2 (0.4ml) and ^1H nmr spectra were recorded between +25 and -110°C.

(b) C_5H_5 Transfer Reactions from Isomer (I) to Pt and Hg

$[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ and *cis*-$[PtCl_2(CO)(PPh_3)]$

A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) was prepared from the reaction of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ (30.7mgs, 0.071 mmol.) and C_5H_5Tl (19.8mgs, 0.073 mmol.) in $CDCl_3$ (350μl) under a N_2 atmosphere and filtered. To it was added a solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ (18.2mgs, 0.033mmol.) in $CDCl_3$ (150μl). ^{31}P nmr investigation of the solution revealed the presence of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$, $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$, $[PtCl(C_5H_5)(CO)(PPh_3)]$, and *cis*-$[PtCl_2(CO)(PPh_3)]$. Integration of the ^{31}P nmr signals allowed the equilibrium constant to be calculated.

$[PtCl(C_5H_5)(CO)(PPh_3)]$ and *cis*-$[PtCl_2(CO)(PMe_2Ph)]$

A solution of $[PtCl(C_5H_5)(CO)(PPh_3)]$ (0.053mmol.) in $CDCl_3$ (350μl) and a solution of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ (12.6mgs, 0.029mmol.) in $CDCl_3$ (150μl) when mixed at ambient temperature gave a similar mixture as above. Again, integration of the ^{31}P nmr signals allowed the equilibrium constant to be calculated and gave a value consistent with that obtained above.

$[PtCl(C_5H_5)(CO)(PEt_3)]$ and *cis*-$[PtCl_2(CO)(PMe_2Ph)]$

Similarly $[PtCl(C_5H_5)(CO)(PEt_3)]$ (0.079mmol.) and *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ (15.2mgs, 0.031mmol.) in $CDCl_3$ equilibrated to give a mixture of *cis*-$[PtCl_2(CO)(PEt_3)]$, $[PtCl(C_5H_5)(CO)(PEt_3)]$, $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$, and *cis*-$[PtCl_2(CO)(PMe_2Ph)]$. The equilibrium constant was calculated as above.

$[PtCl(C_5H_5)(CO)(PPh_3)]$ and *cis*-$[PtCl_2(CO)(PMePh_2)]$

cis-$[PtCl(C_5H_5)(CO)(PPh_3)]$ (15.8mgs, 0.027mmol.) in $CDCl_3$ (200µl) and *cis*-$[PtCl_2(CO)(PMePh_2)]$ (17.2 mgs, 0.035 mmol.) in $CDCl_3$ (200µl) were mixed together under a nitrogen atmosphere at -60°C. ^{31}P nmr investigation showed that there was no reaction at -60°C within 5 hours. Transfer of cyclopentadienyl occurred only on warming to +25°C, giving a mixture of *cis*-$[PtCl_2(CO)(PPh_3)]$, $[PtCl(C_5H_5)(CO)(PPh_3)]$, $[PtCl(C_5H_5)(CO)(PMePh_2)]$, and *cis*-$[PtCl_2(CO)(PMePh_2)]$.

$[PtCl(C_5H_5)(^{13}CO)(PMePh_2)]$ and cis-$[PtCl_2(CO)(PPh_3)]$.

cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ (90% ^{13}CO; 32.6mgs, 0.066 mmol.) and C_5H_5Tl (18.9mgs, 0.070mmol.) were allowed to react in $CDCl_3$ under a nitrogen atmosphere, and the solution was filtered. ^{31}P nmr investigation revealed $[PtCl(C_5H_5)(^{13}CO)(PMePh_2)]$ ($\delta P = +6.3$ppm, $^1J_{PtP} = 1759$ Hz, $^2J_{CP} = 10.5$Hz). A solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ (19.6mgs, 0.035mmol.) was added and ^{31}P nmr spectra were recorded at intervals. Initially the mixture equilibrated to *cis*-$[PtCl_2(^{13}CO)(PMePh_2)]$, $[PtCl(C_5H_5)(^{13}CO)(PMePh_2)]$, $[PtCl(C_5H_5)(^{12}CO)(PPh_3)]$, and *cis*-$[PtCl_2(^{12}CO)(PPh_3)]$, but scrambling of the specificity of the label was appreciable in 6 hours and total overnight. Integration of ^{31}P signals allowed the equilibrium constant to be calculated.

$[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ and *cis*-$[PtBr_2(CO)(PMe_2Ph)]$

$[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ (0.066mmol.) in $CDCl_3$ (350µl) and *cis*-$[PtBr_2(CO)(PMe_2Ph)]$ (23.4mgs, 0.045mmol.) in $CDCl_3$ (150µl) were mixed under a nitrogen atmosphere. Immediate spectroscopic investigation (^{31}P nmr) revealed a mixture of

[$PtBr(C_5H_5)(CO)(PMe_2Ph)$], [$PtCl(C_5H_5)(CO)(PMe_2Ph)$], cis-[$PtBr_2(CO)(PMe_2Ph)$], and one isomer of [$PtBrCl(CO)(PMe_2Ph)$], CO cis to phosphine, (δ = -8.1ppm, $^1J_{PtP}$ = 2832 Hz), which had reached equilibrium within 10 minutes.

[$PtBr(C_5H_5)(CO)(PMe_2Ph)$] and cis-[$PtCl_2(^{13}CO)(PMe_2Ph)$]

Similarly, [$PtBr(C_5H_5)(CO)(PMe_2Ph)$] (0.082mmol.) and cis-[$PtCl_2(^{13}CO)(PMe_2Ph)$] (19.7mgs, 0.045mmol.) were allowed to react in $CDCl_3$ under a nitrogen atmosphere. ^{31}P nmr revealed the presence, within twenty minutes, of an equilibrium mixture of [$PtCl(C_5H_5)(CO)(PMe_2Ph)$], [$PtBrCl(CO)(PMe_2Ph)$] (same isomer as above), [$PtBr(C_5H_5)(CO)(PMe_2Ph)$], cis-[$PtBr_2(CO)(PMe_2Ph)$], and cis-[$PtCl_2(CO)(PMe_2Ph)$], in which the ^{13}CO was randomly distributed amongst all of the products.

[$PtCl(C_5H_5)(CO)(PMePh_2)$] and cis-[$PtBr_2(CO)(PMe_2Ph)$]

[$PtCl(C_5H_5)(CO)(PMePh_2)$] (0.063mmol.) and cis-[$PtBr_2(CO)(PMe_2Ph)$] (25.8mgs, 0.050mmol.) reacted similarly to produce, in less than 10 minutes, [$PtBr(C_5H_5)(CO)(PMePh_2)$] ($\delta p$ = +2.9ppm, $^1J_{PtP}$ = 1780 Hz), [$PtCl(C_5H_5)(CO)(PMePh_2)$], cis-[$PtBr_2(CO)(PMe_2Ph)$], [$PtBrCl(CO)(PMe_2Ph)$] (same isomer as above), [$PtBr(C_5H_5)(CO)(PMe_2Ph)$], [$PtCl(CO)(C_5H_5)(PMe_2Ph)$], cis-[$PtBr_2(CO)(PMePh_2)$] and [$PtBrCl(CO)(PMePh_2)$] (one isomer; CO cis to phosphine; δp = +1.6ppm, $^1J_{PtP}$ = 2924 Hz), with equilibration complete in 30 to 45 minutes.

cis-[$PtBr_2(CO)(PMe_2Ph)$] and *cis*-[$PtCl_2(CO)(PMe_2Ph)$]

A solution of *cis*-[$PtBr_2(CO)(PMe_2Ph)$] (16.3mgs, 0.031 mmol.) in $CDCl_3$ (200μl) and a solution of *cis*-[$PtCl_2(CO)$-(PMe_2Ph)] (13.5 mgs, 0.031 mmol.) in $CDCl_3$ (200μl) were mixed at -60°C. ^{31}P nmr investigation showed that the reaction reached equilibrium in 1½ hours, producing mainly one isomer of [$PtBrCl(CO)(PMe_2Ph)$], (that seen in the previous 3 reactions), *cis*-[$PtBr_2(CO)(PMe_2Ph)$], *cis*-[$PtCl_2(CO)$(PMe_2Ph)] and the other isomer of [$PtBrCl(CO)(PMe_2Ph)$], (CO *cis* to phosphine) as only a minor product. On warming the solution to room temperature, the same ratio of isomers (5:1) was present. ^{31}P nmr at RT:- $\delta = -8.1$ppm, $^1J_{PtP} =$ 2832 Hz and $\delta = -13.1$ppm, $^1J_{PtP} = 2841$ Hz. On performing the reaction at RT with 10.1 mgs of *cis*-[$PtCl_2(CO)(PMe_2Ph)$] (0.023mmol.) and 9.8mgs of *cis*-[$PtBr_2(CO)(PMe_2Ph)$] (0.019 mmol.) a similar result was obtained.

[$PtCl(C_5H_5)(CO)(PMe_2Ph)$] and *cis*-[$PtCl_2(PMe_2Ph)_2$]

[$PtCl(C_5H_5)(CO)(PMe_2Ph)$] (0.067mmol.) and *cis*-[$PtCl_2(PMe_2Ph)_2$] (21.5mgs, 0.040mmol.) were mixed in $CDCl_3$ under a N_2 atmosphere. ^1H nmr investigation showed that no reaction occurred; the only signals detected belonging to the initial complexes.

[$PtCl(C_5H_5)(CO)(PMe_2Ph)$] and *cis*-[$PtCl_2(PPh_3)_2$]

Similarly [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] (0.069mmol.) and *cis*-[$PtCl_2(PPh_3)_2$] (6.6mgs, 0.008mmol.) were mixed in $CDCl_3$ under a N_2 atmosphere. ^1H nmr showed that there was no reaction within 2½ hours. On being left overnight, a ^{31}P

nmr and ^{1}H nmr investigation showed that some of the [PtCl(C_5H_5)(CO)(PMe_2Ph)] had decomposed to its normal decomposition products, and that the only PPh_3- containing material was <u>cis</u>-[$PtCl_2(PPh_3)_2$]. Thus there was no reaction.

<u>[PtCl(C_5H_5)(CO)(PPh_3)] and [PtCl(C_2Cl_3)(CO)($PMePh_2$)]</u>

[PtCl(C_5H_5)(CO)(PPh_3)] (11.1mgs, 0.019mmol.) in $CDCl_3$ (100μl) and [PtCl(C_2Cl_3)(CO)($PMePh_2$)] (11.2mgs, 0.019mmol.) in $CDCl_3$ (200μl) were mixed at -60°C under a nitrogen atmosphere and the reaction was examined by ^{31}P nmr spectroscopy. There was no reaction in 24 hours at RT, and over a period of 1 week [PtCl(C_2Cl_3)(CO)($PMePh_2$)] remained unchanged, while [PtCl(C_5H_5)(CO)(PPh_3)] decomposed.

<u>[PtCl(Ar)(CO)(PMe_2Ph)] and cis-[$PtCl_2$(CO)(PPh_3)]</u>

Solutions of various [PtCl(Ar)(CO)(PMe_2Ph)] isomers (I) in $CDCl_3$ were prepared by standard methods[23,112] and characterised by their ^{31}P nmr spectroscopic parameters. (Ar = <u>o</u>-$MeOC_6H_4$; $\delta = -5.4$ppm, $^1J_{PtP} = 1487$ Hz: Ar = <u>o</u>-ClC_6H_4; $\delta = -7.5$ppm, $^1J_{PtP} = 1541$ Hz, $^2J_{CP} = 8.5$ Hz : Ar = <u>p</u>-$MeO_2CC_6H_4$; $\delta = -5.8$ppm, $^1J_{PtP} = 1410$ Hz). To each solution was added one mol. equivalent of <u>cis</u>-[$PtCl_2$(CO)(PPh_3)] in $CDCl_3$, and the reactions followed by ^{31}P nmr spectroscopy. Transfer of the aryl group to produce [PtCl(Ar)(CO)(PPh_3)] isomer (I) took 2½ hours to reach the equilibrium position with Ar = <u>p</u>-$MeO_2CC_6H_4$ ($\delta = +18.3$ ppm, $^1J_{PtP} = 1483$ Hz), but greater than 1 week for the other two cases. (Ar = <u>p</u>-$MeOC_6H_4$; $\delta = +18.8$ppm, $^1J_{PtP} = 1552$ Hz : Ar = <u>o</u>-ClC_6H_4, $\delta = +16.4$ppm, $^1J_{PtP} = 1607$ Hz). In the case where Ar = o-ClC_6H_4, [PtCl(Ar)(^{13}CO)(PMe_2Ph)] was used, and the label was scrambled after 1 week, although there was no scrambling within 12 hrs., during which time there had been substantial transfer of the aryl group.

[PtCl(C_5H_5)(CO)(PMe_2Ph)] and $HgCl_2$

[PtCl(C_5H_5)(CO)(PMe_2Ph)] (0.065mmol.) and $HgCl_2$ (16.8 mgs, 0.062mmol.) were mixed in $CDCl_3$ under a N_2 atmosphere. ^{1}H nmr examination showed that cis-[$PtCl_2$(CO)(PMe_2Ph)] and C_5H_5HgCl were produced over a period of several hours.

(c) Bis-σ-cyclopentadienyl complexes and transfer reactions

Cis-[Pt(η^1-C_5H_5)$_2$(CO)(PPh_3)]

cis-[$PtCl_2$(CO)(PPh_3)] (32.2mgs, 0.058mmol.) and C_5H_5Tl (63.0mgs, 0.234mmol.) were stirred together in $CDCl_3$ solution (0.5ml) under a nitrogen atmosphere. The reaction was monitored by ^{1}H and ^{31}P nmr spectrometry. Resonances assigned to [Pt(C_5H_5)$_2$(CO)(PPh_3)] (table 3) grew in strength, as those due to [PtCl(C_5H_5)(CO)(PPh_3)] diminished. Increasing quantities of decomposition products were also apparent in solution after 2 hours, and the bis-cyclopentadienyl complex could not be obtained in a pure state.

cis-[Pt(C_5H_5)$_2$(CO)(PPh_3)] and cis-[$PtCl_2$(CO)(PPh_3)]

cis-[$PtCl_2$(CO)(PPh_3)] (27.7mg, 0.050mmol.) and C_5H_5Tl (49.3mgs, 0.183mmol.) were stirred together in $CDCl_3$ (400µl) under nitrogen for 2 hours. After filtration, ^{1}H nmr investigation of the orange solution revealed the main product to be cis-[Pt(C_5H_5)$_2$(CO)(PPh_3)] (55%). A solution of cis-[$PtCl_2$(CO)(PPh_3)] (15.2mg, 0.027mmol.) in $CDCl_3$ (100µl) was added. ^{1}H nmr investigation now revealed

[$PtCl(C_5H_5)(CO)(PPh_3)$] as the main, and only cyclopentadienyl-containing product.

cis-[$Pt(C_5H_5)_2(CO)(PMe_2Ph)$] and cis-[$PtBr_2(CO)(PMe_2Ph)$]

cis-[$PtBr_2(CO)(PPhMe_2)$] (26.4mgs, 0.051mmol.) and C_5H_5Tl (18.4mgs, 0.068mmol.) were stirred together in $CDCl_3$ (500μl) under nitrogen for 45 minutes. After filtration, ^{31}P nmr investigation revealed a mixture of [$PtBr(C_5H_5)$-$(CO)(PMe_2Ph)$] and cis-[$Pt(C_5H_5)_2(CO)(PMe_2Ph)$] in the approximate ratio of 5:3. cis-[$PtBr_2(CO)(PMe_2Ph)$] (15.9mgs, 0.031mmol.) was added as a $CDCl_3$ (200μl) solution and ^{31}P nmr investigation showed only [$PtBr(C_5H_5)(CO)(PMe_2Ph)$] and some excess cis-[$PtBr_2(CO)(PMe_2Ph)$] present.

cis-[$Pt(C_5H_5)_2(CO)(PMePh_2)$] + cis-[$PtCl_2(CO)(PMe_2Ph)$]

cis-[$PtCl_2(CO)(PMePh_2)$] (31.3mgs, 0.064mmol.) and C_5H_5Tl (22.2mgs, 0.082mmol.) were stirred in $CDCl_3$ (500μl) under nitrogen for 45 minutes. After filtration, ^{31}P nmr investigation revealed a mixture of [$PtCl(C_5H_5)(CO)(PMePh_2)$] and cis-[$Pt(C_5H_5)_2(CO)(PMePh_2)$] in a ratio of 3:1. cis-[$PtCl_2(CO)(PMe_2Ph)$] (7.0mgs, 0.016mmol.) in $CDCl_3$ (100μl) was added and ^{31}P nmr investigation showed the presence of only [$PtCl(C_5H_5)(CO)(PMePh_2)$] and [$PtCl(C_5H_5)(CO)(PMe_2Ph)$].

(d) Asymmetrically Substituted Cyclopentadienyl (organo) platinum Complexes

Solutions of [$PtCl(C{\equiv}CR)(CO)L$], Cl trans to L (R = Me, L = $PMePh_2$; R = Ph, L = PMe_2Ph) and [$PtCl(Ar)(CO)(PMePh_2)$], Cl trans to $PMePh_2$, (Ar = Ph, $C_6H_4CO_2Me$-p) were prepared in situ as follows.[150]

$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$)

The complex *cis*-$[PtCl_2(CO)(PMePh_2)]$ (20.0mg, 0.040 mmol.), $[NEt_4]Cl$ (3.3mg, 0.020mmol.) and $Hg(C{\equiv}CMe)_2$ (5.7mg, 0.020 mmol.) were dissolved together in 0.5ml $CDCl_3$. A clear yellow solution and a silver grey precipitate formed. The precipitate, $[Et_4N]_2[Hg_2Cl_6]$, was filtered off. ^{31}P nmr investigation of the solution showed the presence of a single product, $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$), (see table 11).

$[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl *trans* to PMe_2Ph)

cis-$[PtCl_2(CO)(PMe_2Ph)]$ (17.0mg, 0.039 mmol.), $[NEt_4]Cl$ (3.3mg, 0.020mmol.) and $Hg(C{\equiv}CPh)_2$ (8.2mg, 0.020mmol.) reacted similarly in 0.5ml $CDCl_3$ to produce $[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl *trans* to PMe_2Ph), (see table 11).

$[PtCl(Ph)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$)

cis-$[PtCl_2(C_2H_4)(PMePh_2)]$ (20.0mg, 0.040mmol.) and $HgPh_2$ (14.4mg, 0.040mmol.) were mixed in $CDCl_3$ solution (0.5ml) and allowed to react for 1 hour. The solution was filtered and a ^{31}P nmr spectrum showed it to be a *cis*/*trans* mixture of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$, ($^{31}P$ nmr at -60°C δ = 0·0ppm, $^1J_{PtP}$ = 4940 Hz and δ = +0.1ppm, $^1J_{PtP}$ = 4993 Hz) in a ratio of 10:3. Carbon monoxide was bubbled through the solution, followed by N_2, and then the solution was allowed to stand at room temperature until ^{31}P nmr spectroscopic examination showed that it was pure $[PtCl(C_6H_5)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (δ = 1.2ppm, $^1J_{PtP}$ = 3928 Hz at -60°C).

$[PtCl(C_6H_4CO_2Me\text{-}\textit{p})(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$)

cis-$[PtCl_2(C_2H_4)(PMePh_2)]$ (20.0mg, 0.040mmol.) and $Hg(C_6H_4CO_2Me\text{-}\textit{p})_2$ (19.1mg, 0.040mmol.) were allowed to react in 0.5ml $CDCl_3$ for several hours. The solution was filtered and a ^{31}P nmr spectrum showed it to be $[Pt_2Cl_2(C_6H_4CO_2Me\text{-}\textit{p})_2(PMePh_2)_2]$ (^{31}P nmr at -60°C $\delta = -1.4$ppm, $^1J_{PtP} = 4901$ Hz and $\delta = -1.2$ppm, $^1J_{PtP} = 4930$ Hz). Carbon monoxide was bubbled through the solution, followed by N_2, and then it was allowed to stand at room temperature until ^{31}P nmr spectroscopic examination revealed it to be the desired isomer of $[PtCl(C_6H_4CO_2Me\text{-}\textit{p})(CO)(PMePh_2)]$ ($\delta = -2.6$ppm, $^1J_{PtP} = 3826$ Hz at -60°C).

$[Pt(\eta^1\text{-}C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$)

A solution of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$, (Cl *trans* to $PMePh_2$), (0.061mmol.) in 0.5ml $CDCl_3$ was allowed to react with TlC_5H_5 (16.4mg, 0.061mmol.) for 10 minutes at room temperature. Spectroscopic investigation (^{31}P and ^1H nmr) of the solution revealed it to be pure $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$. (tables 4 and 5).

$[Pt(\eta^1\text{-}C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (C_5H_5 *trans* to PMe_2Ph)

A similar reaction was performed using $[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl *trans* to PMe_2Ph) (0.039 mmol.) and TlC_5H_5 (12.2mg, 0.045mmol.). ^{31}P nmr examination of the solution showed that the only product was $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (C_5H_5 *trans* to PMe_2Ph). (table 5).

$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ and $Hg(C_5H_5)_2$

A $CDCl_3$ solution of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (0.040mmol.) and a $CDCl_3$ solution of $Hg(C_5H_5)_2$ (13.4mg, 0.040mmol.) were mixed at -60°C and allowed to react at room temperature. Initially, the complex $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$(identified by ^{31}P nmr) was produced, but subsequent reactions led to the production of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I), and a small amount of *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$.

$[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ and $HgCl_2$

$HgCl_2$ (25.0mg, 0.093mmol.) was added to a solution of $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$, (0.040mmol.) in 0.5ml. $CDCl_3$ at -60°C. A ^{31}P nmr. investigation showed that within 45 minutes this had reacted to produce $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$).

$[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ and Ph_3PAuCl

A $CDCl_3$ solution of $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (0.061mmol.) was added to a $CDCl_3$ solution of Ph_3PAuCl (22.5mg, 0.046mmol.) at room temperature. ^{31}P nmr investigation showed that there was no reaction, other than normal decomposition of the cyclopentadienyl platinum complex.

$[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ and *cis*-$[PtCl_2(CO)(PMePh_2)]$

A solution of *cis*-$[PtCl_2(CO)(PMePh_2)]$ (13.8mg, 0.028 mmol.) in 0.2ml $CDCl_3$ was mixed with a solution of

$[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (0.039mmol.) at room temperature. ^{31}P nmr investigation of the mixture revealed the presence of $[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl *trans* to PMe_2Ph), $[PtCl(C_5H_5)(CO)(PMePh_2)]$, ($C_5H_5$ *trans* to $PMePh_2$), $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ and *cis*-$[PtCl_2(CO)(PMePh_2)]$.

$[Pt(C_5H_5)(Ph)(CO)(PMePh_2)]$, ($C_5H_5$ *trans* to $PMePh_2$)

TlC_5H_5 (11.5mg, 0.043mmol.) was added to a solution of $[PtCl(Ph)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (0.0405mmol.) in 0.5ml $CDCl_3$. After 15 minutes at room temperature, spectroscopic examination showed that the major product was $[Pt(C_5H_5)Ph(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$)]. ^{31}P and ^1H nmr data are given in tables 4 and 5. A minor byproduct was identified by ^{31}P nmr spectroscopy as *cis*-$[PtPh_2(CO)(PMePh_2)]$ (^{31}P nmr at 25°C, $\delta = +2.5$ppm, $^1J_{PtP}=$ 1611 Hz[157]).

$[Pt(C_5H_5)(C_6H_4CO_2Me$-*p*$)(CO)(PMePh_2)]$ (C_5H_5*trans* to $PMePh_2$)

A similar reaction was carried out between TlC_5H_5 (10.9mg, 0.040mmol.) and $[PtCl(C_6H_4CO_2Me$-*p*$)(CO)(PMePh_2)]$ (0·040mmol.) to produce $[Pt(C_5H_5)(C_6H_4CO_2Me$-*p*$)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$).

$[Pt(C_5H_5)(C_6H_4CO_2Me$-*p*$)(CO)(PMePh_2)]$ and *cis*-$[PtCl_2(^{13}CO)(PMe_2Ph)]$

A solution of $[Pt(C_5H_5)(C_6H_4CO_2Me$-*p*$)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$) (0.040mmol.) in 0.3ml $CDCl_3$ was mixed with a solution of cis-[$PtCl_2(^{13}CO)(PMe_2Ph)$] (14.3mg, 0.033mmol.) in 0.3ml $CDCl_3$ at room temperature. After 15 minutes, ^{31}P nmr spectroscopic examination of the solution revealed the presence of equal amounts of [$PtCl(C_6H_4CO_2Me$-p)-(CO)($PMePh_2$)] (Cl trans to $PMePh_2$) and [$PtCl(C_5H_5)(^{13}CO)$-(PMe_2Ph)] (C_5H_5 trans to PMe_2Ph).

(e)η^5-Cyclopentadienyl Complexes

[$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2$]Cl

The complex cis-[$PtCl_2(PMe_2Ph)_2$] (30.2mg, 0.054mmol.) and TlC_5H_5 (16.9mg, 0.063mmol.) were stirred together suspended in $CDCl_3$ (0.5ml) under a N_2 atmosphere for 2 hours. The orange-yellow solution was filtered (to remove TlCl and unreacted TlC_5H_5) into an nmr tube. ^{31}P and ^1H nmr spectra (tables 6 and 7) indicated the presence in solution of only [$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2$]Cl.

[$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2$]$SO_3CF_3$

$AgSO_3CF_3$ (30.0mg, 0.117mmol.) was added to a solution of [$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2$]Cl (0.049mmol.) prepared as above, and allowed to react at room temperature for 5 minutes. The solution was then filtered and ^1H and ^{31}P nmr spectra (tables 6, 7) showed that replacement of Cl^- by $SO_3CF_3^-$ did not affect the parameters.

[$Pt(\eta^5-C_5H_5)(PMePh_2)_2$]Cl

cis-[$PtCl_2(PMePh_2)_2$] (28.8mg, 0.043mmol.) and C_5H_5Tl (13.5 mg, 0.050mmol.) similarly reacted in $CDCl_3$ in 2 hours to produce [$Pt(\eta^5-C_5H_5)(PMePh_2)_2$]Cl. (tables 6, 7).

$[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]Cl$

cis-$[PtCl_2(PPh_3)_2]$ (28.8mg, 0.036mmol.) and TlC_5H_5 (10.6mg, 0.039mmol.) were mixed in $CDCl_3$ (0.5ml) under a N_2 atmosphere. After 3 days reaction, spectroscopic examination revealed the major species to be $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]Cl$ (tables 6, 7).

$[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$

$AgSO_3CF_3$ (17.0mg, 0.066mmol.) was added to a solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) (0.065mmol.) in $CDCl_3$ under N_2. After 1 hour, the solution was filtered and ^1H and ^{31}P nmr spectroscopic examination revealed the presence of $[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$ as the only species present (tables 6 and 7).

$[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]SO_3CF_3$

$AgSO_3CF_3$ (20.5mg, 0.080mmol.) and $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) (0·057mmol.) reacted similarly in $CDCl_3$ to produce $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]SO_3CF_3$ (tables 6, 7).

$[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]$ Cl and $HgCl_2$

$HgCl_2$ (8.4mg, 0.032mmol.) was added to a solution of $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]Cl$ (0.054mmol.) in $CDCl_3$ (0.5ml) and the solution examined by ^1H nmr spectroscopy. As well as unreacted starting material, ($[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]Cl$), resonances were observed from C_5H_5HgCl (δ 6.1ppm) and cis-$[PtCl_2(PMe_2Ph)_2]$(Phosphine methyl resonance : δ 1.76ppm, J_{PtH}= 34.5 Hz, H_{PH} = 11.0 Hz), within twenty minutes.

$[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ and $HgCl_2$

$HgCl_2$ (15.1mg, 0.056mmol.) was added to a solution of $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ (0.065mmol.) in $CDCl_3$ (0.5ml) and the solution examined by ^1H nmr spectroscopy. After 3 hours at room temperature, 50% of the π-complex had reacted and been replaced by *cis*-$[PtCl_2(PMe_2Ph)_2]$.

CHAPTER 3

ACETYLIDE AND ARYL TRANSFER REACTIONS AND CARBONYL INSERTION

INTRODUCTION

Platinum Acetylides

In the last thirty years a wide range of metal acetylide complexes have been prepared, and the chemistry of such compounds has been the subject of a recent review.[164] Platinum acetylides are well-known, particularly complexes of the type <u>trans</u>-$[Pt(C{\equiv}CR)_2L_2]$[165] and <u>trans</u>-$[Pt(C{\equiv}CR)(X)L_2]$,[165, 166] (L = tertiary phosphine, X = halide). Oxidative addition of I_2, IBr, ICN, CF_3I and MeI to <u>trans</u>-$[Pt(C{\equiv}CR)(X)L_2]$ has been demonstrated,[167] where the ease of oxidative addition followed the order $R = Me > H > CF_3$, $X = C{\equiv}CR > Cl$. The platinum acetylides were found to be less susceptible to oxidative addition reactions than their methyl platinum analogues.

Recently, complexes of the type <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and $[PtCl(C{\equiv}CR)(CO)L]$, C≡CR <u>trans</u> to CO, have been prepared by a new preparative route utilising $Hg(C{\equiv}CR)_2$ compounds, to give better selectivity.[150,153] The production of $[PtCl(C{\equiv}CR)(CO)L]$, C≡CR <u>trans</u> to CO, was surprising, since previous reactions of <u>cis</u>-$[PtCl_2(CO)L]$ with phenyl, alkyl or substituted aryl mercurials appeared to produce only $[PtCl(R)(CO)L]$, R <u>trans</u> to L.[23,110-112] In fact it was found that the isomer with C≡CR <u>trans</u> to L was initially formed, but that further reaction occurred to produce <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ which reacted with $HgCl_2$ to form the isomer with C≡CR <u>trans</u> to CO (fig. 15).[150,153]

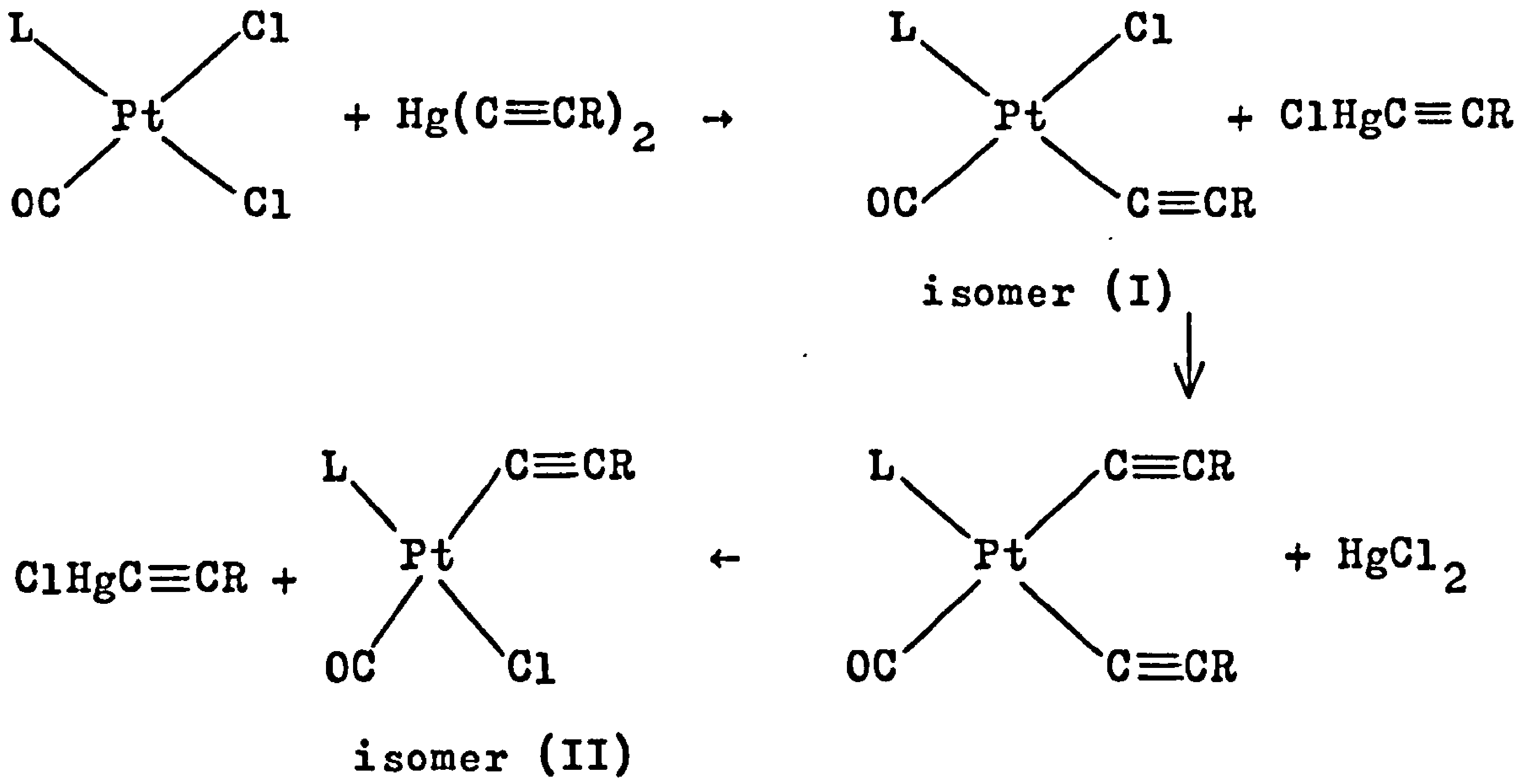
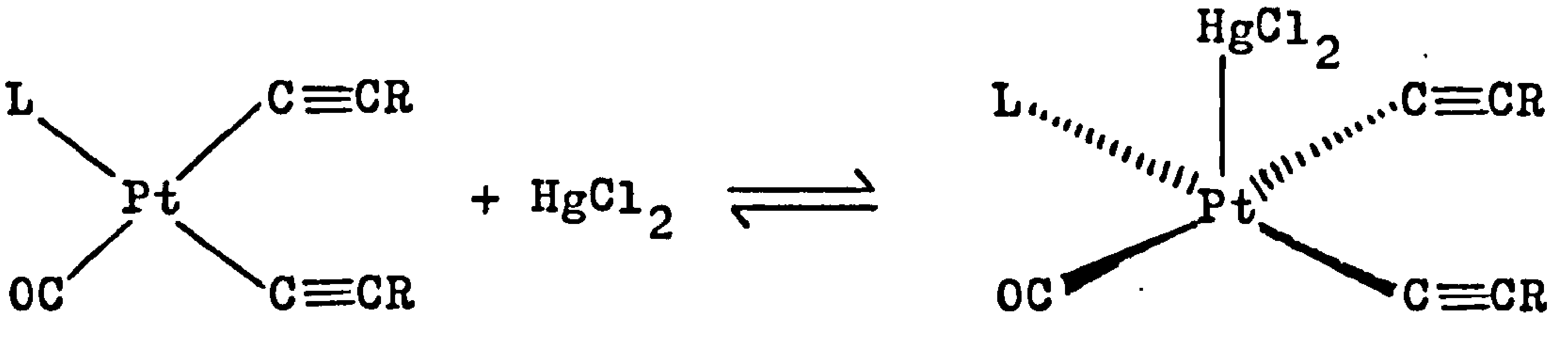


figure 15. (L = $PMePh_2$, R = Me,Ph)

The $[PtCl(C{\equiv}CR)(CO)L]$, $C{\equiv}CR$ <u>trans</u> to L, isomer (I), reacted very quickly with $ClHgC{\equiv}CR$, and was virtually undetectable in $CDCl_3$, even at low temperature, but was observed as the first intermediate when the reaction was performed in THF. The <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgCl_2$ formed a fluxional system whose ^{31}P nmr parameters varied with the extent of reaction and changed with temperature, broadening at low T, with one satellite broadening more than the other. This was interpreted as a rapid equilibrium between <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$, $HgCl_2$ and an associated intermediate, <u>A</u>. The same equilibrium was obtained independantly by mixing <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgCl_2$. The associated species <u>A</u> was thought to be a five or six-coordinate platinum complex, and a five-coordinate platinum mercury adduct was favoured, (fig. 16).



A

figure 16.

This was preferred since there are a number of precedents for such adducts of $HgCl_2$ and transition metals, for example $[RhCl(1,5\text{-}C_8H_{12})]_2.2\ HgCl_2$ which is completely dissociated in acetone solution.[168]

When the reaction was performed in THF, conversion of the equilibrium in figure 16 into [PtCl(C≡CR)(CO)L] isomer (II) was very slow compared to $CDCl_3$, thus it was suggested that good coordinating solvents would block the axial sites on <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and prevent formation of the associated adduct <u>A</u>.

It was also suggested that the production of [PtCl(C≡CR)-(CO)L] isomer (II) from cis-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgCl_2$ occurs by an oxidative addition/reductive elimination mechanism. When a mixed acetylide complex, [Pt(C≡CR)-$(C{\equiv}CR^1)$(CO)L], (C≡CR <u>trans</u> to L, CO <u>cis</u> to L), and $HgCl_2$ were allowed to react, the initial products were $[PtCl(C{\equiv}CR^1)(CO)L]$ isomer (II) and ClHgC≡CR, showing that the acetylide <u>trans</u> to phosphine was cleaved directly. Both <u>cis</u>- and <u>trans</u>- oxidative additions of $HgCl_2$ were considered possible (fig. 17).

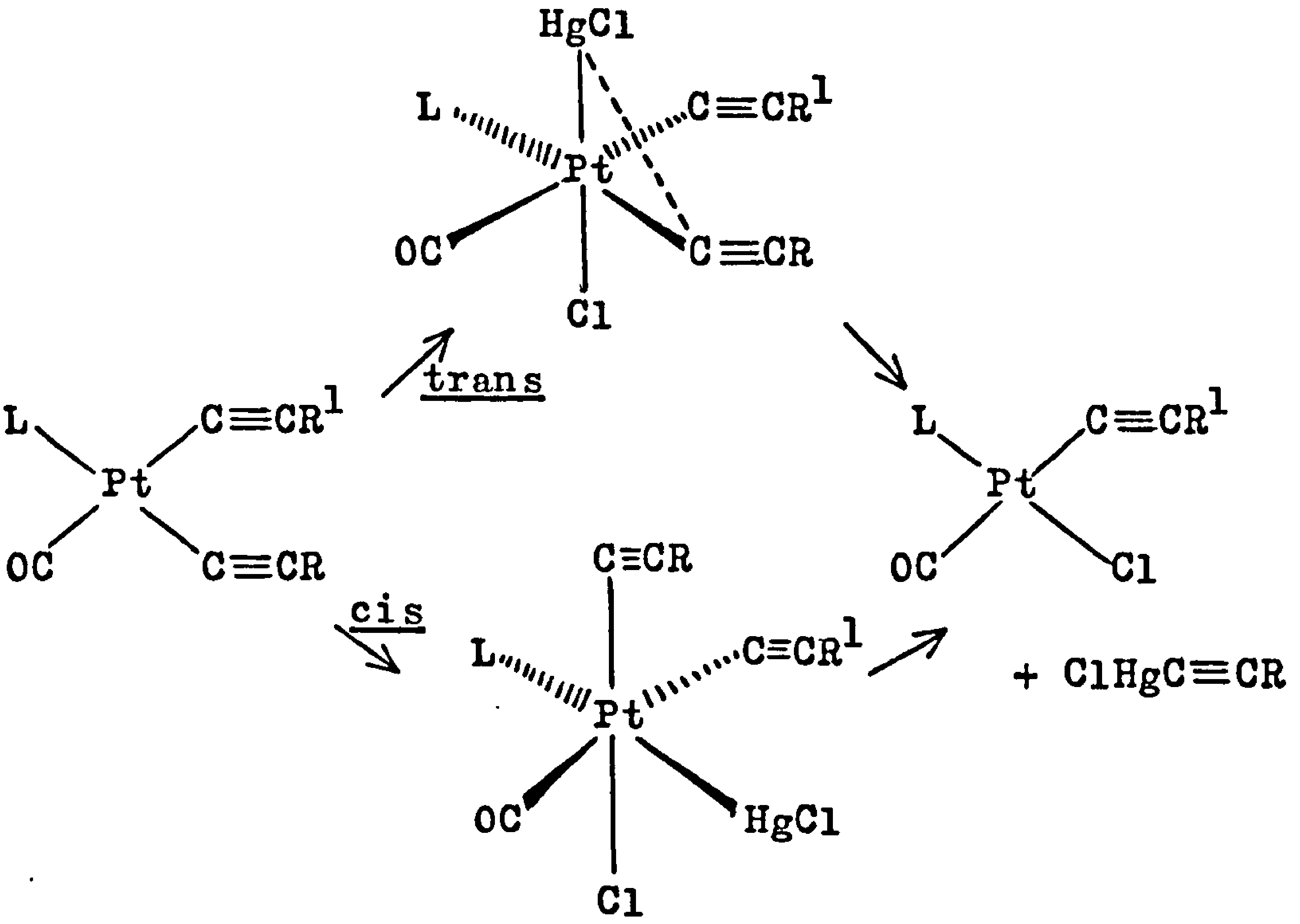
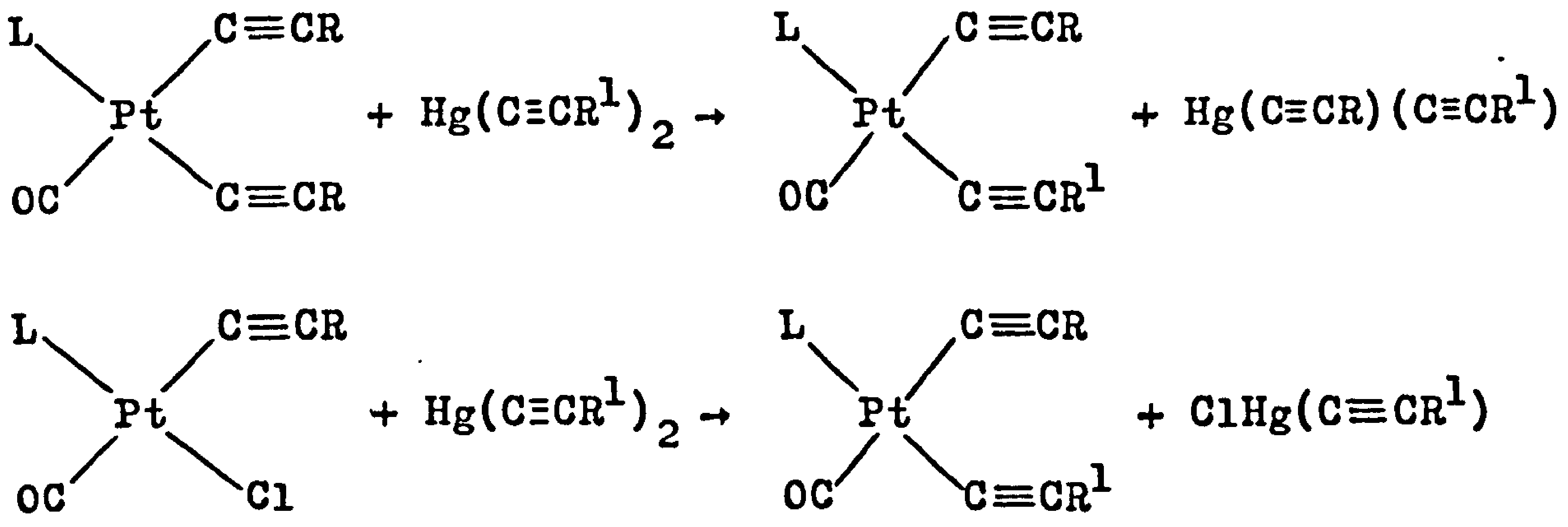


figure 17.

The formation of cis-[Pt(C≡CR)$_2$(CO)L] from [PtCl(C≡CR)-(CO)L] isomer (I) and ClHg(C≡CR) was also considered to be via an oxidative addition/reductive elimination mechanism because a good coordinating solvent considerably slowed the reaction. Several intermediates resulting in the observed products are possible, but a trans-oxidative addition of ClHg(C≡CR) was favoured.[153] The formation of [PtCl(C≡CR)-(CO)L] isomer (I) from cis-[PtCl$_2$(CO)L] and Hg(C≡CR)$_2$ was suggested as being by an S_E2 (cyclic) mechanism, principally because no substantial slowing of this step was observed when the reaction occurred in a good coordinating solvent, and it was believed that an S_E2(cyclic) mechanism might be less inhibited than an oxidative addition, by coordination of the solvent.

It was found that reactions of the bisethynylmercurials could be carried out in the presence of [Et$_4$N]Cl, which symmetrises the $ClHgC{\equiv}CR$ byproduct to $Hg(C{\equiv}CR)_2$, (thus making both acetylide groups available for transfer to platinum) and $[Et_4N]_2[Hg_2Cl_6]$ (which, being insoluble in organic solvents, is easily separated from the desired product). In this way, by controlling the amount of $Hg(C{\equiv}CR)_2$ and $[Et_4N]Cl$, solutions of <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and $[PtCl(C{\equiv}CR)(CO)L]$ isomer (II) could be made free of $ClHgC{\equiv}CR$ byproduct.

Exchange reactions of acetylides were also studied.[150,153] The reaction of <u>cis</u>-$[Pt(C{\equiv}CR)_2(CO)L]$ and $Hg(C{\equiv}CR^1)_2$ produced initially only one isomer of $[Pt(C{\equiv}CR)(C{\equiv}CR^1)$-$(CO)L]$, CO <u>cis</u> to L, and the same isomer was produced by the reaction between $[PtCl(C{\equiv}CR)(CO)L]$ isomer (II) and $Hg(C{\equiv}CR^1)_2$.



Both of these reactions were considered to proceed via an S_E2(cyclic) mechanism, although it was noted that the <u>cis</u>-oxidative addition/reductive elimination which is related to it by a strong Hg-Pt interaction was indistinguishable from the S_E2 (cyclic) mechanism, fig. 18.

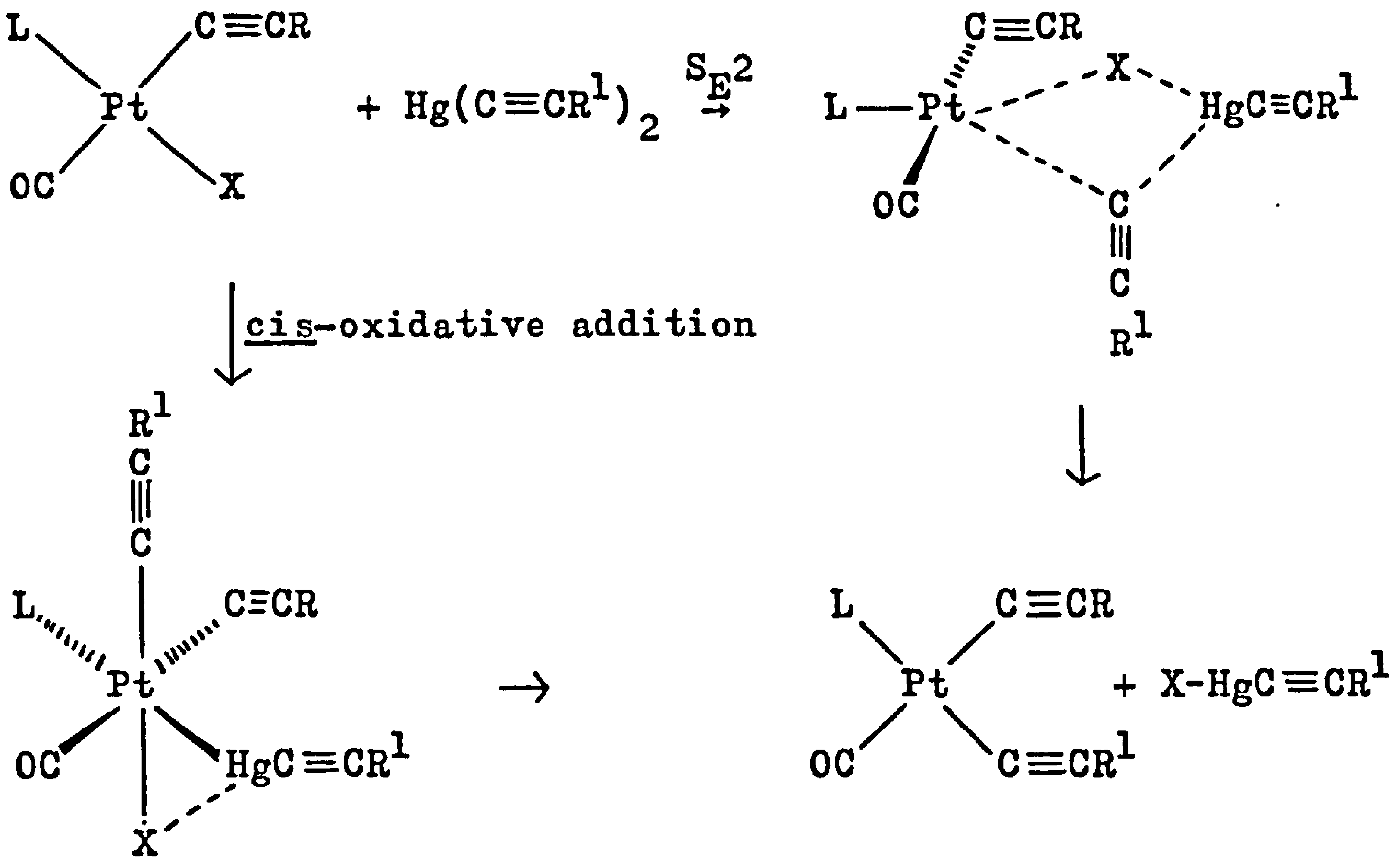


Figure 18. (X = Cl or C≡CR)

When $Ph_3PAuC\equiv CR$ was used instead of the mercurial, reaction with <u>cis</u>-$[PtCl_2(CO)L]$ was not stereospecific.[160] Low temperature nmr experiments showed that both isomer(I) and isomer (II) of $[PtCl(C\equiv CR)(CO)L]$ were formed initially, and that they reacted preferentially with $L^1AuC\equiv CR$ to form <u>cis</u>-$[Pt(C\equiv CR)_2(CO)L]$, which then transferred an acetylide to unused <u>cis</u>-$[PtCl_2(CO)L]$ to produce only isomer (II), (fig.19).

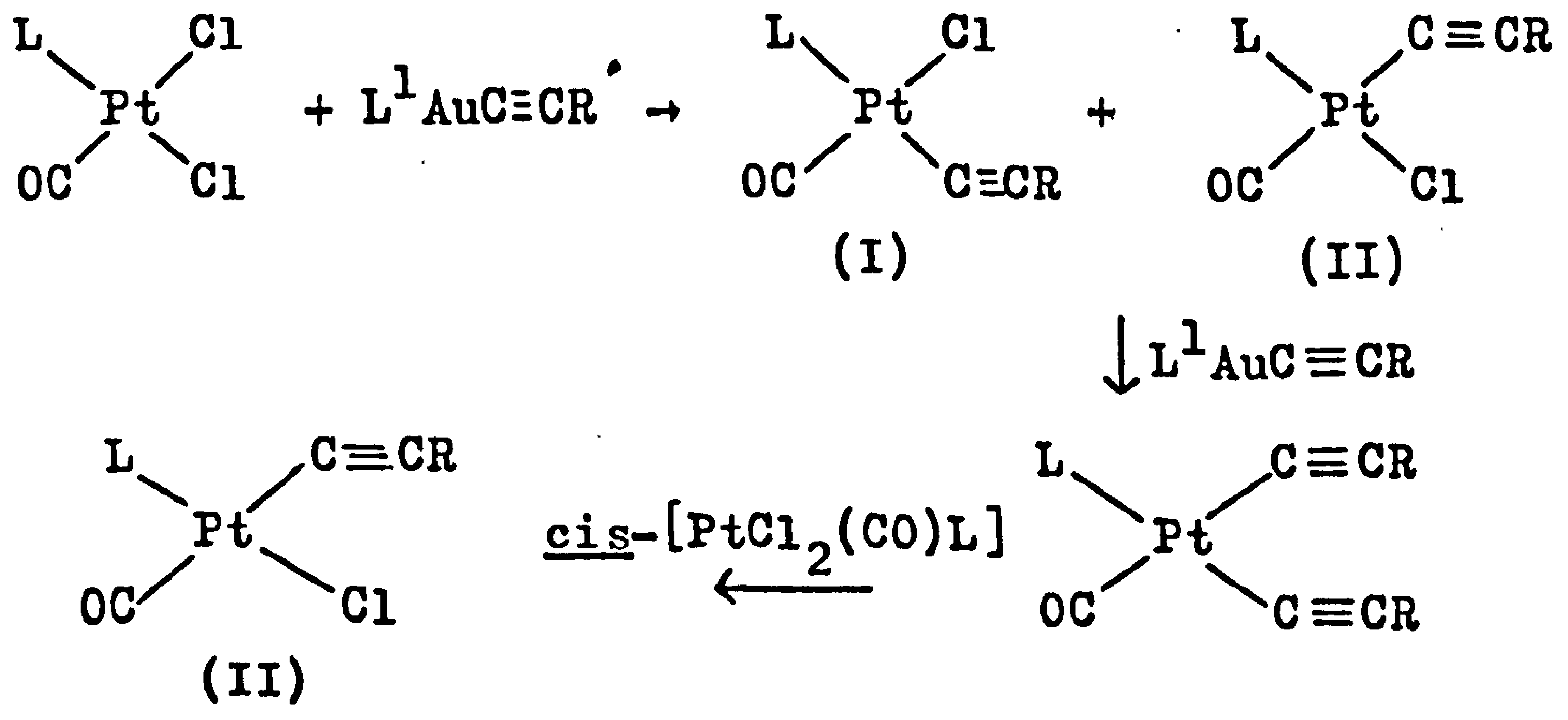
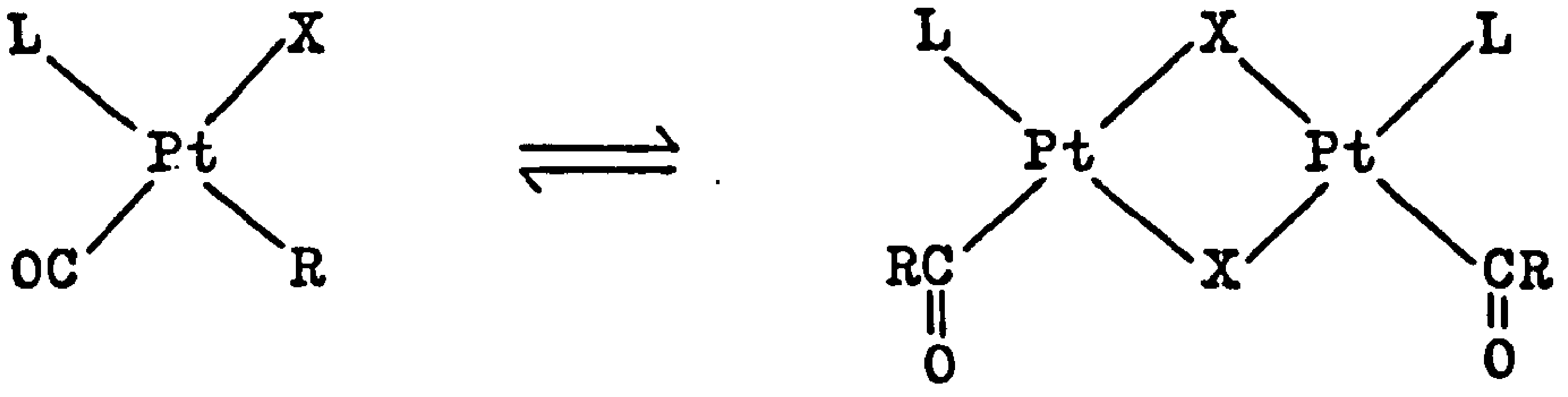


figure 19.

The lack of specificity in which chloride was initially replaced could not be explained, although it was pointed out that, in addition to an S_E2 (cyclic) reaction and cis-oxidative addition/reductive elimination at Pt, there was also the possibility of oxidative addition/reductive elimination at Au. It was suggested that competing reactions, with no one reaction favoured, were occurring.

Carbonyl Insertion at Square-Planar Platinum (II)

Anderson and Cross have shown that only one isomer of [PtCl(R)(CO)L], isomer (I) with R trans to L, undergoes carbonyl insertion, and exists in equilibrium with the halide bridged inserted dimer (IV).[169]



(I) (IV)

The other two isomers of [PtX(R)(CO)L], ((II) with R trans to CO and (III) with R trans to X) slowly interconvert via reversible CO loss and (I) and (IV) slowly interconvert via reversible loss of L[23]. Isomer (I) appeared to be the most thermodynamically stable form.

The position of the equilibrium between isomer (I) and inserted dimer (IV) is affected by the nature of the organic group, the halide and the phosphine. It was found that there was a decrease in the extent of insertion for the series $R = Et > Ph > Me > CH_2Ph$, with $R = CH_2Ph$ existing as 100% isomer (I) in solution.[23] The inserted dimer, (IV), was favoured by stronger bridging halides, X = I > Br > Cl.[110] Neutral ligands, L, were found to exert an effect by both electronic and steric factors. The extent of insertion followed the trans-influence series for L = $PEt_3 > PMe_2Ph > PMePh_2 > PPh_3 > AsMePh_2 > AsPh_3$, but bulkier phosphines, $P(C_6H_{11})_3$ and $P(C_6H_4Me\text{-}o)_3$, which electronically resemble PEt_3 and PPh_3 respectively, did not fit the sequence. With L = $P(C_6H_{11})_3$ and $P(C_6H_4Me\text{-}o)_3$, isomer (I) was favoured for steric reasons, and it appeared that the trans influence dominated equilibrium positions up to a critical ligand size, when steric effects became important.[110] This critical size apparently being a cone angle greater than 145° (for PPh_3) but less than 170° (for $P(C_6H_{11})_3$).

Recently more detailed work has been reported by Cross and Gemmill on a series of substituted aryl compounds, to investigate electronic and steric effects of the R-group on the equilibrium position.[112,153] They found that in a series of meta- and para- substituted aryl isomer (I) complexes, $[PtCl(C_6H_4Y)(CO)L]$, insertion was inhibited by electron-withdrawing substituents and promoted by electron-donating substituents. The electronic effects of the aryl groups on the insertion reaction were found to be as important as any of the other factors (effect of X and L), with variations in the equilibrium from 0% (I) ($C_6H_4NMe_2\text{-}p$) to 100% (I) ($C_6H_4CN\text{-}p$). The order for promotion of carbonyl insertion of meta- and para- substituted aryl groups was found to follow the sequence of Hammett σ constants, showing that it is the overall electron-donating or -withdrawing properties which influence the reaction.

Ortho- substituted aryl groups did not insert, and thus do not fit in the sequence, and this was thought to be a steric effect. The bulky *ortho* group would block the migration of the aryl group.

Methods of promoting insertion by displacing the equilibrium have been used to make groups which appear to exist as 100% isomer (I) insert, by removing complex (IV). Thus, addition of phosphine to a solution of $2[PtCl(R)(CO)L]$ isomer (I) $\rightleftharpoons$ $[Pt_2(COR)_2Cl_2L_2]$ (IV) removes the inserted dimer by bridge cleavage to form *trans*-$[PtCl(COR)L_2]$. When phosphine is slowly added to a solution of benzyl isomer (I), the insertion product *trans*-$[PtCl(COCH_2Ph)L_2]$ is formed, indicating that there must be undetectable amounts of (IV) in equilibrium with (I). Fast addition of phosphine leads to nucleophilic substitution at (I), displacing CO and producing *trans*-$[PtCl(CH_2Ph)L_2]$.[23] Phosphine addition, however, fails to promote insertion with some other organic groups and leads only to CO displacement. Added L can thus react with either side of the equilibrium, either by nucleophilic substitution at (I) or by dimer cleavage, depending on the position of the equilibrium and the size of the rate constants K_3L and K_2L (fig. 20).

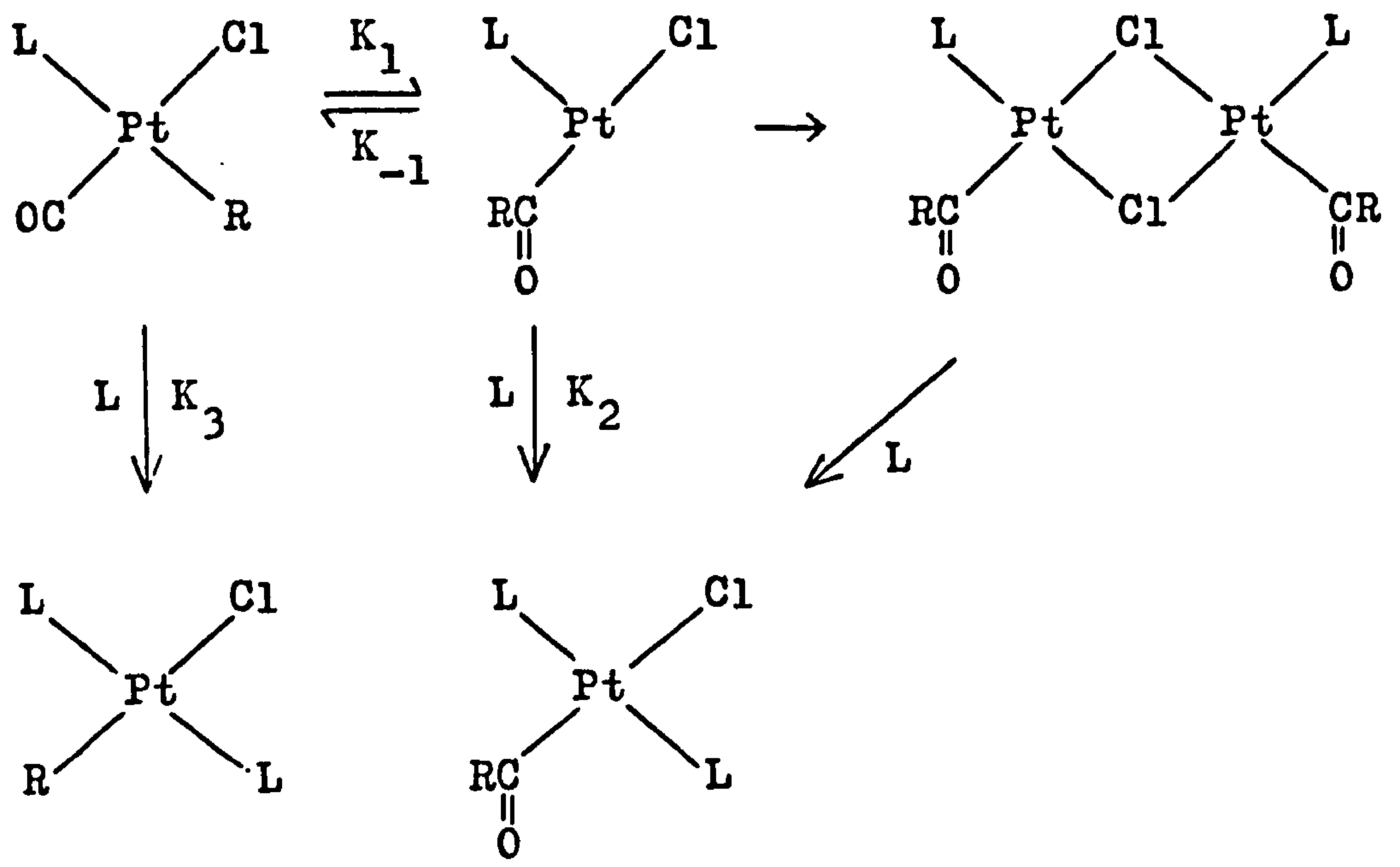


figure 20.

A second nucleophile-assisted method involves the addition of Cl^- to displace the equilibrium,[170] by cleaving inserted dimer (IV) and forming cis-$[PtCl_2(COR)L]^-$. Thus C_6H_4CN-p isomer (I) formed cis-$[PtCl_2(COC_6H_4CN\text{-}p)L]^-$ on addition of Cl^-, but did not insert on addition of phosphine, losing CO to produce trans-$[PtCl(C_6H_4CN\text{-}p)L_2]$.[153] Cl^- is a poorer nucleophile for substitution at square-planar Pt^{II} than phosphine, but is a good nucleophile for bridge-cleavage in Pt^{II} dimers, thus Cl^- addition can promote insertion in cases where phosphine addition fails.

The best method for promoting CO insertion at isomer (I), however, appears to be replacing Cl^- by Br^- or I^-. The softer halides form stronger bridges in dimers, and organic groups which are reluctant to insert as $[PtCl(R)(CO)L]$ isomer (I) readily insert as $[PtI(R)(CO)L]$ isomer (I). A number of R-groups which exist as 100% isomer (I) in solution and methods to promote their insertion are shown in table 8.

Table 8. [PtCl(R)(CO)L] 100% isomer (I) in solution ($CDCl_3$ at Room temperature) and methods for promoting insertion to $[Pt_2(COR)_2Cl_2L_2]$.

		Insertion by :-			
L	R	Adding L	Adding Cl^-	Changing halide to I^-	Ref.
$P(C_6H_4Me-\underline{o})_3$	Ph	No	-	-	110
$AsMePh_2$	Ph	Yes	-	-	110
$AsPh_3$	Ph	Yes	-	-	110
$PMePh_2$	CH_2Ph	Yes	-	-	23
$PMePh_2$	$C_6H_4CN-\underline{p}$	No	Yes	Yes	112, 153, 170.
$PMePh_2$	$C_6H_4Me-\underline{o}$	No	Yes	Yes	112, 153, 170.
$PMePh_2$	$C_6H_4OMe-\underline{o}$	No	-	Yes	112, 153, 170.
$PMePh_2$	C_2Cl_3	No	No	No	153

RESULTS AND DISCUSSION

Reactions of $[PtCl(\eta^1-C_5H_5)(CO)L]$ isomer (I) and Organomercurials

$[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I) reacted with $Hg(C{\equiv}CMe)_2$ at -60°C to produce the same isomer of $[Pt(C{\equiv}CMe)(C_5H_5)(CO)L]$ as did the reaction between $[PtCl(C{\equiv}CMe)(CO)L]$ isomer (II), (Cl _trans_ to L), and $Hg(C_5H_5)_2$, but a similar amount of $[PtCl(C{\equiv}CMe)(CO)L]$ isomer (II) appeared simultaneously. Followed by ^{31}P nmr spectroscopy, the reaction continued until finally only _cis_-$[Pt(C{\equiv}CMe)_2(CO)L]$ and C_5H_5HgCl were present (fig. 21).

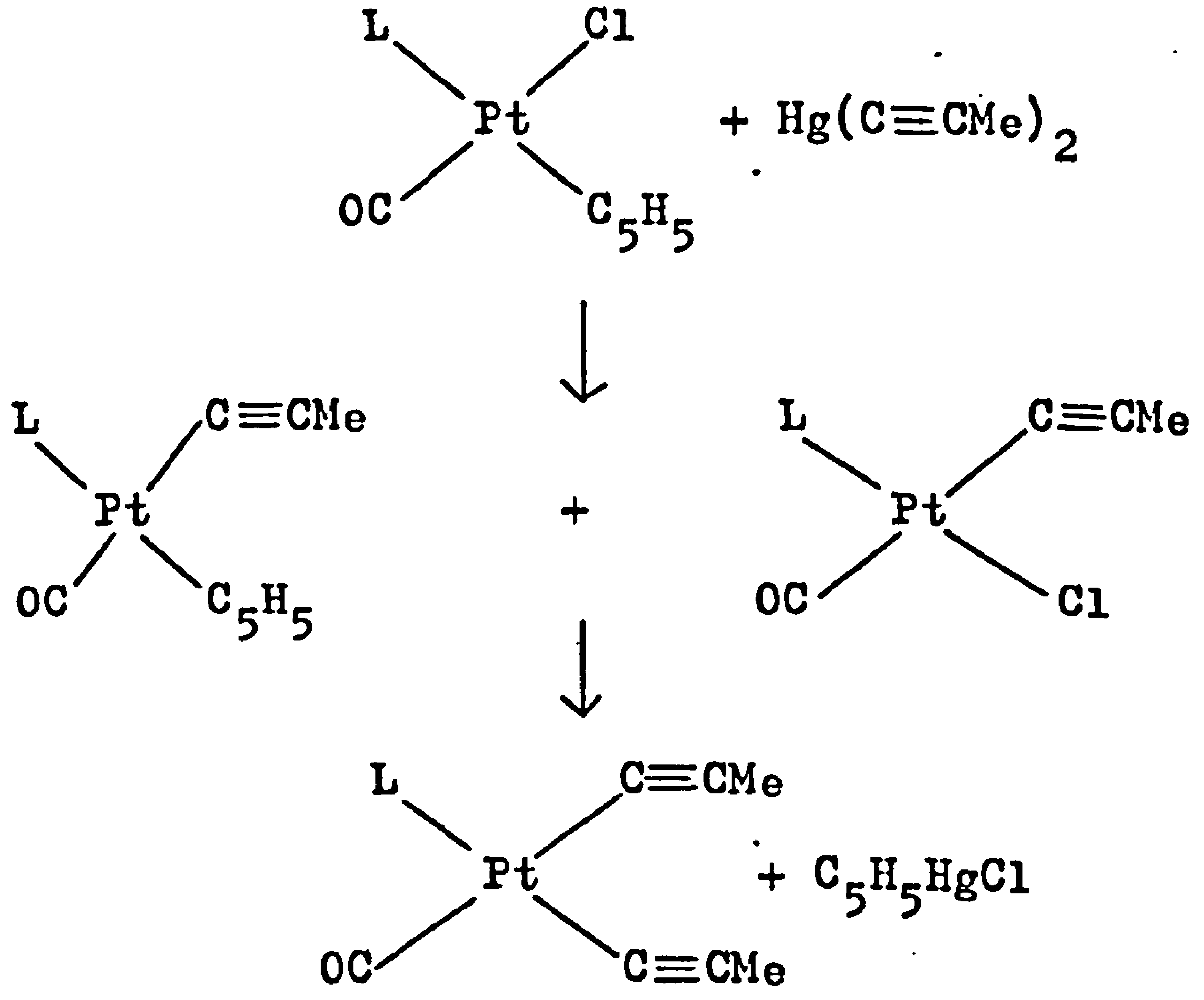
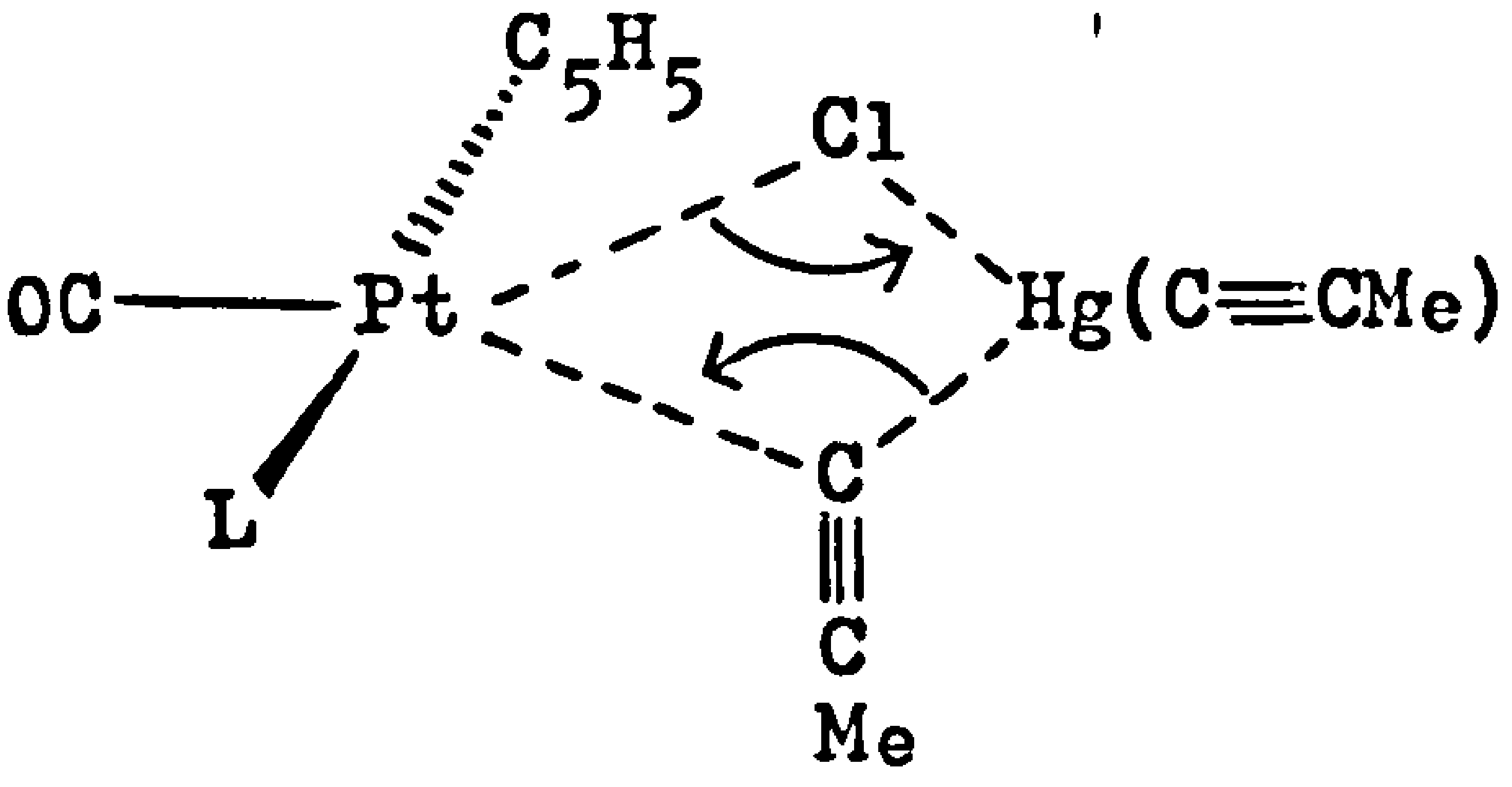


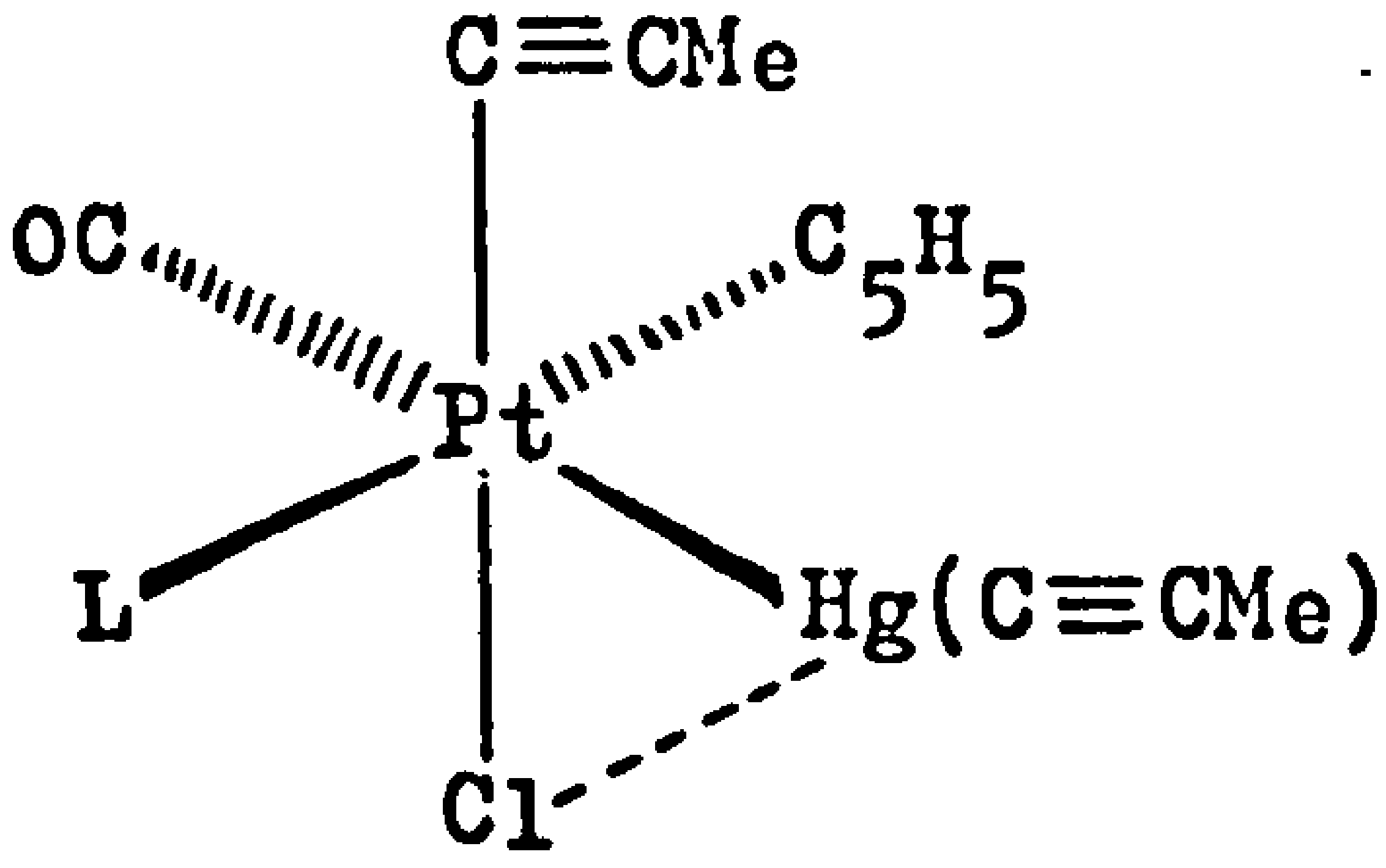
figure 21.

The formation of $[Pt(C_5H_5)(C{\equiv}CMe)(CO)L]$ can be accounted for by a replacement of the S_E2 (cyclic) type, with transition state B. Although the halide replaced is _trans_ to CO, it is the only halide present. Only one _cis_-oxidative addition/reductive elimination intermediate, C, could lead to this product, and that is the one where Hg displaces the

Cl and is trans to CO. No other intermediate except that obtained by a trans-oxidative addition of $Hg(C{\equiv}CMe)_2$ could lead to $[Pt(C_5H_5)(C{\equiv}CMe)(CO)L]$ by a concerted cis-reductive elimination, and a trans-addition is unlikely under these conditions.

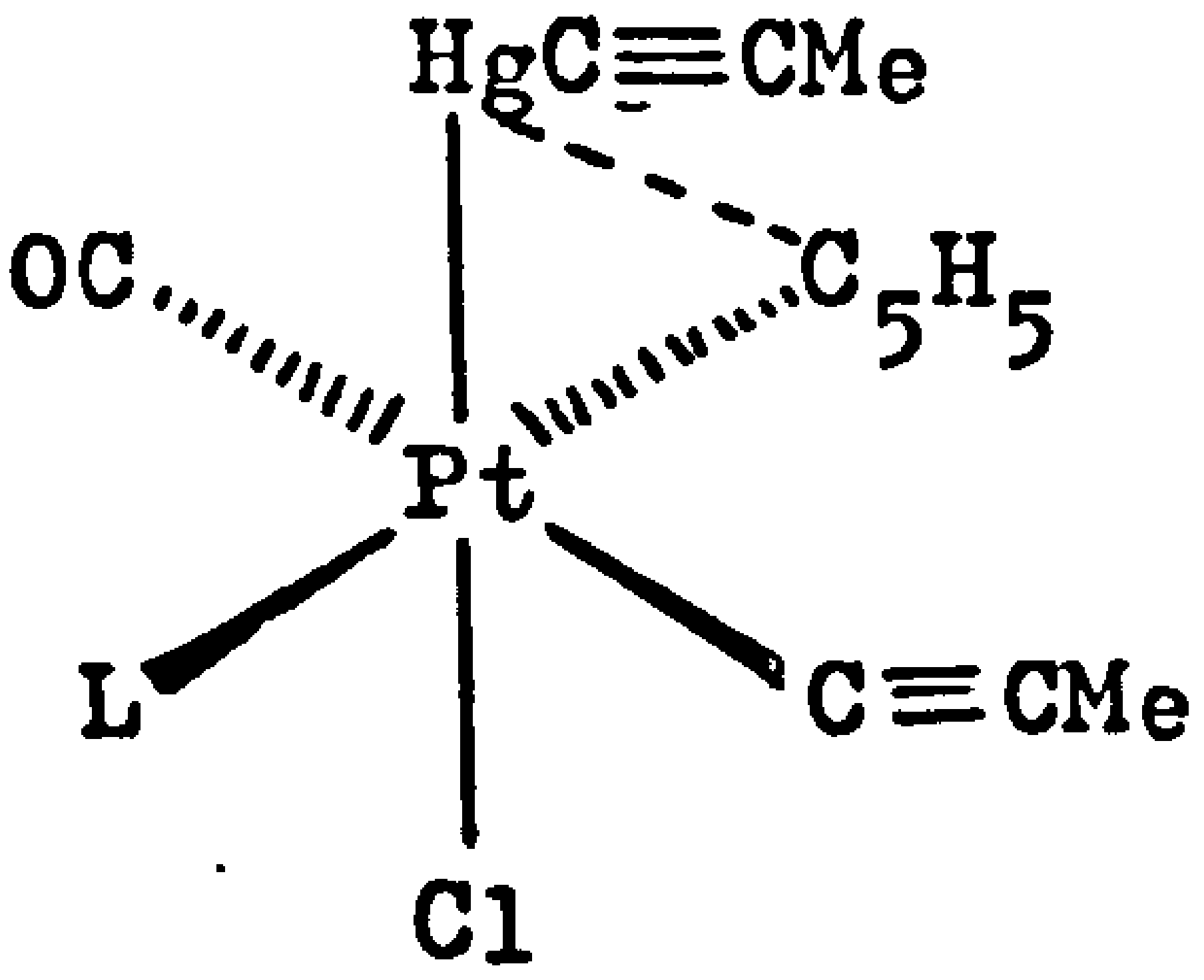


B



C

The formation of $[PtCl(C{\equiv}CMe)(CO)L]$ isomer (II), if it is a one-step process, is possible by a single specific oxidative addition of $Hg(C{\equiv}CMe)_2$ to platinum to form intermediate D, followed by reductive elimination of $C_5H_5HgC{\equiv}CMe$.



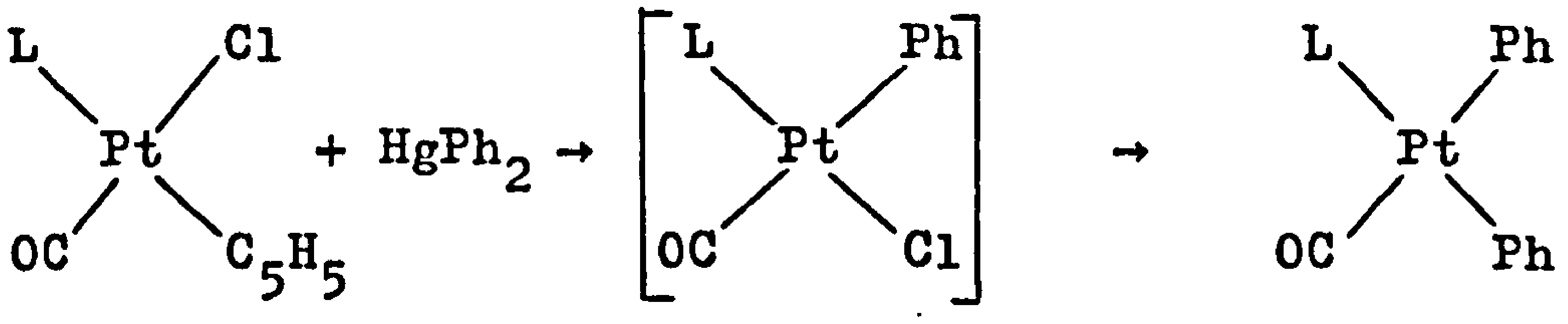
D

Both $ClHgC{\equiv}CMe$ and $C_5H_5HgC{\equiv}CMe$ are presumably also present at the intermediate stages of this reaction, so a variety of steps are possible for the final processes.

The analogous reaction carried out between $[PtCl(C_5H_5)-(CO)(PMePh_2)]$ isomer (I) and $HgPh_2$ was not as clean, or easy to interpret, possibly in part due to the fact that it took much longer. With $HgPh_2$ there was still a significant amount of cyclopentadienyl isomer (I) present after 7 hours at room temperature, whereas, with $Hg(C{\equiv}CMe)_2$ the reaction reached completion in 30 seconds at room temperature.

When $HgPh_2$ was added to $[PtCl(C_5H_5)(CO)L]$ isomer (I), ($L = PMePh_2$), at -60°C there was no reaction. On brief warming of the mixture to room temperature and cooling again to -60°C, a peak was present in the ^{31}P nmr spectrum at -1.2ppm. This is the chemical shift of $[PtCl(Ph)(CO)L]$ isomer (II) at -60°C, but the signal was too weak to observe $^1J_{PtP}$ coupling. After about 1 hour at room temperature, there was about 10% reaction to produce cis-$[PtPh_2(CO)L]$. After this, a number of other platinum complexes were obtained, most of which could be identified by their ^{31}P nmr parameters, (table 13). These included, $[Pt(\eta^5-C_5H_5)(COPh)L]$, trans-$[PtCl(Ph)L_2]$, trans-$[PtCl(COPh)L_2]$, a small amount of $[PtCl(Ph)(CO)L]$ isomer (I) and two unknown species, one at +5.3ppm whose $^1J_{PtP}$ varied from 5026 to 5049 Hz, and one at -18.8ppm which appeared to be a triplet with coupling of 13.6 Hz.

The production of cis-$[PtPh_2(CO)L]$ could have occurred in a similar way to one of the routes to cis-$[Pt(C{\equiv}CMe)_2(CO)L]$ with $Hg(C{\equiv}CMe)_2$, via $[PtCl(Ph)(CO)L]$ (II) if that was the species initially detected. No $[Pt(C_5H_5)Ph(CO)L]$, (C_5H_5 trans to L), was detected at any point during the reaction, so the other route through this may not have occurred. This would suggest the following reaction scheme as most likely:-



$HgPh_2$ has previously been shown to react with [PtCl(Ph)-(CO)L] (II) to form cis-[$PtPh_2$(CO)L].[153] The reaction of cyclopentadienyl isomer (I) to give phenyl isomer (II) would involve an oxidative addition/reductive elimination similar to that proposed for the reaction of $Hg(C{\equiv}CMe)_2$, with an intermediate similar to D.

Complexes trans-[PtCl(Ph)L_2] and trans-[PtCl(COPh)L_2] did not appear until more than four hours had passed, and presumably arose from subsequent reactions of cis-[$PtPh_2$-(CO)L], involving phosphine exchanges, and perhaps also organomercuric halide byproduct. The small amount of [PtCl(Ph)(CO)L] (I) was produced even later. [Pt(η^5-C_5H_5)-(COPh)L] was produced to an appreciable degree earlier in the reaction. (After 3 hours there was as much of this as there was cis-[$PtPh_2$(CO)L] and [PtCl(C_5H_5)(CO)L]). This compound is also produced in the reaction between an equilibrium mixture of [PtCl(Ph)(CO)L] (I) and [$Pt_2(COPh)_2Cl_2L_2$] (IV) and TlC_5H_5. For carbonyl insertion the phenyl and carbonyl ligands should be cis to each other. The production of [Pt(η^5-C_5H_5)(CO)L] could have come about by reactions involving cyclopentadienyl mercury byproduct and phenyl platinum complexes, but this is not likely. A more plausible reaction sequence is shown in fig. 22.

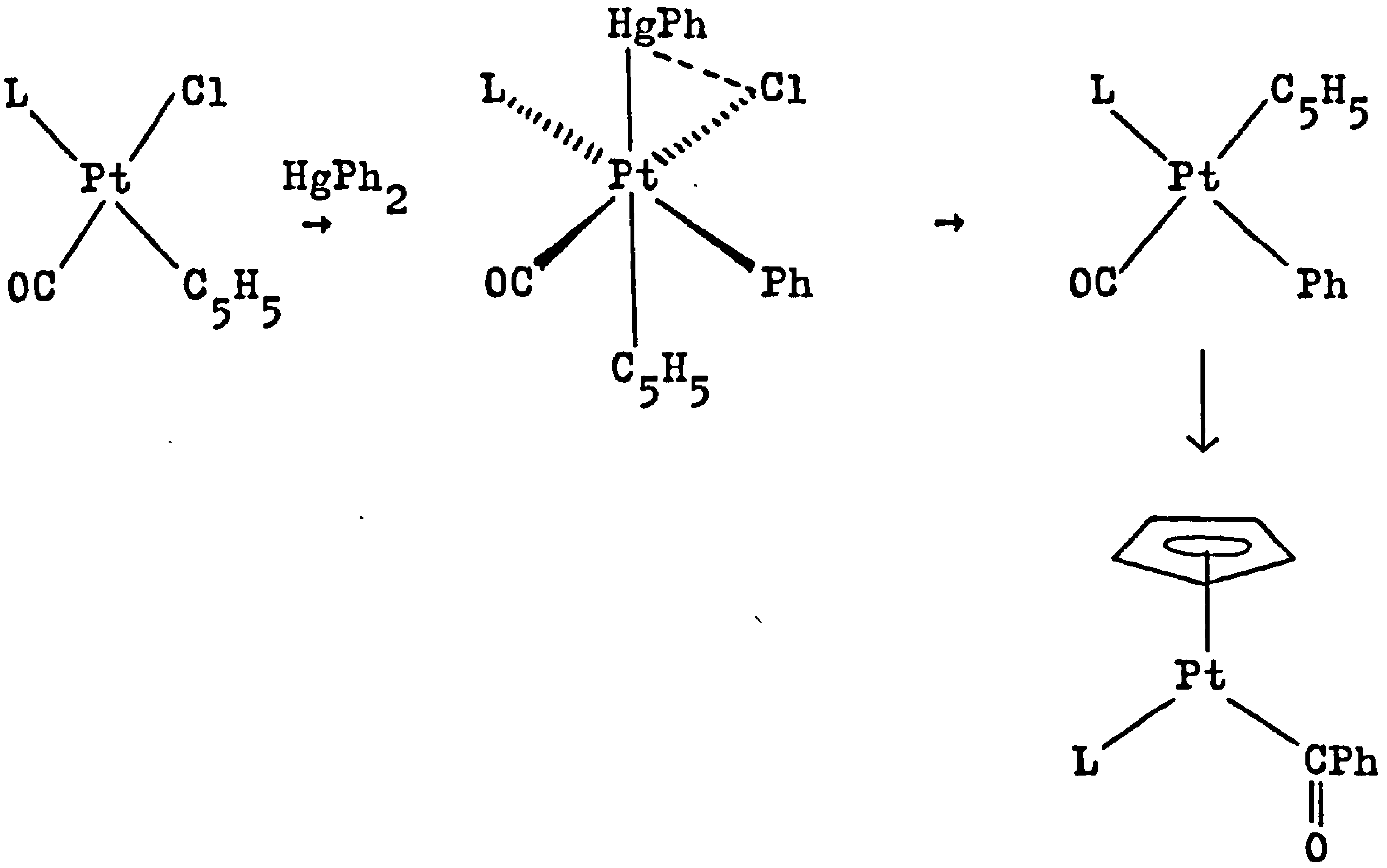


figure 22.

σ-π rearrangements of cyclopentadienyl rings are facile with a suitable leaving group, in this case a migrating phenyl group.

The unidentified species at $\delta p = -5.3$ppm is also produced early in the reaction. As the reaction progressed, the $^1J_{PtP}$ coupling constant increased from 5026Hz (3 hrs. reaction) to 5037 Hz (7 hrs.) to 5049 Hz (overnight reaction). This variation in coupling constant is reminiscent of the situation found with *cis*-[Pt(C≡CR)$_2$(CO)L] in the presence of $HgCl_2$; the transient species had a variable coupling constant with extent of reaction.[153] It is possible, but not any more than speculation, that this species at -5.3ppm involves association of mercuric byproduct. The other unidentified species is unusual in that it appears to be a triplet, but there is no other signal in the ^{31}P spectrum which accompanies it, as there should be if the triplet is a result of P-P coupling.

Cis-bisacetylide carbonyl phosphine platinum (II) Complexes

It was originally believed that site migrations of resident ethynyl groups occurred during formation and exchange reactions of $[Pt(C\equiv CMe)(C\equiv CPh)(CO)L]$,[171] and that these indicated the operation of unique oxidative addition/reductive elimination reactions. Site migrations of the ethynyl groups were based on $^5J_{PH}$ values for $C\equiv CMe$ protons. $[PtCl(C\equiv CMe)(CO)L]$ isomer (II) had a 5-bond phosphorus-proton coupling constant of 1.5 Hz, which was thought to be characteristic of a $C\equiv CMe$ group cis to phosphine. The mixed-bisacetylide complex made from $[PtCl(C\equiv CMe)(CO)L]$ (II) and $Hg(C\equiv CPh)_2$ was found to have $^5J_{PH}$ = 3.5 Hz, and it was concluded that $C\equiv CMe$ was now trans to phosphine. Similarly the product from $[PtCl(C\equiv CPh)(CO)L]$ (II) and $Hg(C\equiv CMe)_2$ had $^5J_{PH}$ = 1.5 Hz, which was considered to indicate that $C\equiv CMe$ was cis to phosphine and $C\equiv CPh$ was trans to phosphine.

However, the production of $[Pt(\eta^1\text{-}C_5H_5)(C\equiv CMe)(CO)L]$, ($C_5H_5$ trans to phosphine) from $[PtCl(C\equiv CMe)(CO)L]$ (II) and TlC_5H_5, which had a 5-bond phosphorus-proton coupling of 3.0 Hz to a $C\equiv CMe$ group cis to phosphine cast some doubt on this. The C_5H_5 J_{PH} of 4.5 Hz was indicative of C_5H_5 trans to L, and this was considered to be a reliable indication of the geometry of $[Pt(\eta^1\text{-}C_5H_5)(C\equiv CMe)(CO)L]$, and site migration was considered unlikely with TlC_5H_5 as the organic group transfer reagent (see chapter 2).

A solution of cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ was prepared by the symmetrisation method, using one equivalent of $Hg(C{\equiv}CMe)_2$ and one equivalent of $[Et_4N]Cl$ to prepare a clean sample free of mercury containing byproduct. The ^{13}C nmr spectrum was recorded and selective ^1H decoupling experiments were performed, which showed that the methyl group with the smaller $^5J_{PH}$ value, (1.95 Hz), was on the acetylide trans to phosphine, and the methyl group with the larger $^5J_{PH}$ value (3.3 Hz) was on the acetylide cis to phosphine. The ^{13}C and ^1H nmr data for cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ is shown in fig. 23. The two isomers of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, CO cis to phosphine, were also prepared, by reacting $[PtCl(C{\equiv}CR)(CO)L]$ isomer (II) with 0.5 equivalents of $Hg(C{\equiv}CR^1)_2$ and 0.5 equivalents of $[Et_4N]Cl$. ^{13}C nmr spectra were recorded at -60°C to prevent isomerisation reactions, and selective ^1H decoupling experiments were performed. These showed that the complex formed from $[PtCl(C{\equiv}CMe)(CO)L]$ (II) and $Hg(C{\equiv}CPh)_2$, with $^5J_{PH}$ of 2.8 Hz, had $C{\equiv}CMe$ cis to phosphine and $C{\equiv}CPh$ trans to phosphine; and the complex formed from $[PtCl(C{\equiv}CPh)(CO)L]$ (II) and $Hg(C{\equiv}CMe)_2$, had $C{\equiv}CMe$ trans to phosphine and $C{\equiv}CPh$ cis to phosphine. The ^{13}C nmr data for cis-$[Pt(C{\equiv}CMe)_2(CO)L]$ and both isomers of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]$ is given in table 9, and the ^1H nmr data in table 10.

The results of the ^{13}C nmr selective decoupling experiments showed that site migration of a resident ethynyl group did not occur; that in bis-acetylide complexes of this type, a $C{\equiv}CMe$ cis to phosphine has a larger $^5J_{PH}$ value (typically > 3 Hz) than a $C{\equiv}CMe$ trans to phosphine

Figure 23. ^{13}C and ^{1}H nmr parameters of cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] on a Bruker WP 200 SY spectrometer at 25°C.

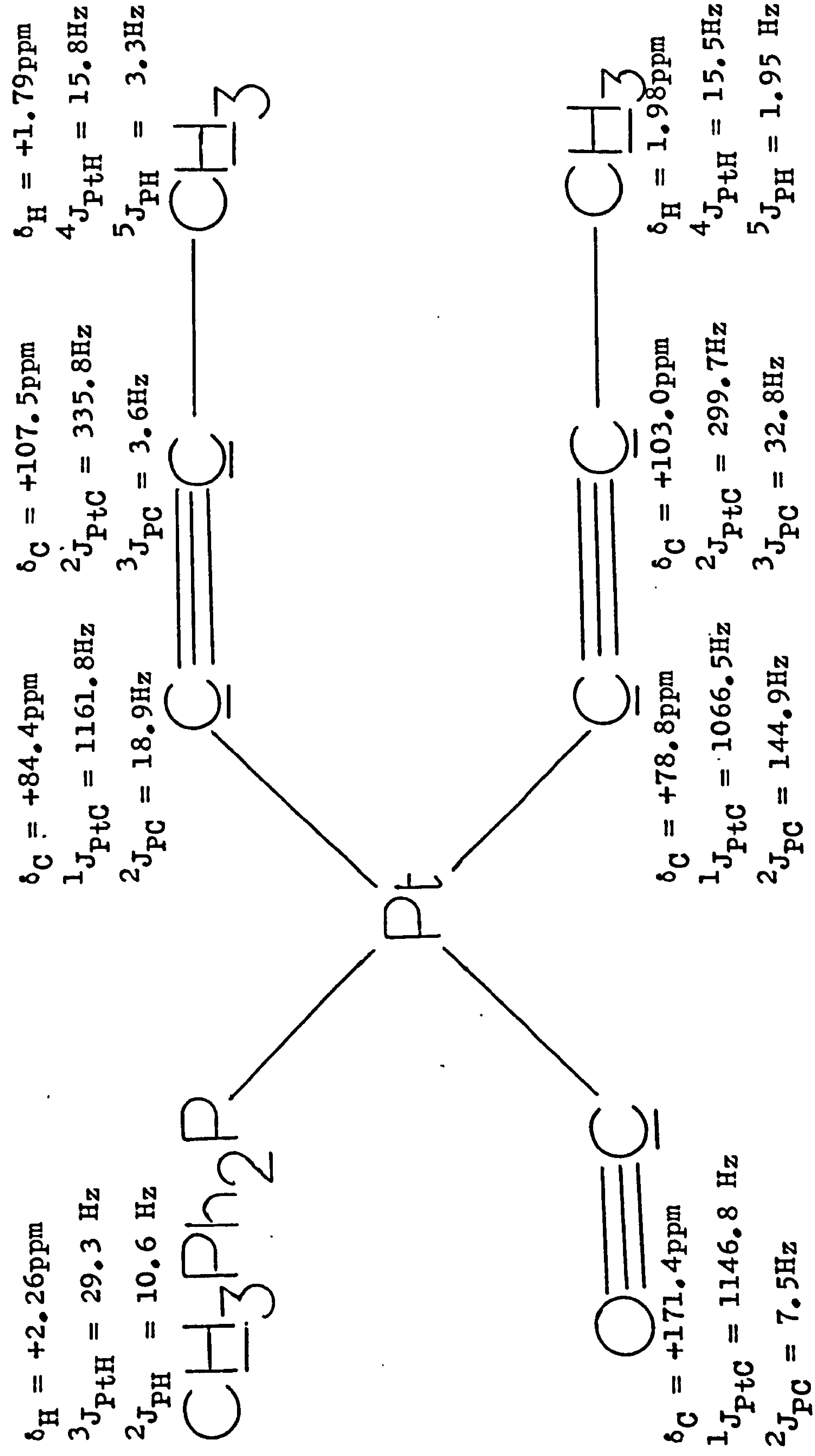


Table 9:- ^{13}C nmr data on complexes *cis*-[Pt(C≡CR)(C≡CR^1)(CO)L], (R = R^1 = Me; R = Me, R^1 = Ph).

Compound L = PMePh$_2$		δC_α (ppm)	δC_β (ppm)	$^1J_{PtC}$ (Hz)	$^2J_{PtC}$ (Hz)	$^2J_{PC}$ (Hz)	$^3J_{PC}$ (Hz)
Cis-[Pt(C≡CMe)$_2$(CO)L] (a)	Acetylide *trans* to CO	+84.4	+107.5	1161.8	335.8	18.9	3.6
	Acetylide *trans* to L	+78.8	+103.0	1066.5	299.7	144.9	32.8
	CO	+171.4	-	1146.8	-	7.5	-
[Pt(C≡CMe)(C≡CPh)(CO)L] (b)	Acetylide *trans* to CO	+82.7	+108.3	1151	(c)	18.7	< 5
C≡CPh *trans* to L	Acetylide *trans* to L	+93.3	+108.0	1068	(c)	143.4	30.6
	CO	+170.7	-	1155.3	-	8.0	-
[Pt(C≡CMe)(C≡CPh)(CO)L] (b)	Acetylide *trans* to CO	+97.0	+111.5	1172	(c)	18.5	2.9
C≡CMe *trans* to L	Acetylide *trans* to L	+78.3	+103.9	(c)	291	144	32.3
	CO	+170.9	-	1169.8	-	8.0	-

(a) At 25°C
(b) At -60°C
(c) Unresolved.

Table 10:- ^1H nmr of C≡CMe bis-organoplatinum complexes, $[PtR(C{\equiv}CMe)(CO)(PMePh_2)]$, in $CDCl_3$ at 25°C, on a Perkin-Elmer R32 90 MHz spectrometer.

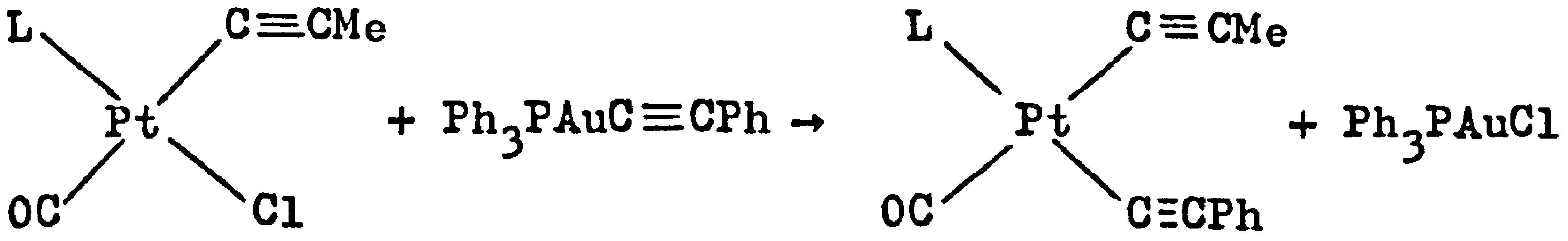
	C≡CMe proton signals			PMePh$_2$ methyl protonsignals		
Complex, (L = Ph$_2$MeP)	δ (ppm)	$^4J_{PtH}$(Hz)	$^5J_{PH}$(Hz)	δ(ppm)	$^3J_{PtH}$(Hz)	$^2J_{PH}$(Hz)
<u>cis</u>-$[Pt(C{\equiv}CMe)_2(CO)L]$	+1.85$^{(a)}$ +2.04$^{(b)}$	15.5 14.0	3.25 2.0	+2.33	29.0	11.0
$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]^{(c)}$ C≡CMe <u>trans</u> to L	+2.06	(d)	1.5	+2.36	29.0	10.6
$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]$ C≡CPh <u>trans</u> to L	+1.88	16.0	3.5	+2.38	30.0	11.0
$[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)L]$ $C_6H_4CO_2Me\text{-}\underline{p}$ <u>trans</u> to L	+1.79	16.5	3.0	+2.43	20.5	10.3
$[Pt(C_5H_5)(C{\equiv}CMe)(CO)L]$ C_5H_5 <u>trans</u> to L	+1.91	16.0	3.0	+2.33	28.5	10.5

(a) <u>cis</u> to phosphine; (b) <u>trans</u> to phosphine; (c) reference 153;

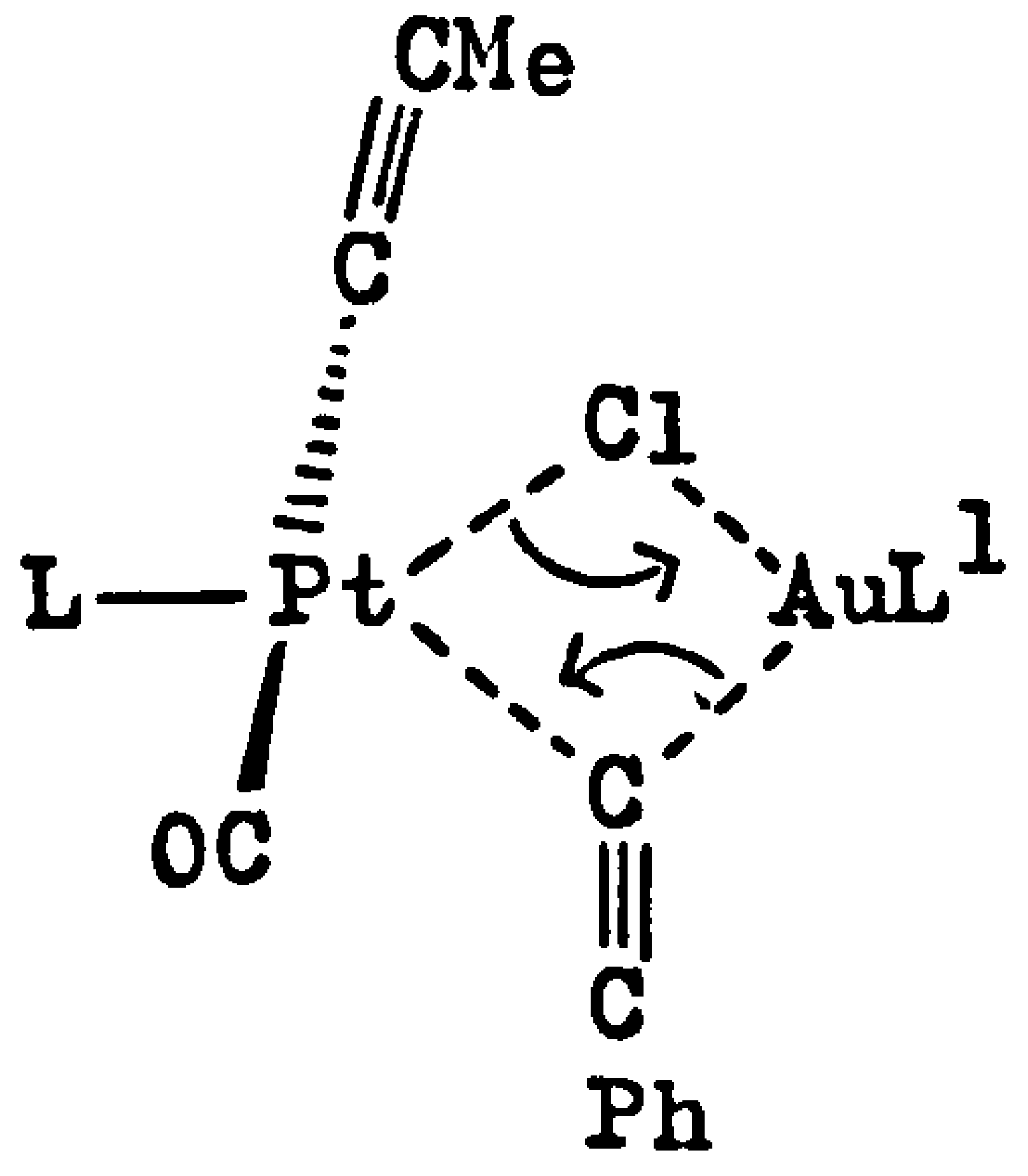
(d) unresolved.

(typically < 2 Hz). This meant that the original interpretation based on site migration of a resident ethynyl group was false, and this was later changed to include the possibility of S_E2 (cyclic) reactions.[172] The reactions are now considered to be as described in the introduction to this chapter.

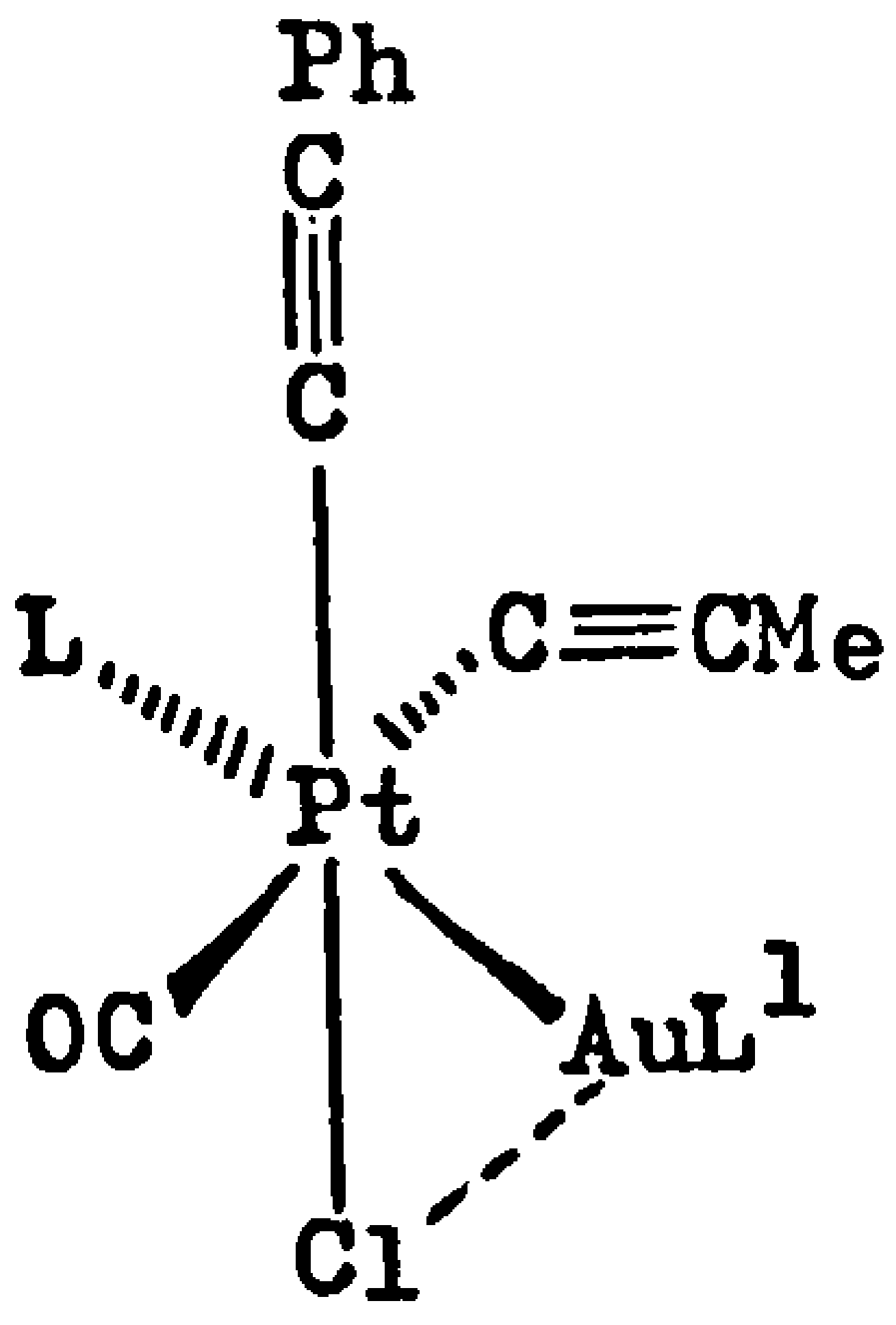
The reaction of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) with $Ph_3PAu(C{\equiv}CPh)$ progressed smoothly at -20°C to produce Ph_3PAuCl and one isomer of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, that with C≡CPh trans to phosphine.



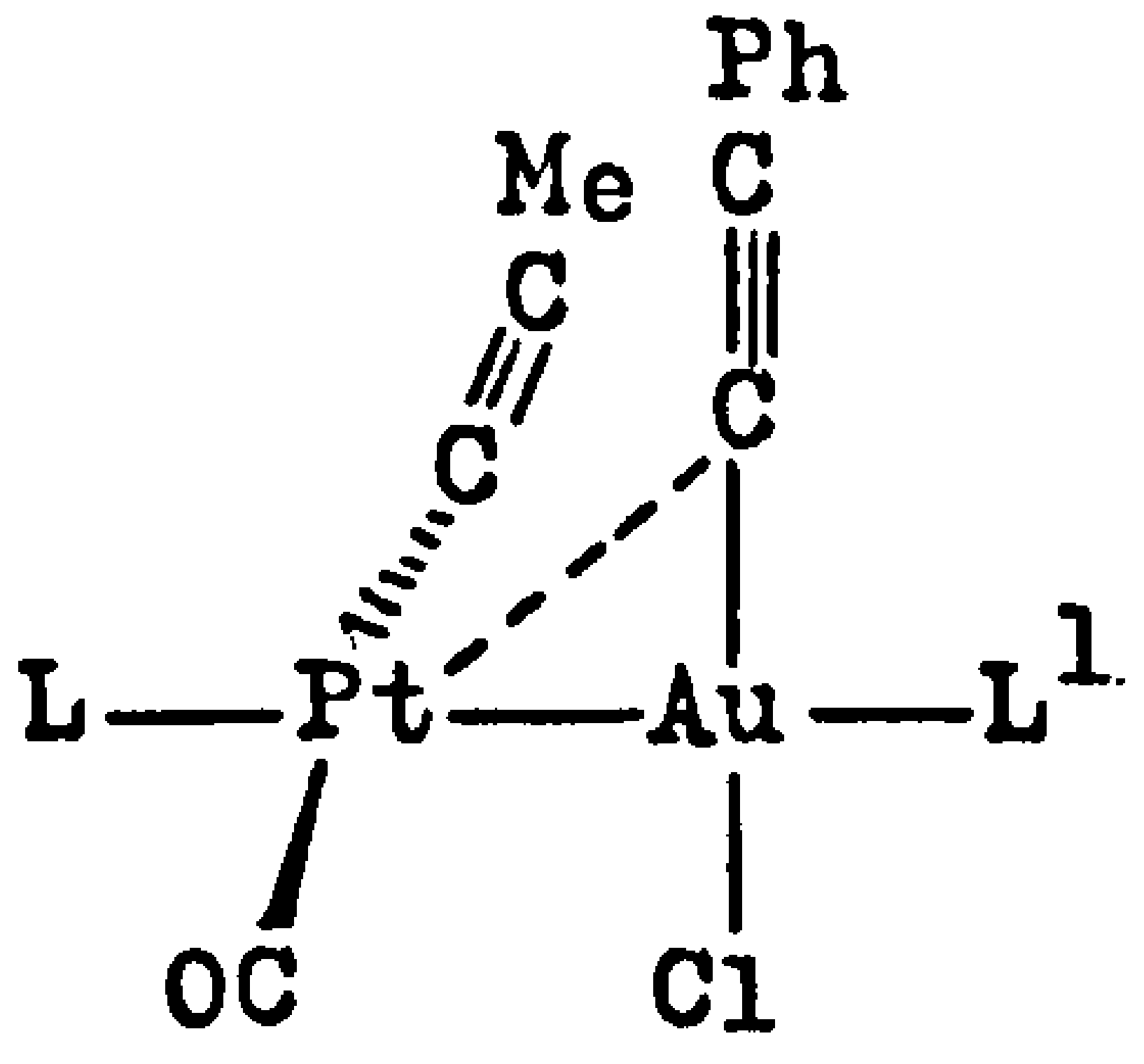
This is also the isomer produced by reaction of $Hg(C{\equiv}CPh)_2$ (1.0 equivalent) or $Hg(C{\equiv}CPh)_2$ and $[Et_4N]Cl$ (0.5 equivalents of each).[150,153] The chloride trans to phosphine has been directly replaced by C≡CPh, which is consistent with an S_E2 (cyclic) mechanism, transition state E, or a cis-oxidative addition/reductive elimination reaction with intermediate F. Intermediate F is the one related to E by Pt-Au bond formation. In the case of $Ph_3PAu(C{\equiv}CPh)$ there is also a possibility of oxidative addition of the Pt-Cl bond to Au, a route not open to mercury acetylides, and this would have an intermediate of type G.



E



F



G

It is not possible to distinguish between these three routes. In this reaction, transfer of $C\equiv CR$ from Au to Pt was stereospecific, unlike the reaction between cis-$[PtCl_2(CO)L]$ and $L^1AuC\equiv CR$,[160] but in this case only one halide is present. The halide trans to L in cis-$[PtCl_2(CO)L]$ would be the one expected to be replaced by an S_E2 (cyclic) mechanism or a cis-oxidative addition to platinum, thus the isomer (II) initially formed in the reaction of cis-$[PtCl_2(CO)L]$ and $L^1AuC\equiv CR$ may have been by oxidative addition of platinum-chloride (trans to CO) to Au, although it might be expected that the platinum-chloride trans to L would be the one involved in this type of reaction also.

$[Pt(C\equiv CMe)(C\equiv CPh)(CO)L]$, $C\equiv CMe$ trans to L, was much more stable when prepared from $L^1Au(C\equiv CPh)$ than when prepared by action of $Hg(C\equiv CPh)_2$. The bis-acetylide was completely stable to isomerisation, even in the presence of Ph_3PAuCl, at < 0°C overnight. This contrasts with its behaviour in the presence of other platinum complexes when isomerisation is extremely rapid or in the presence of even a small amount of mercury-containing byproduct, when isomerisation proceeds at a reasonable rate at ambient temperatures, and slowly at -60°C. There was no broadening of the ^{31}P nmr signal of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]$ or cis-$[Pt(C{\equiv}CMe)_2(CO)L]$ in the presence of L^1AuCl, and there was no cleavage of acetylide. In the presence of $HgCl_2$, the ^{31}P nmr signals broaden due to interaction between Pt and Hg, to form a 5-coordinate adduct,[153] and an acetylide is cleaved to form $ClHgC{\equiv}CR$ and isomer (II). Clearly there is no such interaction between Pt and Au.

Reactions of $[Pt(C{\equiv}CR)(C{\equiv}CR^1)(CO)L]$ with Platinum Complexes

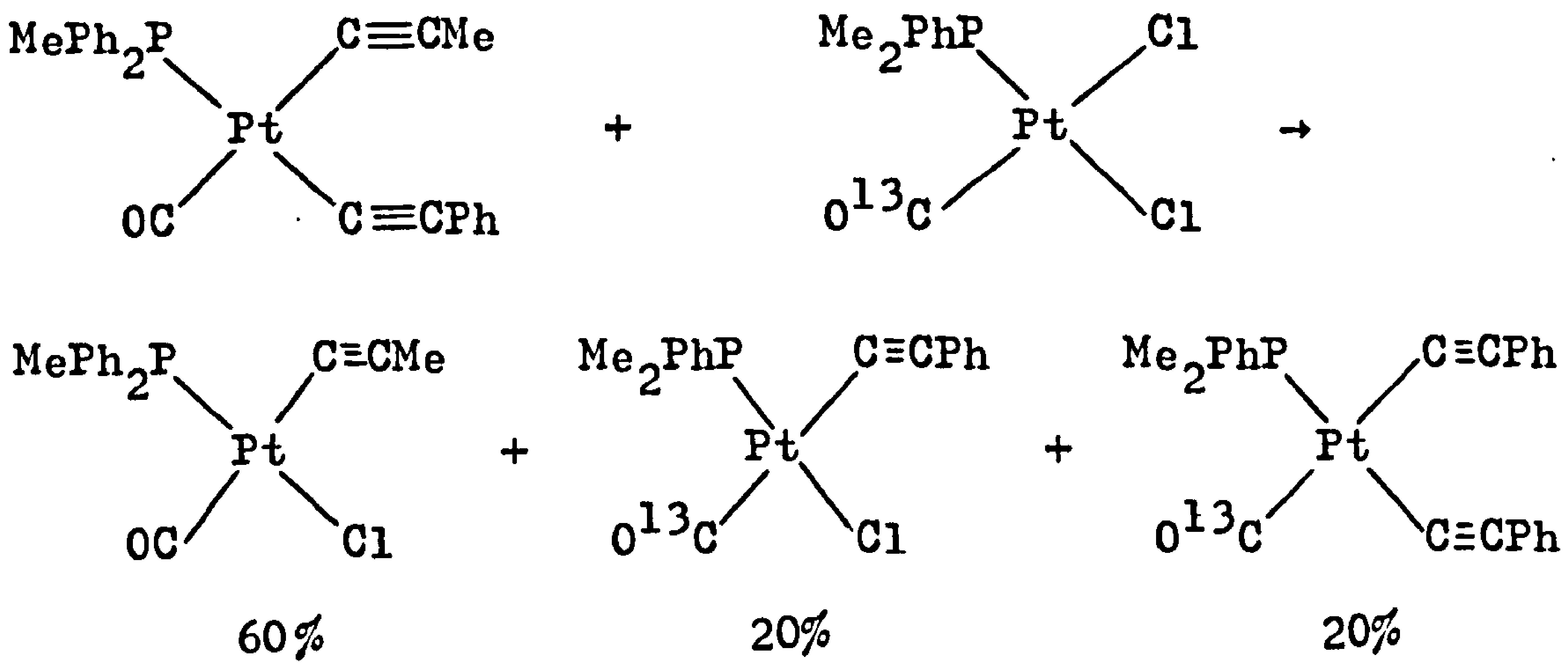
a) With cis-$[PtCl_2(^{13}CO)L^1]$

A solution of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CPh$ trans to phosphine, prepared from $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (II) by the symmetrization method was mixed at -60°C with slightly more than one equivalent of cis-$[PtCl_2(^{13}CO)(PMe_2Ph)]$. The mixture was observed for 6 hours at -60°C by ^{31}P nmr spectroscopy, by which time a little under 50% of the $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$ was used. Warming briefly to room temperature speeded the reaction, the reaction having proceeded to $>70\%$ with only 1 minute at room temperature. The initial products of reaction were $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II), $[PtCl(C{\equiv}CPh)(^{13}CO)(PMe_2Ph)]$ isomer (II) and cis-$[Pt(C{\equiv}CPh)_2(^{13}CO)(PMe_2Ph)]$ (parameters in table 11) and these remained the major products throughout the reaction.

Once more than 70% of the starting material had been used, the products were present in the proportions shown below.

Table 11:- ^{31}P nmr spectra of platinum acetylide complexes in $CDCl_3$ at -60°C.

Complex	δ (ppm)	$^1J_{PtP}$ (Hz)
$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II)	-4.0	3240
$[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ isomer (II)	-3.9	3185
$[PtCl(C{\equiv}CMe)(CO)(PMe_2Ph)]$ isomer (II)	-15.1	3132
$[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ isomer (II)	-15.2	3090
trans-$[PtCl(C{\equiv}CMe)(PMePh_2)_2]$	+5.6	2532
trans-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$	+5.2	2508
cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$	-2.8	2107
cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$	-2.7	2091
cis-$[Pt(C{\equiv}CPh)_2(CO)(PMe_2Ph)]$	-15.4	2055
$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$ $C{\equiv}CMe$ trans to $PMePh_2$	- 2.6	2079
$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$ $C{\equiv}CPh$ trans to $PMePh_2$	- 2.7	2115



After this, minor products became apparent, and these were [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CMe *trans* to phosphine, [PtCl(C≡CPh)(CO)(PMePh$_2$)] isomer (II) and [PtCl(C≡CMe)(^{13}CO)(PMe$_2$Ph)] isomer (II). Throughout the experiment, the ^{13}CO label remained specific to complexes of PMe$_2$Ph. The lack of phosphine and CO scrambling suggests that the minor products arise from isomerisation of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], and reaction of the new isomer with *cis*-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)]. The amount of *cis*-[Pt(C≡CPh)$_2$(^{13}CO)(PMe$_2$Ph)] decreases and the amount of [PtCl(C≡CPh)(^{13}CO)(PMe$_2$Ph)] increases, presumably by reaction of the initial bis-acetylide with unreacted *cis*-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)].

The primary products must be [PtCl(C≡CMe)(CO)(PMePh$_2$)] (II) and [PtCl(C≡CPh)(^{13}CO)(PMe$_2$Ph)] (II), formed by transferring C≡CPh from the position *trans* to phosphine in [Pt(C≡CMe)(C≡CPh)(CC)(PMePh$_2$)] to the position *trans* to CO in cis-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)]. Formation of *cis*-[Pt(C≡CPh)$_2$(^{13}CO)(PMe$_2$Ph)] must be at least a two-step process. The transfer of C≡CPh from [Pt(C≡CMe)(C≡CPh)(CO)L] to *cis*-

$[PtCl_2(^{13}CO)L^1]$ could be by an S_E2 (cyclic) mechanism, however this would involve different sites on each platinum, with the acetylide trans to phosphine being transferred as expected for an S_E2 (cyclic) reaction, but the chloride trans to ^{13}CO being transferred, which is unexpected, (fig. 24).

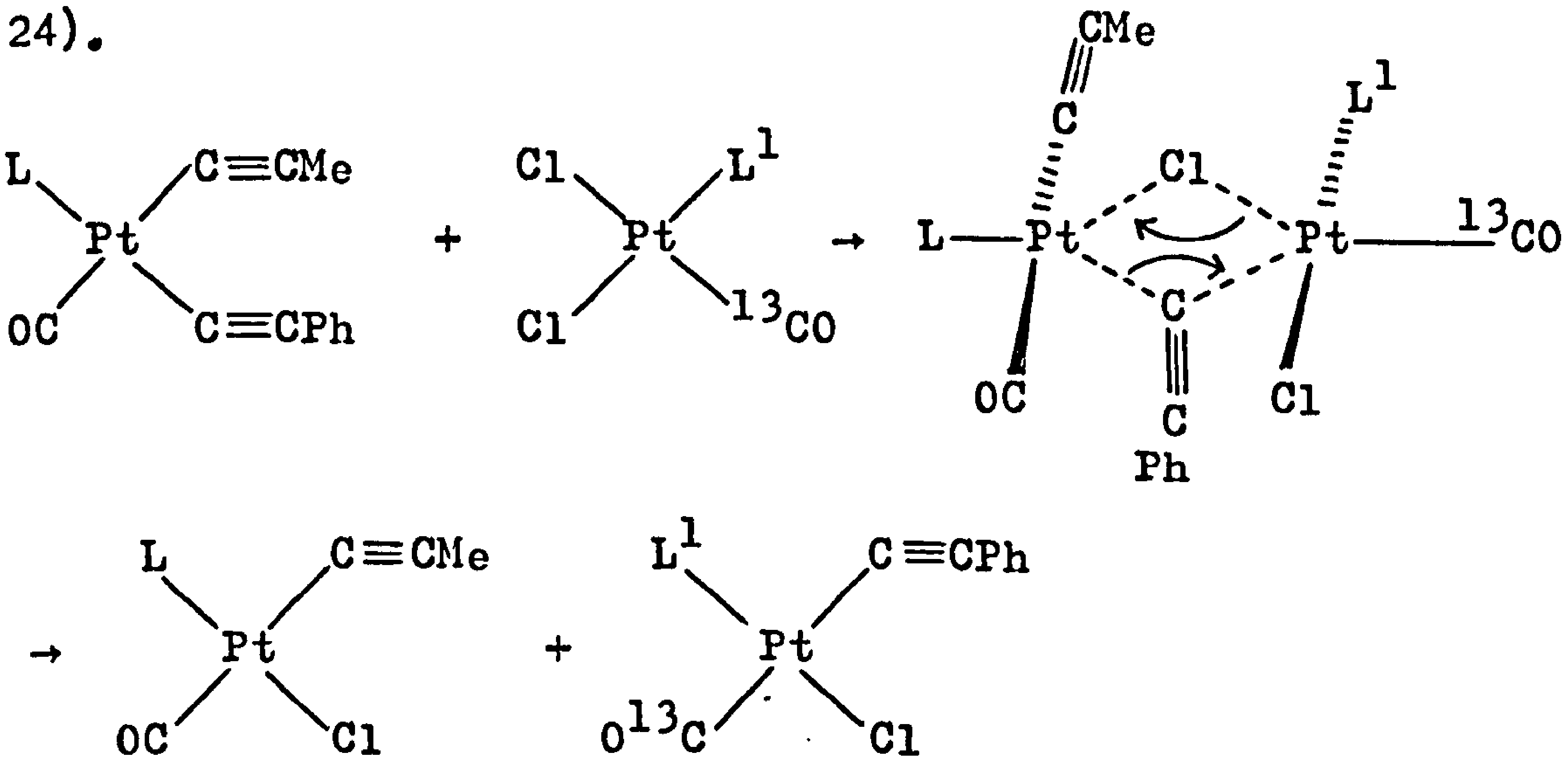


figure 24.

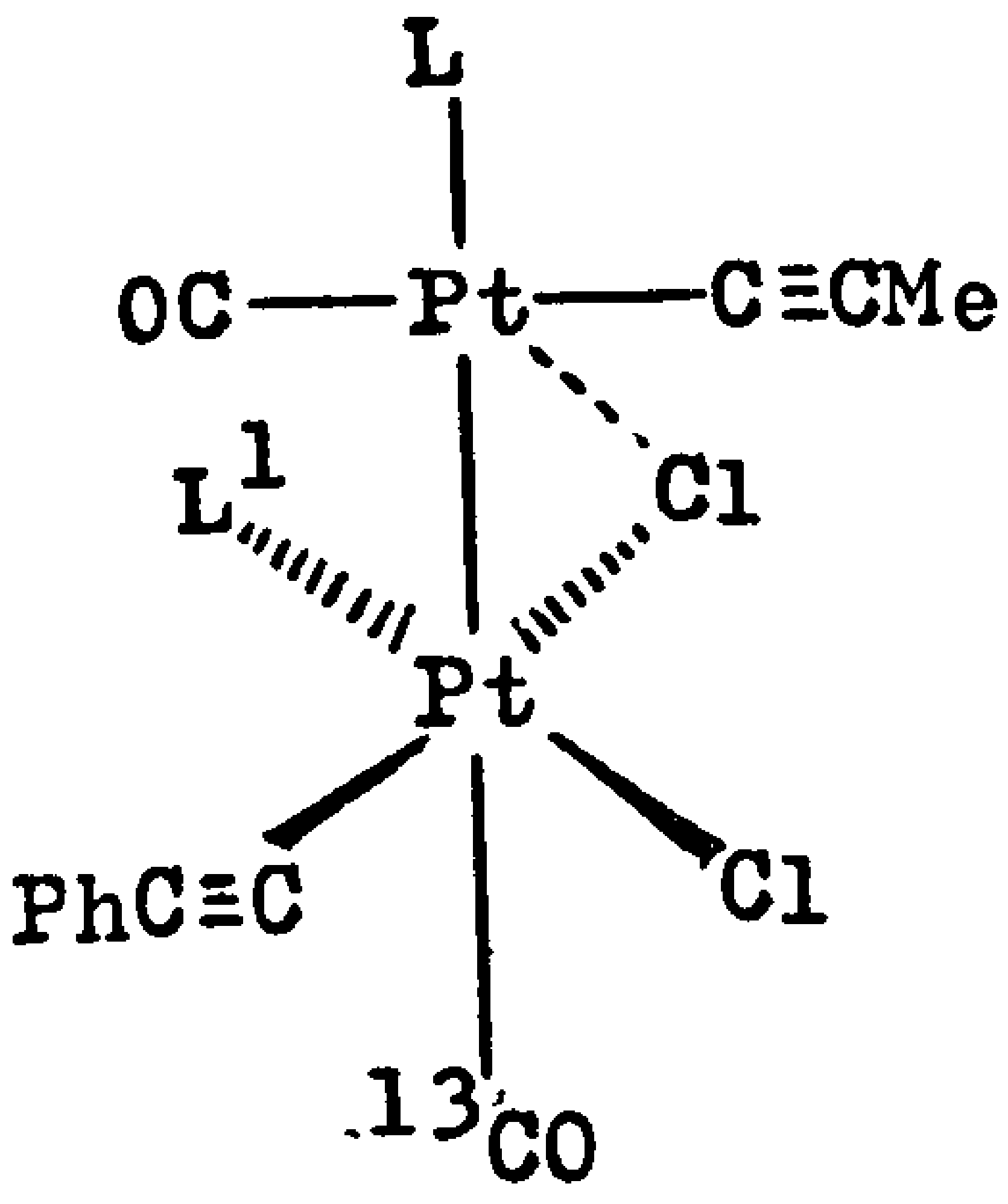
This is similar to the reaction of cis-$[Pt(C_5H_5)_2(CO)L]$ with cis-$[PtCl_2(CO)L^1]$ where the cyclopentadienyl trans to CO was transferred to a position trans to phosphine. Both reactions are anomalous compared to a transfer which is considered to be an S_E2 (cyclic) reaction,

cis-$[PtPh_2(CO)L]$ + cis-$[PtCl_2(CO)L^1]$ → $[PtClPh(CO)L]$ (II) + $[PtClPh(CO)L^1]$ (I)

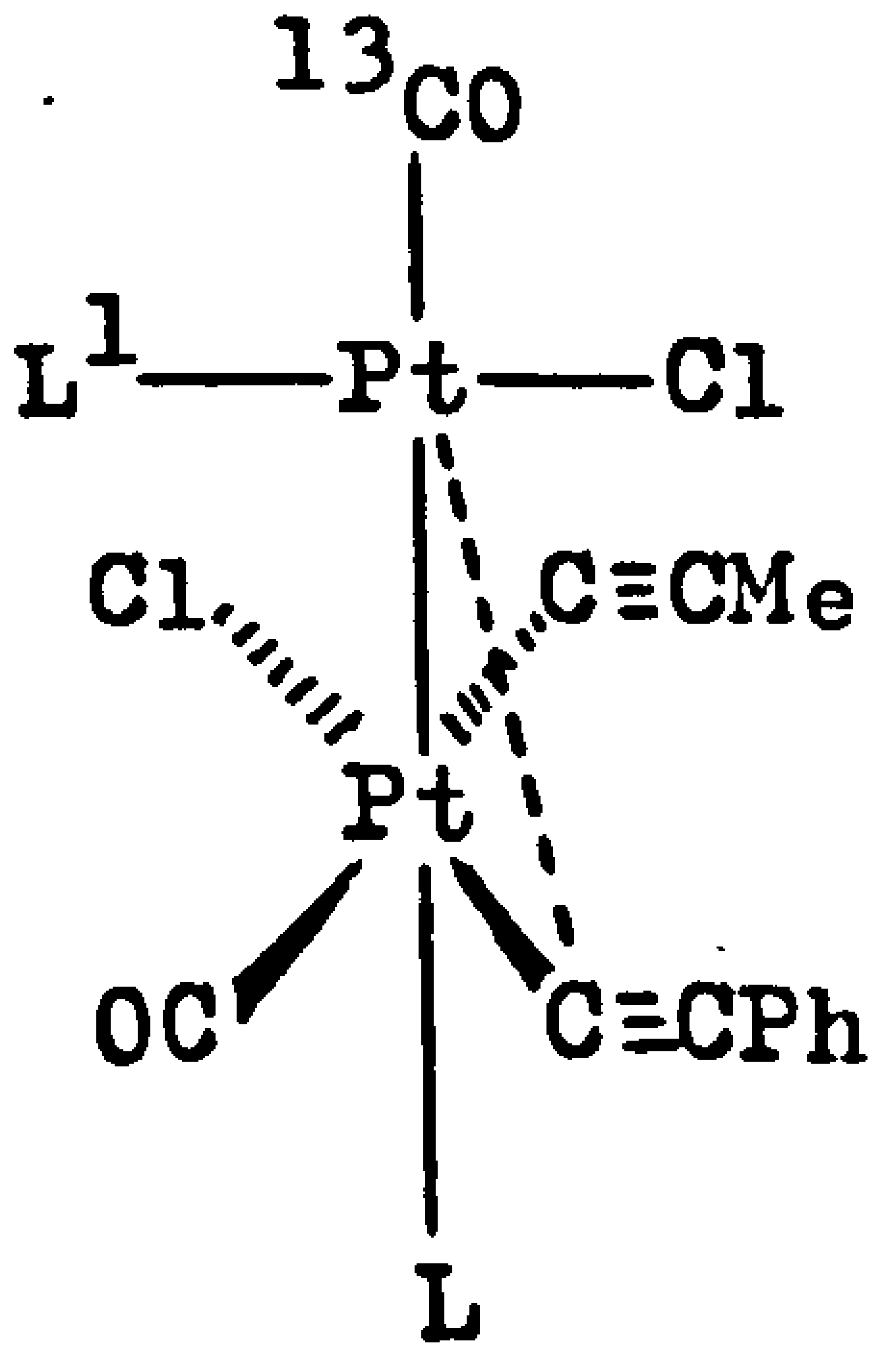
In this case, the groups transferred are both trans to phosphine as would be expected for an S_E2 (cyclic) mechanism.

The production of $[PtCl(C{\equiv}CMe)(CO)L]$ isomer (II) and $[PtCl(C{\equiv}CPh)(^{13}CO)L^1]$ (II) could be explained by a number of different cis-oxidative addition/reductive elimination routes, depending on which complex has the more nucleophilic platinum atom and is oxidatively added to. $[Pt(C{\equiv}CMe)$-

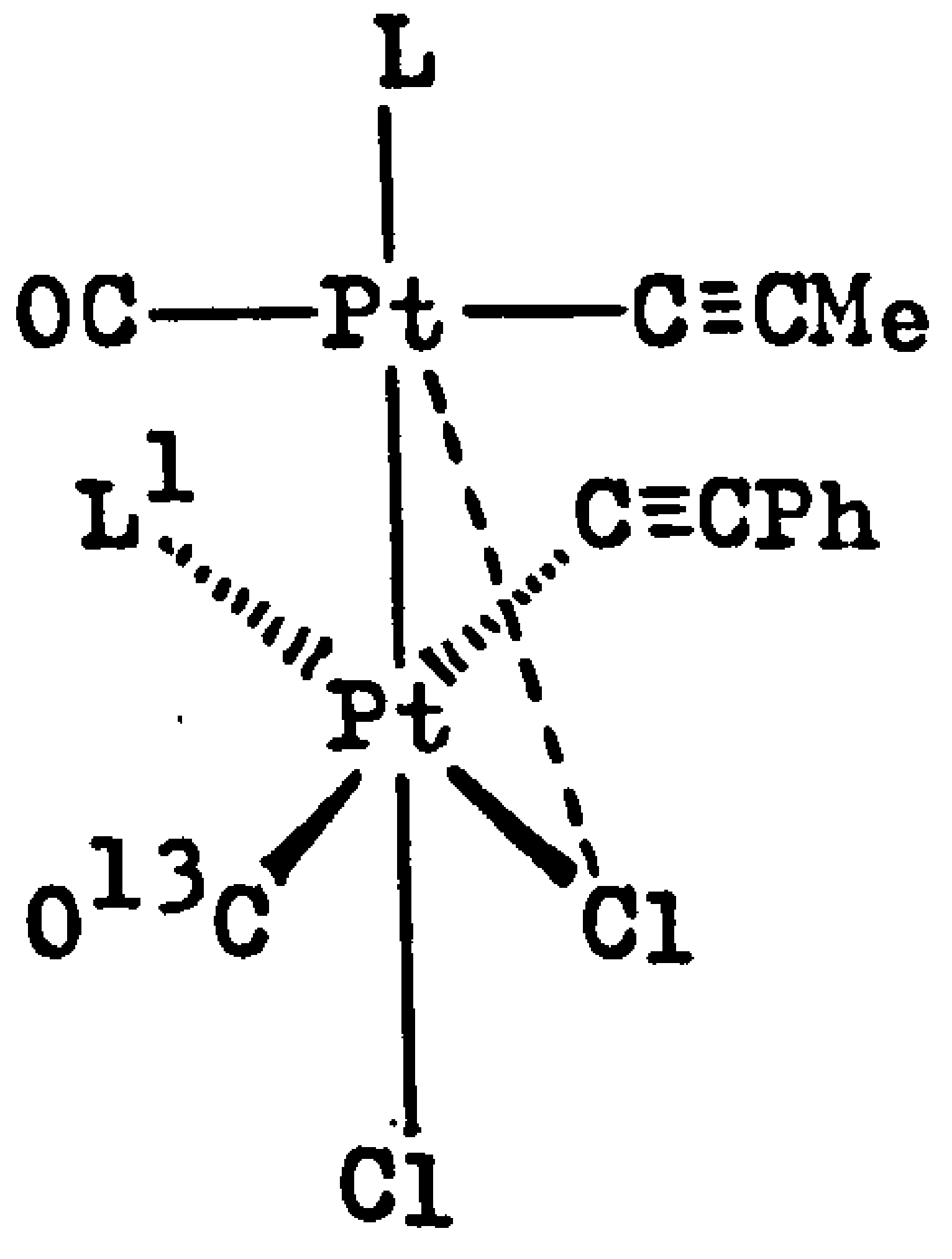
(C$\equiv$CPh)(CO)($PMePh_2$)] has two σ-donating organic groups, with higher trans influences than chlorides and hence more electron donating than chlorides, but cis-[$PtCl_2$(^{13}CO)-(PMe_2Ph)] has the more basic and electron donating phosphine. Also, since CO is a π-acceptor ligand in which the amount of π-back-bonding from metal to ligand can vary from complex to complex, depending on the other ligands, it is not possible to decide on which platinum atom is more nucleophilic. Oxidative addition of Pt-C$\equiv$CPh to cis-[$PtCl_2$(^{13}CO)L^1] would produce intermediate H by displacement of Cl trans to ^{13}CO by Pt and addition of Pt-Cl to [Pt(C$\equiv$CMe)(C$\equiv$CPh)(CO)L] would produce intermediate J by displacement of C$\equiv$CPh by Pt. These two intermediates are the ones related to the S_E2(cyclic) transition state. A third intermediate, K, is also possible by addition of Pt-C$\equiv$CPh and displacement of Cl trans to ^{13}CO by C$\equiv$CPh.



H



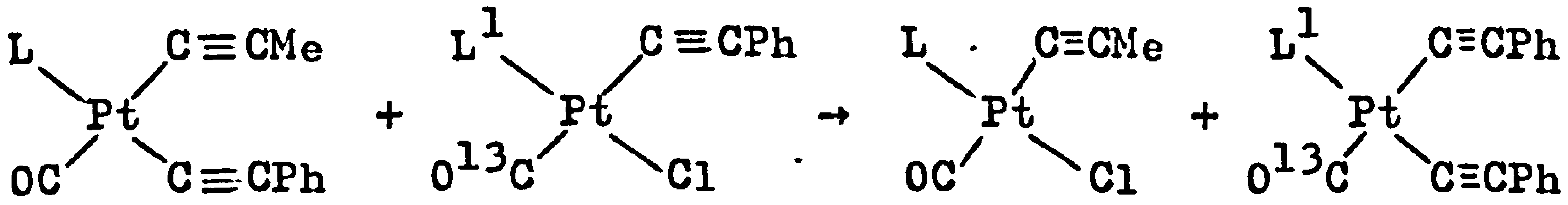
J



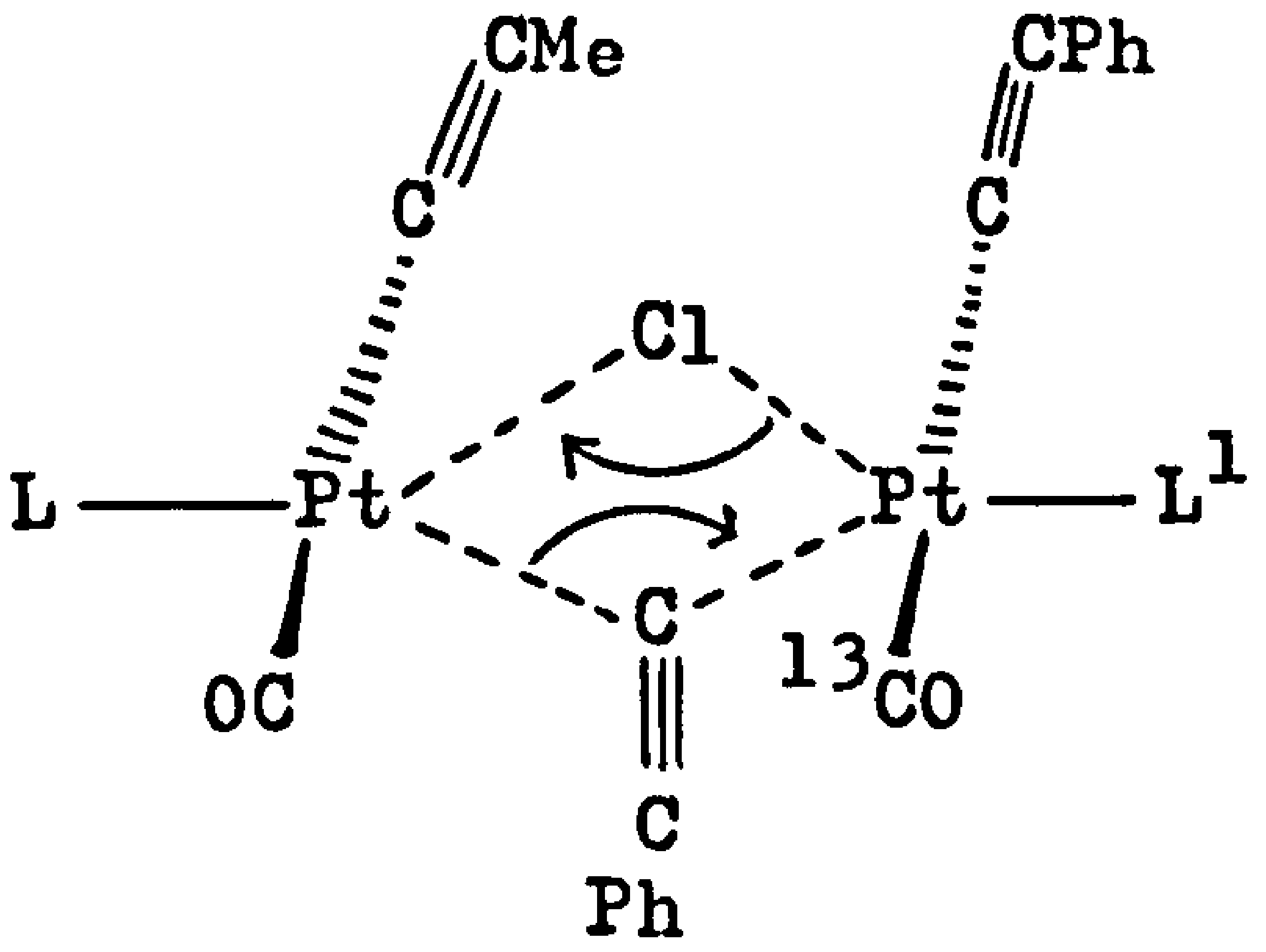
K

Intermediate J is unlikely, since C$\equiv$CMe could be reductively eliminated instead of C$\equiv$CPh, although in this case the elimination is symmetry restricted to produce [PtCl(C$\equiv$CPh)(CO)L] isomer (III), CO trans to L, which is not observed. The other two intermediates H and K involve displacement of the group *trans* to ^{13}CO in each case, and this is also not expected from an oxidative additon; the Cl *trans* to phosphine in *cis*-[PtCl$_2$(^{13}CO)L^1] is the one expected to be attacked either by S$_E$2 or oxidative addition reactions. Both *H* and *K* involve oxidative addition to *cis*-[PtCl$_2$(^{13}CO)L^1] however, so it appears that the most probable oxidative-addition routes involve addition to *cis*-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)].

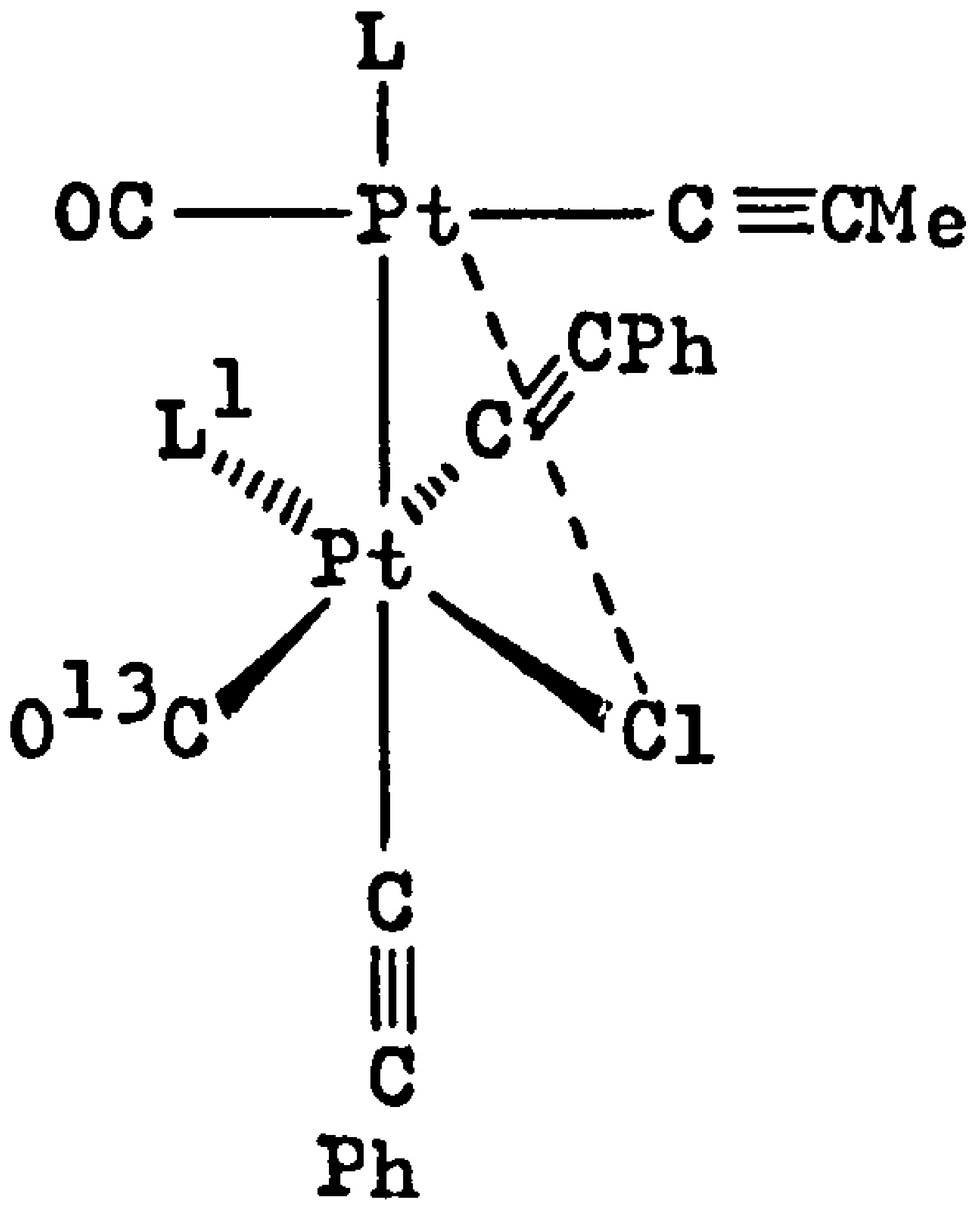
The production of a substantial amount of *cis*-[Pt(C≡CPh)$_2$-(^{13}CO)(PMe$_2$Ph)] must arise from a secondary reaction of [PtCl(C≡CPh)(^{13}CO)(PMe$_2$Ph)] (II) and [Pt(C≡CMe)(C≡CPh)(CO)-(PMePh$_2$)].



Acetylide isomer (II) complexes do not disproportionate, so the only source of C≡CPh is starting material. In this case C≡CPh is transferred from a site *trans* to phosphine in [Pt(C≡CMe)(C≡CPh)(CO)L], and Cl is transferred from a site *trans* to phosphine in [PtCl(C≡CPh)(^{13}CO)L^1], which is consistent with an S$_E$2 (cyclic) mechanism with transition state *L*. The two possible *cis*-oxidative addition intermediates related to the S$_E$2 (cyclic) transition state could produce more than one set of products on reductive elimination. The only intermediate with a unique reductive elimination to give the observed products is *M*.



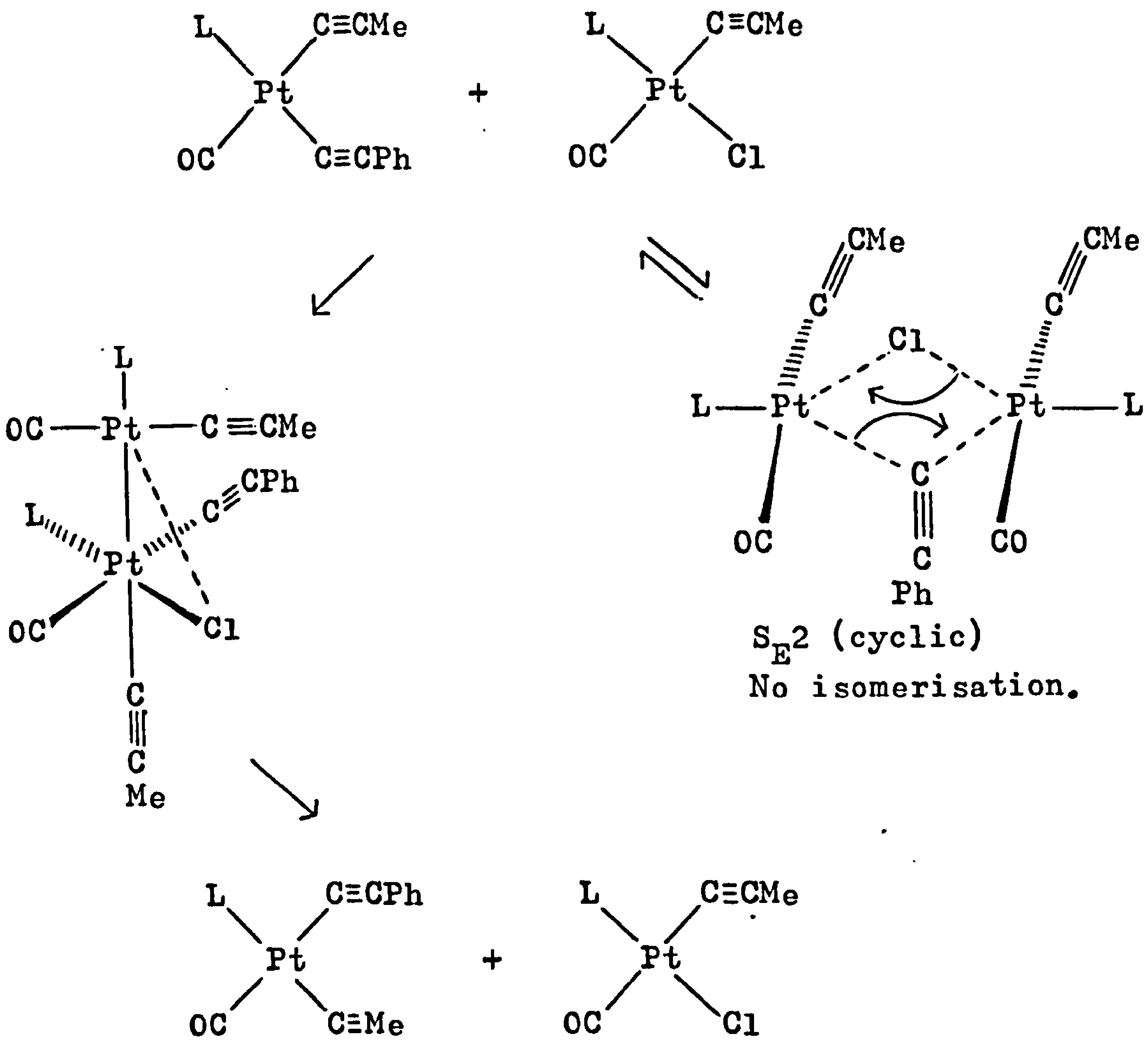
L



M

Although the two S_E2 (cyclic) transition states, fig. 24 and L are different, the oxidative addition intermediates, K and M are very similar.

Intermediate M is formed by addition of Pt–C≡CPh (from the mixed acetylide complex) to $[PtCl(C{\equiv}CPh)(^{13}CO)L^{1}]$ with displacement of C≡CPh *trans* to ^{13}CO. The analogous reaction with $[PtCl(C{\equiv}CMe)(CO)L]$ would provide a possible mechanism for the extremely rapid isomerisation of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L]$, provided the reaction was an oxidative addition/reductive elimination involving an intermediate analogous to M. An S_E2 (cyclic) reaction would exchange C≡CMe for Cl directly, and would not cause isomerisation (fig. 25).



oxidative addition/reductive elimination.

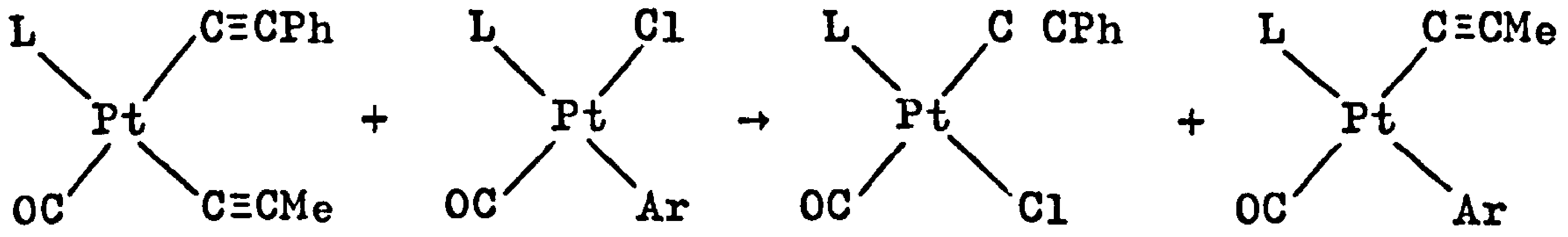
Isomerisation.

Figure 25.

The isomerisation of [Pt(C≡CMe)(C≡CPh)(CO)L] in this reaction is perhaps indicative of oxidative addition/reductive elimination reactions being more plausible than S_E2 (cyclic) reactions for transfer of C≡CR in the system [Pt(C≡CR)(C≡CR^1)(CO)L] + <u>cis</u>-[$PtCl_2(^{13}CO)L^1$].

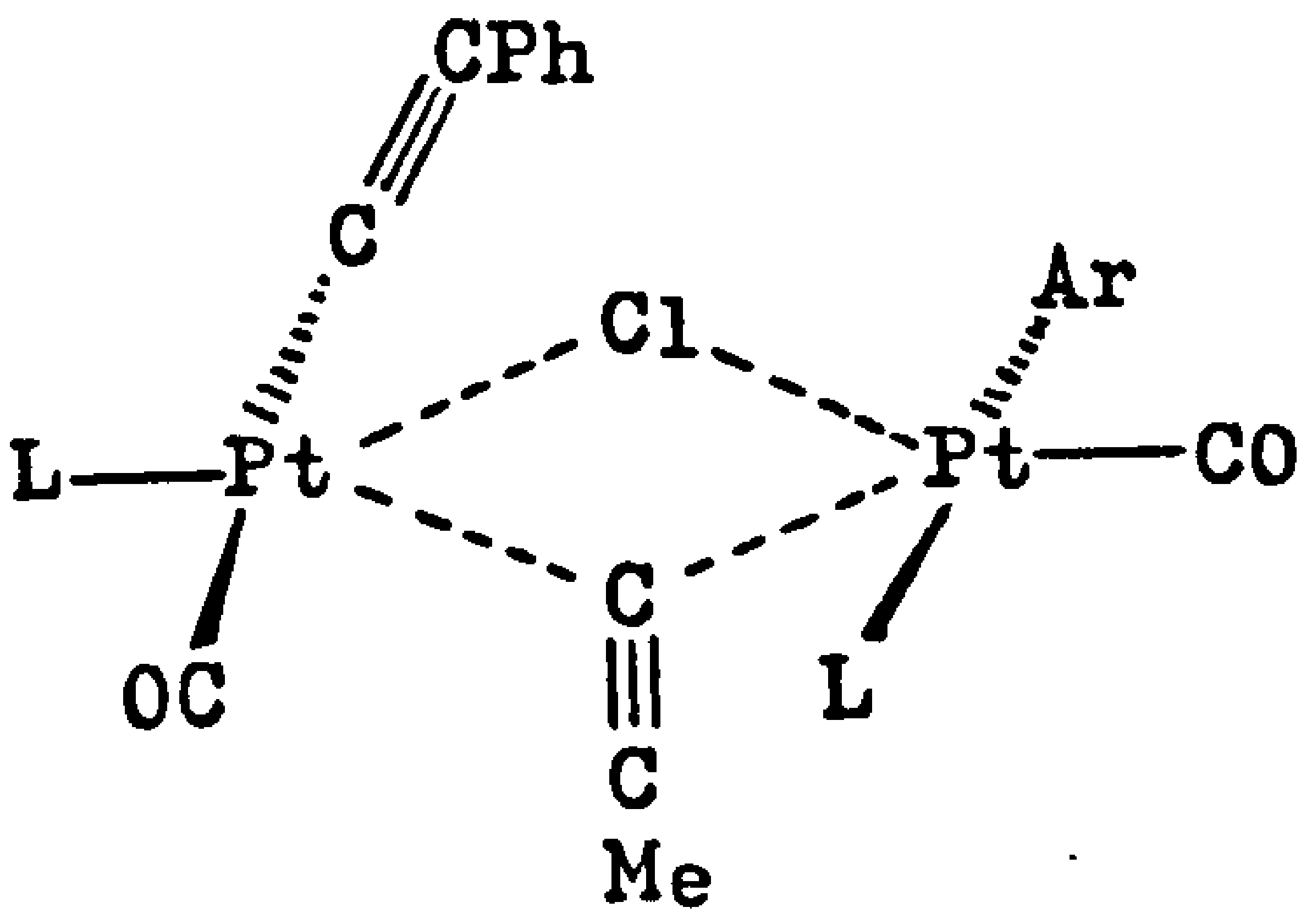
b) With $[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)}]$ isomer (I)

A solution of $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)}]$, $\mathrm{C{\equiv}CMe}$ trans to phosphine, prepared from $[\mathrm{PtCl(C{\equiv}CPh)(CO)(PMePh_2)}]$ (II) by the symmetrization method was mixed at -60°C with a solution of $[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)}]$ isomer (I). The reaction was observed by ^{31}P nmr spectroscopy and after 7 hours at -60°C, 60% of the starting material was consumed. The initial products were $[\mathrm{PtCl(C{\equiv}CPh)(CO)(PMePh_2)}]$ (II) and a species identified as $[\mathrm{Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)}]$, $\mathrm{C{\equiv}CMe}$ trans to CO, (table 12). After this time, isomerisation of $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)}]$ was becoming apparent, (ratio of isomers ca. 5 to 1).

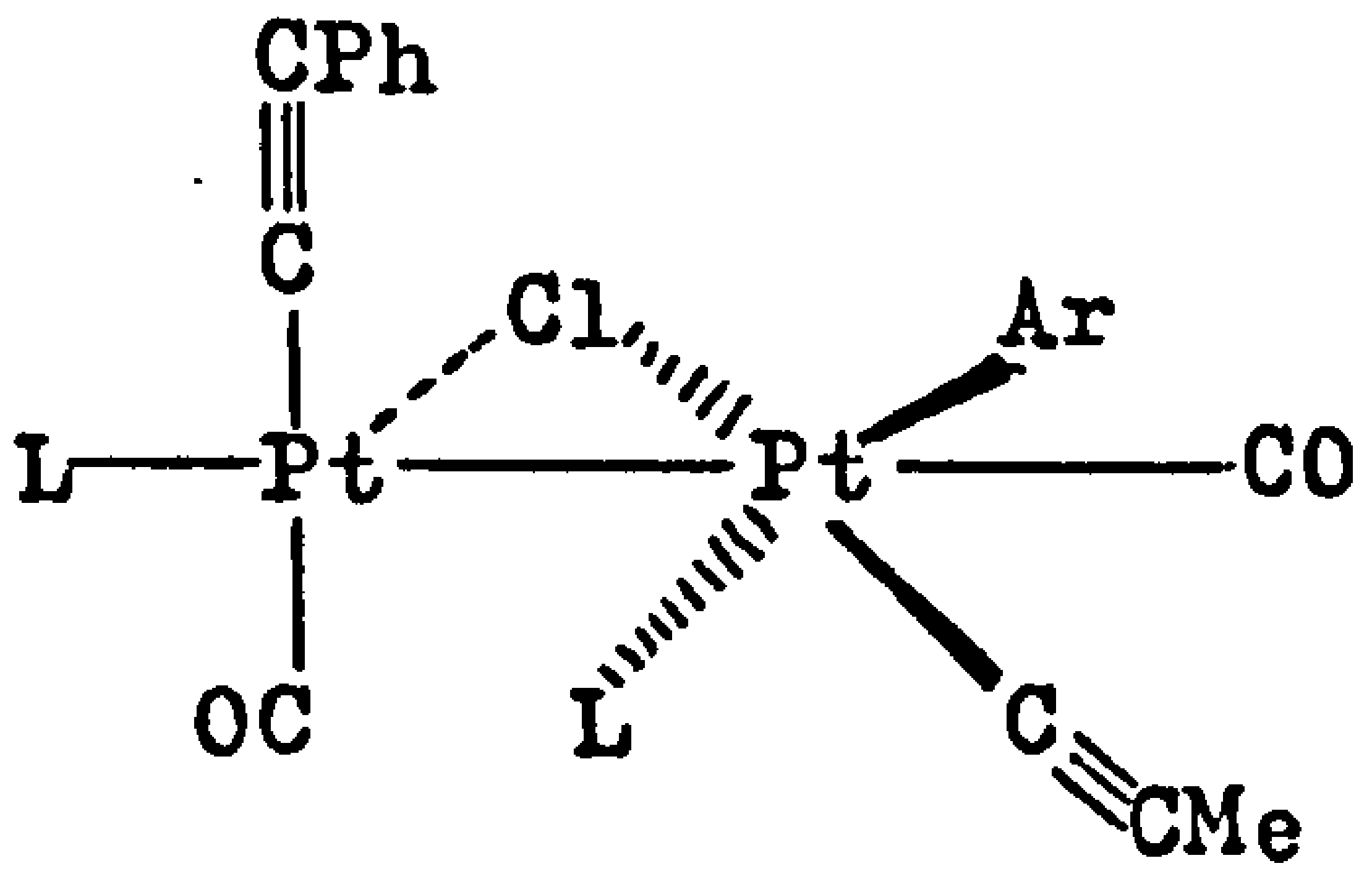


L = $\mathrm{PMePh_2}$, Ar = $\mathrm{C_6H_4CO_2Me\text{-}\underline{p}}$.

$[\mathrm{PtAr(C{\equiv}CMe)(CO)L}]$, Ar trans to L, was the only mixed acetylide aryl complex observed. In this reaction, the acetylide trans to phosphine has been exchanged with a chloride trans to CO, but this is the only chloride present in the system. Assuming this to be a single-step process, the reaction can be accounted for by an S_E2 (cyclic) mechanism with transition state N, or by a cis-oxidative addition/reductive elimination with intermediate P. This is the oxidative addition/reductive elimination reaction related to S_E2 (cyclic), with addition of $\mathrm{Pt{-}C{\equiv}CMe}$ to aryl isomer (I) and displacement of chloride by Pt.



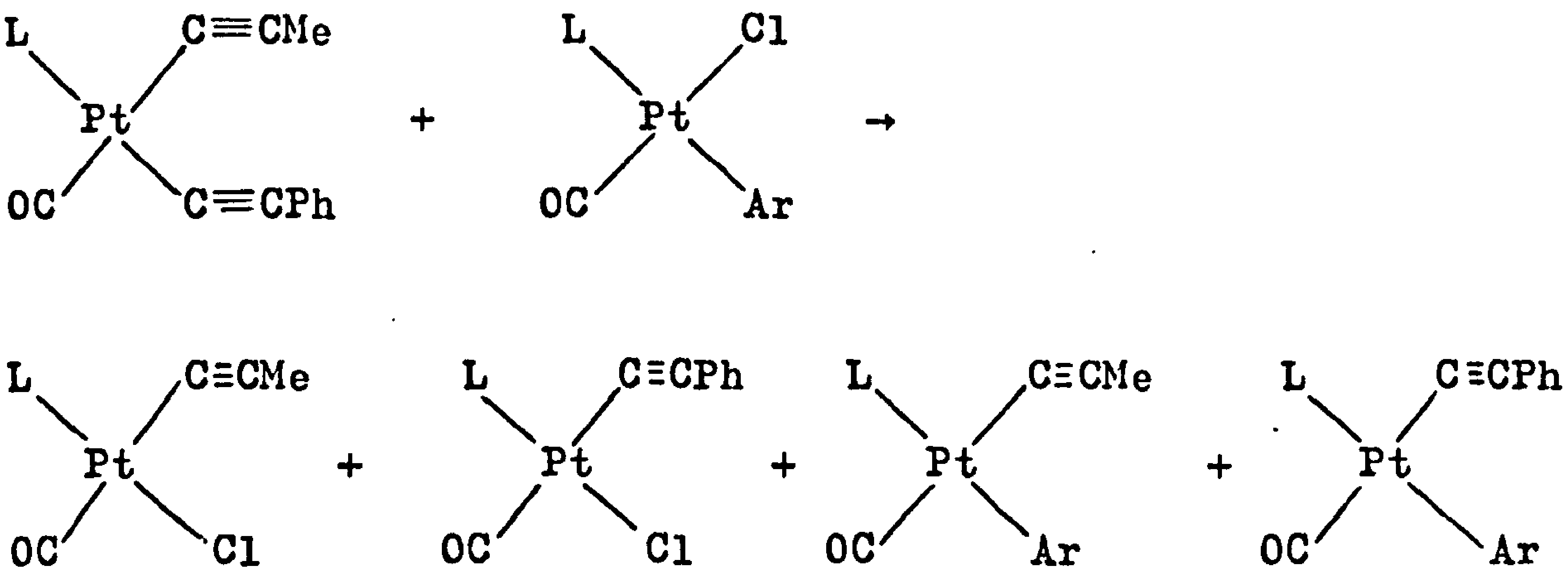
N



P

The other possible cis-oxidative addition intermediate related to the S_E2 (cyclic) transition state, i.e. the intermediate formed by addition of Pt-Cl to the bis-acetylide complex with displacement of $C\equiv CMe$ by Pt, need not produce only the observed products on reductive elimination. No other cis-oxidative additions could give the observed products on reductive elimination.

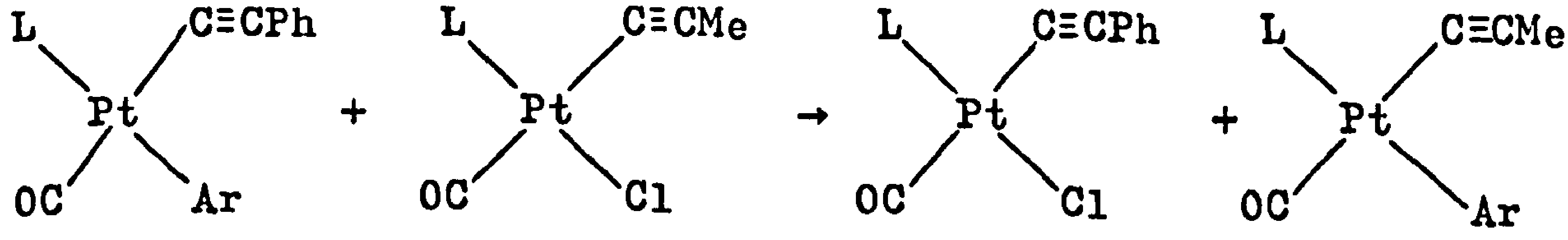
When the other isomer of $[Pt(C\equiv CMe)(C\equiv CPh)(CO)(PMePh_2)]$, that with $C\equiv CPh$ trans to phosphine, and $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ isomer (I) were allowed to react under similar conditions the same stereospecificity was not observed. Almost equal amounts of $[PtCl(C\equiv CMe)(CO)(PMePh_2)]$ (II), $[PtCl(C\equiv CPh)(CO)(PMePh_2)]$ (II), $[PtAr(C\equiv CMe)(CO)(PMePh_2)]$, Ar trans to phosphine, and $[PtAr(C\equiv CPh)(CO)(PMePh_2)]$, Ar trans to phosphine, were produced as initial products. After 5½ hours at -60°C, only 25% of the starting material was consumed.



At this time, isomerisation of $[Pt(C\equiv CMe)(C\equiv CPh)(CO)(PMePh_2)]$ was not appreciable (ratio of isomers ca. 10 to 1). On warming briefly to room temperature isomerisation was rapid, (less than 2 minutes to reach a ratio of isomers of 2 to 1) and the amount of $[PtCl(C\equiv CMe)(CO)L]$ (II) and $[PtAr(C\equiv CPh)(CO)L]$ increased faster than the other two products. These two species are the ones which would be expected by analogy with the previous reaction.

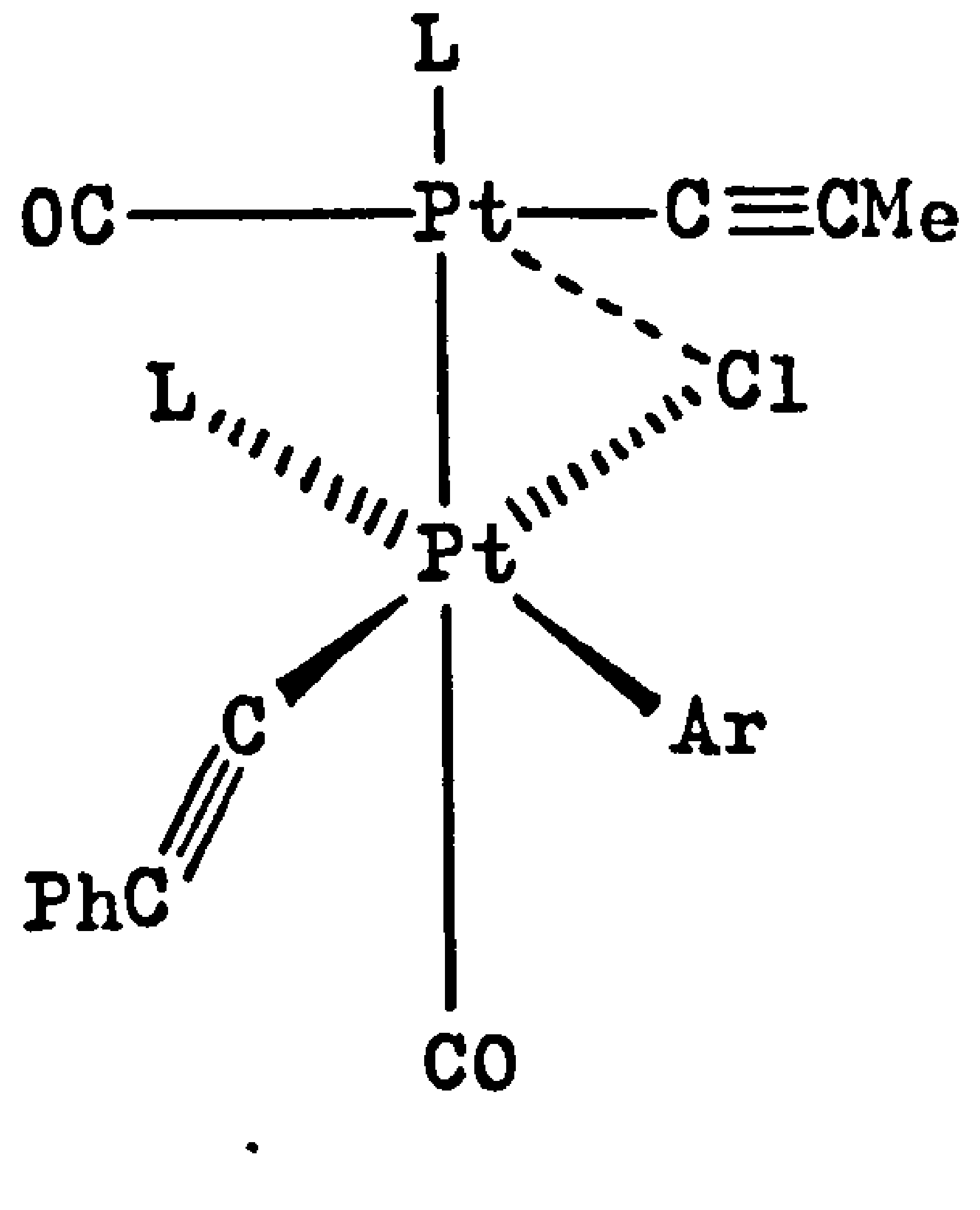
There are a number of possible explanations for this difference in the reaction of the two different isomers.

(i) The reaction could be the same as with the first isomer, producing $[PtCl(C\equiv CMe)(CO)L]$ isomer (II) and $[PtAr(C\equiv CPh)(CO)L]$, Ar <u>trans</u> to L, but that these compounds are less stable than $[PtCl(C\equiv CPh)(CO)L]$ isomer (II) and $[PtAr(C\equiv CMe)(CO)L]$ for some reason, and there is a second, fast aryl transfer reaction:-

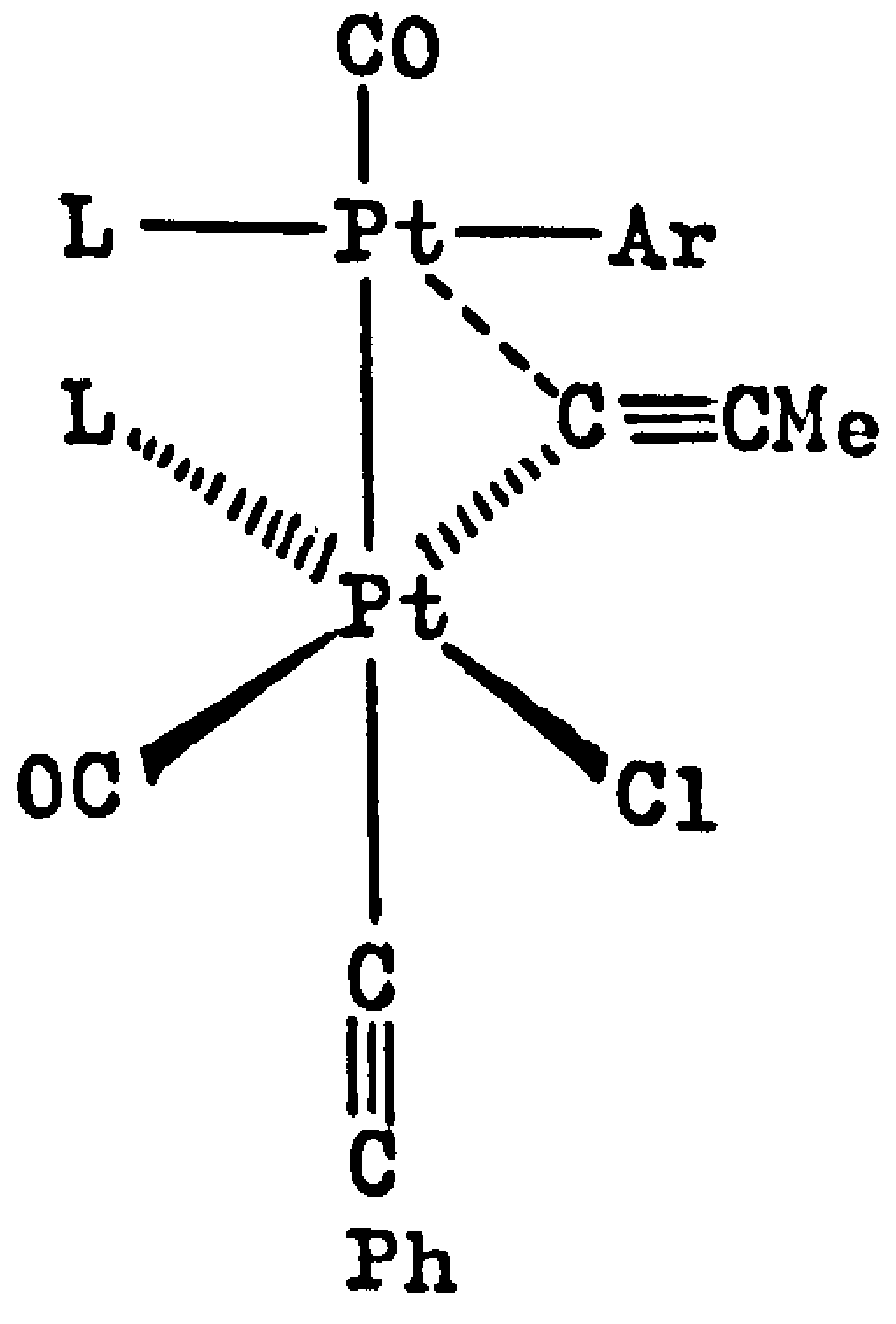


(ii) The two isomers of $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L}]$ react at different rates, that with $\mathrm{C{\equiv}CMe}$ trans to phosphine reacting faster than the rate of isomerisation, that with $\mathrm{C{\equiv}CPh}$ trans to phosphine reacting at a comparable rate to isomerisation, by the mechanisms previously suggested. This would account for the stereospecific reaction of $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L}]$, with $\mathrm{C{\equiv}CMe}$ trans to phosphine, as $\mathrm{C{\equiv}CMe}$ would be transferred to aryl isomer (I) faster than the material could isomerise. $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L}]$, $\mathrm{C{\equiv}CPh}$ trans to phosphine, would react at a similar rate to its rate of isomerisation, but the minor isomer would react faster than the major isomer and lead to all four observed products.

(iii) With $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)L}]$, $\mathrm{C{\equiv}CPh}$ trans to phosphine, another oxidative addition/reductive elimination route operates to give $[\mathrm{PtCl(C{\equiv}CPh)(CO)L}]$ (II) and $[\mathrm{PtAr(C{\equiv}CMe)(CO)L}]$ in addition to the S_E2 (cyclic)/ indistinguishable oxidative addition route for the production of $[\mathrm{PtCl(C{\equiv}CMe)(CO)L}]$ (II) and $[\mathrm{PtAr(C{\equiv}CMe)(CO)L}]$.



P'



Q

Intermediate P' is the one equivalent to intermediate P for the reaction of the other isomer. Intermediate Q comes from oxidative addition of Pt - Cl to bisacetylide, with Cl displacing C≡CPh. Reductive elimination from P' would account for [PtCl(C≡CMe)(CO)L] (II) and [PtAr(C≡CPh)(CO)L], while reductive elimination from Q would account for [PtCl-(C≡CPh)(CO)L] (II) and [PtAr(C≡CMe)(CO)L].

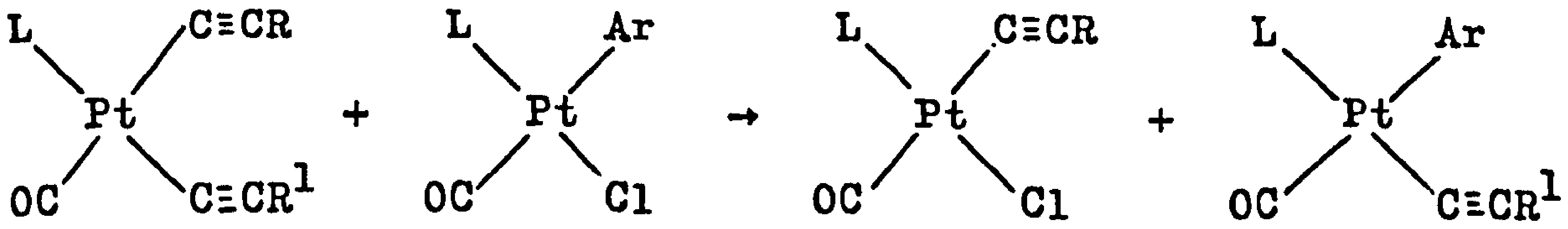
Although any of the above reasons, (i), (ii) and (iii), may account for the difference observed in the reactions of the two isomers of [Pt(C≡CMe)(C≡CPh)(CO)L] with aryl isomer (I), this was the only example of such a difference in the reactions of the two isomers found, and perhaps this reaction should be repeated before such explanations are invoked.

The isomerisation of [Pt(C≡CR)(C≡CR^1)(CO)L] in the above reactions is possible by the same route proposed in the reaction with cis-[PtCl$_2$(CO)L], namely a reaction between starting material and acetylide isomer (II).

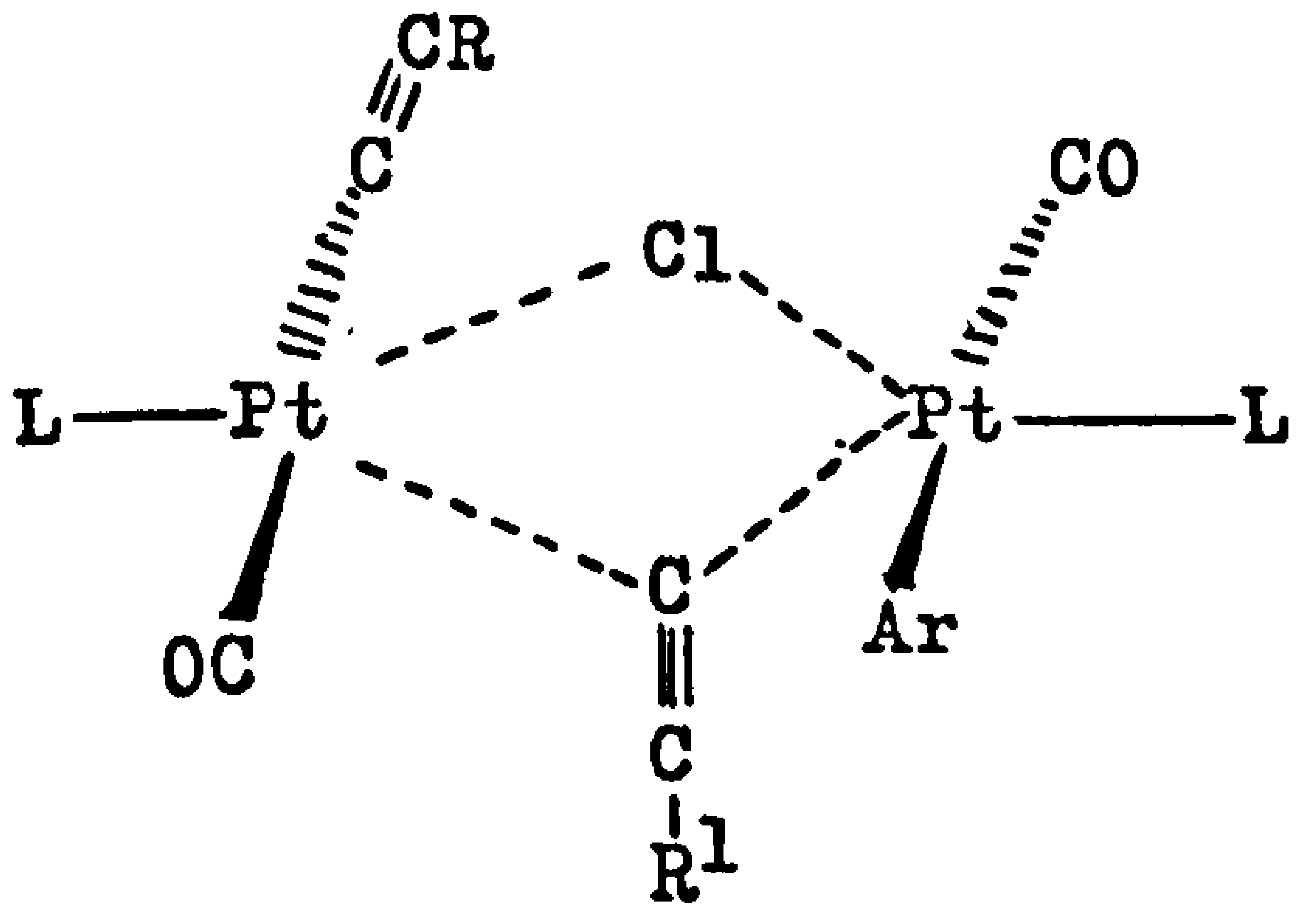
c) With [PtCl(C$_6$H$_4$CO$_2$Me-p)(CO)(PMePh$_2$)] isomer (II)

A solution of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh trans to phosphine, was mixed at -60°C with a solution of [PtCl(C$_6$H$_4$CO$_2$Me-p)(CO)(PMePh$_2$)] isomer (II) and the reaction was observed by ^{31}P nmr spectroscopy. The initial products were [PtCl(C≡CMe)(CO)(PMePh$_2$)] isomer (II) and a species identified as [Pt(C$_6$H$_4$CO$_2$Me-p)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh trans to PMePh$_2$, (table 12). On brief warming of the mixture to room temperature, large amounts of the other isomer of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] appeared, and also some $[\mathrm{PtCl(C{\equiv}CPh)(CO)(PMePh_2)}]$ isomer (II). The amount of $[\mathrm{PtCl(C{\equiv}CMe)(CO)(PMePh_2)}]$ (II) present was much more than the amount of $[\mathrm{Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CPh)(CO)(PMePh_2)}]$ detected; presumably this latter species was decomposing or was not very soluble in $\mathrm{CDCl_3}$ at -60°C.

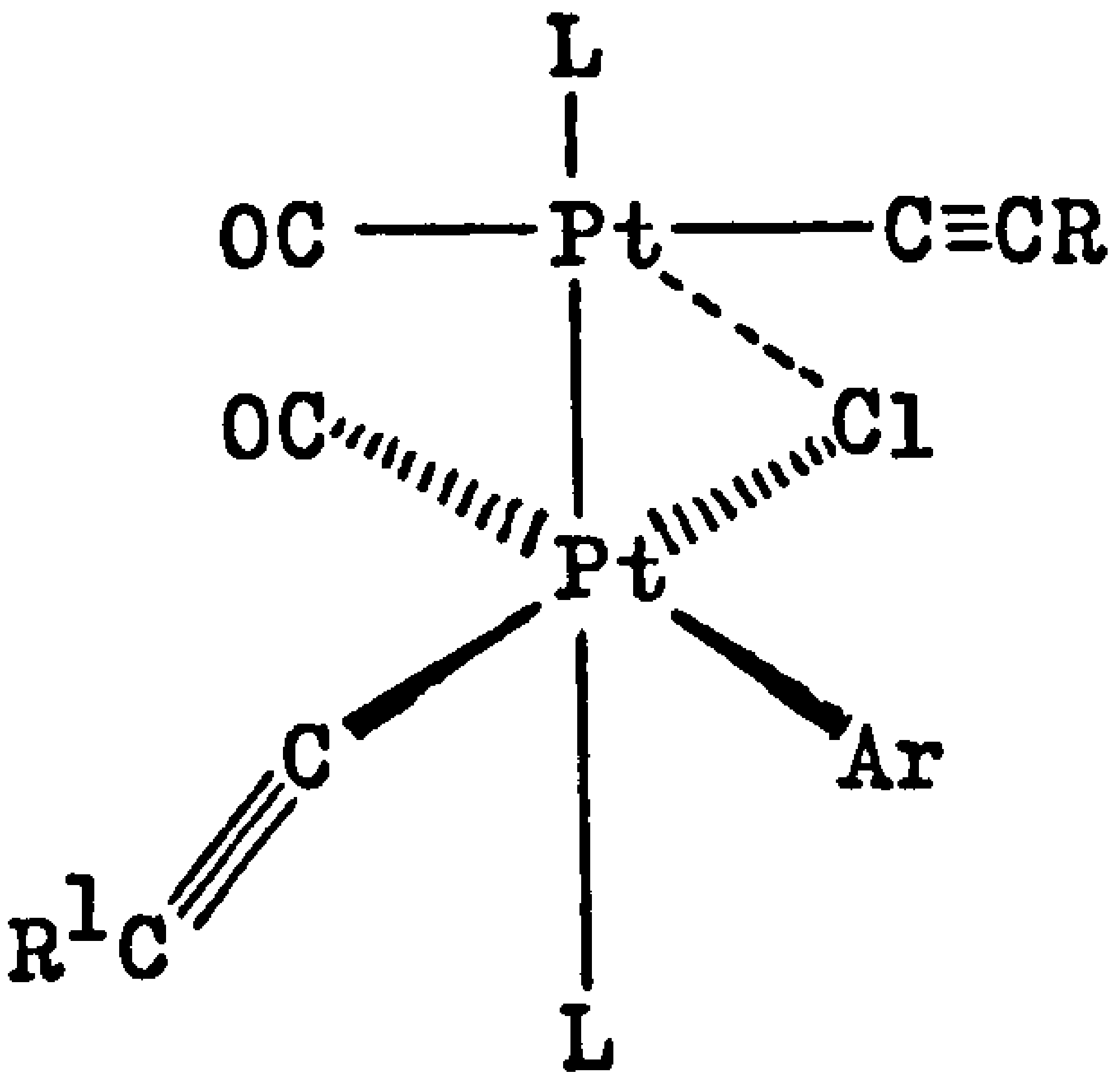
When the same reaction was performed with the other isomer of $[\mathrm{Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)}]$, i.e. the isomer with $\mathrm{C{\equiv}CMe}$ *trans* to $\mathrm{PMePh_2}$, the initial products were $[\mathrm{PtCl(C{\equiv}CPh)(CO)(PMePh_2)}]$ isomer (II) and a species, which was too weak to determine its platinum-phosphorus coupling constant, at + 0.2 ppm. This was assigned as $[\mathrm{Pt(C_6H_4CO_2\text{-}Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)}]$, $\mathrm{C{\equiv}CMe}$ *trans* to $\mathrm{PMePh_2}$, by analogy with the reaction of the other isomer. Again, on warming to room temperature, isomerisation of $[\mathrm{Pt(C{\equiv}CMe)\text{-}(C{\equiv}CPh)(CO)(PMePh_2)}]$ was rapid, and $[\mathrm{PtCl(C{\equiv}CMe)(CO)\text{-}(PMePh_2)}]$ isomer (II) also began to appear. The amount of $[\mathrm{Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)}]$ was again much less than the $[\mathrm{PtCl(C{\equiv}CPh)(CO)(PMePh_2)}]$ (II).



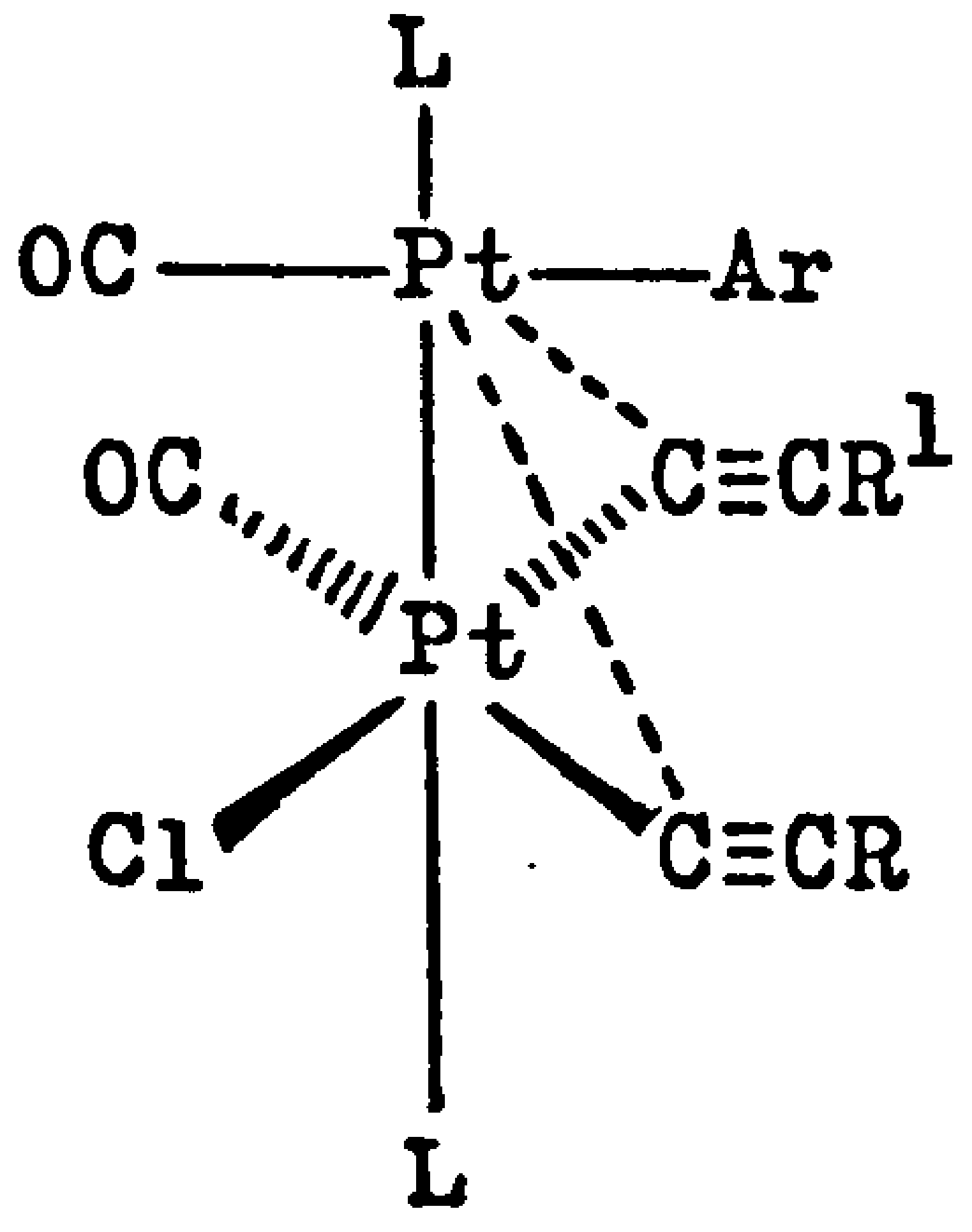
This reaction involves an exchange of groups *trans* to phosphine, which is consistent with an S_E2 (cyclic) mechanism:-



The only cis-oxidative addition/reductive elimination routes capable of giving the products are the ones whose intermediates are related to the above transition state by Pt-Hg bond formation:-



R



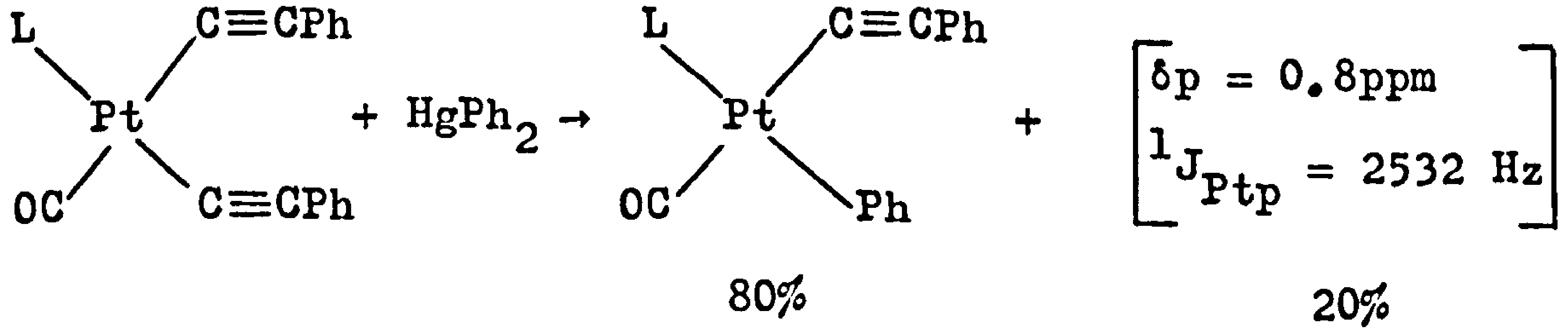
S

Intermediate R, formed by addition of Pt—$C\equiv CR^1$ to aryl isomer (II), with displacement of Cl by Pt gives the observed products. The other intermediate, S, formed by addition of Pt—Cl to bisacetylide complex can give the observed products on reductive elimination of $C\equiv CR^1$, but could also eliminate $C\equiv CR$ to form $[PtAr(C\equiv CR)(CO)L]$ and $[PtCl(C\equiv CR^1)(CO)L]$ isomer (III), which are not observed. However, a specific reductive elimination of $C\equiv CR^1$ cannot be ruled out.

In these reactions $[PtCl(C\equiv CR)(CO)L]$ isomer (II) is again present, providing a route for the rapid isomerisation of the mixed bis-acetylide complexes, $[Pt(C\equiv CR)(C\equiv CR^1)(CO)L]$, which are stable to isomerisation when pure, and in the absence of mercury byproduct. That this is the mechanism of isomerisation is supported by the fact that a mixture of cis-$[PtPh_2(CO)(PMePh_2)]$ and $[Pt(C\equiv CMe)(C\equiv CPh)(CO)(PMePh_2)]$, $C\equiv CPh$ trans to phosphine, not only does not react, but the bisacetylide isomerises much more slowly, with only 30% isomerisation in 20 minutes at room temperature. That any isomerisation is observed at all may be due to the cis-$[PtPh_2(CO)(PMePh_2)]$ being contaminated with small amounts of $[PtCl(Ph)(CO)(PMePh_2)]$ isomers (I) and (II), which should react in the same way as the corresponding $C_6H_4CO_2Me$-p complexes and provide a small amount of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) to cause isomerisation.

Reactions of cis-$[Pt(C{\equiv}CR)_2(CO)(PMePh_2)]$ with $HgPh_2$

When a solution of cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$, prepared by the symmetrization route using $Hg(C{\equiv}CPh)_2$ and $[Et_4N]Cl$, was mixed with a solution of $HgPh_2$ at -60°C there was no reaction in 2½ hours. On warming the mixture, a slow reaction proceeded, the initial product being $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, Ph trans to phosphine, (table 12). A second, unidentified product also became apparent, with ^{31}P nmr parameters of $\delta = +0.8$ ppm, $^1J_{PtP} = 2532$ Hz at room temperature. After 3 hours at room temperature, 70% of the starting material was consumed, and the products were in the ratio shown below, (based on the intensity of peaks in the ^{31}P nmr spectrum).



On being left to react further overnight, cis-$[PtPh_2(CO)(PMePh_2)]$, trans-$[PtCl(Ph)(PMePh_2)_2]$ and trans-$[PtCl(COPh)(PMePh_2)_2]$ were also produced; the amount of $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$ decreased relative to the unknown species.

Table 12:- ^{31}P nmr parameters of mixed arylacetylide platinum complexes in $CDCl_3$ at -60°C.

Complex, L = $PMePh_2$, Ar = $C_6H_4CO_2Me$-*p*	δ (ppm)	J_{PtP} (Hz)
[PtAr(C≡CMe)(CO)L], C≡CMe *trans* to L	+0.1	2418
[PtAr(C≡CPh)(CO)L], C≡CPh *trans* to L	+0.5	2439
[PtPh(C≡CMe)(CO)L], C≡CMe *trans* to L	+1.1	2449
[PtPh(C≡CPh)(CO)L], Ph *trans* to L$^{(a)}$	+0.2	1389
[PtPh(C≡CMe)(CO)L], Ph *trans* to L$^{(b)}$	+0.2	1398
[PtAr(C≡CMe)(CO)L], Ar *trans* to L$^{(c)}$	-0.1	1444
[PtAr(C≡CPh)(CO)L], Ar *trans* to L	-0.2	1431
$[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CMe)_2L_2]$ (d)	+0.2	4104
$[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CPh)_2L_2]$	+0.3	4176

Parameters at 25°C :-

(a) -0.1 ppm, 1368 Hz.

(b) 0.0 ppm, 1369 Hz.

(c) -0.4 ppm, 1419 Hz.

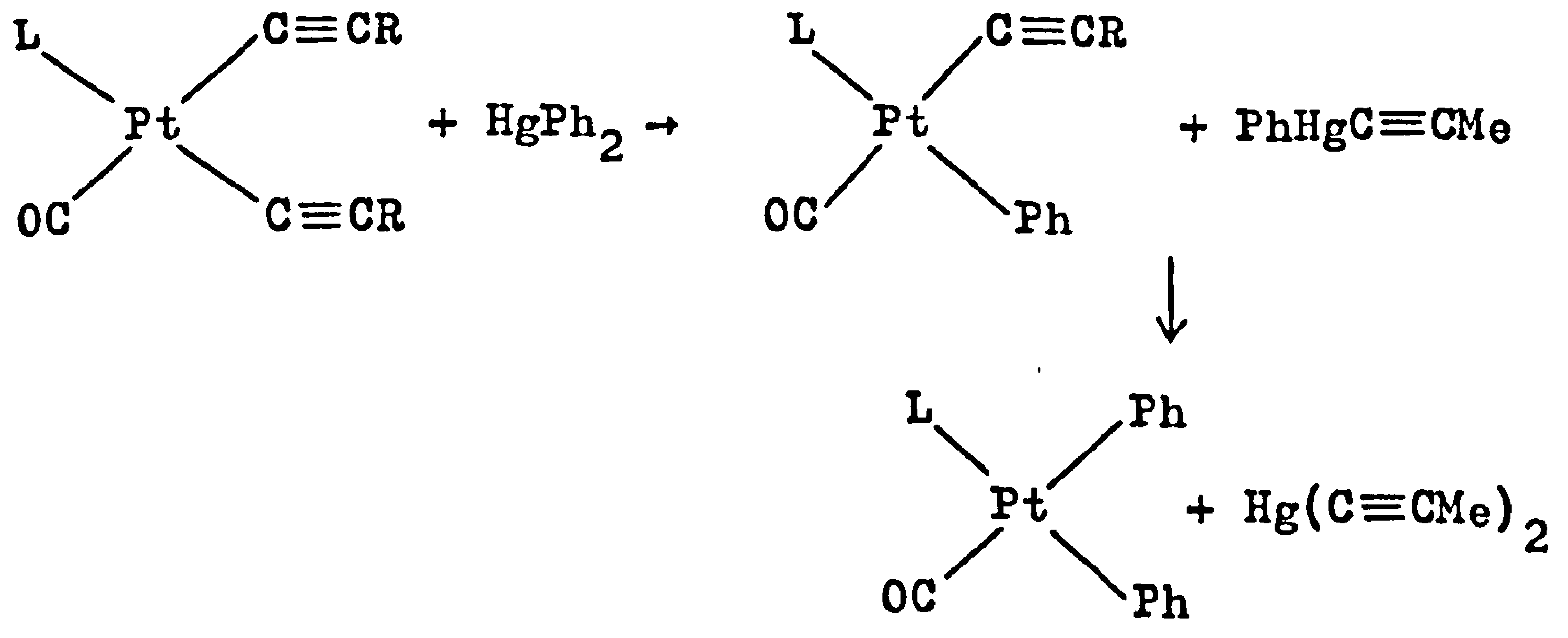
(d) +0.1 ppm, 4161 Hz.

The ^{31}P nmr parameters of the unknown complex are typical of a trans-bisphosphine platinum complex, e.g. :- trans-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$ has parameters $\delta = +5.1$ppm, $^1J_{PtP} = 2546$ Hz and trans-$[PtCl_2(PMePh_2)_2]$ parameters $\delta = +4.3$ ppm, $^1J_{PtP} = 2541$ Hz. Acetylide groups appear to have a similar nmr cis-influence to chlorides, e.g.:- $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I), $\delta = +6.8$ppm, $^1J_{PtP} = 1402$ Hz and $[Pt(Ph)(C{\equiv}CPh)(CO)(PMePh_2)]$, $\delta = -0.1$ ppm, $^1J_{PtP} = 1368$ Hz. This suggests that the unknown species, $\delta = +0.8$ ppm, $^1J_{PtP} = 2532$ Hz, could be trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$.

When solutions of cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$, prepared by the symmetrization route, and $HgPh_2$ were mixed, the reaction was more complicated. In one case, 30% of the starting material was consumed in 20 minutes at room temperature, producing, initially, only $[Pt(Ph)(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to phosphine, (table 12). Other products subsequently appeared and, after 3 hours at room temperature, all of the cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ had been consumed. $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ accounted for 40% of the total ^{31}P intensity of the products. Other products were:- an unknown species, with $\delta = +8.0$ ppm, $^1J_{PtP} = 2428$ Hz (at RT), trans-$[PtCl(C{\equiv}CMe)(PMePh_2)_2]$, trans-$[PtCl(Ph)(PMePh_2)_2]$ and cis-$[PtPh_2(CO)(PMePh_2)]$, which were all of approximately equal intensity after the reaction had been left overnight, (tables 11, 13).

In a second reaction, which contained some excess $(Et_4N]Cl$, $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, was again the initial product, along with an unidentified species with $\delta = +1.2$ ppm, ${}^1J_{PtP} = 2583$ Hz (at room temperature). This is similar to the unknown compound produced in the $C\equiv CPh$ reaction, thus it could be trans-$[Pt(C\equiv CMe)_2(PMePh_2)_2]$. Other products also appeared later, including the anion cis-$[PtCl_2(COPh)(PMePh_2)]^-$, (presumably from reactions involving the excess chloride), and trans-$[PtCl(C\equiv CMe)(PMePh_2)_2]$. After 2 hours at room temperature, 80% of the cis-$[Pt(C\equiv CMe)_2(CO)(PMePh_2)]$ had been consumed. After 4 to 5 hrs., cis-$[PtPh_2(CO)(PMePh_2)]$ had become the major product, and trans-$[PtCl(Ph)(PMePh_2)_2]$ had also appeared.

Complexes such as trans-$[PtCl(Ph)L_2]$, trans-$[PtCl(COPh)L_2]$, trans-$[PtCl(C\equiv CR)L_2]$, trans-$[Pt(C\equiv CR)_2L_2]$ etc. can be considered as decomposition products, since they are formed as a result of phosphine liberation. In each case, $[PtPh(C\equiv CR)(CO)L]$ is the initial product, and subsequent reaction of this with organomercury byproduct could form cis-$[PtPh_2(CO)L]$:-

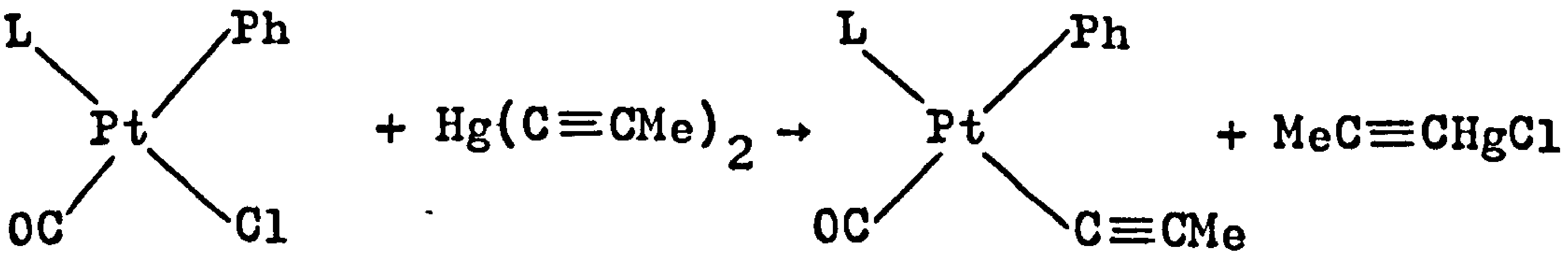


When a solution of cis-$[PtPh_2(CO)(PMePh_2)]$ was mixed with a solution of $Hg(C\equiv CMe)_2$, there was no reaction within 12 hours at room temperature, except for some decomposition, and production of *trans*-$[PtCl(Ph)(PMePh_2)_2]$, thus obviously any *cis*-$[PtPh_2(CO)(PMePh_2)]$ produced in the above scheme would be relatively stable in the presence of $Hg(C{\equiv}CMe)_2$ byproduct.

The reaction between *cis*-$[Pt(C{\equiv}CR)_2(CO)L]$ and $HgPh_2$ gives the product expected for an S_E2(cyclic) reaction, but several *cis*-oxidative addition/reductive elimination reactions would also lead to the observed product, $[PtPh(C{\equiv}CR)(CO)L]$, Ph *trans* to L. The reaction of $[PtPh(C{\equiv}CR)(CO)L]$ with $PhHgC{\equiv}CR$ byproduct to produce *cis*-$[PtPh_2(CO)L]$ is less likely to be an S_E2 (cyclic) mechanism, since the group *trans* to CO is replaced, than a *cis*-oxidative/reductive elimination sequence, of which several are possible.

Complexes $[PtR(C{\equiv}CR^1)(CO)L]$, $C{\equiv}CR^1$ *trans* to L.

$Hg(C{\equiv}CMe)_2$ reacts rapidly at room temperature with $[PtCl(Ph)(CO)(PMePh_2)]$, Ph *trans* to CO, (isomer (II)), to form mainly $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, the ^{31}P nmr characteristics of which indicate that Ph is *trans* to CO, (table 12).



The reaction did not stop at this point; a large amount of *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ was produced, presumably by a reaction between $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ and $MeC{\equiv}CHgCl$ byproduct. Some *trans*-$[PtCl(Ph)(PMePh_2)_2]$ was also produced later.

$[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (II) reacted similarly with $Hg(C{\equiv}CMe)_2$ to produce $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to $PMePh_2$, but with lesser amounts of side-products. Only a small amount of trans-$[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(PMePh_2)_2]$ was produced in this reaction, and no cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ was detected. The complex, $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to phosphine, is the one which was observed in the reaction between $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to $PMePh_2$, and $[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (II).

The reaction of $[PtCl(Ar)(CO)L]$ isomer (II), (Ar = Ph, $C_6H_4CO_2Me\text{-}\underline{p}$; L = $PMePh_2$), with $Hg(C{\equiv}CMe)_2$ to replace the chloride directly with $C{\equiv}CMe$ is consistent with an S_E2 (cyclic) mechanism. A cis-oxidative addition of $Hg(C{\equiv}CMe)_2$, with Hg displacing the chloride is also possible, and this is the oxidative addition/reductive elimination mechanism related to S_E2(cyclic) by Pt–Hg bond formation. However, in the reaction between cis-$[PtCl_2(CO)L]$ and $Hg(C{\equiv}CR)_2$, forming $[PtCl(C{\equiv}CR)(CO)L]$, $C{\equiv}CR$ trans to L, (isomer (I)), it was considered that an S_E2 (cyclic) mechanism operated.[153] This reaction is very similar to the one between $[PtCl(Ar)(CO)L]$ (II) and $Hg(C{\equiv}CMe)_2$, therefore an S_E2 (cyclic) mechanism is perhaps more plausible, (fig. 26).

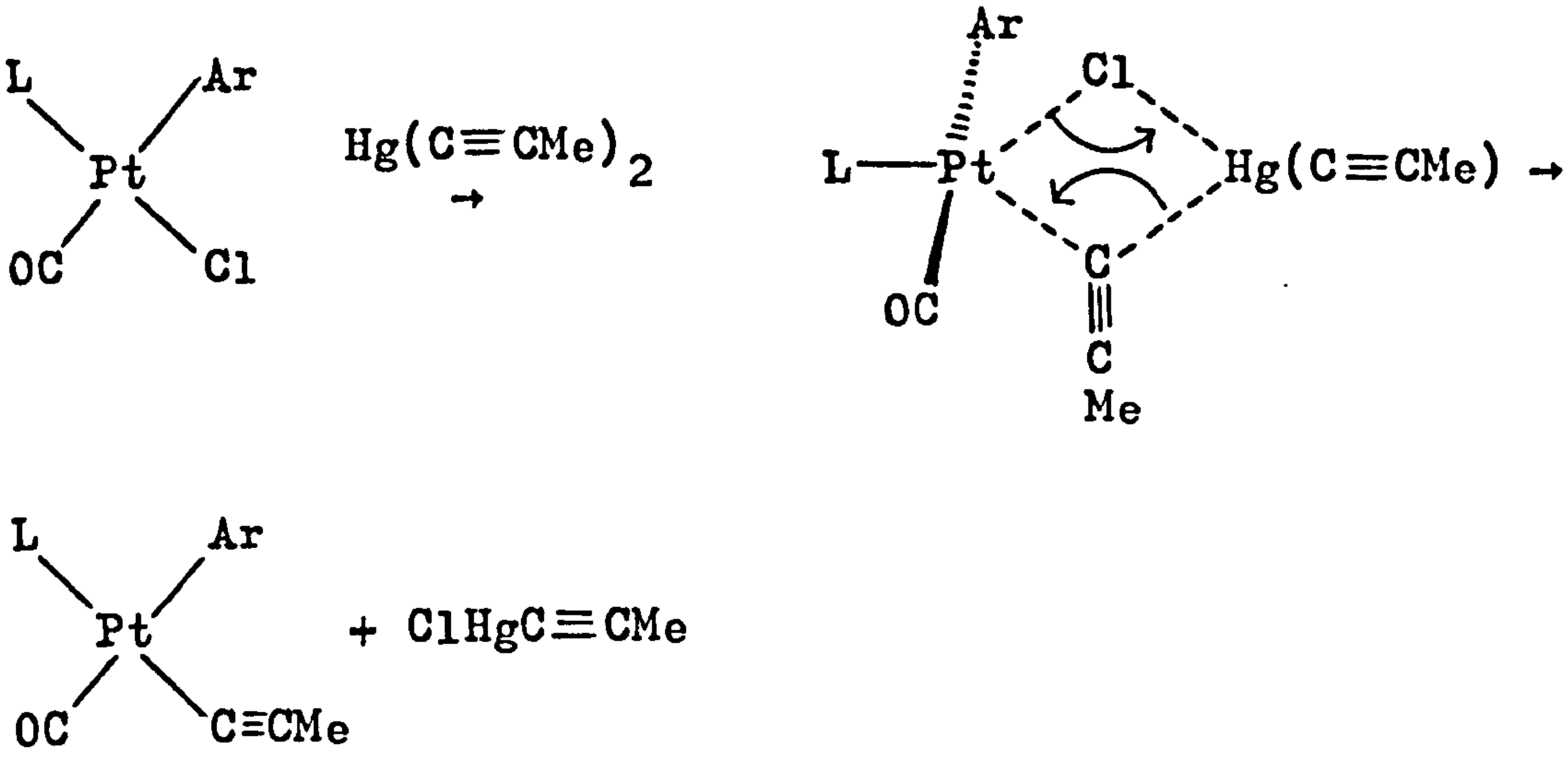
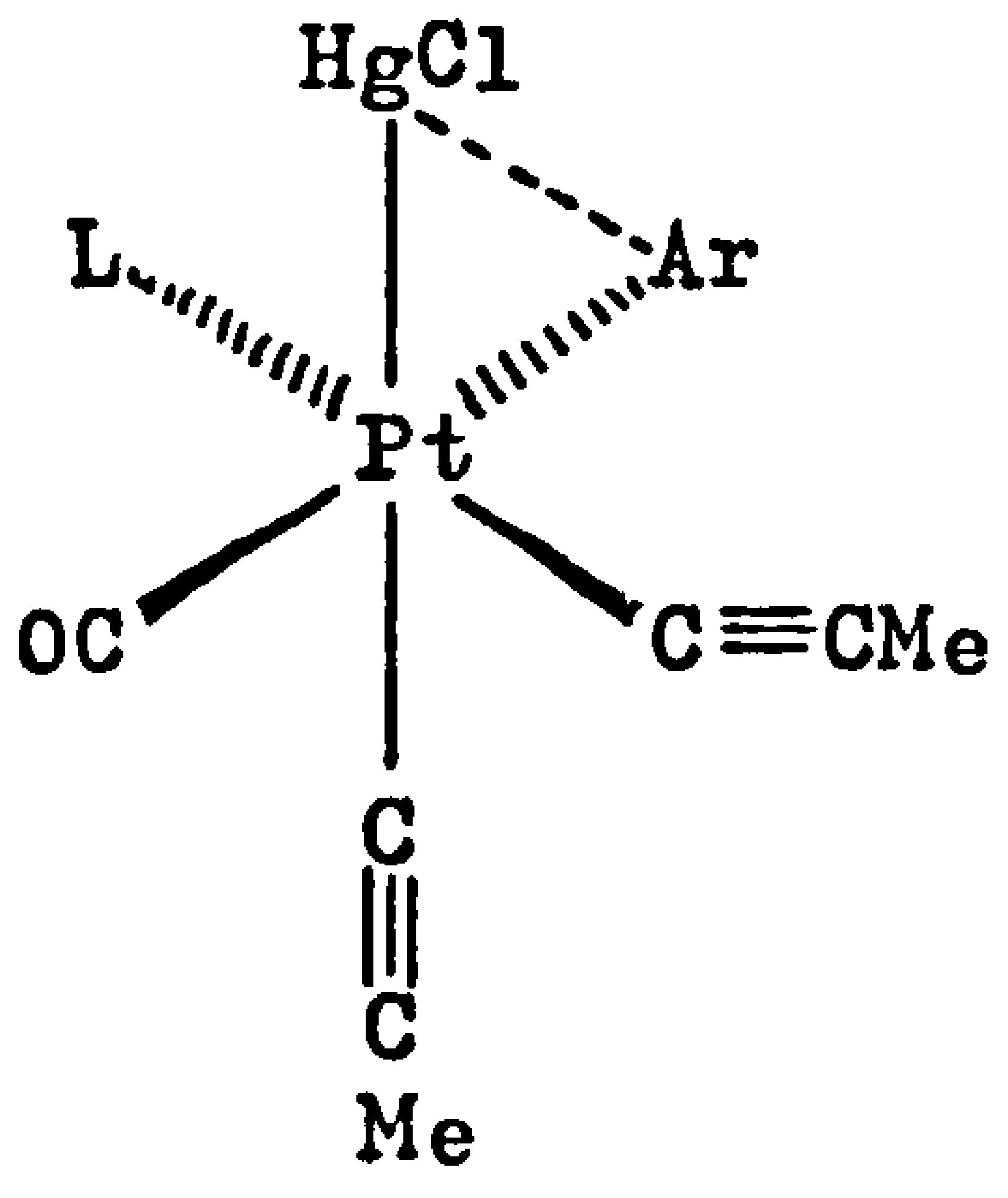
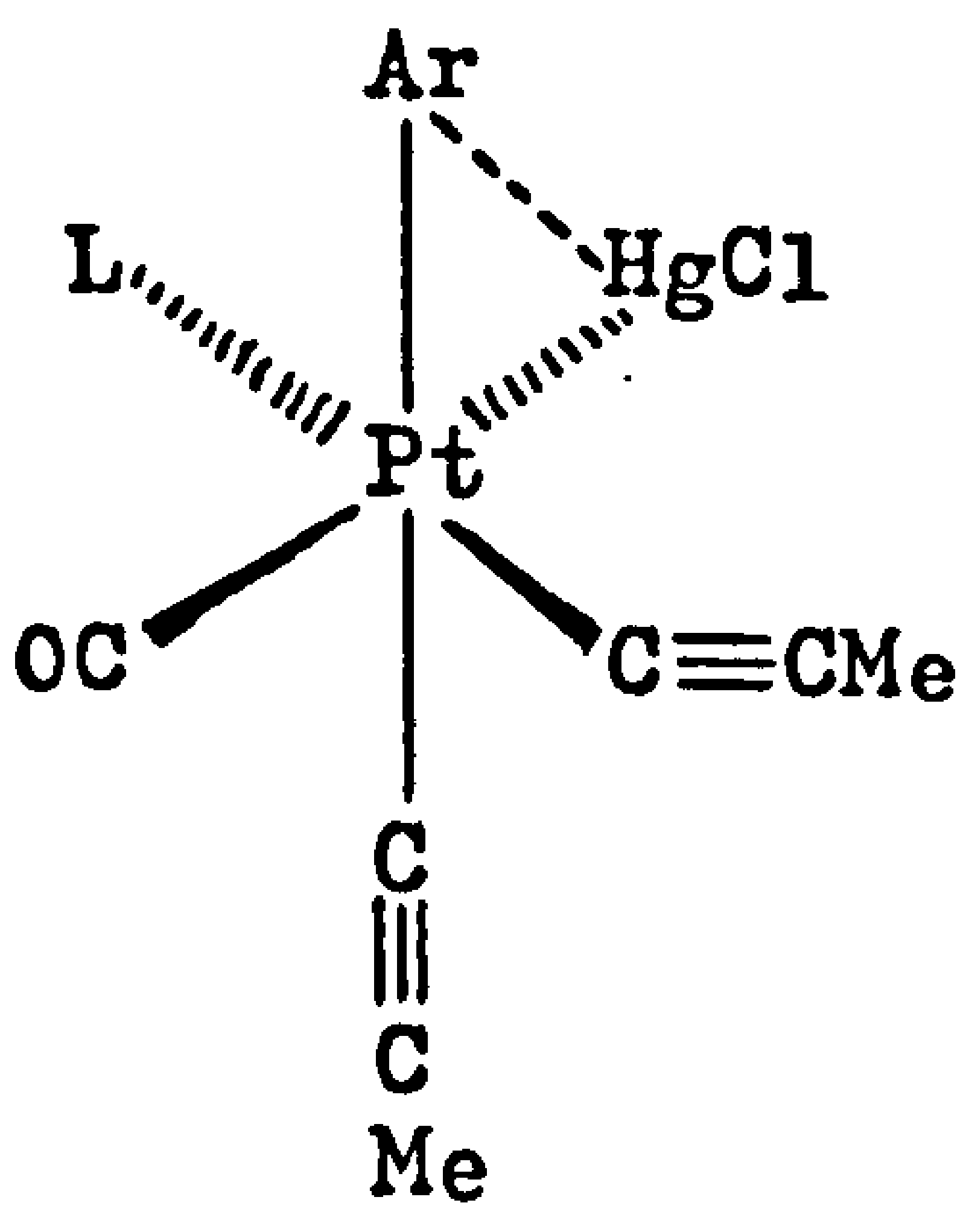


figure 26

In the case where Ar = Ph, large amounts of cis-$[Pt(C\equiv CMe)_2(CO)(PMePh_2)]$ were produced; this is most likely to be an oxidative addition/reductive elimination reaction between $[PtPh(C\equiv CMe)(CO)L]$ and $ClHg(C\equiv CMe)$. Several intermediates leading to the observed products are possible, but in the analogous reaction of $[PtCl(C\equiv CMe)(CO)L]$ isomer (I) with $ClHg(C\equiv CMe)$ to give cis-$[Pt(C\equiv CMe)_2(CO)L]$, a trans-oxidative addition/cis-reductive elimination route was favoured.[153] In the reaction of $[PtPh(C\equiv CMe)(CO)L]$ and $ClHg(C\equiv CMe)$ such a route, via intermediate T is possible, although cis-oxidative addition of $ClHg{-}C\equiv CMe$ with displacement of Ph by Hg giving intermediate U or displacement of $C\equiv CMe$ (on Pt) by $C\equiv CMe$, which also leads to intermediate T, would also lead to the observed products.



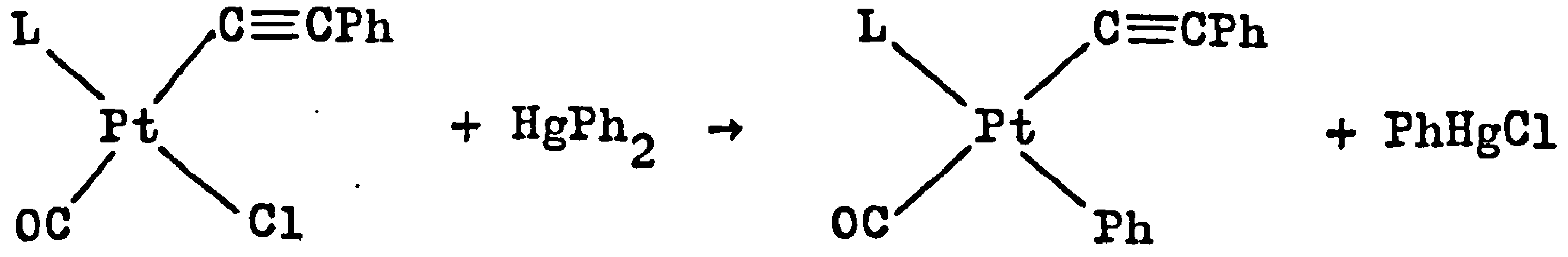
T



U

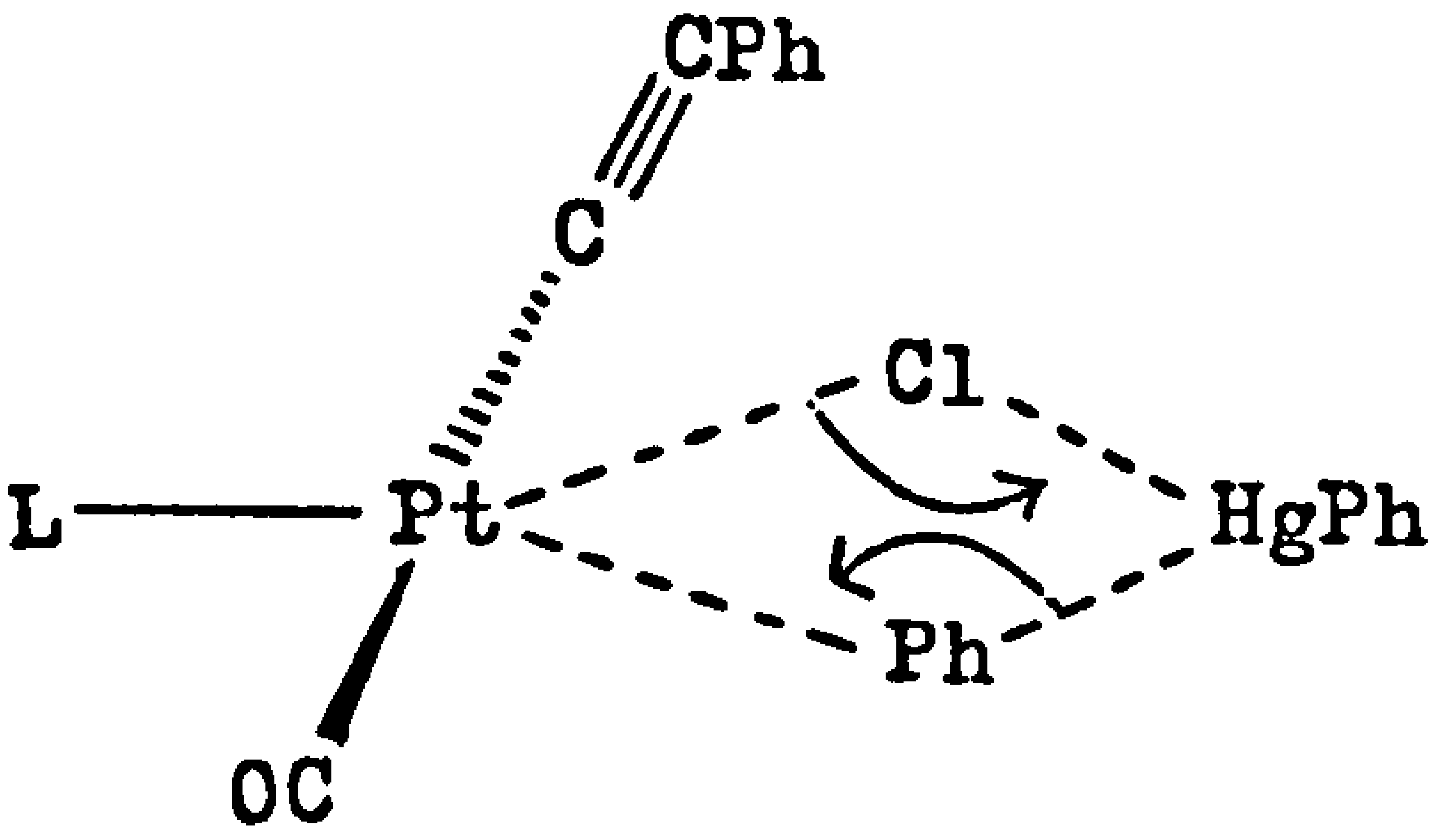
$[PtCl(C{\equiv}CR)(CO)(PMePh_2)]$ isomer (II) and $HgPh_2$

$[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ isomer (II) reacts slowly at -20°C, rapidly at room temperature, with $HgPh_2$ to produce a species with ^{31}P nmr parameters (at 25°C) of $\delta = -0.1$ ppm, $^1J_{PtP} = 1368$ Hz. This is consistent with Ph trans to $PMePh_2$, and this species is assigned as $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$.



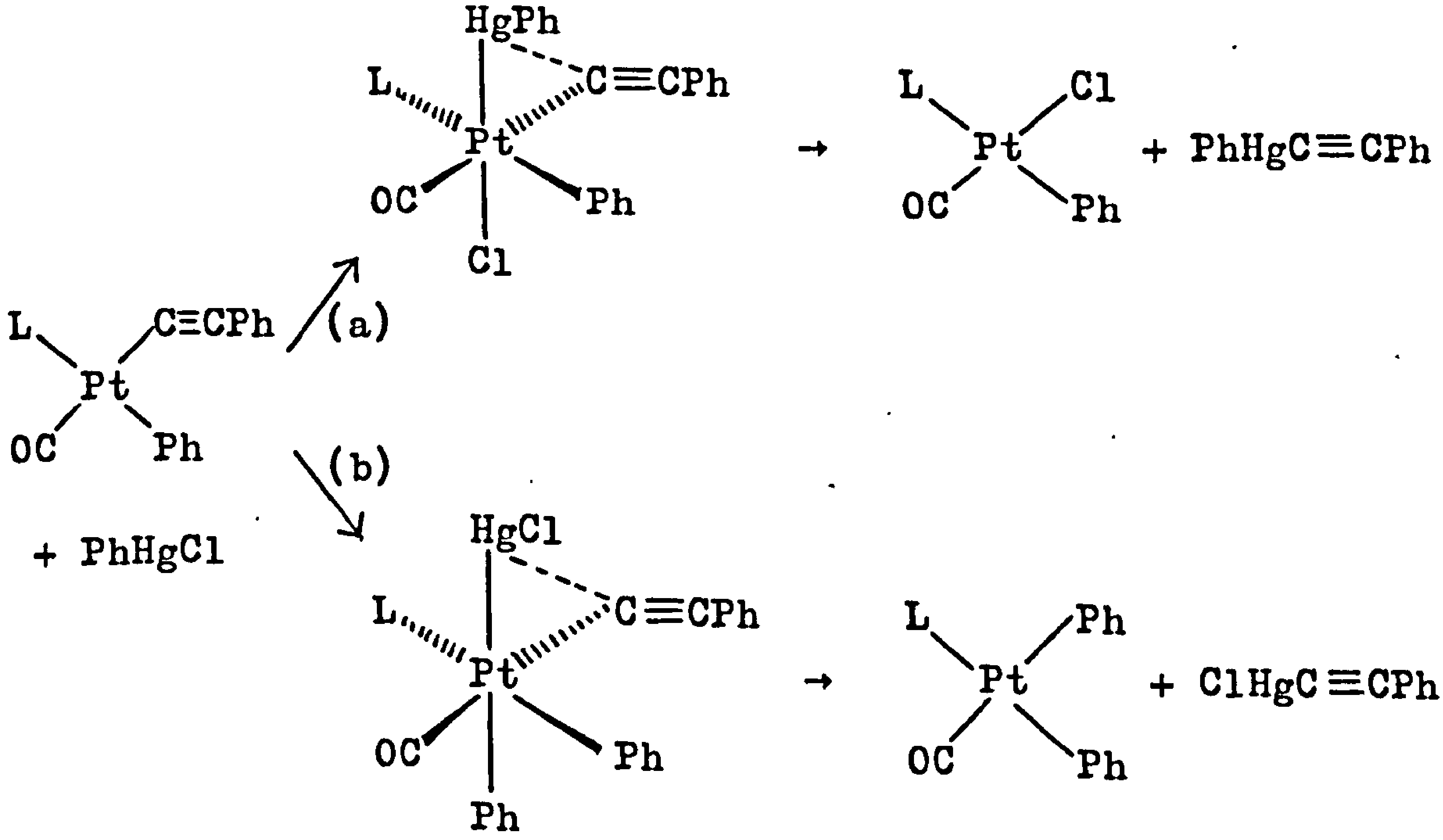
$[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$ was the only product, initially, but on being left at room temperature it decomposed, producing considerable amounts of $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$, cis-$[PtPh_2(CO)(PMePh_2)]$, $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and trans-$[PtCl(Ph)(PMePh_2)_2]$, (table 13).

$[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$ is the product expected from an S_E2 (cyclic)mechanism, via a transition state below:-



S_E2 (cyclic) transition state.

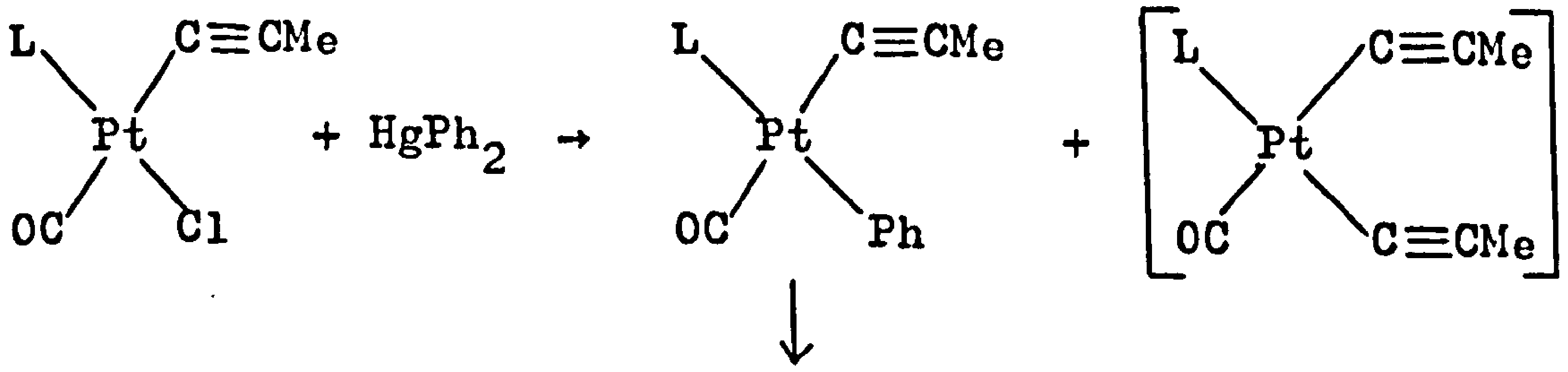
The decomposition products could arise from subsequent reactions of [$PtPh(C\equiv CPh)(CO)(PMePh_2)$] with the PhHgCl byproduct, probably by oxidative addition/reductive elimination sequences. Oxidative addition of the Hg-Ph bond to [$PtPh(C\equiv CPh)(CO)(PMePh_2)$] could produce cis-[$PtPh_2(CO)(PMePh_2)$], while oxidative addition of the Hg-Cl bond could produce [$PtCl(Ph)(CO)(PMePh_2)$] (I) which would, in turn, produce [$Pt_2(COPh)_2Cl_2(PMePh_2)_2$] by insertion, (fig. 27).



(a) trans-oxidative addition of Hg-Cl.
(b) cis-oxidative addition of Hg-Ph.

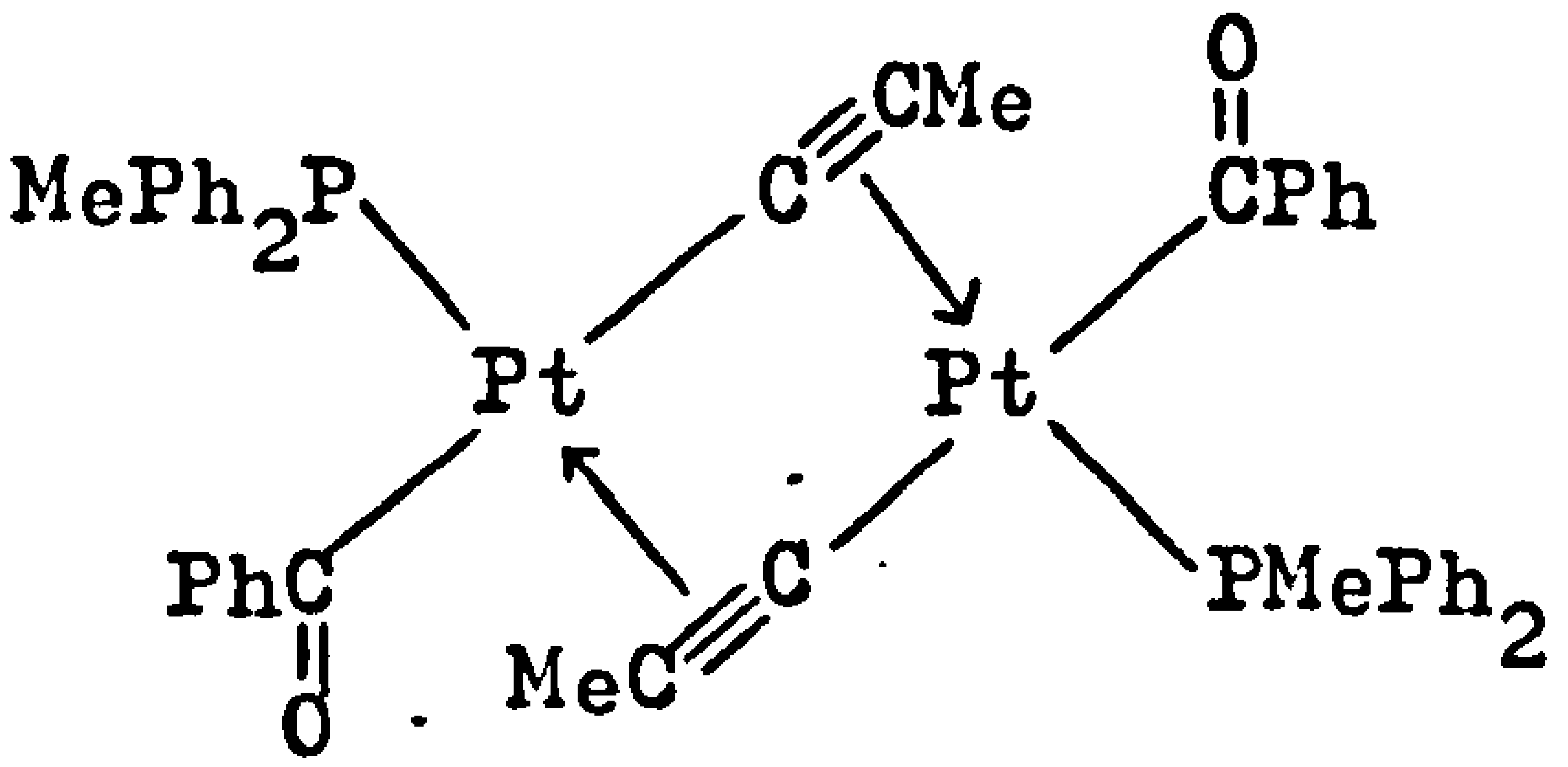
Figure 27.

When a similar reaction was performed with [PtCl(C≡CMe)(CO)($PMePh_2$)] isomer (II) and $HgPh_2$, both [PtPh(C≡CMe)(CO)($PMePh_2$)], Ph trans to $PMePh_2$, (table 12) and cis-[Pt($C{\equiv}CMe)_2$(CO)($PMePh_2$)] were initially produced, (in approximately equal amounts at 40% reaction). From then on, the amount of cis-[Pt($C{\equiv}CMe)_2$(CO)($PMePh_2$)] decreased, while the [PtPh(C≡CMe)(CO)($PMePh_2$)] increased. After 3 minutes reaction at room temperature another species began to grow in which had ^{31}P parameters, at -60°C, of δ = +0.2 ppm, $^1J_{PtP}$ = 4104 Hz, and had broad platinum satellites. This material grew in slowly and appeared to be formed from [PtPh(C≡CMe)(CO)($PMePh_2$)]. At 15 mins reaction (at RT), the ratio of [PtPh(C≡CMe)(CO)($PMePh_2$)] to unknown species (based on the intensities of their ^{31}P signals) was 2 to 1. The only other material present at this time was a small amount of [PtCl(Ph)(CO)($PMePh_2$)](I). After 1 hr. at 25°C, the ratio of the two species had changed to 1 to 2, approximately, but by then the solution contained large amounts of [PtCl(Ph)(CO)($PMePh_2$)] (I), [$Pt_2(COPh)_2Cl_2$($PMePh_2)_2$], trans-[PtCl(Ph)($PMePh_2)_2$] and trans-[PtCl(COPh)($PMePh_2)_2$].

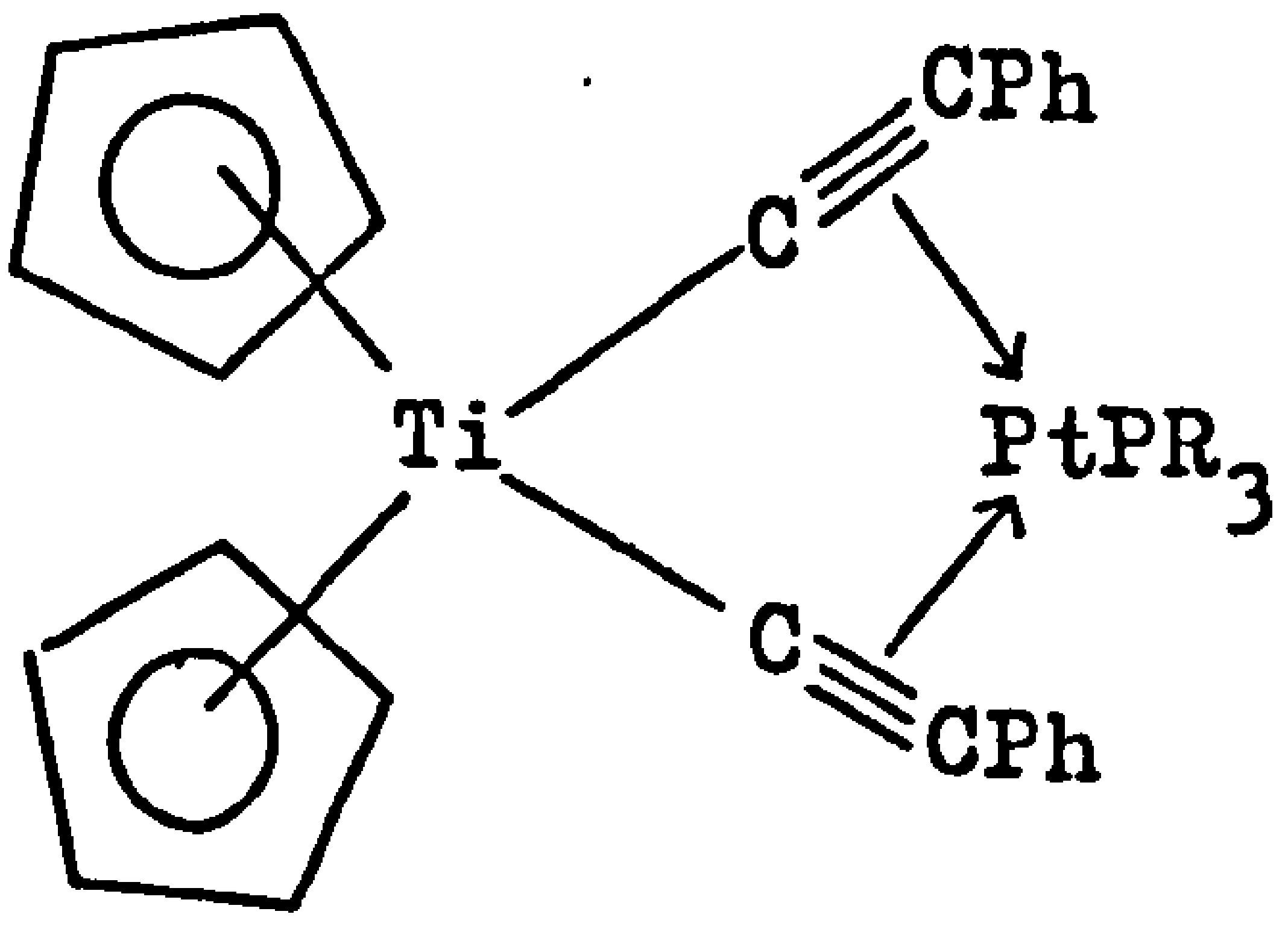


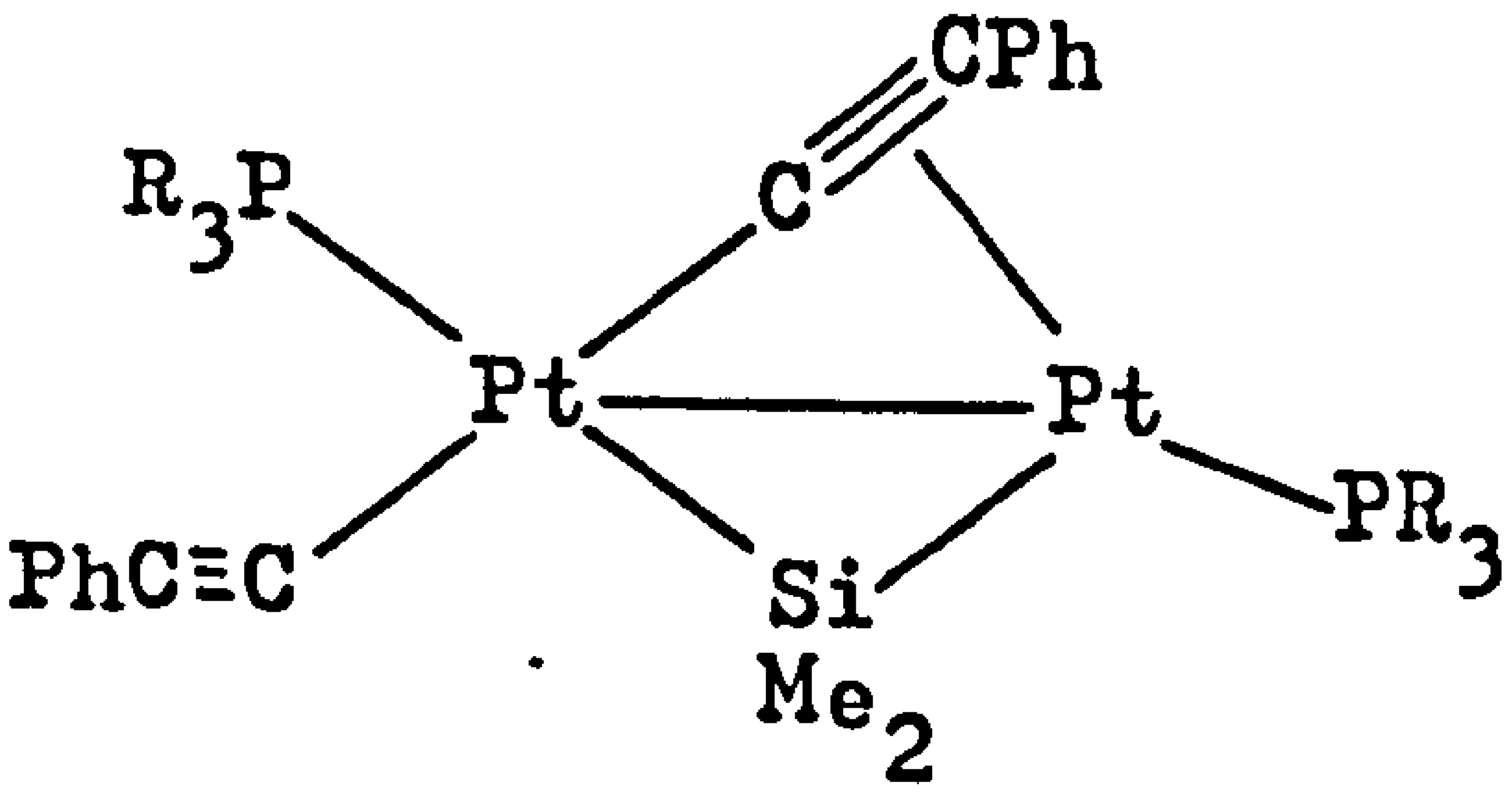
δ = +0.2 ppm, $^1J_{PtP}$ = 4104 Hz.

The species with parameters $\delta = +0.2$ ppm, ${}^1J_{PtP} = 4104$ Hz has a coupling constant indicative of a bridged platinum dimer. For example, $[Pt_2(SCH_2Ph)_2(COPh)_2(PMePh_2)_2]$ has ${}^1J_{PtP} = 4048$ Hz.[173] This, and the result of the reaction between $[PtClPh(CO)(PMePh_2)]$ isomer (I) and $Hg(C{\equiv}CMe)_2$, described later in this chapter, in which this species is also formed, suggests that it is a carbonyl inserted dimer with bridging acetylides, probably in equilibrium with the complex $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, as shown below:-



This type of acetylide-bridge is known, for example in the product formed from the reaction of $[(\eta^5-C_5H_5)_2Ti-(C{\equiv}CPh)_2]$ and $[Pt(C_2H_4)(PR_3)]$ in which C_2H_4 is lost, and the C≡CPh groups on Ti π-bond to platinum, and in the platinum-bonded complex, $[Pt_2(\sigma-C{\equiv}CPh)\{\mu-(1-\sigma,1,2-\pi-C{\equiv}CPh)\}(\mu-SiMe_2)(PR_3)_2]$ complex, which has been isolated and had its structure confirmed by X-ray crystallography.[174]



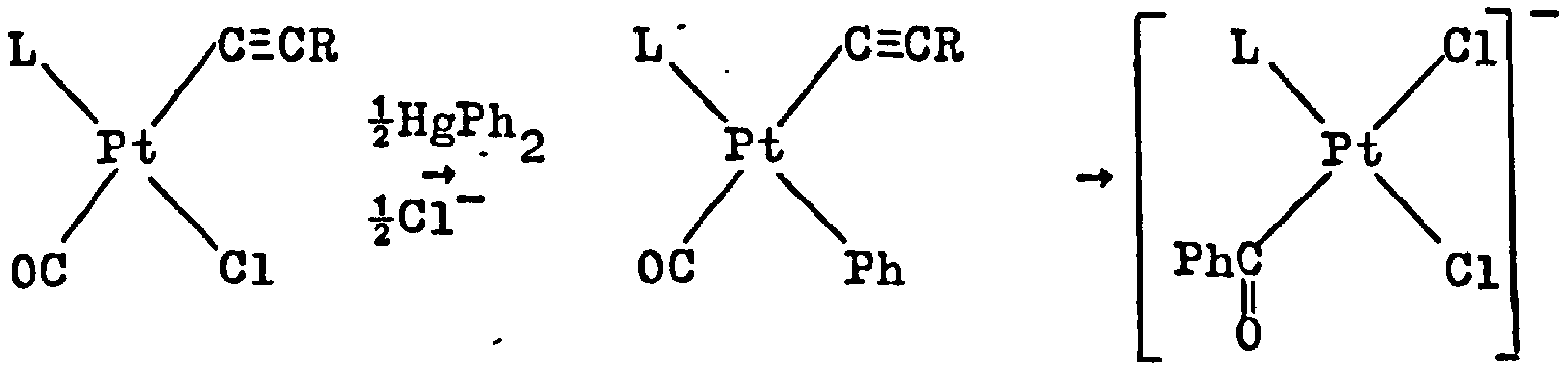


The reason for initial production of <u>cis</u>-[Pt($C\equiv CMe)_2$(CO)($PMePh_2$)] in the above reaction is not clear, nor indeed is the source of the extra $C\equiv CMe$, since no species are produced which do not contain $C\equiv CMe$ (i.e. no species detectable by ^{31}P nmr spectroscopy).

The symmetrization method has been used to prepare acetylide complexes, [PtCl($C\equiv CR$)(CO)L] isomer (II) and <u>cis</u>-[Pt($C\equiv CR)_2$(CO)L], because the reaction is clean, and mercury byproduct can be removed as the insoluble $[Et_4N]_2[Hg_2Cl_6]$. In the above reactions, the products rapidly decomposed, presumably as a result of reactions with PhHgCl byproduct. In an effort to prevent such decomposition, the reactions were repeated using 0.5 equivalents of $HgPh_2$ and 0.5 equivalents of $[Et_4N]Cl$, with the hope that all of the phenyl groups on mercury would be transferred to give [PtPh($C\equiv CR$)-(CO)L] and $[Et_4N]_2[Hg_2Cl_6]$.

When [PtCl($C\equiv CPh$)(CO)($PMePh_2$)] isomer (II) was mixed with 0.5 equivalents of $HgPh_2$ and $[Et_4N]Cl$, 50% of the isomer (II) reacted within 3 minutes at room temperature to produce only [PtPh($C\equiv CPh$)(CO)($PMePh_2$)], Ph <u>trans</u> to $PMePh_2$. After this, a species with parameters $\delta = -5.5$ ppm, $^1J_{PtP} = 4955$ Hz (at -60°C) grew in. This species is the anionic carbonyl insertion product, <u>cis</u>-[$PtCl_2$(COPh)-($PMePh_2$)]$^-$ which has previously been obtained by addition of Cl^- to [PtCl(Ph)(CO)($PMePh_2$)] isomer (I).[170] <u>cis</u>-[$PtCl_2$(COPh)($PMePh_2$)]$^-$ became the major product after 3 hours at room temperature, with the only other observable species being <u>trans</u>-[PtCl($C\equiv CPh$)($PMePh_2)_2$] and the unknown species, (δ = +0.8 ppm, $^1J_{PtP}$ = 2532 Hz) which was suggested to be trans-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$].

Similarly, when [PtCl(C≡CMe)(CO)(PMePh$_2$)] isomer (II) was mixed with 0.5 equivalents of HgPh$_2$ and [Et$_4$N]Cl, [PtPh(C≡CMe)(CO)(PMePh$_2$)], Ph trans to PMePh$_2$, was the first product, but both cis-[PtCl$_2$(COPh)(PMePh$_2$)]$^-$ and cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] soon began to be produced. cis-[PtCl$_2$(COPh)(PMePh$_2$)]$^-$ rapidly became the major product, and only a little [PtPh(C≡CMe)(CO)(PMePh$_2$)] was left. A small amount of the dimeric species, [Pt$_2$-(COPh)$_2$(μ-C≡CMe)$_2$(PMePh$_2$)$_2$] also appeared at the latter stages of the reaction.



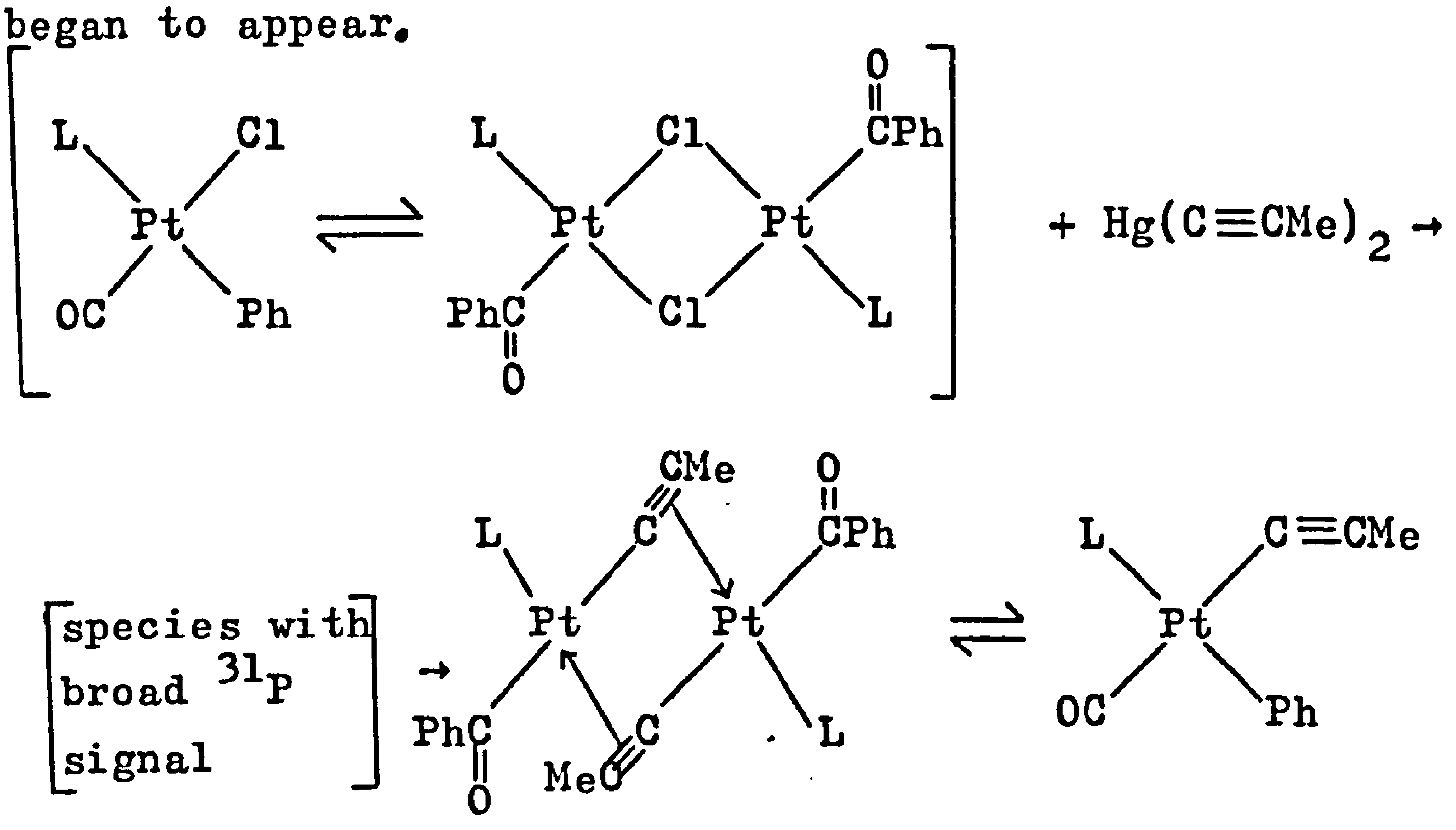
In these reactions, Cl$^-$ does not merely symmetrize the PhHgCl byproduct, but instead seems to displace C≡CR from [PtPh(C≡CR)(CO)(PMePh$_2$)] and promote carbonyl insertion. In this case, the symmetrization method has not worked as it was expected to.

In fact, when the symmetrization method was used to prepare [PtCl(CO)(Ph)(PMePh$_2$)] isomer (I) by reacting cis-[PtCl$_2$(CO)(PMePh$_2$)] with 0.5 equivalents of HgPh$_2$ and [Et$_4$N]Cl, it was found that about 50% of the starting material did not react, and the rest produced cis-[PtCl$_2$(COPh)(PMePh$_2$)]$^-$. This means that Cl$^-$ must have cleaved [Pt$_2$(COPh)$_2$Cl$_2$(PMePh$_2$)$_2$], (in equilibrium with isomer (I)), faster than it symmetrized the PhHgCl. Thus it appears that the symmetrization method for preparing platinum complexes is limited to the preparation of complexes which can not react with Cl^-.

$[PtCl(Ar)(CO)(PMePh_2)]$ isomer (I) and $Hg(C{\equiv}CR)_2$

$[PtCl(Ar)(CO)(PMePh_2)]$ isomer (I), Ar *trans* to $PMePh_2$, exists in equilibrium with $[Pt_2(COAr)_2Cl_2(PMePh_2)_2]$ in solution. When Ar=Ph, the equilibrium position at 38°C is 54% dimer, 46% monomer and when Ar = $C_6H_4CO_2Me$-*p*, it is 12% dimer and 88% monomer.[112] Low temperature tends to displace the equilibrium towards the inserted dimer.

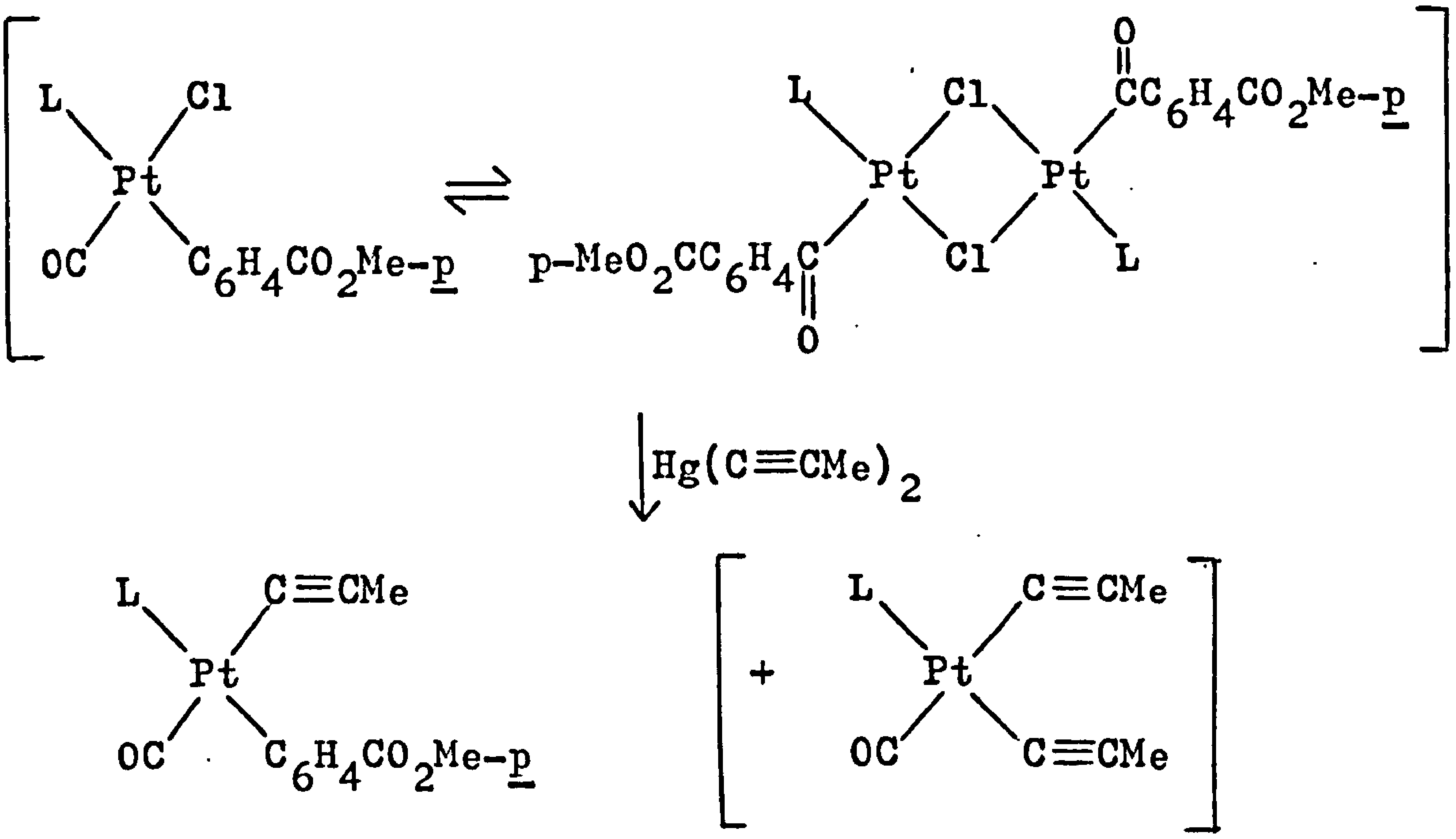
When a mixture of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$, which had been allowed to equilibrate, was mixed with $Hg(C{\equiv}CMe)_2$ at -60°C, the initial product was a species with a very broad peak and satellites with $\delta = +0.5$ppm, $^1J_{PtP} = 4113$ Hz. The parameters of this species varied as the reaction progressed, changing to $\delta = +0.3$ ppm, $^1J_{PtP} = 4108$ Hz after 1 hour at -60°C. This was the major product, and the spectrum did not change over a further 1½ hours at -60°C, and the peaks remained broad. However, when the solution was warmed very briefly to room temperature and cooled again, the peak was found to be sharp, although the satellites were broadened. The parameters had changed to $\delta = +0.2$ ppm, $^1J_{PtP} = 4106$ Hz, which are those of the complex identified as $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CMe)_2(PMePh_2)_2]$. Some *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ had also appeared. After 10 minutes at room temperature $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, had grown in, (to half of the ^{31}P intensity of the dimer) and the amount of cis-$[Pt(C\equiv CMe)_2(CO)(PMePh_2)]$ had also increased. Later, both $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ began to appear.



The final ratio of $[Pt_2(COPh)_2(\mu\text{-}C\equiv CMe)_2(PMePh_2)_2]$ to $[PtPh(C\equiv CMe)(CO)(PMePh_2)]$ obtained in this reaction was the same as that obtained in the reaction of $[PtCl(C\equiv CMe)(CO)(PMePh_2)]$ isomer (II) with $HgPh_2$, (a 2:1 ratio in the ^{31}P intensities, which is equivalent to a 1 to 1 mixture of complexes). This implies that the two species are in equilibrium with each other.

When $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ isomer (I) was used, which is largely isomer (I) at equilibrium with $[Pt_2(COC_6H_4CO_2Me\text{-}p)_2Cl_2(PMePh_2)_2]$, the initial product was $[Pt(C_6H_4CO_2Me\text{-}p)(C\equiv CMe)(CO)(PMePh_2)]$, $C_6H_4CO_2Me$-p trans to $PMePh_2$ (table 12). The geometry of this complex was substantiated by its ^1H nmr spectrum, with $^5J_{PH} = 3$ Hz showing that C≡CMe is cis to phosphine, (table 10).

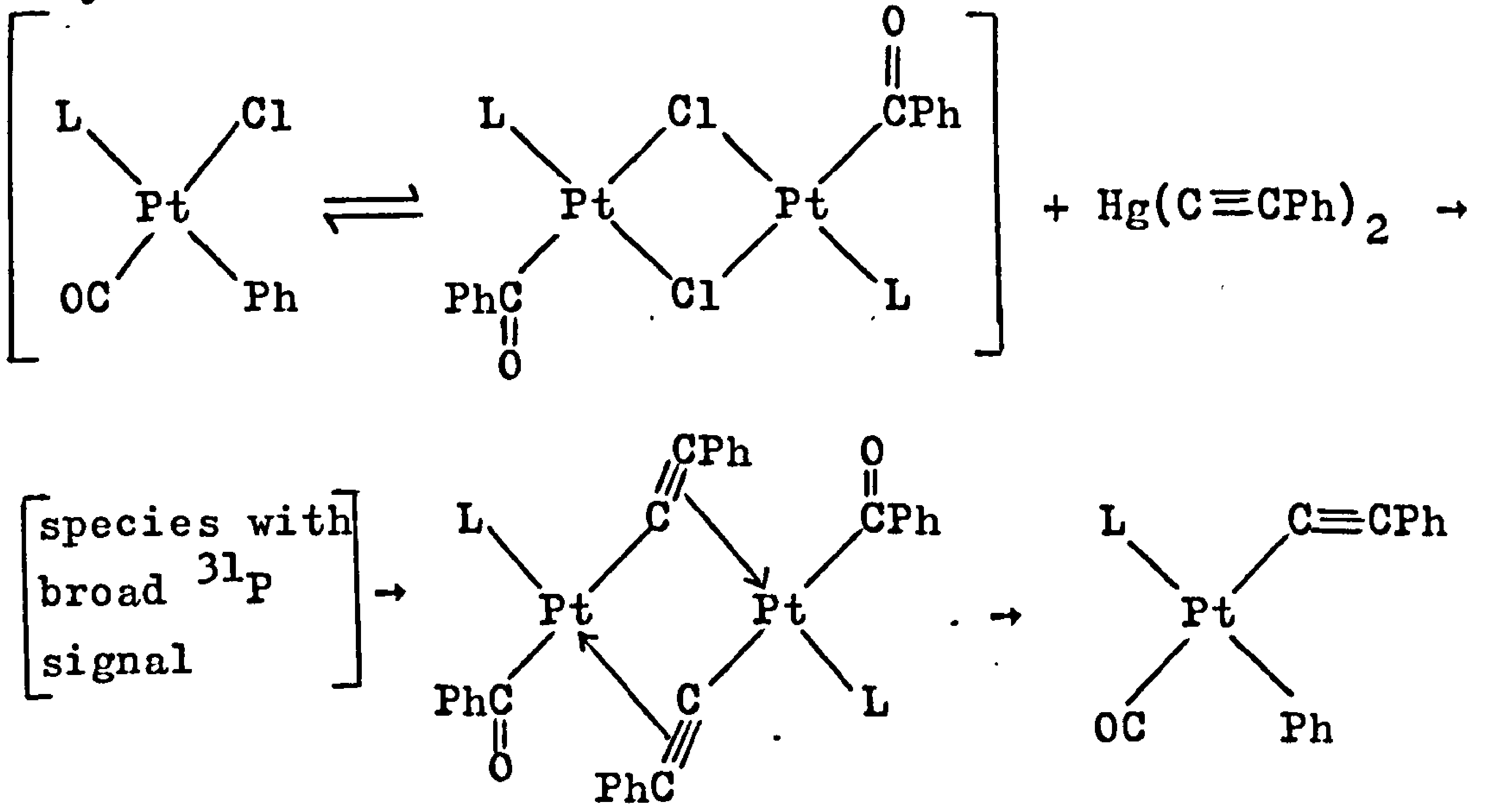
Some cis-[$Pt(C{\equiv}CMe)_2(CO)(PMePh_2)$] grew in later, but at no time was any species seen which would correspond to the acetylide bridged species obtained when Ar = Ph.



produced later.

The reaction between [$PtCl(Ph)(CO)(PMePh_2)$] isomer (I) equilibrated with [$Pt_2(COPh)_2Cl_2(PMePh_2)_2$] and $Hg(C{\equiv}CPh)_2$ followed a similar course to the reaction with $Hg(C{\equiv}CMe)_2$. The initial products, at -60°C, were a species with broad peak and satellites, δ = +0.9 ppm, $^1J_{PtP}$ = 4168 Hz, and a small amount of [$PtPh(C{\equiv}CPh)(CO)(PMePh_2)$], Ph trans to $PMePh_2$. As the reaction progressed, the parameters of the new species changed to δ = +0.3 ppm, $^1J_{PtP}$ = 4176 Hz and the peak became sharp. This species is identified as the C≡CPh bridged dimer, [$Pt_2(COPh)_2$-(μ-$C{\equiv}CPh)_2(PMePh_2)_2$]. cis-[$Pt(C{\equiv}CPh)_2(CO)(PMePh_2)$] also grew in. On warming the reaction mixture to room temperature, the amount of [$PtPh(C{\equiv}CPh)(CO)(PMePh_2)$] steadily increased and the [$Pt_2(COPh)_2(\mu$-$C{\equiv}CPh)_2(PMePh_2)_2$]

decreased until there was none left. Thus the equilibrium position in this reaction must lie completely on the side of $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, and this is supported by the fact that no $C{\equiv}CPh$ bridged dimer was observed in the reaction of $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ (II) with $HgPh_2$, only uninserted monomer.



When $Ph_3PAu(C{\equiv}CPh)$ was used instead of $Hg(C{\equiv}CPh)_2$, the dimer $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CPh)_2(PMePh_2)_2]$ was produced directly, and had a sharp ^{31}P signal, $\delta = +0.3$ ppm, $^1J_{PtP} = 4172$ Hz. There was no broadness associated with the dimer's signals at any time. The reaction followed a similar course, with $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, being produced, although in this case a second, unknown complex, with parameters $\delta = -2.7$ppm, $^1J_{PtP} = 3297$ Hz was a minor ($<20\%$) product.

The broad species obtained when $Hg(C{\equiv}CMe)_2$ and $Hg(C{\equiv}CPh)$ reacted with $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) had ^{31}P parameters very similar to $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2(PMePh_2)_2]$, and indeed, eventually the signals sharpened to produce the acetylide-bridged dimers. No broad species was obtained when $Ph_3PAu(C{\equiv}CPh)$ was used instead of the mercurial, $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2(PMePh_2)_2]$ being produced right away. This is similar to the situation when cis-$[PtCl_2(CO)(PMePh_2)]$ reacted at low temperature with $Hg(C{\equiv}CR)_2$. A transient species, with broad ^{31}P nmr peak and satellites, and parameters slightly different from cis-$[Pt(C{\equiv}CR)_2(CO)(PMePh_2)]$ was obtained. The ^{31}P nmr parameters of the transient varied with the course of the reaction, just as those of the broad species obtained in the above reactions do. The transient was suggested to be an equilibrium between cis-$[Pt(C{\equiv}CR)_2(CO)(PMePh_2)]$, $HgCl_2$ and an adduct of these two compounds, thought to be 5-coordinate.

Since $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2(PMePh_2)_2]$ is the first product, it would appear that $Hg(C{\equiv}CMe)_2$ and $Hg(C{\equiv}CPh)_2$ react with the inserted dimer $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ rather than with isomer (I). The broad species first obtained in the ^{31}P nmr could then be due to an interaction of $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2(PMePh_2)_2]$ with $ClHgC{\equiv}CR$, or an equilibrium between these two species and an associated adduct. The fact that no broadness was observed when $Ph_3PAuC{\equiv}CPh$ was used would tend to support some sort of Pt-Hg interaction.

It is not only in cases where an equilibrium between platinum complex, mercury complex and an adduct occurs that shifts in the ^{31}P parameters of platinum complexes are obtained. Parameter shifts, particularly in the case of bis-organoplatinum complexes containing an acetylide can occur in the presence of bisorganomercury or organomercuric halide compounds. E.g:- cis-[$Pt(C\equiv CMe)_2(CO)(PMePh_2)$] has ^{31}P parameters, at -60°C, of $\delta = -2.8$ ppm, $^1J_{PtP} =$ 2107 Hz, but in the presence of PhHgCl or C_5H_5HgCl these can vary to $\delta = -3.2$ ppm, $^1J_{PtP} = 2121$ Hz. Similarly, [$Pt(C_5H_5)(C\equiv CMe)(CO)(PMePh_2)$] has ^{31}P parameters of $\delta = -2.1$ ppm, $^1J_{PtP} = 1872$ Hz, but in the presence of C_5H_5HgCl this changes to $\delta = -2.3$ ppm, $^1J_{PtP} = 1880$ Hz. Whether this is a direct interaction between Pt and Hg, or an interaction between platinum-coordinated acetylide and Hg, it is not possible to say.

In contrast to phenyl isomer (I), the $C_6H_4CO_2Me$-p complex did not give an acetylide-bridged dimer on reaction of $Hg(C\equiv CMe)_2$ with [$PtCl(C_6H_4CO_2Me$-p$)(CO)(PMePh_2)$] isomer (I), not even as an intermediate on the way to [$Pt(C_6H_4CO_2$-Me-p$)(C\equiv CMe)(CO)(PMePh_2)$], aryl trans to phosphine. Instead, this seemed to be formed directly from isomer (I). The reason may be that, in this case, the equilibrium between [$Pt(C_6H_4CO_2Me$-p$)(Cl)(CO)(PMePh_2)$] isomer (I) and inserted dimer, [$Pt_2(COC_6H_4CO_2Me$-p$)_2Cl_2(PMePh_2)_2$] lies too far on the isomer (I) side, such that $Hg(C\equiv CMe)_2$ reacts with it preferentially. It is possible that $Hg(C\equiv CMe)_2$ reacts with inserted dimer to form an analogous $C\equiv CMe$ bridged complex, but that this de-inserts to [$Pt(C_6H_4CO_2Me$-p$)$-$(C\equiv CMe)(CO)(PMePh_2)$] so quickly that it is not observed.

The combination of the results of these reactions, and those between [$PtCl(C\equiv CR)(CO)(PMePh_2)$] (II) and $HgPh_2$, enable the scheme in figure 28 to be drawn up.

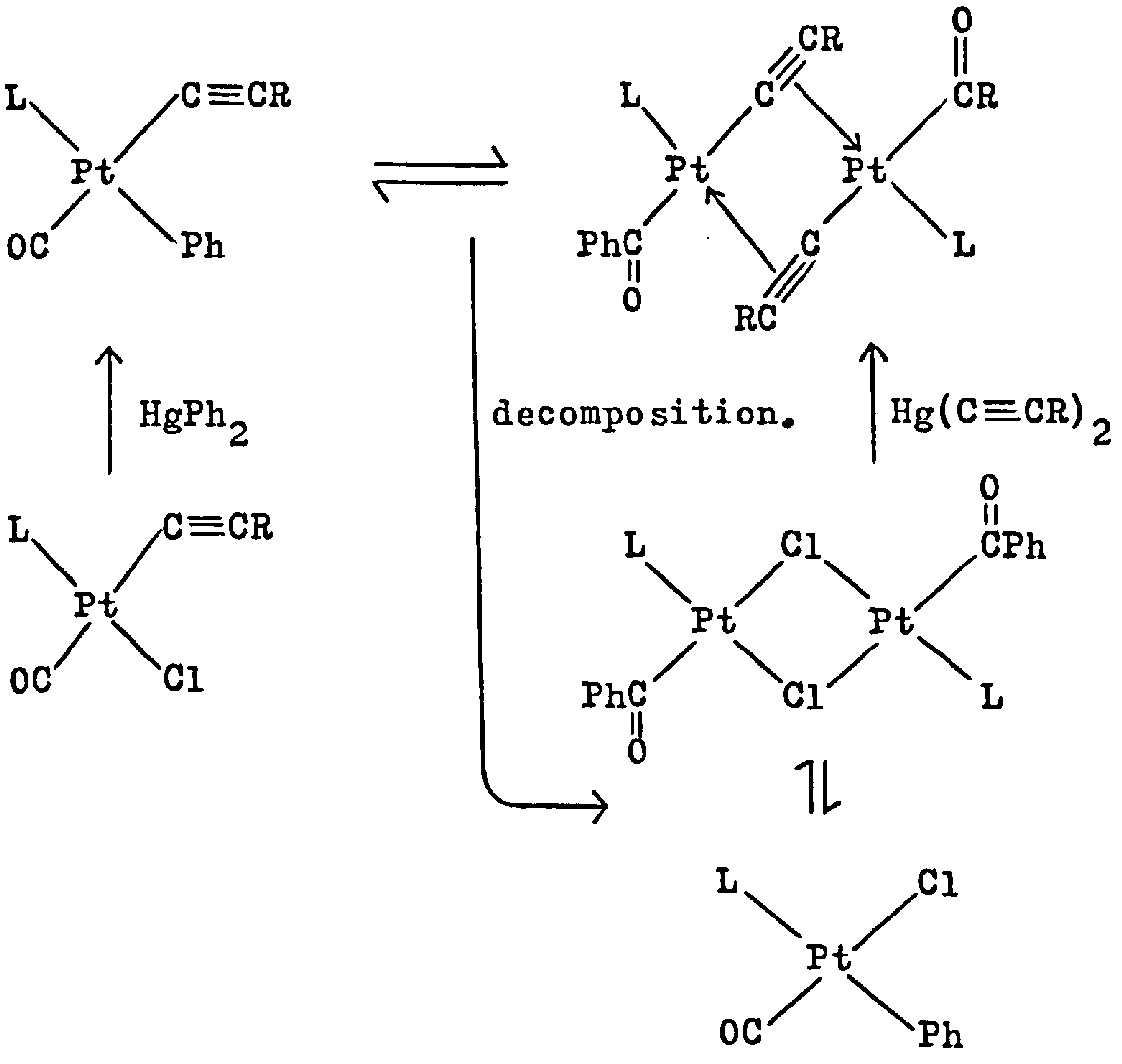


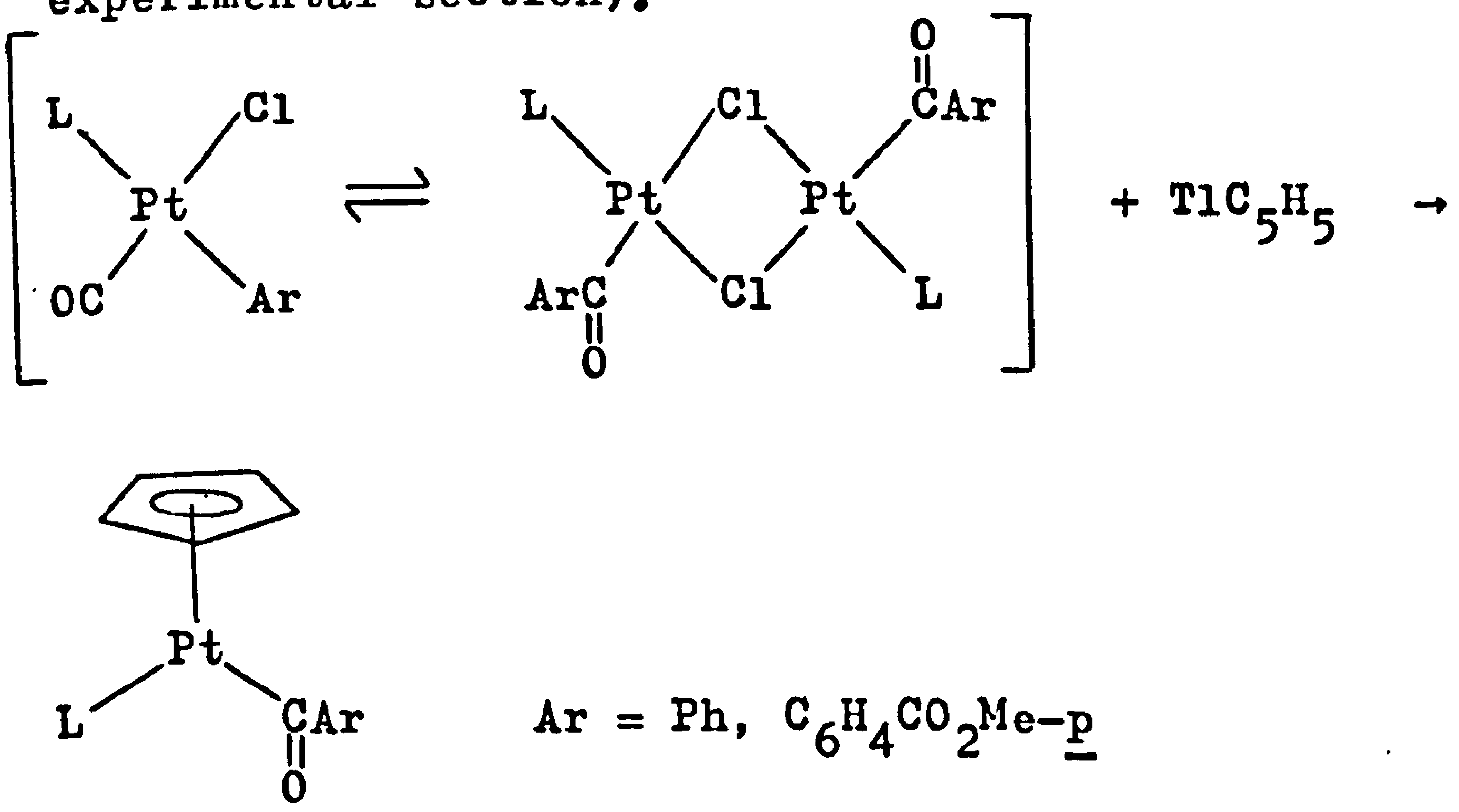
figure 28

From the equilibrium positions between [PtPh(C≡CR)(CO)-L] and $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CR)_2L_2]$, it can be seen that a bridging C≡CMe group is marginally worse, and a bridging C≡CPh group is considerably worse, than a bridging Cl for promoting carbonyl insertion.

$[PtCl(R)(CO)(PMePh_2)]$ isomer (I) and TlC_5H_5

When an equilibrated solution of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ was allowed to react with TlC_5H_5 at room temperature the major product was a species, with ^{31}P nmr parameters at 25°C of δ = -6.2 ppm, $^1J_{PtP}$ = 5687 Hz. A small amount of trans-$[PtCl(Ph)(PMePh_2)_2]$ was also produced. Similarly, an equilibrated solution of $[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$

isomer (I) and $[Pt_2(COC_6H_4CO_2Me\text{-}\underline{p})_2Cl_2(PMePh_2)_2]$ reacted with TlC_5H_5 at room temperature to produce a species with $\delta = -5.9$ ppm, $^1J_{PtP} = 5659$ Hz as the major product, although some cis-$[Pt(C_6H_4CO_2Me\text{-}\underline{p})_2(CO)(PMePh_2)]$ was also produced. A ^1H nmr spectrum showed that a π-cyclopentadienyl complex was present in solution, with the C_5H_5 protons coupled to one phosphorus atom, ($J_{PH} = 2.0$ Hz), and one platinum atom, ($J_{PtH} = 13.0$ Hz). Wardle produced the complex $[Pt(\eta^5\text{-}C_5H_5)(COPh)(Bu^n_3P)]$, with ^1H nmr parameters, $\delta = +5.70$ ppm, $J_{PH} = 1.5$ Hz, $J_{PtH} = 13.0$ Hz, from the reaction of $[Pt_2(COPh)_2Cl_2(Bu^n_3P)_2]$ and TlC_5H_5.[175] Thus, the two new species produced in the above reactions are identified as $[Pt(\eta^5\text{-}C_5H_5)(COPh)(PMePh_2)]$ and $[Pt(\eta^5\text{-}C_5H_5)(COC_6H_4CO_2Me\text{-}\underline{p})(PMePh_2)]$ respectively, (nmr data in experimental section).



Ar = Ph, $C_6H_4CO_2Me\text{-}\underline{p}$

TlC_5H_5 could have reacted, either by bridge-cleavage of $[Pt_2(COAr)_2Cl_2(PMePh_2)_2]$ to give $[Pt(\eta^5\text{-}C_5H_5)(COAr)\text{-}(PMePh_2)]$ directly, or with isomer (I) to give, initially a σ-cyclopentadienyl complex, $[PtAr(\eta^1\text{-}C_5H_5)(CO)(PMePh_2)]$, Ar <u>trans</u> to $PMePh_2$, which then inserted with a σ-π migration of the cyclopentadienyl ring to give $[Pt(\eta^5-C_5H_5)(COAr)(PMePh_2)]$.

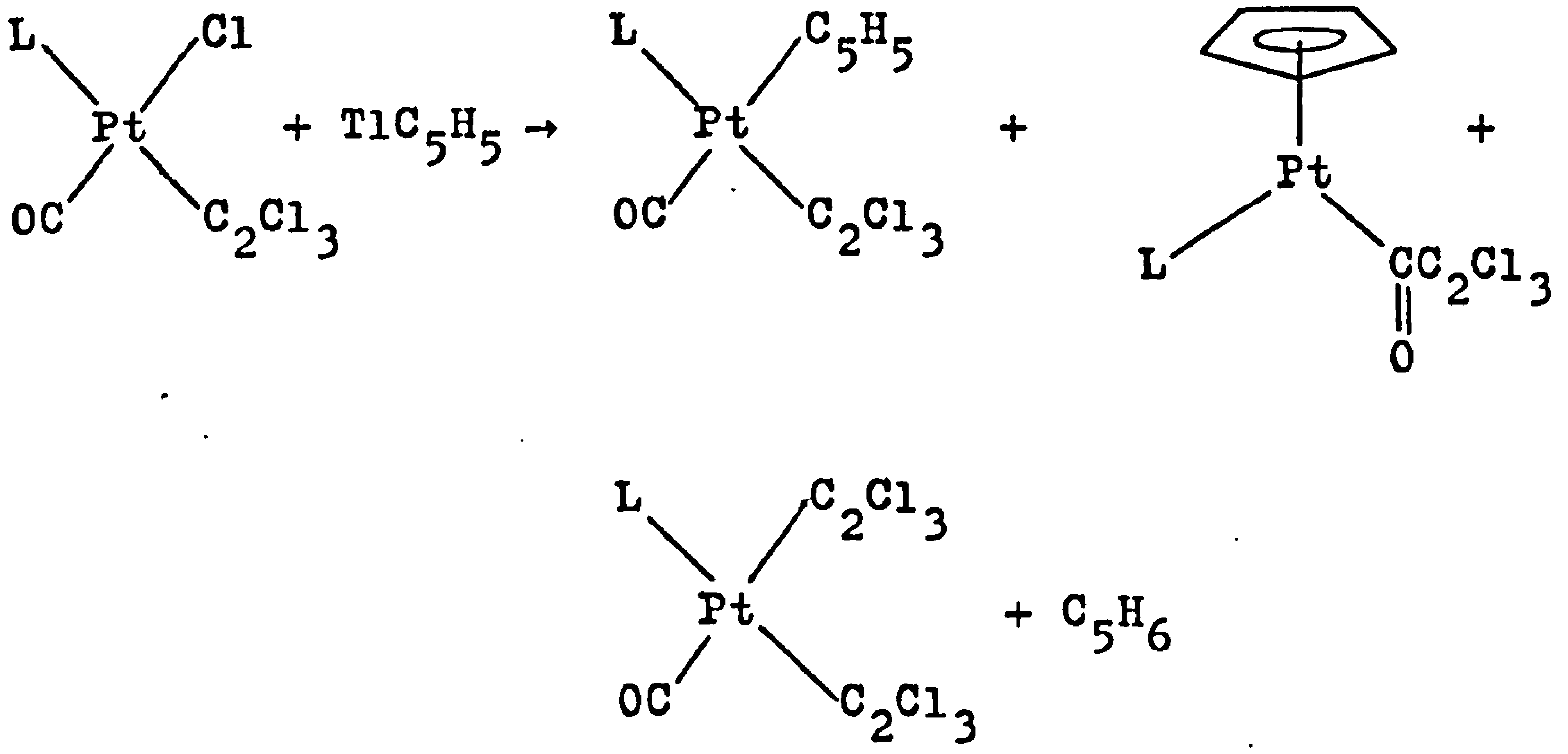
A similar reaction was attempted on two isomer (I) compounds which do not insert, $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ isomer (I) and $[PtCl(C_6H_4Cl-\underline{o})(CO)(PMePh_2)]$ isomer (I). C_2Cl_3 isomer (I) does not insert, even on addition of Cl^- or $PMePh_2$, or on changing the Cl to I and adding phosphine. Other ortho-aryls have been made to insert by Cl^- addition, or by changing Cl to I, but no attempts have been made with $C_6H_4Cl-\underline{o}$ isomer (I).

The reaction between $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ isomer (I) and TlC_5H_5 was found to be non-reporoducible. The reaction is not a simple substitution of Cl by C_5H_5, as more than 1 equivalent of C_5H_5Tl is required to consume all of the C_2Cl_3 isomer (I). When $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ isomer (I) and 1 equivalent of TlC_5H_5 were mixed at room temperature for 10 minutes, less than 30% of the isomer (I) reacted. The products, identified by ^{31}P nmr spectroscopy, were <u>cis</u>-$[Pt(C_2Cl_3)_2(CO)(PMePh_2)]$ and a species (at -60°C) $\delta = -5.9$ ppm, $^1J_{PtP} = 5249$ Hz. When more TlC_5H_5 was added at room temperature and allowed to react for 20 minutes, this new species and <u>cis</u>-$[Pt(C_2Cl_3)_2(CO)(PMePh_2)]$ (table 13) were the only complexes present, in a 3 to 1 ratio. A ^1H nmr spectrum showed that a π-cyclopentadienyl complex was present. ^1H parameters were $\delta = +5.62$ ppm, $J_{PH} = 1.5$ Hz, $J_{PtH} = 13.0$ Hz, (doublet of triplets), typical of a $\pi-C_5H_5$ ring, with phosphine methyl protons at $\delta = +2.00$ ppm, $^2J_{PH} = 11.5$ Hz, $^3J_{PtH} = 30.0$hz. It is clear that the π-complex in the ^1H nmr corresponds to the major species in the ^{31}P nmr. The ^1H nmr also showed that there was a large amount of C_5H_6 present.

When $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ isomer (I) and 1 equivalent of TlC_5H_5 were mixed and left at room temperature, both <u>cis</u>-$[Pt(C_2Cl_3)_2(CO)(PMePh_2)]$ and the π-cyclopentadienyl complex were produced, but in addition a species with δ = -0.3ppm, $^1J_{PtP}$ = 2015 Hz was produced. This appeared to correspond to a σ-cyclopentadienyl complex in the ^1H nmr, δ = +6.15 ppm, J_{PH} = 4.0 hz, J_{PtH} = 36.0 Hz, typical of a σ-C_5H_5 <u>trans</u> to phosphine, with phosphine methyl protons at δ = +2.14 ppm, $^2J_{PH}$ = 10.5 Hz. Again, C_5H_6 was present in the ^1H nmr spectrum. On addition of a second equivalent of TlC_5H_5, all of the isomer (I) disappeared and eventually <u>cis</u>-$[PtCl(C_2Cl_3)(PMePh_2)_2]$ and <u>trans</u>-$[PtCl(C_2Cl_3)(PMePh_2)_2]$ grew in (table 13). The parameters of the π-cyclopentadienyl complex at 25°C were δ = -6.6 ppm, $^1J_{PtP}$ = 5289 Hz.

The π-cyclopentadienyl complex could be either $[Pt(\eta^5-C_5H_5)(COC_2Cl_3)(PMePh_2)]$ or $[Pt(\eta^5-C_5H_5)(C_2Cl_3)(PMePh_2)]$, depending on whether C_2Cl_3 inserted on addition of TlC_5H_5, or on whether CO was simply displaced. The ^1H nmr parameters of $[Pt(\eta^5-C_5H_5)(COC_6H_4CO_2Me$-<u>p</u>$)(PMePh_2)]$ are very similar, but little difference is expected between the parameters of inserted aroyl and uninserted aryl π-cyclopentadienyl complexes. The σ-cyclopentadienyl complex has parameters typical of a C_5H_5<u>trans</u> to phosphine, when it is expected that C_5H_5 would replace Cl, which is <u>trans</u> to CO. However, J_{PH} in <u>cis</u>-$[Pt(C_5H_5)_2(CO)(PPh_3)]$ for the two rings is 3.5 and 5.0 Hz, hence J_{PH} = 4.0 Hz is not inconsistent with C_5H_5 trans to CO. $^1J_{PtP}$ = 2015 Hz is consistent with a bis-organoplatinum complex with CO and $PMePh_2$ cis to each other, and either C_2Cl_3 or C_5H_5 trans to $PMePh_2$. Thus, the σ-cyclopentadienyl complex is probably $[Pt(C_2Cl_3)(\eta^1-C_5H_5)(CO)(PMePh_2)]$, C_2Cl_3 trans to $PMePh_2$.

It is possible, then, that the reaction between C_2Cl_3 isomer (I) and TlC_5H_5 is as follows:-

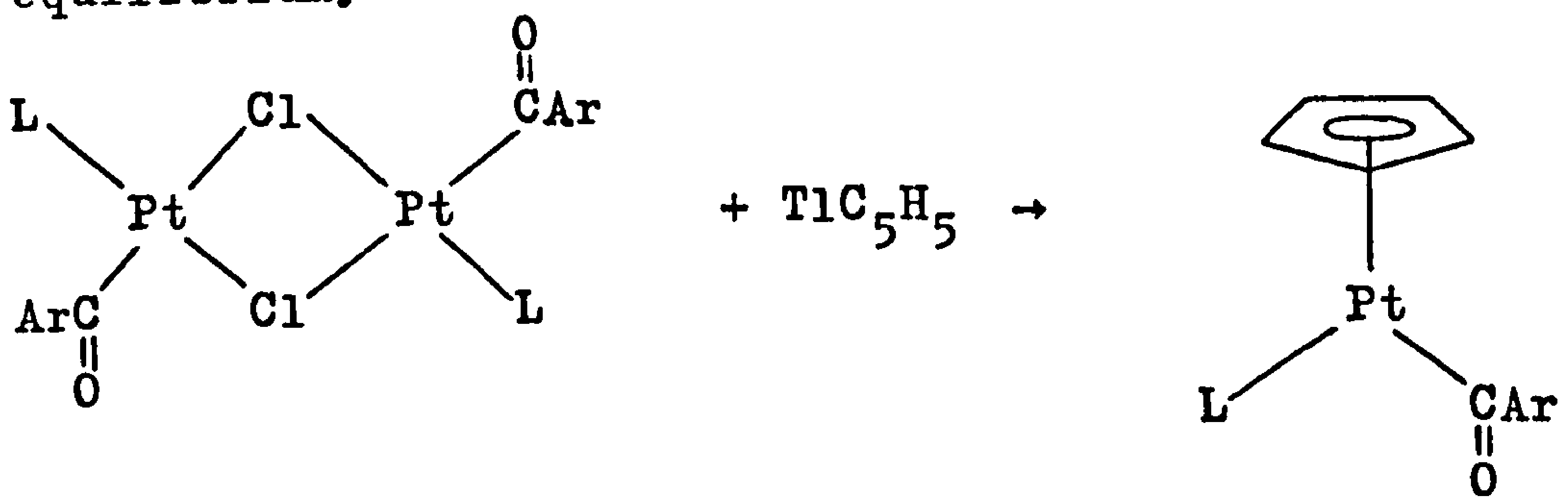


The reaction does not simply replace Cl by C_5H_5 and then promote CO insertion, as had been hoped, by σ-π interconversion of the ring, although this may be occurring to a certain extent.

$[PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)]$ isomer (I) did not appear to react with TlC_5H_5 at all. The isomer (I) slowly disappeared, and other species grew in to the ^{31}P nmr spectrum, but one of these was $[PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)]$ isomer (II). The others had parameters δ = -3.9 ppm, $^1J_{PtP}$ = 4879 Hz, δ = -3.7ppm, $^1J_{PtP}$ = 4868 Hz and δ = -0.4 ppm, $^1J_{PtP}$ = 1833 Hz. Isomers (II) and (I) can interconvert slowly by reversible loss of phosphine, although normally (II) → (I) rather than (I) → (II).

The other products are most likely to be $[Pt_2(C_6H_4Cl\text{-}\underline{o})_2\text{-}Cl_2(PMePh_2)_2]$, *cis* and *trans* isomers, and *cis*-$[Pt(C_6H_4Cl\text{-}\underline{o})_2\text{-}(CO)(PMePh_2)]$, although it is also possible that $\delta = -0.4$ ppm, $^1J_{PtP} = 1833$ Hz could be $[Pt(C_6H_4Cl\text{-}\underline{o})(\eta^1\text{-}C_5H_5)(CO)\text{-}(PMePh_2)]$, but it is unlikely.

The results with C_2Cl_3 and $C_6H_4Cl\text{-}\underline{o}$ isomers (I) would indicate that, with Ph and $C_6H_4CO_2Me\text{-}\underline{p}$, TlC_5H_5 reacts with the inserted dimer, rather than the isomer (I) side of the equilibrium.



There does not appear to be any equilibrium between inserted and uninserted material. $[Pt(\eta^5\text{-}C_5H_5)(COAr)\text{-}(PMePh_2)]$ appears to be 100% of the product, and no $[PtAr(\eta^1\text{-}C_5H_5)(CO)(PMePh_2)]$ is detectable, either in equilibrium, or as an intermediate. Thus this seems to be more favourable towards insertion than leaving isomer (I) to insert, but is not as good as Cl^- addition. This method depends on having some $[Pt_2(COAr)_2Cl_2(PMePh_2)_2]$ in equilibrium with isomer (I).

Table 13:- ^{31}P nmr data; in CDCl$_3$ at 25°C.

Complex	δ (ppm)	$^{1}J_{PtP}$ (Hz)
$[\mathrm{PtCl(Ph)(CO)(PMePh_2)}]$ (I)	+6.8	1404
$[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)}]$(I)	+6.2	1435
$[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMe_2Ph)}]$(I)	-5.8	1410
$[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PPh_3)}]$(I)	+18.3	1483
$[\mathrm{PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)}]$(I)	+4.2	1571
$[\mathrm{PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMe_2Ph)}]$(I)	-7.5	1541
$[\mathrm{PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PPh_3)}]$ (I)	+16.4	1607
$[\mathrm{PtCl(C_6H_4OMe\text{-}\underline{o})(CO)(PMe_2Ph)}]$(I)	-5.4	1487
$[\mathrm{PtCl(C_6H_4OMe\text{-}\underline{o})(CO)(PPh_3)}]$(I)	+18.8	1552
$[\mathrm{PtCl(C_2Cl_3)(CO)(PMePh_2)}]$(I)	+1.0	1801
$[\mathrm{PtCl(Ph)(CO)(PMePh_2)}]$ (II)	-1.7	3920
$[\mathrm{PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)}]$(II)	-2.6	3826
$[\mathrm{PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)}]$ (II)	-2.7	3746
$[\mathrm{Pt_2(COPh)_2Cl_2(PMePh_2)_2}]$	-3.3	5317
$[\mathrm{Pt_2(COC_6H_4CO_2Me\text{-}\underline{p})_2Cl_2(PMePh_2)_2}]$	-3.1	5232
$[\mathrm{Pt_2Cl_2Ph_2(PMePh_2)_2}$	-1.1 -0.9	5010 5050
$[\mathrm{Pt_2Cl_2(C_6H_4CO_2Me\text{-}\underline{p})_2(PMePh_2)_2}$	-1.4 -1.2	4901 4930

cont./

Table 13 (contd.) :-

^{31}P nmr data; in $CDCl_3$ at 25°C.

Complex	δ (ppm)	$^1J_{PtP}$(Hz)
cis-$[PtPh_2(CO)(PMePh_2)]$	+2.4	1604
trans-$[PtCl(Ph)(PMePh_2)_2]$	+8.7	3010
trans-$[PtCl(C_6H_4CO_2Me\text{-}p)(PMePh_2)_2]$	+8.6	2923[a]
trans-$[PtCl(COPh)(PMePh_2)_2]$	+5.1	3212
cis-$[Pt(C_6H_4CO_2Me\text{-}p)_2(CO)(PMePh_2)]$	+1.3	1657
$[Et_4N]$cis-$[PtCl_2(COPh)(PMePh_2)]$	-6.1	5004
cis-$[Pt(C_2Cl_3)_2(CO)(PMePh_2)]$	-2.5	2053
cis-$[PtCl(C_2Cl_3)(PMePh_2)_2]$	-4.6 -0.2	3992[b] 2040
trans-$[PtCl(C_2Cl_3)(PMePh_2)_2]$	+6.7	2772
cis-$[PtCl_2(CO)(PMePh_2)]$	-0.2	2946
cis-$[PtCl_2(CO)(PMe_2Ph)]$	-10.4	2847
cis-$[PtBr_2(CO)(PMe_2Ph)]$	-11.2	2820
cis-$[PtCl_2(CO)(PEt_3)]$	+22.4	2792
cis-$[PtCl_2(CO)(PPh_3)]$	+9.8	3061
cis-$[PtCl_2(PMePh_2)_2]$	-0.9	3625
cis-$[PtCl_2(PMe_2Ph)_2]$	-15.3	3546
cis-$[PtCl_2(PEt_3)_2]$	+9.1	3515
cis-$[PtCl_2(PPh_3)_2]$	+14.3	3673
cis-$[PtCl_2(C_2H_4)(PMePh_2)]$	+2.4	3191

(a) At -60°C. (b) $^2J_{PP}$ = 19.2 Hz.

EXPERIMENTAL

^{31}P nmr spectra were recorded in $CDCl_3$ solution using a Varian XL-100 spectrometer operating in the Fourier Transform mode. Chemical shifts are positive to low field of external 85% H_3PO_4. ^1H nmr spectra were recorded in $CDCl_3$ solution on a Perkin-Elmer R32 90MHz continuous wave spectrometer, with TMS locking signal. ^{13}C nmr spectra were obtained on a Bruker WP200SY spectrometer operating at 50.32MHz in the Fourier transform mode. Chemical shifts were measured relative to $CDCl_3$ at +77.0 ppm.

Solutions of $[PtCl(C{\equiv}CR)(CO)L]$ isomer (II), $[PtCl(Ar)(CO)L]$ isomer (II) and $[PtCl(Ar)(CO)L]$ isomer (I) were prepared in situ as previously described. Other platinum complexes and organomercurials were prepared as previously described. $Ph_3PAu(C{\equiv}CPh)$ was prepared by the same method as $Ph_3PAuC_5H_5$, namely by the reaction of Ph_3PAuCl with $PhC{\equiv}CH$ and NaOEt in EtOH.[160]

[PtCl(C_5H_5)(CO)(PMePh$_2$)] isomer (I) and Hg(C≡CMe)$_2$

To a solution of [PtCl(C_5H_5)(CO)(PMePh$_2$)], (0.040mmol.) in $CDCl_3$ (0.3 ml) was added a solution of Hg(C≡CMe)$_2$, (11.3mg, 0.040mmol.) in $CDCl_3$ (0.3ml) at -60°C under an atmosphere of nitrogen. Initially equal amounts of [Pt(C_5H_5)(C≡CMe)(CO)(PMePh$_2$)] (C_5H_5 <u>trans</u> to PMePh$_2$) and [PtCl(C≡CMe)(CO)(PMePh$_2$)] (Cl <u>trans</u> to PMePh$_2$) were produced, (identified by ^{31}P nmr), but eventually, after 4 hours at -60°C, the major products were <u>cis</u>-[Pt(C≡CMe)$_2$-(CO)(PMePh$_2$)] (^{31}P and ^1H nmr) and C_5H_5HgCl (δ_H = +6.16 ppm). The same reaction, when performed at 25°C, reached completion in 30 seconds, and passed through the same intermediates.

[PtCl(C_5H_5)(CO)(PMePh$_2$)] isomer (I) and HgPh$_2$

A solution of [PtCl(C_5H_5)(CO)(PMePh$_2$)] (0.061mmol.) in $CDCl_3$ (0.3ml) was mixed with a solution of HgPh$_2$ (21.6mg, 0.061mmol.) in $CDCl_3$ (0.3ml) under a nitrogen atmosphere at -60°C. Since no reaction occurred at this temperature the solution was warmed to room temperature, and examined periodically by ^{31}P nmr spectroscopy. After 1 hour, some <u>cis</u>-[PtPh$_2$(CO)(PMePh$_2$)] was present, (ca. 10% of ^{31}P intensity). After 7 hours a number of complexes were present : [Pt(η^5-C_5H_5)(COPh)(PMePh$_2$)], <u>cis</u>-[PtPh$_2$(CO)-(PMePh$_2$)], [PtCl(C_5H_5)(CO)(PMePh$_2$)] (I), a species with parameters δ = -5.3 ppm, $^1J_{PtP}$ = 5037 Hz, a species at -18.8ppm, with no $^1J_{PtP}$ visible, which appeared to be a triplet (13.6 Hz peak separation), <u>trans</u>-[PtCl(Ph)-(PMePh$_2$)$_2$], <u>trans</u>-[PtCl(COPh)(PMePh$_2$)] and a small amount of [PtCl(Ph)(CO)(PMePh$_2$)] (I). Overnight, the cyclopentadienyl isomer (I) disappeared. Early in the reaction, before any cis-[$PtPh_2(CO)(PMePh_2)$] had formed, a peak was observed in the ^{31}P nmr spectrum (recorded at -60°C) at -1.2ppm, which could have corresponded to [PtCl(Ph)(CO)($PMePh_2$)] isomer (II), but this was too weak to observe $^1J_{PtP}$ satellites.

cis-[$Pt(C{\equiv}CMe)_2(CO)(PMePh_2)$]

cis-[$PtCl_2(CO)(PMePh_2)$] (100.0mg, 0.202mmol.), $Hg(C{\equiv}CMe)_2$ (56.5mg, 0.202mmol.) and [Et_4N]Cl (33.5mg, 0.202mmol.) were allowed to react in $CDCl_3$ (1.5ml) for 10 minutes, the yellow solution was then filtered to remove $[Et_4N]_2[Hg_2Cl_6]$, and ^1H and ^{13}C nmr spectra were recorded. Selective decoupling experiments were then performed. ^{13}C nmr data is given in table 9, and in figure 23 with ^1H nmr data, which is also given in table 10. ^{31}P nmr data is in table 11.

[$Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)$], $C{\equiv}CPh$ trans to $PMePh_2$

cis-[$PtCl_2(CO)(PMePh_2)$] (100.0mg, 0.202mmol.), $Hg(C{\equiv}CMe)_2$ (28.3mg, 0.101mmol.) and [Et_4N]Cl (16.8mg, 0.101mmol.) were allowed to react in $CDCl_3$ (1.5ml) for 10 minutes. The solution was filtered and then a solution of $Hg(C{\equiv}CPh)_2$ (41.0mg, 0.101mmol.) and [Et_4N]Cl (16.8mg, 0.101mmol.) in $CDCl_3$ (0.5ml) was added. The solution was filtered after 2 minutes and then frozen to stop scrambling reactions. ^1H and ^{13}C nmr spectra were recorded and selective decoupling experiments were performed at -60°C to slow down decomposition and ligand scrambling. ^{13}C nmr data is given in table 9, ^1H nmr data in table 10, ^{31}P nmr data in table 11.

[Pt(C≡CPh)(C≡CMe)(CO)(PMePh$_2$)], C≡CMe trans to PMePh$_2$

Similarly, cis-[PtCl$_2$(CO)(PMePh$_2$)] (100.0mg, 0.202mmol.), Hg(C≡CPh)$_2$ (41.0mg, 0.101mmol.) and [Et$_4$N]Cl (16.8mg, 0.101mmol.) were reacted in CDCl$_3$ (1.5ml), followed by Hg(C≡CMe)$_2$ (28.3mg, 0.101mmol.) and a further 16.8mg of [Et$_4$N]Cl (0.101mmol.). After filtration, ^{1}H and ^{13}C nmr spectra were recorded at -60°C and selective decoupling experiments were performed. ^{13}C nmr data is given in table 9, ^{1}H in table 10, ^{31}P in table 11.

[PtCl(C≡CMe)(CO)(PMePh$_2$)] isomer (II) and Ph$_3$PAu(C≡CPh)

[PtCl(C≡CMe)(CO)(PMePh$_2$)] (II) was made *in situ* as previously described. To a solution of [PtCl(C≡CMe)(CO)-PMePh$_2$)] (0.040mmol.) in CDCl$_3$ (0.25ml) was added a solution of Ph$_3$PAu(C≡CPh), (25.0mg, 0.045mmol.) in CDCl$_3$ (0.25ml) at -60°C. The reaction was slow at -60°C with only 10% reaction in 1 hour. On warming to -20°C it reached completion in 1 hour, producing one isomer of [Pt(C≡CMe)-(C≡CPh)(CO)(PMePh$_2$)]. (^{31}P nmr at -60°C -2.6 ppm, $^1J_{PtP}$= 2113 Hz) and Ph$_3$PAuCl (δ = +32.7 ppm). ^{1}H nmr at room temperature showed that the isomer of [Pt(C≡CMe)(C≡CPh)-(CO)(PMePh$_2$)] was the one with C≡CPh trans to phosphine. (^{1}H nmr at 25°C; $\delta_{C≡CMe}$ = +1.88 ppm, $^4J_{PtH}$ = 16.0 Hz, $^5J_{PH}$ = 3.5 Hz, δ_{PMePh_2} = +2.38 ppm, $^3J_{PtH}$ = 30.0 Hz, $^2J_{PH}$ = 11.0 Hz). The bis-acetylide complex was stable at -40 to 0°C overnight, with no isomerisation occurring during this time.

cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] and Ph$_3$PAuCl

A solution of cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] (0.040mmol.) in CDCl$_3$ (0.3ml), prepared by the symmetrization method, was mixed with a solution of Ph$_3$PAuCl (20.0mg, 0.040mmol.) in CDCl$_3$ (0.3ml) at room temperature. Followed by ^{31}P nmr, there was no transfer of C≡CMe from Pt to Au in 2½ hours. The only reaction observed was the normal decomposition of cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] to trans-[PtCl(C≡CMe)(PMePh$_2$)$_2$] overnight, accompanied by some exchange of phosphines. No Ph$_3$PAu(C≡CMe) was detected.

[Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh trans to L, and cis-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)]

A solution of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh trans to PMePh$_2$, (0.050 mmol.) in CDCl$_3$ (0.5ml) was mixed at -60°C with a solution of cis-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)], 60% ^{13}CO-labelled, (23.5mg, 0.054mmol.) in CDCl$_3$ (0.3ml), and the reaction was followed by ^{31}P nmr spectroscopy. After 6 hours at -60°C, 50% of the [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] had been consumed. The mixture was warmed to room temperature for 1 minute, then cooled again to -60°C. ^{31}P nmr investigation revealed the presence of [PtCl(C≡CMe)(CO)(PMePh$_2$)] isomer (II), [PtCl(C≡CPh)(^{13}CO)(PMe$_2$Ph)] isomer (II) and cis-[Pt(C≡CPh)$_2$(^{13}CO)(PMe$_2$Ph)] in a ratio of 3:1:1, along with unreacted cis-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)] and [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] ($<$ 30% of the original amount). The other isomer of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] had begun to appear; the ratio of the two isomers,

$C{\equiv}CPh$ trans to L and $C{\equiv}CMe$ trans to L being approximately 4:1. On warming to room temperature for a further 2 minutes, all of the $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$ was consumed. Reactions of the other isomer, with $C{\equiv}CMe$ trans to L, complicated the spectrum, however the amount of cis-$[Pt(C{\equiv}CPh)_2(^{13}CO)(PMe_2Ph)]$ decreased by reacting with cis-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ to produce more $[PtCl(C{\equiv}CPh)(^{13}CO)-(PMe_2Ph)]$. $[PtCl(CO)(C{\equiv}CPh)(PMePh_2)]$ isomer (II) and $[PtCl(C{\equiv}CMe)(^{13}CO)(PMe_2Ph)]$ (II) were apparent among the products, as minor species, in a ratio of approx. 1:3 with the corresponding initial products $[PtCl(CO)(C{\equiv}CMe)(PMePh_2)]$ (II) and $[PtCl(C{\equiv}CPh)(^{13}CO)(PMe_2Ph)]$ (II). (^{31}P data is in table 11).

$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to L, and $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ isomer (I).

Similarly, a solution of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)-(PMePh_2)]$, $C{\equiv}CMe$ trans to $PMePh_2$, (0.050mmol.) in $CDCl_3$ (0.3ml) was mixed at -60°C with a solution of $[PtCl(C_6H_4CO_2-Me\text{-}p)(CO)(PMePh_2)]$, prepared *in situ*, (0.040mmol.) in $CDCl_3$ (0.3ml) and the reaction was followed by ^{31}P nmr spectroscopy. The initial products were $[PtCl(C{\equiv}CPh)(CO)-(PMePh_2)]$ isomer (II) and a species with parameters δ = -0.1 ppm, $^1J_{PtP}$ = 1444 Hz, identified as $[Pt(C_6H_4CO_2Me\text{-}p)-(C{\equiv}CMe)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to CO, (table 12). After 7 hours at -60°C, 60% of the starting material had been consumed, and isomerisation of $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)-(PMePh_2)]$ was becoming appreciable.

[Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh *trans* to L, and [PtCl(C$_6$H$_4$CO$_2$Me-*p*)(CO)(PMePh$_2$)] isomer (I)

In a similar manner, a solution of [Pt(C≡CMe)(C≡CPh)-(CO)(PMePh$_2$)], C≡CPh *trans* to PMePh$_2$, (0.050mmol.) in CDCl$_3$ (0.5ml) was mixed with a solution of [PtCl(C$_6$H$_4$CO$_2$ Me-*p*)(CO)(PMePh$_2$)] isomer (I), (0.040mmol.) in CDCl$_3$ (0.3ml) at -60°C, and the reaction was followed by ^{31}P nmr spectroscopy. Initial products (in almost equal amounts) were [PtCl(C≡CMe)(CO)(PMePh$_2$)] isomer (II), [PtCl(C≡CPh)-(CO)(PMePh$_2$)] isomer (II), and species with parameters δ = -0.2 ppm, $^1J_{PtP}$ = 1431 Hz and δ = -0.1 ppm, $^1J_{PtP}$ = 1442 Hz, identified as [Pt(C$_6$H$_4$CO$_2$Me-*p*)(C≡CPh)(CO)(PMePh$_2$)] and [Pt(C$_6$H$_4$CO$_2$Me-*p*)(C≡CMe)(CO)(PMePh$_2$)] respectively, C≡CR *trans* to CO, (table 12). After 5½ hours at -60°C, only 25% of the starting material had been used up, and isomerisation of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)] was not appreciable. On warming briefly to room temperature (2 minutes) isomerisation was rapid (2 to 1 ratio of isomers) and the product ratio was about 2:1 in favour of [PtCl-(C≡CMe)(CO)(PMePh$_2$)] (II) and [Pt(C$_6$H$_4$CO$_2$Me-*p*)(C≡CPh)(CO)-(PMePh$_2$)] over [PtCl(C≡CPh)(CO)(PMePh$_2$)] (II) and [Pt(C$_6$H$_4$CO$_2$Me-*p*)(C≡CMe)(CO)(PMePh$_2$)].

[Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh *trans* to L, and [PtCl(C$_6$H$_4$CO$_2$Me-*p*)(CO)(PMePh$_2$)] isomer (II)

A solution of [Pt(C≡CMe)(C≡CPh)(CO)(PMePh$_2$)], C≡CPh *trans* to PMePh$_2$, (0.050mmol.) in CDCl$_3$ (0.5ml) was mixed with a solution of [PtCl(C$_6$H$_4$CO$_2$Me-*p*)(CO)(PMePh$_2$)] isomer (II)

(0.040 mmol.), prepared in situ, in $CDCl_3$ (0.3ml) at -60°C, and the reaction was followed by ^{31}P nmr spectroscopy. Initial products were $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) and a species with parameters $\delta = +0.5$ ppm, $^1J_{PtP} = 2439$ Hz, identified as $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CPh$ trans to phosphine. On warming briefly to room temperature (for 2 minutes), isomerisation of $[Pt(C{\equiv}CMe)$-$(C{\equiv}CPh)(CO)(PMePh_2)]$ became appreciable (5 to 3 ratio of isomers) and some $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ isomer (II) was also produced (1 to 3 ratio with $C{\equiv}CMe$ isomer (II)). The amount of $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CPh)(CO)(PMePh_2)]$ detectable was much less than the acetylide isomer (II), and no other species were present.

$[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to L, and $[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (II).

Similarly $[Pt(C{\equiv}CMe)(C{\equiv}CPh)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to $PMePh_2$, (0.050mmol.) in $CDCl_3$ (0.3ml) was mixed with $[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (II), (0.040mmol.) in $CDCl_3$ (0.3ml) at -60°C and the reaction was followed by ^{31}P nmr spectroscopy. Initial products were $[PtCl(C{\equiv}CPh)$-$(CO)(PMePh_2)]$ isomer (II) and a species at $\delta = +0.2$ ppm, too weak to determine $^1J_{PtP}$, which was assigned as $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to $PMePh_2$. On brief warming to room temperature, isomerisation of the mixed bis-acetylide complex became appreciable, and $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (II) also began to appear.

[Pt(C≡CMe)(C≡CPh)(CO)($PMePh_2$)], C≡CPh *trans* to L, and *cis*-[$PtPh_2$(CO)($PMePh_2$)]

Ph_2Hg (14.4mg, 0.040mmol.) was reacted with a solution of [PtCl(Ph)(CO)($PMePh_2$)] isomer (II), (0.040mmol.), prepared *in situ*, for 15 minutes. The solution was filtered and a ^{31}P nmr investigation showed that it was mainly *cis*-[$PtPh_2$(CO)($PMePh_2$)] (>90%), with small amounts of *trans*-[PtCl(Ph)($PMePh_2$)$_2$], and [PtCl(Ph)(CO)($PMePh_2$)] isomers (I) and (II) present. This was mixed with a solution of [Pt(C≡CMe)(C≡CPh)(CO)($PMePh_2$)], C≡CPh *trans* to $PMePh_2$, (0.050mmol.) at -60°C. There was no reaction at -60°C in 2 hours, and on warming to room temperature no reactions except isomerisation of [Pt(C≡CMe)(C≡CPh)(CO)($PMePh_2$)] (about 30%), disappearance of byproducts, [PtCl(Ph)(CO)($PMePh_2$)] isomers (I) and (II), and formation of a small amount of [PtCl(C≡CMe)(CO)($PMePh_2$)] isomer (II) and a species at δ = +0.2 ppm occurred in 20 minutes.

cis-[Pt(C≡CPh)$_2$(CO)(PMePh)] and $HgPh_2$

A solution of $HgPh_2$ (14.4mg, 0.040mmol.) in $CDCl_3$ (0.3ml) was mixed with a solution of *cis*-[Pt(C≡CPh)$_2$(CO)($PMePh_2$)] (0.040mmol.), prepared by the symmetrization method, in $CDCl_3$ (0.3ml) at -60°C and the reaction was followed by ^{31}P nmr spectroscopy. After 2½ hours at -60°C there was no reaction. On warming to room temperature, there was a slow reaction to produce initially [PtPh(C≡CPh)(CO)($PMePh_2$)], Ph *trans* to $PMePh_2$, (table 12). Subsequently, another species grew in with ^{31}P parameters δ = +0.9 ppm,

${}^1J_{PtP}$ = 2494 Hz (at -60°C). After 3 hours at room temperature, 70% of the starting material had been consumed; [PtPh(C≡CPh)(CO)(PMePh$_2$)] accounted for 80% of the products and the unidentified species for 20%. On leaving the solution overnight the products were: the unidentified species (^{31}P nmr at RT:- δ = +0.8 ppm, ${}^1J_{PtP}$ = 2532 Hz), _cis_-[PtPh$_2$(CO)(PMePh$_2$)], _trans_-[PtCl(Ph)(PMePh$_2$)$_2$], [PtPh(C≡CPh)(CO)(PMePh$_2$)]and _trans_-[PtCl(COPh)(PMePh$_2$)].

cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] and HgPh$_2$

a) A solution of HgPh$_2$ (14.4mg, 0.040mmol.) in CDCl$_3$ (0.3ml) was mixed with a solution of _cis_-[Pt(C≡CMe)$_2$-(CO)(PMePh$_2$)] (0.040mmol.) in CDCl$_3$ (0.3ml) and the reaction was followed by ^{31}P nmr spectroscopy. After 20 minutes at room temperature, 30% of the starting material had been consumed and the only detectable product was [PtPh(C≡CMe)(CO)(PMePh$_2$)], Ph _trans_ to PMePh$_2$, (table 12). Subsequently, other species grew in, all the starting material being consumed within 3 hours and [PtPh(C≡CMe)-(CO)(PMePh$_2$)] accounting for 40% of the ^{31}P intensity. Other products were an unidentified species with ^{31}P nmr parameters δ = +8.0 ppm, ${}^1J_{PtP}$ = 2428 Hz (at room temperature), _trans_-[PtCl(C≡CMe)(PMePh$_2$)$_2$], _trans_-[PtCl(Ph)(PMePh$_2$)$_2$] and _cis_-[PtPh$_2$(CO)(PMePh$_2$)], all of which were of equal intensity after the reaction had been left overnight.

b) When the reaction was repeated using the same quantities and conditions, except that there may have been excess [Et$_4$N]Cl present, added in the production of cis-[Pt(C≡CMe)$_2$-(CO)(PMePh$_2$)] by the symmetrization method, (an excess of

2.8mgs, 0.4 equiv.), the reaction took a slightly different course. The first products were [PtPh(C≡CMe)(CO)-(PMePh$_2$)], Ph trans to PMePh$_2$, and an unknown species with ^{31}P parameters δ = +1.2 ppm, $^1J_{PtP}$ = 2583 Hz (at RT), followed by cis-[PtCl$_2$(COPh)(PMePh$_2$)]$^-$ and trans-[PtCl-(C≡CMe)(PMePh$_2$)$_2$]. After 2 hours at room temperature, 80% of the starting material had been consumed, and the above products accounted for 50%, 25%, 14% and 11% of the products respectively (measured as a % of the total ^{31}P intensity of the products). On being left for a further several hours at room temperature, cis-[PtPh$_2$(CO)(PMePh$_2$)] became the major product, and trans-[PtCl(Ph)(PMePh$_2$)$_2$] also appeared.

cis-[PtPh$_2$(CO)(PMePh$_2$)] and Hg (C≡CMe)$_2$

A CDCl$_3$ solution of [PtCl(Ph)(CO)(PMePh$_2$)] isomer (II), (0.040 mmol.) was allowed to react with HgPh$_2$ (14.4mg, 0.040mmol.) until ^{31}P nmr investigation revealed the solution to be cis-[PtPh$_2$(CO)(PMePh$_2$)]. The solution was filtered and mixed at -60°C with a CDCl$_3$ solution of Hg(C≡CMe)$_2$ (11.3mg, 0.040mmol.), and the reaction was followed by ^{31}P nmr spectroscopy. After 12 hours at room temperature, 67% of the cis-[PtPh$_2$(CO)(PMePh$_2$)] was unchanged, and the only other platinum complex present was trans-[PtCl(Ph)-(PMePh$_2$)$_2$].

[PtCl(Ph)(CO)(PMePh$_2$)] isomer (II) and Hg(C≡CMe)$_2$

[PtCl(Ph)(CO)(PMePh$_2$)] isomer (II), (0.040mmol.) and Hg(C≡CMe)$_2$ (11.4mg, 0.040mmol.) were mixed in CDCl$_3$ (0.5ml) at -60°C and the reaction was observed by ^{31}P nmr spectroscopy. No reaction occurred in 30 minutes at -60°C, but on warming to room temperature, there was a rapid reaction to produce initially [$PtPh(C{\equiv}CMe)(CO)(PMePh_2)$], $C{\equiv}CMe$ trans to $PMePh_2$, (table 12). However, large amounts of cis-[$Pt(C{\equiv}CMe)_2(CO)(PMePh_2)$] and some trans-[$PtCl(Ph)(PMePh_2)_2$] were produced in less than 10 minutes at room temperature.

[$PtCl(C_6H_4CO_2Me$-p)(CO)($PMePh_2$)] isomer (II) and $Hg(C{\equiv}CMe)_2$

[$PtCl(C_6H_4CO_2Me$-p)(CO)($PMePh_2$)] isomer (II), (0.040 mmol.) and $Hg(C{\equiv}CMe)_2$ (11.4mg, 0.040mmol.) reacted similarly in $CDCl_3$ (0.5ml) to produce [$Pt(C{\equiv}CMe)(C_6H_4CO_2$-Me-p)(CO)($PMePh_2$)], $C{\equiv}CMe$ trans to $PMePh_2$, (table 12). A small amount of trans-[$PtCl(C_6H_4CO_2Me$-p)$(PMePh_2)_2$] was also produced.

[$PtCl(C{\equiv}CPh)(CO)(PMePh_2)$] isomer (II) and $HgPh_2$

A solution of [$PtCl(C{\equiv}CPh)(CO)(PMePh_2)$] isomer (II), (0.040mmol.) prepared by the symmetrization method, in $CDCl_3$ (0.3ml) was mixed with a solution of $HgPh_2$ (14.4mg, 0.040 mmol.) in $CDCl_3$ (0.2ml) at -60°C. There was no reaction detectable by ^{31}P nmr spectroscopy at -60°C in 1 hour. Reaction began to proceed at -20°C, the initial product being a species with $\delta = +0.1$ ppm, $^1J_{PtP} = 1381$ Hz at -20°C, identified as [$PtPh(C{\equiv}CPh)(CO)(PMePh_2)$], Ph trans to $PMePh_2$, (table 12). After 1 hour at -20°C and a further 15 minutes at +25°C, this was the only product and all of the [$PtCl(C{\equiv}CPh)(CO)(PMePh_2)$] (II) had been consumed. On being left at room temperature for 7 hours, there was considerable decomposition, other products being [$Pt_2(COPh)_2Cl_2(PMePh_2)_2$], cis-[$PtPh_2(CO)(PMePh_2)$], [$PtCl(Ph)(CO)$-

$(PMePh_2)]$ isomer (I) and trans-$[PtCl(Ph)(PMePh_2)_2]$, (table 13).

$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) and $HgPh_2$

Similarly, a solution of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II), (0.040mmol.) in $CDCl_3$ (0.3ml) and a solution of $HgPh_2$ (14.4mg, 0.040mmol.) in $CDCl_3$ (0.2ml) were mixed at -60°C. There was no reaction in $1^1/4$ hours at -60°C, so the mixture was warmed to room temperature. Initially, a species with $\delta = +0.2$ ppm, $^1J_{PtP} = 1399$ Hz (at -60°C), identified as $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ Ph trans to $PMePh_2$, and cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ were produced. After 1 minute at room temperature, ca. 40% of the $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (II) had been consumed, and the products were present in equal amounts. After a further 1 minute at room temperature, the amount of $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ increased, relative to cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$, which appeared to have reached its maximum concentration. After 3 minutes at room temperature, another species began to appear, with parameters $\delta = +0.2$ ppm, $^1J_{PtP} = 4104$ Hz, which had broad $^{195}Pt-^{31}P$ satellites. This material grew in slowly, and the cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ disappeared. After 15 minutes at room temperature, the solution contained mainly $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ and +0.2ppm, $^1J_{PtP} = 4104$ Hz in a 2 to 1 ratio of ^{31}P intensity, with a tiny amount of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) present. After 1 hour at room temperature, the ratio of ^{31}P intensities was approximately 1 to 2, and large amounts of $[PtCl(Ph)(CO)(PMePh_2)]$ (I),

$[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$, trans-$[PtCl(Ph)(PMePh_2)_2]$ and trans-$[PtCl(COPh)(PMePh_2)_2]$ were present.

$[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ isomer (II) and $HgPh_2$ (0.5 equiv.) and $[Et_4N]Cl$ (0.5 equiv.)

A solution of $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ isomer (II) (0.043mmol.) in $CDCl_3$ (0.3ml) was mixed at -60°C with a solution of $HgPh_2$ (10.0mg, 0.022mmol.) and $[Et_4N]Cl$ (4.4mg, 0.022 mmol.) in $CDCl_3$ (0.3ml) and the reaction was observed by ^{31}P nmr spectroscopy. After 3 minutes at room temperature, 50% of the isomer (II) had reacted to form $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$. After a further 10 minutes at room temperature, a species with parameters $\delta = -5.5$ ppm, $^1J_{PtP} = 4955$ Hz, identified as cis-$[PtCl_2(COPh)(PMePh_2)]^-$ began to grow in. On standing for 3 hours at room temperature, this became the major product, with some trans-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$ and $\delta = +0.8$ ppm, $^1J_{PtP} = 2532$ Hz (at 25°C), proposed to be trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$, growing in later.

$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II) and $HgPh_2$ (0.5 equiv.) and $[Et_4N]Cl$ (0.5 equiv.)

Similarly $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer (II), (0.040mmol.), $HgPh_2$ (7.2mg, 0.020mmol.) were mixed in $CDCl_3$ (0.6ml) at -60°C. There was no reaction until the mixture was warmed to -10°C, when $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, began to appear. After 30 minutes at

-10°C and a further 30 minutes at 0°C, there was still 80% of the isomer (II) present. On warming to +10°C for 15 minutes, cis-$[PtCl_2(COPh)(PMePh_2)]^-$ and cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ appeared. After 50 minutes at +10°C, cis-$[PtCl_2(COPh)(PMePh_2)]^-$ was the major product. After 1 hour 20 minutes at +10°C and 30 minutes at room temperature, very little $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$ was left, and a little of the dimeric species, $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CMe)_2(PMePh_2)_2]$ was present.

cis-$[PtCl_2(CO)(PMePh_2)]$ and $HgPh_2$ (0.5 equiv.) and $[Et_4N]Cl$ (0.5 equiv.)

cis-$[PtCl_2(CO)(PMePh_2)]$ (20.0mg, 0.040mmol.), $HgPh_2$ (7.2mg, 0.020mmol.) and $[Et_4N]Cl$ (3.4mg, 0.020mmol.) were mixed in $CDCl_3$ (0.5ml) and after 10 minutes the solution was filtered and examined by ^{31}P nmr spectroscopy. The solution was found to consist of cis-$[PtCl_2(COPh)(PMePh_2)]^-$ (ca. 53%), cis-$[PtCl_2(CO)(PMePh_2)]$ (42%) and $[PtCl(CO)(Ph)(PMePh_2)]$ isomer (I) (5%).

$[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $Hg(C{\equiv}CMe)_2$

A $CDCl_3$ solution of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I), (0.040mmol.) was allowed to equilibrate with its insertion product, $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ at -60°C. (The ratio of ^{31}P intensities was 1 to 5). A solution of $Hg(C{\equiv}CMe)_2$ (11.4mg, 0.040mmol.) in $CDCl_3$ (0.3ml) was then added at -60°C and the reaction was followed by ^{31}P nmr spectroscopy. Initially, a species with very broad satellites and main peak, with $\delta = +0.5$ppm, $^1J_{PtP} = 4113$ Hz was produced. As the reaction progressed, the parameters changed to

$\delta = +0.3$ppm, $^1J_{PtP} = 4108$ Hz, but the peaks remained broad. After 1 hour at -60°C this was the major product (>90%) and the spectrum did not change over a further 1½ hours. On warming the solution to room temperature for 1 minute and then cooling again to -60°C, the peak had sharpened up, the satellites were a little broad and the parameters had changed to $\delta = +0.2$ ppm, $^1J_{PtP} = 4106$ Hz, i.e. the parameters for $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CMe)_2(PMePh_2)_2]$. A little cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ had also appeared. After 10 minutes at room temperature $[PtPh(C{\equiv}CMe)(CO)(PMePh_2)]$, Ph trans to $PMePh_2$, had grown in (to half the ^{31}P intensity of the dimer) and the amount of cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ had also increased. On keeping at room temperature no further change occurred until $[PtCl(Ph)(CO)(PMePh_2)]$ (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ started to grow in again.

$[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (I) and $Hg(C{\equiv}CMe)_2$

A $CDCl_3$ solution (0.3ml) of $[PtCl(C_6H_4CO_2Me\text{-}\underline{p})(CO)(PMePh_2)]$ isomer (I), (0.040mmol.) was allowed to equilibrate with $[Pt_2(COC_6H_4CO_2Me\text{-}\underline{p})_2Cl_2(PMePh_2)_2]$ at -60°C. (The ratio of ^{31}P intensities was 10 to 1). A solution of $Hg(C{\equiv}CMe)_2$ (11.4mg, 0.040mmol.) was added at -60°C and the reaction was followed by ^{31}P nmr spectroscopy. The initial product was $[Pt(C_6H_4CO_2Me\text{-}\underline{p})(C{\equiv}CMe)(CO)(PMePh_2)]$, $C{\equiv}CMe$ trans to CO, (identified by ^{31}P nmr and corroborated by ^1H nmr, tables 10, 12). After 4 hours at -60°C and 10 seconds at room temperature this was the only product. After 15 minutes at room temperature some cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ also appeared.

$[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $Hg(C{\equiv}CPh)_2$

A $CDCl_3$ solution (0.3ml) of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I), (0.040 mmol.) was allowed to equilibrate with $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ at -60°C. (The ratio of ^{31}P intensities was 1 to 5). A solution of $Hg(C{\equiv}CPh)_2$ (16.4mg, 0.040mmol.) in $CDCl_3$ (0.3ml) was added and the reaction was observed at -60°C by ^{31}P nmr spectroscopy. The initial products were a species with parameters $\delta = +0.9$ ppm, $^1J_{PtP} = 4168$ Hz, which was very broad, and a small amount of $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$, Ph *trans* to $PMePh_2$. As the reaction progressed, the unknown species' peak sharpened up, and the parameters changed to $\delta = +0.3$ ppm, $^1J_{PtP} = 4176$ Hz, and this is identified as $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CPh)_2(PMePh_2)_2]$. *cis*-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ also grew in. After 2½ hours at -60°C and 3 minutes at room temperature $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CPh)_2(PMePh_2)_2]$ and $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$ were present in a ratio of 2 to 1 (based on ^{31}P intensities). On warming to room temperature for 45 minutes, only $[PtPh(C{\equiv}CPh)(CO)(PMePh_2)]$ was present, and $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ started to grow in again. Eventually, these two complexes and *trans*-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$ were the only species present.

$[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $Ph_3PAu(C{\equiv}CPh)$

A similar reaction was performed using an equilibrium mixture of $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I) and $[Pt_2(COPh)_2Cl_2(PMePh_2)_2]$ (0.040mmol. of Pt) with $Ph_3PAu(C{\equiv}CPh)$ (23.2mgs, 0.041 mmol.) in $CDCl_3$ (0.6ml) at -60°C. The initial products were $[Pt_2(COPh)_2(\mu\text{-}C{\equiv}CPh)_2(PMePh_2)_2]$, with sharp peaks and parameters δ = +0.3 ppm, $^1J_{PtP}$ = 4172 Hz, and [PtPh(C≡CPh)(CO)(PMePh$_2$)], Ph trans to PMePh$_2$, δ = +0.3 ppm, $^1J_{PtP}$ = 1386 Hz. As the reaction proceeded the amount of [PtPh(C≡CPh)(CO)(PMePh$_2$)] increased and dimer decreased. Another species, with parameters δ = -2.7 ppm, $^1J_{PtP}$ = 3297 Hz was also produced.

[PtCl(Ph)(CO)(PMePh$_2$)] isomer (I) and TlC$_5$H$_5$

A solution of [PtCl(Ph)(CO)(PMePh$_2$)] isomer (I) in equilibrium with [Pt$_2$(COPh)$_2$Cl$_2$(PMePh$_2$)$_2$] at room temperature was prepared (0.040mmol. of Pt). The ratio of ^{31}P intensities was 1 to 2, which is equivalent to a 1 to 1 mole ratio. TlC$_5$H$_5$ was added (12.0mgs, 0.045mmol.) at room temperature and after 20 minutes the solution was filtered and a ^{31}P nmr spectrum showed that it contained largely one species, δ = -6.2 ppm, $^1J_{PtP}$ = 5687 Hz, identified as [Pt(η^5-C$_5$H$_5$)(COPh)(PMePh$_2$)], with a small amount of trans-[PtCl(COPh)(PMePh$_2$)$_2$].

[PtCl(C$_6$H$_4$CO$_2$Me-p)(CO)(PMePh$_2$)] isomer (I) and TlC$_5$H$_5$

Similarly, TlC$_5$H$_5$ (11.6mg, 0.043mmol.) was added to an equilibrated mixture of [PtCl(C$_6$H$_4$CO$_2$Me-p)(CO)(PMePh$_2$)] isomer (I) and [Pt$_2$(COC$_6$H$_4$CO$_2$Me-p)$_2$Cl$_2$(PMePh$_2$)$_2$], (0.040mmol. of Pt) in CDCl$_3$ (0.5ml) at -60°C. ^{31}P nmr showed that there was no reaction in 2 hours at -60°C. On warming to room temperature, the major product was a species, δ = -5.9 ppm, $^1J_{PtP}$ = 5659 Hz (at 25°C), identified as [Pt(η^5-C$_5$H$_5$)-(COC$_6$H$_4$CO$_2$Me-p)(PMePh$_2$)]. ^{1}H nmr at 25°C, δ = +5.58 ppm, J_{PH} = 2.0 Hz, J_{PtH} = 13.0 Hz (C$_5$H$_5$), δ = +3.90 ppm, (CH$_3$ of C$_6$H$_4$CO$_2$Me-p) and δ_H = +2.03 ppm, $^2J_{PH}$ = 11.0 Hz, $^3J_{PtH}$

unresolved. Some <u>cis</u>-[Pt($C_6H_4CO_2Me$-<u>p</u>)$_2$(CO)($PMePh_2$)] was also produced, (table 13).

<u>[PtCl(C_2Cl_3)(CO)($PMePh_2$)] isomer (I) and TlC_5H_5</u>

a) [PtCl(C_2Cl_3)(CO)($PMePh_2$)] isomer (I), (24.4mg, 0.040mmol.) and TlC_5H_5 (10.9mg, 0.040mmol.) were mixed in $CDCl_3$ (0.5 ml) at room temperature. The solution rapidly became yellow, and was filtered, after 10 minutes and a ^{31}P nmr spectrum was obtained at -60°C. This showed that ca. 70% of the isomer (I) was unreacted, and the only other species present were <u>cis</u>-[Pt(C_2Cl_3)$_2$(CO)($PMePh_2$)] and δ = -5.9 ppm, $^1J_{PtP}$ = 5249 Hz. More TlC_5H_5 was added (21.8mg, 0.080 mmol.), and the mixture was reacted at room temperature for 20 minutes, filtered and ^{31}P spectrum recorded at -60°C. The solution contained only δ = -6.0 ppm, $^1J_{PtP}$ = 5254 Hz and <u>cis</u>-[Pt(C_2Cl_3)$_2$(CO)($PMePh_2$)] in a 3 to 1 ratio. A ^1H nmr spectrum at room temperature showed the presence of C_5H_6 and a π-cyclopentadienyl species with δ = +5.62 ppm, J_{PH} = 1.5 Hz, J_{PtH} = 13.0 Hz (d of t.), (C_5H_5) and δ = +2.00 ppm, $^2J_{PH}$ = 11.5 Hz, $^3J_{PtH}$ = 30.0 Hz (d. of t.) ($PMePh_2$ methyl H's).

b) Similarly [PtCl(C_2Cl_3)(CO)($PMePh_2$)] isomer (I), (24.4mg, 0.040mmol.) and TlC_5H_5 (10.9mg, 0.040mmol.) were reacted in $CDCl_3$ (0.5ml) at room temperature for 6 hours. A ^{31}P nmr spectrum at -60°C revealed the presence of <u>cis</u>-[Pt(C_2Cl_3)$_2$(CO)($PMePh_2$)], -5.8 ppm, $^1J_{PtP}$ = 5249 Hz and a species with δ = -0.4 ppm, $^1J_{PtP}$ = 2047 Hz in a ratio of 4:3:2 approximately. A ^1H nmr spectrum at room temperature showed that C_5H_6 was present.

c) Similarly $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ isomer (I), (24.4mg, mg, 0.040mmol.) and TlC_5H_5 (10.9mg, 0.040mmol.) were allowed to react in $CDCl_3$ (0.5ml) at room temperature. After 10 hours there had been very little reaction although the solution was orange-yellow and contained TlCl. A ^1H nmr showed the presence of C_5H_6. After 23 hours, isomer (I) was still 65% of the ^{31}P intensity, with the most abundant product a species at $\delta = -0.3$ ppm, $^1J_{PtP} = 2015$ Hz. A ^1H nmr spectrum contained a large amount of C_5H_6, and a σ-cyclopentadienyl species, $\delta = +6.15$ ppm, $J_{PH} = 4.0$ Hz, $J_{PtH} = 36.0$ Hz (d of t.) (C_5H_5) and $\delta = +2.14$ ppm, $^2J_{PH} = 10.5$ Hz, $^3J_{PtH}$ unresolved (d), ($PMePh_2$ methyl H's). A further 10.9mg of TlC_5H_5 (0.040mmol.) was added, and after 12 hours at room temperature, a ^{31}P nmr spectrum at -60°C contained $\delta = -0.4$ ppm, $^1J_{PtP} = 2045$ Hz; cis-$[Pt(C_2Cl_3)_2(CO)(PMePh_2)]$; $\delta = -5.8$ ppm, $^1J_{PtP} = 5249$ Hz and cis-$[PtCl(C_2Cl_3)(PMePh_2)_2]$. Eventually some trans-$[PtCl(C_2Cl_3)(PMePh_2)_2]$ also grew in, (table 13).

$[PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)]$ isomer (I) and TlC_5H_5

TlC_5H_5 (10.9mg, 0.040mmol.) was added to a solution of $[PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)]$ isomer (I) at room temperature.

The solution was investigated periodically by ^{31}P nmr spectroscopy. In 3 days at room temperature there was no reaction, but after 1 week some other species began to grow in. By 2½ weeks, only 35% of the isomer (I) was left. Products were species with parameters $\delta = -3.9$ ppm, $^1J_{PtP} = 4879$ Hz and $\delta = -3.7$ ppm, $^1J_{PtP} = 4868$ Hz, a species with parameters $\delta = -0.4$ ppm, $J_{PtP} = 1833$ Hz and $[PtCl(C_6H_4Cl\text{-}\underline{o})(CO)(PMePh_2)]$ isomer (II).

CHAPTER 4

FORMATION AND REACTIONS OF A NOVEL, ASYMMETRICALLY SUBSTITUTED, BINUCLEAR PLATINUM COMPLEX.

RESULTS AND DISCUSSION

The Decomposition of Cyclopentadienyl isomer (I)

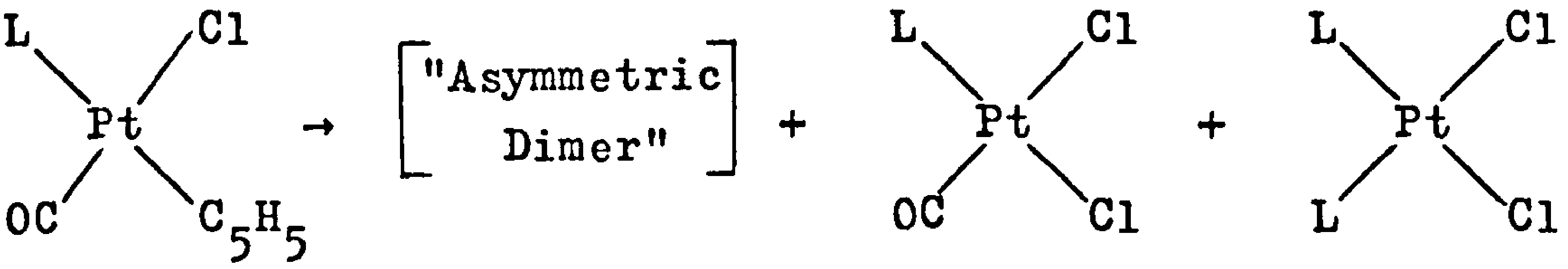
The decomposition of cyclopentadienyl isomer (I) complexes in solution leads to the formation of a novel dinuclear platinum complex. When a $CDCl_3$ solution of $[PtCl(\eta^1-C_5H_5)(CO)(PPh_3)]$ isomer (I), C_5H_5 trans to PPh_3, was left at room temperature for three days a ^{31}P nmr spectroscopic investigation showed that only 34% of the isomer (I) remained. The products of decomposition were cis-$[PtCl_2(CO)(PPh_3)]$ (25% of the ^{31}P intensity of the products), cis-$[PtCl_2(PPh_3)_2]$ (10%), a species with parameters δ = +20.7 ppm, $^1J_{PtP}$ = 3435 Hz (8%) and a species whose ^{31}P nmr parameters showed it to be a dimer, probably with a platinum-platinum bond (57%). The parameters of the dimer are:-

δ = +9.1 ppm, doublet $^3J_{PP}$ = 9.4 Hz, $^1J_{PtP}$ = 5006 Hz, $^2J_{PtP} < 20$ Hz.

δ = +34.0 ppm, doublet $^3J_{PP}$ = 9.4 Hz, $^1J_{PtP}$ = 5505 Hz, $^2J_{PtP}$ = 862 Hz.

The dimeric nature of this complex is indicated by the coupling of each phosphine to two platinum atoms, and the size of the long-range platinum-phosphorus coupling to the low-field phosphine indicates that the complex probably has a platinum-platinum bond.

A similar dimer was obtained when $[PtCl(\eta^1-C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) was allowed to decompose in solution. After 1 day at room temperature in $CDCl_3$, only 33% of the ^{31}P intensity was isomer (I), the remainder being the asymmetrically substituted dimer (33%), cis-[$PtCl_2(CO)$-(PMe_2Ph)] (20%) and cis-[$PtCl_2(PMe_2Ph)_2$] (10%). On being left for three days cis-[$PtCl_2(PMe_2Ph)_2$] became the major product.



The ^{31}P parameters of the "Asymmetric Dimer" obtained from [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] are given in table 14. The formation of "Asymmetric Dimer" is not light-induced, since a solution of [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) kept in the dark decomposed at the same rate, and to the same products, as a solution exposed to daylight. Neither is it dependant on $CDCl_3$, since solutions of [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] (I) in acetone and in benzene also produced "Asymmetric Dimer", cis-[$PtCl_2(CO)(PMe_2Ph)$] and cis-[$PtCl_2(PMe_2Ph)_2$]; although the decomposition was slower than in $CDCl_3$.

The decomposition of [$PtCl(C_5H_5)(CO)(PMePh_2)$] isomer (I) is not accelerated by bubbling either nitrogen, oxygen, carbon monoxide or carbon dioxide through a $CDCl_3$ solution, nor is it affected by addition of H_2O. This would seem to suggest that the decomposition of cyclopentadienyl isomer (I) complexes is via either intramolecular or intermolecular reactions of the platinum complexes alone, rather than reactions with air or moisture etc.

Other Routes to "Asymmetric Dimers"

The "Asymmetric Dimers" can be made in higher yield by allowing cis-[$PtX_2(CO)L$] to react with 2 equivalents of TlC_5H_5. cis-[$PtCl_2(CO)(PPh_3)$] on some occasions produced cis-$[Pt(C_5H_5)_2(CO)(PPh_3)]$ on reaction with 2 TlC_5H_5, but in the majority of attempts, the reaction led largely to "Asymmetric Dimer", usually 70-90% of the total ^{31}P intensity. The species with parameters $\delta = +20.7$ ppm, $^1J_{PtP} = 3435$ Hz was also always produced. This was also obtained from the decomposition of $[PtCl(C_5H_5)(CO)(PPh_3)]$, isomer (I).

The reaction of cis-$[PtCl_2(CO)(PEt_3)]$ with 2 equivalents of TlC_5H_5 also produced an "Asymmetric Dimer" complex, whose ^{31}P nmr parameters are given in table 14. In this case, the "Asymmetric Dimer" was produced as 97% of the ^{31}P intensity, with only one other, minor, species present in solution with parameters $\delta = +9.2$ ppm, $^1J_{PtP} = 5185$ Hz. cis-$[PtCl_2(CO)(PMe_2Ph)]$ reacted with 2 TlC_5H_5 in $CDCl_3$ to produce an "Asymmetric Dimer", the same one produced by decomposition of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I). However, in this case a large number of other products was also obtained, and "Asymmetric Dimer" at no time accounted for more than 50% of the ^{31}P intensity except on one occasion, when it accounted for 83% of the ^{31}P intensity. Normally $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$, cis-$[PtCl_2(PMe_2Ph)_2]$ and unidentified species with parameters $\delta = -5.3$ ppm, $^1J_{PtP} = 2827$ Hz and $\delta = -6.6$ ppm, $^1J_{PtP} = 3090$ Hz were also produced. Also cis-$[Pt(\eta^1\text{-}C_5H_5)_2(CO)(PMe_2Ph)]$ and a species with parameters $\delta = -13.9$ ppm, $^1J_{PtP} = 2211$ Hz were transient products en route to the "Asymmetric Dimer". The reaction of cis-$[PtBr_2(CO)(PMe_2Ph)]$ with 2 equivalents of TlC_5H_5 produced an "Asymmetric Dimer" with different

^{31}P nmr parameters to the one produced from cis-[$PtCl_2(CO)$-(PMe_2Ph)], showing that the "Asymmetric Dimers" contain halide. The parameters are shown in table 14. Other products were [$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ and species with parameters δ = -7.4 ppm, $^1J_{PtP}$ = 2802 Hz and δ = -8.8 ppm, $^1J_{PtP}$ = 3072 Hz. These two species are presumably the Br analogues of δ = -5.3 ppm, $^1J_{PtP}$ = 2827 Hz and δ = -6.6 ppm, $^1J_{PtP}$ = 3090 Hz, since the latter two species begin to grow in after 2 days at room temperature. cis-[$PtBr_2(PMe_2Ph)_2$] is also produced and later cis-[$PtBr(Cl)(PMe_2Ph)_2$], thus there appears to be Br/Cl exchange in some of the species. The only source of Cl in this reaction is the $CDCl_3$ solvent. cis-[$Pt(C_5H_5)_2(CO)(PMe_2Ph)$] and the species with δ = -13.9 ppm, $^1J_{PtP}$ = 2211 Hz were again transient products en route to "Asymmetric Dimer".

^{31}P nmr parameters of other "Asymmetric Dimers" were obtained in other types of reactions, and are shown in table 14. Addition of [Bu_4N]I to the "Asymmetric Dimer", produced by reaction of cis-[$PtCl_2(CO)(PPh_3)$] and 2CpTl, formed a new "Asymmetric Dimer" with different ^{31}P nmr parameters. Addition of [Bu_4N]I to a $CDCl_3$ solution of [$Pt(\eta^5-C_5H_5)(CO)(PMe_2Ph)$]$SO_3CF_3$ formed an "Asymmetric Dimer", whose parameters differed from those formed by cis-[$PtCl_2(CO)(PMe_2Ph)$] and cis-[$PtBr_2(CO)(PMe_2Ph)$]. Similarly, addition of [Et_4N]Cl to [$PtCl(C_5H_5)(CO)(PMePh_2)$] produced some "Asymmetric Dimer", as a minor product, along with cis-[$PtCl_2(PMePh_2)_2$] and some other unidentified species.

Table 14 :- ^{31}P nmr of "Asymmetric Dimer" complexes in $CDCl_3$ at 25°C.

Phosphine	Halide	δP_1 (ppm)	$^1J_{PtP}$ (Hz)	$^2J_{PtP}$ (Hz)	δP_2 (ppm)	$^1J_{PtP}$ (Hz)	$^2J_{PtP}$ (Hz)	$^3J_{PP}$ (Hz)
PPh_3 (a)	Cl	+34.0	5505	862	+9.1	5006	unresolved (b)	9.4
$PMePh_2$	Cl	+19.5	5480	863	-8.4	4824	32.2	8.2
PMe_2Ph	Cl	+10.0	5367	872	-25.1	4690	31.0	7.2
PEt_3	Cl	+35.7	5302	858	+7.7	4618	unresolved (b)	5.7
PPh_3	I	+33.8	5533	835	+8.1	4925	unresolved (b)	9.3
PMe_2Ph	Br	+9.3	5399	852	-25.1	4683	24.4	7.3
PMe_2Ph	I	+7.7	5378	842	-25.3	4657	25	7.0

(a) ^{13}C nmr at 25°C in $CDCl_3$:- δ_{CO} = +191.1 ppm, $^2J_{P_2C}$ = 4.3 Hz, $^1J_{PtC}$ = 1625 and 723 Hz; $\delta_{C_5H_5}$ = +95.3 ppm, J_{PC} = 2.5 Hz (d).

(b) Unresolved means that $^2J_{PtP}$ satellites were hidden under the main doublet.

Structure of the "Asymmetric Dimers" from Spectroscopic Parameters

The ^{31}P nmr parameters of all of the "Asymmetric Dimers" show that these are all related species. The spectra of each are similar, as shown in figure 29.

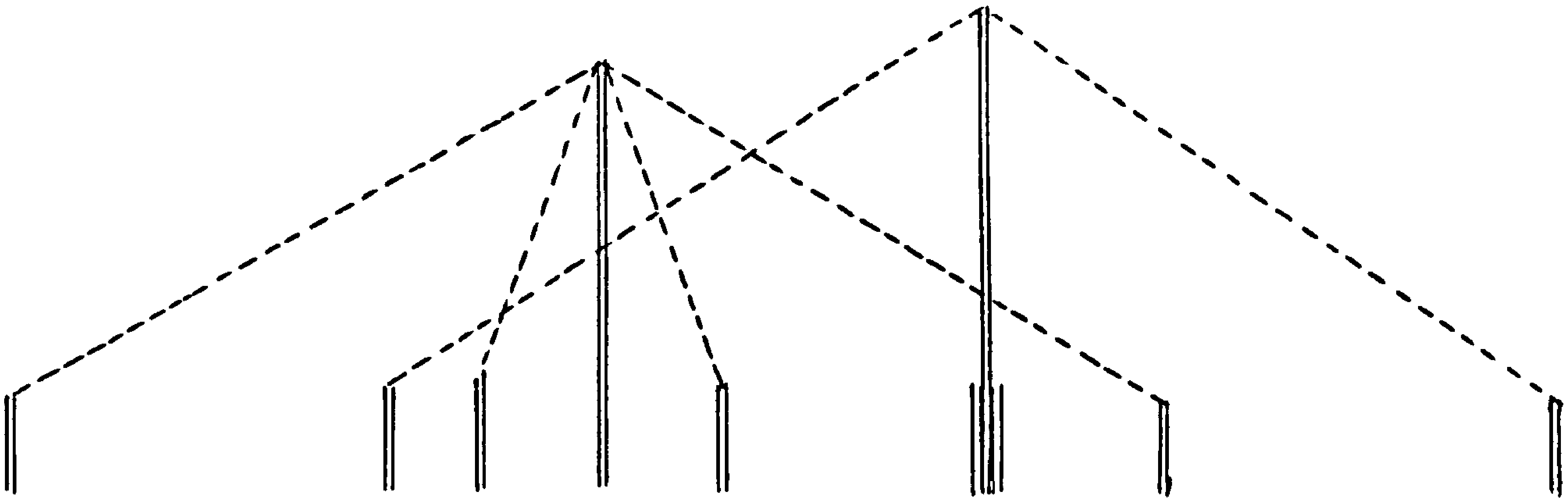
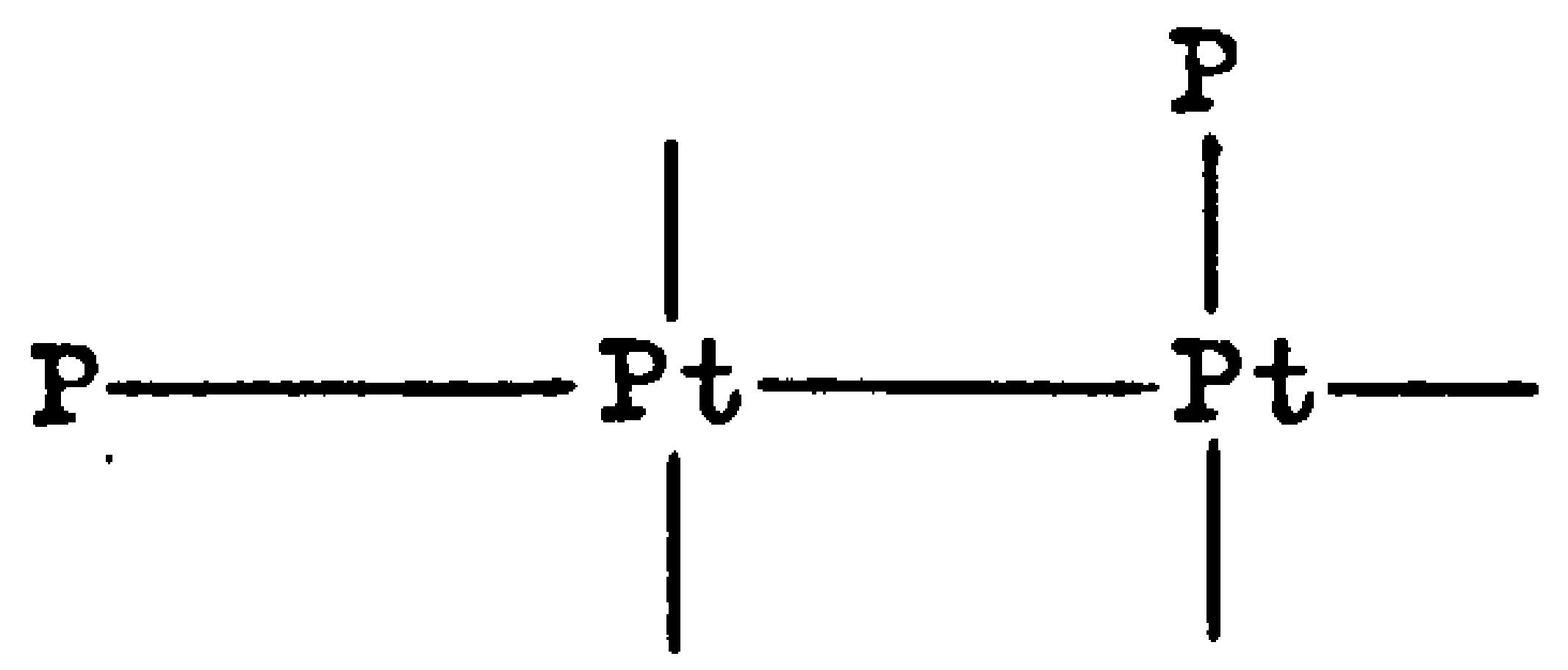
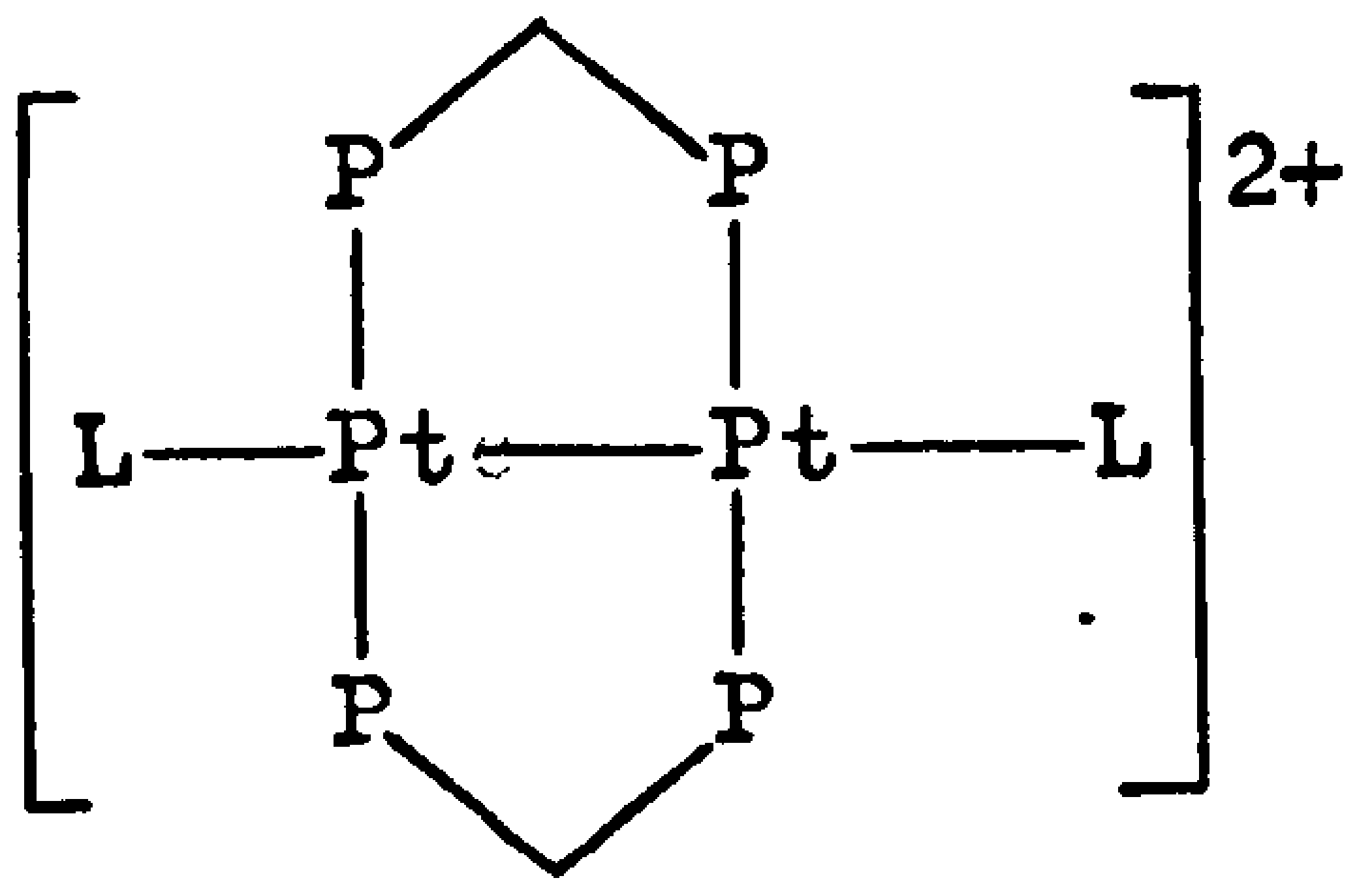


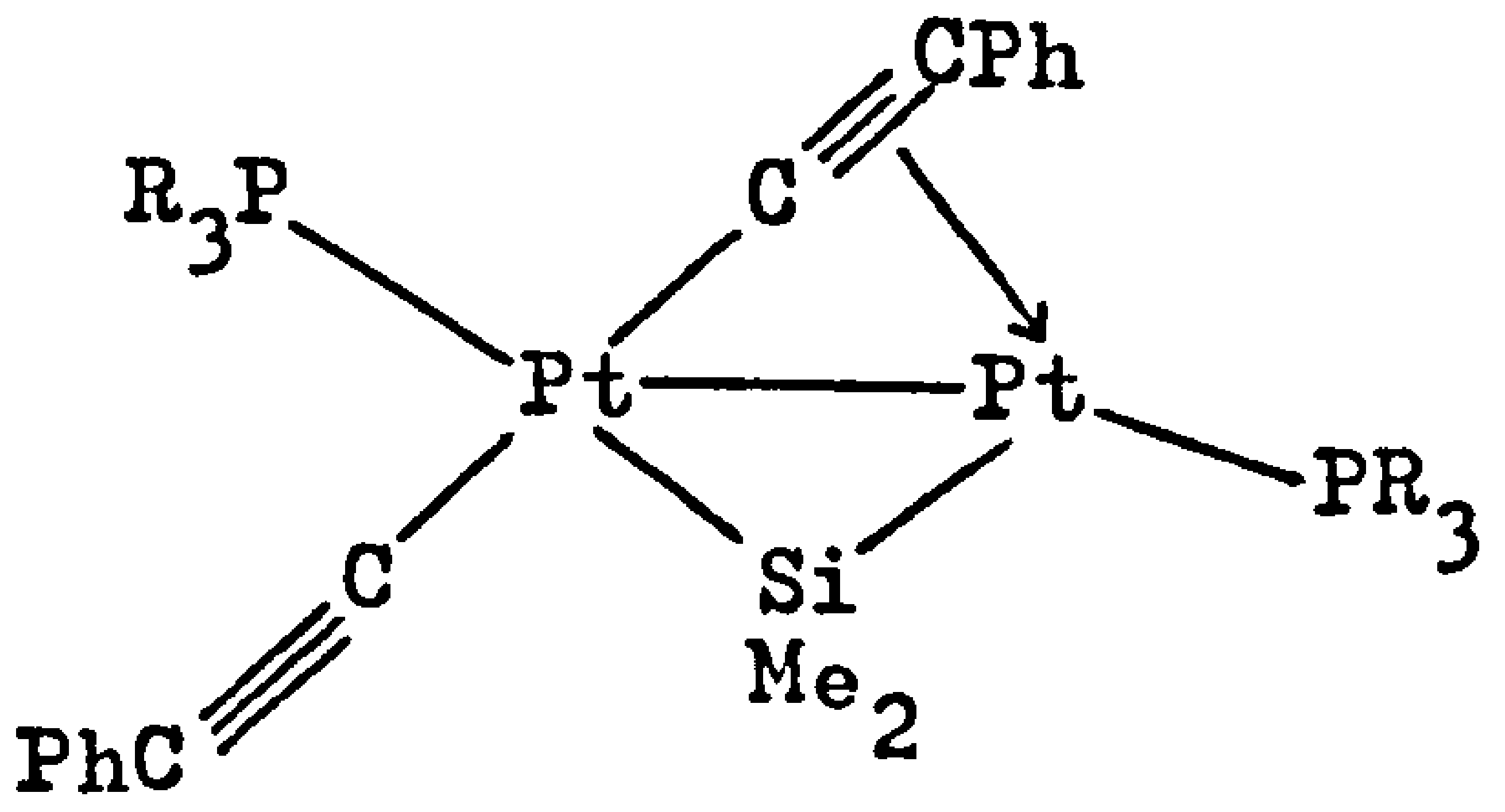
figure 29.

The phosphine with the more downfield chemical shift has the larger one-bond platinum-phosphorus coupling constant (5300 to 5530 Hz) and also has a large, long-range platinum-phosphorus coupling (835 to 870 Hz). The upfield phosphine has the smaller one-bond platinum-phosphorus coupling (4620 to 5000 Hz), and has a very small long-range platinum-phosphorus coupling constant (less than 32 Hz). One-bond $^{195}Pt-^{31}P$ coupling constants vary as expected with changing the phosphine, i.e. $PPh_3 > PMePh_2 > PMe_2Ph > PEt_3$. However, long-range $^{195}Pt-^{31}P$ coupling constants do not vary in this way, being 862, 863, 872 and 858 Hz respectively. Such large values are typical of a phosphine trans to a platinum-platinum bond. The other phosphine must then be cis to a platinum-platinum bond, since the long-range $^{195}Pt-^{31}P$ coupling is so small, viz:-



Such large $^2J_{PtP}$ values have been found in other platinum dimers with platinum-platinum bonds, for example in complexes of the type $[Pt_2(\mu\text{-dppm})_2L_2]^{2+}$, $^2J_{PtP}$ = 750 Hz when L = $PMePh_2$ and 650 Hz when L = PMe_2Ph,[74] for the phosphine, L, <u>trans</u> to the Pt-Pt bond, and only 120 Hz and 100 Hz respectively for the dppm phosphorus atoms <u>cis</u> to the Pt-Pt bond.





L = $PMePh_2$, PMe_2Ph $\qquad$ $PR_3 = P(C_6H_{11})_3$, $PMeBu^t_2$

In this case, there are large changes in $^2J_{PtP}$ on changing the phosphine, unlike the "Asymmetric Dimer", but there are two phosphines, <u>trans</u> to the Pt-Pt bond, and to each other through the Pt-Pt bond. The acetylide-bridged dimer $[Pt_2(\sigma\text{-}C{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SiMe_2)(PR_3)_2]$ has a non-linear P-Pt-Pt-P skeleton with PPtPt angles of 165.2° and 148.0°, and $^2J_{PtP}$ values of 308 Hz and 0 Hz for PR_3 = $P(C_6H_{11})_3$ and 312 Hz and 11 Hz for $PR_3 = PMeBu^t_2$.[174] In this case, the phosphine with large $^2J_{PtP}$ is not fully <u>trans</u> to the Pt-Pt bond, and the other phosphine is not fully <u>cis</u>, yet there is a large difference in $^2J_{PtP}$ values.

When the "Asymmetric Dimers" are prepared from ^{13}CO-labelled cis-$[PtCl_2(CO)L]$, ($L = PPh_3$ and PMe_2Ph), the upfield phosphine signal in the ^{31}P nmr spectrum is broadened by ^{13}C - ^{31}P coupling, and the downfield doublet is unaffected. The ^{13}C - ^{31}P coupling is not resolved, but is less than the $^{3}J_{PP}$ coupling of ca. 9 Hz, hence the carbon monoxide and phosphine ligands must be of approximately cis-geometry. A trans ^{13}C - ^{31}P coupling would be much larger; $^{2}J_{CP}$ values of 150 to 160 Hz for phosphine trans to CO are known.[154] Thus, it appears that "Asymmetric Dimer" complexes contain only one CO per dimer, which shows ^{13}C - ^{31}P coupling to the phosphine with the small $^{2}J_{PtP}$ value.

A ^{1}H nmr spectrum of the "Asymmetric Dimer" produced by reaction of cis-$[PtCl_2(CO)PPh_3)]$ and 2 TlC_5H_5 in $CDCl_3$ for two days contained C_5H_6 and a signal at $\delta = +5.75$ ppm, a doublet of doublets, $J_{PH} = 1.0$ and 1.8 Hz with broad, unresolved platinum satellites, "J_{PtH}" = 11.5 Hz. This corresponds to a π-cyclopentadienyl ring coupling to two different phosphorus atoms. It is not possible to distinguish the platinum-proton couplings to see whether the C_5H_5 ring couples to only one, or to both, platinum atoms. The ^{1}H nmr spectrum is shown in fig. 30, (π-cyclopentadienyl signal only). From integration of the amounts of C_5H_5 protons and C_5H_6 protons, there were approximately 1.5 equivalents of cyclopentadiene present for every π-cyclopentadienyl ring. A minor species was also present, at $\delta = +4.95$ ppm, a triplet, $J_{PH} = 3.0$ Hz, $J_{PtH} = 25.8$ Hz.

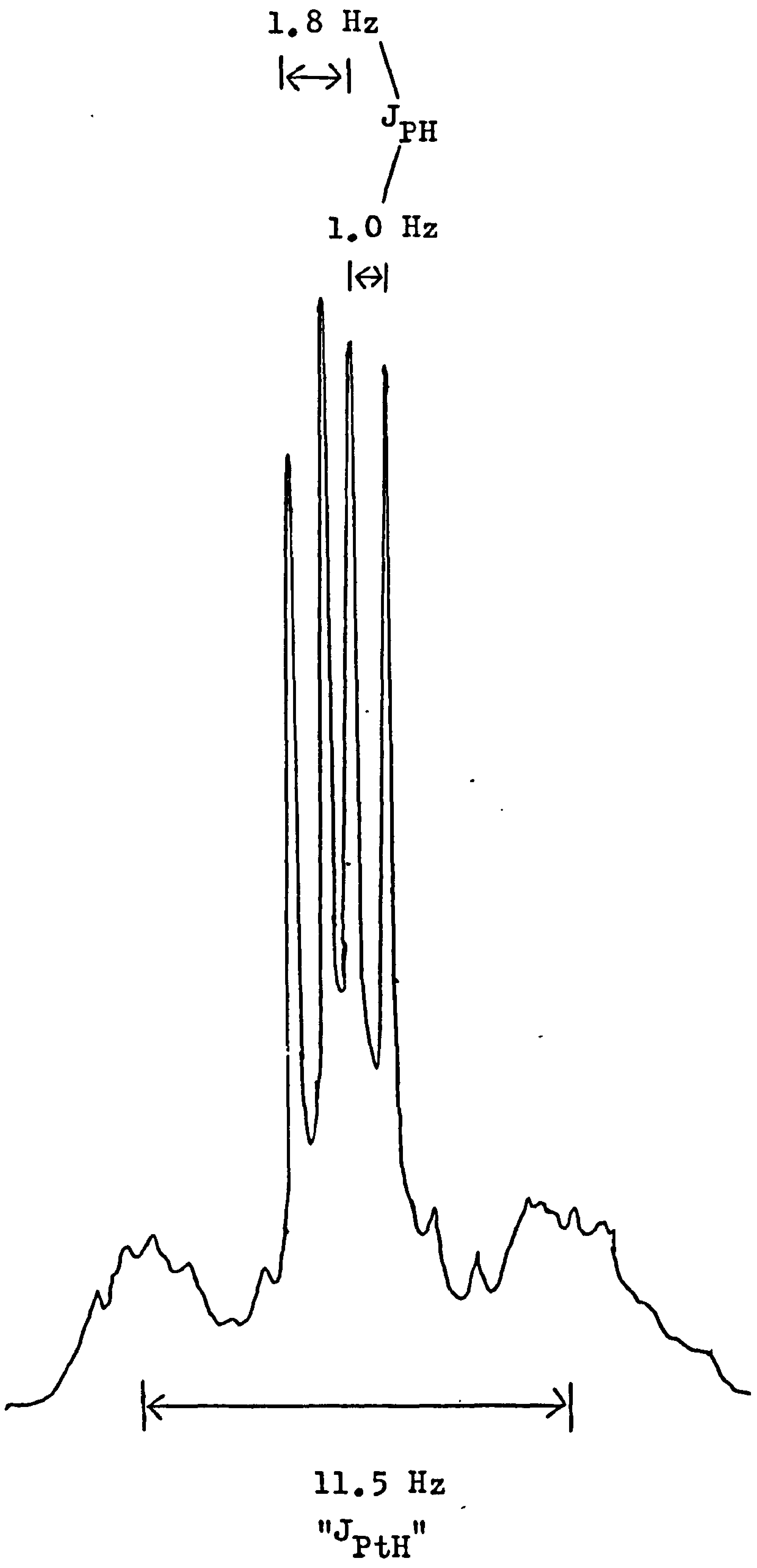


figure 30. ^1H nmr spectrum of C_5H_5 region of "Asymmetric Dimer" at δ = +5.75 ppm.

When the reaction between cis-$[PtCl_2(CO)(PEt_3)]$ and 2 TlC_5H_5 was followed by ^1H nmr spectroscopy, the initial product was $[PtCl(C_5H_5)(CO)(PEt_3)]$ isomer (I). After 3 hours, the solution also contained some cis-$[Pt(C_5H_5)_2(CO)(PEt_3)]$, (see table 3 for ^1H nmr parameters) and a peak at $\delta = +5.81$ ppm, a doublet of doublets, $J_{PH} = 1.0$ and 1.7 Hz, with broad, unresolved platinum satellites, "J_{PtH}" = 11.0 Hz. After 24 hours, this was the major species in solution. As the "Asymmetric Dimer" grew in to the spectrum, so did C_5H_6. From integration, about 1.5 equivalents of C_5H_6 were present for every π-cyclopentadienyl ring. Integration of PEt_3 signals showed that the "Asymmetric Dimer" contained only one C_5H_5 ring per dimer molecule. A minor species with parameters $\delta = +5.70$ ppm, doublet, $J_{PH} = 1.6$ Hz, $J_{PtH} = 11.0$ Hz was also present. This corresponded to a species in the ^{31}P nmr spectrum with parameters $\delta = + 9.2$ ppm, $^1J_{PtP} = 5185$ Hz.

The ^1H nmr parameters of the "Asymmetric Dimers" are in table 15. Comparison of the spectra with a spectrum of freshly cracked and distilled cyclopentadiene in $CDCl_3$ showed that the C_5H_6 was not coordinated to platinum in "Asymmetric Dimer" solutions. Formation of "Asymmetric Dimers" by decomposition of isomer (I) is also accompanied by production of C_5H_6, as was formation of "Asymmetric Dimers" in the reactions of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I) with Cl^- and $[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)]^+$ with I^-.

Table 15:- ^1H nmr of "Asymmetric Dimer" complexes in $CDCl_3$ at 25°C.

Phosphine	Halide	C_5H_5 protons		
		δ(ppm)	J_{PH} (Hz)	"J_{PtH}"
PPh_3	Cl	+5.75	1.8 and 1.0	11.5
PEt_3	Cl	+5.81	1.7 and 1.0	11.0
PMe_2Ph (a)	Cl	+5.73	1.6 and 1.0	11.0
PMe_2Ph	I	+5.64	1.7 and 0.8	(b)

(a) PMe_2Ph - methyl protons = δ = +1.93 ppm, $^2J_{PH}$ = 11.0 Hz, $^3J_{PtH}$ = 45.0 Hz and δ = +1.78 ppm, $^2J_{PH}$ = 10.5 Hz, $^3J_{PtH}$ = 44.0 Hz.

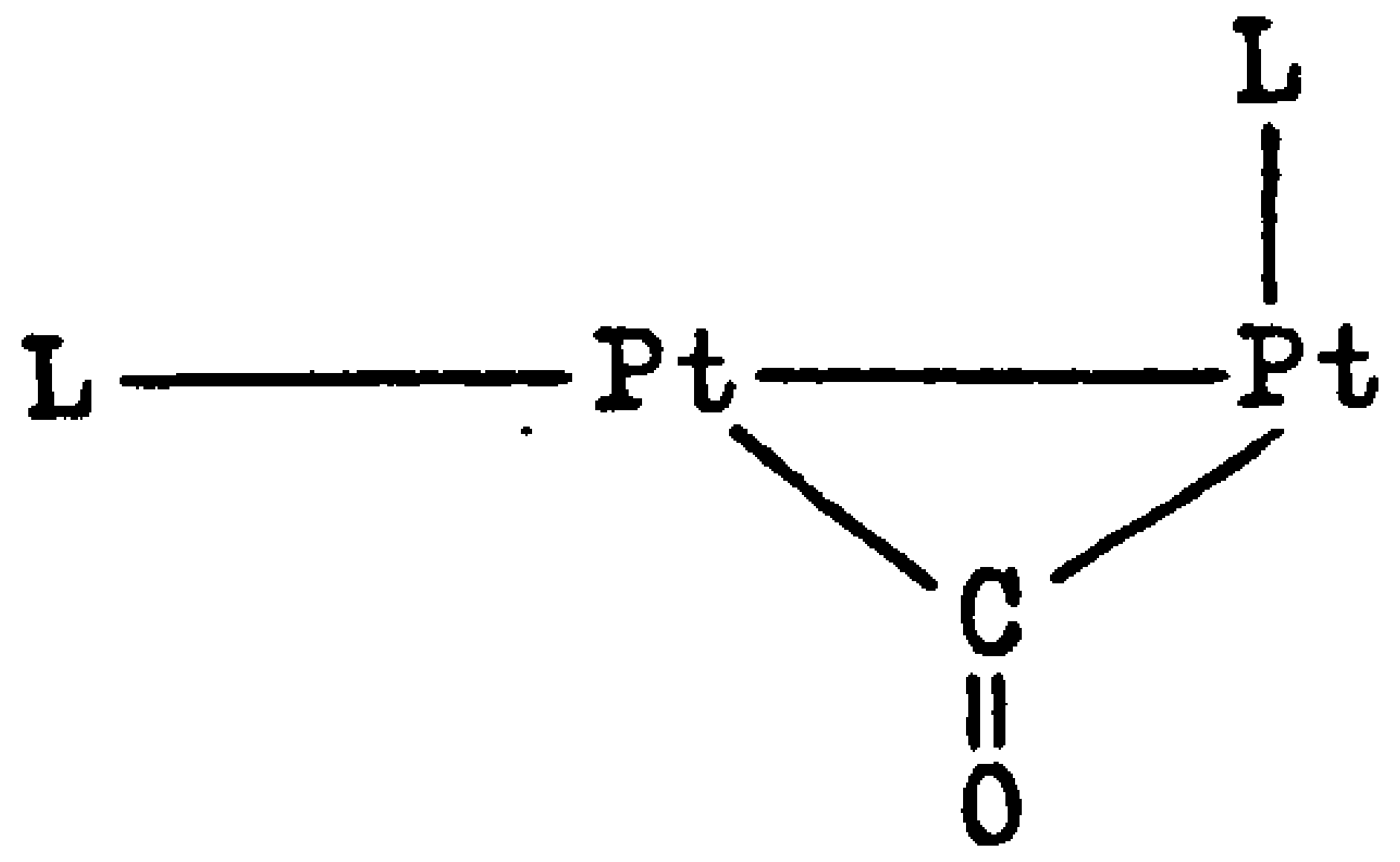
(b) Unresolved.

An impure solid sample of "Asymmetric Dimer" was isolated from the reaction of $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) and TlC_5H_5, by freeze-drying the $CDCl_3$ solution diluted with benzene. A KBr disc i.r. spectrum of this solid had a medium strong, broad absorbance at $1805cm^{-1}$, which is characteristic of a bridging CO ligand. No absorptions typical of a terminal CO could be observed. The i.r. spectrum of a $CHCl_3$ solution was also obtained, and this too had a broad absorbance at $1800cm^{-1}$, indicating that CO is bridging in solution as well as in the solid.

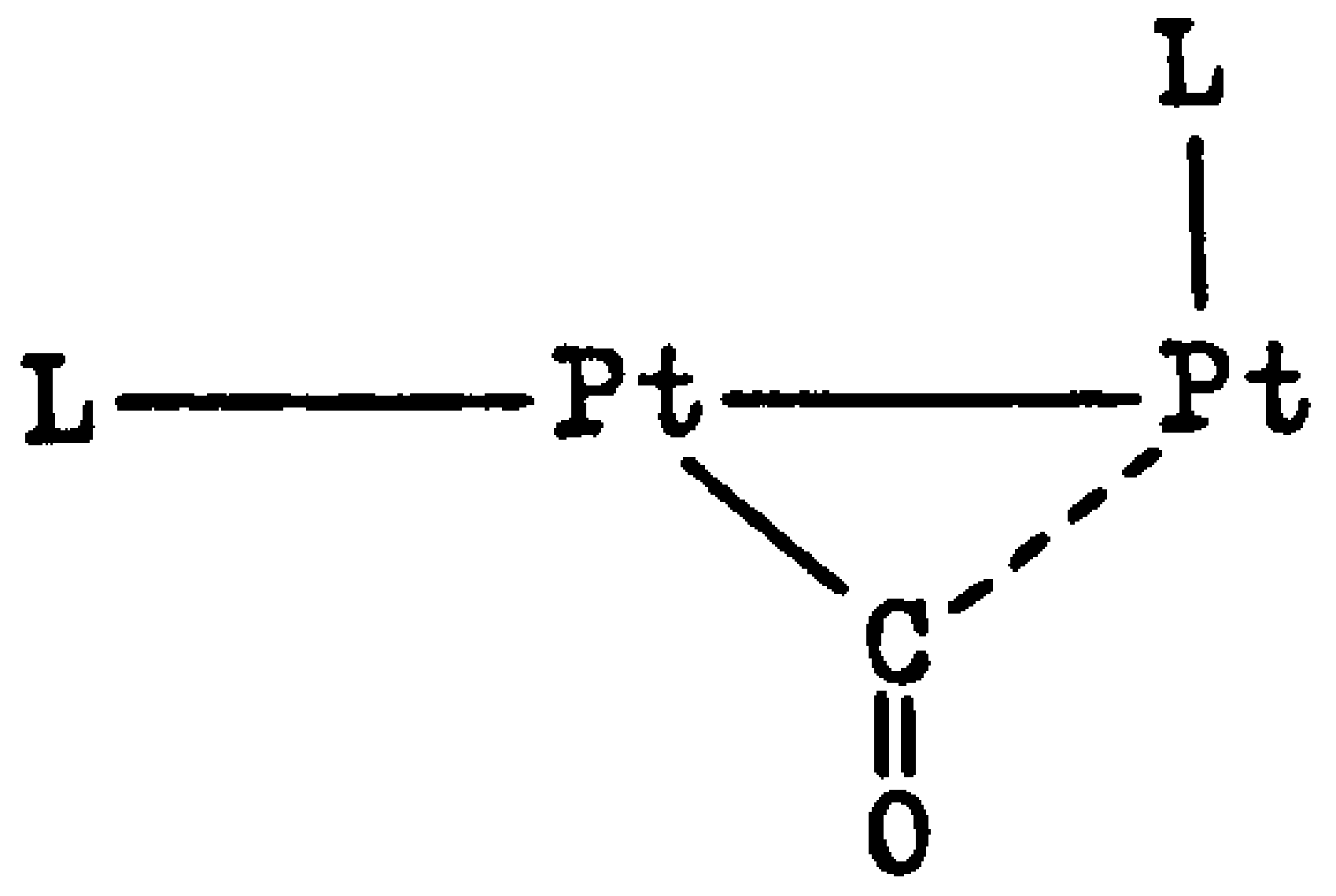
A ^{13}C nmr spectrum of the solid material dissolved in $CDCl_3$ contained a peak at $\delta = +95.3$ ppm, a doublet, $J_{PC} = 2.5$ Hz, and a large number of peaks at $\delta = +127.6$ to $+134.9$ ppm, attributable to aryl carbon atoms. No peak could be observed corresponding to a CO ligand, even on addition of $Cr(acac)_3$ to decrease spin-relaxation times. When a sample of "Asymmetric Dimer" was made from cis-$[PtCl_2(^{13}CO)(PPh_3)]$, (60% enriched with ^{13}CO), an additional peak was observed at $\delta = +191.1$ ppm, a doublet, $J_{PC} = 4.3$ Hz, with two sets of platinum satellites, $J_{PtC} = 1625$ Hz and 723 Hz. This peak was weak compared to the aryl carbon peaks, but was enhanced, (with a slight altering of parameters), on addition of $Cr(acac)_3$.

The peak in the ^{13}C nmr spectrum at +191.1 ppm is in the range typical of a carbonyl ligand. The two platinum-carbon coupling constants, of 1625 Hz and 723 Hz, indicate that the CO is bridging, which is consistent with the i.r. spectrum. A coupling constant of 723 Hz is too large to be a two-bond coupling constant, e.g.:- in $[Pt_2(C_5H_5)_2(CO)_2]$,

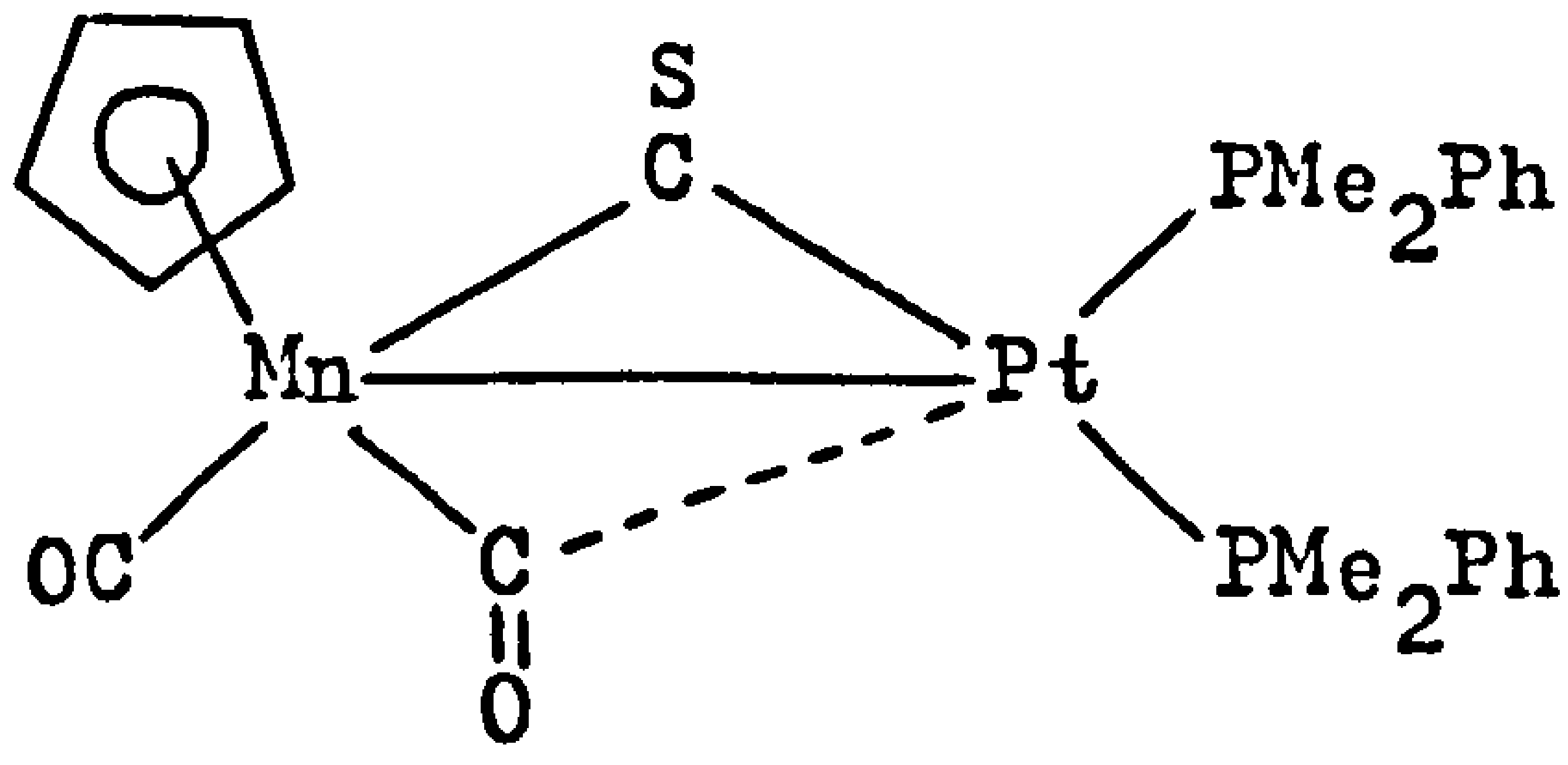
$^1J_{PtC}$ = 2446 Hz and $^2J_{PtC}$ = 102 Hz.[176] Both platinum-carbon coupling constants are thus one-bond coupling constants, and the carbonyl ligand more or less symmetrically bridges the two platinum atoms, as below:-



The CO couples to only one of the two phosphine ligands, J_{PC} = 4.3 Hz, which is consistent with the ^{31}P nmr data, where only the upfield phosphine (i.e. that <u>cis</u> to the Pt-Pt bond) couples to ^{13}CO. Neither phosphine can be in a position <u>trans</u> to the CO, since $^2J_{PC}$ values of 140 to 160 Hz are typical of this arrangement.[154] An unsymmetrical bridging mode like that shown below is also unlikely.

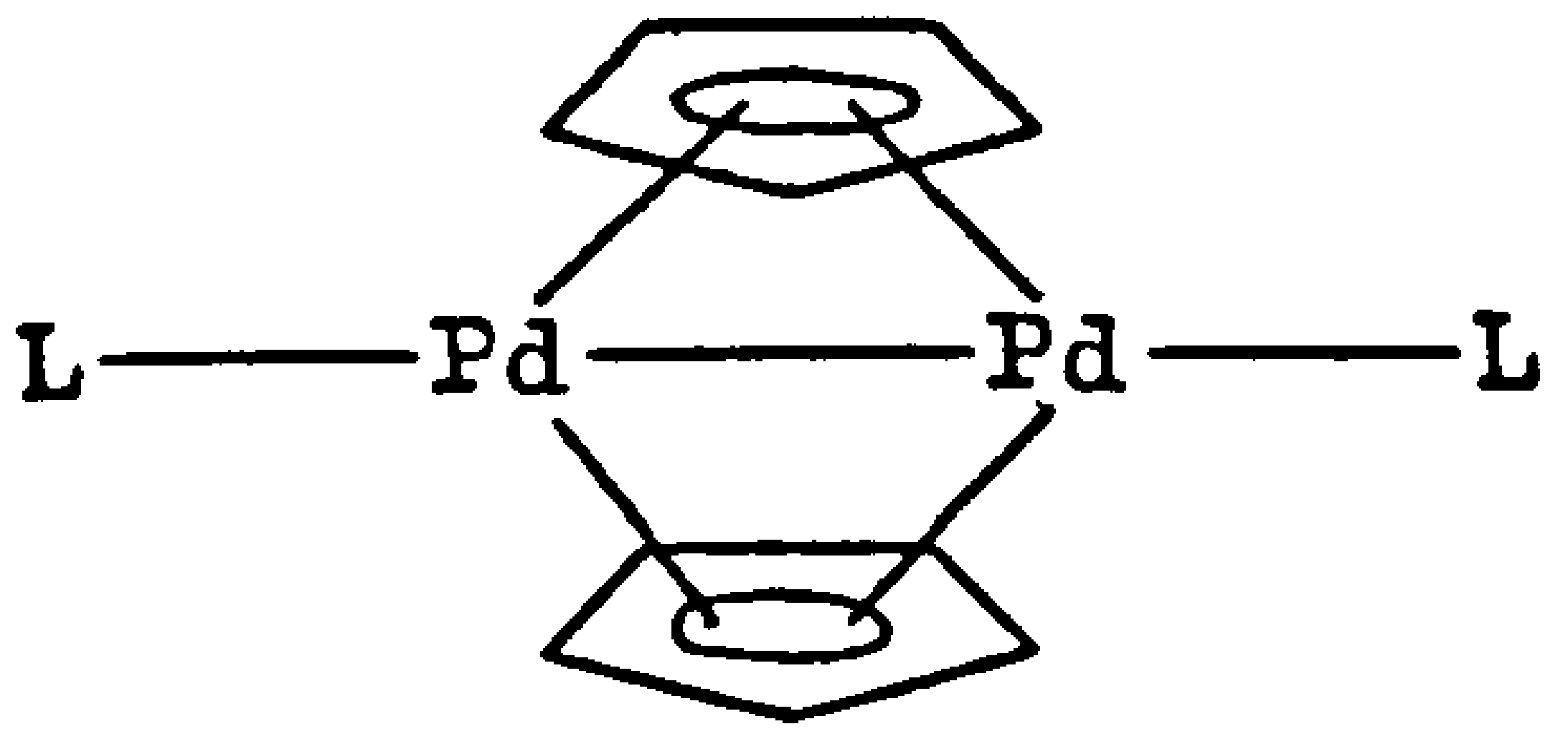


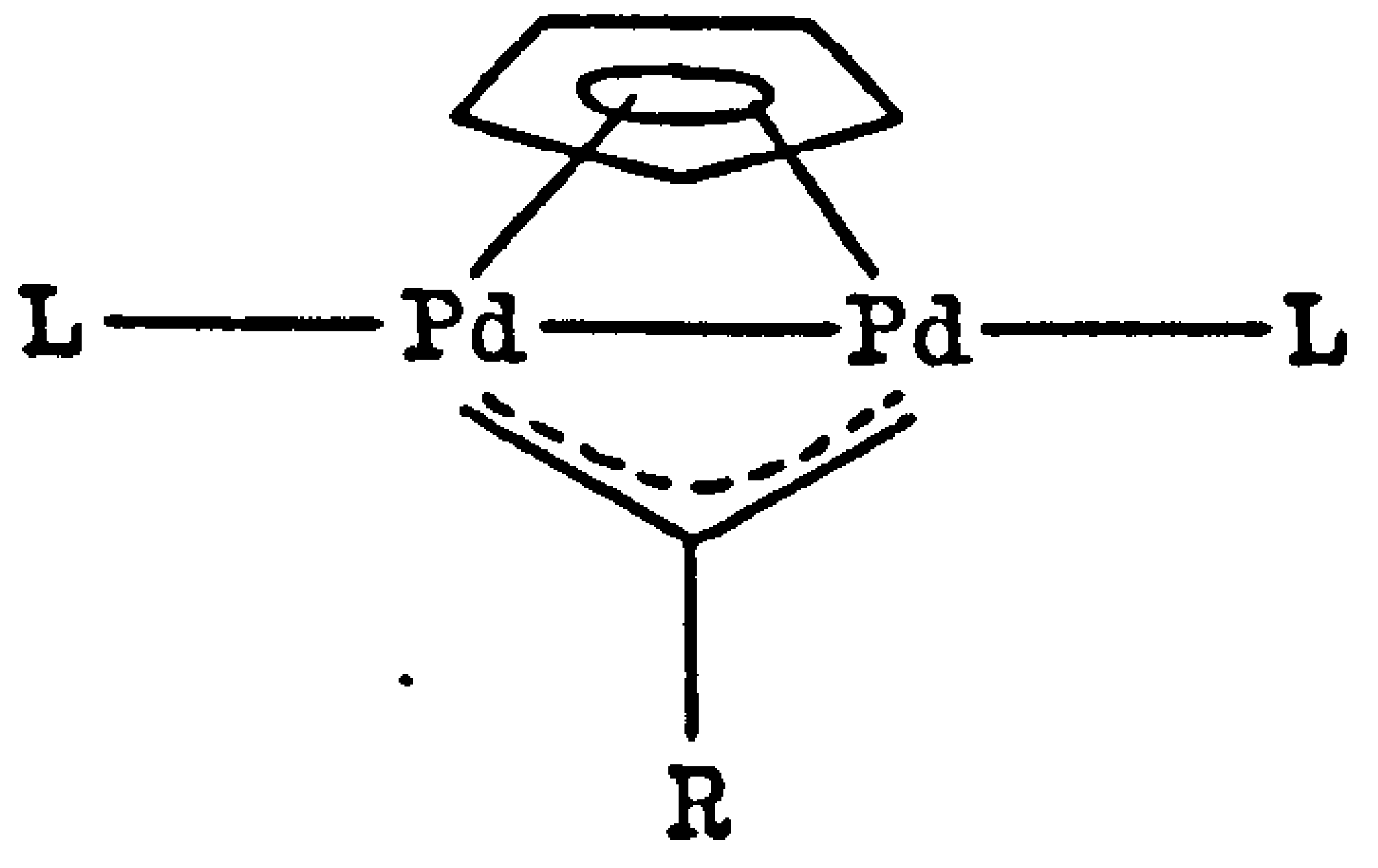
In similar complexes, like [MnPt(μ-CS)(CO)$_2$(PMe$_2$Ph)$_2$-(η^5-C$_5$H$_5$)], with a semi-bridging interaction of CO with Pt, a much smaller platinum-carbon coupling constant of 77 Hz was found.[177]

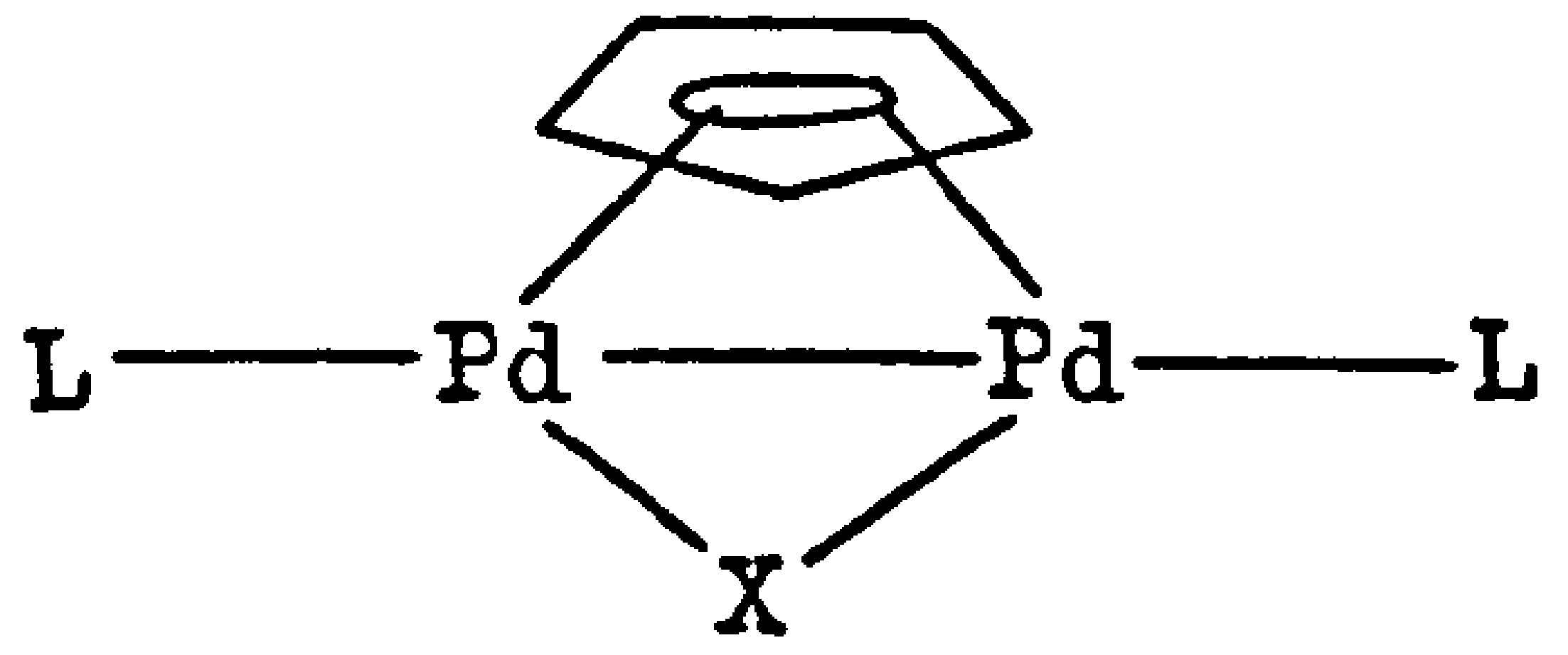


A ^{13}CO ligand trans to a halide has a $^{1}J_{PtC}$ value in the range 1650 - 1900 Hz, while a ^{13}CO ligand trans to an organic group typically has $^{1}J_{PtC}$ = ca. 900 Hz.[154] An organic group cis to ^{13}CO tends to increase $^{1}J_{PtC}$.

The peak at +95.3 ppm showed no platinum-carbon coupling, but is in the range for a π-bonded cyclopentadienyl ring. A wide range of platinum complexes containing a CO group or C_5H_5 rings are shown in table 16, and the chemical shifts lie in the range +90 to +95 ppm, for π-bonded rings, with J_{PtC} ranging from 3 to 30 Hz. This contrasts with σ-bonded C_5H_5 rings, with δ in the range +110 to +117 ppm, and coupling constants of 35 to 100 Hz. The C_5H_5 group in the "Asymmetric Dimer" is thus unlikely to be σ-bonded. There is a possibility that the C_5H_5 group could be bridging the two platinum atoms, as in complexes of the type below, studied extensively by Werner, which have a metal-metal bond and a C_5H_5 ring symmetrically bridging between the metals.[178-181]







L = tertiary phosphine
X = halide

In these complexes, the PPdPd bond angle is almost linear, and the coordination of the C_5H_5 rings has been shown, by X-ray structure determination, to be trihapto, i.e. η^3-C_5H_5, via an allylic type bonding system.[182]

Table 16:- ^{13}C nmr spectra of Cyclopentadienyl and Carbonyl Complexes of Platinum.

Complex		δ(ppm)	$^{1}J_{PtC}$ (Hz)	$^{2}J_{PtC}$ (Hz)	Ref.
$[Pt(C_2H_4)(\eta^1-C_5H_5)(\eta^5-C_5H_5)]$	$\eta^5-C_5H_5$	+94.5	17	-	176
$[Pt_2(\eta^5-C_5H_5)_2(\mu-C_{10}H_{10})]$	$\eta^5-C_5H_5$	+90.7	13	7	176
$[Pt(CO)(\eta^1-C_5H_5)(\eta^5-C_5H_5)]$	$\eta^5-C_5H_5$ CO	+94.8 +162.1	11 2494	- -	176
$[Pt_2(CO)_2(\eta^5-C_5H_5)_2]$	CO	+164.1	2446	102	176
$[Pt(CO)(Me)(\eta^5-C_5H_5)]$	$\eta^5-C_5H_5$ CO	+94.1 +163.4	8.4 2459	- -	90,91
$[Pt_2Cl_4(CO)_2]^{2-}$	CO	+159.2	2000	48	72
$[Pt(Me)(P(OMe)_3)(\eta^5-C_5H_5)]$	$\eta^5-C_5H_5$	+93.2	3.8	-	90
$[Pt(Me)(\eta^1-C_5H_5)(COD)]$	$\eta^1-C_5H_5$	+115.2	87.8	-	90
$[Pt(\eta^1-C_5H_5)_2(COD)]$	$\eta^1-C_5H_5$	+116.5	96.8	-	90

cont./

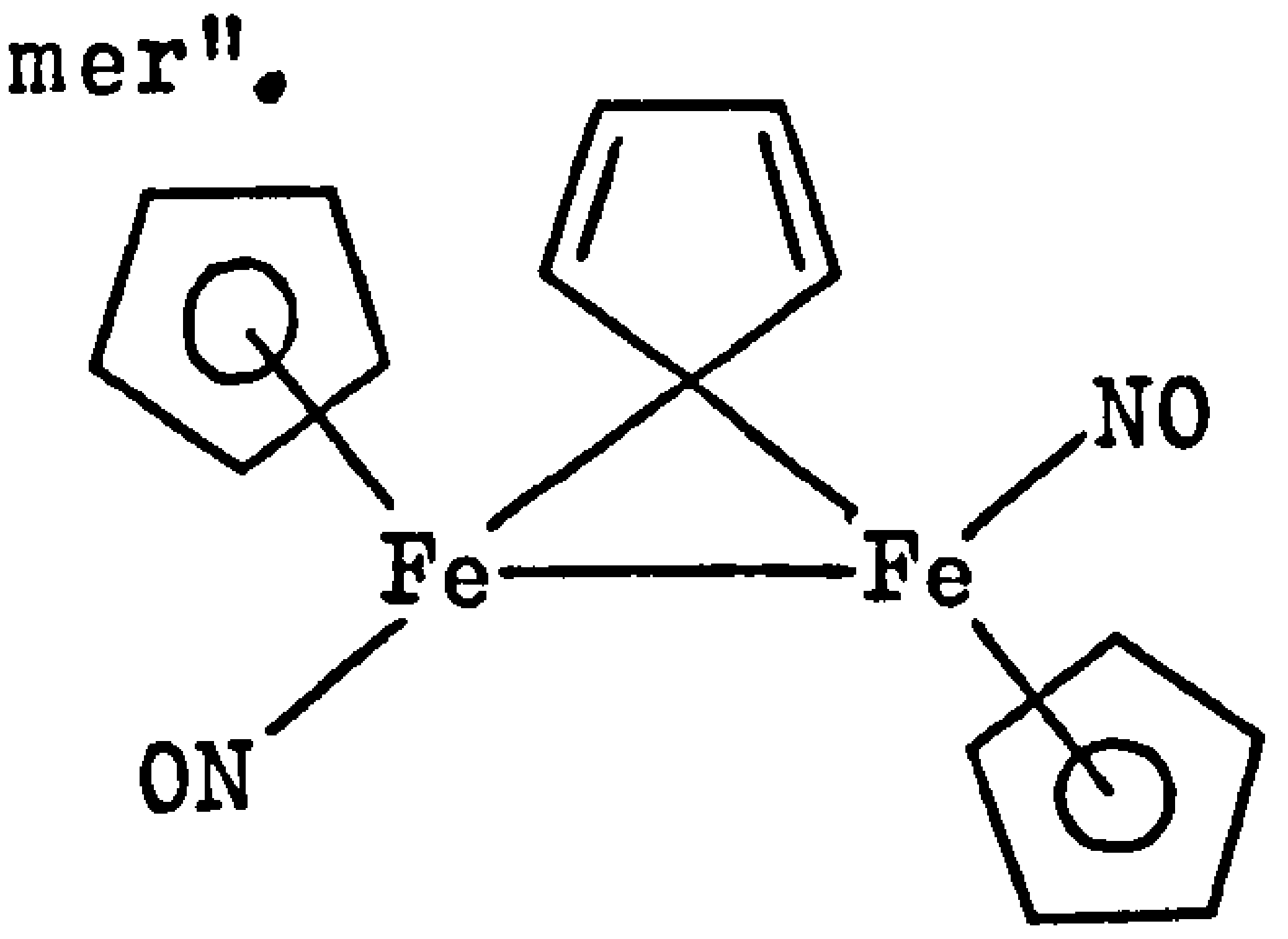
Table 16 (contd.)

^{13}C nmr spectra of Cyclopentadienyl and Carbonyl Complexes of Platinum.

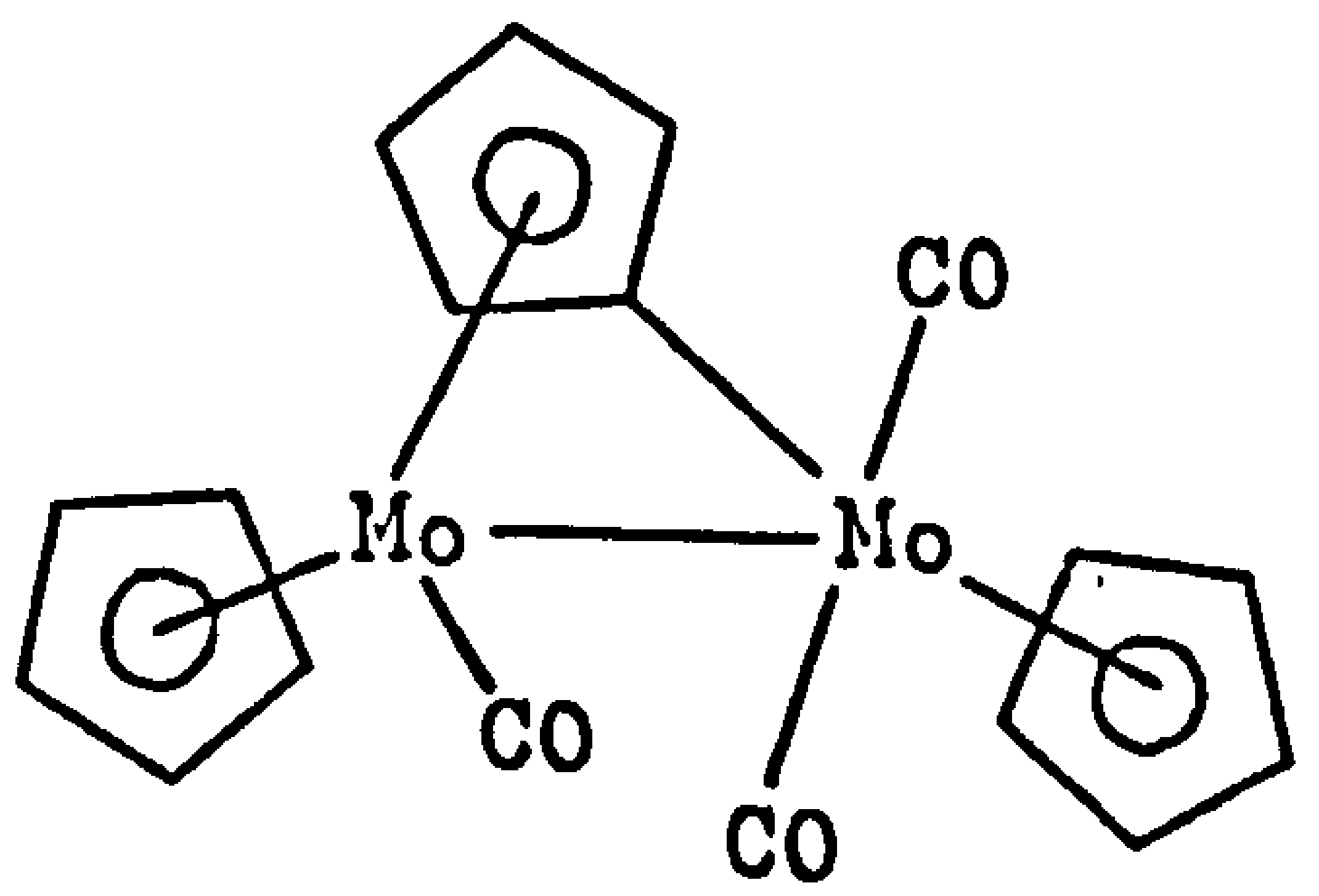
Complex		δ(ppm)	$^{1}J_{PtC}$ (Hz)	$^{2}J_{PtC}$ (Hz)	Ref.
trans-[Pt(CNBu^{t})$_2$ (η^1-allyl) (η^1-C_5H_5)]	η^1-C_5H_5	+111.4	35	-	91
cis-[Pt(CNBu^{t})$_2$ (η^1-allyl) (η^1-C_5H_5)]	η^1-C_5H_5	+114.9	76	-	91
[Pt(η^3-allyl) (η^5-C_5H_5)]	η^5-C_5H_5	+90.7	31	-	91
[Pt$_2$(μ-allyl) (μ-C_5H_5)(PMe$_3$)$_2$]	μ-C_5H_5	+84.6	25.7	-	183
[Pt$_2$(μ-allyl) (μ-C_5H_5)(PPr$_3^{i}$)$_2$]	μ-C_5H_5	+84.9	27.9	-	183

The ^{13}C nmr spectra of bridging C_5H_5 groups in platinum complexes of the type $[Pt_2(\mu\text{-allyl})(\mu\text{-}C_5H_5)L_2]$ has chemical shifts in the range +84 to +85 ppm, and J_{PtC} values of 25 to 28 Hz,[183] (see table 16).

The ^{13}C nmr data for the "Asymmetric Dimer" is most consistent with a π-bonded, terminal cyclopentadienyl ring. No platinum-carbon coupling could be observed, and some of the $\pi\text{-}C_5H_5$ rings in complexes in table 16 have low values of J_{PtC}, e.g. 3.8 Hz for $[Pt(Me)(P(OMe)_3(\eta^5\text{-}C_5H_5)]$. A bridging C_5H_5 is also less likely in view of the bridging CO ligand, and the need for one phosphine to be bent away from the platinum-platinum bond. The ^1H nmr spectrum of the "Asymmetric Dimer" is also most consistent with a π-bonded C_5H_5. In "Werner-type" complexes, like the two in table 16, J_{PtH} values are in the range 27 to 31 Hz, with J_{PH} in the range 1.8 to 2.4 Hz.[183] In the "Asymmetric Dimer", the ^1H and ^{13}C nmr spectra demonstrate that other types of bridging cyclopentadienyl, found in dimers of other metals,[184] can not be present. The bridging C_5H_4 units, either $\eta^1,\eta^1\text{-}\mu\text{-}C_5H_4$, or $\eta^1,\eta^5\text{-}\mu\text{-}C_5H_4$, in the complexes below do not have equivalent ^1H or C atoms, as in the "Asymmetric Dimer".

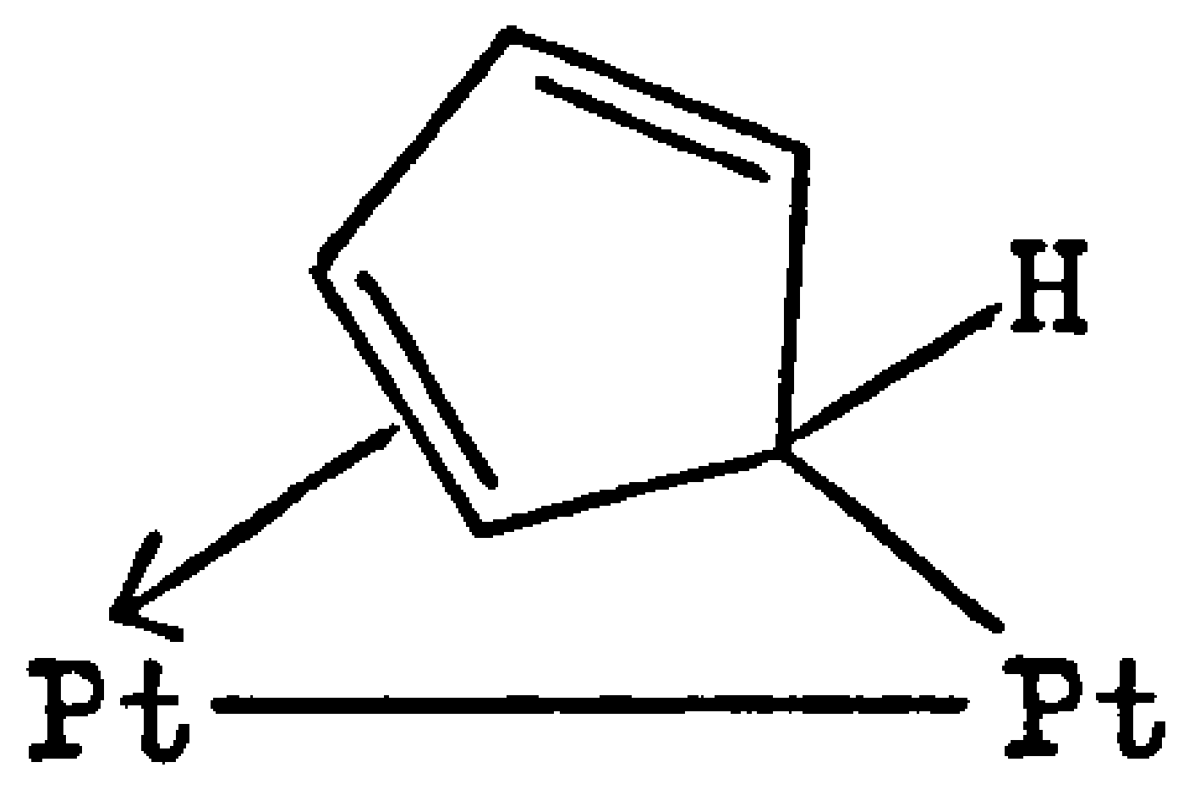


$\eta^1,\eta^1\text{-}\mu\text{-}C_5H_4$



$\eta^1,\eta^5\text{-}\mu\text{-}C_5H_4$

A fluxional $\eta^1,\eta^2-\mu-C_5H_5$ group would be possible, but this would be expected to show a set of satellites with J_{PtH} typical of a σ-bonded C_5H_5 ring, 25 to 40 Hz, and to show a second set of platinum satellites due to coupling



through the double-bond. "Ring-whizzing" of such a C_5H_5 group might also be expected to be a higher energy process than for a simple, σ-bonded ring in $[PtCl(C_5H_5)(CO)L]$ isomer (I). The low temperature ^1H nmr spectrum of "Asymmetric Dimer" was obtained. At -60°C the C_5H_5 peak was broadened such that J_{PH} could not be resolved, but the broadening was no more than that expected due to solvent-stiffening. "J_{PtH}" could still be observed at this temperature. Furthermore, this bridging mode is very similar to that in the "Werner-type" dimeric complexes, and might have the same steric constraint that it would be difficult to bend a phosphine-platinum bond far enough away from the platinum-platinum bond to account for a small $^2J_{PtP}$ value.

Although the C_5H_5 protons couple to both phosphorus atoms in the "Asymmetric Dimer", the C_5H_5 carbon atoms only couple to one phosphine, J_{PC} = 2.5 Hz. Coupling to the other phosphorus atom is either zero or very small.

To summarise, the spectroscopic data gives the following information on the "Asymmetric Dimer".

The "Asymmetric Dimer" has a platinum-platinum bond with one phosphine trans to the platinum-platinum bond and one cis to it. The two phosphines are on different platinum atoms, since J_{PP} is too small for cis-phosphines on the same platinum atom. The "Asymmetric Dimer" has a bridging carbonyl, which is cis to both phosphines, and only couples to the phosphine cis to the platinum-platinum bond. There is only one C_5H_5 ring in the dimer, and this is a π-bonded terminal ring. The "Asymmetric Dimer" must also contain halide, since a change in the ^{31}P nmr parameters is obtained on changing the halide present.

A possible structure of the "Asymmetric Dimer" is shown in fig. 31.

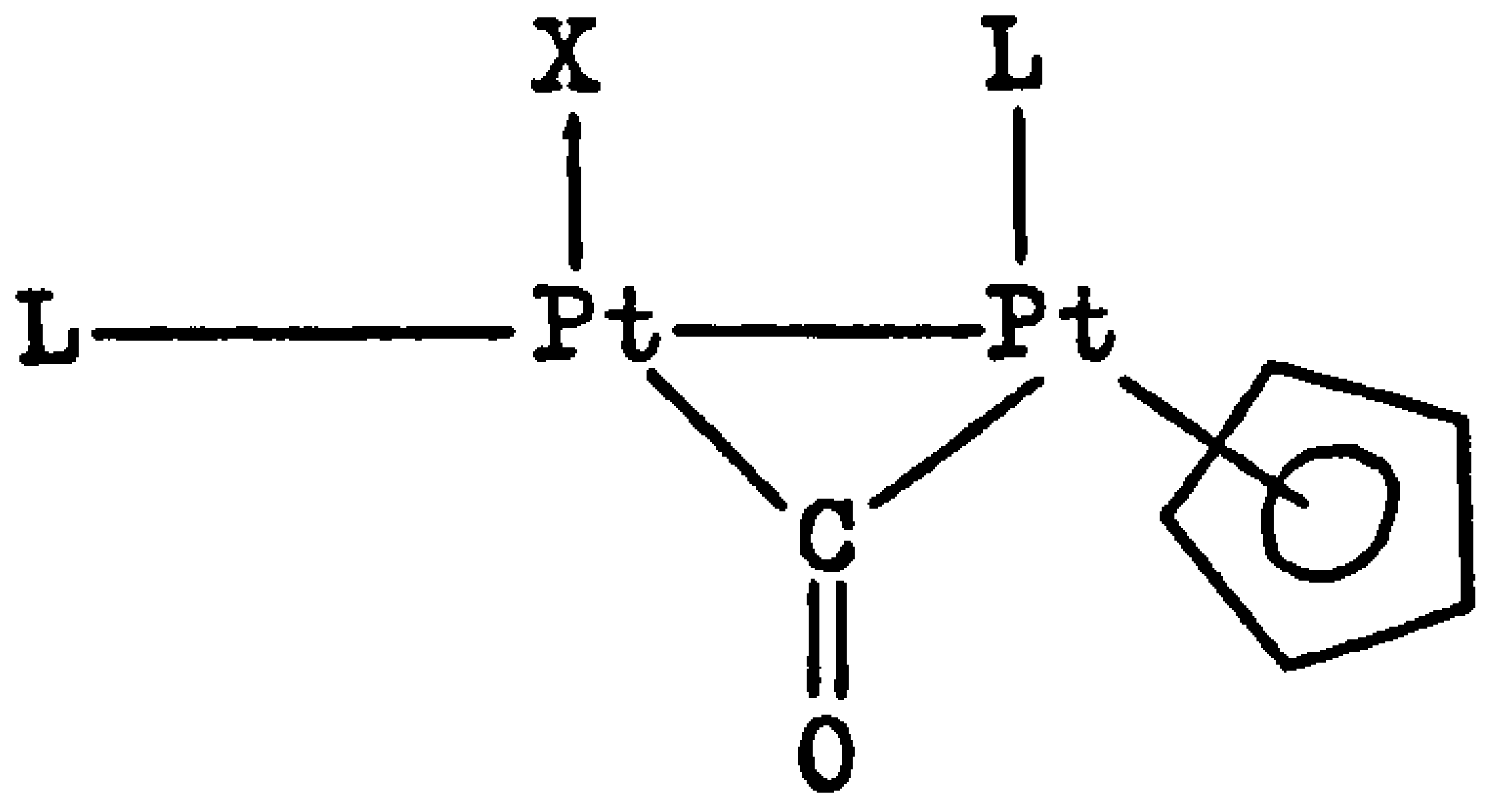


figure 31.

A minor variation of the structure in figure 31 may also be a possibility, (figure 32), and this is more consistent with the ^{13}C data, having CO trans to X and the organic group.

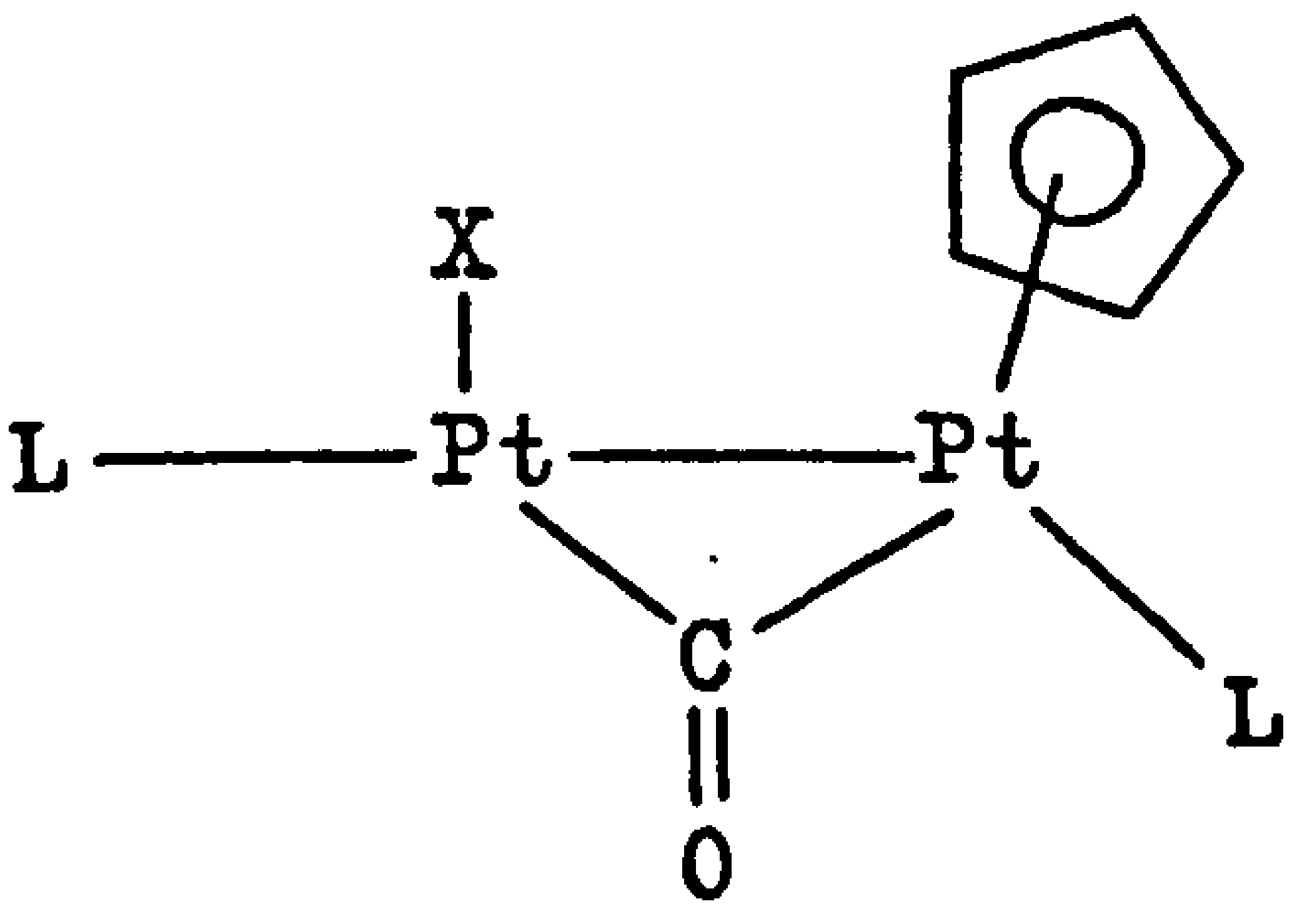
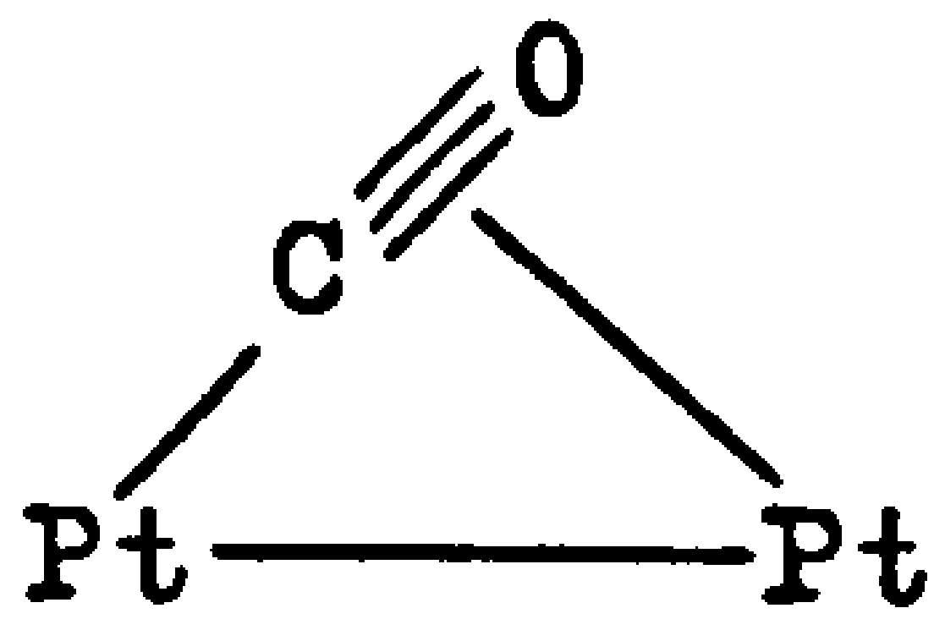


figure 32.

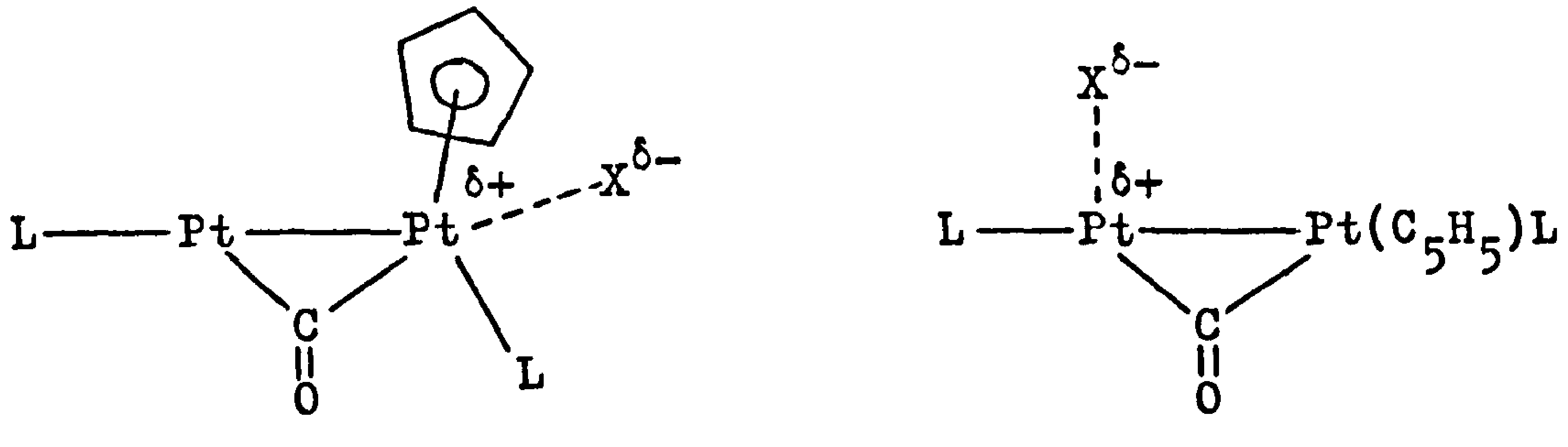
The phosphine with the small $^2J_{PtP}$ value need not be bent at 90° to the platinum-platinum bond to achieve a value of < 30 Hz. In $[Pt_2(\sigma\text{-}C{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SiMe_2)(PR_3)_2]$, PPtPt angles of 165.2° and 148.0° lead to $^2J_{PtP}$ values of 308 Hz and 0 Hz respectively.[174] The C_5H_5 ligand is fairly large and bulky; Tolman[185] gives it a cone angle of 136°, and PPh_3 a cone angle of 145°. Also, whereas phosphines can frequently mesh with each other and occupy less space than their cone angles indicate, the C_5H_5 has a very large steric demand, e.g.:- in complexes such as $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$, the geometry is pseudo-octahedral with C_5H_5 occupying 3 coordination sites, and PRuCl bond angles of 89.1° and 90.4° and a PRuP bond angle of 103.9° were found.[186] Thus, in either structure proposed for the "Asymmetric Dimer", the C_5H_5 ring would have a large enough steric demand to bend the platinum-phosphorus bond away from the platinum-platinum bond.

The only inconsistency in the structures in figures 31 and 32 is the absence of a Pt-Cl absorbance in the i.r. spectrum. The i.r. spectrum of the impure "Asymmetric Dimer" isolated material was obtained as a KBr disc, but no Pt-Cl stretch was observed. The i.r. spectrum was also obtained as a nujol mull, in case there had been Cl/Br exchange with the KBr disc, but again no absorbance could be found. A polythene disc was also used, which allowed the i.r. spectrum to be observed down to $180 cm^{-1}$, but there was no peak present.

Metal-chloride stretching frequencies increase as the oxidation state of the metal increases and the coordination number decreases.[187] Thus, in the proposed structure for the "Asymmetric Dimer", the platinum-chloride stretch should be at lower frequency than in four-coordinate platinum (II) complexes, where ν_{PtCl} lies in the range 270 - 340 cm^{-1}, depending on the other ligands present.[11] Some platinum (I) dimers with platinum-platinum bonds and terminal chlorides are known. For example, in $[Pt_2Cl_4(CO)_2]^{2-}$, Pt-Cl stretches are 315 and 310cm^{-1} for Cl trans to CO and 269 and 240cm^{-1} for Cl trans to platinum.[188] The complex $[Pt_2Cl_2(\mu\text{-}CO)\text{-}(\mu\text{-}dppm)_2]$ has ν_{Pt-Cl} at 229cm^{-1}, and it is suggested that the presence of a carbonyl bridge decreases ν_{Pt-Cl}.[189] This latter complex has an unusually low ν_{CO} of 1638 cm^{-1}, and it is suggested that CO is acting as a 4-electron donor bridge.



It seems unlikely that the Pt-Cl stretch in the "Asymmetric Dimer" could occur at less than 180cm^{-1}, yet no such absorbance can be observed. Even if the halide was bridging instead of terminal, and thus with a lower ν_{Pt-Cl}, it should still be possible to observe the stretch in the i.r. spectrum. Another possibility is that the halide is not bonded to platinum, but is ionic. Although the ^{31}P nmr parameters change on altering the halide, the effect on the upfield phosphine, (on the same platinum as C_5H_5), is greater than the effect on the downfield phosphine, (on the same platinum as the halide). This could be caused by a closely associated halide/dimer ion pair, where the two platinum atoms are formally platinum (o) and platinum (II), and would lead to a structure of the type in figure 33(a), or a semi-ionic bond between platinum and halide as in (b).



(a) (b)

figure 33.

It is interesting to note that changing the solvent has a larger effect on the "Asymmetric Dimer" ^{31}P parameters than changing the halide, (see table 17). In fact, changing from $CDCl_3$ to benzene has as large an effect on the downfield phosphine's $^{1}J_{PtP}$ as changing the phosphine from PPh_3 to PMe_2Ph. However, there does not seem to be any rationalisation of this effect, since acetone, THF, benzene and methylene chloride all alter the ^{31}P parameters in the same direction.

"Asymmetric Dimer" and $AgSO_3CF_3$

The addition of a silver salt to an ionic complex should remove the halide as AgX and leave the cationic complex unchanged. However, addition of $AgSO_3CF_3$ to a $CDCl_3$ solution of "Asymmetric Dimer" caused immediate decomposition to a number of species. These were:- a species which appeared to be an AA'X pattern, ^{31}P parameters $\delta = 0.2$ppm, $^{1}J_{PtP} = 3774$ Hz, $^{2}J_{PtP} = -156$ Hz and $^{3}J_{PP} = 140$ Hz (signs

Table 17:- ^{31}P nmr of "Asymmetric Dimer" complexes in different solvents at 25°C.

Phosphine	Halide	Solvent	δP_1 (ppm)	$^1J_{PtP}$ (Hz)	$^2J_{PtP}$ (Hz)	δP_2 (ppm)	$^1J_{PtP}$ (Hz)	$^2J_{PtP}$ (Hz)	$^3J_{PP}$ (Hz)
PMe_2Ph	Cl	$CDCl_3$	+10.0	5367	872	-25.1	4690	31.0	7.2
PMe_2Ph	Cl	THF (a)	+8.7	5294	911	-24.4	4787	31.8	6.8
PMe_2Ph	Cl	$(CH_3)_2CO$ (a)	+9.3	5334	903	-24.2	4712	30.0	6.5
PPh_3	Cl	$CDCl_3$	+34.0	5505	862	+9.1	5006	unres.	9.4
PPh_3	Cl	C_6H_6 (a)	+33.4	5369	878	+9.7	5084	unres.	9.4
PPh_3	Cl	CH_2Cl_2 (a)	+33.5	5455	869	+9.5	5015	unres.	9.6

(a) C_6D_6 added as a locking signal.

THF = tetrahydrofuran.

unres. = unresolved, (<25 Hz).

are relative only); $[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]^+$ (table 7), an unidentified species at $\delta = +4.9$ ppm and $[Pt(\eta^5-C_5H_5)(PPh_3)_2]^+$ (table 7). Some Ph_3PO was also produced.

$AgSO_3CF_3$ removing the chloride from the "Asymmetric Dimer" structure in figure 32 would leave a coordinatively unsaturated molecule which might react in two ways. Either the molecule could break up, and $[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]^+$ is equivalent to one end of the proposed "Asymmetric Dimer" structure, or the C_5H_5 might move into a bridging position and form a complex as shown in figure 34 below.

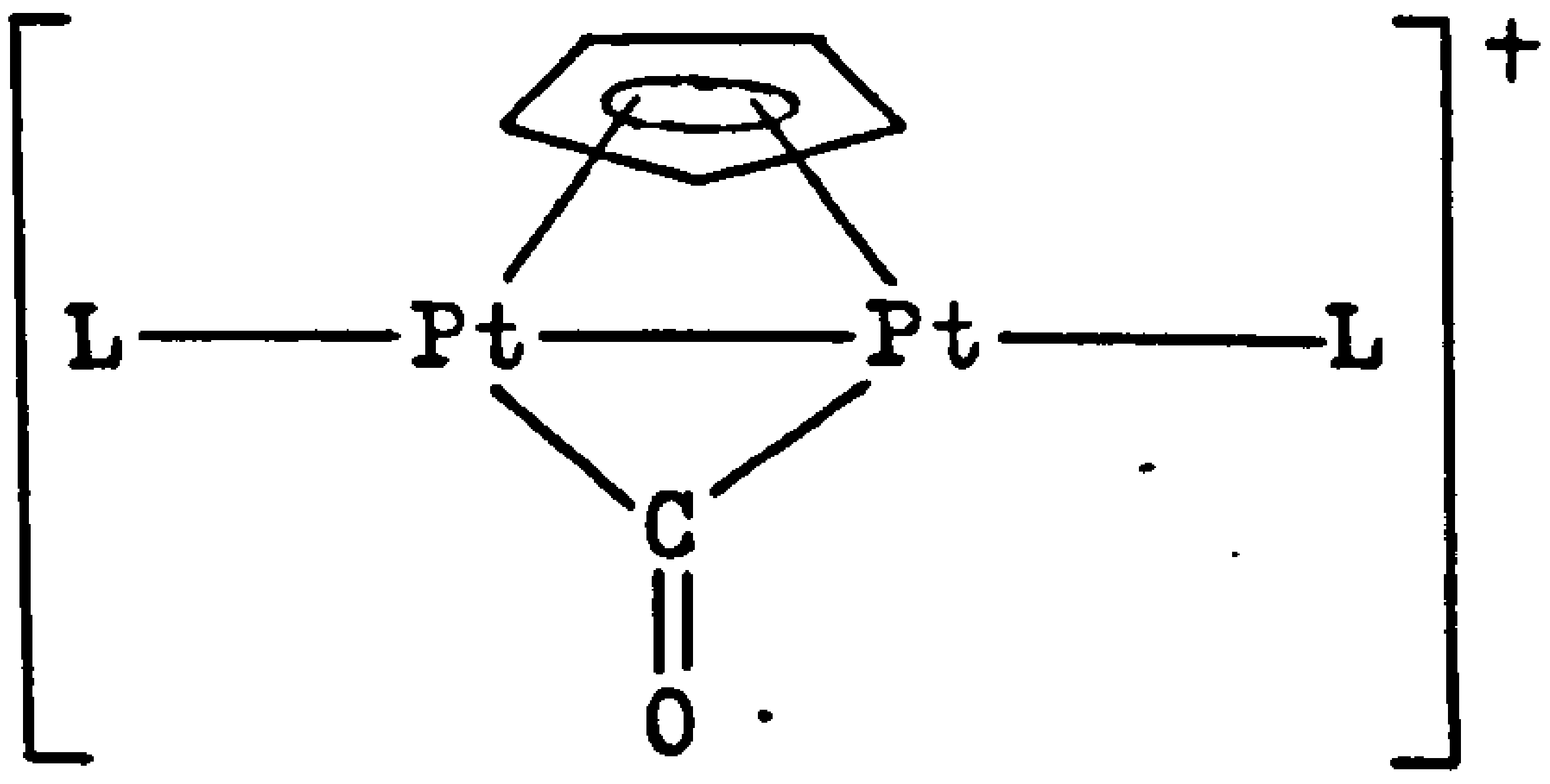


figure 34.

The compound in figure 34 is similar to those made by Werner with a bridging C_5H_5 and metal-metal bond, and a complex such as fig. 34 would exhibit an AA'X pattern in its ^{31}P spectrum. Although the reaction with $AgSO_3CF_3$ was complicated, it can thus be interpreted on the basis of the "Asymmetric Dimer" having the structure shown in figure 32.

Should some of the "Asymmetric Dimer" break up on removal of chloride, $[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]^+$ could be produced along with an unsaturated fragment $[PtPPh_3]$, which could release phosphine to produce $[Pt(\eta^5-C_5H_5)(PPh_3)_2]^+$, by CO displacement, and Ph_3PO by oxidation.

"Asymmetric Dimer" and added phosphine or arsine

When phosphine was added to a solution of "Asymmetric Dimer" at low temperature, the dimer was not cleaved, as normally happens on adding phosphine to a dimer. For example, on addition of PMe_2Ph to $[Pt_2Cl_4(PMe_2Ph)_2]$, the dimer is cleaved to give, initially $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ at low temperature.[190] Addition of PPh_3 to the "Asymmetric Dimer" made from <u>cis</u>-$[PtCl_2(CO)(PPh_3)]$ produced a new dimeric platinum complex containing three phosphines and a metal-metal bond. Two of the phosphorus atoms had very similar chemical shifts, and gave rise to a 2nd order pattern for the central peaks (66% of Pt with I=0), but the ^{195}Pt satellites were 1st order. The other phosphine was far enough away in chemical shift from the other two to give a 1st order pattern. The ^{31}P nmr parameters at -60°C of this species are:-

δ = +27.5 and +27.3ppm (2P atoms), with 1st order ^{195}Pt satellites:-

P_1 $^1J_{PtP}$ = 3025 Hz, J_{PP} = 23.7 Hz (doublets).

P_2 $^1J_{PtP}$ = 4646 Hz, $^2J_{PtP}$ = 850 Hz, J_{PP} = 23.7 and 11.9 Hz (d of d.).

δ = + 10.1 ppm (1P), $^1J_{PtP}$ = 4738 Hz, $^2J_{PtP}$ = 22.2 Hz, J_{PP} = 9.8 Hz (d).

This new dimer is stable at -60°C in the presence of excess PPh_3, and the peaks for the dimer and PPh_3 are sharp, indicating that there is no phosphine exchange occurring.

A ^{1}H nmr spectrum at -60°C had a broad signal at +5.40 ppm, neither phosphorus-proton or platinum-proton coupling being resolved. At +10°C, the signal began to show some doublet structure, with J_{PH} = 1.2 Hz, but each peak of the doublet appeared to be broadened by further couplings.

Although the new dimer is stable at -60°C in the presence of excess PPh_3, on warming to room temperature it reacts further. With a brief warming to room temperature the first cleavage products observed were $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ and a species with parameters δ = +12.7 ppm, $^1J_{PtP}$ = 3550 Hz, (at -60°C) which is identified as $[Pt(PPh_3)_3(CO)]$, (^{31}P nmr in toluene at -80°C, +12.3 ppm, $^1J_{PtP}$ = 3537 Hz).^{191} On warming to room temperature for 30 minutes, $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ was the major product.

$$\begin{array}{l}\text{"Asymmetric Dimer"} \xrightarrow{PPh_3} \text{"New Dimer"} \xrightarrow{PPh_3} [Pt(PPh_3)_3(CO)] + \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad [Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+\end{array}$$

The ^{31}P parameters show that the new dimer has one phosphine (P_2) <u>trans</u> to a platinum bond, with a second phosphine (P_1) <u>cis</u> to it on the same platinum atom. The third phosphine (P_3) is on the other platinum atom. P_2 couples to P_1 (23 Hz, typical coupling of <u>cis</u>-phosphines) and to P_3 (9.8 to 11.9 Hz), but P_1 and P_3 do not couple to each other. The new dimer still contains C_5H_5 (detected by ^{1}H nmr) and CO, since both of these are present in the fragments after cleavage. This suggests the following structure for the new dimer,

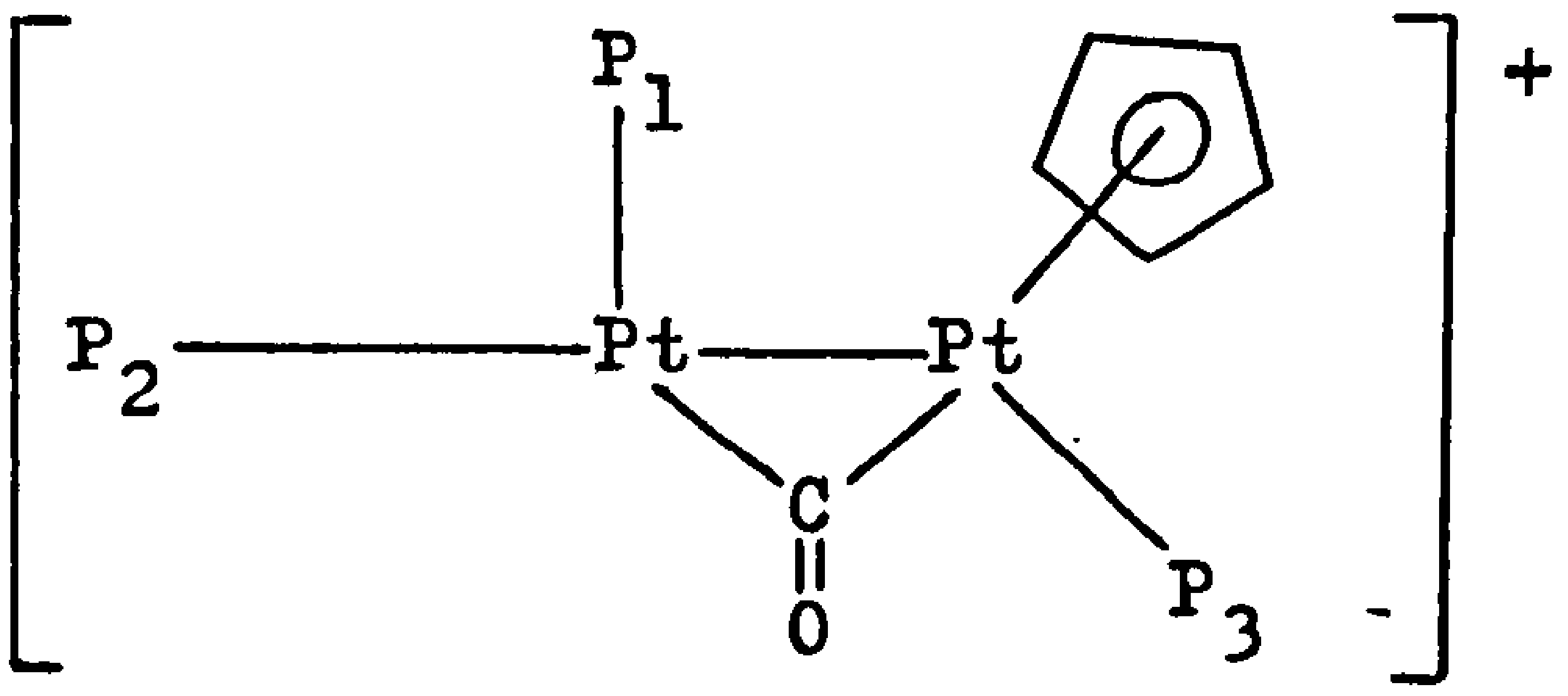


figure 35.

This would then be obtained from "Asymmetric Dimer" by substitution of Cl by PPh_3. Cleavage of the dimer in figure 35 by excess phosphine could then produce $[Pt(PPh_3)_3(CO)]$ and $[Pt(\eta^5-C_5H_5)(PPh_3)_2]^+$, which were the first species observed. The above structure is supported by the result of using ^{13}CO-labelled "Asymmetric Dimer". The spectrum of the new dimer obtained from PPh_3 addition to ^{13}CO-labelled "Asymmetric Dimer" (PPh_3 and Cl) was first order with the following parameters,

P_1 +27.6 ppm (d of d), $^2J_{CP}$= 113 Hz, $^2J_{PP}$ = 23.4 Hz with $^1J_{PtP}$ = 3028 Hz.

P_2 +26.9 ppm, (d of d), $^2J_{PP}$ = 23.0 Hz, $^3J_{PP}$ = 11.8 Hz, with $^1J_{PtP}$ = 4625 Hz and $^2J_{PtP}$ = 855 Hz.

P_3 +10.0 ppm, (broad d.) $^2J_{CP}$ small and $^3J_{PP}$ small, unresolved with $^1J_{PtP}$ = 4742 H z.

The ^{13}C - ^{31}P coupling of 113 Hz between ^{13}CO and P_1 shows that these two groups are almost fully trans to each other. The ^{13}C - ^{31}P coupling constant in [PtCl(R)(CO)L] isomer (III), CO trans to L, is about 150 Hz.[154] The small coupling of ^{13}CO to P_3 suggests that the CO ligand is still in a bridging position, as this is the same phosphine that ^{13}CO couples to in "Asymmetric Dimer".

Addition of PPh_3 to the "Asymmetric Dimer" produced from cis-$[PtCl_2(CO)(PMe_2Ph)]$ at -60°C also produced a new dimer containing three phosphine ligands and a platinum-platinum bond, analogous to the previous one. This had parameters, at -60°C, of,

P_1 +29.2ppm, $^1J_{PtP}$ = 2818 Hz, $^2J_{PP}$ = 22.0 Hz (d)

P_2 -3.1 ppm, $^1J_{PtP}$ = 4360 Hz, $^2J_{PtP}$ = 851 Hz, $^2J_{PP}$ = 22.0 Hz and $^3J_{PP}$ = 9.7 Hz (d of d).

P_3 -22.2 ppm, $^1J_{PtP}$ = 4320 Hz, $^2J_{PtP}$ = 14.2 Hz, $^3J_{PP}$ = 9.1 Hz (d).

From the chemical shifts of the phosphines, it is clear that P_1 is PPh_3 and P_2 and P_3 are PMe_2Ph. This species was also stable at -60°C in the presence of excess PPh_3 and was the major product after being left at < -60°C for 12 hours. During this time some $[PtCl(PMe_2Ph)_3]^+$, $PhMe_2PO$ and some $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ were produced, along with a species which is apparently either another isomer of the dimer with one PPh_3 and two PMe_2Ph ligands or the analogous dimer with three PMe_2Ph ligands. Only P_1 and P_3 could be observed, and these were obviously PMe_2Ph (by their chemical shifts). The parameters were :-

P_1 -5.4ppm, $^1J_{PtP}$ = 2670 Hz, $^2J_{PP}$ = 20.6 Hz (d).

P_2 unobserved

P_3 -20.8ppm, $^1J_{PtP}$ = 4370 Hz, $^2J_{PtP}$ not observed, $^3J_{PP}$ = 10.4 Hz (d).

On warming to room temperature, the major products were $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ and cis-$[PtCl_2(PMe_2Ph)_2]$.

A similar dimer was obtained on addition of $AsPh_3$ to the "Asymmetric Dimer" made from <u>cis</u>-$[PtCl_2(CO)(PPh_3)]$. In this case, only two phosphorus signals were obtained in the low temperature ^{31}P nmr spectrum, corresponding to P_2 and P_3 in previous dimers, with $AsPh_3$ replacing P_1. The parameters at -60°C were:-

P_2 +28.8ppm, $^1J_{PtP}$ = 4937 Hz, $^2J_{PtP}$ = 795 Hz, $^3J_{PP}$ = 11.6 Hz (d).

P_3 +9.4ppm, $^1J_{PtP}$ = 4669 Hz, $^2J_{PtP}$ = 24.8 Hz, $^3J_{PP}$ = 11.6 Hz (d).

Whereas addition of PPh_3 to "Asymmetric Dimer" was rapid, the addition of $AsPh_3$ was slow, and reversible. When a solution of the new dimer with one $AsPh_3$ and two PPh_3 was left standing at -60°C "Asymmetric Dimer" was regenerated, presumably via loss of $AsPh_3$ and oxidation of this to Ph_3AsO. This is consistent with added ligand (PPh_3 or $AsPh_3$) substituting the chloride which can return to coordinate to form "Asymmetric Dimer" if the added ligand is lost. Addition of $AgSO_3CF_3$ to the dimer containing one $AsPh_3$ and two PPh_3 ligands did not alter its parameters, and the compound was stable at room temperature. Its parameters at 25°C were:-

P_2 +29.6ppm, $^1J_{PtP}$ = 4976 Hz, $^2J_{PtP}$ = 834 Hz, $^3J_{PP}$ = 11.6 Hz (d).

P_3 +8.9ppm, $^1J_{PtP}$ = 4705 Hz, $^2J_{PtP}$ = 33.0 Hz, $^3J_{PP}$ = 11.6 Hz (d).

These results show that the ligand added to "Asymmetric Dimer" is the one which is trans to CO in the new dimer formed, and the reaction is best described, as shown by figure 36, as a substitution reaction.

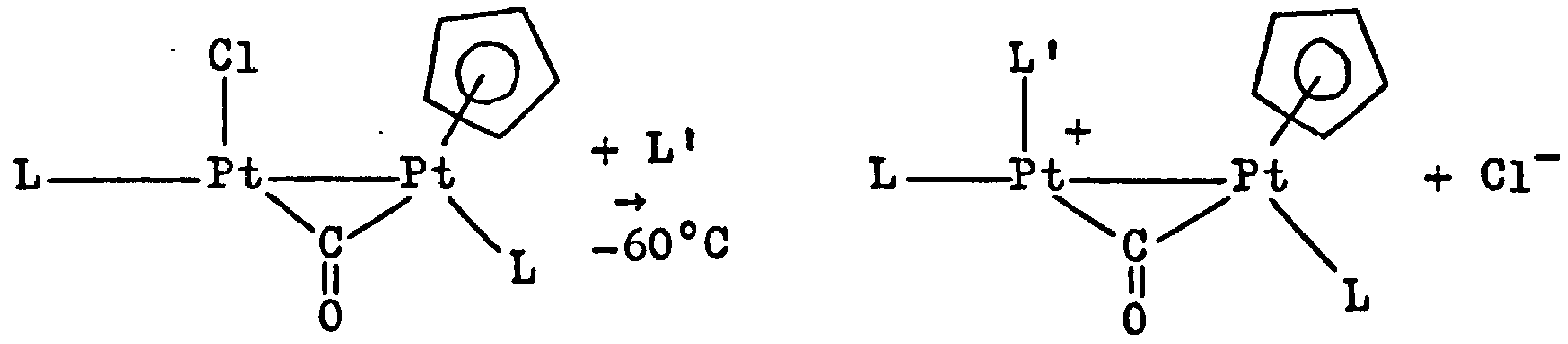
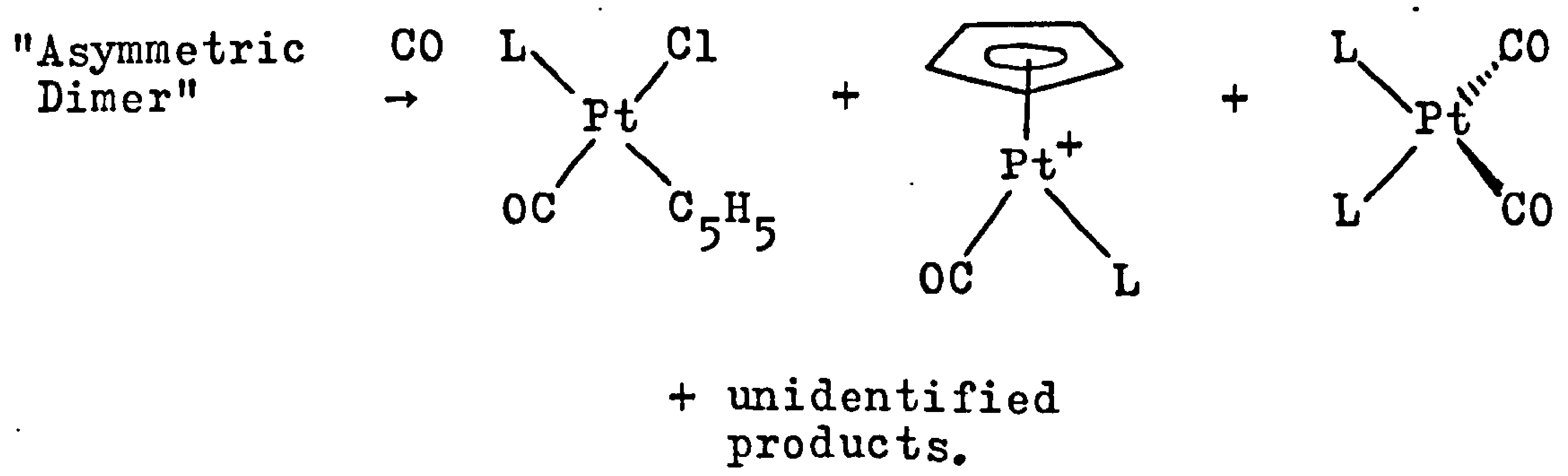


figure 36.

"Asymmetric Dimer" and CO

When carbon monoxide was passed through a solution of "Asymmetric Dimer", (made from cis-[$PtCl_2(CO)(PPh_3)$]), at -60°C, the dimer was cleaved to give a large number of products. The major products were [$PtCl(C_5H_5)(CO)(PPh_3)$] isomer (I), an unidentified species with ^{31}P parameters δ = +16.1 ppm, $^1J_{PtP}$ = 3823 Hz, and [$Pt(\eta^5-C_5H_5)(CO)(PPh_3)$]$^+$. Less abundant products were a species, δ = +19.3ppm, $^1J_{PtP}$ = 3402 Hz, a species δ = +5.5ppm, $^1J_{PtP}$ = 3079 Hz, $^3J_{PtP}$ = 110 Hz, a species δ = +7.8ppm, $^1J_{PtP}$ = 3203 Hz identified as [$Pt(PPh_3)_2(CO)_2$], (^{31}P nmr in toluene at -80°C, +7.7ppm, $^1J_{PtP}$ = 3232 Hz),[191] and the new dimer produced by PPh_3 addition to "Asymmetric Dimer". The byproduct with parameters +20.7ppm, $^1J_{PtP}$ = 3435 Hz, produced when the "Asymmetric Dimer" is made, also seemed to increase in intensity. On warming the solution to room temperature this byproduct and [$PtCl(C_5H_5)(CO)(PPh_3)$] isomer (I) were the major species present, along with some "Asymmetric Dimer" which had been regenerated.

The reaction was repeated using ^{13}CO-labelled "Asymmetric Dimer" to try and identify any products containing CO. However, on bubbling CO through a solution of ^{13}CO-labelled "Asymmetric Dimer" at -60°C, all of the ^{13}CO was lost from the dimer while 64% was still uncleaved. At this time, none of the cleavage products appeared to contain ^{13}CO either. The same cleavage products were obtained as in the previous reaction.



The identified products are not inconsistent with the structure in figure 32 proposed for the "Asymmetric Dimer", but the complexity and large number of products makes it difficult to draw any definite conclusions about this reaction.

Irreproducibility of "Asymmetric Dimer" Reactions

It has already been stated that reactions producing "Asymmetric Dimer" are not reproducible, with both the yield and the byproducts being variable. Reactions between cis-$[PtCl_2(CO)(PPh_3)]$ and 2 equivalents of TlC_5H_5 gave, on occasion, a high yield of cis-$[Pt(C_5H_5)_2(CO)(PPh_3)]$ which was used in the cyclopentadienyl transfer studies, (chapter 2). More often the reaction gave "Asymmetric Dimer" as 70% to 90% of the total ^{31}P intensity of the products when performed on an nmr scale, (ca. 0.055mmol. of cis-$[PtCl_2(CO)(PPh_3)]$ in 0.5ml $CDCl_3$), and less on a larger scale. The most frequently encountered byproduct was the species with parameters δ = +20.7 ppm, $^1J_{PtP}$ = 3435 Hz. Other common byproducts were cis-$[PtCl_2(PPh_3)_2]$ and Ph_3PO, which indicate that some loss of phosphine from platinum can often occur during the reaction. The rate of formation of "Asymmetric Dimer" from cis-$[PtCl_2(CO)(PPh_3)]$ and 2 equivalents of TlC_5H_5 also varied considerably, from as little as 4 hours to longer than 2 days in reactions where conditions appeared to have been the same.

a) Stoicheometric Effects

Varying the amount of TlC_5H_5 used, provided it was more than 1 equivalent, did not appear to affect the yield of "Asymmetric Dimer" ultimately obtained, although it may have had an effect on the rate of the reaction. cis-$[PtCl_2(CO)(PPh_3)]$ and 2.17 equivalents of TlC_5H_5 in $CDCl_3$ produced a solution containing "Asymmetric Dimer" (75% of the ^{31}P intensity), the species with δ = +20.7 ppm, $^1J_{PtP}$ = 3435 Hz (19%) and $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) (6%) after 23 hours. cis-$[PtCl_2(CO)(PPh_3)]$ and 1.50 equivalents of TlC_5H_5, in an identical volume of solvent and concentration of platinum complex, under identical conditions, produced a solution mixture after 2 days which was identical to that obtained from 2.17 equivalents of TlC_5H_5 after 23 hours. cis-$[PtCl_2(CO)(PPh_3)]$ and 1.00 equivalents of TlC_5H_5, under identical conditions, produced, initially only $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I), but after 3 days produced a solution containing "Asymmetric Dimer" (37%), isomer (I)

(31%), cis-[$PtCl_2(CO)(PPh_3)$] (16%), cis-[$PtCl_2(PPh_3)_2$] (9%) and δ = +20.7 ppm.

b) Solvent Effects

$CDCl_3$ and D_2O were shaken together over a five hour period, then the solvents were separated and the $CDCl_3$ was used without drying first. An nmr tube was filled with D_2O and heated for the same period, then dried in an oven. When cis-[$PtCl_2(CO)(PPh_3)$] and TlC_5H_5 (2.07 equivalents) were allowed to react in this $CDCl_3$, "Asymmetric Dimer" was produced as normal. The ^1H nmr spectrum showed that there was no deuterium present in either C_5H_6 or the C_5H_5 of "Asymmetric Dimer", hence neither water present in the solvent, nor on the glass of the nmr tube, is the source of the proton in C_5H_6, and does not influence the course of the reaction.

Using $CHCl_3$ which had been dried by passing down a column of silica gel and had been treated with $MgSO_4$, and then had N_2 bubbled through to remove dissolved O_2, gave the same result as using $CDCl_3$ for the solvent. cis-[$PtCl_2(CO)(PPh_3)$] and TlC_5H_5 (2.25 equivalents) in treated $CHCl_3$ produced a mixture of "Asymmetric Dimer" (84% of ^{31}P intensity) and the species with parameters +20.7 ppm, $^1J_{PtP}$ = 3435 Hz. However, when $CHCl_3$ which was not treated in any way was used, the reaction between cis-[$PtCl_2(CO)$-(PPh_3)] and TlC_5H_5 produced a mixture of "Asymmetric Dimer" and a new species with parameters +11.1 ppm, $^1J_{PtP}$ = 5644 Hz. The new species was initially the major product, but after 5 days "Asymmetric Dimer" had increased relative to it, and a second new species, with parameters +18.8 ppm,

$^1J_{PtP}$ = 3092 Hz had also appeared.

Since the presence of moisture in $CDCl_3$ had no effect on the reaction, it could not be the presence of H_2O in the $CHCl_3$ which led to the production of the new complexes. $CHCl_3$ contains 2% v/v ethanol as a preservative, while $CDCl_3$ does not. When cis-[$PtCl_2(CO)(PPh_3)$] and 2 TlC_5H_5 were allowed to react in $CDCl_3$ to which some EtOH had been added, the new species with parameters +11.1 ppm, $^1J_{PtP}$ = 5613 Hz was the major product, with some "Asymmetric Dimer" and the other new species, +18.8 ppm, $^1J_{PtP}$ = 3075 Hz.

Similar results were obtained when cis-[$PtCl_2(CO)(PPh_3)$] and 2 TlC_5H_5 were allowed to react in $CDCl_3$ to which MeOH or Bu^nOH had been added. In each case, the new species, parameters +10.9 ppm $^1J_{PtP}$ = 5531 Hz (in $CDCl_3$ + MeOH), and +11.2 ppm $^1J_{PtP}$ = 5622 Hz (in $CDCl_3$ + BuOH) was the major product, and the other new species, parameters +19.1ppm, $^1J_{PtP}$ = 3017 Hz (in $CDCl_3$ + MeOH) and +18.7 ppm, $^1J_{PtP}$ = 3075 Hz (in $CDCl_3$ + BuOH) was also produced. The highest yield of the new complex with large J_{PtP} was obtained in the presence of BuOH. Either the presence of alcohol inhibits "Asymmetric Dimer" formation, or encourages the formation of a new platinum complex.

When a large scale reaction between cis-[$PtCl_2(CO)(PPh_3)$] and 2 TlC_5H_5 was performed in $CHCl_3$ no "Asymmetric Dimer" was produced. The only product was isolated as a yellow oil, and proved to be the new species, with parameters in $CDCl_3$ of δ = +11.2 ppm, $^1J_{PtP}$ = 5632 Hz, contaminated with a small amount of Ph_3PO. A ^1H nmr spectrum of this yellow oil showed that the complex contained a π-C_5H_5 ring, coupled to one phosphine, at +5.61 ppm, J_{PtH} = 13.2 Hz,

J_{PH} = 1.3 Hz (d). On leaving this species in $CDCl_3$ for 1 week, it reacted further to produce large amounts of "Asymmetric Dimer", Ph_3PO and a small amount of the other new species, +18.8 ppm, $^1J_{PtP}$ = 3089 Hz. A similar species was obtained in a large scale reaction between cis-$[PtCl_2(CO)(PEt_3)]$ and 2 TlC_5H_5 in $CHCl_3$ along with "Asymmetric Dimer". This had ^{31}P parameters δ = +12.2 ppm, J_{PtP} = 5223 Hz and ^1H nmr parameters δ = +5.74ppm, J_{PtH}= 11.5Hz, J_{PH}= 1.4Hz (d).

The species, δ = +11.2 ppm, $^1J_{PtP}$ = 5632 Hz must be a complex which can change into "Asymmetric Dimer" with time, and hence must contain CO, and have Cl^- present either coordinated, or as a counterion, in addition to PPh_3 and π-C_5H_5. The simplest compound fulfilling these requirements would be $[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]^+Cl^-$, but the parameters for this complex are known, and this cannot be the new complex. Other, monomeric complexes are unlikely, since $[Pt(\eta^5-C_5H_5)Cl(PPh_3)]$ is unknown, and there is no way in which this could convert to "Asymmetric Dimer" without CO being present. An impure solid was obtained which was mainly the species with parameters δ = +11.2 ppm, $^1J_{PtP}$ = 5632 Hz (67% of the total intensity) which was contaminated with Ph_3PO (17%) and the other species, +18.8 ppm, $^1J_{PtP}$ = 3089 Hz (16%). A KBr disc i.r. spectrum of this solid had a strong absorbance at 1630cm^{-1} (broad). It seems likely that this species is a dimer, symmetrically substituted, with one phosphine and one C_5H_5 on each platinum. No two-bond platinum-phosphorus coupling could be observed, but this does not exclude the possibility of having a platinum-

platinum bond. The PPtPt angle could be such that $^2J_{PtP}$ is very small or zero. The most plausible structure for this compound is shown in fig. 37.

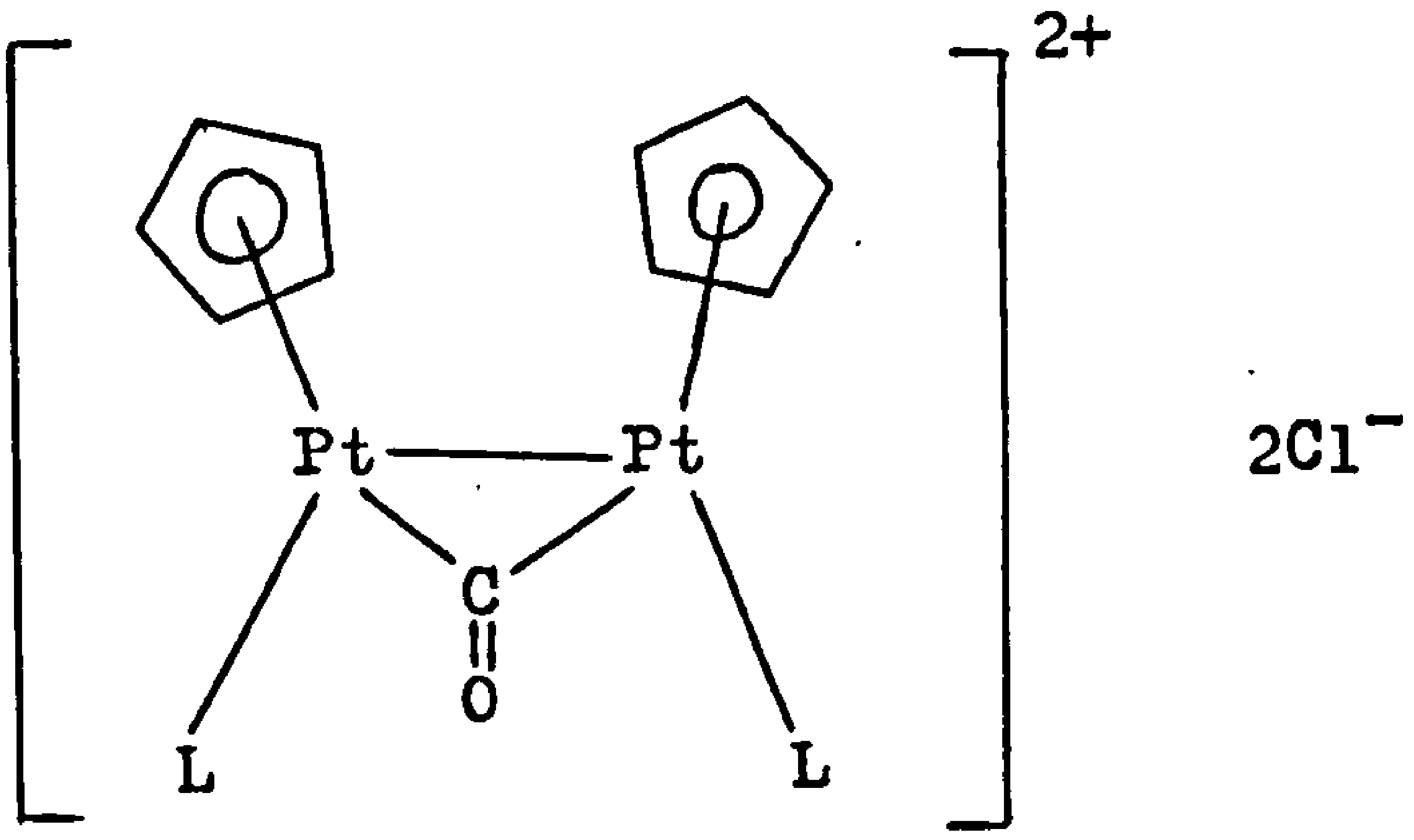
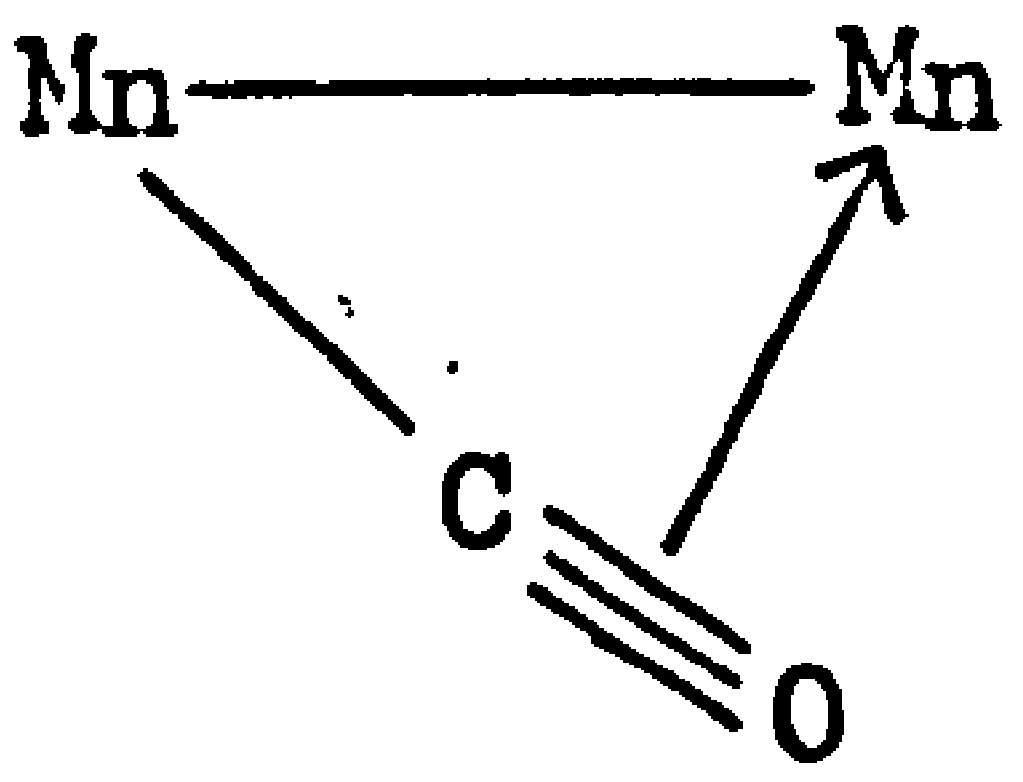


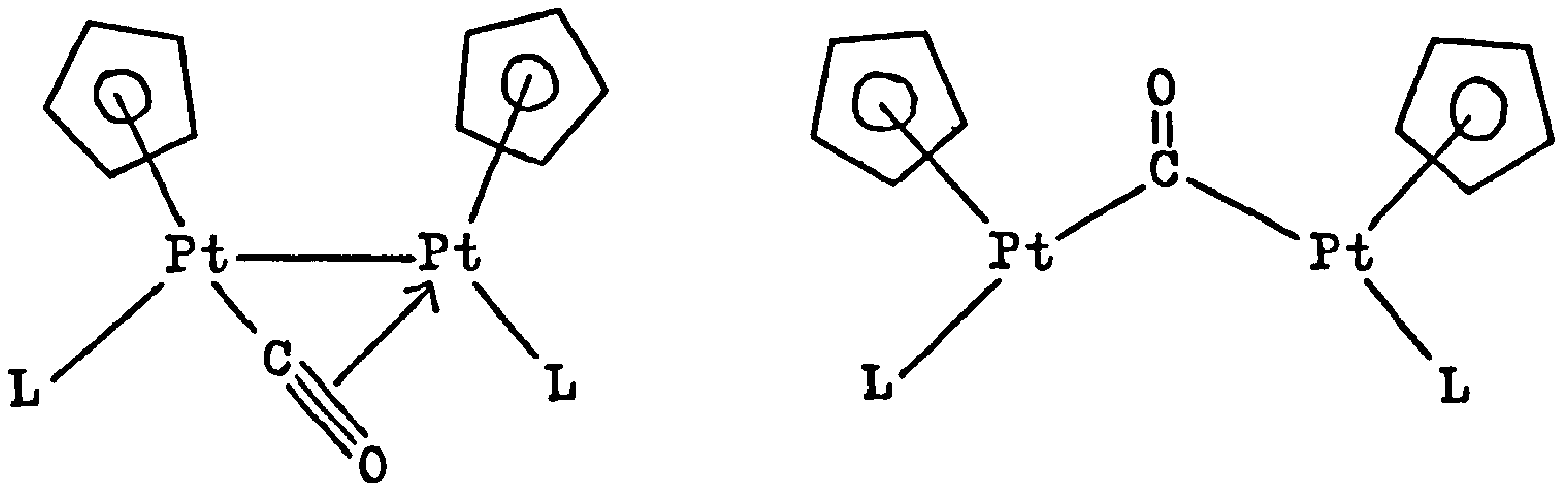
figure 37

The structure in fig. 37 allows each platinum to conform to the 18-electron rule. However, the low value of ν_{CO} is not consistent with this, as a positive charge on the complex should increase ν_{CO} by reducing the amount of back-bonding from platinum. The absorbance is at 1630cm^{-1}, which is very similar to the frequency for the complex $[Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, where ν_{CO} is 1638cm^{-1}, which was proposed to have a 4 electron CO bridge and platinum-platinum bond.[189] This type of carbonyl bridge was first discovered in $[Mn_2(CO)_5(\mu\text{-}dppm)_2]$, which had ν_{CO} = 1645cm^{-1} for the bridging CO, and was shown, by X-ray structural analysis to be a 4-electron bridge of the type below.[192]



Such a bridging carbonyl was expected to be fluxional in the complex $[Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, to explain why the

P atoms were equivalent in the ^{31}P nmr spectrum. However, a bridging carbonyl of this type, giving the structure shown in figure 38 (a) would make each platinum 19-electron for a platinum (II) species, which would be cationic with a charge of 2+, or 20-electron for a neutral platinum (I) species.



(a) (b)

figure 38.

There is no evidence to support a platinum-platinum bond in this species, and it is possible to have a carbonyl bridge when no metal-metal bond is present, although this is extremely rare. The palladium (1) dimer, $[Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-}Ph_2AsCH_2\text{-}AsPh_2)_2]$ has been shown, by X-ray structural analysis, to contain a symmetrically bridging CO without a palladium-palladium bond,[193] although the CO stretching frequency, at 1720cm^{-1}, is somewhat higher. This would give a structure, shown in fig. 38 (b), which would be 17-electron and cationic for platinum (II) or 18-electron and neutral for platinum (I).

The platinum (I) dimer, with structure (b) in fig. 38 is a strong possibility, although the absence of chloride is a stumbling block. However, the complex, +11.2 ppm, $^1J_{PtP}$ = 5632 Hz, converts to "Asymmetric Dimer" only very slowly in $CDCl_3$, and solvent participation cannot be ruled out as the source of Cl^-.

It is unlikely that this compound, whatever its structure, is a direct intermediate in the route to "Asymmetric Dimer" from cis-$[PtCl_2(CO)L]$. It was observed only when alcohol was present in the reaction mixture and if the alcohol inhibited a final step to form "Asymmetric Dimer", the new species should react rapidly in $CDCl_3$, (with no alcohol present), but does not do so. However, with the information presently available it is not possible to definitely assign a structure to this compound, or to decide whether it is always an intermediate.

When cis-$[PtCl_2(CO)(PPh_3)]$ and 2 TlC_5H_5 were allowed to react in benzene the reaction produced "Asymmetric Dimer" (parameters in table 17) and the usual byproduct, parameters in benzene $\delta = +20.7$ ppm, $^1J_{PtP} = 3467$ Hz, similar to the reaction in $CDCl_3$. However in benzene the reaction proceeded further to give a new dimeric species, which had a 2nd-order AA'X ^{31}P nmr spectrum, with parameters +7.2 ppm, $^1J_{PtP} = 3806$ Hz, $^2J_{PtP} = -118$ Hz, $^3J_{PP} = 141$ Hz. The sizes of the coupling constants are similar to those of the dimer obtained by addition of $AgSO_3CF_3$ to "Asymmetric Dimer", which was considered to be a "Werner-type" dimer with bridging C_5H_5 and CO ligands. This new dimer is likely to be a similar complex, and it seems plausible that, since it is obtained on further reaction of "Asymmetric Dimer" over a period of days, it arises from CO loss and has the following structure.

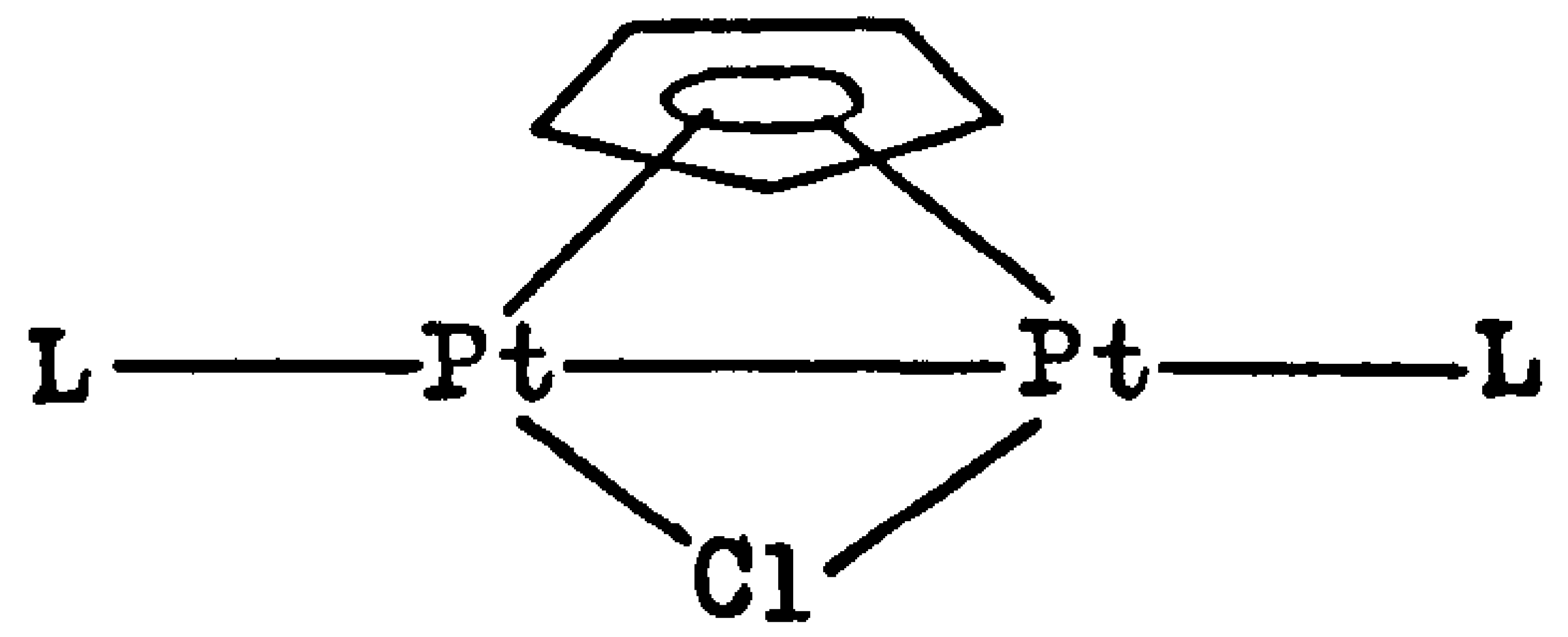


figure 39.

This complex was also obtained as a byproduct in some reactions in $CDCl_3$, and its ^{31}P parameters in $CDCl_3$ are:- $\delta = +6.8$ ppm, $^1J_{PtP} = 3862$ Hz, $^2J_{PtP} = -118$ Hz, $^3J_{PtP} = 141$ Hz. A ^1H nmr spectrum of a solution of "Asymmetric Dimer" containing this species also contained a triplet at +4.98 ppm, with $J_{PH} = 2.9$ Hz and $J_{PtH} = 25.6$ Hz. These parameters are typical of a bridging C_5H_5 group in compounds of this type. $[Pt_2(\mu\text{-}C_5H_5)(\mu\text{-allyl})(PMe_3)_2]$ has ^1H parameters for the C_5H_5 group, +5.59 ppm, $J_{PH} = 2.4$ Hz, $J_{PtH} = 27$ Hz.[183.] This dimer was present in a sample of "Asymmetric Dimer" prepared from <u>cis</u>-$[PtCl_2(^{13}CO)(PPh_3)]$ and exhibited no ^{13}C - ^{31}P coupling in the ^{31}P nmr, and contained no terminal or bridging CO in the ^{13}C nmr spectrum. This dimer appeared to decompose in $CDCl_3$ to produce C_5H_6, as its C_5H_5 signal disappeared from the ^1H nmr spectrum to be replaced by that for C_5H_6, while the "Asymmetric Dimer" remained unchanged.

c) Concentration Effects

The concentration of reaction mixtures did not seem to affect the course of the reaction between <u>cis</u>-$[PtCl_2(CO)$-$(PPh_3)]$ and 2 TlC_5H_5. A 0.032M solution of <u>cis</u>-$[PtCl_2$-$(CO)(PPh_3)]$ reacted with 2 equivalents of TlC_5H_5 to produce "Asymmetric Dimer" (58% of the total ^{31}P intensity), Ph_3PO (16%), the species proposed to be $[Pt_2(\mu\text{-}C_5H_5)(\mu\text{-}Cl)(PPh_3)_2]$

(18%) and the other, usual byproduct with parameters +20.7 ppm, ${}^{1}J_{PtP}$ = 3435 Hz (8%). A 0.097M solution of the same sample of cis-$[PtCl_2(CO)(PPh_3)]$ and 2 equivalents of the same sample of TlC_5H_5 reacted to produce "Asymmetric Dimer" (61%), the species with parameters +20.7 ppm, ${}^{1}J_{PtP}$ = 3435 Hz (25%) and $[Pt_2(\mu-C_5H_5)(\mu-Cl)(PPh_3)_2]$ (14%). The differences between the two reaction concentrations is very small, and is not significant compared to the wide variations obtained in "Asymmetric Dimer" reactions which appear to have identical conditions.

d) Other Effects

The age of the TlC_5H_5 sample used in the reaction also does not appear to have much effect on the outcome. The reaction above with the 0.097M solution of cis-$[PtCl_2(CO)(PPh_3)]$ used a freshly prepared sample of TlC_5H_5, which consisted of bright yellow needles. A similar reaction was performed using an old sample of TlC_5H_5 which had been exposed to air for several months, and was a dull, fawn colour. This produced "Asymmetric Dimer" (74%), +20.7 ppm, ${}^{1}J_{PtP}$ = 3435 Hz (13%) and $[Pt_2(\mu-C_5H_5)(\mu-Cl)(PPh_3)_2]$ (13%).

Miscellaneous Reactions

An attempt was made to produce an "Asymmetric Dimer" with arsine ligands instead of phosphine ligands, by allowing cis-$[PtCl_2(CO)(AsMePh_2)]$ to react with two equivalents of TlC_5H_5. Initially, $[PtCl(C_5H_5)(CO)(AsMePh_2)]$ isomer (I) was produced, (table 1), followed by a species with ${}^{1}H$ parameters δ = +5.85 ppm, J_{PtH} = 13.4 Hz and 5.7 Hz, and a species with parameters δ = +5.56 ppm, J_{PtH} =

12.6 Hz. Some C_5H_6 was also produced. The first of these two species has parameters typical of a π-C_5H_5 in a dimeric platinum complex with a platinum-platinum bond, but cannot be an "Asymmetric Dimer" analogue since the same species was found in the reaction of $[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ with 2 TlC_5H_5. This may be $[Pt_2(C_5H_5)_2(CO)_2]$, which was reported by Fritz and Kreiter to have ^1H nmr parameters, $\delta = +5.5$ ppm, $J_{PtH} = 13.7$ and 6.0 Hz.[194] The other species, which is typical of a monomeric π-C_5H_5 complex, was also observed in the reaction of $[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ with 2 TlC_5H_5. This complex is not $[Pt(CO)(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$, which is known,[176] and may be $[Pt(CO)(\eta^5\text{-}C_5H_5)Cl]$. In addition to these two species, the reaction of $[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ and 2 TlC_5H_5 produced a σ-cyclopentadienyl complex with parameters $\delta = +6.21$ ppm, $J_{PtH} = 41.0$ Hz.

Addition of PPh_3 to the mixture of σ- and π-cyclopentadienyl species obtained in the reaction of $[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ and 2 TlC_5H_5 produced the species with ^{31}P parameters +20.7 ppm, $^1J_{PtP} = 3435$ Hz and $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$, in a ratio of 2 to 1 (based on ^{31}P intensities). This species, produced as a byproduct in many "Asymmetric Dimer" preparations, was also the major product when PPh_3 was added to $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I), with $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ being produced as a minor product. Addition of $AgSO_3CF_3$ to a solution containing this unknown species had no effect, indicating that the complex probably does not contain Cl^-. A ^1H nmr spectrum of the mixture contained only very weak signals, one at +6.26 ppm, a triplet with

J_{PH} about 2 to 2.5 Hz, and J_{PtH} = 40 Hz, and the C_5H_5 signal of $[Pt(\eta^5-C_5H_5)(PPh_3)_2]^+$. These signals were very much weaker than the signals of the phosphine aryl protons, and there was also a strong signal at +7.27 oom amongst the aryl protons which could be $CHCl_3$. If this is the case it indicates that there may have been H/D exchange involving the solvent. If the signal at +6.26 ppm corresponds to the ^{31}P signal at +20.7 ppm, then this unidentified byproduct is a trans-bisphosphine species, and is most likely to be trans-$[Pt(\eta^1-C_5H_5)(PPh_3)_2L]$ where L is unknown, possibly Cl, C_5H_5 or CO.

A number of large-scale reactions were performed in an attempt to isolate "Asymmetric Dimer" in a pure state, but these always resulted in material which was contaminated, often with Ph_3PO or other platinum species, and they are briefly described in the experimental section. From a preparation of "Asymmetric Dimer", from cis-$[PtCl_2(CO)(PPh_3)]$, a hydrogen-deficient, largely organic byproduct was isolated with composition:- C 48.55%, H 2.76%, Cl 3.10% and P 4.11% which gives a ratio of 90C : 60H : 3P : 2Cl. Almost all of the TlC_5H_5 added is consumed, because most of the Tl is recovered as TlCl. This is also the case in reactions producing the material, +11.1 ppm, $^1J_{PtP}$ = 5634 Hz instead of "Asymmetric Dimer".

The proton source for production of C_5H_6 seems most likely to be another C_5H_5, and the production of a hydrogen deficient, carbon rich material supports the earlier experiments which eliminate solvent and moisture as the source. Further work needs to be done on the "Asymmetric Dimer" both to elucidate the mechanism of its formation and relationship to the other dimers mentioned in this chapter, and to corroborate the proposed structure, that in fig. 32. A tentative scheme relating the dimers is shown in fig. 40.

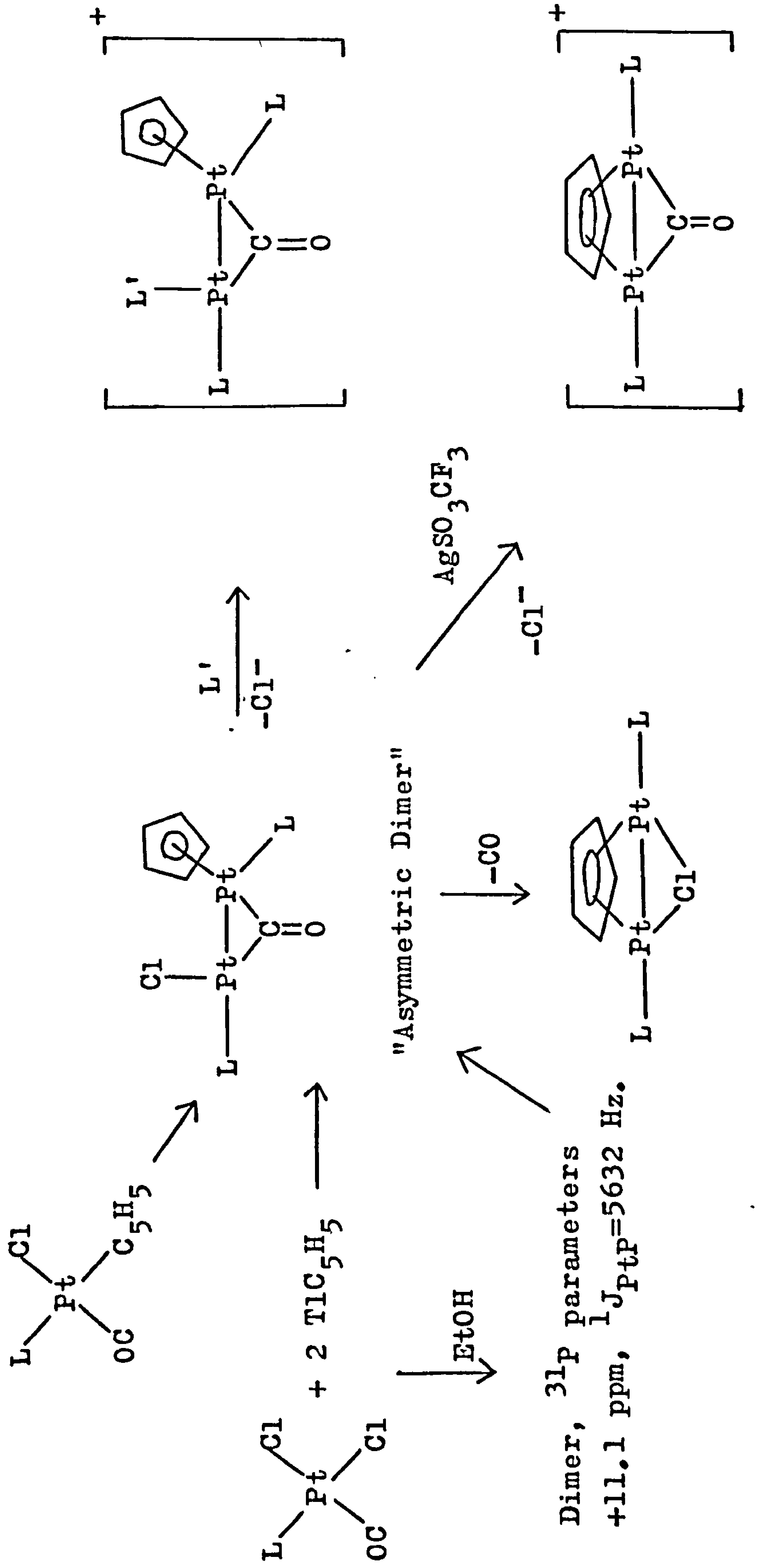

L
Pt
Cl
OC
C5H5
L
Pt
Cl
Cl
OC
+ 2 TlC5H5
EtOH
Dimer, 31P parameters
+11.1 ppm, 1JPtP=5632 Hz.
"Asymmetric Dimer"
L
Pt
Cl
Pt
C
O
L
L'
-Cl−
AgSO3CF3
-Cl−
-CO
L'
+
L
Cl
Pt

figure 40.

EXPERIMENTAL

^{31}P nmr spectra were recorded on a Varian XL 100 spectrometer operating in the Fourier Transform mode with $CDCl_3$ or C_6D_6 locking signal. Chemical shifts are downfield of external 85% H_3PO_4. ^{1}H nmr spectra were obtained on a Perkin-Elmer R32 90 MHz continuous-wave spectrometer with TMS locking signal or on a Varian XL 100 spectrometer with $CDCl_3$ locking signal. ^{13}C nmr spectra were run on a Bruker WP 200 SY spectrometer operating in the Fourier-transform mode at 50.32 MHz, with $CDCl_3$ locking signal. Chemical shifts were measured relative to $CDCl_3$ at 77.0 ppm. Infra red spectra were recorded on a Perkin-Elmer 580 spectrophotometer. All reactions were carried out at room temperature under an atmosphere of nitrogen unless otherwise stated.

Complexes cis-$[PtCl_2(CO)L]$ and TlC_5H_5 were prepared as previously described. $[Bu_4N]_2[Pt_2Cl_4(CO)_2]$ was prepared by the literature method used to prepare $[Pr_4N]_2[Pt_2Cl_4(CO)_2]$[188] and characterised by comparison of its infra red spectrum with the literature spectrum.[72]

Decomposition of $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I)

A solution of $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I), (0.061mmol.) in $CDCl_3$ (0.5ml) was left standing at room temperature for three days. The solution was examined by ^{31}P nmr spectroscopy, and it was found that isomer (I) was now only 34% of the total ^{31}P intensity. The products were cis-$[PtCl_2(CO)(PPh_3)]$ (25% of the intensity of the products), cis-$[PtCl_2(PPh_3)_2]$ (10%), a species with $\delta = +20.7$ ppm, $^1J_{PtP} = 3435$ Hz (8%) and a species with parameters $\delta = +9.1$ ppm, (d) $J_{PP} = 9.4$ Hz, $J_{PtP} = 5006$ Hz and < 20 Hz, $\delta p = +34.0$ ppm, (d) $J_{PP} = 9.4$ Hz, $J_{PtP} = 5505$ Hz and 862 Hz (57%). A ^1H nmr spectrum showed that C_5H_6 was present, along with isomer (I) and "Asymmetric Dimer" (table 15).

Decomposition of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I)

(a) A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), (0·068mmol.) in $CDCl_3$ (0.5ml) was left standing at room temperature for one day. ^{31}P nmr spectroscopic examination showed that isomer (I) was now only 33% of the total ^{31}P intensity, with "Asymmetric Dimer" a further 33% (^{31}P parameters are in table 14), cis-$[PtCl_2(CO)(PMe_2Ph)]$ 20% and cis-$[PtCl_2(PMe_2Ph)_2]$ 10% of the total intensity. On leaving the solution for 3 days, cis-$[PtCl_2(PMe_2Ph)_2]$ became the major species present.

(b) An identical solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), (0.068mmol.) in $CDCl_3$ (0.5ml) decomposed at the same rate to the same products when kept in the dark at room temperature.

(c) A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), (0.075mmol.) in acetone (0.5ml) with 6 drops of C_6D_6 as locking signal was left standing at room temperature for 38 hours. At this time 57% of the ^{31}P intensity was still isomer (I), the other species present being cis-$[PtCl_2(PMe_2Ph)_2]$ (11%), cis-$[PtCl_2(CO)(PMe_2Ph)]$ (9%) and "Asymmetric Dimer" (23%), (see table 17).

(d) A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), (0.077mmol.) in benzene (0.5ml), with C_6D_6 added as a locking signal, was left at room temperature for 38 hours. ^{31}P nmr examination showed that 65% of the ^{31}P intensity was still isomer (I), with the other species present being cis-$[PtCl_2(CO)(PMe_2Ph)]$ (9%), cis-$[PtCl_2(PMe_2Ph)_2]$ (13%) and "Asymmetric Dimer" (12%).

Decomposition of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I)

(a) Nitrogen gas was passed through a solution of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I), (0.052mmol.) in $CDCl_3$ (0.5ml) at room temperature for 2½ hours. A ^{31}P nmr spectrum of the solution showed that it contained only isomer (I). Oxygen gas was passed through the solution for 30 minutes, and the solution was found to contain, in addition to isomer (I), cis-$[PtCl_2(CO)(PMePh_2)]$ (3%) and "Asymmetric Dimer" (9%). A drop of H_2O (approx. 50µl) was added and, after 1 hour, ^{31}P nmr spectroscopic examination of the solution revealed no change in its composition. CO_2 was bubbled through the solution for 2 to 3 minutes (by adding solid CO_2 to the solution), but the composition of the solution did not change. On being left overnight at room temperature, 63% of the ^{31}P intensity was still isomer (I), with cis-[$PtCl_2(CO)(PMePh_2)$] (12%) and "Asymmetric Dimer" (25%) also present.

(b) Carbon monoxide was bubbled through a solution of [$PtCl(C_5H_5)(CO)(PMePh_2)$] isomer (I) (0·060mmol.) for 30 minutes at room temperature. A ^{1}H nmr spectrum showed only the presence of isomer (I). The solution was left under an atmosphere of CO overnight, when ^{31}P nmr examination showed the presence of cis-[$PtCl_2(CO)(PMePh_2)$] (6% of ^{31}P intensity), a species at $\delta = +6.8$ ppm, $^{1}J_{PtP} = 3261$ Hz (12%) and isomer (I) (82%).

cis-[$PtCl_2(CO)(PPh_3)$] and 2 equivalents of TlC_5H_5

cis-[$PtCl_2(CO)(PPh_3)$] (35.1mg, 0.063mmol.) and TlC_5H_5 (35.0mg, 0.130mmol.) were mixed in $CDCl_3$ (0.5ml) under a nitrogen atmosphere. After 2 days at room temperature, ^{31}P nmr examination of the solution showed that it was largely "Asymmetric Dimer" (89% of the total ^{31}P intensity). Other products were the species with parameters $\delta = +20.7$ ppm, $^{1}J_{PtP} = 3435$ Hz and cis-[$PtCl_2(PPh_3)_2$].

cis-[$PtCl_2(CO)(PEt_3)$] and 2 equivalents of TlC_5H_5

cis-[$PtCl_2(CO)(PEt_3)$] (20.0mg, 0.049mmol.) and TlC_5H_5 (38.1mg, 0.141mmol.) were allowed to react in $CDCl_3$ (0.5ml) under an atmosphere of nitrogen. After 1 day at room temperature a ^{31}P nmr spectrum showed that an "Asymmetric Dimer" species had been produced, (parameters in table 14), which accounted for 97% of the ^{31}P intensity. A species with $\delta = +9.2$ ppm, $^{1}J_{PtP} = 5185$ Hz was also produced.

cis-[$PtCl_2(CO)(PMe_2Ph)$] and 2 equivalents of TlC_5H_5

cis-[$PtCl_2(CO)(PMe_2Ph)$] (26.3mg, 0.061mmol.) and TlC_5H_5 (29.0mg, 0.108mmol.) were allowed to react in $CDCl_3$ (0.5ml) under an atmosphere of nitrogen and the reaction was followed by ^{31}P nmr spectroscopy. Initially large amounts of [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) and cis-[$Pt(\eta^1$-$C_5H_5)_2(CO)(PMe_2Ph)$] were produced, along with a species, $\delta = -13.9$ ppm, $^1J_{PtP} = 2211$ Hz. Eventual products were [$Pt(\eta^5$-$C_5H_5)(PMe_2Ph)_2]^+$ (28% of the total ^{31}P intensity), cis-[$PtCl_2(PMe_2Ph)_2$] (24%), $\delta = -5.3$ ppm, $^1J_{PtP} = 2827$ Hz (14%), $\delta = -6.6$ ppm, $^1J_{PtP} = 3090$ Hz (12%) and an "Asymmetric Dimer", (17%), (parameters in table 14).

cis-[$PtBr_2(CO)(PMe_2Ph)$] and 2 equivalents of TlC_5H_5

cis-[$PtBr_2(CO)(PMe_2Ph)$] (26.6mg, 0.051mmol.) and TlC_5H_5 (25.3mg, 0.094mmol.) were allowed to react in $CDCl_3$ (0.5ml) under a nitrogen atmosphere and the reaction was followed by ^{31}P nmr spectroscopy. Initially [$PtBr(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) and cis-[$Pt(\eta^1$-$C_5H_5)_2(CO)(PMe_2Ph)$] were produced, along with a species, $\delta = -13.9$ ppm, $^1J_{PtP} = 2211$ Hz. Eventually, (after 7 hours), the solution contained [$Pt(\eta^5$-$C_5H_5)(PMe_2Ph)_2]^+$ (34% of total ^{31}P intensity), $\delta = -7.4$ ppm, $^1J_{PtP} = 2803$ Hz (23%), $\delta = -8.8$ ppm, $^1J_{PtP} = 3076$ H z (15%) and an "Asymmetric Dimer", (22%), (parameters in table 14). After two days at room temperature the species $\delta = -5.3$ ppm, $J_{PtP} = 2828$ Hz and $\delta = -6.6$ ppm, $^1J_{PtP} = 3090$ Hz, obtained in the previous reaction, also began to appear, followed by cis-[$PtBr_2(PMe_2Ph)_2$] and cis-[$PtBr(Cl)(PMe_2Ph)_2$], (^{31}P parameters:- -13.1 ppm (d)

${}^1J_{PtP}$ = 3523 Hz and -17.1 ppm, ${}^1J_{PtP}$ = 3524 Hz (d) ${}^2J_{PP}$ = 16.6 Hz).

"Asymmetric Dimer" (PPh_3 and Cl) and $[Bu_4N]I$

A solution of "Asymmetric Dimer" was prepared from cis-$[PtCl_2(CO)(PPh_3)]$ (33.6mg, 0.061mmol.) and TlC_5H_5 (32.8mg, 0.126mmol.). ${}^{31}P$ nmr spectroscopic examination showed that "Asymmetric Dimer" was 70% of the total ${}^{31}P$ intensity. A solution of $[Bu_4N]I$ (22.4mg, 0.061mmol.) was then added, and a new "Asymmetric Dimer" with different ${}^{31}P$ parameters, was produced immediately, (table 14).

$[Pt(\eta^5-C_5H_5)(CO)(PMe_2Ph)]\ SO_3CF_3$ and $[Bu_4N]I$

A solution of $[Pt(\eta^5-C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$ (0.069 mmol.) in $CDCl_3$ (0.3ml) was prepared as previously described. A solution of $[Bu_4N]I$ (25.4mg, 0.069mmol.) was then added, and a ${}^{31}P$ nmr spectrum showed the presence of a new "Asymmetric Dimer", parameters in table 14, as 70% of the total ${}^{31}P$ intensity. A ${}^1H$ nmr spectrum was also obtained, (table 15), and indicated the presence of C_5H_6.

$[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I) + $[Et_4N]Cl$.

$[Et_4N]Cl$ (9.8mg, 0.059mmol.) was added to a solution of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I), (0.051mmol.) in $CDCl_3$ (0.5ml). After 19 hours, a ${}^{31}P$ nmr investigation of the solution showed the presence of an "Asymmetric Dimer", (parameters in table 14), as 32% of the total ${}^{31}P$ nmr intensity. The major product was cis-$[PtCl_2(PMePh_2)_2]$ (45%). A ${}^1H$ nmr spectrum showed that C_5H_6 was present.

cis-$[PtCl_2(^{13}CO)(PPh_3)]$ and 2 equivalents of TlC_5H_5

cis-$[PtCl_2(^{13}CO)(PPh_3)]$ (60% labelled with ^{13}CO), (31.5mg, 0.057mmol.) and TlC_5H_5 (29.3mg, 0.109mmol.) were allowed to react in $CDCl_3$ under nitrogen for 2 days. ^{31}P nmr examination revealed the solution to be largely "Asymmetric Dimer", (89% of ^{31}P intensity) with some cis-$[PtCl_2(PPh_3)_2]$. The upfield doublet at δ +9.1 ppm was broadened by ^{13}C - ^{31}P coupling, but the downfield doublet at δ +34.0 ppm was unaffected.

cis-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ and 2 equivalents of TlC_5H_5

Similarly, cis-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ (60% labelled), (25.5mg, 0.059mmol.) and TlC_5H_5 (33.5mg, 0.124mmol.) were allowed to react in $CDCl_3$ (0.5ml). ^{31}P nmr examination revealed the upfield doublet at δ -25.1 ppm to be broadened by ^{13}C - ^{31}P coupling, while the downfield doublet of the "Asymmetric Dimer", at δ +10.0 ppm, was unaffected.

cis-$[PtCl_2(CO)(PPh_3)]$ and 2 equivalents of TlC_5H_5 followed by ^1H nmr.

cis-$[PtCl_2(CO)(PPh_3)]$ (25.1mg, 0.045mmol.) and TlC_5H_5 (26.4mg, 0.098mmol.) were allowed to react in $CDCl_3$ (0.5ml) for 2 days as previously described. A ^1H nmr spectrum showed the presence of C_5H_6, a peak at δ = +5.75 ppm, (doublet of doublets). J_{PH} = 1.8 and 1.0 Hz, with broad, poorly resolved platinum satellites, "J_{PtH}" = 11.5 Hz, attributed to "Asymmetric Dimer", and a minor species at δ = +4.95 ppm, (triplet) J_{PH} = 3.0 Hz, with platinum satellites, J_{PtH} = 25.8 Hz. The relative integrations of C_5H_6 olefinic protons to +5.75 ppm protons was 1.2 to 1.

cis-[$PtCl_2(CO)(PEt_3)$] and 2 equivalents of TlC_5H_5 followed by ^1H nmr

The reaction between *cis*-[$PtCl_2(CO)(PEt_3)$] and 2 equivalents of TlC_5H_5 previously described was followed by ^1H nmr spectroscopy. The initial product was [$PtCl(C_5H_5)(CO)(PEt_3)$] isomer (I),(table 1). After 3 hours reaction, *cis*-[$Pt(C_5H_5)_2(CO)(PEt_3)$], (table 3), C_5H_6 and a species at δ = +5.81 ppm, (doublet of doublets) J_{PH} = 1.7 and 1.0 Hz, with broad platinum satellites, "J_{PtH}" = 11.0 Hz, began to appear. This latter species was identified as "Asymmetric Dimer". After 1 day, "Asymmetric Dimer" was the major platinum-containing product, with integration of phosphine ethyl protons and C_5H_5 protons indicating there were 2 phosphines present for each C_5H_5 ring. The ratio of C_5H_6 olefinic protons to C_5H_5 was 1.2 to 1. A minor species, δ +5.70 Hz, (doublet) J_{PH} = 1.6 Hz, J_{PtH} = 11.0 Hz was also present.

[$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) and TlC_5H_5

A solution of [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) (0.066mmol.) was allowed to react with TlC_5H_5 (0.063mmol.) with vigorous shaking at room temperature for 5 minutes, the solution was then filtered and left standing for 3 days. A ^{31}P nmr spectrum indicated that 83% of the total ^{31}P intensity was "Asymmetric Dimer". A ^1H nmr spectrum was obtained, (table 15), and showed that C_5H_6 was present in addition to "Asymmetric Dimer".

Isolation of "Asymmetric Dimer"

cis-$[PtCl_2(CO)(PPh_3)]$ (198mg, 0.356mmol.) and TlC_5H_5 (96mg, 0.355mmol.) were allowed to react in $CDCl_3$ (3ml) until a ^{31}P nmr spectrum indicated that $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) was the major species present. The solution was filtered and treated with a further 94mg of TlC_5H_5 (0.349mmol.). After 6 hours reaction at room temperature, ^{31}P nmr showed that "Asymmetric Dimer" was the most abundant product (55% of the total ^{31}P intensity). The solution was filtered, diluted with benzene and freeze-dried to yield 180mgs. of brown solid. A KBr disc i.r. spectrum contained no terminal CO absorptions, but had a peak at $1805cm^{-1}$, which was broad, and medium strong. A ^1H nmr spectrum was obtained, showing "Asymmetric Dimer" to be the major species. 80mgs. of the material was dissolved in $CDCl_3$ and a ^{13}C nmr spectrum was recorded, with peaks at $\delta = +95.3$ ppm, doublet $J_{PC} = 2.5$ Hz, and a complex series of peaks at +127.6 to +134.9 ppm. Even on addition of 0.04M $Cr(acac)_3$, no other peaks could be observed. An i.r. spectrum in $CHCl_3$ solution also had the broad absorption at 1800 cm^{-1}, seen in the KBr disc spectrum.

cis-$[PtCl_2(^{13}CO)(PPh_3)]$ + TlC_5H_5; followed by a second equivalent of TlC_5H_5

Similarly, cis-$[PtCl_2(^{13}CO)(PPh_3)]$ (29.1mg, 0.052mmol.), 60% ^{13}CO labelled, and TlC_5H_5 (17.4mg, 0.065mmol.) were allowed to react in $CDCl_3$ (0.5ml) under a nitrogen atmosphere for 1½ hours. The solution was filtered and allowed to react with TlC_5H_5 (13.5mg, 0.050mmol.) for 5 hours, then filtered. A ^1H nmr spectrum showed that

"Asymmetric Dimer" was the major product. A ^{13}C nmr spectrum was obtained and showed a peak at $\delta = +191.1$ ppm, $J_{PtC} = 1625$ and 723 Hz, $J_{PC} = 4.3$ Hz (doublet), weak compared to peaks at +127.6 to +134.9 ppm, and a peak at +95.4 ppm. Addition of 0.04M $Cr(acac)_3$ enhanced the peak at low field, changing its parameters slightly to +190.8 ppm, $J_{PtC} = 1621$ and 723 Hz, $J_{PC} = 3.7$ Hz.

"Asymmetric Dimer" (PPh_3 and Cl) and $AgSO_3CF_3$

A $CDCl_3$ solution of "Asymmetric Dimer" was prepared from cis-$[PtCl_2(CO)(PPh_3)]$ (30.3mg, 0.055mmol.) and TlC_5H_5 (41.4mg, 0.154mmol.) as previously described. The solution was filtered after 50 hours at room temperature when a ^{31}P nmr spectrum showed that "Asymmetric Dimer" was 82% of the total ^{31}P intensity. The major byproduct was the species with parameters $\delta = +20.7$ ppm, $^1J_{PtP} = 3435$ Hz (14%). $AgSO_3CF_3$ (7.8mg, 0.030mmol.) was then added and a ^{31}P nmr spectrum was obtained. The species with $\delta = +20.7$ ppm was unchanged, but the "Asymmetric Dimer" had disappeared to be replaced by a species at +0.2 ppm, with 2nd order satellites in an AA'X pattern which analysed as $^1J_{PtP} = 3774$ Hz, $^2J_{PtP} = -156$ Hz, $^3J_{PP} = 140$ Hz, which was 34% of the total intensity of the products. Other products were $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$ (17%), a species at +4.9 ppm whose satellites could not be found (17%), Ph_3PO (+29.3 ppm) (15%) and $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (10%).

"Asymmetric Dimer" (PPh_3 and Cl) and PPh_3

A $CDCl_3$ solution "Asymmetric Dimer" was prepared from cis-[$PtCl_2(CO)(PPh_3)$] (31.3mg, 0.056mmol.) and TlC_5H_5 (31.0mg, 0.115mmol.) under a nitrogen atmosphere as described previously. ^{31}P nmr examination of the solution showed that "Asymmetric Dimer" was 86% of the total ^{31}P intensity. Other products were [$PtCl(C_5H_5)(CO)(PPh_3)$] isomer (I) (6%), cis-[$PtCl_2(PPh_3)_2$] (5%) and δ = +20.7 ppm (3%). The solution was filtered and a solution of PPh_3 (9.3mg, 0.036mmol.)in $CDCl_3$ (0.1ml) was added at -60°C. The major product was a dimeric species with 3 phosphines, with the following parameters:-

δ = +27.5 ppm and +27.3 ppm (2P atoms, 2nd order pattern with 1st order satellites), P_1 $^1J_{PtP}$ = 3025 Hz, J_{PP} = 23.7 Hz (d).

P_2 $^1J_{PtP}$ = 4646 Hz, $^2J_{PtP}$ = 850 Hz, J_{PP} = 23.7 and 11.9 Hz (d of d).

δ = +10.1 ppm (1P atom), $^1J_{PtP}$ = 4738 Hz, $^2J_{PtP}$ = 22.2 and J_{PP} = 9.8 Hz (d).

Some PPh_3 was also present, and the peak was sharp indicating that there was no exchange process occurring. On warming to room temperature for 5 minutes and cooling again to -60°C, the solution contained $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (13% of the total ^{31}P intensity), and [$Pt(PPh_3)_3(CO)$] (15%) in addition to the new dimer (50%). On warming the solution to room temperature for 30 minutes the major product was $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (81%) with some +20.7 ppm, $^1J_{PtP}$ =

3435 Hz also present (12%) and some Ph_3PO (7%).

A similar reaction was followed by ^1H nmr spectroscopy. On addition of PPh_3 to "Asymmetric Dimer" at -60°C the ^1H nmr spectrum showed a broad peak at $\delta = +5.40$ ppm. On warming to +10°C some coupling began to be resolved, and the peak was a broad doublet at $\delta = +5.43$ ppm, with $J_{PH} = 1.2$Hz.

^{13}CO-labelled "Asymmetric Dimer" (PPh_3 and Cl) and PPh_3

A similar reaction was performed using "Asymmetric Dimer" prepared from cis-$[PtCl_2(^{13}CO)(PPh_3)]$ (31.5mg, 0.056mmol.), 60% ^{13}CO-labelled, and TlC_5H_5 (29.3mg, 0.109 mmol.). The solution was examined by ^{31}P nmr and was found to contain "Asymmetric Dimer" (88% of the total ^{31}P intensity) with minor amounts of +20.7 ppm $^1J_{PtP} = 3435$ Hz (2%), cis-$[PtCl_2(PPh_3)_2]$ (8%) and Ph_3PO (2%). On addition of PPh_3 (9.4mg, 0.036mmol.) in $CDCl_3$ (0.1ml) at -60°C the major product was a dimeric species with parameters:-

+27.6 ppm (d of d) $^2J_{CP} = 113$ Hz, $^2J_{PP} = 23.4$ Hz, $^1J_{PtP} = 3028$ Hz.

+26.9 ppm (d of d) $^2J_{PP} = 23.0$ Hz, $^3J_{PP} = 11.8$ Hz, $^1J_{PtP} = 4625$ Hz and $^2J_{PtP} = 855$ Hz.

+10.0 ppm (broadened d.) $^1J_{PtP} = 4742$ Hz, $^2J_{CP}$ and $^3J_{PP}$ unresolved.

cis-$[PtCl_2(PPh_3)_2]$, +20.7 ppm, PPh_3 and Ph_3PO were also present.

"Asymmetric Dimer" (PMe_2Ph and Cl) and PPh_3

A similar reaction was carried out using "Asymmetric Dimer" prepared from cis-$[PtCl_2(CO)(PMe_2Ph)]$ (28.5mg, 0.066mmol.) and TlC_5H_5 (2 lots, 18.6mg, 0.069mmol. followed by 16.9mg, 0.063mmol.) as described previously. ^{31}P nmr investigation indicated that "Asymmetric Dimer" was 83% of the total ^{31}P intensity, other products being cis-$[PtCl_2(PMe_2Ph)_2]$ (12%) and $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$. A solution of PPh_3 (8.9mg, 0.034mmol.) was added at -60°C and ^{31}P nmr showed that a new dimer with 3 phosphine ligands was the major product (74% of ^{31}P intensity). The parameters for the new dimer were:-

+29.2 ppm (d) $^2J_{PP} = 22.0$ Hz, $^1J_{PtP} = 2818$ Hz.

-3.1 ppm (d of d), $^2J_{PP} = 22.0$ Hz, $^3J_{PP} = 9.7$ Hz, $^1J_{PtP} =$ 4360 Hz and $^2J_{PtP} = 851$ Hz.

-22.2 ppm (d) $^3J_{PP} = 9.1$ Hz, $^1J_{PtP} = 4320$ Hz, $^2J_{PtP} =$ 14.2 Hz.

On being kept overnight at less than -60°C, further reactions produced some $[PtCl(PMe_2Ph)_3]^+$,(15%), $PhMe_2PO$ (6%) and another dimer with three phosphines (8%) as well as the dimer above (63%). The new dimer with 3 phosphines (8% of the total intensity) had parameters for two phosphines, (the third not being observed), as follows:-

-5.4 ppm, (d) $^2J_{PP} = 20.6$ Hz, $^1J_{PtP} = 2670$ Hz.

-20.8 ppm (d) $^3J_{PP} = 10.4$ Hz, $^1J_{PtP} = 4370$ Hz.

On warming to room temperature the major products were $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ and cis-$[PtCl_2(PMe_2Ph)_2]$.

"Asymmetric Dimer" (PPh_3 and Cl) and $AsPh_3$

Similarly, a solution of "Asymmetric Dimer" was prepared from cis-$[PtCl_2(CO)(PPh_3)]$ (31.8mg, 0.057mmol.) and TlC_5H_5 (31.0mg, 0.115mmol.) and was shown, by ^{31}P nmr, to be 82% of the ^{31}P intensity. The other product was the species, δ = +20.7 ppm, $^1J_{PtP}$ = 3435 Hz (18%). A solution of $AsPh_3$ (8.8mg, 0.029mmol.) in $CDCl_3$ (0.1ml) was added at -60°C and this reacted slowly to produce a dimer with the following parameters:-

+28.8 ppm, (d) $^3J_{PP}$ = 11.6 Hz, $^1J_{PtP}$ = 4937 Hz, $^2J_{PtP}$ = 795 Hz (1P).

+9.4 ppm, (d) $^3J_{PP}$ = 11.6 Hz, $^1J_{PtP}$ = 4669 Hz, $^2J_{PtP}$ = 24.8 Hz (1P).

On being left overnight at -80°C, a substantial amount of "Asymmetric Dimer" was regenerated. A further solution of $AsPh_3$ (8.8mg, 0.029mmol.) in $CDCl_3$ (0.1ml) was added at -60°C to give the new dimer as the major product (69% of ^{31}P intensity).

$AgSO_3CF_3$ (8.1mg, 0.032mmol.) was added and the parameters of the new dimer were unchanged. The new dimer was stable at room temperature in the presence of $AgSO_3CF_3$, and had parameters at +25°C of :-

+29.6 ppm, $^3J_{PP}$ = 11.6 Hz, $^1J_{PtP}$ = 4976 Hz, $^2J_{PtP}$ = 834 Hz.

+8.9 ppm, $^3J_{PP}$ = 11.6 Hz, $^1J_{PtP}$ = 4705 Hz, $^2J_{PtP}$ = 33.0 Hz.

"Asymmetric Dimer" (PPh_3 and Cl) and CO

Similarly, a solution of "Asymmetric Dimer" was prepared from cis-$[PtCl_2(CO)(PPh_3)]$ (37.7mg, 0.068mmol.) and TlC_5H_5 (33.7mg, 0.125mmol.) in $CDCl_3$ (0.4ml). A ^{31}P nmr spectrum showed that "Asymmetric Dimer" was 88% of the ^{31}P intensity, the rest being the species with δ = +20.7 ppm, $^1J_{PtP}$ = 3435 Hz, (8%) and cis-$[PtCl_2(PPh_3)_2]$ (4%). Carbon monoxide was bubbled through the solution at -60°C for 4 minutes producing the following species:- $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) (16% of the ^{31}P intensity), +20.7 ppm, $^1J_{PtP}$ = 3435 Hz (17%), +16.1 ppm, $^1J_{PtP}$ = 3823 Hz (16%), $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$ (14%), +19.3 ppm, $^1J_{PtP}$ = 3402 Hz (9%), +5.5 ppm, $^1J_{PtP}$ = 3079 Hz, $^3J_{PtP}$ = 110 Hz (6%), $[Pt(PPh_3)_2(CO)_2]$ (6%), cis-$[PtCl_2(PPh_3)_2]$ (4%), and the new dimer produced in PPh_3 addition to "Asymmetric Dimer" (7%). On warming the solution to room temperature for 2 minutes, only +20.7 ppm, $^1J_{PtP}$ = 3435 Hz; $[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) and "Asymmetric Dimer" were present, in a ratio of ^{31}P intensities of 2:2:1.

The reaction was repeated using ^{13}CO-labelled "Asymmetric Dimer" (60% ^{13}CO). On bubbling CO through the solution briefly at -60°C, the "Asymmetric Dimer" lost the ^{13}CO completely while 64% of it was still uncleaved. None of the products, which were the same as above, showed ^{13}C - ^{31}P coupling.

Variations in Conditions in "Asymmetric Dimer" Reactions

Reactions producing "Asymmetric Dimer" from cis-[$PtCl_2(CO)(PPh_3)$] were performed, varying some of the conditions, and were followed by ^{31}P nmr spectroscopy, unless otherwise stated.

(i) cis-[$PtCl_2(CO)(PPh_3)$] (31.4mg, 0.057mmol.) and TlC_5H_5 (33.2mg, 0.123mmol.) were allowed to react in $CDCl_3$ (0.5ml).

(ii) cis-[$PtCl_2(CO)(PPh_3)$] (29.4mg, 0.053mmol.) and TlC_5H_5 (21.5mg, 0.080mmol.) were allowed to react in $CDCl_3$ (0.5ml).

(iii) cis-[$PtCl_2(CO)(PPh_3)$] (29.5mg, 0.053mmol.) and TlC_5H_5 (14.2mg, 0.053mmol.) were allowed to react in $CDCl_3$ (0.5ml).

(iv) cis-[$PtCl_2(CO)(PPh_3)$] (25.2mg, 0.045mmol.) and TlC_5H_5 (25.2mg, 0.093mmol.) were allowed to react in 0.5ml $CDCl_3$, which had been mixed with D_2O for 5 hours, in an nmr tube which had been filled with D_2O at 80°C for 5 hours, then dried in an oven, before use. The reaction was examined by ^1H nmr spectroscopy.

(v) $CHCl_3$ was dried by passing it down a silica gel column, then by treatment with anhydrous $MgSO_4$. Dissolved oxygen was removed by flushing the $CHCl_3$ with N_2 gas. cis-[$PtCl_2(CO)(PPh_3)$] (28.9mg, 0.052mmol.) and TlC_5H_5 (31.7mg, 0.118mmol.) were allowed to react in 0.5ml of this $CHCl_3$ with 5 drops of C_6D_6 added as a locking signal for ^{31}P nmr.

(vi) *cis*-[$PtCl_2(CO)(PPh_3)$] (27.0mg, 0.049mmol.) and TlC_5H_5 (27.0mg, 0.100mmol.) were allowed to react in $CHCl_3$ (0.5ml) which had not been treated in any way.

(vii) *cis*-[$PtCl_2(CO)(PPh_3)$] (27.4mg, 0.049mmol.) and TlC_5H_5 (30.5mg, 0.113mmol.) were allowed to react in $CDCl_3$ (0.5ml) to which 50μl of EtOH had been added.

(viii) Similarly, *cis*-[$PtCl_2(CO)(PPh_3)$] (28.6mg, 0.052 mmol.) and TlC_5H_5 (29.7mg, 0.110mmol.) were allowed to react in $CDCl_3$ (0.5ml) to which MeOH (50μl) had been added.

(ix) Also, *cis*-[$PtCl_2(CO)(PPh_3)$] (28.5mg, 0.051mmol.) and TlC_5H_5 (30.5mg, 0.113mmol.) were allowed to react in $CDCl_3$ (0.5ml) to which Bu^nOH (50μl) had been added.

(x) *cis*-[$PtCl_2(CO)(PPh_3)$] (29.6mg, 0.053mmol.) and TlC_5H_5 (30.9mg, 0.115 mmol.) were allowed to react in benzene (0.5ml) to which a few drops of C_6D_6 was added as a locking signal for ^{31}P nmr.

(xi) *cis*-[$PtCl_2(CO)(PPh_3)$] (9.0mg, 0.016mmol.) and TlC_5H_5 (9.3mg, 0.034mmol.) were allowed to react in $CDCl_3$ (0.5ml).

(xii) *cis*-[$PtCl_2(CO)(PPh_3)$] (27.0mg, 0.049mmol.) and TlC_5H_5 (26.2mg, 0.097mmol.) were allowed to react in $CDCl_3$ (0.5ml).

(xiii) *cis*-[$PtCl_2(CO)(PPh_3)$] (25.6mg, 0.046mmol.) and an old sample of TlC_5H_5 (24.4mg, 0.090mmol.) were allowed to react in $CDCl_3$ (0.5ml).

cis-$[PtCl_2(CO)(AsMePh_2)]$ and 2 TlC_5H_5

cis-$[PtCl_2(CO)(AsMePh_2)]$ (21.8mg, 0.040mmol.) and TlC_5H_5 (10.9mg, 0.040mmol.) were allowed to react in $CDCl_3$ (0.5ml) under an atmosphere of N_2 for $1^3/4$ hours, when ^1H nmr examination of the solution revealed it to be largely $[PtCl(C_5H_5)(CO)(AsMePh_2)]$ isomer (I) (parameters in table 1). A further 10.9mg of TlC_5H_5 (0.040mmol.) was added, and after 18 hours at room temperature the solution contained, in addition to isomer (I), a C_5H_5 signal at +5.85 ppm, with two sets of platinum satellites, J_{PtH} = 13.4 and 5.7 Hz, and a C_5H_5 signal at +5.56 ppm, J_{PtH} = 12.6 Hz.

$[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ and 2 TlC_5H_5

$[Bu_4N]_2[Pt_2(CO)_2Cl_4]$ (40.0mg, 0.037mmol.) and TlC_5H_5 (20.0mg, 0.074mmol.) were allowed to react in $CDCl_3$ (0.5ml). A dark solution was formed immediately and this was filtered and examined by ^1H nmr spectroscopy. There were initially two species present, a σ-C_5H_5 species at +6.21 ppm, J_{PtH} = 41.0 Hz and a π-C_5H_5 dimeric species, δ = +5.85 ppm, J_{PtH} = 13.3 and 6.0 Hz, in equal intensities. A third species appeared with δ = +5.54 ppm, J_{PtH} = 12.5 Hz, within 2 hours. Addition of PPh_3 (19.9mg, 0.074mmol.) in $CDCl_3$ (0.2ml) to this solution produced the byproduct obtained in "Asymmetric Dimer" reactions with ^{31}P parameters δ = +20.7 ppm, $^1J_{PtP}$ = 3435Hz, and $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ in a ratio of 2 to 1. No C_5H_5 resonances could be observed in the ^1H nmr spectrum.

$[PtCl(C_5H_5)(CO)(PPh_3)]$ isomer (I) and PPh_3

$[PtCl(C_5H_5)(CO)(PPh_3)]$ (0.053mmol.) in $CDCl_3$ (0.3ml) and PPh_3 (13.8mg, 0.053mmol.) in $CDCl_3$ (0.2ml) were mixed at room temperature under a nitrogen atmosphere. The ^{31}P nmr spectrum of the mixture contained the species with parameters +20.7 ppm, $^1J_{PtP}$ = 3435 Hz as the major product (90% of the intensity) and $[Pt(\eta^5-C_5H_5)(PPh_3)_2]$. A ^1H nmr spectrum of this solution contained only weak signals in addition to PPh_3 protons, a triplet at +6.26 ppm, J_{PH} = 2 to 2.5 Hz, J_{PtH} = 40 Hz and $\pi-C_5H_5$ of $[Pt(\eta^5-C_5H_5)(PPh_3)_2]^+$ in a relative ratio of 5 to 1. The relative intensity of PPh_3 aryl protons on this scale was 165, which is much too large. However, in amongst these signals was one at +7.27 ppm, which may be due to $CHCl_3$. Addition of $AgSO_3CF_3$ (16.6mg, 0.065mmol.) had no effect on the ^{31}P nmr spectrum.

Attempted Isolation of "Asymmetric Dimers"

(i) cis-$[PtCl_2(CO)(PEt_3)]$ (204mg, 0.495mmol.) and TlC_5H_5 (274mg, 1.010mmol.) were stirred together in $CHCl_3$ which had been passed down a silica gel column (5ml) under a nitrogen atmosphere for 20 hours. The orange-brown solution was filtered to remove TlCl, and the solvent was removed to yield an oil. The oil was extracted with pentane (50ml) to give a yellow solution and an insoluble black oil. Removal of the pentane produced a yellow-orange oil. Both oils were soluble in $CDCl_3$ and ^1H nmr spectra were recorded. The only species in the solution of the black oil was "Asymmetric Dimer". The yellow oil contained both "Asymmetric Dimer" and a species with $\delta = +5.72$ ppm, doublet $J_{PH} = 1.5$ Hz, $J_{PtH} = 11.0$ Hz, which had ^{31}P parameters $\delta = +12.2$ ppm, $^{1}J_{PtP} = 5223$ Hz, and was 67% of the ^{31}P intensity.

(ii) cis-[$PtCl_2(CO)(PPh_3)$] (500mg, 0.902mmol.) and TlC_5H_5 (500mg, 1.855mmol.) were similarly allowed to react in $CHCl_3$ (10ml.) for 25 hours. A ^{31}P spectrum showed that the species with parameters $\delta = +11.1$ ppm, $^{1}J_{PtP} = 5644$ Hz and "Asymmetric Dimer" were present, in an intensity ratio of 2 to 1. The solution was filtered to remove TlCl, and was then chromatographed on a silica column. A fraction was eluted with a 1 to 2 mixture of diethyl ether and $CHCl_3$ which on evaporation of the solvent yielded a yellow-brown oil. On treatment with hexane a solid was obtained, (75mg) whose ^{31}P spectrum indicated that it was mainly "Asymmetric Dimer" (69% of the intensity) with Ph_3PO (22%) and the byproduct, +20.7 ppm, $^{1}J_{PtP} = 3435$ Hz (9%). The other species was either retained or destroyed on the column.

(iii) Similarly cis-[$PtCl_2(CO)(PPh_3)$] (504mg, 0.909mmol.) and TlC_5H_5 (528mg, 1.959mmol.) were allowed to react in $CDCl_3$ (5ml) for 1 day, when a ^{31}P nmr spectrum showed the solution to be mainly "Asymmetric Dimer" (64%) and Ph_3PO (24%). The solution was filtered and the solvent removed to yield a black oil. The oil was extracted with ether to give an orange solution and an insoluble brown solid (153mg).

A ^{31}P nmr spectrum of the brown solid had no detectable signals and a ^{1}H spectrum only a broad peak in the aryl region, +7.0 to 7.8 ppm. A microanalysis of this material gave a composition of:- C 48.55%, H 2.76%, Cl 3.10 % and P 4.11%, which gives a C/H ratio of 1.48, a C/P ratio of 30.2 and a P/Cl ratio of 1.5 and a relative ratio of 2Cl : 3P : 90C : 60H. Repeated attempts to crystallise the orange solution, which was mainly "Asymmetric Dimer", resulted in an orange semi-solid, contaminated with Ph_3PO.

(iv) <u>cis</u>-$[PtCl_2(CO)(PPh_3)]$ (235mg, 0.424mmol.) and TlC_5H_5 (221.mg, 0.820mmol.) were similarly allowed to react in $CDCl_3$ (5ml) for 1½ days, when a ^{1}H nmr spectrum indicated the solution was mainly "Asymmetric Dimer". The solution was filtered and 178mgs. of TlCl (0.742mmol., 91% of Tl) was recovered. The solvent was removed to give a black oil which was extracted with pentane to give an orange solution and a brown solid (155mg). The brown solid contained "Asymmetric Dimer" (47% of ^{31}P intensity) and Ph_3PO (30%) as the major species, while the orange-solution yielded 44mgs. of solid which contained "Asymmetric Dimer" (40%) and an unknown at δ = +26.1 ppm (47%).

(v) <u>cis</u>-$[PtCl_2(CO)(PPh_3)]$ (504mg, 0.909mmol.) and TlC_5H_5 (488mg, 1.810mmol.) were allowed to react in $CHCl_3$ for 1 day. A ^{31}P spectrum of the solution contained the species at +11.1 ppm, $^{1}J_{PtP}$ = 5640 Hz as the major product (82% of the intensity) with a species at +6.6 ppm. The solution was filtered and 380mg of TlCl (1.585mmol, 88% of Tl) was recovered. The solvent was removed to give a black oil which, on extraction with ether, yielded an orange solution and a golden brown solid. An i.r. spectrum of this solid contained no CO stretch. The orange solution yielded a yellow oil which resisted all attempts at crystallisation. A ^1H nmr spectrum of the yellow oil contained a π-C_5H_5 signal at +5.6 ppm, (doublet) with $J_{PH} = 1.3$ Hz and $J_{PtH} = 13.2$ Hz while a ^{31}P nmr contained the species, $\delta = +11.2$ ppm, $^1J_{PtP} = 5632$ Hz as 89% of the intensity along with Ph_3PO. Eventually, a light brown solid that was largely this material was obtained from an ether solution, and an i.r. spectrum had a strong, broad absorbance at 1630cm^{-1}. A $CDCl_3$ solution of this species slowly produced "Asymmetric Dimer" and Ph_3PO over a period of 1 week.

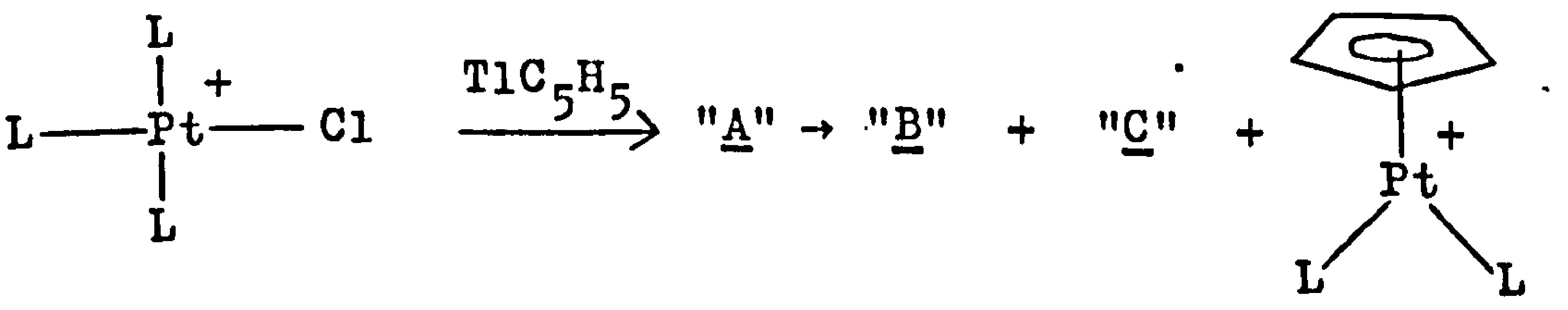
CHAPTER FIVE

TRISPHOSPHINE COMPLEXES OF PLATINUM

RESULTS AND DISCUSSION

[PtCl(PMe$_2$Ph)$_3$]X and TlC$_5$H$_5$

TlC$_5$H$_5$ reacted with [PtCl(PMe$_2$Ph)$_3$]SO$_3$CF$_3$ in CDCl$_3$ to produce initially a trisphosphine platinum complex, A (parameters in table 18), as an intermediate, followed by another trisphosphine platinum complex B, (table 18). Complex B was the major product, but a third trisphosphine complex C (table 18) was also produced, along with [Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]SO$_3$CF$_3$. The ^{1}H nmr spectrum of this mixture did not contain any signals which could be identified as a σ-bonded C$_5$H$_5$ ring. Clearly the simple replacement of Cl by C$_5$H$_5$, which might have been expected from this reaction to give only [Pt(η^1-C$_5$H$_5$)(PMe$_2$Ph)$_3$]SO$_3$CF$_3$ has not occurred. The parameters of B and C are very similar to each other, and are typical of a square-planar trisphosphine platinum complex with a σ-bonded organic group as the fourth ligand. For example, [PtMe(PMe$_2$Ph)$_3$]BF$_4$ has ^{31}P parameters:- δ = -5.7 ppm, $^1J_{PtP}$ = 2682 Hz (d) and δ = -13.1 ppm, $^1J_{PtP}$ = 1831 Hz (t), $^2J_{PP}$ = 24 Hz.[195] The first produced trisphosphine complex, A, has parameters very different from this.



A similar result was obtained when CHCl$_3$ was used as the solvent, thus one possible explanation for the similarity of B and C can be eliminated, namely that B is [Pt(η^1-C$_5$H$_5$)-L$_3$]$^+$ and C is the same compound in which the ring has been deuterated, i.e. $[Pt(\eta^1-C_5D_5)L_3]^+$. Furthermore complex B is produced first, and complex C appears to be formed from it.

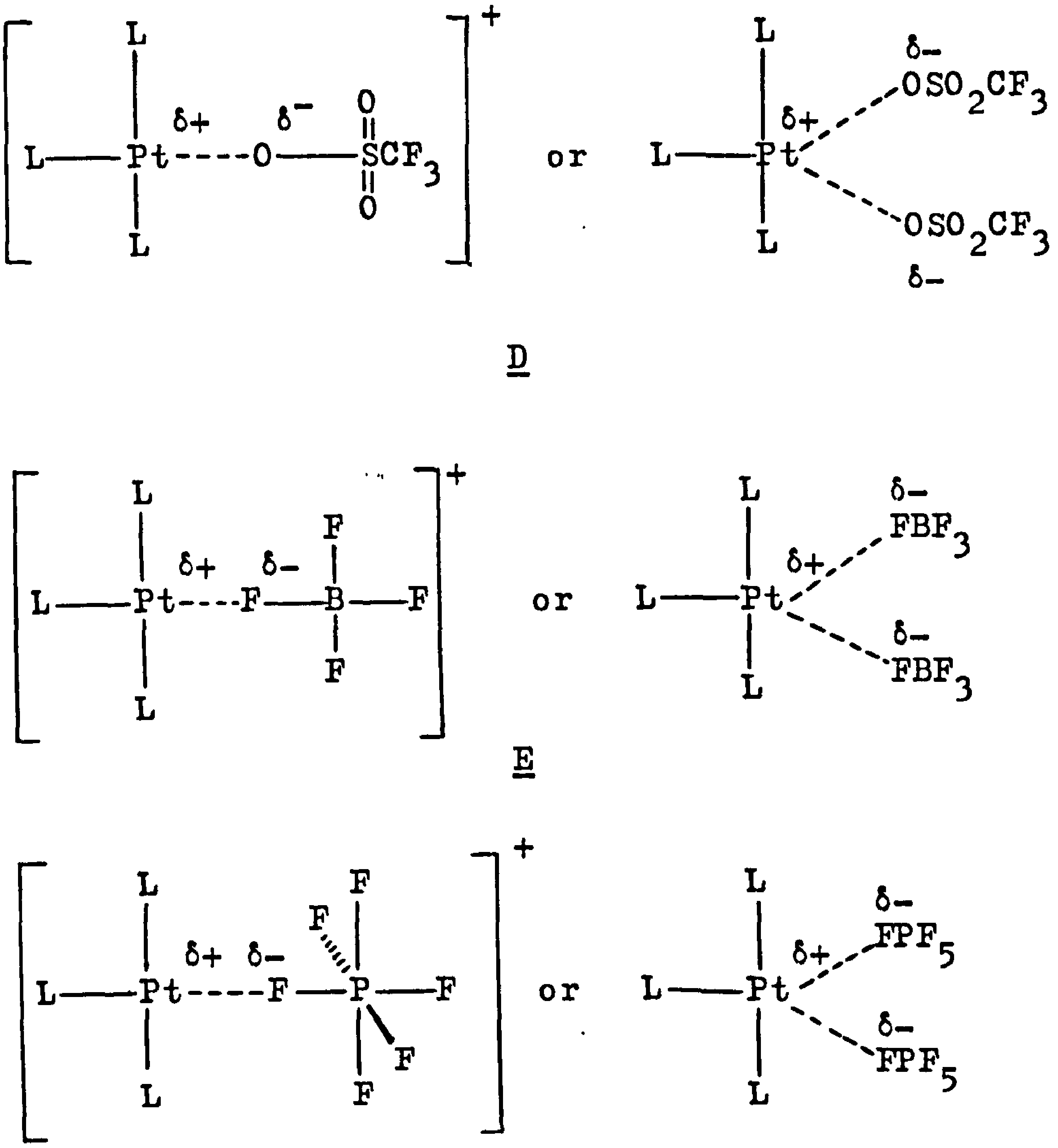
When $[PtCl(PMe_2Ph)_3]Cl$ and TlC_5H_5 were allowed to react, the reaction was more rapid, and although some trisphosphine complex B was produced, it rapidly decomposed. The major products in this case were $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$, $[Pt(PMe_2Ph)_4]^{2+}$ (^{31}P nmr at 25°C:- $\delta = -15.0$ ppm, $^1J_{PtP} =$ 2369 Hz) and $PhMe_2PO$ ($\delta = +34.5$ ppm).

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ does not react with $Hg(C_5H_5)_2$ within 3 days at room temperature. Possibly the three phosphine ligands around platinum create enough steric hinderance to block approach of $Hg(C_5H_5)_2$ via an S_E2 (cyclic) mechanism.

Reactions between $[PtCl(PMe_2Ph)_3]X$ and Silver Salts

The chloride of $[PtCl(PMe_2Ph)_3]SO_3CF_3$ was removed by $AgSO_3CF_3$ to produce a trisphosphine complex, D, with very different ^{31}P parameters to the starting material. The doublet for the two phosphines *trans* to each other has moved downfield although $^1J_{PtP}$ is practically unchanged; while the triplet has moved upfield and $^1J_{PtP}$ has increased by 330 Hz, indicating that the ligand *trans* to this phosphine has a lower *trans*-influence than Cl. Similar complexes, E and F, were produced when $[PtCl(PMe_2Ph)_3]Cl$ was treated with two equivalents of $AgBF_4$ and $AgPF_6$ respectively. The ^{31}P parameters of complexes D, E and F are very similar. There is only a slight difference between $^1J_{PtP}$ values for the doublet, although there is a variation of almost 100 Hz in $^1J_{PtP}$ for the triplet.

Although coordination of $SO_3CF_3^-$ to platinum has been claimed,[196] for the complex $[PtCl(OSO_2CF_3)(PR_3)_2]$, produced by halide abstraction from <u>cis</u>-$[PtCl_2(PR_3)_2]$ by $HOSO_2CF_3$, this could have been $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][SO_3CF_3]_2$, and evidence in favour of coordination is inconclusive. BF_4^- and PF_6^- are generally considered to be non-coordinating anions. The reaction between $[PdCl_2L_2]$ (L = phosphine, arsine or stibine) and $AgPF_6$ in acetone leads to the formation of a complex $[Pt(Me_2CO)_2L_2][PF_6]_2$,[197] thus $[Pt(PMe_2Ph)_3(CDCl_3)]^{2+}$ is a possibility for complexes <u>D</u>, <u>E</u>, and <u>F</u>, but if this is the case there should be virtually no difference in ^{31}P parameters between the complexes. The parameters of complex <u>D</u> in acetone are very similar to those in $CDCl_3$. Since the parameters vary as the anion varies, it is more plausible that there is an interaction between the anion and platinum. $SO_3CF_3^-$ could bond via oxygen as in the example above, but BF_4^- and PF_6^- presumably interact through fluorine. This would give the structures shown in figure 41 as most probable for complexes <u>D</u>, <u>E</u> and <u>F</u>, with 4-coordinate complexes $[PtL_3X]X$ if one anion interacts, or five-coordinate complexes if both interact, $[PtL_3X_2]$. No ^{19}F - ^{31}P coupling is observed, so any interaction must be weak.



D

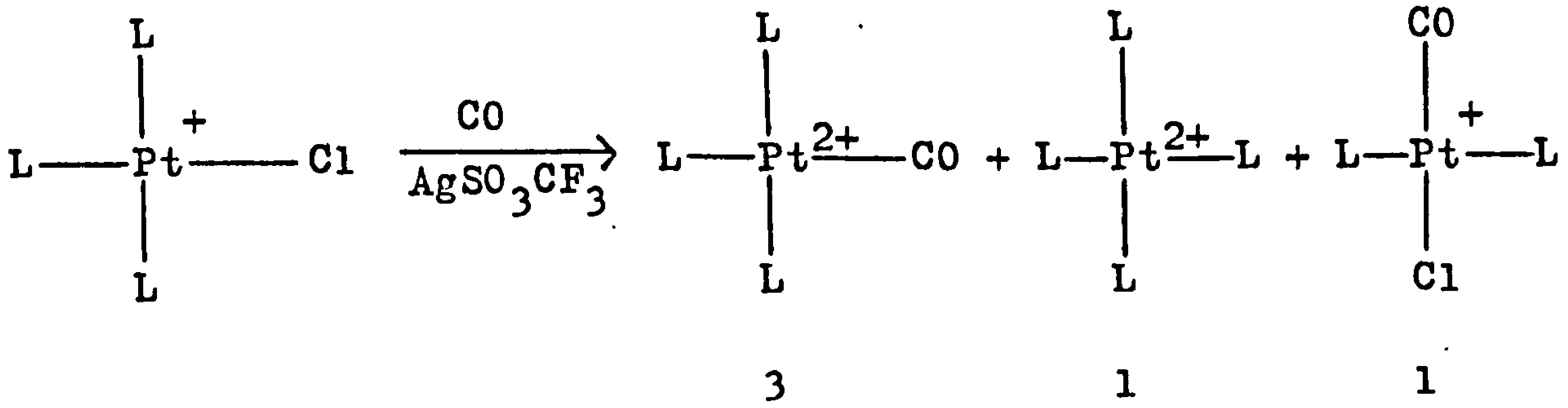
E

F

figure 41.

Reactions of Compex D

When carbon monoxide was bubbled through a solution of $[PtCl(PMe_2Ph)_3]Cl$ in the presence of 2 equivalents of $AgSO_3CF_3$, complex D was initially formed and reacted further to produce $[Pt(CO)(PMe_2Ph)_3][SO_3CF_3]_2$, (parameters in table 19). Both $[Pt(PMe_2Ph)_4]^{2+}$ and trans-$[PtCl(CO)(PMe_2Ph)_2]^+$ were also formed, thus $AgSO_3CF_3$ could not have removed all of the Cl from solution.



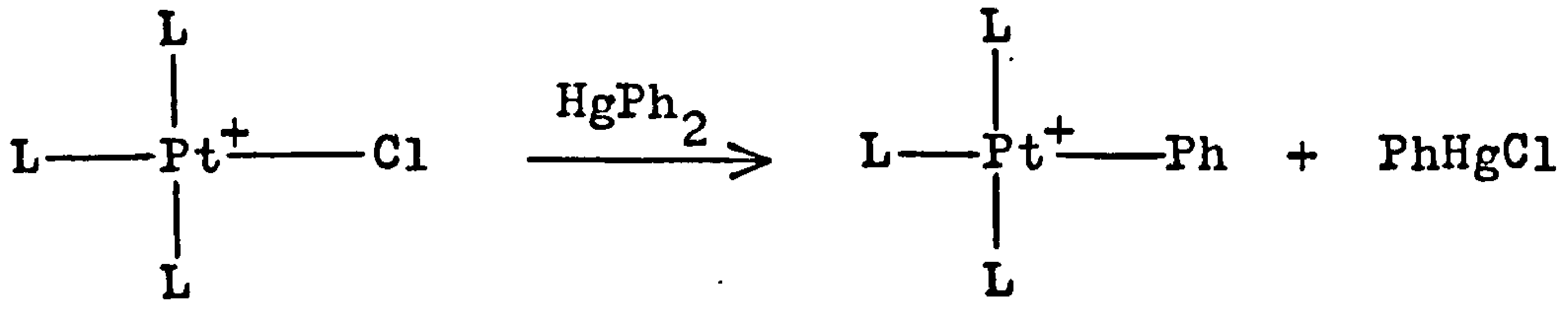
$$\mathrm{L{-}\overset{L}{\underset{L}{Pt^{+}}}{-}Cl} \xrightarrow[\mathrm{AgSO_3CF_3}]{\mathrm{CO}} \underset{3}{\mathrm{L{-}\overset{L}{\underset{L}{Pt^{2+}}}{-}CO}} + \underset{1}{\mathrm{L{-}\overset{L}{\underset{L}{Pt^{2+}}}{-}L}} + \underset{1}{\mathrm{L{-}\overset{CO}{\underset{Cl}{Pt^{+}}}{-}L}}$$

TlC_5H_5 reacted with tris-phosphine platinum complex D very rapidly and almost quantitatively to produce a new tris-phosphine complex, G, (parameters in table 18). Minor products were $[Pt(PMe_2Ph)_4][SO_3CF_3]_2$ and an unknown species, $\delta = -17.4$ ppm, $^1J_{PtP} = 3479$ Hz (at -60°C). Complex G reacted slowly, over 2 days, to produce complex B and complex C, $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ and more $[Pt(PMe_2Ph)_4][SO_3CF_3]_2$. The ^{31}P parameters of G are similar to those of A and it is likely that the two complexes are related.

Since $[Pd(Me_2CO)_2L_2][PF_6]_2$ reacts rapidly with C_5H_6 to form $[Pd(\eta^5\text{-}C_5H_5)L_2][PF_6]$,[197] C_5H_6 was added to a $CDCl_3$ solution of trisphosphine complex D. Although the solution became deeply coloured, very little reaction was detectable by ^{31}P nmr spectroscopy, and the products were $[Pt(PMe_2Ph)_4]^{2+}$ and $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$. C_5H_6 must react with complex D to produce $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ and liberate a molecule of phosphine which then attacks another molecule of complex D, to form $[Pt(PMe_2Ph)_4]^{2+}$.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ and $HgPh_2$ reacted slowly in $CDCl_3$ to produce only one trisphosphine complex, identified as $[PtPh(PMe_2Ph)_3]SO_3CF_3$, ($^{31}P$ parameters in table 19), as the major product and a complex with parameters $\delta = -17.7$ ppm, $^1J_{PtP} = 3529$ Hz. The analogous trisphosphine complex of

$PMePh_2$, $[PtPh(PMePh_2)_3]ClO_4$, has been reported[198] and has similar ^{31}P parameters.

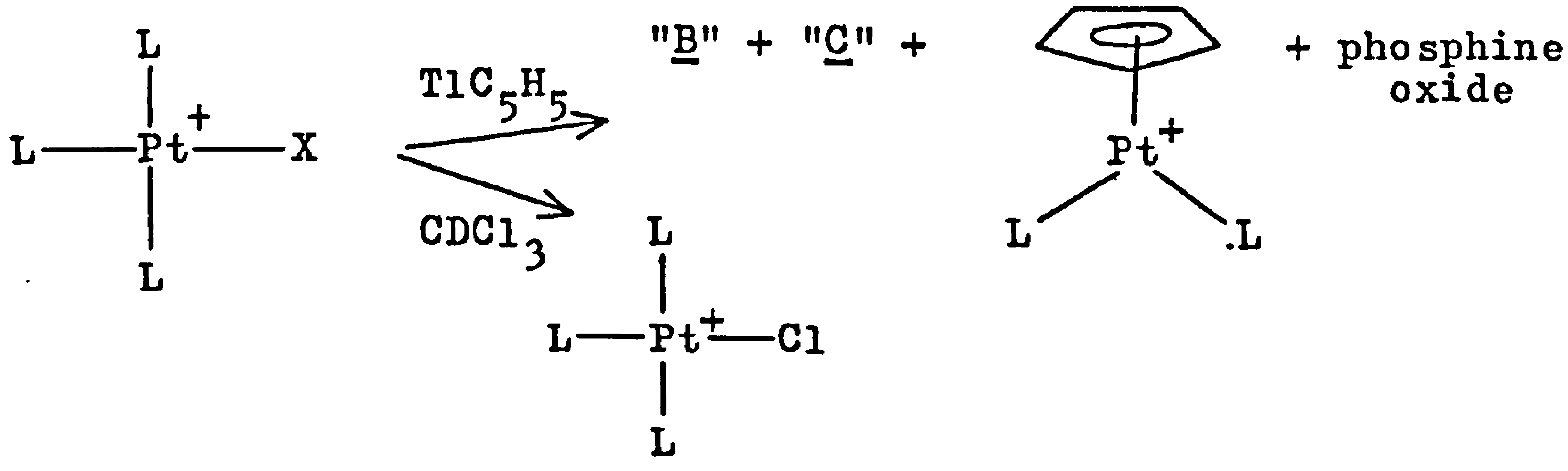


The trisphosphine complex D also reacted with $HgPh_2$, but in this case a new trisphosphine complex, H, was produced (^{31}P parameters in table 18), along with the unidentified complex produced in the previous reaction, and $PhMe_2PO$ which seemed to have been displaced to higher field and to be coupled either to platinum or to mercury, although the intensity of the satellites favours Hg, ($\delta = +30.3$ ppm, $J_{HgP} = 2198$ Hz). Complexes D and H appeared to undergo exchange reactions at room temperature. After 1 month, the solution had reacted to form $[PtPh(PMe_2Ph)_3]SO_3CF_3$ and the unidentified complex, with parameters $\delta = -17.7$ ppm, $^1J_{PtP} = 3529$ Hz. Thus complex H appears to be an intermediate en route to $[PtPh(PMe_2Ph)_3]^+$, analogous to complex G, formed as an intermediate in the reaction of TlC_5H_5 with complex D.

TlC_5H_5 and $[PtX(PMe_2Ph)_3]SO_3CF_3 (X = Br, I)$

$[PtBr(PMe_2Ph)_3]SO_3CF_3$ and $[PtI(PMe_2Ph)_3]SO_3CF$ were prepared by treating trisphosphine complex D with one equivalent of $[Bu_4N]Br$ and $[Bu_4N]I$ respectively. These complexes reacted with TlC_5H_5 in a manner similar to $[PtCl(PMe_2Ph)_3]SO_3CF_3$, producing $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ and complex B initially, with complex C also appearing later, along with $PhMe_2PO$. The ^{31}P signals for $[PtBr(PMe_2Ph)_3]^+$

and $[PtI(PMe_2Ph)_3]^+$ were broadened at room temperature by exchange with liberated phosphine, but were sharp at -60°C. There was one difference in these reactions, however.
As the reaction progressed, the parameters for the tris-phosphine complexes changed, both the triplet and doublet moved downfield while $^1J_{PtP}$ also changed. The ^{31}P parameters seemed to move closer to those for $[PtCl(PMe_2Ph)_3]^+$ as the reaction progressed. This can be explained by a halide exchange of Br or I for Cl from the solvent. Such halogen exchanges have been observed for some other platinum complexes in $CDCl_3$ (see chapter 4). Halogen exchange between $[PtIL_3]^+$ or $[PtBrL_3]^+$ and $[PtClL_3]^+$ might be expected to be rapid, with only one, averaged signal being obtained in the ^{31}P spectrum, even at -60°C.



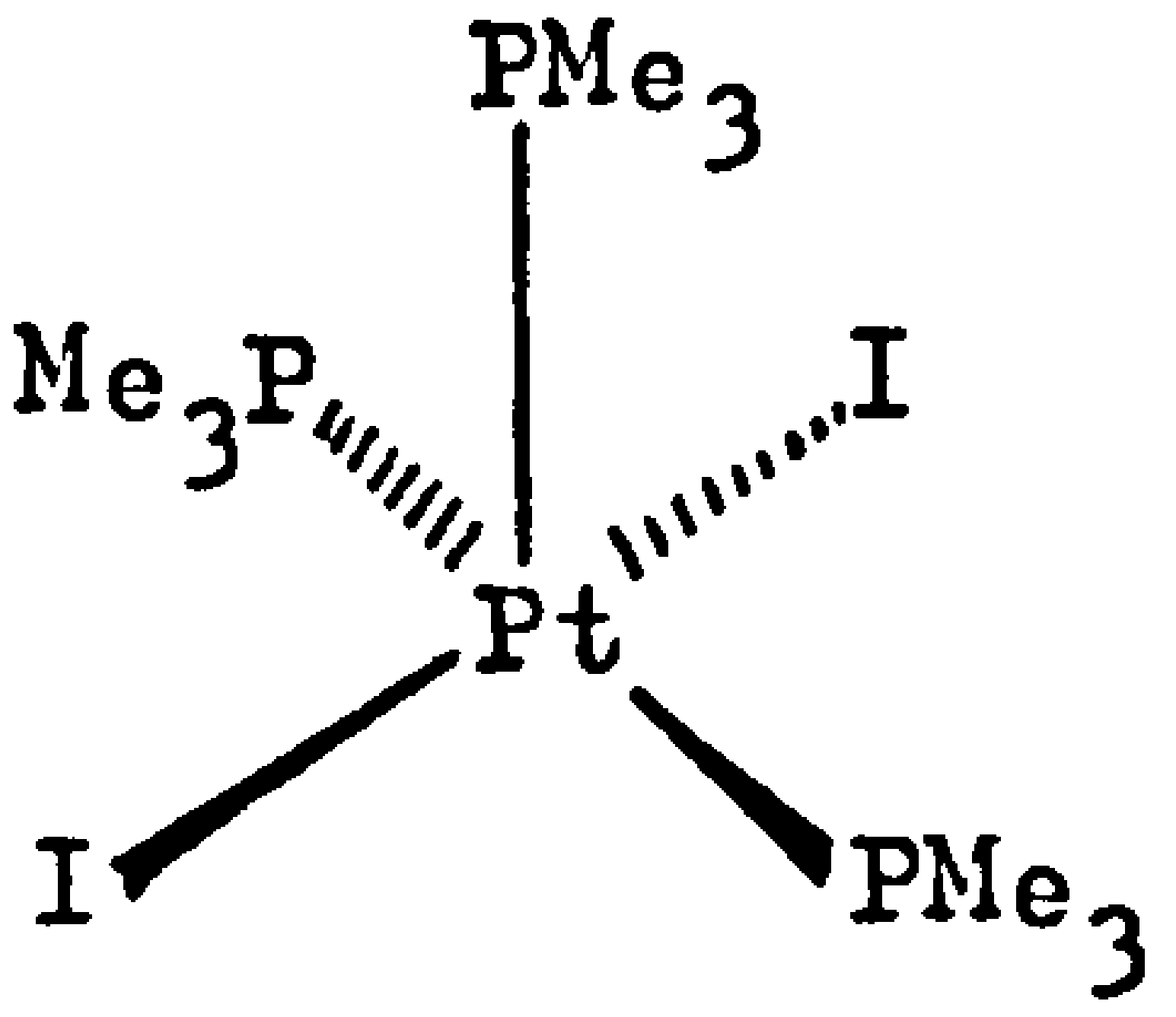
Five-coordinate complexes $[PtX_2L_3]$

Addition of excess $[Bu_4N]I$ to $[PtI(PMe_2Ph)_3]SO_3CF_3$ caused a shift in the ^{31}P parameters of the platinum complex. The peaks were broad at room temperature, but sharp at -60°C. Successive additions of I^- displaced both the doublet and triplet to higher field, and dramatically increased $^1J_{PtP}$ for the triplet by over 270 Hz. Similar behaviour was observed on addition of $[Bu_4N]Br$ to $[PtBr(PMe_2Ph)_3]SO_3CF_3$, although the increase in $^1J_{PtP}$ for the triplet was less dramatic, being only 150 Hz. Most of the shift in nmr parameters occurred on addition of only one equivalent of I^- or Br^-; addition of further halide modifying the parameters only slightly. By contrast $[PtCl(PMe_2Ph)_3]Cl$ has very similar ^{31}P parameters to $[PtCl(PMe_2Ph)_3]SO_3CF_3$. This suggests that five-coordinate trisphosphine complexes $[PtI_2(PMe_2Ph)_3]$ and $[PtBr_2(PMe_2Ph)_3]$ have been formed (parameters in table 19).

The formation of the complexes $[PtBr_2(PMe_2Ph)_3]$ and $[PtI_2(PMe_2Ph)_3]$ has been claimed in the reaction between $[Pt(PMe_2Ph)_4]$ and 1-bromo-ethylbenzene and 2-iodobutane respectively, carried out in benzene,[199] and by addition of PMe_2Ph to $[PtBr_2(PMe_2Ph)_2]$ or $[PtI_2(PMe_2Ph)_2]$ in pentane/CH_2Cl_2.[200] Evidence in favour of five-coordinate complexes was a band at 400 nm in the visible spectrum of $[PtBr_2L_3]$, which was absent in a spectrum of $[PtBrL_3]ClO_4$, and differences between the ^1H nmr parameters of the phosphine methyl protons of $[PtX_2L_3]$ and $[PtXL_3]^+$. However, conflicting results have been obtained, and Cooper and Powell have claimed that addition of PMe_2Ph to $[PtCl_2(PMe_2Ph)_2]$ or $[PtI_2(PMe_2Ph)_2]$ in chloroform produces the four coordinate ionic complexes, $[PtCl(PMe_2Ph)_3]Cl$ and $[PtI(PMe_2Ph)_3]I$.[201] The analogous five-coordinate palladium complex $[PdCl_2(PMe_2Ph)_3]$ has been isolated and its crystal structure obtained. This was found to be square-pyramidal with three phosphines and one chloride in the basal plane.[202]

Recently, Roulet has shown that addition of PMe_3 to $[PtX_2(PMe_3)_2]$ produces the four-coordinate ionic complex

$[PtX(PMe_3)_3]^+X^-$ when X is Cl or Br, and the five-coordinate neutral complex $[PtX_2(PMe_3)_3]$ when X is I.[203] That $[PtI_2(PMe_3)_3]$ is five-coordinate in solution was shown by its ^{31}P nmr spectrum, which differs considerably from that of $[PtI(PMe_3)_3]PF_6$. The doublet and triplet of $[PtI_2(PMe_3)_3]$ are shifted to high field, and $^1J_{PtP}$ for the triplet is increased by 700 Hz. The authors favoured a square-pyramidal geometry with one PMe_3 in the apical position and two basal iodides trans to each other.



An extensive series of complexes $[PtX_2L_3]$ (X = Cl, Br, I; L = 1-R-3,4-dimethyl phosphole) have also recently been reported, and these are all five-coordinate, neutral complexes in solution.[204] A square-based pyramidal geometry was also favoured for these complexes.

Thus, it seems likely that $[PtBr_2(PMe_2Ph)_3]$ and $[PtI_2(PMe_2Ph)_3]$ are five-coordinate complexes, with the most likely geometry being that shown in figure 42 below.

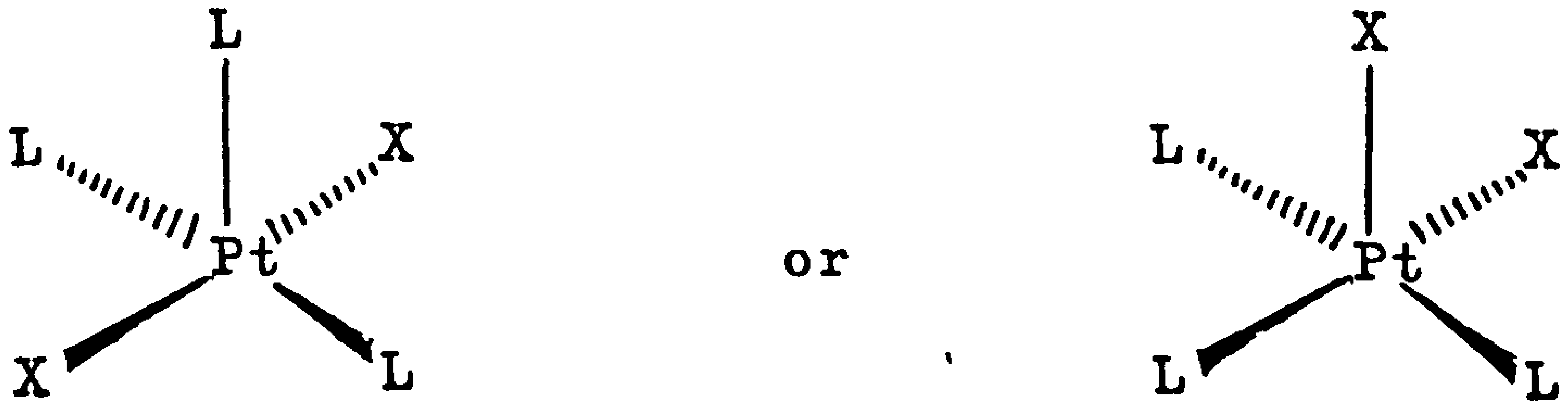


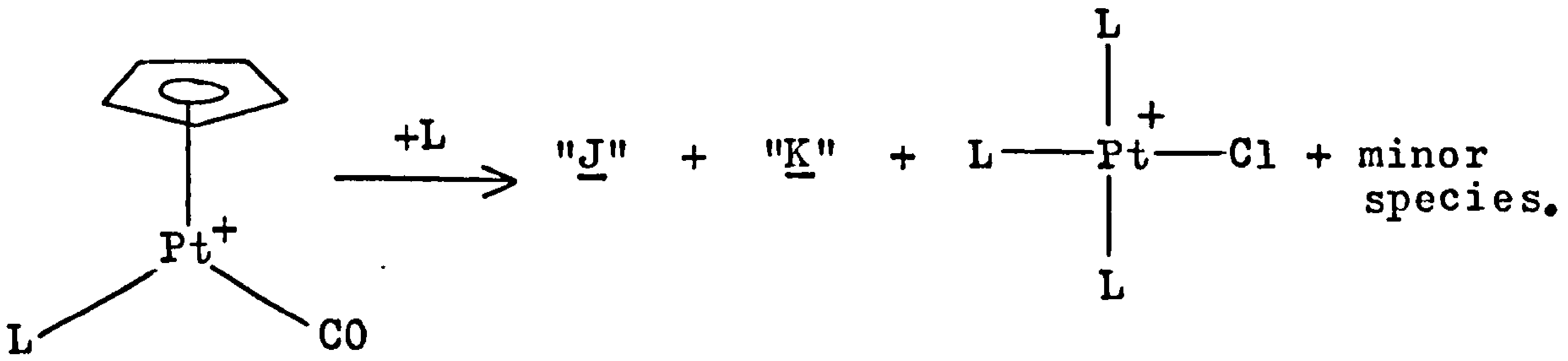
figure 42.

Trisphosphine complexes from addition of phosphine to platinum complexes

When PMe_2Ph was added to $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ the products were complex B and Ph_2MePO, along with a broad peak due to an exchanging system. Addition of sulphur to abstract any free phosphine present removed the broad peak and replaced it with $PhMe_2PS$ and $[PtCl(PMe_2Ph)_3]SO_3CF_3$, plus small amounts of cis-$[PtCl_2(PMe_2Ph)_2]$ and an unidentified complex, $\delta = -5.2$ ppm, $^1J_{PtP} = 2828$ Hz which was previously observed in the reaction of cis-$[PtCl_2(CO)(PMe_2Ph)]$ with two equivalents of TlC_5H_5. On adding PMe_2Ph to $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]$-$SO_3CF_3$ in acetone, complex B was the major product, but this was eventually replaced by $[Pt(PMe_2Ph)_4]^{2+}$.

Addition of PMe_2Ph to $[Pt(\eta^5-C_5H_5)L_2]Cl$ in $CDCl_3$ also produced complex B and $PhMe_2PO$, along with a broad peak due to an exchanging system. Complex C also appeared later and addition of $AgSO_3CF_3$ removed the broad peak, replacing it with $[PtCl(PMe_2Ph)_3]SO_3CF_3$ and another, minor trisphosphine complex, J.

PMe_2Ph reacted with $[Pt(\eta^5-C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$ in $CDCl_3$ to produce two tris-phosphine complexes J and K, (parameters in table 18), $[PtCl(PMe_2Ph)_3]SO_3CF_3$, an unknown complex (parameters in experimental section), $[Pt(\eta^5-C_5H_5)$-$(PMe_2Ph)_2]SO_3CF_3$ and $PhMe_2PO$. The $^1J_{PtP}$ values for complex J are very similar to those of complexes B and C, although both the doublet and triplet are further upfield. Complex K has a remarkably low value of $^1J_{PtP}$ for the phosphine cis to two phosphines. The parameters of complex K are typical of a trisphosphine platinum complex with a carbonyl-inserted organic group as the fourth ligand. For example [Pt(COPh) $(PMePh_2)_3]ClO_4$ has ^{31}P parameters, $\delta = -4.3$ ppm, $^1J_{PtP} = 3015$ Hz (d) and $\delta = -8.7$ ppm, $^1J_{PtP} = 1475$ Hz, (t), $^2J_{PP} = 26$ Hz.[198]

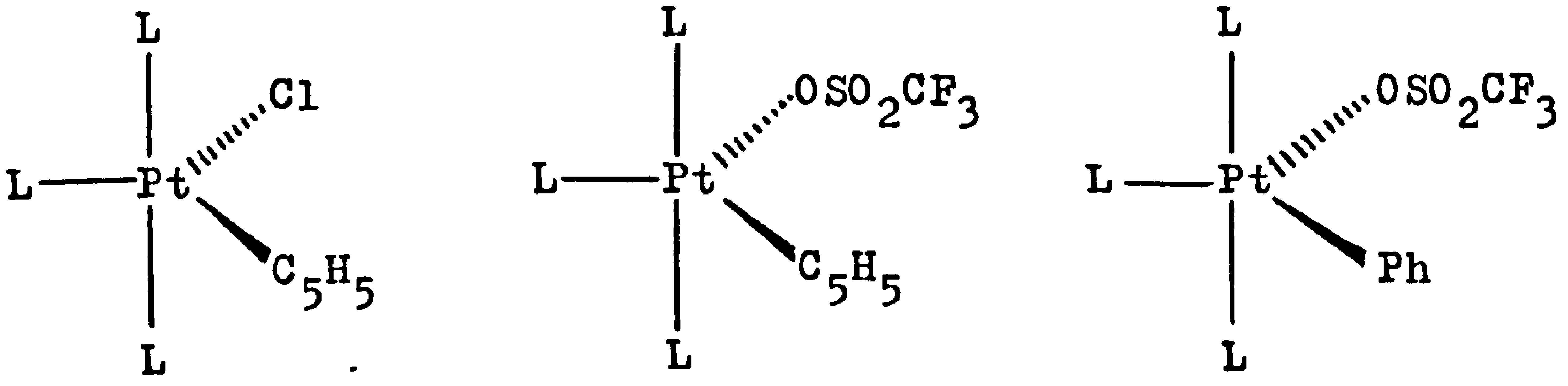


Two other trisphosphine complexes, L and M, were obtained as two of many products when neat phosphine was added to a solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I). Other products were the unknown complex obtained in the previous reaction, $[PtCl(PMe_2Ph)_3]Cl$, $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]Cl$, another unknown complex (parameters in experimental section) and other, minor products. A ^1H nmr spectrum showed that some C_5H_6 had been produced.

Identities of trisphosphine platinum complexes

The chemical shifts of the doublet and triplet signals in the ^{31}P spectra of complexes, A, G and H are similar to those for complexes D, E and F. The latter complexes were considered to be four- or five-coordinate trisphosphine complexes in which the other ligand, or ligands, was the anion SO_3CF_3, BF_4 or PF_6. Complex A was obtained in the reaction between $[PtCl(PMe_2Ph)_3]SO_3CF_3$ and TlC_5H_5 while complex G was obtained in the reaction between complex D and TlC_5H_5. Both A and G were intermediates en route to complexes B and C. Complex H was obtained in the reaction between complex D and $HgPh_2$ as an intermediate en route to

$[PtPh(PMe_2Ph)_3]SO_3CF_3$. Complexes A, G and H have parameters which differ considerably from those of a four-coordinate trisphosphine complex with a σ-bonded organic group as the fourth ligand. It is possible that these complexes are five-coordinate intermediates with either σ-bonded organic groups (C_5H_5 and Ph) or with the organic groups still co-ordinated to Tl or Hg. Possible structures with σ-bonded organic groups are shown in figure 43 below.

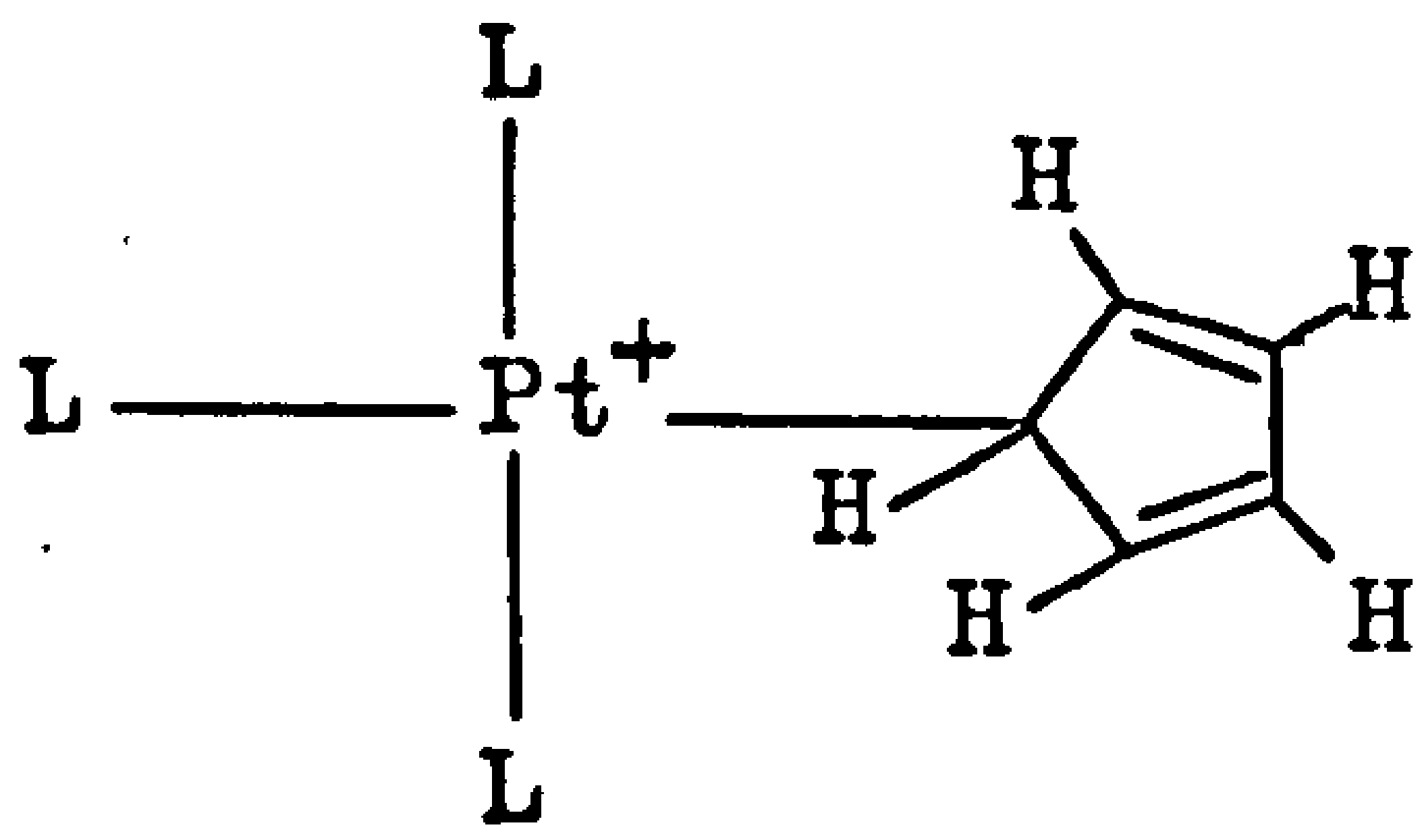


A. G H

figure 43.

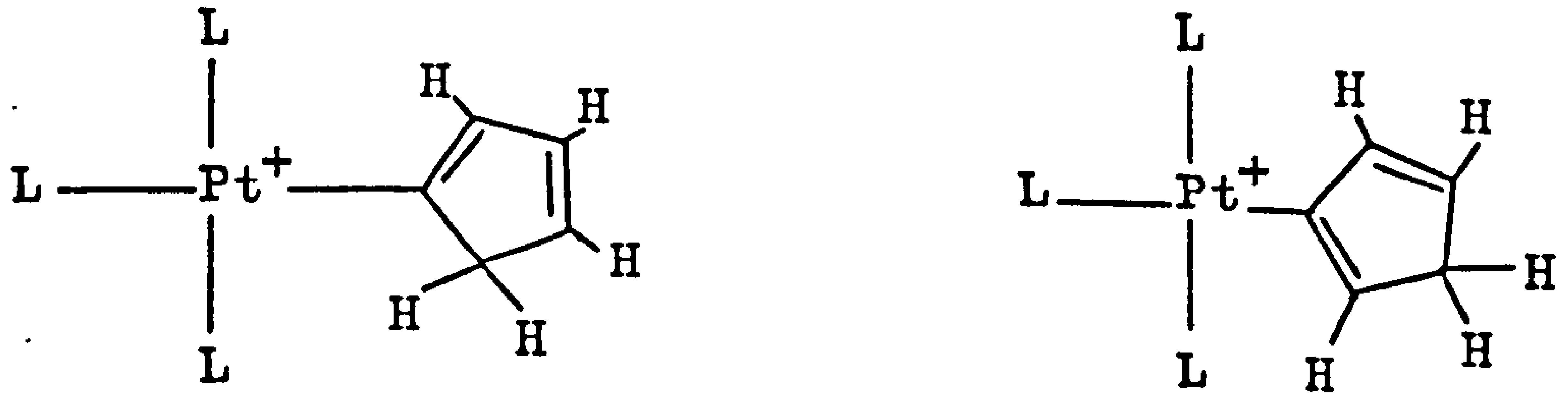
Intermediates in which molecules of TlC_5H_5 or $HgPh_2$ are bonded to platinum, either via a π-bond from the organic group or σ-bonds from both organic group and metal, are also possible, but these would also have to be five-coordinate.

Trisphosphine complexes B, C and J all have very similar ^{31}P parameters, and these are similar to many trisphosphine complexes with a σ-bonded organic group as the fourth ligand.[195] Complex B was produced from the reaction between $[PtCl(PMe_2Ph)_3]^+$ and TlC_5H_5 and the reaction between $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ and PMe_2Ph. Thus the most probable identity for complex B is $[Pt(\eta^1-C_5H_5)(PMe_2Ph)_3]^+$.



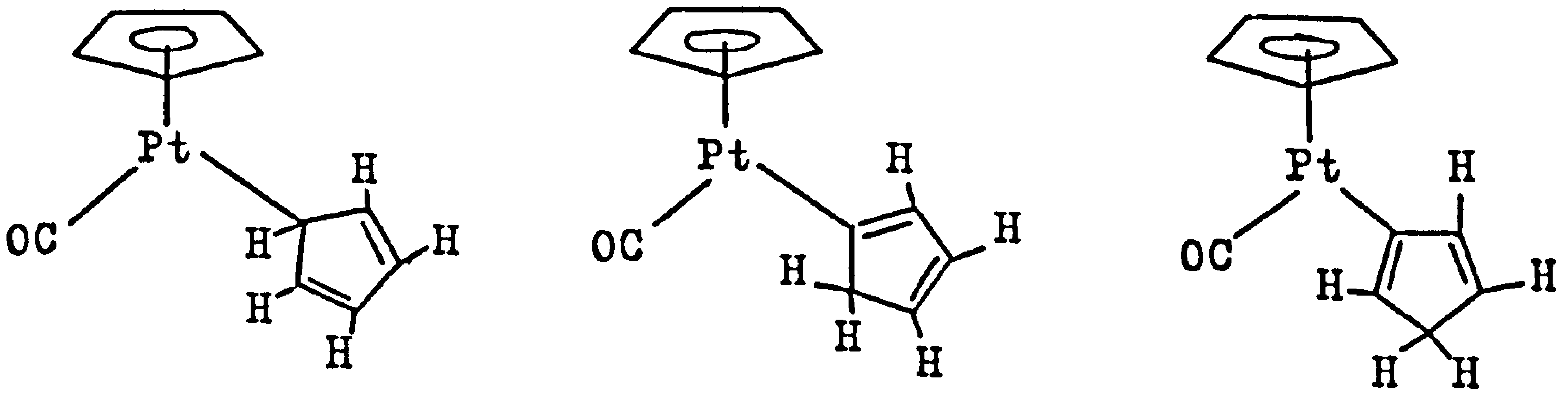
B

Complex C is produced in the same reactions as complex B, but always after complex B. Complex J was obtained as a major product in the reaction between $[Pt\eta^5-C_5H_5)(CO)(PMe_2Ph)]^+$ and PMe_2Ph, and as a minor product in $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ and PMe_2Ph. Complexes C and J could thus be the two vinyl isomers of complex B, which could be formed from B by successive [1,5] sigmatropic rearrangements.



C and J

Such an isomerisation of σ-bonded C_5H_5 rings has been observed with $[Pt(CO)(\eta^1-C_5H_5)(\eta^5-C_5H_5)]$, which slowly converts to its vinyl isomer (a) in solution, which in turn equilibrates with the other vinyl isomer (b).[176] (fig. 44).



(a) (b)

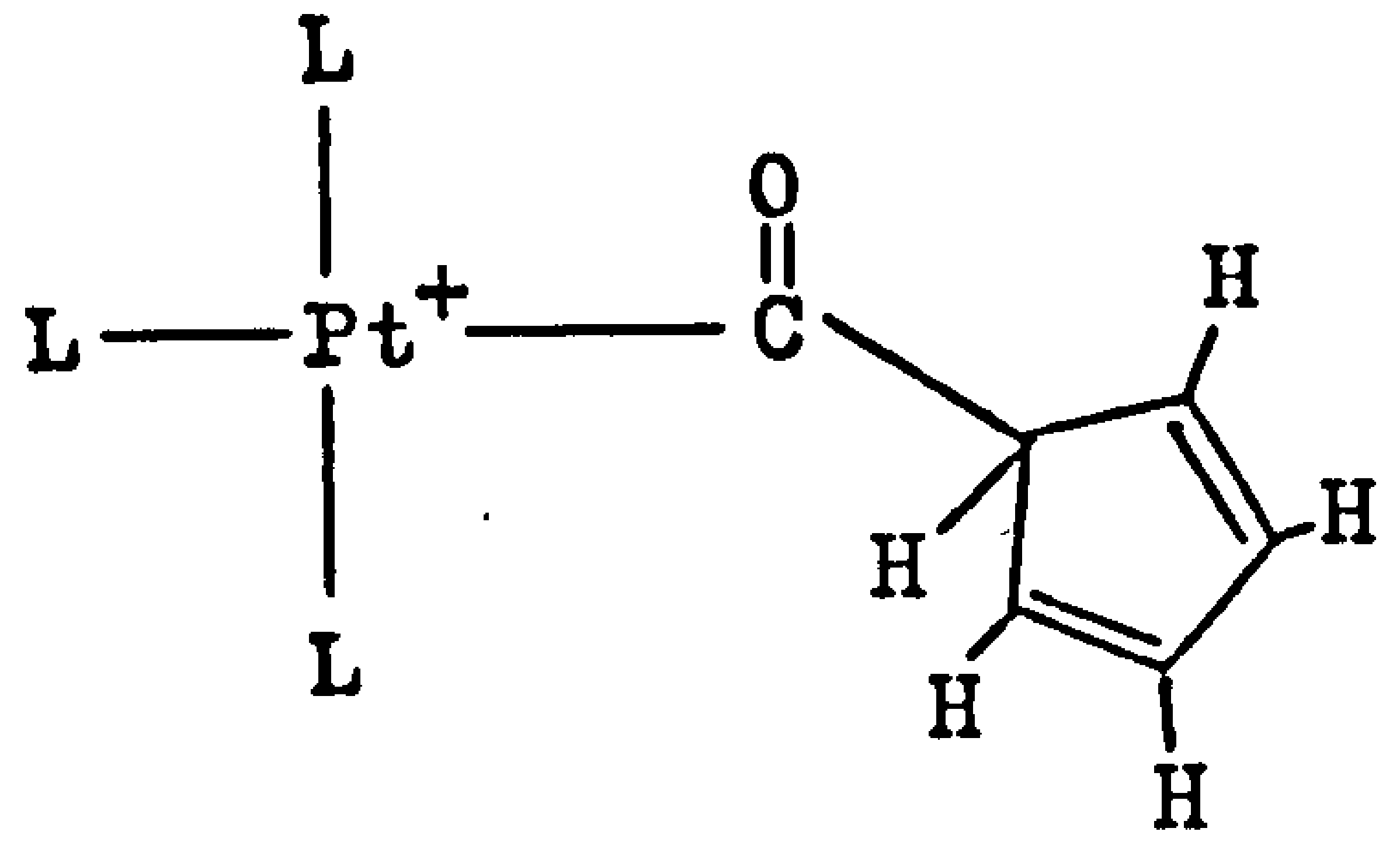
figure 44.

Similar behaviour was observed with [Pt(η-C_2H_4)(η^1-C_5H_5)(η^5-C_5H_5)].

Cyclopentadienyl silane, [(η^1-C_5H_5)SiH_3], also undergoes such isomerisation to vinyl isomers,[205] and theoretical calculations indicate that a 1,2-H shift (equivalent to a [1,5] sigmatropic rearrangement) is the mechanism of isomerisation, and that the vinyl isomers are more stable.[206]

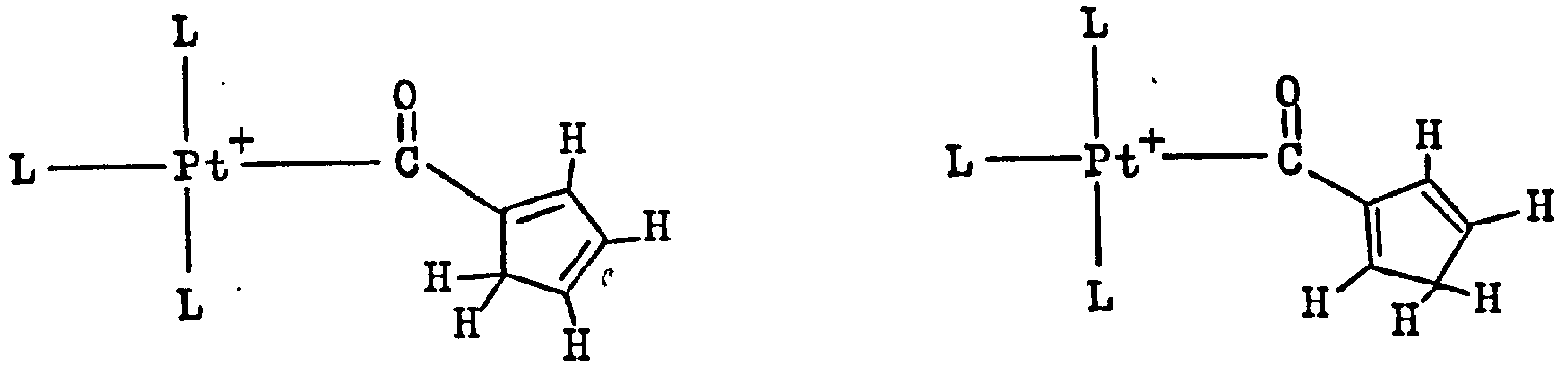
Surprisingly, the cyclopentadienyl isomer (I) complexes, [PtCl(η^1-C_5H_5)(CO)L], appear not to undergo such isomerisation reactions. No ^{31}P or ^1H signals were observed in solutions of isomer (I) which can be attributed to vinyl isomers, although such species could be involved in the decomposition of isomer (I). A vinyl C_5H_5 might react with C_5H_5 from Pt or Tl to abstract a proton and produce C_5H_6, which is obtained in a number of reactions, particularly in the formation of "Asymmetric Dimer".

Complex K, formed from the reaction between [Pt(η^5-C_5H_5)(CO)(PMe_2Ph)]$^+$ and PMe_2Ph has ^{31}P nmr parameters which bear a similar relationship to those of complex B as the parameters of [Pt(COPh)($PMePh_2$)$_3$]$^+$ bear to [Pt(Ph)($PMePh_2$)$_3$]$^+$.[198] The phenyl complex has $^1J_{PtP}$ values of 2798 Hz for the doublet and 1792 Hz for the triplet, while the COPh complex has values of 3015 Hz and 1475 Hz. This suggests that complex K could be a carbonyl inserted species, [Pt(COC_5H_5)(PMe_2Ph)$_3$]$^+$. It was also observed in acetone, thus it cannot have been derived from solvent, and the organic group which can have inserted is C_5H_5.



K

Complexes L and M produced when neat phosphine was added to $[PtCl(\eta^1-C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) may be analogous carbonyl insertion products of the two vinyl isomers of C_5H_5, the differences in $^1J_{PtP}$ in this case could be due to conjugation of the double bonds of the C_5H_5 ring with the carbonyl double bond.



L and M

The identities of the trisphosphine complexes in table 19 are well established, but those in table 18 are only speculative. Of the unknown complexes in table 18, the identifications of B as $[Pt(\eta^1-C_5H_5)(PMe_2Ph)_3]^+$, C as a vinyl isomer of this and K as $[Pt(COC_5H_5)(PMe_2Ph)_3]^+$ seem to be the best established, the rest are less well so. More experiments need to be performed before definite identities can be established for the complexes in table 18, and further studies of the relationships between some of the complexes would also be worthwhile.

Table 18:- ^{31}P nmr of trisphosphine platinum complexes in $CDCl_3$ at 25°C. (Phosphine is PMe_2Ph).

Complex	δ(ppm)	$^1J_{PtP}$ (Hz)		$^2J_{PP}$ (Hz)	Comments
A	-0.7	2490	d	21.9	possibly five-coordinate with C_5H_5 and Cl.
	-24.3	3000	t		
B	-7.6	2620	d	22.6	probably this is $[Pt(\eta^1-C_5H_5)(PMe_2Ph)_3]^+$
	-15.8	1818	t		
C	-8.6	2610	d	22.6	this is probably a vinyl isomer of <u>B</u>
	-16.1	1814	t		
D	+1.0	2360	d	22.1	four or five-coordinate with solvent or SO_3CF_3.
	-25.6	3826	t		
E	+1.2	2357	d	22.2	analogous to <u>D</u> with with BF_4
	-25.8	3896	t		
F	+2.0	2368	d	21.9	analogous to <u>D</u> with PF_6.
	-25.0	3802	t		
G	+0.4	2466	d	21.4	analogous to <u>A</u> with C_5H_5 and SO_3CF_3.
	-23.4	3135	t		
H(a)	-0.4	2397	d	21.5	possibly similar to <u>A</u> with Ph and SO_3CF_3.
	-24.5	3575	t		
J	-12.2	2612	d	26.5	this is possibly a vinyl isomer of <u>B</u>.
	-21.8	1788	t		
K	-11.7	2914	d	26.0	possibly this is $[Pt(COC_5H_5)(PMe_2Ph)_3]^+$
	-21.5	1495	t		

Cont./

Table 18 :- continued

Complex	δ(ppm)	$^1J_{PtP}$ (Hz)		$^2J_{PP}$ (Hz)	Comments
L	-10.6 -20.9	3289 (b)	d t	21.4	this could be a vinyl isomer of K.
M	-11.0 -21.1	3219 1365	d t	22.3	this could be a vinyl isomer of K.

(a) At -60°C

(b) Not resolved.

Table 19:- ^{31}P nmr of trisphosphine platinum complexes in $CDCl_3$ at 25°C.

Complex	δP (ppm)	$^1J_{PtP}$ (Hz)		$^2J_{PP}$ (Hz)
$[Pt(CO)(PMe_2Ph)_3][SO_3CF_3]_2$	-16.1 -21.5	2059 2931	d t	27.0
$[PtPh(PMe_2Ph)_3][SO_3CF_3]$	-8.8 -18.0	2660 1757	d t	22.5
$[PtCl(PMe_2Ph)_3][PF_6]$	-4.1 -17.3	2309 3489	d t	21.5
$[PtCl(PMe_2Ph)_3][SO_3CF_3]$ (a)	-4.0 -16.9	2312 3496	d t	21.4
$[PtBr(PMe_2Ph)_3][SO_3CF_3]$	-7.4 -16.5	2300 3523	d t	20.8
$[PtI(PMe_2Ph)_3][SO_3CF_3]$	-12.9 -20.4	2293 3491	d t	19.9
$[PtBr_2(PMe_2Ph_3]$ (b)	-7.8 -18.3	2311 3675	d t	20.8
$[PtI_2(PMe_2Ph)_3]$ (b)	-15.8 -25.3	2310 3764	d t	19.6
$[PtCl(PMe_2Ph)_3]Cl$ (b)	-3.5 -16.7	2300 3515	d t	21.4

(a) Parameters at -60°C

$\delta = -3.2$ ppm, $^1J_{PtP} = 2287$ Hz (d) $^2J_{PP} = 21.1$ Hz

$\delta = -17.0$ ppm, $^1J_{PtP} = 3489$ Hz (t)

(b) At -60°C.

EXPERIMENTAL

^{31}P nmr spectra were recorded on a Varian XL 100 spectrometer operating in the Fourier Transform mode with a $CDCl_3$ locking signal. ^{1}H nmr spectra were recorded on a Perkin-Elmer R32 90 MHz spectrometer with TMS locking signal. Chemical shifts are positive downfield of external H_3PO_4 (^{31}P) or TMS (^{1}H).

$[PtCl(PMe_2Ph)_3]Cl$

K_2PtCl_4 (9.96g, 0.024 moles) and PMe_2Ph (6.9ml, 0.048 moles) were allowed to react in H_2O/ethanol (80ml/120ml) as previously described to yield cis-$[PtCl_2(PMe_2Ph)_2]$ (9.75g, 72%). Material later crystallised in the H_2O/ethanol solution, and this was filtered off and found to be $[PtCl(PMe_2Ph)_3]Cl$ (2.78g, 17%), identified by its ^{31}P nmr spectrum. I.r., Pt-Cl stretches at 300 cm^{-1} (w) and 370 cm^{-1} (vw).

$[PtCl(PMe_2Ph)_3]SO_3CF_3$

$[PtCl(PMe_2Ph)_3]Cl$ (208mg, 0.306mmol.) was dissolved in $CHCl_3$ to give a pale yellow solution. $AgSO_3CF_3$ (103mg, 0.400mmol.) was added and the solution became colourless. The AgCl and excess $AgSO_3CF_3$ was removed by filtration to leave a solution which eventually yielded a grey-white powder, found to be $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (162mg, 67%). I.r. $\nu_{Pt-Cl} = 310\ cm^{-1}$.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ and TlC_5H_5

(i) $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (30.0mg, 0.038mmol.) and TlC_5H_5 (11.0mg, 0.041mmol.) were allowed to react in $CDCl_3$ (0.5ml) under a N_2 atmosphere and the solution was periodically examined by ^{31}P nmr spectroscopy. After 1 hour, a second trisphosphine platinum complex, complex A, had appeared, ^{31}P parameters in table 18, (12% of the total ^{31}P intensity), along with $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ (1%) and a species identified as $[Pt(PMe_2Ph)_4]^{2+}$, (2%). On being left overnight at room temperature the major product was a new trisphosphine complex, B, (parameters in table 18), (70% of the intensity of the products), along with $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ (13%) and another trisphosphine complex, C, (table 18), (17%). There was still some $[PtCl(PMe_2Ph)_3]^+$, but its peaks were broadened by exchange with another species. A ^1H nmr spectrum contained no identifiable C_5H_5 signals.

(ii) $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (33.5mg, 0.042mmol.) and TlC_5H_5 (14.2mg, 0.053mmol.) were allowed to react in $CHCl_3$ (0.5ml), containing a few drops of C_6D_6, in a similar manner. After 1 day, the solution contained $[PtCl(PMe_2Ph)_3]^+$ (58%), trisphosphine platinum complex B (23%), $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ (8%) and trisphosphine complex A, (11%). After 4 days, all of the starting material had been consumed, and the solution consisted of a mixture of $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ (21%), complex B (34%), complex C (36%) and $PhMe_2PO$, ($\delta = +34.5$ ppm), (9%).

$[PtCl(PMe_2Ph)_3]Cl$ and TlC_5H_5

$[PtCl(PMe_2Ph)_3]Cl$ (33.5mg, 0.049mmol.) and TlC_5H_5 (14.6mg, 0.054mmol.) were allowed to react in $CDCl_3$ under a nitrogen atmosphere at -60°C and the reaction was observed by ^{31}P nmr spectroscopy. After 3 minutes at room temperature $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ accounted for 20% of the ^{31}P intensity, the remainder being starting material. On allowing the solution to warm to room temperature for a further 2 minutes, some of the tris-phosphine platinum complex **B** was also produced, along with $[Pt(PMe_2Ph)_4]^+$ and $PhMe_2PO$. After 25 minutes at room temperature, $[PtCl(PMe_2Ph)_3]^+$ again became the major species present.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ and $Hg(C_5H_5)_2$

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ (22.8mg, 0.029mmol.) and $Hg(C_5H_5)_2$ (10.5mg, 0.032mmol.) were mixed in $CDCl_3$ (0.5ml) under a nitrogen atmosphere at -60°C. ^{31}P nmr spectra showed that no reaction occurred at -60°C in 2½ hours, and on warming to room temperature, no reaction occurred within 3 days.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ and $AgSO_3CF_3$

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ (22.5mg, 0.028mmol.) and $AgSO_3CF_3$ (9.0mg, 0.035mmol.) were mixed in $CDCl_3$ (0.5ml) and a ^{31}P nmr spectrum of the solution showed that it contained only one species, a trisphosphine platinum complex **D**, (parameters in table 18).

$[PtCl(PMe_2Ph)_3]Cl$ and excess $AgBF_4$

20.5mg of $[PtCl(PMe_2Ph)_3]Cl$ (0.030mmol.) and $AgBF_4$ (14.0mg, 0.074 equiv.) were mixed in $CDCl_3$ (0.5ml) and a ^{31}P nmr spectrum of the solution showed that it contained only one species, a trisphosphine complex E, whose parameters are in table 18.

$[PtCl(PMe_2Ph)_3]Cl$ and excess $AgPF_6$

$[PtCl(PMe_2Ph)_3]Cl$ (21.6mg, 0.032mmol.) and $AgPF_6$ (22.4mg, 0.088mmol.) were allowed to react in $CDCl_3$ (0.5ml), and on examination by ^{31}P nmr spectroscopy, the solution was found to contain only one species, a trisphosphine platinum complex, F, (see table 18 for ^{31}P parameters), on being left overnight at room temperature.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ + $AgSO_3CF_3$ + CO

Carbon monoxide was passed through a solution of $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (25.2mg, 0.032mmol.) in $CDCl_3$ (0.5ml) in the presence of $AgSO_3CF_3$ (11.3mg, 0.044mmol.) at room temperature. After 1½ hours all of the starting material was consumed, and the ^{31}P nmr spectrum of the solution contained $[Pt(PMe_2Ph)_4]^{2+}$ (30% of ^{31}P intensity), a trisphosphine complex, identified as $[Pt(CO)(PMe_2Ph)_3]^{2+}$ (58%) and trans-$[Pt(PMe_2Ph)_2(CO)Cl]^+$ (12%). The trisphosphine complex D was formed as an intermediate; after 30 minutes it was the major product, but it completely disappeared after 1½ hours. The ^{31}P nmr parameters of $[Pt(CO)(PMe_2Ph)_3]^{2+}$ are given in table 19.

Complex D and TlC_5H_5

A solution of trisphosphine complex D was prepared, using $[PtCl(PMe_2Ph)_3]Cl$ (31.7mg, 0.047mmol.) and $AgSO_3CF_3$ (32.8mg, 0.128mmol.) as previously described. The solution was filtered and allowed to react with TlC_5H_5 (14.2mg, 0.053mmol.) under a nitrogen atmosphere. The starting material totally disappeared within 2 minutes at room temperature, being replaced mainly by a new trisphosphine platinum complex, G, (parameters in table 18), (83% of the total ^{31}P intensity). Some $[Pt(PMe_2Ph)_4]^{2+}$ (12%) and a species with parameters (at -60°C) $\delta = -17.4$ ppm, $^1J_{PtP} = 3479$ Hz. On being at room temperature the amount of $[Pt(PMe_2Ph)_4]^{2+}$ increased, trisphosphine complex B appeared, and also some $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$. After 2 days at room temperature the solution was composed of $[Pt(PMe_2Ph)_4]^{2+}$ (34%), complex G (34%), $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ (17%), complex B (9%) and complex C (7%).

Complex D and C_5H_6

Similarly, a $CDCl_3$ solution (0.5ml) of complex D was prepared using $[PtCl(PMe_2Ph)_3]Cl$ (35.7mg, 0.052mmol.) and $AgSO_3CF_3$ (0.154mmol.). The solution was filtered and C_5H_6 (freshly cracked and distilled), a total of 45μl (0.557mmol.) was added. The solution became a deep blue colour, but even after 7 hours its ^{31}P nmr spectrum contained only small amounts of $[Pt(PMe_2Ph)_4]^{2+}$ (5%) and $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ (5%) in addition to complex D.

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ and $HgPh_2$

A solution of $[PtCl(PMe_2Ph)_3]SO_3CF_3$ was prepared in situ from $[PtCl(PMe_2Ph)_3]Cl$ (28.9mg, 0.042mmol.) and $AgSO_3CF_3$ (14.1mg, 0.055mmol.) in $CDCl_3$ (0.5ml), filtered and checked by ^{31}P nmr spectroscopy. A solution of $HgPh_2$ (15.1mg, 0.043mmol.) in $CDCl_3$ (0.1ml) was added and the reaction was followed by ^{31}P nmr spectroscopy. After 2 days at room temperature $[PtCl(PMe_2Ph)_3]SO_3CF_3$ still accounted for 69% of the ^{31}P intensity, the remainder being a trisphosphine complex identified as $[PtPh(PMe_2Ph)_3]^+$, (^{31}P parameters in table 19). After 1 month $[PtPh(PMe_2Ph)_3]^+$ was 94% of the ^{31}P intensity, the remainder being a species with parameters $\delta = -17.7$ ppm, $^1J_{PtP} = 3529$ Hz.

Complex D and $HgPh_2$

A solution of complex D in $CDCl_3$ (0.4ml) was prepared as previously described from $[PtCl(PMe_2Ph)_3]Cl$ (30.7mg, 0.045mmol.) and $AgSO_3CF_3$ (36.4mg, 0.142mmol.). After filtering, a solution of $HgPh_2$ (18.3mg, 0.052mmol.) in $CDCl_3$ (0.1ml) was added and the reaction was observed by ^{31}P nmr spectroscopy. No reaction occurred in 1½ hours at -60°C. On being left overnight at room temperature, the solution was found to consist of complex D (72% of the intensity), the species with parameters $\delta = -17.6$ ppm, $^1J_{PtP} = 3529$ Hz (16%) and $PhMe_2PO$ (12%). On running the ^{31}P spectrum at -60°C after 2 days reaction at room temperature, the spectrum contained complex D (37%), a new trisphosphine platinum complex, H, (parameters in table 18), (17%), the species with parameters at -60°C, $\delta = -17.5$ ppm, $^1J_{PtP} = 3488$ Hz, and what appeared to be $PhMe_2PO$, $\delta =$

+30.3 ppm, which appeared to have low intensity satellites with J_{PtP} or J_{HgP} = 2198 Hz. At room temperature only trisphosphine complex <u>D</u> was observed, and its upfield satellite was collapsed; complex <u>H</u> was not visible. After 1 month at room temperature, the solution contained the species with parameters δ = −17.7 ppm, $^1J_{PtP}$ = 3529 Hz and $[PtPh(PMe_2Ph)_3]^+$ as the major signals.

<u>$[PtBr(PMe_2Ph)_3]SO_3CF_3$ and TlC_5H_5</u>

$[PtCl(PMe_2Ph)_3]Cl$ (29.8mg, 0.044 mmol.) and $AgSO_3CF_3$ (32.4mg, 0.126mmol.) were allowed to react in $CDCl_3$ (0.4ml) to produce complex <u>D</u>. The solution was filtered and checked by ^{31}P nmr spectroscopy, then a solution of $[Bu_4N]Br$ (14.7 mg, 0.046mmol.) in $CDCl_3$ (0.1ml) was added to form $[PtBr(PMe_2Ph)_3]SO_3CF_3$ (^{31}P parameters in table 19). TlC_5H_5 (13.4mg, 0.050mmol.) was then added to the solution at room temperature and the reaction was followed by ^{31}P nmr spectroscopy. After 2½ hours reaction the ^{31}P spectrum at room temperature contained $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$, trisphosphine complex <u>B</u> and a broad signal at +6.2 to +7.7 ppm and +15.3 to +17.0 ppm. At −60°C, the broad signal was resolved as a trisphosphine complex with parameters:-

δ = −5.6 ppm (2P) $^1J_{PtP}$ = 2290 Hz, $^2J_{PP}$ = 20.9 Hz (d).

δ = −17.0 ppm (1P) $^1J_{PtP}$ = 3549 Hz, $^2J_{PP}$ = 20.9 Hz (t).

After 1 day at room temperature the amount of $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ and complex <u>B</u> had increased, complex <u>C</u> had also appeared and the parameters of the trisphosphine species, (which gave broad peaks at room temperature), were, at −60°C, :-

$\delta = -4.2$ ppm, $^1J_{PtP} = 2293$ Hz, $^2J_{PP} = 21.4$ Hz (d),
$\delta = -17.2$ ppm, $^1J_{PtP} = 3523$ Hz, $^2J_{PP} = 21.3$ Hz (t).
Some $PhMe_2PO$ had also been produced.

$[PtI(PMe_2Ph)_3]SO_3CF_3$ and TlC_5H_5

$[PtCl(PMe_2Ph)_3]Cl$ (34.0mg, 0.050mmol.) and $AgSO_3CF_3$ (35.2mg, 0.137mmol.) were allowed to react in $CDCl_3$ (0.4ml) to produce complex D. The solution was filtered and then $[Bu_4N]I$ (20.9mg, 0.056mmol.) in $CDCl_3$ (0.1ml) was added to form $[PtI(PMe_2Ph)_3]SO_3CF_3$ (^{31}P parameters in table 19). TlC_5H_5 (14.1mg, 0.052mmol.) was added at room temperature and the reaction was observed by ^{31}P nmr spectroscopy. After 3 hours at room temperature the solution contained $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$, trisphosphine complex B and a trisphosphine complex with broad peaks at room temperature and parameters, at -60°C of:-
$\delta = -9.6$ ppm, $^1J_{PtP} = 2282$ Hz, $^2J_{PP} = 19.6$ Hz (d)
$\delta = -19.7$ ppm, $^1J_{PtP} = 3520$ Hz, $^2J_{PP} = 19.6$ Hz (t).
The peaks were broadened even at -60°C.

After 1 day at room temperature the solution contained complex B (33% of intensity), the trisphosphine species with broad peaks at room temperature (27%), trisphosphine complex C (16%), $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$ (16%) and Ph_2MePO (8%). The parameters of the trisphosphine species had changed to:-
$\delta = -5.3$ ppm, $^1J_{PtP} = 2293$ Hz, $^2J_{PP} = 21.0$ Hz (d),
$\delta = -18.2$ ppm, $^1J_{PtP} = 3519$ Hz, $^2J_{PP} = 21.0$ Hz (t).

$[PtI(PMe_2Ph)_3]SO_3CF_3$ and excess I^-

A solution of complex **D** (0.048mmol.) in $CDCl_3$ (0.4ml) was prepared as previously described. On addition of $[Bu_4N]I$ (18.1mg, 0.049mmol.) in $CDCl_3$ (0.1ml) the solution became a deep yellow colour and a ^{31}P nmr spectrum contained only one species, $[PtI(PMe_2Ph)_3]SO_3CF_3$ (table 19). Addition of more $[Bu_4N]I$ altered the parameters and broadened the spectrum at room temperature. After addition of 21.4mg $[Bu_4N]I$ (0.058mmol.) the ^{31}P nmr parameters (at -60°C) were:-

δ = -14.9 ppm, $^1J_{PtP}$ = 2302 Hz $^2J_{PP}$ = 19.6 Hz (d)
δ = -24.1 ppm, $^1J_{PtP}$ = 3713 Hz $^2J_{PP}$ = 19.6 Hz (t)

On addition of a further portion of $[Bu_4N]I$ (39.0mg, 0.110 mmol.) these altered to:-

δ = -15.6 ppm, $^1J_{PtP}$ = 2308 Hz $^2J_{PP}$ = 19.7 Hz (d)
δ = -25.0 ppm, $^1J_{PtP}$ = 3759 Hz $^2J_{PP}$ = 19.7 Hz (t).

Finally, on addition of more $[Bu_4N]I$ (67.0mg, 0.180mmol.) there was very little change in the parameters, to:-

δ = -15.8 ppm, $^1J_{PtP}$ = 2310 Hz $^2J_{PP}$ = 19.6 Hz (d)
δ = -25.3 ppm, $^1J_{PtP}$ = 3764 Hz, $^2J_{PP}$ = 19.6 Hz (t).

$[PtBr(PMe_2Ph)_3]SO_3CF_3$ and excess Br^-

A solution of $[PtBr(PMe_2Ph)_3]SO_3CF_3$ (0.046mmol.) was prepared in the same way and $[Bu_4N]Br$ (13.7mg, 0.043mmol.) was added to it. The ^{31}P nmr parameters, at -60°C, changed to,

δ = -7.4 ppm, $^1J_{PtP}$ = 2302 Hz, $^2J_{PP}$ = 20.7 Hz (d)
δ = -17.7 ppm, $^1J_{PtP}$ = 3640 Hz, $^2J_{PP}$ = 20.7 Hz (t).

On addition of a further portion of $[Bu_4N]Br$ (54.6mg, 0.170mmol.) these changed to:-

δ = -7.8 ppm, $^1J_{PtP}$ = 2311 Hz, $^2J_{PP}$ = 20.8 Hz (d),

δ = -18.3 ppm, $^1J_{PtP}$ = 3675 Hz, $^2J_{PP}$ = 20.8 Hz (t).

$[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ and PMe_2Ph

(i) A solution of $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ (0.062 mmol.) was prepared as described in chapter 1 and checked by ^{31}P nmr spectroscopy. A solution of PMe_2Ph in $CDCl_3$ (calculated to be 1.0 equivalents) was then added at room temperature. The ^{31}P spectrum contained trisphosphine complex B, some $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$, some $PhMe_2PO$ and a broad peak between -8.0 and -25.0 ppm, presumable species undergoing exchange processes. Excess S_8 was added to the solution, the broad peak disappeared and some $PhMe_2PS$ (δ = +33.0 ppm), $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (the major species), a little cis-$[PtCl_2(PMe_2Ph)_2]$ and a small amount of the species with parameters δ = -5.2 ppm, $^1J_{PtP}$ = 2828 Hz appeared.

(ii) A similar reaction was performed in acetone containing a few drops of C_6D_6. $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ (0.058mmol.) and PMe_2Ph (0.054mmol.) were mixed in acetone (0.5ml) at room temperature. Initially, the major product was trisphosphine complex B, (parameters in acetone were:-

δ = -7.0 ppm, $^1J_{PtP}$ = 2624 Hz, $^2J_{PP}$ = 23.6 Hz (d)

δ = -15.0 ppm, $^1J_{PtP}$ = 1860 Hz, $^2J_{PP}$ = 23.6 Hz (t).

On being left overnight, this disappeared, to be replaced by a complex with parameters $\delta = -13.8$ ppm, $^1J_{PtP} = 2349$ Hz, identified as $[Pt(PMe_2Ph)_4]^{2+}$.

cis-$[PtCl_2(PMe_2Ph)_2]$ and PMe_2Ph

cis-$[PtCl_2(PMe_2Ph)_2]$ (32.7mg, 0.060mmol.) was dissolved in acetone (0.4ml). $AgSO_3CF_3$ (32.1mg, 0.125mmol.) and a solution of PMe_2Ph (15µl, 0.109mmol.) in acetone (150µl) was added and a ^{31}P nmr spectrum showed the presence of one species, $\delta = -13.6$ ppm, $^1J_{PtP} = 2345$ Hz, $[Pt(PMe_2Ph)_4][SO_3CF_3]_2$.

$[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]Cl$ and PMe_2Ph

A solution of $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]Cl$ (0.056mmol.) in $CDCl_3$ (0.4ml) was prepared as described previously. A solution of PMe_2Ph (7.5µl; 0.054mmol.) in $CDCl_3$ (150µl) was added at room temperature. After 2½ hours, the spectrum contained trisphosphine complex **B**, some $PhMe_2PO$ and a broad peak between 0 and -25 ppm, due to species undergoing exchange reactions. Overnight trisphosphine complex **C** also appeared. Addition of $AgSO_3CF_3$ (20.7mg, 0.081mmol.) removed the broad peak and replaced it with $[PtCl(PMe_2Ph)_3]SO_3CF_3$, as the major species present. Another, minor species also appeared, which may have been tris-phosphine complex **J**, (see table 18 for ^{31}P parameters).

$[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$ and PMe_2Ph

A solution of $[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3$ (0.065mmol.) in $CDCl_3$ (0.4ml) was prepared as described in chapter 1. A solution of PMe_2Ph (7.5µl; 0.054mmol.) in $CDCl_3$ (150µl) was added at room temperature and the reaction was followed by ^{31}P nmr spectroscopy. Within 30 minutes virtually all of the starting material was consumed and the major products were trisphosphine complex K, (33% of the total ^{31}P intensity), trisphosphine complex J (24%), $[PtCl(PMe_2Ph)_3]SO_3CF_3$ (16%), a species with parameters $\delta = -6.6$ ppm, $^1J_{PtP} = 3091$ Hz (10%), $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ (5%) and $PhMe_2PO$ (5%). On being left overnight at room temperature the amount of complex J decreased and $[PtCl(PMe_2Ph)_3]SO_3CF_3$ increased.

$[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) and PMe_2Ph

A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), (0.063mmol.) in $CDCl_3$ (0.5ml) was prepared as described previously. Neat PMe_2Ph (8.8µl, 0.063mmol.) was added and the reaction was observed by ^{31}P nmr spectroscopy. The products were, a species with parameters $\delta = -6.6$ ppm, $^1J_{PtP} = 3092$ Hz, seen in the previous reaction, (18% of the total ^{31}P intensity), $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]Cl$ (14%), a species with parameters $\delta = -6.3$ ppm, $^1J_{PtP} = 3395$ Hz, (11%), trisphosphine species L (16%), trisphosphine complex M (16%), (parameters of both are in table 18), $[PtCl(PMe_2Ph)_3]Cl$ (16%), the species with parameters $\delta = -5.3$ ppm, $^1J_{PtP} = 2829$ Hz (5%), encountered in the previous chapter, and $PhMe_2PO$ (4%). A ^1H nmr spectrum contained some C_5H_6.

APPENDIX

MISCELLANEOUS REACTIONS OF CYCLOPENTADIENYL PLATINUM COMPLEXES AND CYCLOPENTADIENYLATING REAGENTS.

RESULTS AND DISCUSSION

Attempts to Promote CO-insertion at Platinum Cyclopentadienyls

Attempts were made to promote carbonyl insertion at $[PtX(C_5H_5)(CO)L]$ isomer (I) by the addition of L or Cl^-. The reactions are described in detail in the experimental section, and none of the reactions were simple or straightforward. A large number of products, many of which remain unidentified, were observed. The addition of phosphine to $[PtX(C_5H_5)(CO)L]$ (L = $PMePh_2$, X = Cl; L = PMe_2Ph, X = Cl,Br) always produced some $[Pt(\eta^5-C_5H_5)L_2]^+$, but the most straightforward of the reactions produced at least another two unidentified complexes which were observed in each reaction. These had parameters as follows,

δ = -8.8 ppm, $^1J_{PtP}$ = 3073 Hz and δ = -8.8 ppm, $^1J_{PtP}$ = 2781 Hz when L was PMe_2Ph and X was Br.

δ = -6.6 ppm, $^1J_{PtP}$ = 3092 Hz and δ = -5.3 ppm, $^1J_{PtP}$ = 2829 Hz when L was PMe_2Ph and X was Cl.

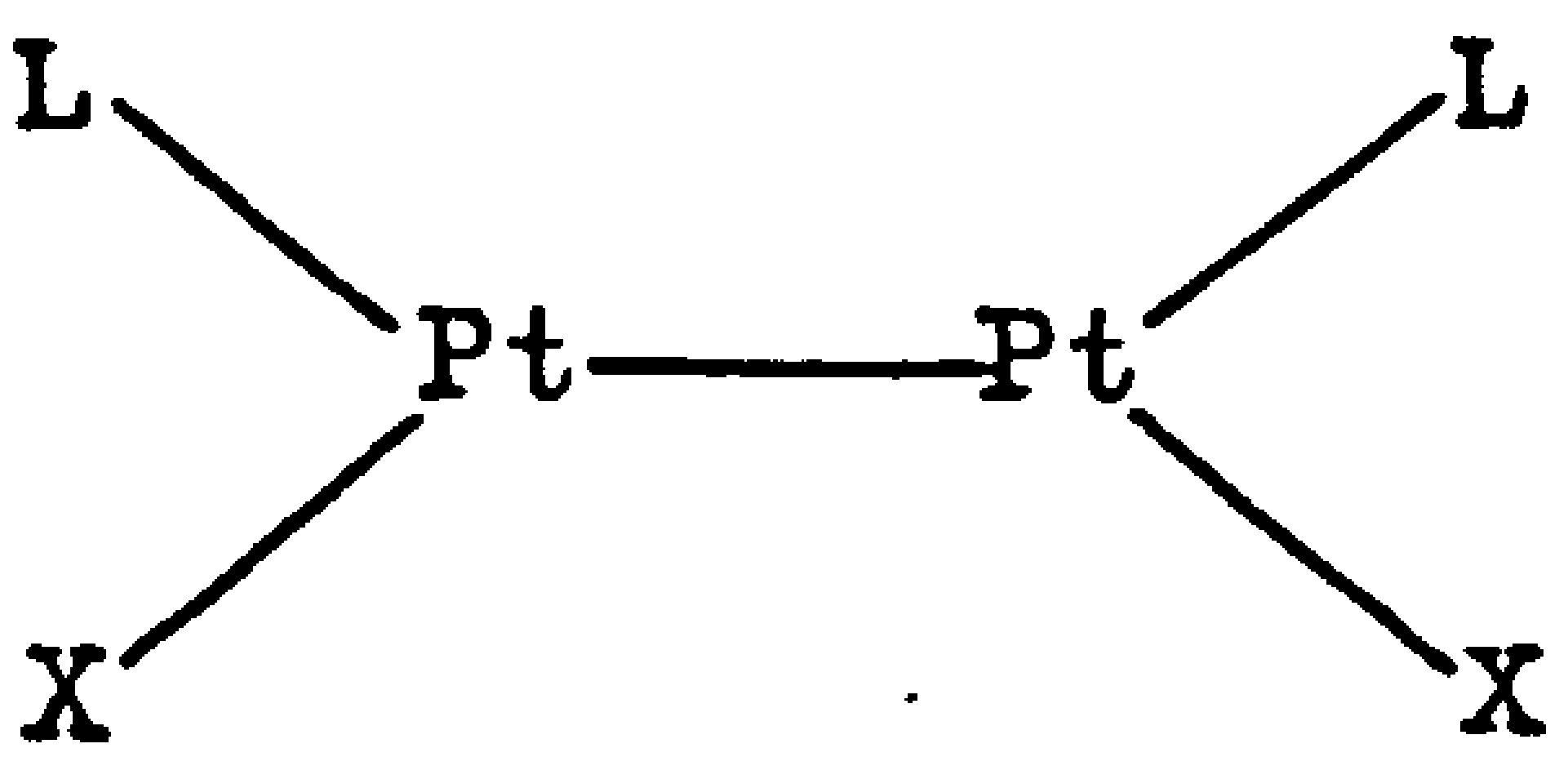
δ = +6.8 ppm, $^1J_{PtP}$ = 3262 Hz and δ = +7.8 ppm, $^1J_{PtP}$ = 2970 Hz when L was $PMePh_2$ and X was Cl.

Possible identities of these complexes are trans-$[PtX(COC_5H_5)L_2]$ and trans-$[PtX(C_5H_5)L_2]$. For example, trans-$[PtCl(COPh)(PMePh_2)_2]$ has δ = +5.1 ppm, $^1J_{PtP}$ = 3215 Hz and trans-$[PtClPh(PMePh_2)_2]$ has δ = +8.7 ppm, $^1J_{PtP}$ = 3010 Hz.[173]

^1H nmr spectra of the reactions showed that C_5H_6 was liberated, so it is also possible that the complexes above do not contain C_5H_5. When L was PMe_2Ph and X was Cl, a complex, thought to be $[Pt(COC_5H_5)L_3]^+$ was observed, and with X = Br an i.r. absorption at 1630cm^{-1} was obtained, thus the possibility that some carbonyl insertion has occurred must be considered.

Addition of $[Et_4N]Cl$ to $[PtCl(\eta^1-C_5H_5)(CO)L]$ isomer (I), (L = $PMePh_2$, PMe_2Ph) produced a large amount of <u>cis</u>-$[PtCl_2L_2]$. When L was $PMePh_2$, "Asymmetric Dimer" was also obtained, along with a complex which appeared to be a symmetrically substituted, platinum-platinum bonded, dimer, with $\delta = -5.7$ ppm, $^1J_{PtP} =$ 5088 Hz, $^2J_{PtP} = 683$ Hz. When L was PMe_2Ph a species with parameters $\delta = -19.7$ ppm, $^1J_{PtP} = 4916$ Hz was obtained, along with a small amount of a symmetrically substituted dimer, also with a platinum-platinum bond, $\delta = -8.8$ ppm, $^1J_{PtP} = 4730$ Hz, $^2J_{PtP} = 413$ Hz, $^3J_{PP} = 8$ Hz (d). This is probably a different type of dimer from the one above. In both reactions C_5H_6 was liberated.

Addition of $[Et_4N]Cl$ to $[Pt(\eta^5-C_5H_5)(CO)(PMe_2Ph]SO_3CF_3$ initially produced $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I), <u>cis</u>-$[PtCl_2(PMe_2Ph)_2]$, "Asymmetric Dimer" and the two complexes obtained by adding Cl^- to isomer (I). Addition of $[Bu_4N]I$ to $[Pt(\eta^5-C_5H_5)(^{13}CO)(PMe_2Ph)]SO_3CF_3$ produced only one species initially, with parameters at -60°C of $\delta = -16.2$ ppm, $^1J_{PtP} =$ 3487 Hz. On warming to room temperature the products were "Asymmetric Dimer", <u>cis</u>- and <u>trans</u>-$[PtI_2(PMe_2Ph)_2]$ (identified by ^{31}P nmr)[207] plus the analogous, iodide containing, symmetrical dimer, with $\delta = -8.6$ ppm, $^1J_{PtP} = 4698$ Hz, $^2J_{PtP} =$ 372 Hz, $^3J_{PP} = 9.4$ Hz (d) and the species with $\delta = -19.7$ ppm, $^1J_{PtP} = 4846$ Hz. The symmetrically substituted dimer was found not to contain C_5H_5 groups, and C_5H_6 was liberated in the reaction. No coupling to ^{13}CO was observed in either complex. The symmetrically substituted dimer may be a complex of the type below.

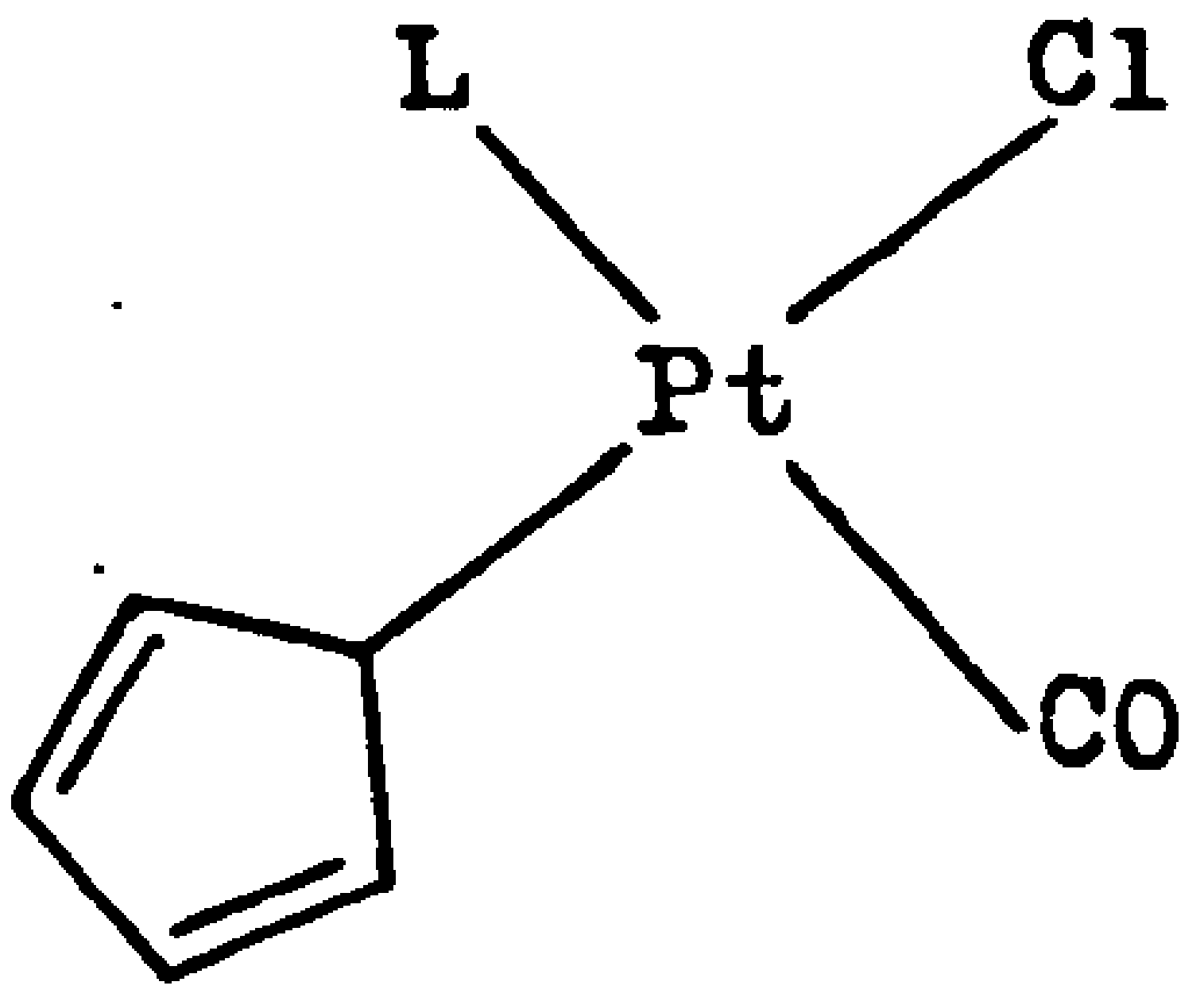


The other complex at ca. -19.7 ppm, could be cis-[PtX_2-(COC_5H_5)L]$^-$, or cis-[$PtCl_2$(C_5H_5)L]$^-$. The complex cis-[$PtCl_2$(COPh)($PMePh_2$)]$^-$ has δ = -6.0 ppm, $^1J_{PtP}$ = 5006 Hz and cis-[$PtCl_2$Ph($PMePh_2$)]$^-$ has δ = -1.4 ppm, $^1J_{PtP}$ = 4757 Hz.[170]

Addition of [Bu_4N]I to [Pt(η^5-C_5H_5)(CO)(PPh_3)]SO_3CF_3 produced, initially [PtI(C_5H_5)(CO)(PPh_3)] isomer (I), but "Asymmetric Dimer" and other unidentified complexes were subsequently produced.

Reactions of Platinum Complexes with Cyclopentadienylating Reagents

trans-[$PtCl_2$(CO)(PMe_2Ph)] reacted with TlC_5H_5 or $Hg(C_5H_5)_2$ to initially produce a complex with δ = -7.5 ppm, $^1J_{PtP}$ = 3274 Hz. Replacement of Cl by C_5H_5 would produce [PtCl-(C_5H_5)(CO)(PMe_2Ph)] isomer (III), C_5H_5 trans to Cl, :-



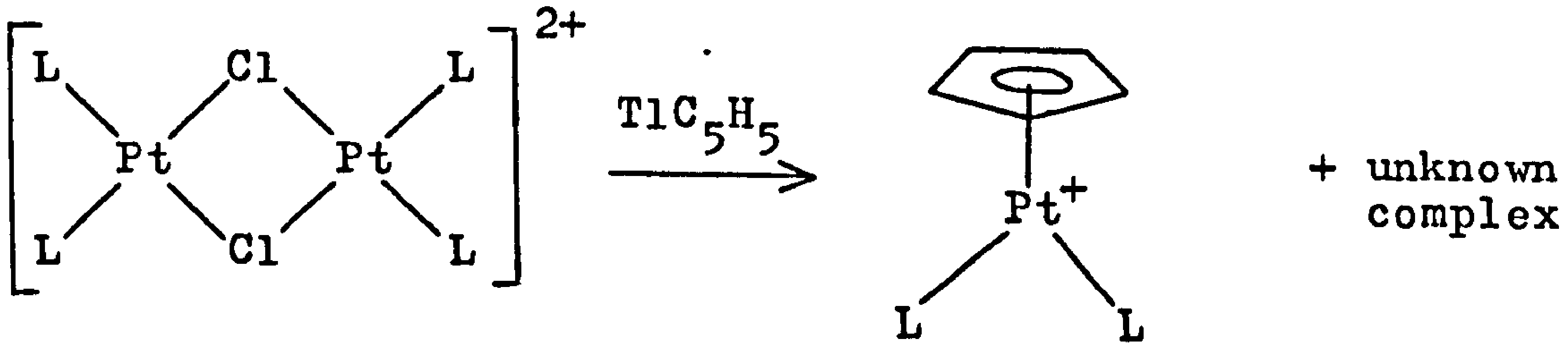
(III)

[PtBr(Ph)(CO)(PMe_2Ph)] isomer (III) has $^1J_{PtP}$ = 3359 Hz, and C_5H_5 has a lower trans-influence than Ph, but a higher cis-influence, thus a $^1J_{PtP}$ value of 3274 Hz would not be unexpected for [PtCl(C_5H_5)(CO)(PMe_2Ph)] isomer (III). With TlC_5H_5 subsequent reactions led to the formation of a large number of products. With $Hg(C_5H_5)_2$ only cis-[$PtCl_2$(CO)-

$(PMe_2Ph)]$, from isomerisation of trans-$[PtCl_2(CO)(PMe_2Ph)]$, and isomer (I) were produced.

trans-$[PtCl(CO)(PMe_2Ph)_2]SO_3CF_3$ and TlC_5H_5 reacted in $CDCl_3$ to produce $[PtCl(PMe_2Ph)_3]SO_3CF_3$, $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]SO_3CF_3$ and an unknown complex. Substantial decomposition must have occurred to liberate phosphine.

The cationic, dimeric complexes $[Pt_2(\mu\text{-}Cl)_2L_4][SO_3CF_3]_2$ reacted with TlC_5H_5 to produce mainly $[Pt(\eta^5\text{-}C_5H_5)L_2]^+$ and an unidentified complex with parameters $\delta = -17.7$ ppm, $^1J_{PtP} = 3529$ Hz ($L = PMe_2Ph$) and $\delta = -6.0$ ppm, $^1J_{PtP} = 3667$ Hz ($L = PMePh_2$). The unknown complexes can not contain C_5H_5, since the complex with $\delta = -17.7$ ppm was a product in the reaction between trisphosphine complex D and $HgPh_2$.



$[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ was formed by the reaction between cis-$[PtCl_2(PMe_2Ph)_2]$ and $Hg(C_5H_5)_2$ as might be expected, but the reaction was very slow. At room temperature the reaction between TlC_5H_5 and cis-$[PtCl_2(PMe_2Ph)_2]$ is rapid, and produces $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$, but at low temperature only two minor products were obtained. These had parameters $\delta = -21.1$ ppm, $^1J_{PtP} = 3512$ Hz and a species with two doublets, $\delta = -7.5$ ppm, $^1J_{PtP} = 1776$ Hz and $\delta = -20.4$ ppm, $^1J_{PtP} = 3539$ Hz, $^2J_{PP} = 14.6$ Hz. On warming to room temperature some $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ was also formed.

$[Pt_2Cl_4(PMe_2Ph)_2]$ reacted with TlC_5H_5 (both 2 and 4 equivalents) to form a large number of products, including $[PtCl_3(PMe_2Ph)]^-$, trans-$[PtCl_2(PMe_2Ph)_2]$ and a dimeric complex with $\delta = -24.8$ ppm, $^1J_{PtP} = 3865$ Hz, $^3J_{PtP} = 20.5$ Hz, presumably halide-bridged. This complex was also a minor product in the reaction between $[Et_4N][PtCl_3(PMe_2Ph)]$ and TlC_5H_5. The reaction between $[Et_4N][PtCl_3(PMePh_2)]$ and TlC_5H_5 produced, among other products, an asymmetrically substituted dimer with a platinum-platinum bond, $\delta = +4.2$ ppm, $^1J_{PtP} = 4965$ Hz, $^2J_{PtP} = 135$ Hz (d) and $\delta = -8.2$ ppm, $^1J_{PtP} = 4806$ Hz, $^2J_{PtP} = 83$ Hz (d), $^3J_{PP} = 3.0$ Hz.

The reaction between cis-$[PtCl_2(CO)(PMe_2Ph)]$ and LiC_5H_5, which was expected to produce $[PtCl(\eta^1\text{-}C_5H_5)(CO)(PMe_2Ph)]$ isomer (II), Cl trans to PMe_2Ph, yielded a larger number of complexes, including isomer (I), and "Asymmetric Dimer", but none of the numerous products could be assigned as isomer (II).

$[PtCl(\eta^1\text{-}C_5H_5)(CO)(PPh_3)]$ isomer (I) and AgF

AgF could replace the Cl of isomer (I) by F, but the F was then rapidly lost and the C_5H_5 ring underwent an $\eta^1\rightarrow\eta^5$- conversion to produce $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$. AgF did not react with $[PtCl(Ph)(CO)(PMePh_2)]$ isomer (I), nor with "Asymmetric Dimer".

EXPERIMENTAL

$[PtCl(\eta^1-C_5H_5)(CO)(PMePh_2)]$ and $PMePh_2$

A solution of $[PtCl(\eta^1-C_5H_5)(CO)(PMePh_2)]$ isomer (I), (0.051mmol.) in $CDCl_3$ (0.5ml) was prepared as described previously. $PMePh_2$ (9.4μl, 0.051mmol.) was added under a nitrogen atmosphere at room temperature. A ^{31}P nmr spectrum after 30 minutes, (recorded at -60°C) showed that the solution contained $[Pt(\eta^5-C_5H_5)(PMePh_2)_2]^+$ (46% of the ^{31}P intensity), a species with parameters $\delta = +9.0$ ppm, $^1J_{PtP} = 3203$ Hz (42%) and a species with parameters $\delta = +7.9$ ppm, $^1J_{PtP} = 2940$ Hz (12%). A ^1H nmr spectrum showed that C_5H_6 was present, along with the π-cyclopentadienyl complex, but no other recognisable signals were observed. On leaving overnight at room temperature, the solution, dark red in colour, contained $[Pt(\eta^5-C_5H_5)(PMePh_2)_2]^+$ (46%), a species with parameters $\delta = +6.8$ ppm, $^1J_{PtP} = 3262$ Hz (46%) and a species, $\delta = +7.8$ ppm, $^1J_{PtP} = 2970$ Hz (at 25°C).

$[PtCl(\eta^1-C_5H_5)(CO)(PMe_2Ph)]$ and PMe_2Ph

The reaction between $[PtCl(\eta^1-C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) and neat PMe_2Ph has already been described.

A solution of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) (0·058 mmol.) in $CDCl_3$ (0.3ml) and a solution of PMe_2Ph (7.9μl, 0.057mmol.) in $CDCl_3$ (0.2ml) were mixed at -60°C under a nitrogen atmosphere. Initially $[PtCl(PMe_2Ph)_3]^+$ was produced, and after 1 hour at -60°C the solution was composed of $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) (28% of ^{31}P intensity), <u>cis</u>-$[PtCl_2(PMe_2Ph)_2]$ (27%), $[Pt(\eta^5-C_5H_5)-(PMe_2Ph)_2]^+$ (17%), a species with parameters, $\delta = -5.7$ ppm,

$^1J_{PtP}$ = 3012 Hz (8%), trisphosphine complex K (7%), $[PtCl(PMe_2Ph)_3]^+$ (6%) and $PhMe_2PO$ (3%). After 2 hours at room temperature the major products were $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ cis-$[PtCl_2(PMe_2Ph)_2]$ and the species at δ = -5.7 ppm. A ^1H nmr spectrum showed that C_5H_6 had been produced.

A similar reaction in acetone solution at room temperature produced mainly cis-$[PtCl_2(PMe_2Ph)_2]$, with a small amount of $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ and a species with parameters δ = -6.6 ppm, $^1J_{PtP}$ = 3137 Hz.

$[PtBr(\eta^1\text{-}C_5H_5)(CO)(PMe_2Ph)]$ and PMe_2Ph

Similarly, a solution of $[PtBr(\eta^1\text{-}C_5H_5)(CO)(PMe_2Ph)]$ isomer (I) (0.058mmol.) in $CDCl_3$ (0.4ml) and a solution of PMe_2Ph (8μl, 0.058mmol.) in $CHCl_3$ (160μl) were mixed at room temperature under an atmosphere of nitrogen. Immediately after mixing, a ^{31}P nmr spectrum showed the presence of species with parameters δ = -8.8 ppm, $^1J_{PtP}$ = 3073 Hz (38%), δ = -8.8 ppm, $^1J_{PtP}$ = 2781 Hz (26%), $[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]^+$ (29%) and $PhMe_2PO$. A ^1H nmr spectrum contained C_5H_6 and an i.r. spectrum, a broad absorbance at 1630cm^{-1}.

$[PtCl(\eta^1\text{-}C_5H_5)(CO)(PMePh_2)]$ and $[Et_4N]Cl$

$[Et_4N]Cl$ (9.8mg, 0.059mmol.) was added to a $CDCl_3$ solution of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ isomer (I) (0·051mmol.) under a N_2 atmosphere. After 18 hours a ^{31}P spectrum showed that the solution contained cis-$[PtCl_2(PMePh_2)_2]$ (43% of ^{31}P intensity), "Asymmetric Dimer" (30%), isomer (I) (11%), a species with two sets of ^{195}Pt satellites, δ = -5.7 ppm,

$^1J_{PtP}$ = 5088 Hz, $^2J_{PtP}$ = 683 Hz (11%). A ^{1}H nmr spectrum contained C_5H_6.

[PtCl(η^1-C_5H_5)(CO)(PMe_2Ph)] and [Et_4N]Cl

[Et_4N]Cl (13.1mg, 0.079mmol.) was added to a $CDCl_3$ solution of [PtCl(C_5H_5)(CO)(PMe_2Ph)] isomer (I) (0.070mmol.) under a N_2 atmosphere. After 18 hours a ^{31}P spectrum of the solution comprised <u>cis</u>-[$PtCl_2$(PMe_2Ph)$_2$] (45% of ^{31}P intensity), a species with parameters δ = -19.7 ppm, $^1J_{PtP}$ = 4916 Hz (36%), a dimeric species with δ = -8.8 ppm, $^1J_{PtP}$ = 4730 Hz, $^2J_{PtP}$ = 413 Hz, $^3J_{PP}$ = 8 Hz (doublets) (12%). A ^{1}H nmr spectrum contained C_5H_6.

[Pt(η^5-C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3 and [Et_4N]Cl

[Et_4N]Cl (14.8mg, 0.089 mmol.) was added to a $CDCl_3$ solution of [Pt(η^5-C_5H_5)(CO)(PMe_2Ph)]SO_3CF_3 (0.068mmol.) under a N_2 atmosphere. The initial products were [PtCl-(C_5H_5)(CO)(PMe_2Ph)] isomer (I), <u>cis</u>-[$PtCl_2$(PMe_2Ph)$_2$], the two complexes in the previous reaction and "Asymmetric Dimer".

[Pt(η^5-C_5H_5)(^{13}CO)(PMe_2Ph)]SO_3CF_3 and [Bu^n_4N]I

[Bu_4N]I (24.4mg, 0.066mmol.) was added to a $CDCl_3$ solution of [Pt(η^5-C_5H_5)(^{13}CO)(PMe_2Ph)]SO_3CF_3 (0.066mmol.), 60% ^{13}CO-labelled, under an atmosphere of N_2 at -60°C. A ^{31}P nmr spectrum at -60°C contained only one species, δ = -16.2 ppm, $^1J_{PtP}$ = 3487 Hz, (56% of ^{31}P intensity) in addition to starting material. On warming to room temperature, the solution contained "Asymmetric Dimer" (32%), a symmetrical dimer, δ = -8.6 ppm, $^1J_{PtP}$ = 4698 Hz, $^2J_{PtP}$ = 372 Hz, $^3J_{PP}$ =

9.4 Hz (d) (32%), a species with parameters δ = -19.7 ppm, $^1J_{PtP}$ = 4846 Hz, (16%) and cis- and trans- $[PtI_2(PMe_2Ph)_2]$ (-16.9 ppm, $^1J_{PtP}$ = 3373 Hz and -22.5 ppm, $^1J_{PtP}$ = 2315 Hz). After several hours, the symmetrical dimer had increased to 40% of the intensity and "Asymmetric Dimer" had decreased to 18%. A ^1H nmr spectrum contained C_5H_6, but no other C_5H_5 signals except "Asymmetric Dimer".

$[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]SO_3CF_3$ and $[Bu_4N]I$.

$[Bu_4N]I$ (21.2mg, 0.057mmol.) was added to a $CDCl_3$ solution of $[Pt(\eta^5-C_5H_5)(CO)(PPh_3)]SO_3CF_3$ (0.057mmol.) under a N_2 atmosphere. The initial product was $[PtI(C_5H_5)(CO)(PPh_3)]$ isomer (I), (see table 2 for ^{31}P parameters), but other species appeared later, including "Asymmetric Dimer", and species with parameters δ = +8.1 ppm, $^1J_{PtP}$ = 2934 Hz; δ = +5.0 ppm, $^1J_{PtP}$ = 3183 Hz; δ = +7.4 ppm, $^1J_{PtP}$ = 3775 Hz and δ = +17.7 ppm, $^1J_{PtP}$ = 3360 Hz, all except the first of which were minor products.

trans-$[PtCl_2(CO)(PMe_2Ph)]$ and TlC_5H_5

$[Pt_2Cl_4(PMe_2Ph)_2]$ (17.0mg, 0.021mmol.) was suspended in $CDCl_3$ (0.4ml.) at -60°C. Carbon monoxide was passed through the suspension for 20 minutes, followed by nitrogen for 1 minute. A ^{31}P nmr spectrum of the solution showed that trans-$[PtCl_2(CO)(PMe_2Ph)]$ (δ = -10.2 ppm, $^1J_{PtP}$ = 2874 Hz) was the only platinum complex present. TlC_5H_5 (15.0mg, 0.056mmol.) was added at -60°C and the reaction was observed by ^{31}P nmr spectroscopy. After 30 seconds at room temperature, 50% of the trans-[$PtCl_2(CO)(PMe_2Ph)$] had reacted, the major product being a species with parameters δ = -7.5 ppm, $^1J_{PtP}$ = 3274 Hz. After a further 30 seconds at room temperature this species was ca. 28% of the ^{31}P intensity, but a large number of minor products, none more than 7% of the ^{31}P intensity, were present. These included [$PtCl_3(PMe_2Ph)$]$^-$ (δ = -21.0 ppm, $^1J_{PtP}$ = 3735 Hz), trans-[$PtCl_2(PMe_2Ph)_2$] (δ = -7.5 ppm, $^1J_{PtP}$ = 2412 Hz), [$Pt(\eta^5-C_5H_5)(PMe_2Ph)_2$]$^+$, cis-[$PtCl_2(CO)$-($PMe_2Ph$)], [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I), $PhMe_2PO$, "Asymmetric Dimer", and species with parameters δ = -12.4 ppm, $^1J_{PtP}$ = 4660 Hz and δ = +0.2 ppm, $^1J_{PtP}$ = 2498 Hz.

trans-[$PtCl_2(CO)(PMe_2Ph)$] and $Hg(C_5H_5)_2$

A solution of trans-[$PtCl_2(CO)(PMe_2Ph)$] (0.065mmol.) in $CDCl_3$ (0.3ml) was prepared as above. $Hg(C_5H_5)_2$ (23.1 mg, 0.070mmol.) in $CDCl_3$ (0.2ml) was added at -60°C, but there was no reaction within 1 hour at this temperature. On warming to room temperature the species with parameters δ = -7.5 ppm, $^1J_{PtP}$ = 3274 Hz, cis-[$PtCl_2(CO)(PMe_2Ph)$] and [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) were all produced. Eventually, isomer (I) was the only product.

trans-[$PtCl(CO)(PMe_2Ph)_2$]SO_3CF_3 and TlC_5H_5

cis-[$PtCl_2(PMe_2Ph)_2$] (32.7mg, 0.060mmol.) and $AgSO_3CF_3$ (16.0 mg, 0.062mmol.) were mixed in $CDCl_3$ (0.5ml) and CO was passed through the solution for 1½ hours to produce trans-[$PtCl(CO)(PMe_2Ph)_2$]SO_3CF_3 (δ = -1.4 ppm, $^1J_{PtP}$ = 1913 Hz). TlC_5H_5 (16.2mg, 0.060mmol.) was added and the reaction was followed by ^{31}P nmr spectroscopy. The products were

$[PtCl(PMe_2Ph)_3]SO_3CF_3$ (58% of ^{31}P intensity), $[Pt(\eta^5-C_5H_5)-(PMe_2Ph)_2]SO_3CF_3$ (22%) and a species with parameters $\delta = -9.0$ ppm, $^1J_{PtP} = 2427$ Hz (20%).

$[Pt_2(\mu-Cl)_2(PMe_2Ph)_4][SO_3CF_3]_2$ and TlC_5H_5

cis-$[PtCl_2(PMe_2Ph)_2]$ (30.2mg, 0.056mmol.) and $AgSO_3CF_3$ (15.8mg, 0.061mmol.) were mixed in $CDCl_3$ (0.5ml) under a nitrogen atmosphere. A ^{31}P nmr spectrum showed the presence of only one species, $[Pt_2Cl_2(PMe_2Ph)_4][SO_3CF_3]_2$ ($\delta = -11.5$ ppm, $^1J_{PtP} = 3758$ Hz; ^1H nmr PMe_2Ph methyl protons, $\delta = +1.84$ ppm, $^2J_{PH} = 11.0$ Hz, $^3J_{PtH} = 39.0$ Hz). TlC_5H_5 (15.4 mg, 0.057mmol.) was added and the reaction followed by ^{31}P nmr spectroscopy. The major product was $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]$ SO_3CF_3, with the species with parameters $\delta = -17.7$ ppm, $^1J_{PtP} = 3529$ Hz and *cis*-$[PtCl_2(PMe_2Ph)_2]$ as minor products.

$[Pt_2(\mu-Cl)_2(PMePh_2)_4][SO_3CF_3]_2$ and TlC_5H_5

A solution of $[Pt_2Cl_2(PMePh_2)_4][SO_3CF_3]_2$ (0.048mmol.), ($\delta = 0.0$ ppm, $^1J_{PtP} = 3821$ Hz) in $CDCl_3$ (0.5ml) was prepared as above. Addition of TlC_5H_5 (19.6mg, 0.073mmol.) produced $[Pt(\eta^5-C_5H_5)(PMePh_2)_2]SO_3CF_3$ and a species with parameters $\delta = -6.0$ ppm, $^1J_{PtP} = 3667$ Hz.

cis-$[PtCl_2(PMe_2Ph)_2]$ and $Hg(C_5H_5)_2$

A solution of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (26.0mg, 0.046mmol.) in $CDCl_3$ (0.3ml) and a solution of $Hg(C_5H_5)_2$ (16.4mg., 0.049 mmol.) in $CDCl_3$ (0.2ml) were mixed at -60°C, but no reaction occurred within 1 hour. On warming to room temperature there was a slow reaction to produce $[Pt(\eta^5-C_5H_5)(PMe_2Ph)_2]^+$.

cis-$[PtCl_2(PMe_2Ph)_2]$ and TlC_5H_5 at low temperature

cis-$[PtCl_2(PMe_2Ph)_2]$ (19.6mg., 0.036mmol.) and TlC_5H_5 (13.7mg, 0.051mmol.) were mixed in $CDCl_3$ under a N_2 atmosphere at -60°C. The solution was warmed from -60°C to 0°C by incremental increasing of the temperature but no reaction occurred. On being left at less than -30°C for 12 hours the solution contained *cis*-$[PtCl_2(PMe_2Ph)_2]$ (92%), a species with parameters δ = -21.1 ppm, $^1J_{PtP}$ = 3512 Hz (at -60°C (4%) and a species, δ = -20.4 ppm, $^1J_{PtP}$ = 3539 Hz (d) and -7.5 ppm, $^1J_{PtP}$ = 1776 Hz (d), $^2J_{PP}$ = 14.6 Hz (4%). There was little change in five days at less than -30°C, with the above two species growing in to 6% and 9% respectively. After being left overnight at room temperature the solution consisted of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (40%), the species with δ = 21.6 ppm, $^1J_{PtP}$ = 3509 Hz (at 25°C), (30%), $[Pt(\eta^5\text{-}C_5H_5)\text{-}(PMe_2Ph)_2]^+$ (20%) and the species, δ = -7.5 ppm, and -20.3 ppm, (d) $^2J_{PP}$ = 13.6 Hz, (10%). ($^1J_{PtP}$ was not resolved).

$[Pt_2Cl_4(PMe_2Ph)_2]$ and TlC_5H_5

(i) $[Pt_2Cl_4(PMe_2Ph)_2]$ (30.3mg, 0.037 mmol.) and TlC_5H_5 (21.6mg, 0.080mmol.) were mixed in $CDCl_3$ (0.5ml) under a N_2 atmosphere. A ^{31}P nmr spectrum, recorded immediately, showed the presence of a large number of species. These included $[PtCl_3(PMe_2Ph)]^-$ (δ = -23.9 ppm, $^1J_{PtP}$ = 3742 Hz at 25°C), (18%), a species with δ = -24.8 ppm, $^1J_{PtP}$ = 3865 Hz, $^3J_{PtP}$ = 20.5 Hz (16%), *trans*-$[PtCl_2(PMe_2Ph)_2]$ (-8.5 ppm, $^1J_{PtP}$ = 2454 Hz), (10%), a species with δ = -14.9 ppm, $^1J_{PtP}$ = 4090 Hz (14%) and a large number of unidentified minor species.

(ii) Similarly $[Pt_2Cl_4(PMe_2Ph)_2]$ (27.2mg, 0.034mmol.) and TlC_5H_5 (36.7mg, 0.136mmol.) were allowed to react in $CDCl_3$, under an atmosphere of nitrogen. The initial products were $[PtCl_3(PMe_2Ph)]^-$ (26%), the complex with δ = -24.8 ppm, $^1J_{PtP}$ = 3865 Hz, $^3J_{PtP}$ = 20.5 Hz (21%), and trans-$[PtCl_2(PMe_2Ph)_2]$ (9%) plus a large number of minor species.

$[Et_4N][PtCl_3(PMe_2Ph)]$ and TlC_5H_5

$[Et_4N]Cl$ (10.9mg, 0.066mmol.) and $[Pt_2Cl_4(PMe_2Ph)_2]$ (26.8mg, 0.033mmol.) were mixed in $CDCl_3$ (0.5ml) to produce $[Et_4N][PtCl_3(PMe_2Ph)]$. TlC_5H_5 (22.3mg, 0.083mmol.) was added at room temperature, but there was little reaction within 1½ hours. On being left overnight a small amount of the species with δ = -24.8 ppm, $^1J_{PtP}$ = 3865 Hz, $^3J_{PtP}$ = 20.5 Hz and a species with δ = -16.6 ppm, $^1J_{PtP}$ = 4575 Hz were formed.

$[Et_4N][PtCl_3(PMePh_2)]$ and TlC_5H_5

A solution of $[Et_4N][PtCl_3(PMePh_2)]$ (0·064mmol.) in $CDCl_3$ (0.5ml) was similarly prepared (δ = -11.4 ppm, $^1J_{PtP}$ = 3837 Hz). TlC_5H_5 (16.9mg, 0.063mmol.) was added and, on leaving overnight a ^{31}P nmr spectrum showed that more than 60% of the intensity was starting material, products being species with parameters δ = -2.6 ppm, $^1J_{PtP}$ = 4698 Hz; δ = -4.9 ppm, $^1J_{PtP}$ = 5465 Hz; a dimer, δ = +4.2 ppm, $^1J_{PtP}$ = 4965 Hz, $^2J_{PtP}$ = 135 Hz (d) and δ = -8.2 ppm, $^1J_{PtP}$ = 4806 Hz, $^2J_{PtP}$ = 83 Hz (d), $^3J_{PP}$ = 3.0Hz and cis-$[PtCl_2(PMePh_2)_2]$.

cis-[$PtCl_2(CO)(PMe_2Ph)$] and LiC_5H_5

Freshly distilled C_5H_6 (616µl, 7.5mmol.) was dissolved in THF (10ml) under a N_2 atmosphere, and 4ml. of 1.88M MeLi solution was added at -40°C and the solution was stirred for 2 hours at less than -30°C. 80µl of the resultant LiC_5H_5 solution (i.e.:- 0.043mmol. LiC_5H_5) was added to a solution of *cis*-[[$PtCl_2(CO)(PMe_2Ph)$] (22.3mg, 0.052mmol.) in $CDCl_3$ (0.5ml) at -60°C. Initially a large number of mostly unidentified complexes was produced. These were a species with parameters δ = -22.2 ppm, $^1J_{PtP}$ = 5284 Hz, (21% of ^{31}P intensity), [$PtCl(C_5H_5)(CO)(PMe_2Ph)$] isomer (I) (13%) and species with δ = -4.2 ppm, $^1J_{PtP}$ = 1915 Hz (11%); δ = -4.4 ppm, $^1J_{PtP}$ = 2072 Hz (11%); δ = -11.0 ppm, $^1J_{PtP}$ = 5487 Hz (13%); δ = -20.7 ppm, $^1J_{PtP}$ = 5780 Hz (11%) and species whose $^1J_{PtP}$ could not be resolved, at -21.5 ppm (8%), -20.2 ppm (6%) and -16.6 ppm (6%). On being left overnight at less than 0°C and then being warmed to room temperature, the composition changed to "Asymmetric Dimer" (30%); species with parameters δ = -17.6 ppm, $^1J_{PtP}$ = 4779 Hz (22%); δ = -17.3 ppm, $^1J_{PtP}$ = 5122 Hz (18%); δ = -13.6 ppm, $^1J_{PtP}$ = 5587 Hz (15%), isomer (I) (8%) and *cis*-[$PtCl_2(PMe_2Ph)_2$] (7%).

[$PtCl(\eta^1-C_5H_5)(CO)(PPh_3)$] isomer (I) and AgF

A large excess of AgF was added to a solution of [$PtCl(C_5H_5)(CO)(PPh_3)$] isomer (I) (0.055mmol.) in $CDCl_3$ (0.5ml) under a N_2 atmosphere. Initially some [$PtF(\eta^1-C_5H_5)(CO)(PPh_3)$] isomer (I) was produced (^{31}P parameters in table 2), followed by [$Pt(\eta^5-C_5H_5)(CO)(PPh_3)$]$^+$.

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