1977

Studies Of Some Organopalladium Compounds

Charles Roderick Milne

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STUDIES OF SOME ORGANOPALLADIUM COMPOUNDS

by

Charles Roderick Cameron Milne

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
September, 1977

ABSTRACT

Some cationic compounds of the type trans-[PdMe(L)-$(PEt_3)_2]PF_6$ have been prepared where L = tertiary phosphine, substituted pyridine, isocyanide, nitrile or carbon monoxide. Various reactions of these coordinated ligands are also reported.

Some cationic compounds of the type $[PdMe(L)diphos]PF_6$ have been prepared where L = tertiary phosphine or para substituted pyridine. The ^{31}P nmr spectra have been run for these compounds. Correlations between J(P-P) and δP and the electronic nature of L are discussed.

The acetylenes $CH_3OOCC{\equiv}CCOOCH_3$ and $CF_3C{\equiv}CCF_3$ insert into the methyl palladium bond of the complexes PdXMe-diphos (X=Cl,NO_3 or (solvent)PF_6) and PdMe(η^5-C_5H_5)PPh_3 to give alkenyl complexes and in some cases butadienyl compounds. For insertion of $CH_3OOCC{\equiv}CCOOCH_3$ into PdXMediphos (X=Cl, NO_3 or (solvent)PF_6) the rate of insertion was anion dependent being in the order (solvent)-PF_6>NO_3>Cl. The implications of this observation as to the nature of the mechanism of insertion is discussed.

Acetylenes substituted with one electron-withdrawing group, R', reacted with the hydrides trans-PdX(H)$(PCy_3)_2$ (X = NO_3 or (solvent)PF_6) to give alkenyl products of the type trans-PdX(RC=CR'(H))$(PCy_3)_2$.

In some cases the geometry of the resulting alkenyl group could be determined. In these cases the observation that all alkenyl groups have a cis geometry is consistent with a migratory insertion step involving a four-centred transition state, in which the disposition of the acetylene relative to the Pd-H bond appears to be dependent on the Pd-H bond polarity.

For the acetylene $CF_3C{\equiv}CCF_3$, the occurrence of a side reaction which competes with insertion and which leads to a palladium(0) acetylene complex is demonstrated.

The carbon bonded imine trans-PdCl($CH_3C{=}N$p-tolyl)-$(PEt_3)_2$ reacts with the acetylene $CH_3OOCC{\equiv}CCOOCH_3$ to form two new compounds, each containing a substituted pyrrole derivative as a ligand. A single crystal X-ray diffraction study was undertaken on one of the products. The structure was refined by full matrix least-squares methods on F to an agreement factor of $R_1=0.046$ employing 5043 observations. The result of this study showed the compound to be trans-chloro(1-para-tolyl-3-oxo-2-E-carbomethoxymethylidene 2,3 dihydro-pyrrole) bis(triethylphosphine)palladium(II).

Infrared, nmr and deuterium exchange studies of the starting material, intermediates and products indicate the starting imine exists as two tautomers, the enamine and the ketimine form. The N-H fragment of the enamine form adds across the triple bond of the acetylene to give an intermediate which then undergoes ring closure with elimination of methanol.

ACKNOWLEDGEMENTS

I would like to thank Dr. Howard C. Clark for his supervision and for his encouragement during those dark moments that occur in the tenure of every graduate student. I would also like to thank the various members of Dr. Clark's group especially Dr. C.S. Wong and Dr. Alan Shaver.

Thanks are also due to Dr. N.C. Payne and the members of the X-ray group for their help and comradeship.

I am also grateful for the friendship of M.E. Olson during the completion of this thesis.

Thank you M.J.E.

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ABBREVIATIONS

(d)	decomposition
diphos	1,2,-bis(diphenylphosphino)ethane
DMA	dimethylacetylenedicarboxylate
Et	ethyl
Me	methyl
n	normal
nmr	nuclear magnetic resonance
o	ortho
p	para
Ph	phenyl
pic	4-picoline
py	pyridine
S	solvent molecule
THF	tetrahydrofuran
TMS	tetramethylsilane
Cy	cyclohexyl
Bu	butyl

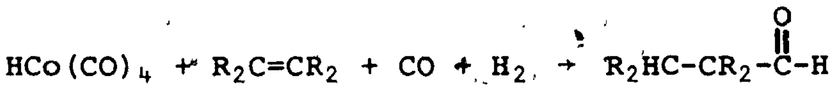
CHAPTER I

INTRODUCTION

The importance of organotransition metal chemistry has recently been manifested by the award of the Nobel prize in chemistry to two of the pioneers in the field, Sir Geoffrey Wilkinson and Ernst Otto Fischer.

This importance stems from the ability of transition metal compounds to perform three tasks.[1,2] Firstly, transition metal complexes can often have vacant coordination sites, allowing substrates to bind to the metal. Secondly, these substrates when bonded to the metal are often activated toward reaction with other molecules. Thirdly, transition metals can stabilize entities which do not normally exist in a "free state". The combination of these three properties allows transition metal compounds to act as catalysts for many reactions. The catalytic reactions of primary importance that transition metal complexes bring about are combination reactions of various unsaturated molecules (such as olefins, acetylenes and carbon monoxide) with each other and other reagents to form, often in a highly specific way, products containing new carbon-carbon bonds.

A typical catalytic system is exemplified by the hydroformylation of olefins using the transition metal compound hydridotetracarbonylcobalt(I) (equation 1).



$$HCo(CO)_4 + R_2C{=}CR_2 + CO + H_2 \rightarrow R_2HC\text{-}CR_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \qquad (1)$$

The catalytic cycle of this reaction has been studied in some detail[5] and the various steps involved are presented in Figure I-1.

Step 1 represents dissociative loss of carbon monoxide to give a coordinatively unsaturated species which can add olefin to give a Co(I) olefin complex (step 2). Migratory insertion (step 3) produces the coordinatively unsaturated alkyl complex which can pick up another mole of carbon monoxide to form the 18-electron complex (alkyl)Co(CO)$_4$ (step 4). Migratory insertion of carbon monoxide produces an acyl metal complex (step 5) which being coordinatively unsaturated can oxidatively add molecular hydrogen to form a Co(III) dihydride (step 6). Reductive elimination of this dihydride gives the aldehyde and regenerates the starting catalyst.

The four key steps in this cycle are dissociation of a ligand to form an unsaturated metal centre, coordination and activation of a substrate, oxidative addition and reductive elimination and migratory insertion.

These same key steps are postulated to occur in the transition metal catalyzed reactions of the hydrogenation, oligomerization, polymerization and isomerization of unsaturated organic molecules.[6] The understanding therefore,

Figure I-1. Hydroformylation of an olefin by $HCo(CO)_4$

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (1)$$

$$HCo(CO)_3 + R_2C{=}CR_2 \rightleftharpoons HCo(CO)_3(R_2C{=}CR_2) \qquad (2)$$

$$HCo(CO)_3(R_2C{=}CR_2) \rightleftharpoons CR_2HCR_2Co(CO)_3 \qquad (3)$$

$$CR_2HCR_2Co(CO)_3 + CO \rightleftharpoons CR_2HCR_2Co(CO)_4 \qquad (4)$$

$$CR_2HCR_2Co(CO)_4 \rightleftharpoons CR_2HCR_2COCo(CO)_3 \qquad (5)$$

$$CR_2HCR_2COCo(CO)_3 + H_2 \rightleftharpoons CR_2HCR_2COCo(CO)_3(H_2) \qquad (6)$$

$$CR_2HCR_2COCo(CO)_3(H_2) \longrightarrow CR_2HCR_2CHO + HCo(CO)_3 \qquad (7)$$

of the electronic and steric factors which control these four key steps is necessary to design the best catalyst for a particular process.

Work in this laboratory has centred around the understanding of the nature of the coordinated substrate[7,8] and also the nature of the migratory insertion reaction.[9,10] Complexes of platinum(II) are ideal for studying these facets of the catalytic cycle because the low lability and high thermal stability of Pt(II) compounds[11] allow the detection and isolation of many of the intermediates proposed in the catalytic cycle and allow, the preparation of many complexes containing coordinated unsaturated organic molecules. However, these very factors which make Pt(II) compounds suitable for the investigation of the steps of the catalytic cycle may also render them inert to subsequent reactions.

We hoped that by working on the analagous palladium(II) compounds, the greater lability of palladium(II) complexes[12] would allow us to extend the range and types of reactions which occur for platinum complexes.

The studies described in this thesis have attempted to examine the nature and behavior of molecules coordinated to palladium and the nature of the migratory insertion step into palladium-carbon and palladium-hydrogen bonds by unsaturated organic molecules.

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CHAPTER II

PREPARATION OF AND REACTIONS OF SOME METHYLPALLADIUM(II) CATIONIC COMPLEXES

a) Introduction

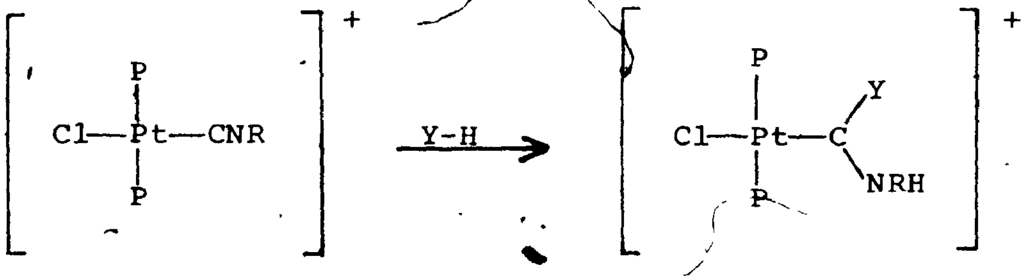
It is generally accepted that in order for a transition metal complex to be catalytically active, a vacant coordination site must be available for substrates to bind.[1,2] On coordination the substrate often readily undergoes reactions towards which it would otherwise be inactive.[1,2] Creation of a vacant coordination site can be achieved in a variety of ways. One method, which has been exploited by this research group, is to remove a coordinated chloride ligand with the silver salt of a non-coordinating anion to create a solvated complex (equation 1).

$$\text{M-Cl} \quad + \quad \text{AgY} \longrightarrow [\text{M-solvent}]^{+}\text{Y}^{-} \quad + \quad \text{AgCl} \qquad (1)$$

The solvent is then readily displaced by neutral ligands to give a cationic species [M-L]Y.

The chloride ion in trans-PtClMeL_2 (where L = tertiary phosphine or arsine) is labile due to the high trans-influence of the methyl group.[3,4] Thus, in a polar solvent such as methanol or acetone the chloride ion is readily removed by $AgPF_6$ to give the solvated cation trans-$[PtMe(S)L_2]PF_6$.[5] The addition of a donor ligand L', such as PR_3, AsR_3, py, CO, CNR or RCN, to a solution of the solvated cation results in displacement of the solvent and formation of the cationic compound trans-$[PtMe(L')L_2]PF_6$.[4]

In addition, the coordinated ligand often can undergo reactions. For example, coordinated isocyanide is susceptible to nucleophilic attack by alcohols and amines[6,7] leading to the formation of a variety of Pt(II) carbene complexes (equation 2).[8]



(2)

$Y = NR'_2, OR'$

Reaction of the solvated cation with acetylenes leads to various types of products depending on the nature of the substituents on acetylene and the reaction conditions employed.[9,10,11,12] In some instances where the acetylene is a dialkyl or diaryl acetylene, the π-bonded acetylene complex may be isolated.[9,11] However these complexes are often susceptible to attack by nucleophilic protic solvents such as methanol to give methyl vinyl ether compounds.[11]

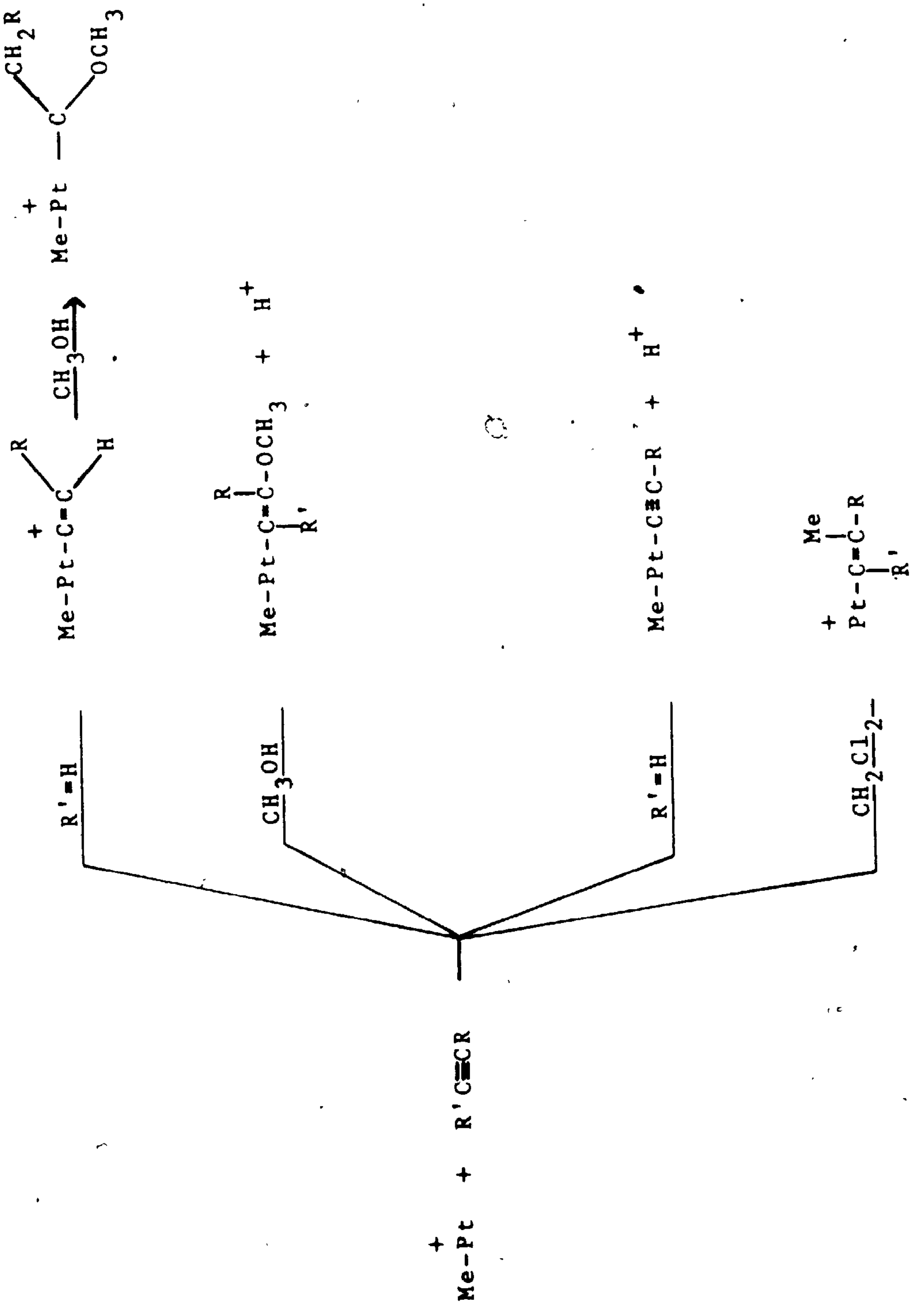
When terminal acetylenes are reacted with the solvated cation, carbene formation occurs.[9,10,12] These and some other reactions of acetylenes with the solvated cation are summarized in Figure II-1.

Reaction of the solvated cation with nitriles usually leads to the product in which the nitrile is bonded to the metal via the lone pair of the nitrogen. However in some instances coordination occurs in a π fashion. If the fluorinated nitriles C_6F_5CN or NCC_6F_4CN are used and the reaction carried out in an alcoholic medium, imino ethers are produced in some instances.[13,14]

Thus the chemistry of unsaturated organic molecules coordinated to Pt(II) is diverse.

It was our intention to extend this work to Pd(II) methyl compounds, partly to examine the differences and similarities between Pt and Pd, and partly to pave the way toward the study of insertion reactions of acetylenes into Pd-carbon bonds. The system <u>trans</u>-$PdClMe(PEt_3)_2$ was used as well as, somewhat later, the system PdClMediphos. The latter system was also interesting in that in a series of complexes $[PdMe(MR_3)diphos]^+$ (R = alkyl, aryl M = P, As, Sb), relationships among the ^{31}P chemical shifts, the phosphorus coupling constants, and the electronic and steric nature of MR_3 could be established.

Figure II-1. Some reactions of acetylenes with methylplatinum cations. For the sake of clarity other ligands on platinum are omitted.



Me-Pt⁺ + R'C≡CR
R'=H
CH₃OH
R'=H
CH₂Cl₂
Me-Pt⁺-C=C(R)(H)
CH₃OH
Me-Pt⁺—C(CH₂R)(OCH₃)
Me-Pt-C(R')=C(R)-OCH₃ + H⁺
Me-Pt-C≡C-R + H⁺
Pt⁺-C(R')=C(Me)-R

b) Results and Discussion

(i) Preparation of the solvated cations trans-[PdMe(S)(PEt$_3$)$_2$]PF$_6$ and [PdMe(S)diphos]PF$_6$

The compound trans-PdClMe(PEt$_3$)$_2$ reacted smoothly, in a coordinating solvent such as tetrahydrofuran or acetone, with AgPF$_6$ to give a colourless solution and a thick precipitate of AgCl. The solution which contained the solvated cation was temperature sensitive and rapidly decomposed above 5°C. Addition of a donor ligand L gave a temperature stable solution and the product trans-[PdMeL(PEt$_3$)$_2$]PF$_6$ could often be isolated as white air stable crystals. Analytical data for bistriethylphosphine compounds are presented in Table II-1, infrared data in Table II-2 and ^{1}H nmr data in Table II-3.

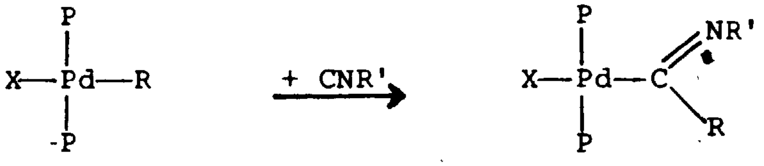
The compound PdClMediphos also reacted smoothly in a coordinating solvent with AgPF$_6$ to give on filtration, solutions of the solvated cation. These solutions were also temperature sensitive but not to the same extent as the bistriethylphosphine cationic solutions. Addition of a donor ligand gave stable solutions from which air stable white crystals of the form [PdMeLdiphos]PF$_6$ could be isolated. Analytical data for these compounds are presented in Table II-4.

(ii) Reaction of trans-[PdMe(S)(PEt$_3$)$_2$]PF$_6$ and [PdMe(S)diphos]PF$_6$ with para-tolylisocyanide.

From the addition of one equivalent of p-tolylisocyanide to a solution of the solvated cation trans-

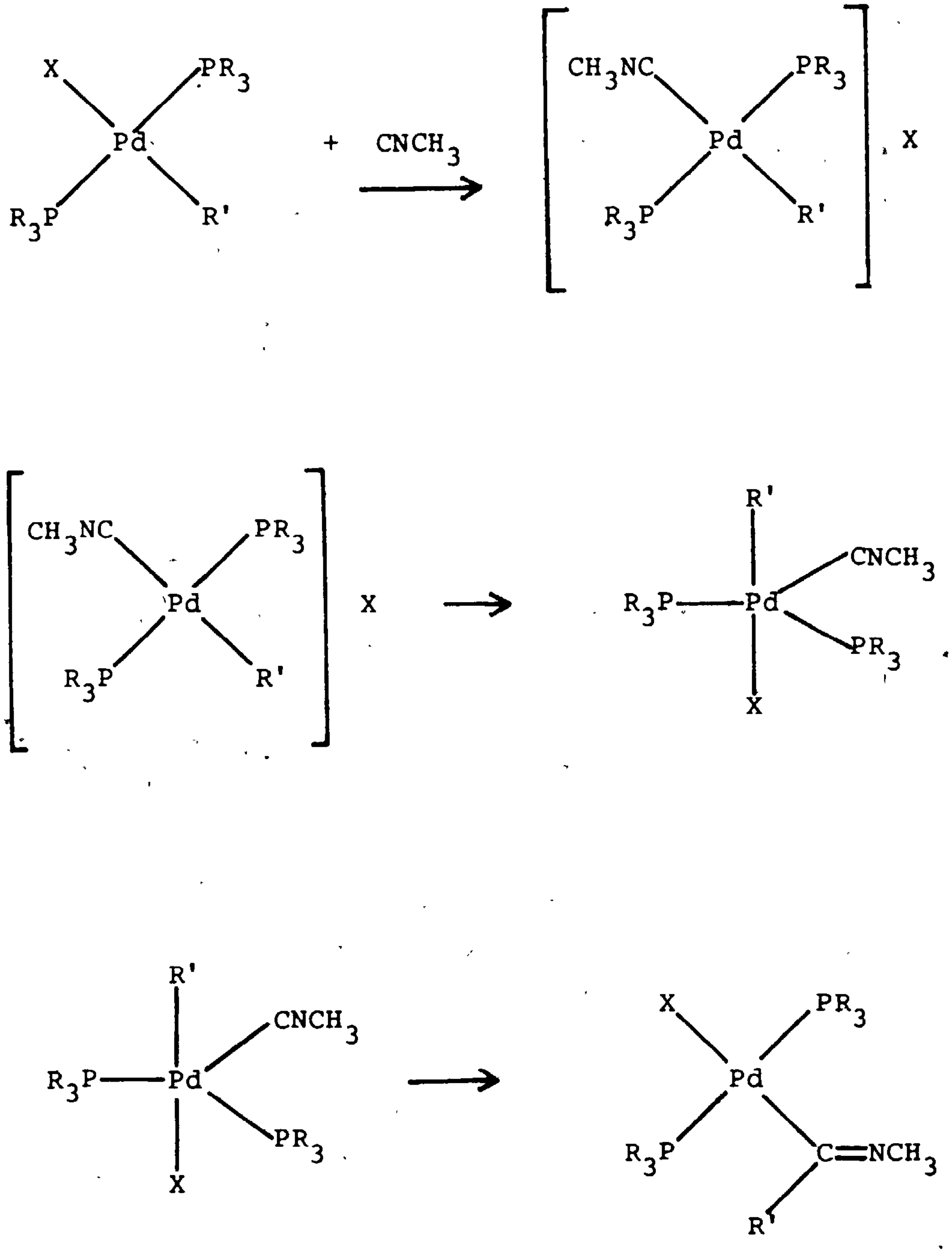
$[PdMe(S)(PEt_3)_2]PF_6$, the isocyanide cation trans-$[PdMe(CNR)(PEt_3)_2]PF_6$ could be isolated. It was characterized by its infrared and ^1H nmr spectra. In the infrared a sharp intense signal at 2171 cm^{-1} is indicative of $\nu(C{\equiv}N)$. In addition a band at 1503 cm^{-1} due to the $\delta(CH_3)$ of the tolyl methyl and a band at 839 cm^{-1} due to $\nu(P\text{-}F)$ of the PF_6^- anion are observed. The ^1H nmr spectrum has peaks at 1.08 and 1.80 ppm indicative of trans triethylphosphine ligands and a peak at 0.05 ppm due to the protons of the methyl group bonded to the palladium atom. This latter resonance is split into a triplet with relative intensities of 1:2:1, due to coupling to the mutually trans phosphorus atoms. The aromatic protons of the p-tolyl group appear as a singlet at about 7 ppm while the tolyl methyl protons appear as a singlet at about 2.3 ppm.

Isocyanide readily inserts into the alkyl group of square planar palladium compounds of the type trans-$PdXR(PR'_3)_2$ (X = Cl,Br,I) to give a carbon bonded imine (equation 3).[15,16,17]



(3)

Figure II-2. Proposed mechanism for isocyanide insertion for square planar complexes of the type $\mathrm{PtX(R')(PR_3)_2}$. R' = alkyl, X = Cl, Br, I.


X
PR3
Pd
R3P
R'
+ CNCH3
CH3NC
PR3
Pd
R3P
R'
X
CH3NC
PR3
Pd
R3P
R'
X
R'
CNCH3
R3P
Pd
PR3
X
R'
CNCH3
R3P
Pd
PR3
X
X
PR3
Pd
R3P
C=NCH3
R'

However, the cationic isocyanide complex prepared here did not undergo insertion even upon refluxing in acetone for 48 hours. Addition of a trace of a good coordinating ligand such as PEt_3 or pyridine, however, caused insertion to occur and the compound trans-Pd[CH_3C=Np-tolyl]Cl$(PEt_3)_2$ could be isolated on quenching with LiCl.

Treichel and Hess[18] have proposed the existence of a five coordinate intermediate in the mechanism of insertion of isocyanide into the platinum-carbon bond of the ionic complexes [PtR(CNR')$(PEt_3)_2$]X [R = Me, X = I; R = Ph, X = Cl, Br or I] (Figure II-2). In this five coordinate intermediate the isocyanide and the methyl group would most likely be cis to each other a necessary criterion for migratory insertion. Similar conclusions were arrived at by Christian and Clark for the insertion reaction of isocyanide into the platinum-hydrogen bond of trans-PtCl(H)$(PEt_3)_2$.[19]

It would appear that for the cationic compound prepared here, the isocyanide and the methyl group cannot form a five coordinate intermediate because the PF_6^- anion cannot coordinate. However, addition of a donor ligand allows the formation of a cationic five coordinate species in which the isocyanide and methyl group are cis to one another. Thus, insertion can take place.

The reaction of p-tolylisocyanide with the cation [PdMe(S)diphos]PF_6 resulted in the formation of gums which subsequently decomposed. However, if a solution of

TABLE II-1

Analytical and Physical Data for <u>Trans</u> bistriethylphosphine Palladium Compounds[a]

Compound	Colour	M.p.	%C		%H		%N	
			Found	Calc.	Found	Calc.	Found	Calc.
$[PdMe(py)L_2]PF_6$	white	110(d)	36.72	37.15	6.50	6.56	2.55	2.41
$[PdMe(pic)L_2]PF_6$	white	118-119(d)	38.75	38.30	6.52	6.77		
$[PdMeL_3]PF_6$	white	105(d)	36.61	36.75	7.62	7.79		
$[(PdMeL_2)_2NC-C_6F_4-CN](PF_6)_2$	pale yellow	80-82(d)	33.05	33.88	5.23	5.51	2.21	2.32
$[PdMe(CNR)L_2]PF_6$	white	94(d)	40.66	40.69	6.34	6.51	2.38	2.26
$PdCl(CH_3C{=}NR)L_2$	white	106-107(d)	49.53	49.42	7.74	7.90	2.65	2.74
$[PdCl(C(CH_3)NRH)L_2]Cl$	white	176-177(d)	45.72	46.06	7.63	7.50	2.52	2.56
$[PdMe(C(NRH)NMe_2)L_2]PF_6$	white	110-111(d)	41.21	41.50	7.05	7.07	4.43	4.21
$[PdMe(C(NRH)NMeH)L_2]PF_6$	white	135-136(d)	40.69	40.52	6.73	6.92	4.26	4.31

[a] R = *p*-tolyl; L = PEt_3

TABLE II-2.

Infrared Data[a,b,c] for <u>Trans</u> bistriethylphosphine Palladium Compounds

Compound	
$[\mathrm{PdMe(CO)L_2}]\mathrm{PF_6}$	ν(CO) 2130, ν(P-F) 835
$[\mathrm{PdMe(CNR)L_2}]\mathrm{PF_6}$	$\nu(\mathrm{C{\equiv}N})$ 2171, ν(P-F) 839
$[\mathrm{PdMe(C(NRH)NMe_2)L_2}]\mathrm{PF_6}$	ν(N-H) 3346, δ(N-H) 1596, $\nu(\mathrm{C}\overset{---}{=}\mathrm{N})$ 1542, ν(P-F) 837
$[\mathrm{PdMe(C(NRH)NMeH)L_2}]\mathrm{PF_6}$	ν(N-H) 3425,3332, δ(N-H) 1610,1604, $\nu(\mathrm{C}\overset{---}{=}\mathrm{N})$ 1546, ν(P-F) 836
$\mathrm{PdCl(CH_3C{=}NR)L_2}$	$\nu(\mathrm{C{=}N})$ 1599
$[\mathrm{PdCl(C(CH_3)NRH)L_2}]\mathrm{Cl}$	ν(N-H) 3494,3414, δ(N-H) 1615, $\nu(\mathrm{C}\overset{---}{=}\mathrm{N})$ 1547
$[\mathrm{(PdMeL_2)_2NC{-}C_6F_4{-}CN}]\mathrm{(PF_6)_2}$	$\nu(\mathrm{C{\equiv}N})$ 2272, ν(P-F) 840

[a] All spectra recorded as nujol mulls

[b] All values in cm^{-1}

[c] R = <u>p</u>-tolyl; L = $\mathrm{PEt_3}$

TABLE II-3. ^{1}H NMR Data for Trans-bistriethylphosphine Palladium Compounds[a,b,c]

Compound		δ(Pd-CH$_3$)	^{3}J(P-H)	Other Resonances
[PdMe(py)L$_2$]PF$_6$		0.25	6.5	
[PdMe(pic)L$_2$]PF$_6$		0.29	6.5	δ(CH$_3$) 2.49
[PdMeL$_3$]PF$_6$		0.14	^{4}7.2	
[PdMe(CO)L$_2$]PF$_6$		0.43	7.5	
[{PdMeL$_2$}$_2$NCC$_6$F$_4$CN](PF$_6$)$_2$		0.45	6.5	
[PdMe(CNR)L$_2$]PF$_6$		0.05	6.6	δ(CH$_3$) 2.28 δ(phenyl) 6.98
PdCl(CH$_3$C=NR)L$_2$				δ(C-CH$_3$) 2.49 δ(CH$_3$-tolyl) 2.29 δ(phenyl) 7.0-7.7
[PdCl(C(CH$_3$)NRH)L$_2$]Cl				δ(C-CH$_3$) 3.16 δ(CH$_3$-tolyl) 2.23 δ(phenyl) 7.0-8.6 δ(N-H) 15.29
[PdMe(C(NRH)NMe$_2$)L$_2$]PF$_6$	I	-0.13	6.5	δ(CH$_3$-tolyl) 2.28 δ(N-CH$_3$) 3.22,3.63 δ(N-H) 7.98 δ(phenyl) 6.95-7.8
	II	-0.14	6.5	2.28 3.28,3.71 -- 6.95-7.8
[PdMe(C(NRH)NMeH)L$_2$]PF$_6$	III	0.09	6.3	δ(CH$_3$-tolyl) 2.28 δ(N-CH$_3$) 3.32 ^{2}J(N-H)=5.0 δ(N-H) 8.58 δ(phenyl) 6.9-8.0
	IV	-0.20	6.5	2.28 3.08 5.0 8.16 6.9-8.0
	V	-0.19	6.5	2.28 3.22 5.0 8.16 6.9-8.0

[a] Chemical shifts in positive ppm downfield from TMS; coupling constants in Hz.

[b] L = PEt$_3$; R = para-tolyl.

[c] Compounds also had resonances between 1-3 ppm indicative of trans triethylphosphine ligands.

TABLE II-4.

Analytical and Physical Data for Cationic Complexes of the Type [PdMe(L)diphos]PF_6

A. L = para C_5H_4N-X

		%C		%H	
X	Melting Point (°C)	Found	Calculated	Found	Calculated
H	165(d)	51.78	51.67	4.36	4.29
Me	151-152(d)	52.35	52.24	4.41	4.49
NMe_2	159-161(d)	51.73	51.89	4.72	4.74
CN	154-155(d)	51.31	51.55	4.21	4.06
$COOCH_3$	160-162(d)	50.62	50.93	4.13	4.27
$COCH_3$	159-160(d)	51.33	51.95	4.25	4.32

B. L = R_3M, M = P,As,Sb

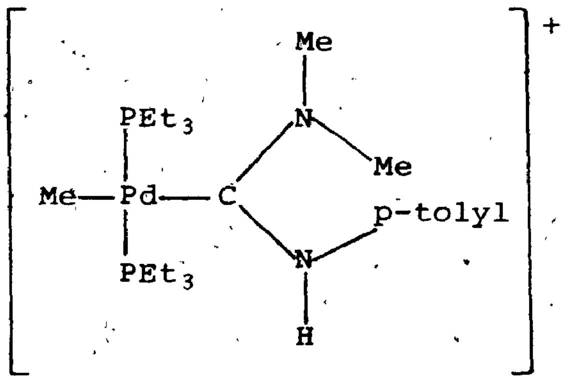
L					
PPh_3	128-129(d)	58.08	58.30	4.45	4.56
PEt_3	159(d)	51.02	50.58	5.15	5.36
$PMePh_2$	122-124(d)	56.12	55.54	5.31	4.66
PMe_2Ph	143-145(d)	52.56	52.53	4.84	4.77
$PnBu_3$	117(d)	54.14	54.02	6.30	6.28
$P(C_6F_5)_3$	109(d)	44.14	44.87	2.36	2.26
PCy_3	126(d)	56.74	56.58	6.24	6.25
$AsPh_3$	139-141(d)	55.77	55.66	4.32	4.36
$SbPh_3$	143(d)	53.20	53.10	4.28	4.16
$PMe_2C_6F_5$	168-169(d)	46.91	47.08	3.76	3.73
P(o-tolyl)$_3$	113-115(d)	59.18	59.44	5.08	4.95

this cation in acetone was made up in an nmr tube and one equivalent of isocyanide added at -15°C, an ^{1}H nmr spectrum was obtained which was consistent with the formation of the cation $[PdMe(CNR)diphos]PF_6$. The signal for the methyl bonded to the palladium atom comes at 0.49 ppm and is a doublet of doublets due to coupling to the trans phosphorus atom and to the cis phosphorus atom. Because both couplings are present the isocyanide must be coordinated since in the solvated cation only the trans coupling is observed. On warming to 5°C this peak shifted to 2.12 ppm, the region where a methyl on an imine is usually found.[17] Quenching of this solution with LiCl afforded the insertion product $PdCl[CH_3C{=}N$p-tolyl] - diphos in good yield. This ready insertion is probably due to the presence of the phosphine ligand diphos. Because the phosphine occupies cis sites the isocyanide coordinates cis to the methyl group. There is now no need for formation of a five coordinate intermediate to produce this cis arrangement and insertion can occur spontaneously.

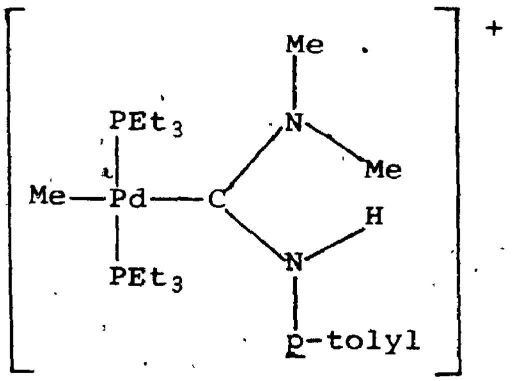
As mentioned in the introduction coordinated isocyanide is often susceptible to nucleophilic attack by alcohols and primary and secondary amines to give carbene complexes. The amines NMe_2H and $NMeH_2$ readily added across the C≡N bond of the isocyanide ligand in trans-[PdMe(CNp-tolyl)-$(PEt_3)_2]PF_6$. For the amine NMe_2H the carbene complex trans-[PdMe[C(NMe_2)(NHp-tolyl)]$(PEt_3)_2]PF_6$ was isolated in good yield. The infrared spectrum of this product has bands at 3346 cm^{-1}(ν(N-H)), at 1596 cm^{-1} (δ(N-H)), at 1542 cm^{-1}(ν(C---N)), at 1506 cm^{-1} due to the methyl rock of the p-tolyl methyl, and at 837 cm^{-1}(ν(P-F)).

In the ^{1}H nmr spectrum two sets of signals are observed in the ratio of 7:1. Each set has resonances between 1 and 3 ppm characteristic of trans triethylphosphine ligands. In addition each set has two singlets at around 3.6 ppm due to the methyl groups on the nitrogen; a singlet at 2.3 ppm due to the p-tolyl methyl protons, and a peak at 8 ppm due to the amino proton. The methyl group on the palladium appears, for both sets of signals, at around 0.13 ppm upfield from TMS as a triplet of relative intensities of 1:2:1 due to coupling to the trans phosphorus atoms. The aromatic protons of the p-tolyl group appear as an AB quartet.

Two sets of signals are observed because of restricted rotation about the carbene carbon nitrogen bond to give the two isomers I and II.



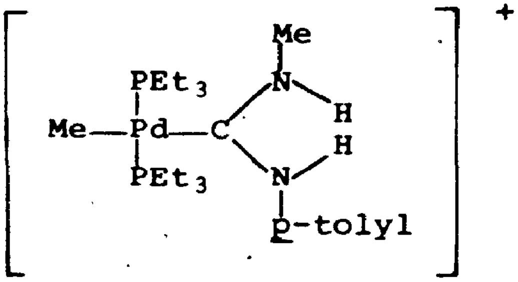
I



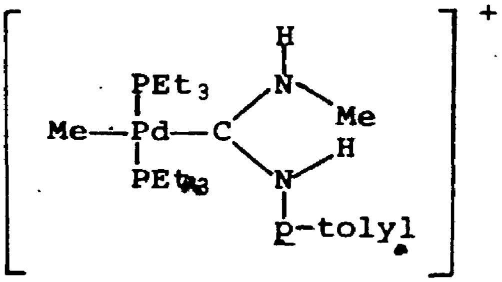
II

This hindered rotation about a heteroatom carbene carbon bond is very common for both secondary and primary carbenes.[7] The smaller set of signals is probably due to I and the larger set due to II on account of the steric interactions being greater for I between the p-tolyl group and one of the amino methyl groups versus the interaction between a hydrogen and the amino methyl group in II.

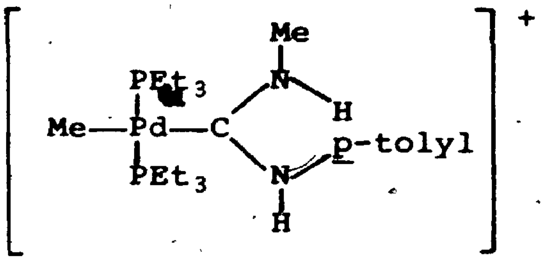
Addition of $NMeH_2$ across the coordinated isocyanide triple bond also occurred readily to give the carbene cation trans-$[PdMe(C(NMeH)(Np\text{-tolyl }H)(PEt_3)_2]PF_6$. Now four isomers are possible III, IV, V and VI, three of which are detectible in the ^1H nmr. Again on steric arguments the most abundant isomer is assigned structure III, the next most abundant structure IV and the least abundant structure V. No attempt was made to study the dependence of the isomer distribution on temperature or on polarity of solvent.[20]



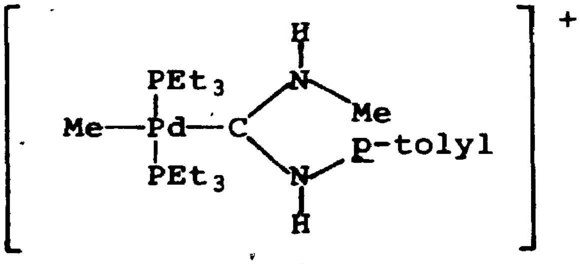
III



IV



V



VI

Despite refluxing in ethanol or methanol for 48 hours the isocyanide cation trans-[PdMe(CNp-tolyl)(PEt$_3$)$_2$]PF$_6$ failed to form carbene complexes.

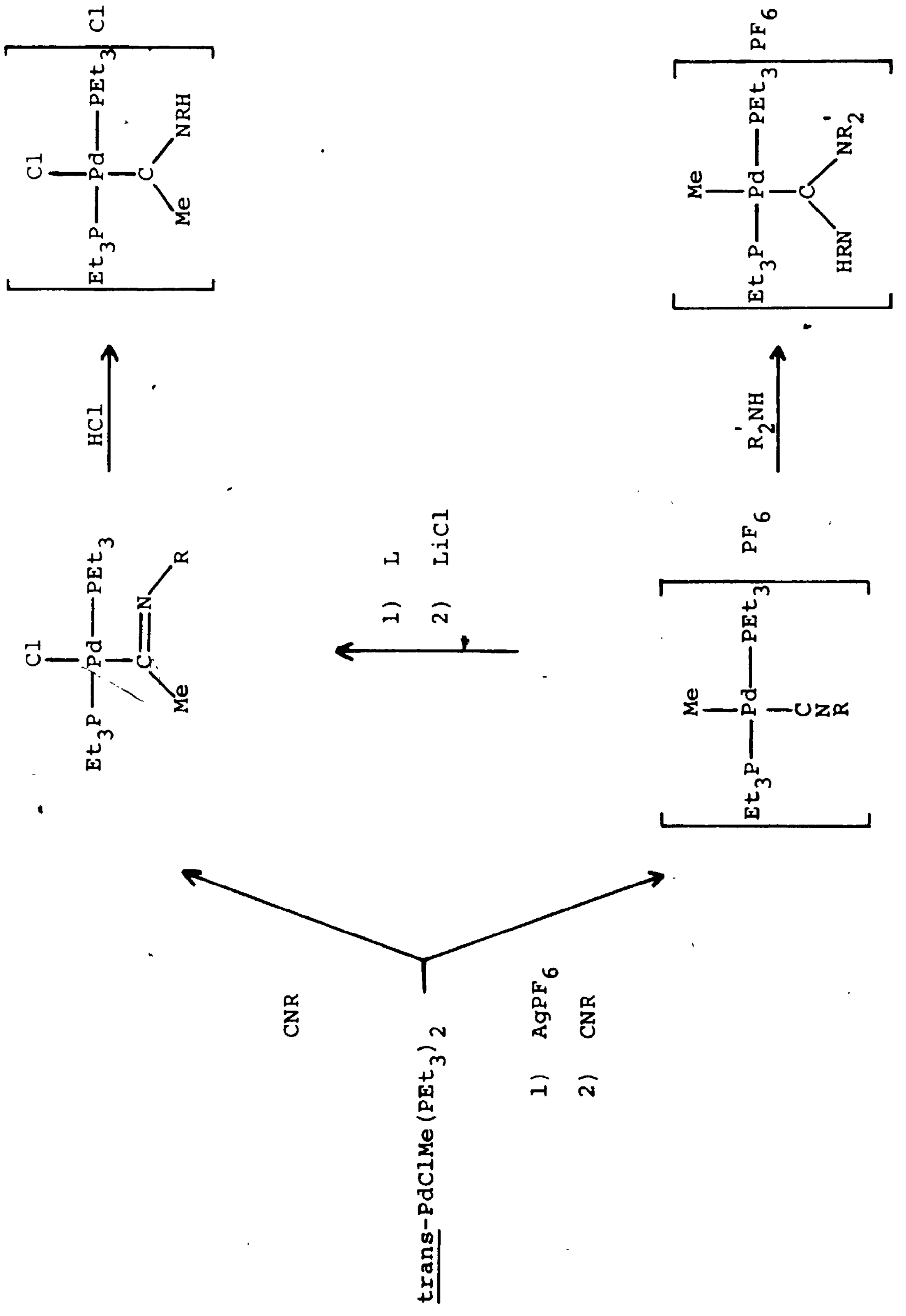
As mentioned earlier isocyanides insert into complexes of the type trans-PdClMe(PR$_3$)$_2$. The compound trans-PdClMe(PEt$_3$)$_2$ was no exception and reaction with p-tolylisocyanide at room temperature in dichloromethane afforded the imine trans-PdCl[MeC=Np-tolyl](PEt$_3$)$_2$. Addition of HCl to this imine produced the cationic carbene complex trans-[PdCl(C(Me)(Np-tolyl H)) (PEt$_3$)$_2$]Cl. This carbene formation is characterized in the infrared by the drop in ν(C-N) from 1599 cm^{-1} to 1560 cm^{-1} and the appearance of ν(N-H) at 3419 and 3499 cm^{-1}. Corresponding changes occur in the ^{1}H nmr spectrum.

These reactions of isocyanide with palladium methyl cations are summarized in Figure II-3.

(iii) Reaction of trans-[PdMe(S)(PEt$_3$)$_2$]PF$_6$ with carbon monoxide.

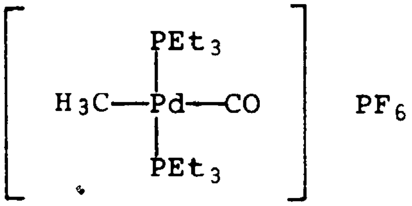
Passage of carbon monoxide through a methanol solution of the solvated cation trans-[PdMe(S)(PEt$_3$)$_2$]PF$_6$ at -30°C caused a precipitation of white crystals. These crystals were stable at -5°C but at higher temperatures decomposed in a matter of 2-3 hours preventing their elemental analysis. The infrared spectrum of these crystals shows a strong absorbance at 2130 cm^{-1} indicative of a coordinated terminal CO group. The ^{1}H nmr spectrum of these crystals in dichloromethane solution at -10°C has

Figure II-3. Some reactions of para-tolylisocyanide with methylpalladium compounds.


trans-PdClMe(PEt3)2
CNR
1) AgPF6
2) CNR
1) L
2) LiCl
HCl
R'2NH
Cl
PF6
PF6
Et3P
PEt3
Pd
Me
NRH
NR'2
HRN
CNR

signals between 1-3 ppm indicative of <u>trans</u> triethylphosphine ligands. In addition there is a resonance at 0.43 ppm which is a triplet of relative intensities 1:2:1 due to a methyl group on a palladium atom coupled to <u>trans</u> phosphorus atoms.

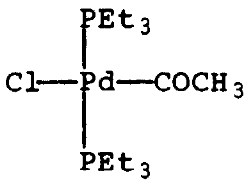
A reasonable structure for these crystals is VII.



$$\left[\begin{array}{c} PEt_3 \\ | \\ H_3C-Pd-CO \\ | \\ PEt_3 \end{array}\right] PF_6$$

VII

On warming to 0°C the ^1H nmr spectrum changes. The 1:2:1 triplet at 0.43 ppm slowly disappears and is replaced by a 1:2:1 triplet at 2.32 ppm. In addition the chemical shifts of the protons of the triethylphosphine groups change slightly although the basic pattern remains the same indicating that the phosphorus atoms are still mutually <u>trans</u>. Addition of LiCl to this solution followed by workup afforded the known compound VIII.[25]



$$\begin{array}{c} PEt_3 \\ | \\ Cl-Pd-COCH_3 \\ | \\ PEt_3 \end{array}$$

VIII

Thus it appears that the compound VII undergoes spontaneous insertion at 5°C to give the acyl complex which may be isolated by quenching with LiCl.

Addition of donor ligands to a solution of VII at -5°C resulted in displacement of carbon monoxide rather than insertion, thwarting attempts to follow the reaction kinetics of insertion.

The change of $\nu(C{\equiv}O)$ from the free ligand value is only 14 cm^{-1} indicating that there is little back donation of electron density from the palladium d orbitals into the π^* orbitals of the carbon monoxide ligand.[21] This lack of π donation, presumably a consequence of the cationic charge, may explain why only three other well characterized Pd(II) carbon monoxide compounds have been reported in the literature.[22,23,24]

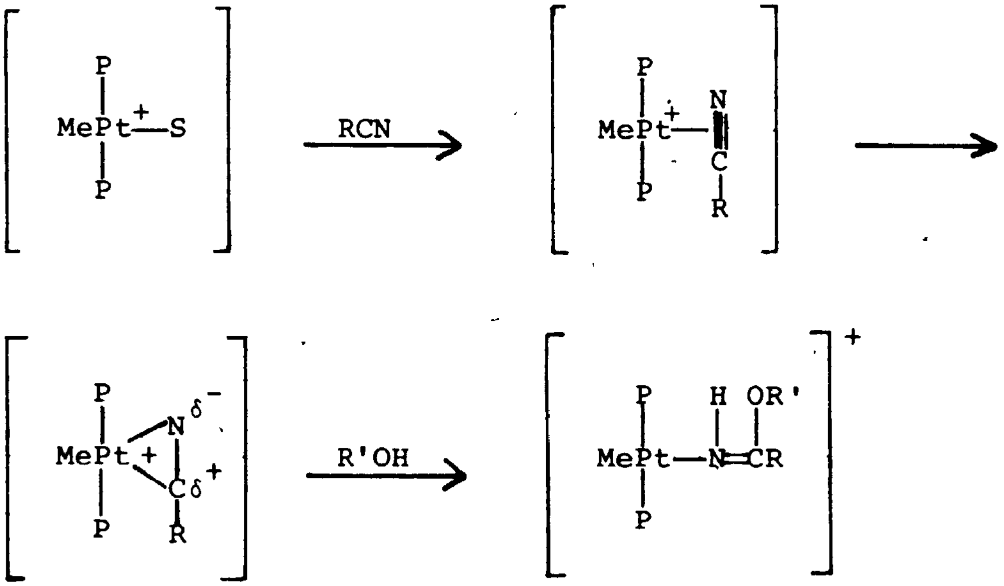
Reaction of carbon monoxide with the solvated cation $[PdMe(S)diphos]PF_6$ led only to decomposition. Interestingly Booth and Chatt[25] found that although trans-$PdClMe(PEt_3)_2$ could readily be carbonylated to give the acyl compound VIII, PdBrMediphos decomposed under similar conditions. In light of the ready insertion of isocyanide into the Pd-carbon bond of $[PdMe(S)diphos]PF_6$ it would appear that multiple insertion of CO occurs to give unstable products.

iv) Reaction of trans-$[PdMe(S)(PEt_3)_2]PF_6$ with organonitriles

Addition of aromatic nitriles substituted in the para position to solutions of the cation trans-$[PdMe(S)(PEt_3)_2]$-PF_6 gave only sticky oils which could not be identified. However, the use of the fluorinated nitrile $NC\text{-}C_6F_4\text{-}CN$ gave a crystalline product, $[PdMe(PEt_3)_2]_2(NC\text{-}C_6F_4CN)(PF_6)_2$.

The $\nu(C{\equiv}N)$ of this compound in the infrared came at

2272 cm^{-1} indicative of a σ bonded nitrile.[26] This product failed to add the elements of ROH to form imino ethers and also failed to form imino ethers even if it was prepared in an alcoholic solvent. This failure to form imino ethers is in contrast to Pt(II) cations[13,14] but is consistent with work on some Rh(III) cations.[27] The formation of an imino ether is thought to proceed through an intermediate in which the nitrile is bonded in a π fashion to the metal, followed by attack of the alcohol on this π bonded nitrile (equation 4).



(4)

If the nitrile is bonded in a σ fashion, rearrangement to the π bonded form cannot occur, rendering the complex inert to imino ether formation. In the case of the Rh(III) cationic work it was postulated that the lifetime of the π bonded intermediate was short and that it quickly rearranged to form the σ bonded compound before imino ether formation could occur. It would appear that this is also true for palladium(II) cations. This is supported by the high ν(C≡O) in trans-$[PdMe(CO)(PEt_3)_2]PF_6$. The lack of back donation from the metal causes the high stretching frequency. It may be that this same lack of back donation renders the π complexed nitrile so unstable with respect to the σ bonded form that the lifetime of the π bonded form is too short for imino ether formation to occur.

v) Reaction of trans-$[PdMe(S)(PEt_3)_2]PF_6$ with substituted acetylenes

A large variety of substituted acetylenes were allowed to react with solutions of the solvated cation trans-$[PdMe(S)(PEt_3)_2]PF_6$. In no instance could π acetylene, carbene or vinyl ether complexes be isolated. Even the acetylene 3-butyne-1-ol failed to form the cyclic carbene compound. As the formation of both the latter type of compounds is thought to proceed through a π bonded acetylene intermediate it is reasonable to suggest that as in the case of the fluorinated nitrile work such π bonded complexes are particularly shortlived for palladium(II) compounds because of the lack of π back donation from the metal. Even if they are formed the acetylene may not be activated enough to undergo nucleophilic attack as do the Pt(II) cations.

vi) Discussion of the ^{31}P nmr spectra of compounds of the type $[PdMe(L)diphos]PF_6$.

As mentioned earlier, cationic complexes of the type $[PdMe(L)diphos]PF_6$ could readily be prepared. The ^{31}P nmr spectra for a large number of these cations were run for L = tertiary phosphine, arsine or stibine and for L = pyridines substituted in the para position. The data obtained from these spectra are contained in Table II-5.

The proton decoupled ^{31}P nmr spectrum when L = substituted pyridine contains two resonances, a doublet at around -60 ppm and a doublet at around -40 ppm. The low field signal is due to the phosphorus atom trans to the pyridine, P^2, while the high field signal is due to the phosphorus atom cis to the methyl group P^1, a reflection of the higher trans influence of methyl versus pyridine.[4] The doublet appearance of each signal is due to the coupling between the two phosphorus atoms and is of the order of 24 Hz.

The changes in the values of the ^{31}P chemical shifts and $|J(P^1-P^2)|$ are small as the para substituent is varied, however regular trends are observed. The ^{31}P chemical shifts increase while $|J(P^1-P^2)|$ decreases as the donating ability of the para substituent on the pyridine increases. Plots of the chemical shift of the trans phosphorus atom P^2, the cis phosphorus atom P^1 and $|J(P^1-P^2)|$ versus the Hammett substituent constant[28] (ρ) of the para substituent

TABLE II-5

^{31}P NMR Data for Cationic Complexes of the Type $[PdMe(L)diphos]PF_6$[a,b]

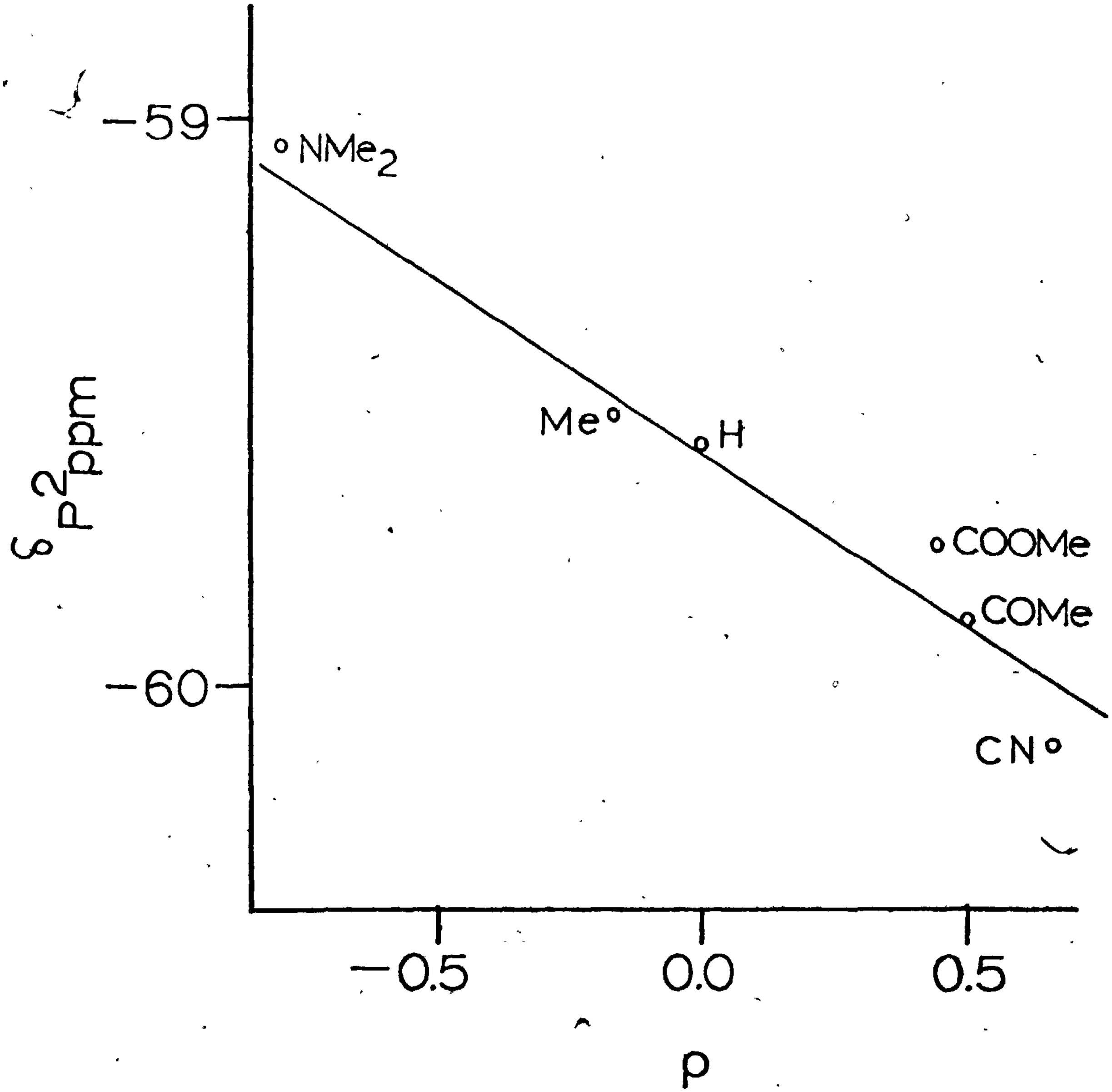
L	δP^1	δP^2	δP^L	$\lvert J(P^1-P^2)\rvert$	$\lvert J(P^1-P^L)\rvert$	$\lvert J(P^2-P^L)\rvert$
PPh_3	-43.02	-58.16	-29.35	27.35	32.72	365.69
$PMePh_2$	-42.61	-56.68	- 9.98	26.58	33.25	372.9
PMe_2Ph	-42.73	-56.07	5.92	27.05	33.42	380.87
P*n*-Bu$_3$	-42.03	-54.84	- 8.72	25.97	31.61	365.0
PEt_3	-42.30	-55.10	-16.97	26.14	32.02	363.75
PCy_3	-39.01	-55.02	-30.14	24.95	30.20	346.4
$P(C_6F_5)_3$	-42.96	-60.41	25.56	29.60	30.40	399.90
$PMe_2C_6F_5$	-42.61	-57.99	5.13	27.47	33.60	393.95
P(*o*-tolyl)$_3$	-38.75	-55.75	-25.50	25.50	31.02	354.93
$AsPh_3$	-43.35	-59.38		27.54		
$SbPh_3$	-46.16	-60.76		29.91		
Py-H[c]	-39.02	-59.57		23.20		
Py-CH_3	-38.66	-59.52		23.00		
Py-NMe_2	-37.50	-59.04		22.59		
Py-CN	-39.84	-60.10		23.81		
Py-$COOCH_3$	-39.51	-59.75		23.55		
Py-$COCH_3$	-39.64	-59.89		23.71		

[a] Spectra recorded in CH_2Cl_2 using 1% phosphoric acid as an external standard. Chemical shifts are in ppm and coupling constants in Hz.

[b] P^L refers to the ligand L, P^1 to the phosphorus atom cis to L and P^2 to the phosphorus atom trans to L.

[c] Pyridine derivatives substituted in the para position.

Figure II-4. Plot of δP^2 vs. the Hammett substituent constant, ρ, for compounds of the type [PdMe(py-X)diphos-]PF_6. X refers to a substituent in the para position of the pyridine.



δ_{P^2} ppm
−59
−60
NMe$_2$
Me
H
COOMe
COMe
CN
−0.5
0.0
0.5
ρ

Figure II-5. Plot of δP^1 vs. the Hammett substituent constant, ρ, for compounds of the type [PdMe(py-X)diphos]PF_6. X refers to a substituent in the *para* position of the pyridine.

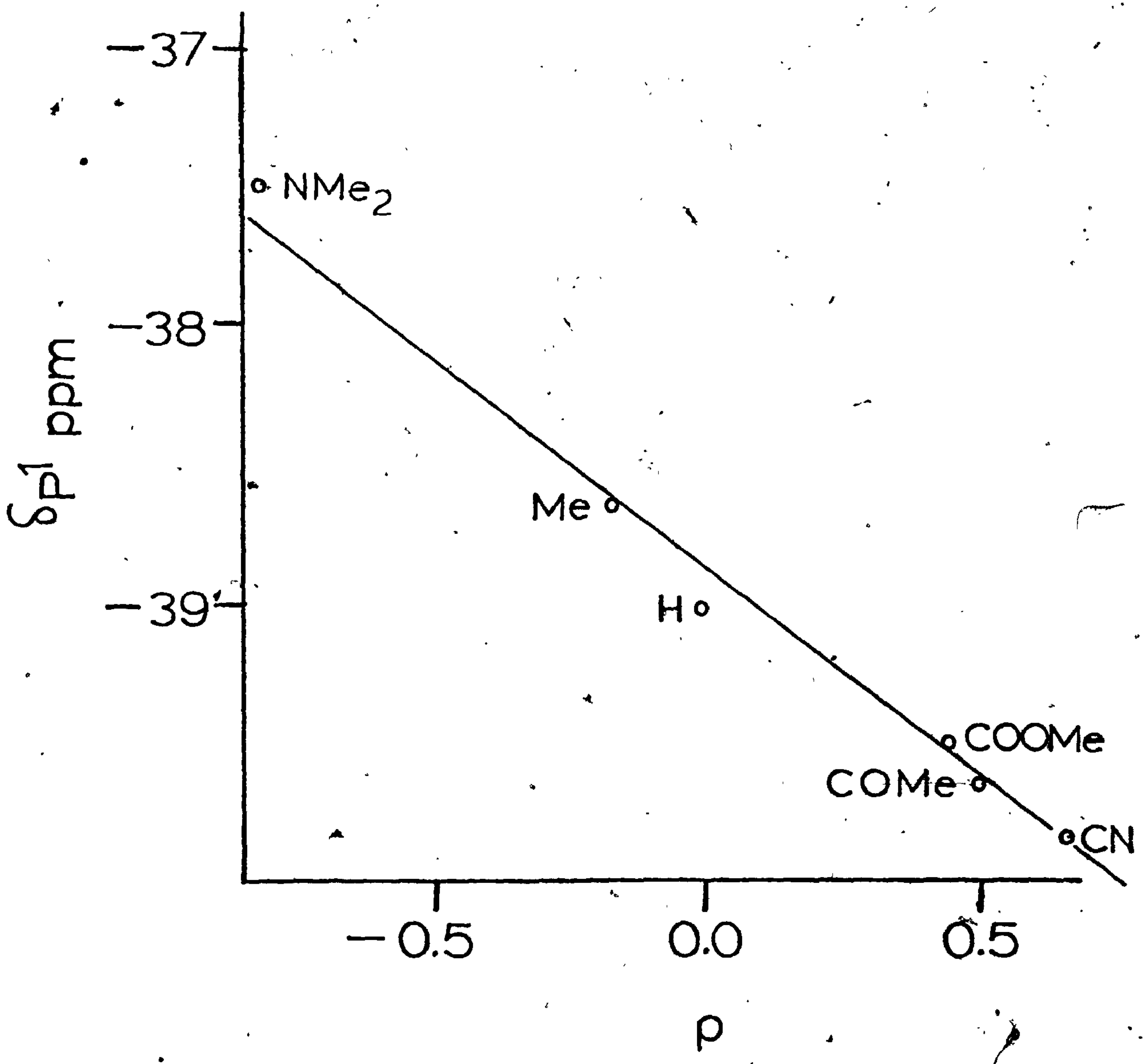
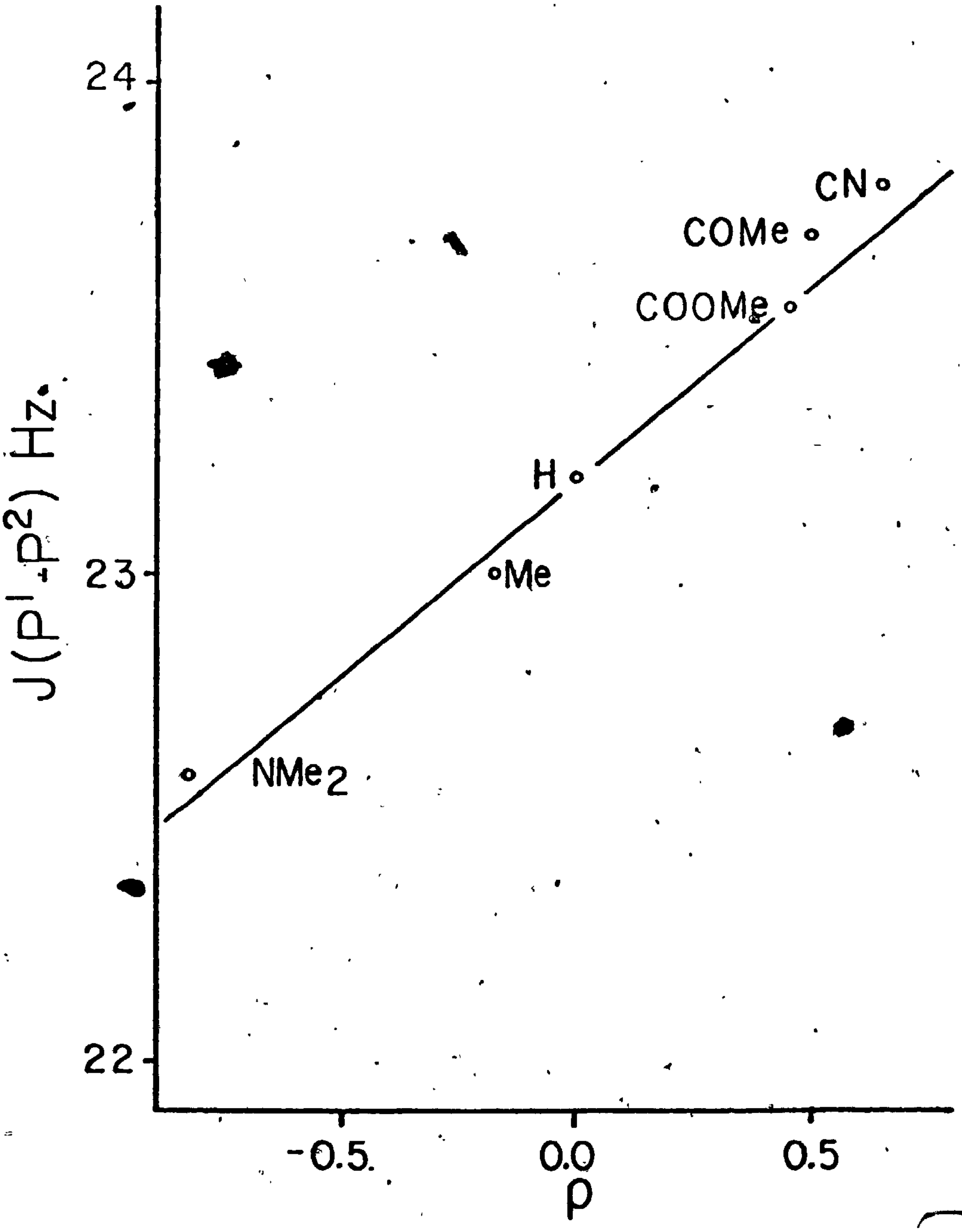

−37
−38
−39
δ_{P^1} ppm
NMe$_2$
Me
H
COOMe
COMe
CN
−0.5
0.0
0.5
p

Figure II-6. Plot of $|J(P^1-P^2)|$ vs. the Hammett substituent constant, ρ , for compounds of the type $[PdMe(py\text{-}X)diphos]PF_6$. X refers to a substituent in the *para* position of the pyridine.


J(P¹-P²) Hz.
24
23
22
CN
COMe
COOMe
H
Me
NMe2
-0.5
0.0
0.5
ρ

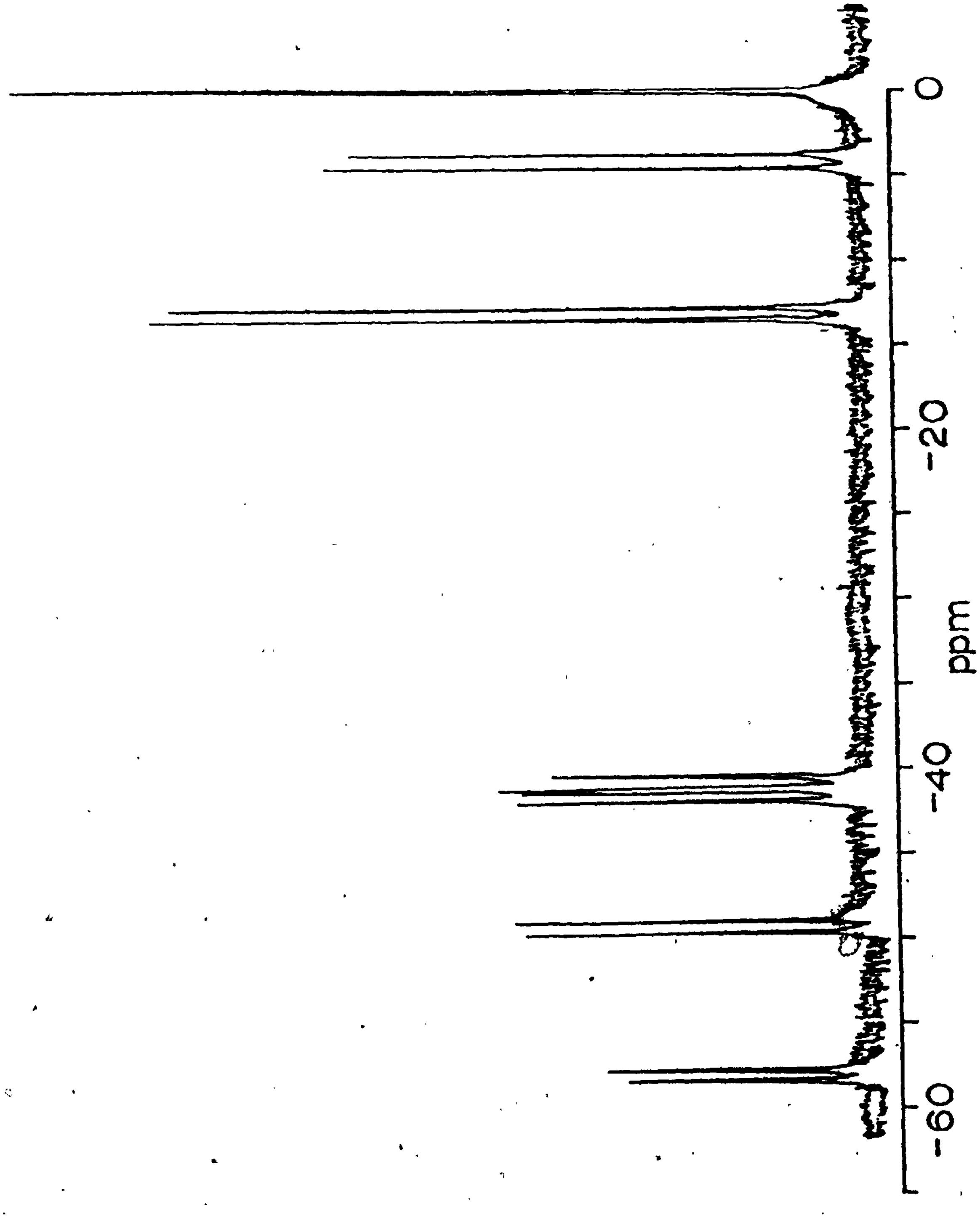
of the pyridine yield straight lines (Figures II-4, II-5 and II-6). Interestingly the changes in chemical shift for the cis phosphorus atom are greater than for the trans phosphorus atom. Usually the trans influence is much greater than for the cis influence.[4]

On coordination the ^{31}P chemical shift of a tertiary phosphine generally decreases from the free ligand value.[29] The reason for this behaviour is not well understood but it has been suggested that it is mainly due to the strong donor σ bond from the phosphorus to the metal.[30,31] In this case it is reasonable to say that the downfield shift of the ^{31}P chemical shifts as the para substituent on the pyridine becomes more electron-withdrawing, implies that the phosphorus atoms are able to bind more tightly to the metal. In other words, the phosphorus atoms do not have to compete so much with the pyridine for the Pd orbitals and are thus able to donate more strongly.

Similarly $|J(P^1-P^2)|$ increases as the substituent on the pyridine becomes more electron-withdrawing presumably because the phosphorus atoms being more tightly bonded to the palladium have more orbital overlap with each other resulting in a larger $|J(P^1-P^2)|$.[29]

A typical proton decoupled ^{31}P nmr spectrum for complexes of the type $[PdMe(L)diphos]PF_6$, L = PR_3, is shown in Figure II-7. The phosphorus atom trans to L, P^2, appears as a doublet of doublets at around -58 ppm.

Figure II-7. Typical ^{31}P nmr spectrum for a compound of the type $[PdMe(P^L)diphos]PF_6$. In this case P^L is P<u>n</u>-Bu_3. Spectrum was run at a sweepwidth of 5000 Hz in dichloromethane solution. The lowfield resonance is due to P^2 , the middle resonance to P^1 and the highfield signal to P^L.


0
-20
-40
-60
ppm

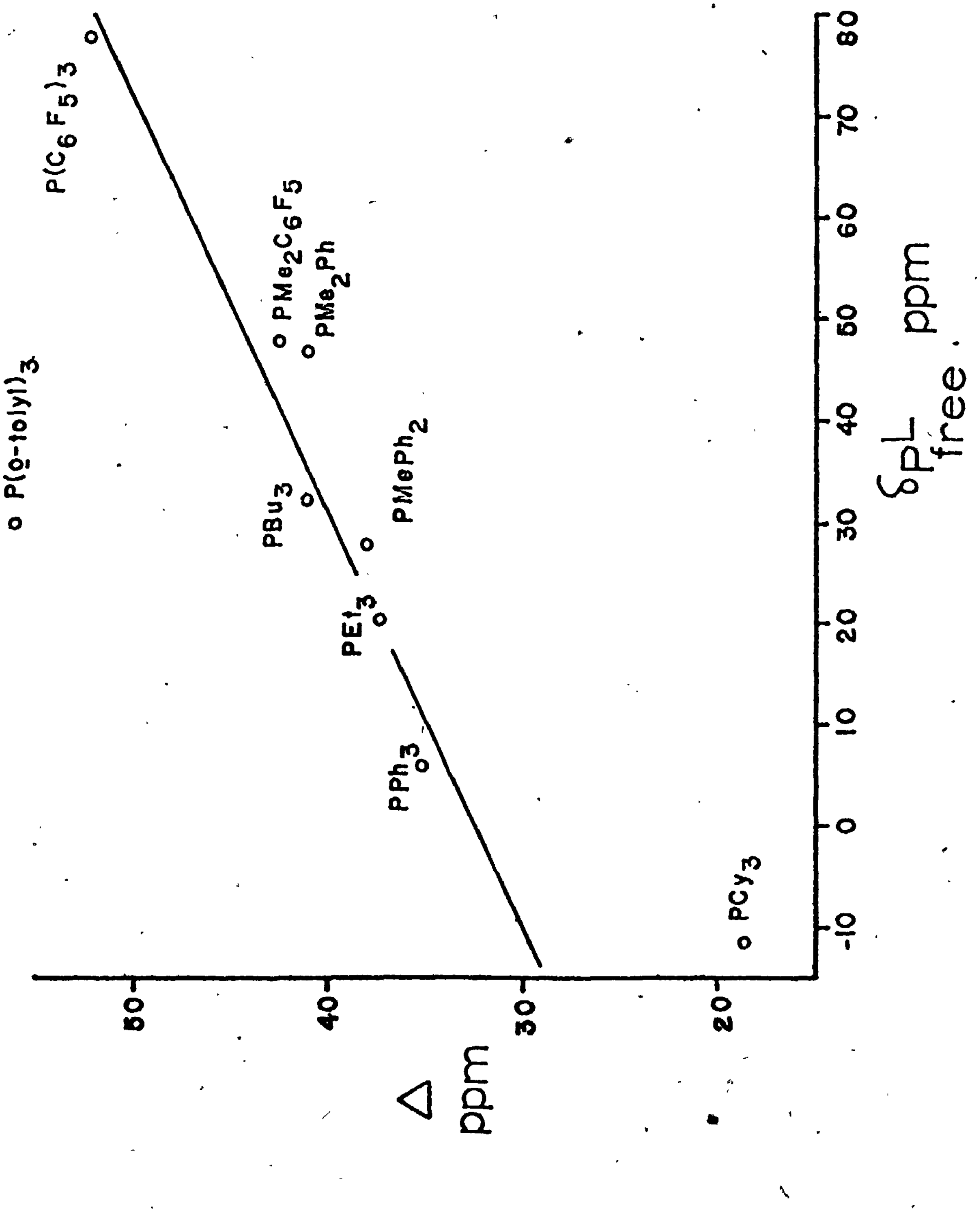
The large coupling constant (≈370 Hz) is due to coupling to the phosphorus atom, P^L, of the trans ligand[32,33] L while the small coupling constant (≈30 Hz) is due to the coupling to the cis phosphorus nucleus[32,33] P^1. δP^1 appears at around -40 ppm and also consists of a doublet of doublets due to coupling to the two non-equivalent cis phosphorus atoms P^2 and P^L. The chemical shift of P^L varies depending on the nature of the groups on the ligand but always is upfield from P^1 and P^2. It consists of a doublet of doublets with a large trans coupling constant to P^2 and a small cis coupling constant to P^1.

Thus from each ^{31}P nmr spectrum six parameters can be obtained; δP^1, δP^2, δP^L, $|J(P^1-P^2)|$, $|J(P^1-P^L)|$ and $|J(P^2-P^L)|$. The relationship between these parameters and the electronic and steric properties of L could then be determined.

The change in ^{31}P chemical shift, Δ, of P^L on coordination from its value for the free ligand was plotted against the free ligand value[34] (Figure II-8). A general trend was observed in that the greater the ^{31}P chemical shift of the free phosphine, the greater the change in chemical shift on coordination. Such a trend has been noticed previously for coordination complexes of transition metals by Shaw and co-workers, but no explanation of why this trend should exist has been proposed.[35,36]

The chemical shift of P^2 was plotted against the

Figure II-8. Plot of the difference in ^{31}P nmr chemical shift of P^L from its free value on coordination (Δ), vs. the chemical shift of P^L on coordination, P^L_{free} for compounds of the type $[PdMe(P^L)diphos]PF_6$.

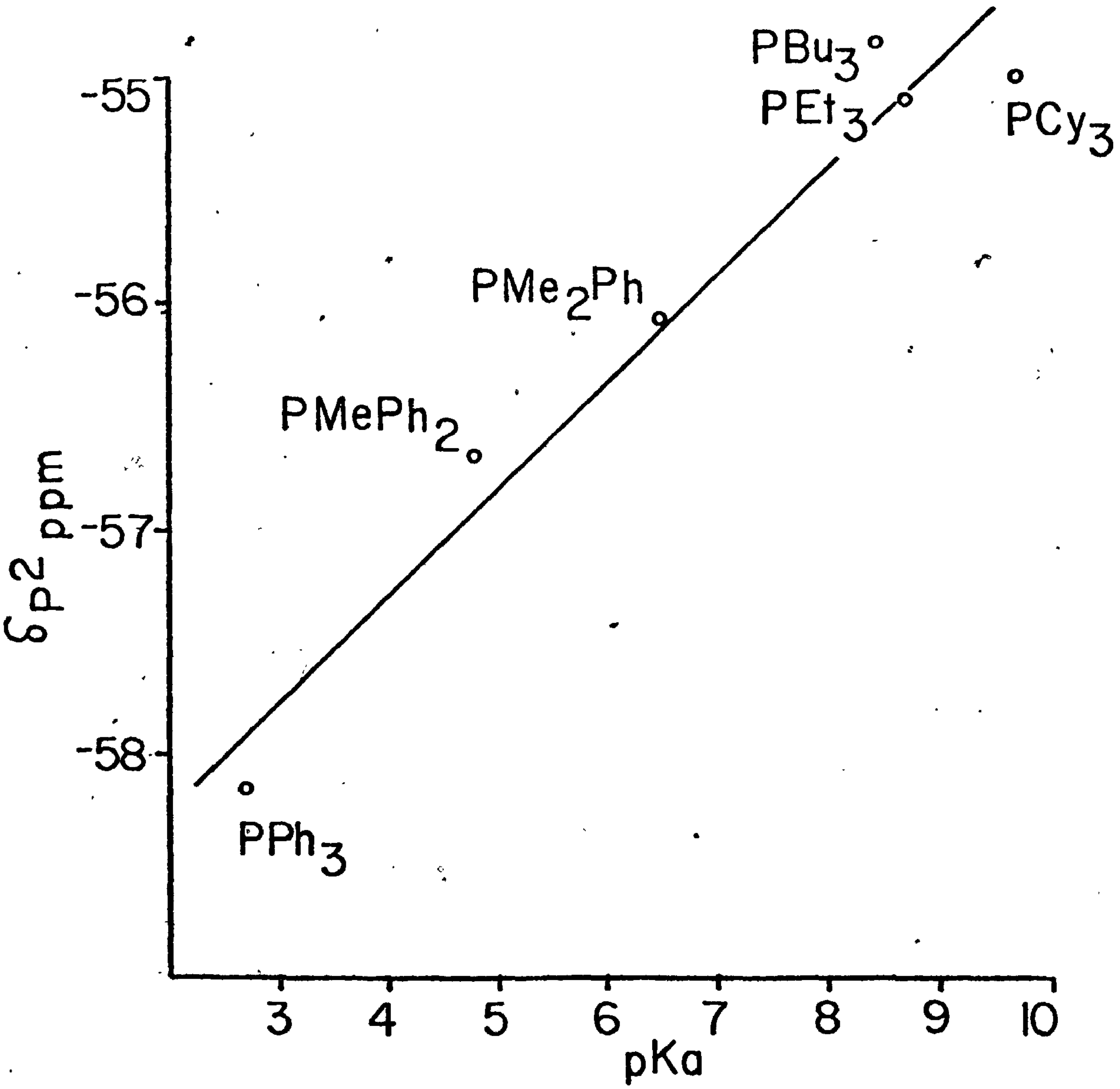

Δ ppm
20
30
40
50
δ_{P} L_{free} ppm
-10
0
10
20
30
40
50
60
70
80
$P(C_6F_5)_3$
$PMe_2C_6F_5$
PMe_2Ph
$P(\underline{o}\text{-tolyl})_3$
$PMePh_2$
PBu_3
PEt_3
PPh_3
PCy_3

basicity of the ligand L as determined by titration of the free phosphine with acid.[37] (Figure II-9) There exists a fairly good linear correlation in that δP^2 decreases as the basicity of L decreases. This is consistent with the results obtained on the substituted pyridine cations. The greater the donor strength of L the greater the chemical shift of the other phosphorus atoms.

Alternatively the chemical shift of P^2 could be plotted against the A_1 carbonyl stretching frequency in the compound $Ni(CO)_3(PR_3)$. Tolman has suggested that changes in this stretching frequency are solely dependent on the electronic nature of L.[38] A low value of $\nu(C{\equiv}O)$ implies that the ligand L is a good donor while a high value of $\nu(C{\equiv}O)$ is associated with a poor electron donor. This plot was far from linear but showed a general trend in that the greater the stretching frequency the greater the chemical shift of P^2, a trend similar to that observed for the substituted pyridines.

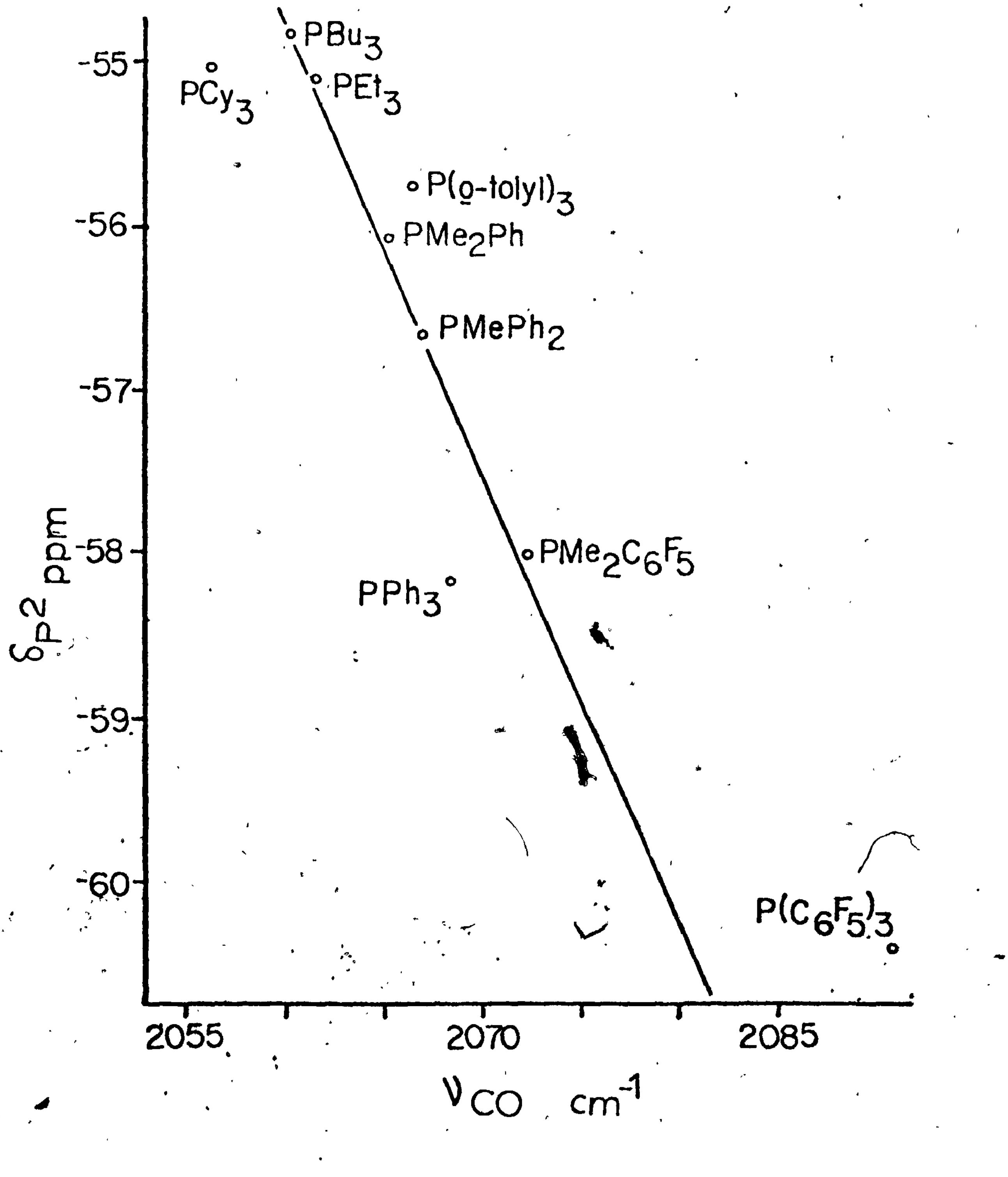
In addition δP^2 decreases for the series PPh_3, $AsPh_3$, $SbPh_3$ reflecting the order of donor strength; $PPh_3 > AsPh_3 > SbPh_3$. The chemical shift of P^1, the phosphorus atom cis to L, tended to decrease as the donor ability of L decreased. Thus, for the series PPh_3, $AsPh_3$, $SbPh_3$ the chemical shift of P^1 followed the order $PPh_3 > AsPh_3 > SbPh_3$. Also the chemical shift of P^1 followed the order $PCy_3 > P\underline{n}\text{-}Bu_3 > PEt_3 > PMe_2Ph > PPh_3$, the same order as the donor ability of the phosphine.

Figure II-9. Plot of δP^2 vs. the pKa of P^L for compounds of the type $[PdMe(P^L)diphos]PF_6$



δ_{P^2} ppm
-55
-56
-57
-58
3
4
5
6
7
8
9
10
pKa
PBu$_3$
PEt$_3$
PCy$_3$
PMe$_2$Ph
PMePh$_2$
PPh$_3$

Figure II-10. Plot of δP^2 vs. νCO for compounds of the type $[PdMe(P^L)diphos]PF_6$. νCO refers to the infrared stretching frequency of the A_1 carbonyl mode in the compound $Ni(CO)_3P^L$.



PBu3
PEt3
PCy3
P(o-tolyl)3
PMe2Ph
PMePh2
PMe2C6F5
PPh3
P(C6F5)3
-55
-56
-57
-58
-59
-60
δP2 ppm
2055
2070
2085
νCO cm-1

However there is also a tendency for the chemical shift of P^1 to shift to higher field if the steric bulk of L is large. For example δP^1 for L = PCy_3 is very high compared to δP^1 for L = PEt_3 or P<u>n</u>-Bu_3 although the donor strength of PCy_3 is only marginally better than that of PEt_3. Similarly δP^1 for L = P(<u>o</u>-tolyl)$_3$ is also very high compared to PPh_3 even though the donor ability of P(<u>o</u>-tolyl)$_3$ is not much better than that of PPh_3. In fact δP^1 for L = P(<u>o</u>-tolyl)$_3$ is greater than δP^1 for PCy_3 even though PCy_3 is by far the stronger donor. Again, δP^1 for $P(C_6F_5)_3$ is greater than δP^1 for PPh_3 although $P(C_6F_5)_3$ is the poorer donor. The common factor linking PCy_3, $P(C_6F_5)_3$ and P(<u>o</u>-tolyl)$_3$ is that they are all very bulky ligands with cone angles[39] of 170°, 184° and 192° respectively compared to 132° for PEt_3 and 145° for PPh_3. It would seem reasonable to say that if L = a bulky phosphine, L competes with the phosphine ligand <u>cis</u> to it, P^1, preventing P^1 from approaching the metal to equilibrium bonding distance. As P^1 is being prevented from achieving best overlap with the metal, its ^{31}P chemical shift increases as was observed in the case of increasing the donor ability of a substituted pyridine.

$|J(P^1-P^2)|$ also tends to follow the trend observed for L = substituted pyridine. As L becomes a better donor $|J(P^1-P^2)|$ decreases. However, $|J(P^1-P^2)|$ will be a function of the bonding strengths of both P^1 and P^2. Therefore, ligands which because of their steric bulk make δP^1 high will show abnormalities in $|J(P^1-P^2)|$. Thus $|J(P^1-P^2)|$ for L = P(<u>o</u>-tolyl)$_3$ is abnormally low and the order of PMe_2Ph and $PMePh_2$ are reversed perhaps because of the small cone angle of PMe_2Ph.

Thus, in conclusion, it is apparent that both ^{31}P chemical shifts and $^{31}P-^{31}P$ coupling constants are dependent not only on the donor ability of the ligands attached to the metal but also on their steric bulk. A more thorough study is needed however, to conclusively establish the trends observed here.

c) Experimental

Reactions were generally carried out under an inert atmosphere but rigorous techniques were not observed. 'Spectro'grade solvents were used without further purification.

Infrared spectra were recorded on a Perkin Elmer 621 Spectrometer as nujol mulls or in dichloromethane solution.

^1H nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer or on a Varian XL-100 spectrometer using either dichloromethane or tetramethylsilane as internal lock. All chemical shifts are reported in parts <u>per</u> million downfield from TMS. ^{19}F nmr spectra were recorded on the HA-100 spectrometer at 94.1 MHz using "Freon-11" ($CFCl_3$) as an internal reference-lock signal. ^{19}F chemical shifts are reported in parts <u>per</u> million upfield from $CFCl_3$. ^{31}P nmr spectra were recorded on the XL-100 spectrometer at 45.1 MHz using

1% phosphoric acid as an external reference signal.*

Microanaylses were obtained from Chemalytics Inc., Tempe, Arizona or from Spang Inc. Ann Arbor, Michigan.

Tertiary phosphines were prepared by standard methods[40] and p-tolylisocyanide was prepared by the method of Ziehn.[41]

Substituted pyridines were purchased from Aldrich Inc., $PdCl_2$ from Fisher Scientific Company, $AgPF_6$ from Cationics Inc., and methyllithium, as an ether solution, from Alpha Products Inc.

(i) Preparation of trans-$PdCl_2(PEt_3)_2$[42]

To a suspension of $PdCl_2$ (5.0 g) in 100 ml. of water was added a solution of 6.62 g of PEt_3 in 50 ml. of ethanol. The mixture was stirred for 24 hours to give a yellow precipitate. The precipitate was filtered and washed with water to give trans-$PdCl_2(PEt_3)_2$. Yield was 10.81 g. (93%).

(ii) Preparation of trans-$PdClMe(PEt_3)_2$.

A solution of $PdCl_2(PEt_3)_2$ (5.00 g) in 60 ml. of diethyl ether was chilled to 0°C. The solution was stirred and 26 ml. of a 1.86 M solution of methyllithium in ether was added dropwise. The solution turned orange and then white. After two hours the reaction mixture was hydrolyzed with 30 ml. of water. The ether layer was decanted and the aqueous layer extracted with three 50 ml. portions of ether. The combined ether layers were washed with water and then dried over $MgSO_4$. The solution was filtered through Celite and the solvent removed on a rotary

---

* Downfield shifts from this reference are in negative p.p.m.; upfield shifts in positive p.p.m.

evaporator to give white crystals of $PdMe_2(PEt_3)_2$. Yield was 3.42 g. (76%). Immediately 40 ml. of methanol was added followed by 0.65 ml. of acetyl chloride. After the effervescence ceased the solvent was removed under vacuum to give trans $PdClMe(PEt_3)_2$ as white crystals. Yield was 3.10 g. (86%).

(iii) Preparation of PdClMe(diphos).

Trans-$PdClMe(PEt_3)_2$ (3.0 g) and 1,2,-bis(diphenylphosphino)ethane (3.03 g) were dissolved in 40 ml. of dichloromethane and the solution was stirred for two hours. The solution, which smelt strongly of triethylphosphine, was stripped to dryness on a rotary evaporator to give a sticky white gum. This gum was pumped on under high vacuum while being heated to 80°C for forty-eight hours, to give a white solid. The solid was then dissolved in dichloromethane and filtered. Addition of ether yielded white crystals which were collected and washed with ether. Yield was 3.21 g. (76%).

(iv) Preparation of trans-$[PdMe(py)(PEt_3)_2]PF_6$.

A solution of trans-$PdClMe(PEt_3)_2$ (0.300 g) in 20 ml. of tetrahydrofuran was chilled to -20°C. $AgPF_6$ (0.192 g) in 10 ml. of tetrahydrofuran was added. A flocculent precipitate of silver chloride formed immediately. The solution was stirred for 30 minutes and then filtered through a cold frit into a chilled receiving vessel. To the filtrate was added pyridine (0.061 ml.) and the clear colourless solution was warmed to room temperature. The solvent was removed on a rotary evaporator and the residue crystallized from dichloromethane/ether solution to give white needles. Yield was 0.351 g. (79%).

(v) Preparation of trans-[PdMe(CN p-tolyl)$(PEt_3)_2$]PF_6.

The solvated cation [PdMe(THF)$(PEt_3)_2$]PF_6 was made *in situ* as above and one equivalent of p-tolylisocyanide was added at -20°C. After warming to room temperature the solvent was removed under vacuum and the white solid crystallized from dichloromethane/ether. Yield was 85%.

(vi) Preparation of trans-[PdMe(CO)$(PEt_3)_2$]PF_6.

The solvent cation trans-[PdMe(S)$(PEt_3)_2$]PF_6 was made as described previously except that methanol was used in place of tetrahydrofuran as the solvent. The solution containing the cation was cooled to -30°C and carbon monoxide bubbled through. After a few minutes white crystals began to precipitate and the reaction was complete after 20 mins. The crystals were collected on a cold frit at -20°C and dried in a stream of dry nitrogen. The crystals were air stable but decomposed in a few hours if warmed to room temperature. Yield was 72%.

(vii) Insertion of CO to give trans-PdCl$(COCH_3)(PEt_3)_2$.

Trans-[PdMeCO$(PEt_3)_2$]PF_6 (0.300 g) was dissolved in dichloromethane at room temperature. After 5 minutes LiCl (0.50 g) in methanol was added. The solvents were removed on a rotary evaporator and the solid extracted with hexane. On cooling this hexane solution, large white plates formed whose nmr and infrared spectra were identical to those of an authentic sample of trans-$PdCl(COCH_3)(PEt_3)_2$ prepared by the method of Chatt and Shaw.[25] Yield was 67%.

(viii) Preparation of trans-$[Pd(Me)[C(NH\ p\text{-tolyl})(NHMe)](PEt_3)_2]PF_6$.

Trans-$[Pd(Me)(CN\ p\text{-tolyl})(PEt_3)_2]PF_6$ (0.300 g) was dissolved in 20 ml. of dichloromethane and monomethylamine bubbled through the solution for 10 mins. The solvent was removed on a rotary evaporator and the product recrystallized from dichloromethane/ether to give fluffy white crystals. Yield was 0.261 g (83%).

In a similar manner trans-$[Pd(Me)(C(NH\ p\text{-tolyl})(NMe_2))P(Et_3)_2]PF_6$ was prepared in 79% yield.

(ix) Preparation of trans-$PdCl[C(CH_3)=N\ p\text{-tolyl}](PEt_3)_2$.

To a solution of trans-$Pd(Me)Cl(PEt_3)_2$ (0.500 g) in dichloromethane was added para-tolylisocyanide (0.149 g). The solution was stirred for 12 hours during which time the colour changed from yellow to orange-brown. The solvent was removed and the solid recrystallized from n-pentane at -15° to give white plates of the imidoyl. Yield was 0.532 g (82%).

(x) Preparation of trans-$[PdCl(C(CH_3)NH\ p\text{-tolyl})(PEt_3)_2]Cl$.

A few drops of 6 M hydrochloric acid were added to an acetone solution containing trans-$PdCl[C(CH_3)=N\ p\text{-tolyl}](PEt_3)_2$ (0.200 g). The solvent was removed in vacuo and the solid recrystallized from dichloromethane/diethyl ether to give the carbene in 87% yield.

(xi) Preparation of $[PdMePEt_3diphos]PF_6$.

To a suspension of PdClMediphos (0.110 g) in tetrahydrofuran (20 ml.) at -20°C was added $AgPF_6$ (0.046 g) in 3 ml. of THF. A thick white precipitate of AgCl immediately formed. The solution was filtered through a cold frit into a receiving vessel chilled to 0°C. PEt_3 (0.021g) was added to the filtrate and the solution warmed to room temperature. Removal of the solvent followed by recrystallization from dichloromethane/diethyl ether yielded white crystals of the cation in 85% yield.

Other cationic species of the type $[PdMe(L)diphos]PF_6$ were made in a similar fashion.

(xii) Preparation of $PdCl[C(CH_3)=N$p-tolyl]diphos.

To a solution of PdClMediphos (0.300 g) in dichloromethane (20 ml.) was added one equivalent of para-tolylisocyanide. The solution was stirred for 24 hours and then filtered. The filtrate was concentrated to about 5 ml. and then diethyl ether added to give cream coloured crystals of the imine. Yield was 0.247 g (68%) m.p. 196-198 Analytical data: Found (calculated) %C: 61.98(62.45) %H: 5.21(5.06) %N: 2.11(2.08). Infrared in cm^{-1}: $\nu(C=N)$ 1598, 1592. ^1H nmr ($CDCl_3$) $\delta 2.24$ (CH_3-tolyl), $\delta 2.14$ (CH_3) J(P-H) = 4.1, 1.9 Hz.

d)

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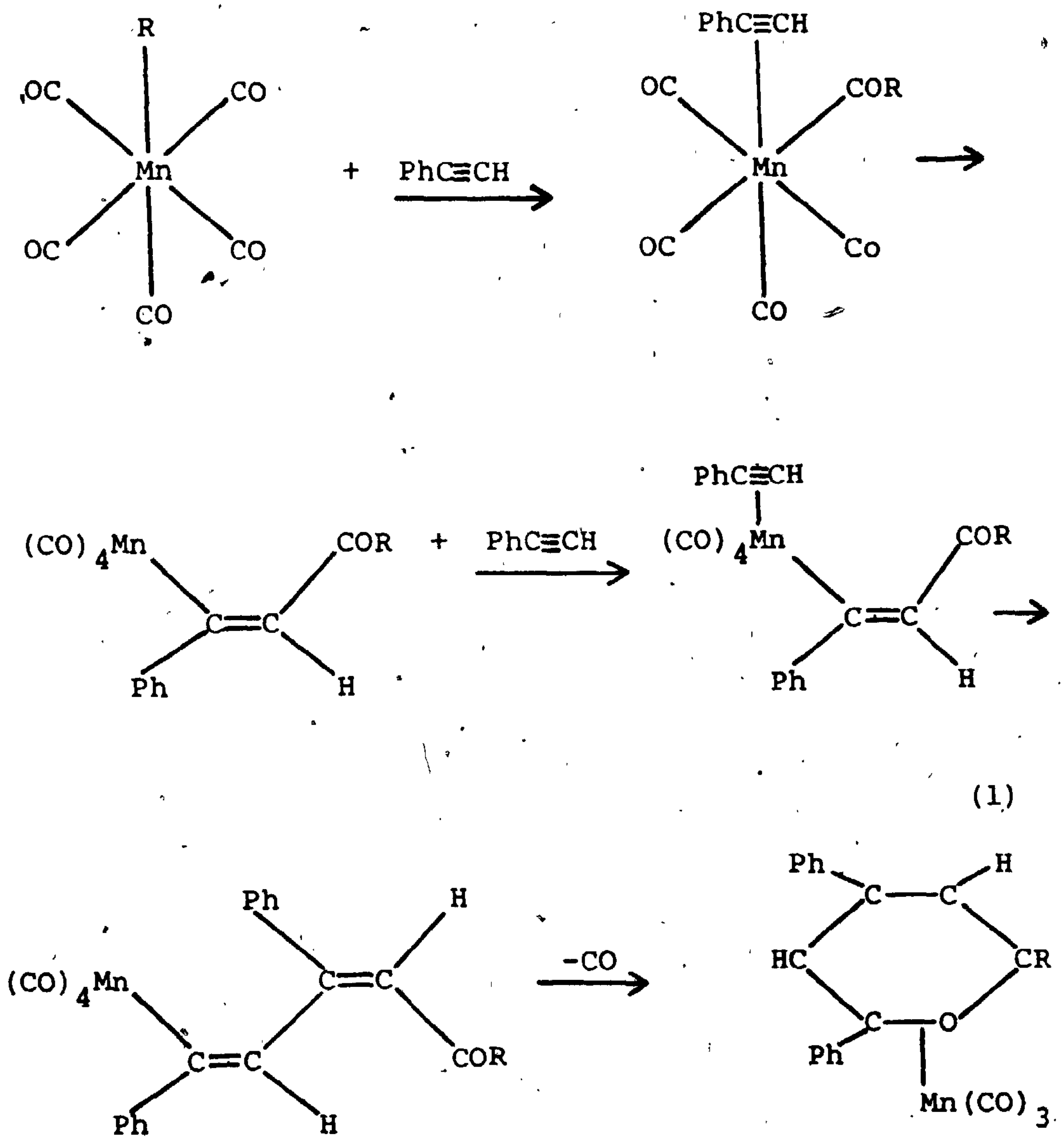
CHAPTER III

REACTIONS OF METHYLPALLADIUM COMPOUNDS WITH SUBSTITUTED ACETYLENES

a) Introduction

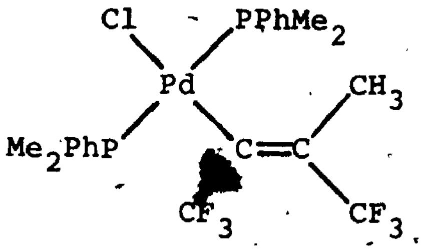
As mentioned in Chapter I the migratory insertion of unsaturated organic molecules into metal-carbon or metal-hydrogen bonds is thought to be one of the key steps in many transition metal catalyzed reactions.[1] Attempts to study the insertion step by starting with a stable alkyl metal derivative are often hampered by either a lack of reactivity or by the complexity of the ensuing reaction.

For example, Booth and Hargreaves have studied the reaction of acetylenes with $MnMe(CO)_5$.[2] Rather than simple insertion of the acetylene into the $Mn-CH_3$ bond to give the vinylic product, CO insertion occurred first to give the acyl derivative. This was followed by acetylene insertion to give the vinyl ketone derivative. Small amounts of a product resulting from a double insertion were also obtained in one instance (equation 1). A similar type of reaction sequence has been used to explain the formation of lactonyl compounds from the reaction of $MeCo(CO)_4$ with acetylenes.[3]



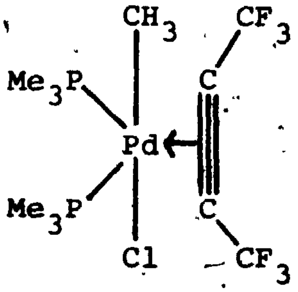
(1)

Clark and Puddephatt have investigated the reactivity of some fluorinated olefins and acetylenes toward methylplatinum compounds of the type $PtClMe(PR_3)_2$.[4] In a few instances a product derived by migratory insertion was obtained. For example, *trans*-$PtClMe(PMe_2Ph)_2$ was heated to 70° for 24 hours with an 8-fold excess of $CF_3C{\equiv}CCF_3$ to give the vinylic product I.



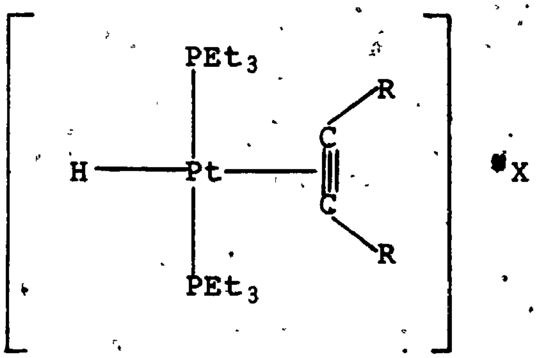
I

Incorporation of a second mole of acetylene to give a σ-butadienyl derivative did not occur. The authors isolated the five coordinate π-bonded acetylene complex II, and thus concluded that formation of a five coordinate intermediate was essential for the insertion reaction.[5]



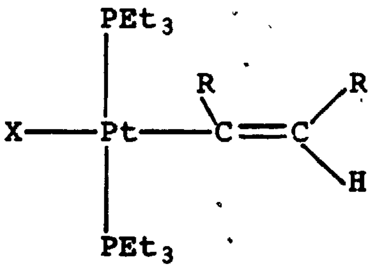
II

Subsequent work by Clark[6,7,8] on insertions of acetylenes into Pt-H bonds demonstrated that insertion occurred from a four coordinate species. Thus for *trans*-$PtX(H)(PEt_3)_2$ the rate of insertion was much greater for X = NO_3 than X = Cl and greater still for X = PF_6 (solvent). This implied that displacement of the anion by the acetylene to form a four coordinate cationic species III, was rate determining.



III

Rearrangement of this four coordinate species to place the acetylene cis to the hydride group followed by migratory insertion gives the vinylic product IIIa.



IIIa

Subsequently Clark and Jablonski[9] noticed a similar anion dependence on rate in the reaction of PtXMediphos with substituted acetylenes. Only mono insertions occurred and then only with the acetylenes $CF_3C{\equiv}CCF_3$ and MeOOCC≡ CCOOMe (DMA).

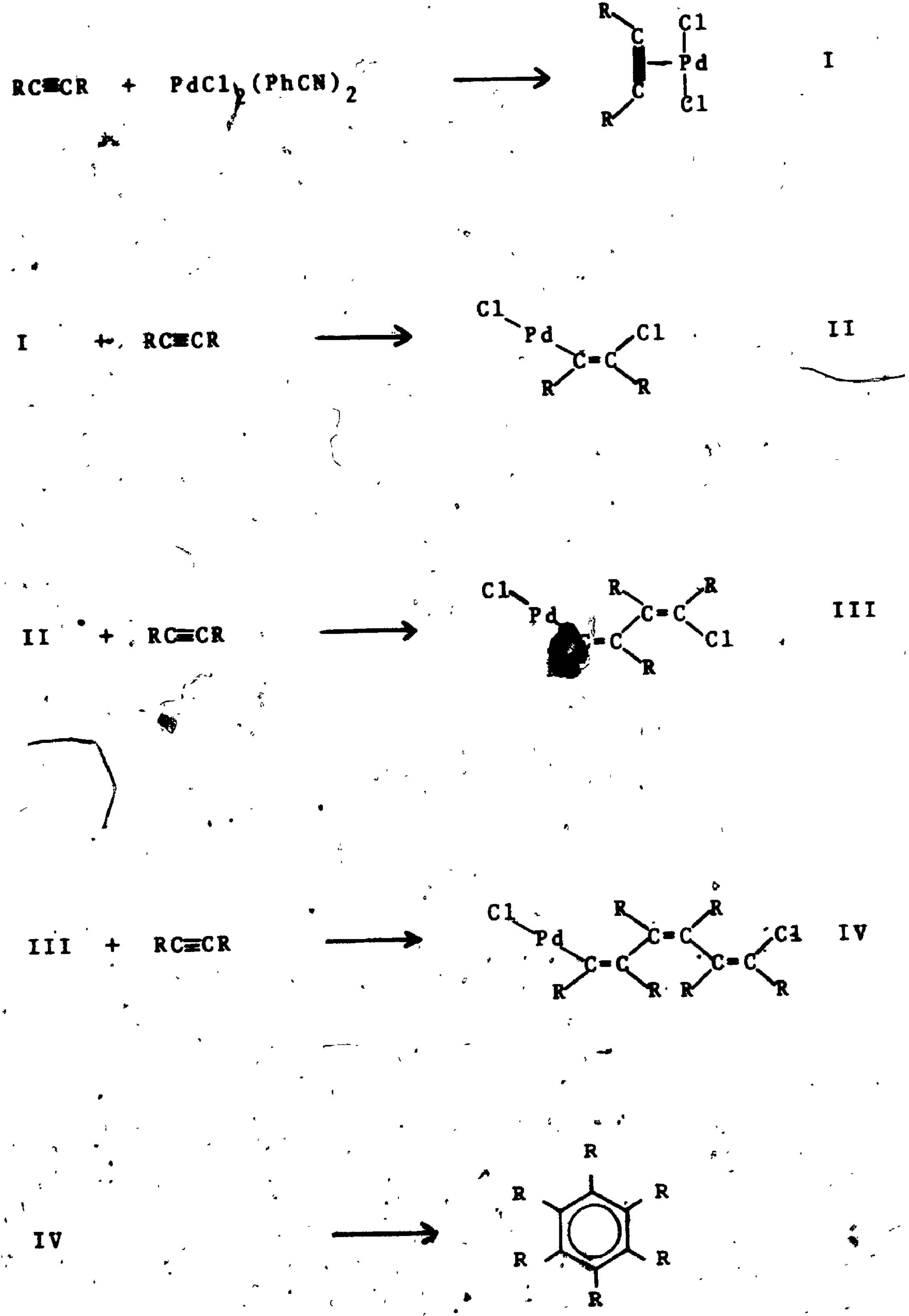
We thought that since the $Pd-CH_3$ bond is weaker than the $Pt-CH_3$ bond[10] and since organopalladium compounds are generally more reactive than the corresponding organoplatinum compounds[11], investigation into the reactions of substituted acetylenes with palladium species containing an alkyl group would be rewarding.

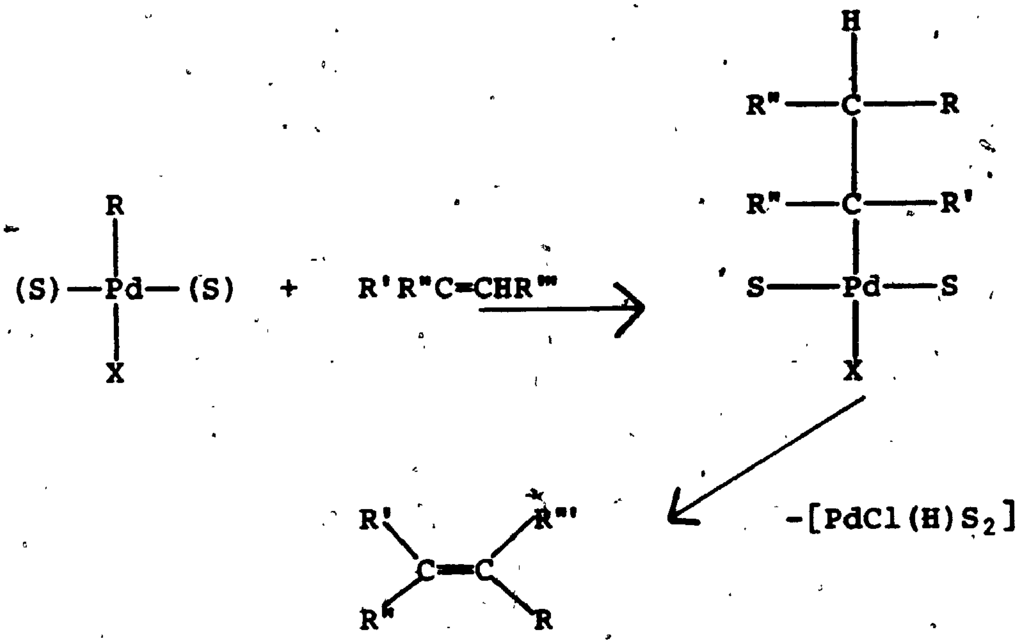
Work by Maitlis[12] and by Heck[13,14] has indicated the palladium carbon bond is indeed very susceptible to insertions by acetylenes and olefins.

Maitlis studied the reaction of bis-benzonitrile palladium chloride with substituted acetylenes. Rapid reactions occurred to give a variety of products, the nature of which depended on the reaction conditions and stoichiometry. In some instances a hexa-substituted benzene derivative formed by trimerization of the acetylene was obtained. This process was tho[illegible] to occur by insertion of an acetylene into a palladium-chlorine bond to give a σ-vinylic complex, followed by fast insertions of acetylene into the Pd-vinylic bond to produce σ-hexatrienyl complexes which could eliminate halide to form the substituted benzene derivative (Figure III-1).

Heck investigated the reaction of $RPdX(solvent)_2$, prepared in situ, with olefins. The products obtained were olefins in which a hydrogen of the original olefin had been replaced by the alkyl group of the starting palladium compound. The mechanism was postulated to involve insertion of the olefin into the Pd-R bond to give an alkyl derivative which then β-eliminated to give the the substituted olefin and a palladium hydride (equation 2).

Figure III-1. Reaction Scheme for the trimerization of acetylenes by trans-$PdCl_2(PhCN)_2$


RC≡CR + PdCl2(PhCN)2
I
I + RC≡CR
II
II + RC≡CR
III
III + RC≡CR
IV
IV
Cl
Pd
R



(2)

However although these systems were reactive, they were difficult to characterize fully. In both cases the intermediates were not always observed and in the case of the acetylene oligomerizations the first insertion steps could not always be followed.

Therefore we considered that the system *trans*-PdXMe-$(PR_3)_2$ analogous to the platinum system studied by Clark and Puddephatt, would be

a) more reactive than the corresponding platinum system

b) not so reactive, so that intermediate species could be isolated and characterized.

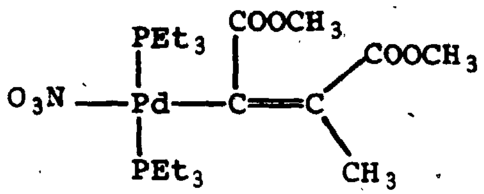
Although Clark and Puddephatt had observed no reaction of tetrafluoroethylene with *trans*-$PdClMe(PMe_2Ph)_2$[4], by changing the anion *trans* to the methyl group to a more weakly coordinating anion such as NO_3^- we hoped to increase the reactivity of the compound toward insertion of acetylenes as had been found for both the platinum-hydrogen and platinum-alkyl compounds.

This chapter deals with the results of the reactions of acetylenes with systems containing a palladium-methyl bond.

b) Results

Solutions of the cation trans-$[PdMe(S)(PEt_3)_2]^+$ prepared from trans-$PdClMe(PEt_3)_2$ and $AgPF_6$ in a coordinating solvent, were extremely temperature sensitive, quickly decomposing at room temperature to give $[PdMe(PEt_3)_3]PF_6$ as the only isolatable product. Reaction of solutions of this cation at 0°C with acetylenes (either in excess of in stoichiometric quantities) gave only the decomposition product $[PdMe(PEt_3)_3]PF_6$.

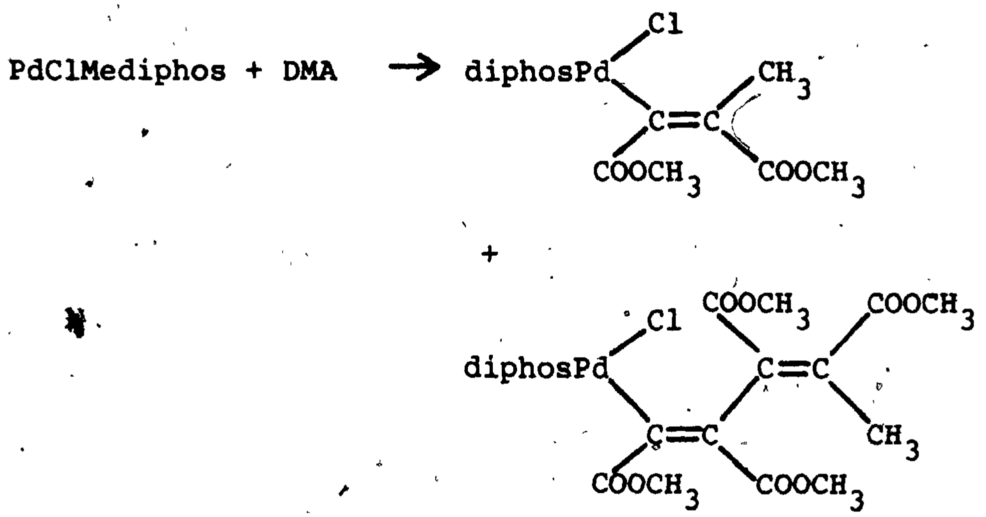
In order to stabilize the system while still retaining sufficient reactivity, the compound trans-$PdNO_3Me(PEt_3)_2$ was made. The weakly coordinating NO_3^- ion should prevent the disproportionation reaction but should not be so tightly held as to prevent coordination of an acetylene. Although a variety of acetylenes were allowed to react with the nitrate, in only one instance could a product of insertion be isolated. The acetylene $MeOOCC{\equiv}CCOOMe$ (DMA) gave a mono inserted product IV.



IV

Again to prevent the disproportion reaction, a chelating phosphine, 1,2-bis(diphenylphosphino)ethane was used in place of the unidentate phosphine PEt_3. The compound PdBrMediphos had been made previously by the reaction of $PdBr_2$diphos with the Grignard reagent MeMgBr.[15] Repetition of this preparation resulted in low yields of impure product. A more convenient preparation was achieved by the metathical replacement of 2 moles of PEt_3 by diphos in the compound trans-PdClMe$(PEt_3)_2$, to give PdClMediphos in 75% yield.

At room temperature PdClMediphos failed to react with substituted acetylenes and the starting material was recovered. However at 80° in dichloromethane it reacted with one equivalent of DMA to give a mixture of starting material, an alkenyl derivative(V) and a σ-butadienyl product(VI) (equation 3). If two equivalents of DMA were used only the butadienyl VI was obtained in high yields.

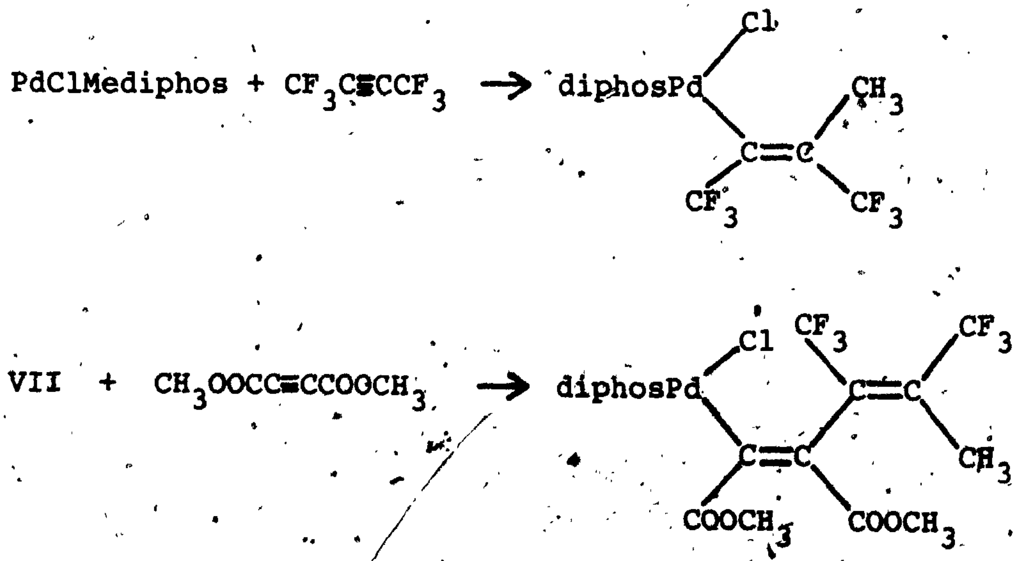


V

VI

(3)

The acetylene hexafluoro-2-butyne also reacted with PdClMediphos at high temperatures but gave only the alkenyl product VII and no butadienyl product even if large excesses of acetylene and long reaction times were employed. However, VII reacted slowly at high temperatures with DMA to give signals in the ^{1}H nmr which indicated the formation of a mixed σ-butadienyl compound VIII (equation 4). Unfortunately at the temperatures at which this reaction took place extensive decomposition also occurred, rendering isolation of a pure sample of VIII impossible.



VII

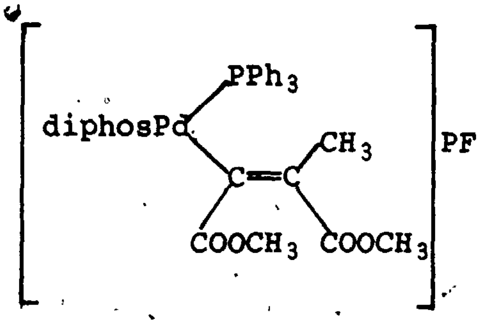
(4)

VIII

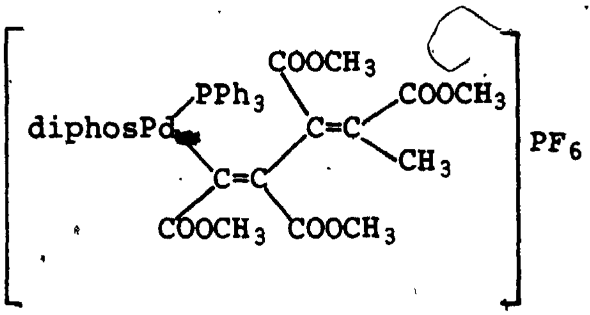
In contrast, if $PdNO_3$Mediphos(IX) was used in place of the chloro complex, insertions occurred much more readily.

At room temperature, one equivalent of DMA reacted smoothly with IX to give only the alkenyl derivative X, analogous to V, the reaction being complete in about 30 minutes. If two equivalents of DMA were used the butadienyl complex XI, analogous to VI, was obtained at room temperature after about 3 hours. Hexafluoro-2-butyne also reacted with IX at room temperature and one atmosphere pressure to give the alkenyl product XII, analagous to VII. A second insertion did not occur, but if the alkenyl derivative XII, was reacted with DMA at room temperature a slow insertion occurred to give the butadienyl product XIII, analagous to VIII.

The solvated cation $[PdMe(S)diphos]PF_6$ XIV could readily be made <u>in situ</u>, in acetone or in tetrahydrofuran by the reaction of PdClMediphos with $AgPF_6$. Solutions of this cation were fairly stable up 10°C but at higher temperatures decomposed to an orange oil. DMA reacted readily with solutions of this cation at 0-10°C, to give the alkenyl insertion product XV, if one equivalent of acetylene were used, or the butadienyl product XVI with two equivalents of acetylene. The products were isolated as triphenylphosphine adducts.

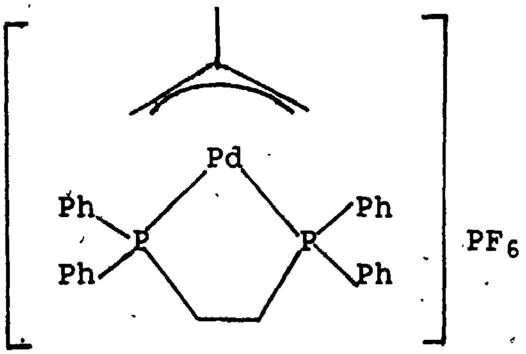


XV



XVI

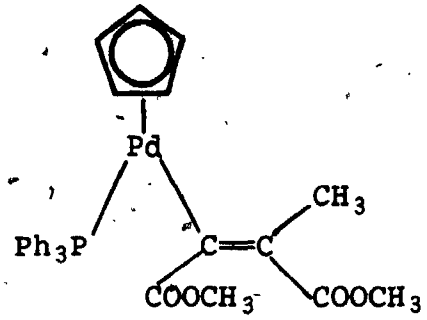
Allene also reacted with the cation XIV, to give the π-allyl cation XVII.



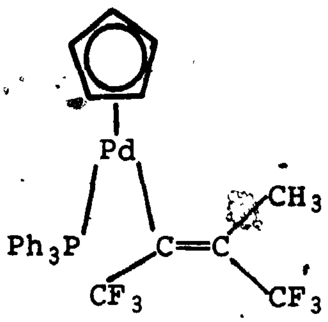
XVII

Incorporation of a further molecule of DMA to form a trienyl derivative or a cyclized product did not occur regardless of the nature of the anion. Substituted acetylenes having one or no electronwithdrawing substituents failed to react with the diphos complex, again regardless of the nature of the anion.

The compound PdMe(η^5-C_5H_5)PPh_3 reacted smoothly with DMA or $CF_3C\equiv CCF_3$ in dichloromethane solution to give the alkenyl derivatives XVIII and XIX respectively. Further reaction with excess acetylene to give butadienyl complexes did not occur. Less reactive acetylenes failed to insert and starting materials were recovered.



XVIII



XIX

Analytical results and physical properties of the new compounds are presented in Table III-1

c) NMR and Infrared Spectroscopic Data for the New Compounds

The ^1H nmr spectra of the compounds PdX(alkenyl)diphos or [Pd(alkenyl)PPh_3diphos]PF_6 are fairly straightforward. The diphos ligand gives a resonance in the region 7-8 ppm due to the phenyl protons and a signal at 2-3 ppm due to the methylene protons. This latter resonance appears as a very broad signal due to the inequivalence of the protons and to the coupling to the non-equivalent phosphorus atoms. For the alkenyl products of DMA there are two distinct peaks in the region of 3-4 ppm due to the $COOCH_3$ groups, and for the butadienyl products there are four such signals. The alkenyl or butadienyl methyl protons appear as a singlet in the region 0.7-2 ppm. It is not possible to assign the exact configuration of the alkenyl or butadienyl groups, nor is it possible to assign unambiguously each particular methoxy signal to a particular methoxy group.

TABLE III-1

Analytical and Physical Data for Some Alkenyl and Butadienyl Palladium Complexes[a]

Compound	Colour	m.p.°C	%C		%H	
			Found	Calc.	Found	Calc.
Trans-$PdNO_3[RC{=}C(R)CH_3](PEt_3)_2$	white	85-86	40.89	40.57	6.35	6.93
$PdCl[RC{=}CR(RC{=}C(R)CH_3)]$diphos	white	124-127(d)	56.78	55.86	4.51	4.68
$PdCl[CF_3C{=}C(CF_3)CH_3]$diphos	white	198-200(d)	51.97	51.91	3.71	3.79
$PdNO_3[RC{=}C(R)CH_3]$diphos	white	98-100(d)	54.82	54.75	4.44	4.59
$PdNO_3[RC{=}CR(RC{=}C(R)CH_3)]$diphos	white	170-171(d)	54.11	54.08	4.56	4.54
$PdNO_3[CF_3C{=}C(CF_3)CH_3]$diphos	white	209-210(d)	49.92	50.00	3.61	3.63
$PdNO_3[RC{=}CR(CF_3C{=}C(CF_3)CH_3]$diphos	white	213-214(d)	49.81	50.11	3.73	3.72
$[Pd\{RC{=}C(R)CH_3\}PPh_3$diphos$]PF_6$	white	140-141(d)	57.23	57.29	4.40	4.53
$[Pd\{RC{=}CR(RC{=}C(R)CH_3)\}Ph_3$diphos$]PF_6$	white	130-131(d)	56.60	56.52	4.31	4.49
$[Pd\{CH_2C(CH_3)CH_2\}$diphos$]PF_6$	white	194-195(d)	51.21	51.06	4.35	4.40
$Pd[RC{=}C(R)CH_3](\eta^5{-}C_5H_5)PPh_3$	maroon	138-140(d)	64.43	65.00	5.26	5.41
$Pd[CF_3C{=}C(CF_3)CH_3](\eta^5{-}C_5H_5)PPh_3$	red	148-150(d)	54.20	54.99	3.85	3.70

[a] R = $COOCH_3$

TABLE III-2. ^1H and ^{19}F NMR Data for Some Alkenyl and Butadienyl Palladium Complexes[a,b,c]

Complex	δ(CH_3)	Other Resonances
Trans-$PdNO_3[RC=C(R)CH_3](PEt_3)_2$	2.20 $^3J(P-H)=2.0$	δ(OCH_3) 3.66,3.68
$PdCl[RC=CR(RC=C(R)CH_3)]diphos$	1.44	δ(OCH_3) 3.07,3.54,3.56,3.69
$PdNO_3[RC=C(R)CH_3]diphos$	1.80	δ(OCH_3) 3.39,3.42
$PdNO_3[RC=CR(RC=C(R)CH_3)]diphos$	1.56	δ(OCH_3) 3.11,3.40,3.49,3.69
$[Pd\{RC=C(R)CH_3\}PPh_3diphos]PF_6$	0.96	δ(OCH_3) 2.89,3.32
$[Pd\{RC=CR(RC=C(R)CH_3)\}PPh_3diphos]PF_6$	0.67	δ(OCH_3) 2.92,3.22,3.52,3.69
$PdCl[CF_3C=C(CF_3)CH_3]diphos$	1.56 $^qJ(F-H)=1.9$	δCF_3 59.06 $J(F-F)=13.6$ $J(P-F)=2.4$ δCF_3 47.41 $J(F-F)=13.6$ $J(P-F)=13.6$
$PdNO_3[CF_3C=C(CF_3)CH_3]diphos$	1.42 $^qJ(F-H)=1.42$	δCF_3 62.16 $J(F-F)=14.2$ δCF_3 50.32 $J(F-F)=14.2$ $J(P-F)=14.2$, 2.6
$PdNO_3[RC=CR(CF_3C=C(CF_3)CH_3)]diphos$	2.08 $^qJ(F-H)=2.1$	δ(OCH_3) 3.54 δCF_3 59.46 $J(F-F)=13.4$ 3.58 δCF_3 54.23 $J(F-F)=13.4$
$Pd[RC=C(R)CH_3](\eta^5-C_5H_5)PPh_3$	1.36	δ(OCH_3) 3.04,3.28 δ($\eta^5-C_5H_5$) 5.39 $J(P-H)=1.8$
$Pd[CF_3C=C(CF_3)CH_3](\eta^5-C_5H_5)PPh_3$	1.88 $^qJ(F-H)=2.2$	δCF_3 60.61 $J(F-F)=14.8$ δCF_3 50.04 $J(F-F)=14.8$ $J(P-F)=2.2$ δ($\eta^5-C_5H_5$) 5.70 $J(P-H)=2.0$

[a] Spectra recorded in $CDCl_3$; ^1H nmr chemical shifts in positive ppm downfield from TMS; coupling constants in H_3.

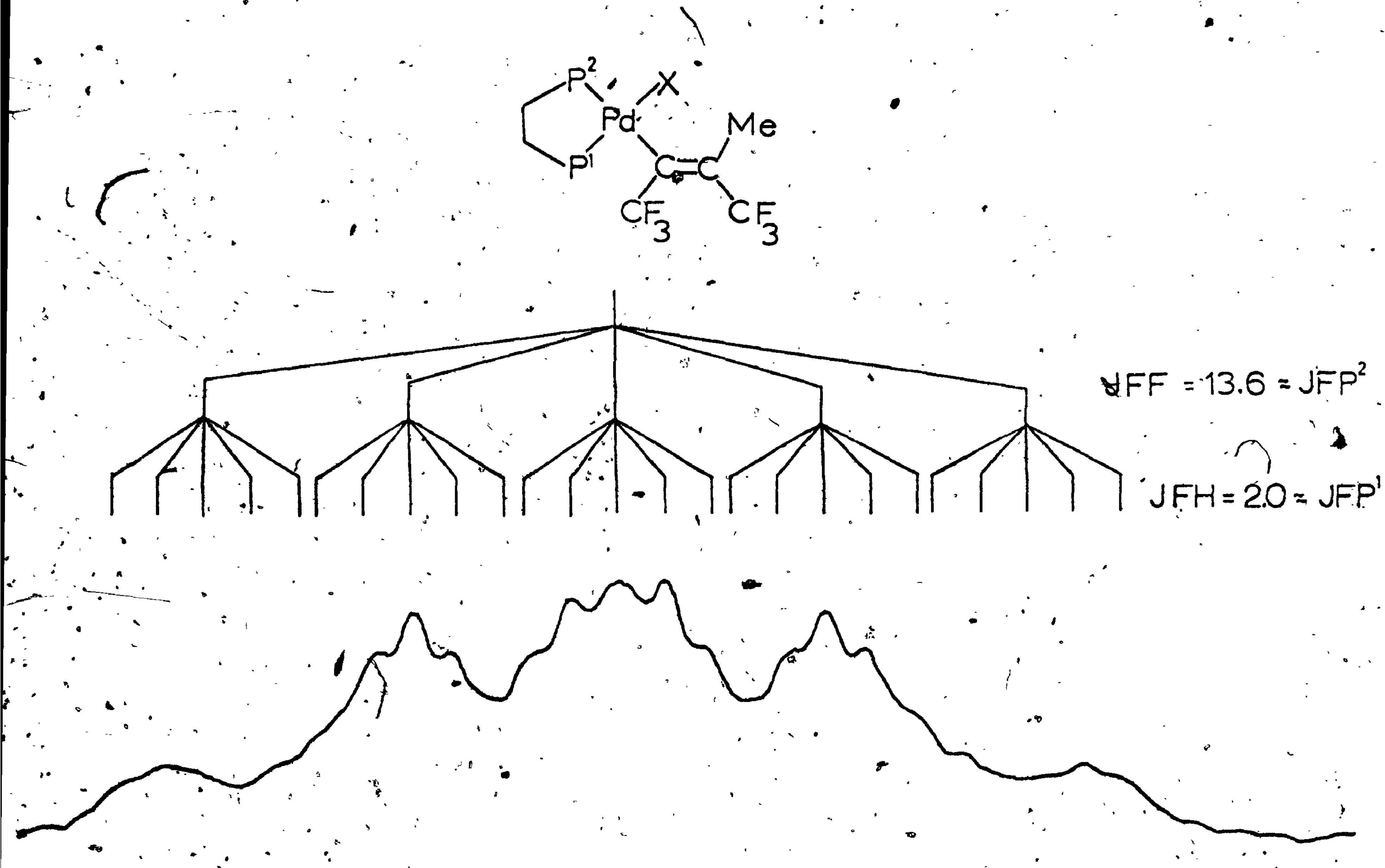
[b] $R = COOCH_3$.

[c] Compounds also contained phosphine hydrogen resonances.

The ^{1}H nmr spectra of the alkenyl derivatives obtained from insertion of $CF_3C{\equiv}CCF_3$ into the methyl group have, in addition to the signals of the diphos ligand, a peak at about 1.5 ppm due to the alkenyl methyl protons. This signal is a quartet because of coupling to one of the vinylic CF_3 groups. The ^{19}F nmr spectra each have two resonances corresponding to two chemically different CF_3 groups, with a mutual coupling constant of about 14 Hz. This large J(F-F) determines unambiguously, that the two CF_3 groups are cis to each other about the alkenyl double bond.[16] The high field CF_3 resonance can be assigned to the CF_3 group on the β vinyl carbon atom.[4] The low field resonance can be assigned to the CF_3 group on the α vinyl carbon atom.[4] This low field resonance appears as a quintet of quintets (Figure III-2). The fluorine atoms are coupled not only to the other set of fluorine atoms but to the vinylic methyl hydrogen atoms, the trans phosphorus atom and to the cis phosphorus atom. The coupling to the trans phosphorus atom is of the same magnitude as the coupling to the β fluorine atoms giving rise to a quintet of spacings of about 14 Hz. The coupling to the cis phosphorus atom is of the same magnitude as the coupling to the alkenyl methyl hydrogens and thus each part of the quintet is split into a further quintet with spacings of about 2 Hz.

The stereochemistry of this vinylic group is retained in the insertion of DMA into $PdNO_3[CF_3C{=}CCF_3(CH_3)]$diphos

Figure III-2. Partial ^{19}F nmr spectrum of $PdNO_3[CF_3C{=}CCF_3$-$(CH_3)]$diphos. Spectrum of the signal at 50.32 ppm run at 100 Hz sweepwidth.


P²
Pd
X
P¹
C=C
Me
CF₃
CF₃
JFF = 13.6 ≈ JFP²
JFH = 2.0 ≈ JFP¹

2

(XII). The J(F-F) value is 13.4 Hz consistent with <u>cis</u> CF_3 groups. However, the J(P-F) values drop to 0 Hz for both CF_3 groups because of the lengthening distance between the coupled nuclei.

The alkenyl product $(\eta^5-C_5H_5)Pd[CH_3OOC=CCOOCH_3(CH_3)]-PPh_3$ exhibits resonances in the proton nmr at 7.0 ppm due to the phosphine phenyl protons, at 5.39 ppm (J(P-H) = 1.8 Hz) due to the $\eta^5-C_5H_5$ ring protons[17] and at 3.04 and 3.28 ppm to the two carbomethoxy groups. The vinylic methyl group appears as a singlet at 1.36 ppm. The ^1H nmr spectrum of $(\eta^5-C_5H_5)Pd[CF_3C=CCF_3(CH_3)]PPh_3$ has peaks at 7.0 ppm due to the phosphine phenyl protons and a signal at 5.70 ppm (J(P-H) = 2.0 Hz) due to the $\eta^5-C_5H_5$ ring protons. The vinylic methyl hydrogens appear as a quartet (J(F-H) = 2.2 Hz) at 1.88 ppm.

The ^{19}F spectrum consists of two equally intense sets of signals corresponding to two CF_3 groups with a mutual coupling constant of 14.8 Hz. The large J(F-F) implies that they are <u>cis</u> to each other about the alkenyl double bond.[16] On closer examination each peak of the quartet at low field (50.04 ppm) is a quintet with spacings af 2.2 Hz. This is due to coupling to the alkenyl methyl hydrogens and to the phosphorus nucleus of the triphenyl phosphine. The coupling constants are of the same magnitude giving rise to a quintet rather than a doublet of quartets. ^1H and ^{19}F nmr data for the new compounds are contained in Table III-2 .

The infrared spectra of the insertion products of DMA all contain a broad intense peak at about 1710 cm^{-1} corresponding to the ketonic stretching vibration of the ester functions. The $CF_3C{\equiv}CCF_3$ insertion products all show strong bonds between 1100-1400 cm^{-1} due to carbon-fluorine stretching modes.[17] Both types of products show a weak absorption at about 1610 cm^{-1} attributable to carbon-carbon double bond stretching vibrations. The nitrato derivatives all have a strong band at 1270 cm^{-1} indicating that the nitrate is coordinated[18], while the cationic derivatives have a strong band at 840 cm^{-1} and a sharp band at 555 cm^{-1} characteristic of the PF_6^- anion.

Infrared data are presented in Table III-3 .

d) Discussion

Generally the systems studied were not as reactive toward insertion of substituted acetylenes into the palladium-carbon bond as had been hoped. Only the acetylenes substituted with two electron-withdrawing groups, CF_3 or $COOCH_3$, inserted and this insertion ceased after two molecules of acetylene had been incorporated. The cis complex PdXMediphos was much more reactive than the trans complex $PdXMe(PEt_3)_2$. Similarly Puddephatt[19] found that PdClMe(bipy) reacted with $CF_3C{\equiv}CCF_3$ at room temperature to give the alkenyl complex, while Hagihara[20] found that trans-$PdI(R')(PR_3)_2$, R' = methyl or alkynyl, reacted with DMA only in refluxing dioxane, to give only the alkenyl compounds and not butadienyl ones. This difference in

TABLE III-3

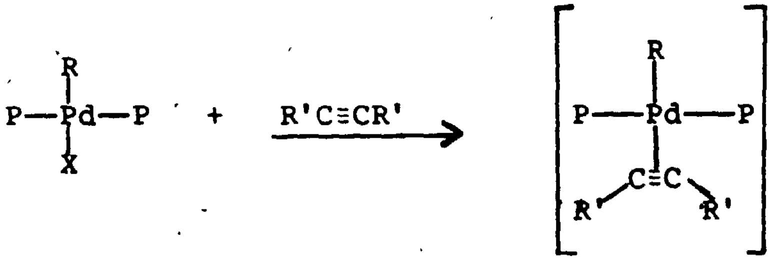
Infrared Data for Some Alkenyl and Butadienyl Palladium Complexes[a,b]

Compound	ν(C=C)	ν(C=O)	ν(NO$_3$)	ν(CF$_3$)	ν(PF$_6$)
Trans-$PdNO_3[RC{=}C(R)CH_3](PEt_3)_2$	1590	1708	1280		
$PdCl[RC{=}CR(RC{=}C(R)CH_3)]$diphos	1608	1708			
$PdNO_3[RC{=}C(R)CH_3]$diphos	1624	1715	1274		
$PdNO_3[RC{=}CR(RC{=}C(R)CH_3)]$diphos	1634	1712	1275		
$[Pd\{RC{=}C(R)CH_3\}PPh_3$diphos$]PF_6$	1603	1703			840,555
$[Pd\{RC{=}CR(RC{=}C(R)CH_3)\}PPh_3$diphos$]PF_6$	1617	1712			841,555
$PdCl[CF_3C{=}C(CF_3)CH_3]$diphos	1627			1278,1236,1141,1119	
$PdNO_3[CF_3C{=}C(CF_3)CH_3]$diphos	1625		1278	1278,1236,1140,1118	
$PdNO_3[RC{=}CR(CF_3C{=}C(CF_3)CH_3)]$diphos	1586	1711	1280	1276,1235,1144,1104	
$Pd[RC{=}C(R)CH_3](\eta^5\text{-}C_5H_5)PPh_3$	1608	1712			
$Pd[CF_3C{=}C(CF_3)CH_3](\eta^5\text{-}C_5H_5)PPh_3$	1615			1278,1230,1160,1111	

[a] All values in cm^{-1}; spectra recorded as nujol mulls.

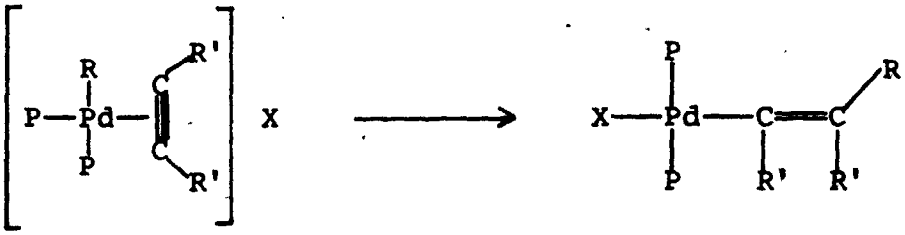
reactivity may be due to the nature of the intermediate in the insertion step. The mechanism of insertion may very well be as follows.

1) displacement of the anion by the acetylene to form a four coordinate cationic species (equation 5).
2) rearrangement of this four coordinate complex to a complex in which the acetylene is <u>cis</u> to the alkyl group (equation 6).
3) migratory insertion to give the alkenyl complex followed by recoordination of the anion (equation 7).



(5)

(6)



(7)

For the system PdXMediphos, once the acetylene has displaced the anion, it occupies a site <u>cis</u> to the methyl and thus does not require any further rearrangement about palladium in order to insert. However for the system trans $PdXMe(PR_3)_2$ if the acetylene displaces the anion to form a four coordinate intermediate, a further reaction must occur for the acetylene to insert. It may be that this trans-cis isomerism is the rate determining step for species of the type $PdXMe(PR_3)_2$. This result is substantiated by the difference in reactivity of $[PdMe(CNR)(PEt_3)_2]^+$ and $[PdMe(CNR)diphos]^+$ toward formation of an imine. The diphos cation undergoes insertion to give the imine at 10°C whereas the triethylphosphine cation, in the absence of added ligand is stable toward insertion in refluxing ethanol.

The rate of insertion of DMA into the complexes PdXRdiphos (R = CH_3 or alkenyl) was extremely dependent on the nature of the anion X. This rate dependence is summarized in Table III-4 and would seem to suggest that displacement of X by acetylene plays an important role in the reaction. A reaction sequence for the insertions is presented in Figure III-3.

Presumably when X = NO_3 or solvent, the displacement of X occurs readily so that the rate determining step is likely to be the actual insertion reaction. Thus the formation of alkenyl versus butadienyl products depends on the relative rates of steps B and D in Figure III-3. The Pd-CH_3 bond is most likely weaker than the Pd-alkenyl bond especially if the alkenyl ligand contains

TABLE III-4

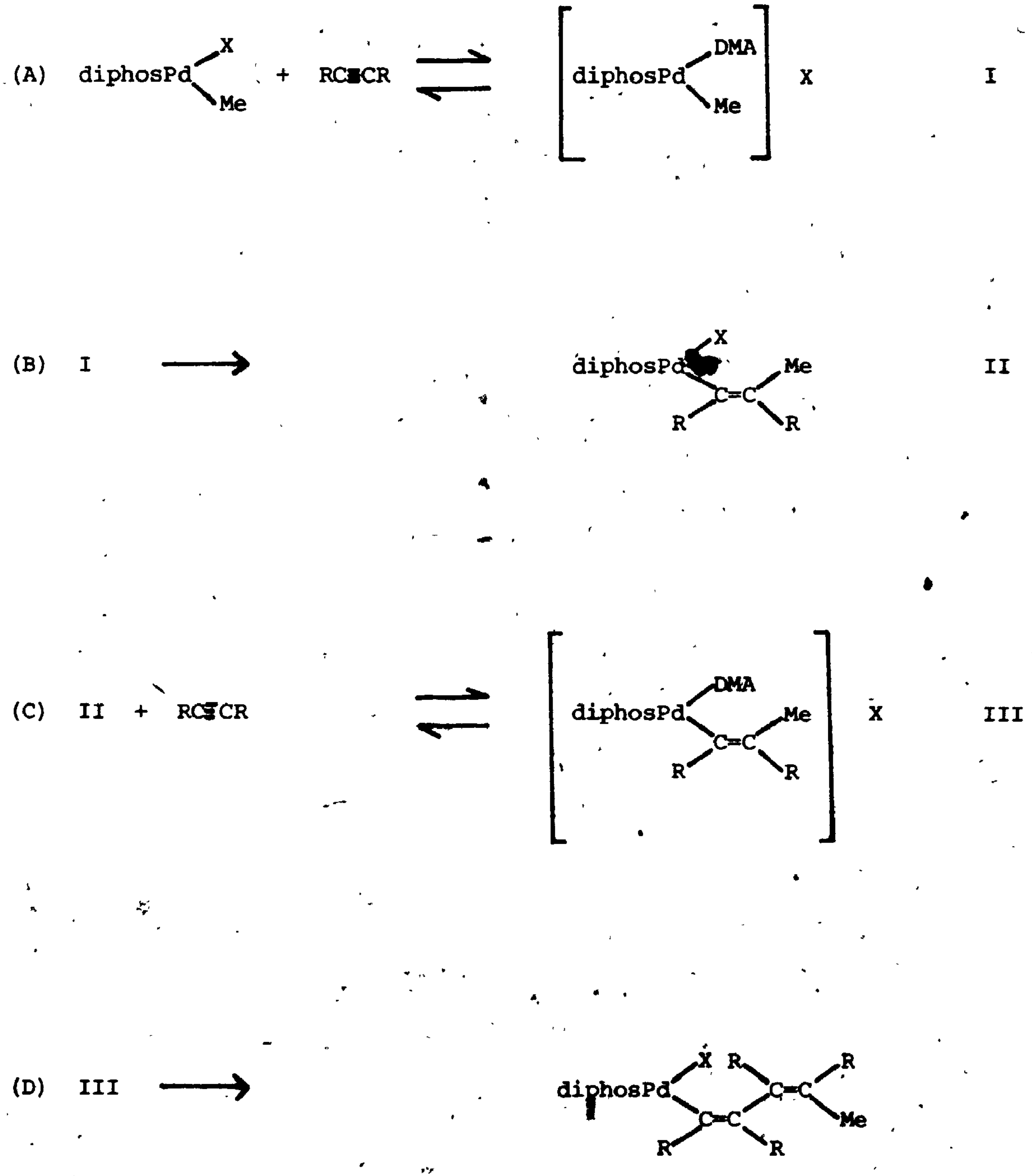
Relative Rates of Acetylene Insertion of Complexes of the Type $PdX(R)diphos^a$

X	R	T°C	Time hours	Solvent	R'C≡CR'
Cl	CH_3	85	3	CD_2Cl_2	DMA[b] (2 equivalents)
NO_3	CH_3	22	0.5	CD_2Cl_2	DMA
PF_6(THF)	CH_3	10	0.15	THF	DMA
Cl	CH_3	85	4	CD_2Cl_2	$CF_3C{\equiv}CCF_3$ (1.5 equivalents)
NO_3	CH_3	22	1.5	CD_2Cl_2	$CF_3C{\equiv}CCF_3$ (1.5 equivalents)
NO_3	$CH_3OOCC{=}C(COOCH_3)CH_3$	22	3	CD_2Cl_2	DMA
PF_6(THF)	$CH_3OOCC{=}C(COOCH_3)CH_3$	10	0.5	THF	DMA
NO_3	$CF_3C{=}C(CF_3)CH_3$	22	30	CD_2Cl_2	DMA

[a] Times obtained by monitoring the ^1H nmr spectrum of 0.10 g of PdX(R)diphos in 0.5 ml. of solvent until complete disappearance of the starting material resonances.

[b] Time for double insertion to give the butadienyl complex.

Figure III-3. Reaction scheme for the formation of butadienyl complexes from PdXMediphos and the acetylene DMA. R = $COOCH_3$



(A)
diphosPd
X
Me
+
RC≡CR
diphosPd
DMA
Me
X
I
(B)
I
diphosPd
X
Me
C=C
R
R
II
(C)
II
+
RC≡CR
diphosPd
DMA
Me
C=C
R
R
X
III
(D)
III
diphosPd
X
R
C=C
R
Me
C=C
R
R

electron-withdrawing groups. For example the platinum-carbon bond in trans-$PtXMe(PR_3)_2$ is readily cleaved by HCl, while the platinum-carbon bond in $Pt(ClC{=}CCl_2)X(PPh_2Me)_2$ remains intact.[22] Similarly the compound trans-$PdNO_3Me(PEt_3)_2$ decomposes over a period of a few days if exposed to air at room temperatures but trans-$PdNO_3[CH_3OOCC{=}CCOOCH_3(CH_3)](PEt_3)_2$ appears to be indefinitely stable under these conditions.

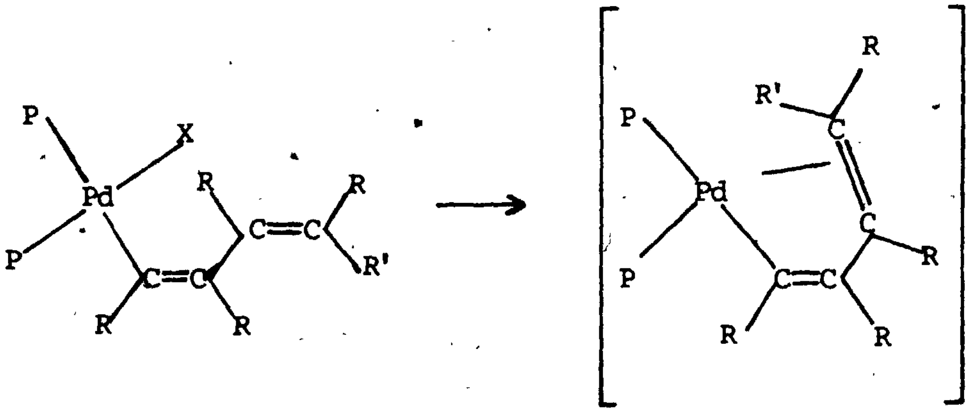
Thus step B predominates resulting firstly in the formation of the alkenyl product. Subsequently in a slower step the σ-butadienyl is formed if two equivalents of acetylene are used. When X = Cl however, the rate of the displacement of Cl^- (A+C) becomes significant so that there is less distinction between reactions B and D. Consequently both alkenyl and butadienyl products are formed.

This dependence of rate of insertion upon the nature of the anion in Pd(II) and Pt(II) complexes has been observed elsewhere. Maitlis[23] found that the species $PdCl(H)(PR_3)_2$ failed to react with conjugated dienes to give the corresponding π-allyl cations. However if the solvated cation $[Pd(H)S(PR_3)_2]^+$ was used a quick insertion took place to give the π-allyl. Clark[6-9] has shown that the insertion of acetylenes into Pt-H bonds in systems of the type $PtX(H)(PR_3)_2$ is dependent on the nature of X. The rate being in the order (solvent) $PF_6 > NO_3 > Cl$.

The nature of the acetylene was also important in determining the rate of reaction. The acetylene $CF_3C{\equiv}CCF_3$ inserted more slowly than DMA into the $Pd{-}CH_3$ bond and no butadienyl product was formed. Also DMA inserted into the Pd-alkenyl bond of $Pd[CF_3C{=}CCF_3(Me)]$ more slowly than into the Pd-alkenyl bond of $Pd[CH_3OOCC{=}CCOOCH_3(CH_3)]$.

Thus DMA is the more reactive acetylene and alkenyls produced from insertion of DMA into a $Pd{-}CH_3$ bond are more reactive than vinyls produced from insertion of $CF_3C{\equiv}CCF_3$ into a $Pd{-}CH_3$ bond.

The failure of either acetylene to produce a product containing 3 moles of acetylene per palladium atom was disappointing but can be rationalized in two ways. Possibly the incorporation of a large number of electron-withdrawing groups on the butadienyl ligand increases the stability of the Pd-carbon bond resulting in a decrease in reactivity. Alternately, once a σ-butadienyl fragment has been formed the double bond at the end of the chain competes with free acetylene for the vacant coordination site produced by displacement of the anion. (equation 8).



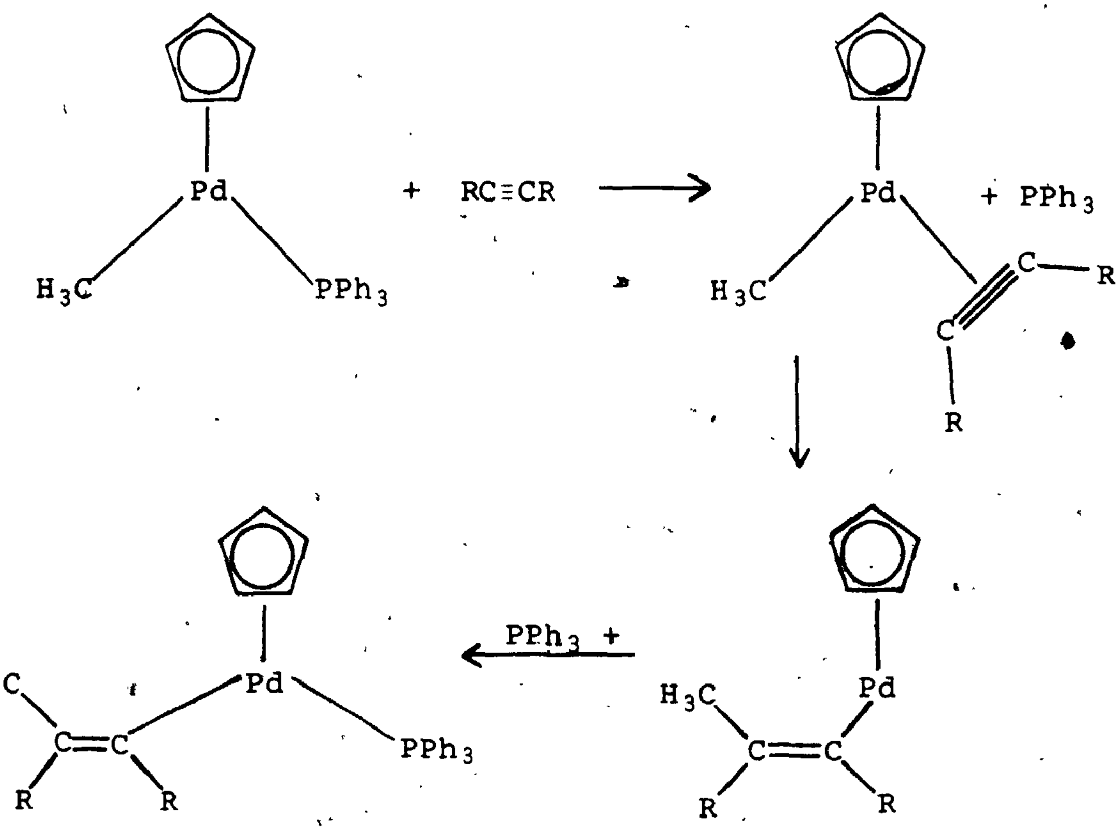
(8)

However, we have no evidence for such coordination in this system.

The magnitude of the J(F-F) of the alkenyl compounds derived from insertion of $CF_3C{\equiv}CCF_3$ into the Pd-CH_3 bond indicated that the CF_3 groups were mutually cis. This implies that cis addition across the triple bond has occurred. Cis addition of metal-hydrides and of metal alkyls to unsaturated organic compounds is thought to be the usual case.[4-9] However there exists the possibility that addition is actually trans and this trans product isomerizes to produce the cis product. Studies by Schwartz[24] on several vinylic Rh(III) complexes has shown that in certain cases isomerization is possible. However isomerization was always from a cis compound to a trans compound. Moreover the formation of the insertion products reported here could be conveniently followed in the ^1H nmr. In no instance were signals observed which corresponded to the presence of a trans alkenyl or butadienyl product.

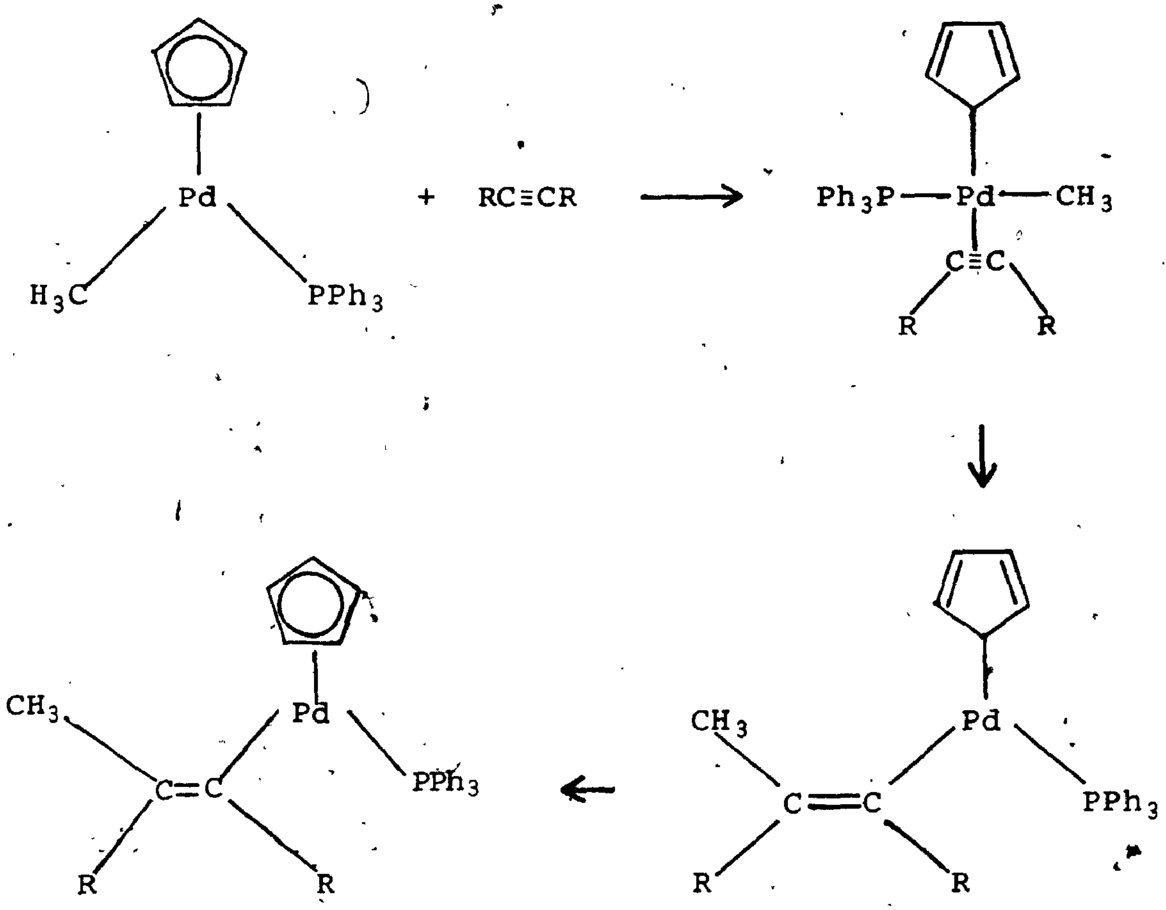
The compound PdMe(η^5-C_5H_5)PPh_3 also reacted with $CF_3C{\equiv}CCF_3$ and DMA to give only the alkenyl compounds. The stereochemistry of the alkenyl group, derived from insertion of $CF_3C{\equiv}CCF_3$, indicated, with the previously mentioned reservations that the addition across the triple bond was cis.

As the starting compound is an 18-electron complex it is coordinatively saturated.[25] To allow the acetylene to complex and insert, a vacant coordination site must be created. There are two possible ways in which this may be achieved. The first way is displacement of the phosphine ligand by the acetylene, followed by insertion and recombination of the free phosphine with the metal centre (equation 9).



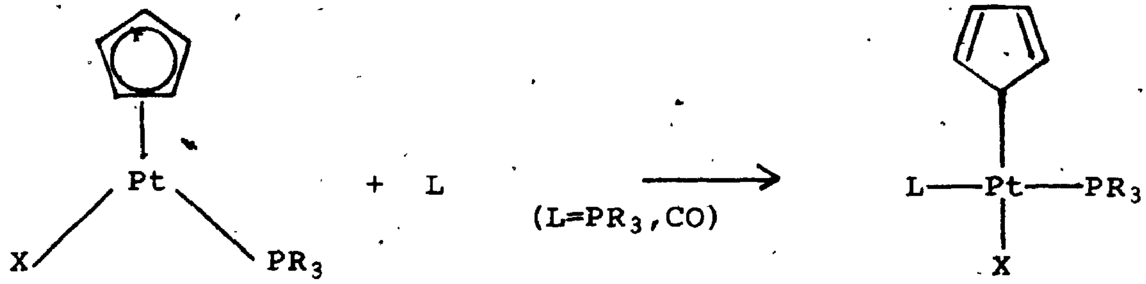
(9)

Alternatively, and more likely, the coordination of the acetylene causes the η^5-C_5H_5 ring to change its mode of bonding to a σ-cyclopentadienyl type. The Pd is now in only a 14-electron configuration and coordination of the acetylene is now possible to give a 16-electron complex. Insertion leads to a 14-electron alkenyl complex allowing the σ-cyclopentadienyl ring to revert to a η^5-C_5H_5 type reforming an 18-electron compound (equation 10).



(10)

This interconversion of a η^5-C_5H_5 ring to the σ-bonding type has been well documented for square planar d^8 systems, by Cross and Wardle[26]. They found that compounds of the type $PtX(\eta^5\text{-}C_5H_5)PR_3$ (X = alkyl, Cl or aryl) would react with a donor ligand to form the square planar σ-bonded cyclopentadienyl complexes (equation 11).



(11)

The corresponding Pd species were too unstable to isolate, however, but ^{1}H nmr evidence implied the existence of such σ-bonded cyclopentadienyls.

e) Experimental

i) Preparation of trans-$PdNO_3Me(PEt_3)_2$

To a solution of trans-$PdClMe(PEt_3)_2$ (0.300 g) in acetone (20 ml.), was added silver nitrate (0.129 g) in 3 ml. of water. The solution was stirred and then filtered to remove the thick precipitate of silver chloride. The filtrate was taken to dryness on a rotary evaporator and the residue in dichloromethane passed through a column of florisil. The eluate was collected and the solvent removed to give the nitrate as a white solid. Yield was 0.304 g (95%).

ii) Preparation of trans-$PdNO_3[CH_3OOCC{=}CCOOCH_3(CH_3)]$-$(PEt_3)_2$

Trans-$PdNO_3Me(PEt_3)_2$ (0.200 g) and $CH_3OOCC{\equiv}CCOOCH_3$ (0.058 ml) were stirred in dichloromethane for 12 hours to give a yellow solution. Removal of the solvent gave a sticky oil which was chromatographed on silica gel using diethyl ether as the eluent. The title compound was contained in the second band of the thick layer chromatography plate. The compound was separated from the silica gel by extraction with acetone to give on evaporation white crystals.

Yield was 0.081 g (35%).

iii) Preparation of $PdNO_3$Mediphos

To a suspension of PdClMediphos (0.300 g) in acetone at 0°C was added silver nitrate (0.091 g) in 3 ml of water. A thick white precipitate of silver chloride was noticed. After 30 minutes, the solution was filtered through celite and the filtrate taken to dryness on a rotary evaporator. The residue was dissolved in dichloromethane and passed through a short column containing florisil. Diethyl ether was added to the eluate causing the formation of white crystals.

Yield was 0.245 g (78%).

iv) Preparation of $PdCl[CH_3OOCC{=}CCOOCH_3(C(COOCH_3){=}C(COOCH_3)CH_3)]$diphos

PdClMediphos (0.300 g) and DMA (0.066 ml) were dissolved in dichloromethane (10 ml) and transferred to a thick walled Carius tube. The tube was sealed and heated to 85°C for 3 hours. The tube was cooled, opened and the contents filtered. The solvent volume was reduced and ether was added to produce white crystals of the title compound.

Yield was 0.210 g (56%).

v) Preparation of $PdCl[CF_3C{=}CCF_3(CH_3)]$diphos

Hexa-fluoro-2-butyne (0.175 g) was condensed onto PdClMediphos (0.300 g) in dichloromethane (10 ml) in a Carius tube. The tube was sealed, heated for 3 hours at 85°C and then cooled. The tube was opened and the contents filtered. Addition of ether to the filtrate precipitated white crystals.

Yield was 0.251 g (65%).

vi) Preparation of $PdNO_3[CH_3OOCC{=}CCOOCH_3(CH_3)]$diphos

To an acetone or dichloromethane solution of $PdNO_3$Mediphos (0.250 g) was added DMA (0.053 ml). The solution was stirred for 20 minutes and then stripped to dryness. The residue was recrystallized from dichloromethane/diethyl ether to give off-white crystals of the title compound.

Yield was 0.233 g (75%).

vii) Preparation of $PdNO_3[CH_3OOCC{=}CCOOCH_3(C(COOCH_3){=}C(COOCH_3)CH_3)]$diphos

To an acetone or dichloromethane solution of $PdNO_3$Mediphos (0.250 g) was added DMA (0.106 ml). The solution was stirred for 3 hours and then stripped to dryness. The residue was recrystallized from dichloromethane/ether to give off-white crystals of the title compound.

Yield was 0.261 g (70%).

viii) Preparation of $[Pd[CH_3OOCC{=}CCOOCH_3(CH_3)]PPh_3$-diphos]$PF_6$

PdClMediphos (0.300 g) was suspended in 20 ml. of tetrahydrofuran and the flask and its contents cooled to -15°C. Silver hexafluorophosphate (0.136 g) dissolved in 10 ml. of tetrahydrofuran was added slowly. An immediate precipitate of silver chloride appeared and the solution was stirred for 15 minutes. The contents of the flask were then filtered through a cold frit containing a pad of celite, into a flask chilled to 0°C, to give a clear colourless solution. DMA (0.066 ml.) was added and the solution was stirred for 15 minutes. Triphenylphosphine (0.141 g) in 10 ml. of tetrahydrofuran was added and then the solvent was removed. The residue was recrystallized from dichloromethane/diethyl ether to give fluffy white crystals.

Yield was 0.463 g (80%).

ix) Preparation of $[Pd[CH_3OOCC{=}CCOOCH_3(C(COOCH_3){=}CCOOCH_3(CH_3))]PPh_3diphos]PF_6$

The solvated cation $[PdMe(S)diphos]PF_6$ was made in situ as above and DMA (0.133 g) was added. The solution was stirred at 0°C for one hour and then triphenylphosphine (0.141 g) was added. The solvent was then removed by a rotary evaporator and the residue recrystallized from dichloromethane/diethyl ether to give white crystals.

Yield was 0.458 g (70%).

x) Preparation of $PdNO_3[CH_3OOCC{=}CCOOCH_3(C(CF_3){=}C(CF_3)CH_3)]diphos$[27]

$PdNO_3[CF_3C{=}C(CF_3)CH_3]diphos$ (0.100 g) and DMA (0.017 ml.) were dissolved in dichloromethane (3 mls.) and the solution stirred for 48 hours. Addition of ether gave a white precipitate of the butadienyl compound.

Yield was 0.089 g (75%).

xi) Preparation of $PdMe(\eta^5{-}C_5H_5)PPh_3$

$PdCl(\eta^5{-}C_5H_5)PPh_3$ (1.0 g) was dissolved in 50 ml. of toluene and the solution was cooled to -78°C. 2.5 ml. of a 1.84 M solution of methyllithium in ether was slowly added. As the solution was warmed to 0°C its original dark green colour changed to orange-red. After the solution was stirred for an hour at 0°C the excess methyllithium was hydrolyzed with ice-cold water. The contents of the flask were transferred to a separatory funnel and the organic layer put aside. The aqueous layer was extracted with three 50 ml. portions of diethyl ether and the combined organic layers were washed with 50 ml. of water. After drying over $MgSO_4$ the organic layers were stripped to dryness. The orange residue was recrystallized from toluene/hexane to give orange-red crystals.

Yield was 0.69 g (72%).

xii) Preparation of $Pd[CH_3OOCC{=}CCOOCH_3(CH_3)](\eta^5\text{-}C_5H_5)\text{-}PPh_3$

A solution of $PdMe(\eta^5\text{-}C_5H_5)PPh_3$ (0.300 g) and DMA (0.082 ml) in dichloromethane was stirred for 12 hours. The original orange-red solution darkened to a brown-red colour. The solvent was removed and the oily residue was chromatographed on a silica gel column. Elution with pentane followed by benzene gave some brown material which was not characterized. Elution with diethyl ether gave a deep red eluent which was collected and stripped to dryness to give a crystalline mass. Recrystallization from toluene/-pentane gave needle-shaped maroon crystals.

Yield was 0.237 g (60%).

xiii) Preparation of $Pd[CF_3C{=}CCF_3(CH_3)](\eta^5\text{-}C_5H_5)PPh_3$

A one-necked round bottomed flask equipped with a serum cap, was charged with a solution of $PdMe(\eta^5\text{-}C_5H_5)PPh_3$

(0.300 g) in 10 ml of dichloromethane. The flask was evacuated via a syringe needle and hexafluoro-2-butyne introduced to produce a pressure slightly greater than one atmosphere. The solution was stirred for 12 hours during which time the colour of the solution changed from red to reddish brown. On removal of the solvent a reddish oil remained, which was chromatographed on silica gel, using a 1:4 mixture of toluene/pentane as the eluent. A pinkish-red band came off which was collected and evaporated to dryness. Recrystallization of the residue from pentane/toluene gave burgundy red crystals.

Yield was 0.220 g (54%).

xiv) Preparation of $PdNO_3[CF_3C{=}CCF_3(CH_3)]$diphos

A solution of $PdNO_3$Mediphos (0.300 g) in dichloromethane (10 ml.) was stirred for 4 hours under an atmosphere of hexafluoro-2-butyne. The solution was then filtered through celite and diethyl ether added to the filtrate to give white crystals of the title compound. Yield was 0.240 g (62%).

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CHAPTER IV

THE REACTION OF TRANS-$PdNO_3(H)(PCy_3)_2$ and TRANS-$[Pd(H)(CH_3CN)(PCy_3)_2]PF_6$ WITH SOME DISUBSTITUTED ACETYLENES

a) Introduction

The insertion step in the catalyzed hydrogenation of olefins and acetylenes has been studied in some detail for Pt(II) hydride complexes.[1,2,3] Thus, Clark and Wong have examined the reactivity of substituted acetylenes toward insertion into the Pt-hydride bond of the system trans-$PtX(H)(PEt_3)_2$ [X = Cl , NO_3^- or (solvent) PF_6]. Evidence was presented for a mechanistic pathway which may involve either four or five coordinate intermediates, depending on the nature of the ligand trans to the hydridic hydrogen, and on the coordinating ability of the acetylene. Both of these pathways at one point, bring the hydridic hydrogen and the substrate cis to one another on the metal, and from this arrangement migratory insertion may take place.

The reactions of Pt(II) hydrides with disubstituted acetylenes are ideal for determining the stereochemical course of the insertion step. From the ^1H and ^{19}F nmr spectra of the alkenyl products the cis or trans geometry about the alkenyl bond can be determined. In addition for an unsymmetrical acetylene the disposition of the acetylene substituents with respect to the α and β positions of the alkenyl product can often be determined. The determination of these factors provides considerable information on the nature of the insertion step.

Similarly Clark and Attig have examined the reactions of the solvated cation trans-$[PtH(S)(PCy_3)_2]PF_6$ with disubstituted acetylenes.[1] The bulky phosphine groups had a marked effect on the insertion reaction. Clearly, then, the reaction will be affected by the ligands on metal and by the nature of the metal itself. We were therefore interested in examining the reactions of disubstituted acetylenes with palladium hydrides in order to compare their behaviour with that of the analagous platinum hydrides. However, the number of stable well characterized, palladium hydrides are few.

Attempts to prepare palladium hydrides by using conventional reducing reagents such as hydrazine hydrate or sodium borohydride with compounds of the type trans-$PdCl_2(PR_3)_2$ have led only to decomposition. Glockling[4] has prepared trans-$PdCl(H)(PEt_3)_2$ by using trimethylgermane as the reducing agent (equation 1).

$$\underline{\text{trans}}\text{-}PdCl_2(PEt_3)_2 + GeMe_3H \rightarrow \underline{\text{trans}}\text{-}PdCl(H)(PEt_3)_2 \qquad (1)$$

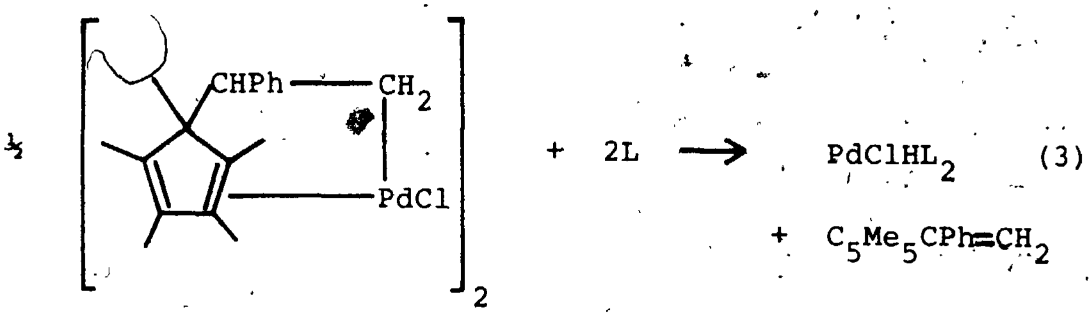
Repetition of this preparation did indeed lead to this hydride but it was extremely unstable and difficult to handle. Uchida[5] has reported the preparation of trans-

$PdCl(H)(PPh_3)_2$ by the oxidative addition of HCl to $Pd(PPh_3)_4$ (equation 2).

$$Pd(PPh_3)_4 + HCl \xrightarrow{-50°C} \underline{trans}\text{-}PdCl(H)(PPh_3)_2 \qquad (2)$$

This procedure could not be repeated by either myself or by other members of our research group.

Maitlis[6,7] has prepared palladium hydrides <u>in situ</u> by β elimination processes (equation 3).



Green[8,9,10] has prepared a number of palladium hydrides of the type $\underline{trans}\text{-}PdCl(H)(PR_3)_2$, where R is a bulky substituent such as cyclohexyl or isopropyl, by using a nickel hydride as the reducing agent(equation 4).

$$\underline{trans}\text{-}Ni(BH_4)H(PR_3)_2 + \underline{trans}\text{-}PdCl_2(PR'_3)_2 + PR_3 \rightarrow$$

$$\underline{trans}\text{-}PdCl(H)(PR_3)_2 + \underline{trans}\text{-}NiCl(H)(PR_3)_2 + B_2H_6 \qquad (4)$$

These hydrides are particularly stable, a property which has been attributed to the steric bulk of the phosphine ligands.[8]

Recently Saito[11,12] reported the preparation of trans-$PdNO_3(H)(PCy_3)_2$ by the reduction of $Pd(NO_3)_2(PCy_3)_2$ with $NaBH_4$. The high yield of this reaction is probably due to the high stability of the product and because the starting material is quite soluble compared to the chloride complex allowing rapid reduction.

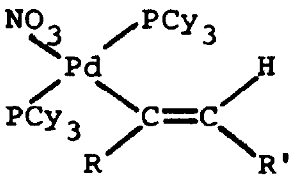
Our repetition of this procedure also resulted in high yields. The hydride was air stable in the solid state but rapidly decomposed in solutions that were not oxygen-free. Because of its ease of preparation and handling we decided to investigate the reactions of this hydride with disubstituted acetylenes. In addition, the reactions would be directly comparable to those of the analagous platinum system.[1]

b) Results

The palladium hydride trans-$PdNO_3(H)(PCy_3)_2$, I, was prepared by the method of Saito and Morigama.[12] The brown product obtained from this procedure could be purified by washing with small amounts of ice-cold acetone, to give a white powder.

The hydride I reacted smoothly in dichloromethane with disubstituted acetylenes bearing one electron-withdrawing group, to give alkenyl compounds (equation 5).

I + $RC\equiv CR'$ $\longrightarrow$



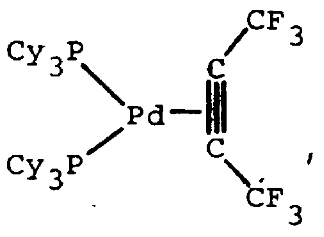
(5)

In each case reaction was complete after about four hours and the products could be isolated as cream coloured crystals. In all instances, the presence of only one product was detected both during and after the reaction. The yields were always at least 65%, indicating that the insertion reaction was by far the dominant one.

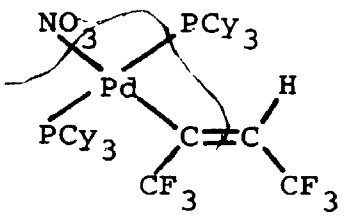
The acetylene $CH_3C{\equiv}CPh$ failed to react with I, while the acetylenes $PhC{\equiv}CH$ and $PhC{\equiv}CPh$ reacted to produce mixtures which showed olefinic hydrogen resonances in their ^1H nmr spectra. However, work up of these reaction mixtures produced only red oils whose ^1H nmr spectra did not display any olefinic hydrogen resonances.

If I was allowed to react with acetylenes substituted with two electron-withdrawing groups the reaction was considerably more complicated. For the reaction of I with DMA, no products could be isolated. After one equivalent of DMA had been added to a dichloromethane solution of the hydride, the ^1H nmr spectrum showed the presence of many methyl ester resonances, two alkenyl hydrogen resonances as well as the hydride signal of the starting material I. Further addition of DMA resulted in the disappearance of the hydride signal, an increase in complexity of the methyl ester signals and the formation of yet another alkenyl hydrogen resonance. Further product characterization could not be achieved.

If hexafluoro-2-butyne was allowed to react with I in dichloromethane at one atmosphere pressure the colour of the solution lightened. After two hours an infrared spectrum of a portion of this solution displayed a band at 2143 cm^{-1} due to ν(Pd-H) of residual I, and a new band at 1762 cm^{-1} due to the formation of the zero-valent species $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$(II). After 8 hours the hydride signal had completely disappeared leaving the strong band at 1762 cm^{-1} and a weaker band at 1616 cm^{-1} due to some alkenyl product. If the same reaction was carried out in an nmr tube at 2-3 atmospheres pressure of $CF_3C{\equiv}CCF_3$ the alkenyl product III was obtained, although in a poor yield.



II



III

The zero-valent acetylene compound II could be prepared quantitatively in a pure form if proton sponge[13] was added to the reaction solution. When $CF_3C{\equiv}CCF_3$ was bubbled through a benzene solution of I in the presence of proton sponge an immediate precipitate of proton sponge•HNO_3 was observed. From the solution white crystals of II could be obtained on addition of methanol. In a similar manner the zero-valent acetylene complex $Pd(CH_3OOCC{\equiv}CCOOCH_3)$-$(PCy_3)_2$ (IV) was prepared.

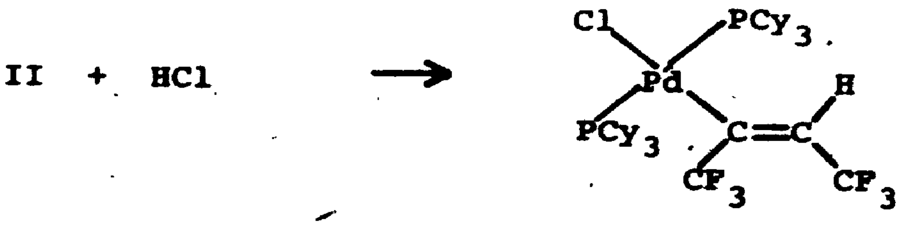
The hydridochloride complex <u>trans</u>-$PdCl(H)(PCy_3)_2$ (V)[8] could be prepared by treating the hydridonitrate(I) with a ten fold excess of Et_4NCl in benzene. Compound V failed to react with substituted acetylenes at room temperature in dichloromethane solution. However, the solvated cation $[Pd(H)CH_3CN(PCy_3)_2]PF_6$ (VI) could be prepared by treatment of V with $AgPF_6$ in acetonitrile solution. The cation VI could be isolated as white air stable crystals in 65-70% yields.

Acetylenes containing one electron-withdrawing substituent reacted with this solvated cation VI in a variety of solvents at room temperature to give alkenyl products, isolated as the neutral chloride complexes by quenching the reaction solutions with LiCl.

The rate of reaction was solvent dependent, being in the order CH_2Cl_2 > acetone > CH_3CN.

Reaction of VI with the acetylene DMA or $CF_3C{\equiv}CCF_3$ produced complicated mixtures from which no single compound could be isolated.

The zero-valent compound II reacted with one equivalent of HCl (generated by the action of methanol on acetyl chloride) to give the alkenyl Pd(II) compound VII (equation 6).



(6)

VII

TABLE IV-1

Analytical and Physical Data for Trans-bistricyclohexylphosphine Palladium Compounds[a]

Compound	Colour	mp°C	%C		%H	
			Found	Calc.	Found	Calc.
$PdNO_3[CH_3C{=}C(COOCH_3)H]L_2$	white	140-142(d)	59.21	59.42	8.60	8.81
$PdNO_3[PhC{=}C(COOCH_3)H]L_2$[b]	white	134-135(d)	64.23	64.48	8.88	8.43
$PdNO_3[PhC{=}C(CF_3)H]L_2$	cream	155-157(d)	59.46	60.03	8.24	8.06
$PdNO_3[HC{=}C(COOCH_3)H]L_2$	cream	110-112(d)	58.81	58.97	8.54	8.60
$PdCl[CH_3C{=}C(COOCH_3)H]L_2$	white	145-146(d)	61.68	61.43	9.02	9.12
$PdCl[PhC{=}C(COOCH_3)H]L_2$	white	139-141(d)	63.72	63.42	8.61	8.80
$PdCl[PhC{=}C(CF_3)H]L_2$	cream	165-167(d)	62.24	61.86	8.22	8.25
$[Pd(H)(CH_3CN)L_2]PF_6$	white	145-146(d)	53.64	53.40	8.33	8.20
$PdNO_3[CF_3C{=}C(CF_3)H]L_2$	white	173-174(d)	53.88	53.81	7.61	7.51
$PdCl[CF_3C{=}C(CF_3)H]L_2$	white	181-183(d)	55.02	55.45	7.41	7.74
$Pd[CF_3C{\equiv}CCF_3]L_2$	white	148-149(d)	57.86	57.90	7.84	7.96
$Pd[CH_3OOCC{\equiv}CCOOCH_3]L_2$	cream	135-137(d)	62.58	62.30	9.18	8.90
$PdCl[HC{=}C(COOCH_3)H]L_2$	white	117-119(d)	61.23	60.95	8.95	9.02

[a] $L = PCy_3$

[b] Analyzed as $PdNO_3[PhC{=}C(COOCH_3)H]L_2 \cdot C_6H_6$

The zero-valent compound IV also reacted with one equivalent of HCl to give mixtures of products, some of which appeared to be alkenyl derivatives. No product could be isolated in a pure state.

Analytical results and physical properties of the new compounds are presented in Table IV-1.

c) Discussion of the ^{1}H, ^{19}F and infrared spectroscopic data for the new compounds.

The ^{1}H nmr spectra (Table IV-2) of the alkenyl products trans-PdX(alkenyl)$(PCy_3)_2$ (X = Cl or NO_3) all contain an intense broad signal between 1.0 and 2.5 ppm, due to the 66 hydrogens of the cyclohexyl rings of the phosphine ligands. The resonance for the alkenyl proton for each product appears between 5.5 and 9.0 ppm. For the products derived from insertion of the acetylenes $RC{\equiv}CCOOCH_3$, R = Me or Ph the signal for the vinylic proton appears as a broad singlet, hence nothing further can be said about the stereochemical arrangement of the alkenyl substituents. For R=H however, two vinylic hydrogen resonances are observed (Figure IV-1). One signal is a doublet of triplets centred at 8.69 ppm [J(P-H)=6.0 Hz J(H-H)=16 Hz] and the other signal a doublet centred at 5.90 ppm [J(H-H)=16 Hz]. Irradiation of the signal at 8.69 ppm causes the signal at 5.90 ppm to collapse to a singlet and irradiation of the signal at 5.90 ppm causes the signal at 8.69 to collapse to a triplet of relative intensities 1:2:1. The large value of J(H-H) necessitates

TABLE IV-2

^{1}H and ^{19}F nmr Data for Compounds of the Type Trans-PdX[$R^1C=C(R^2)H$](PCy_3)$_2$[a]

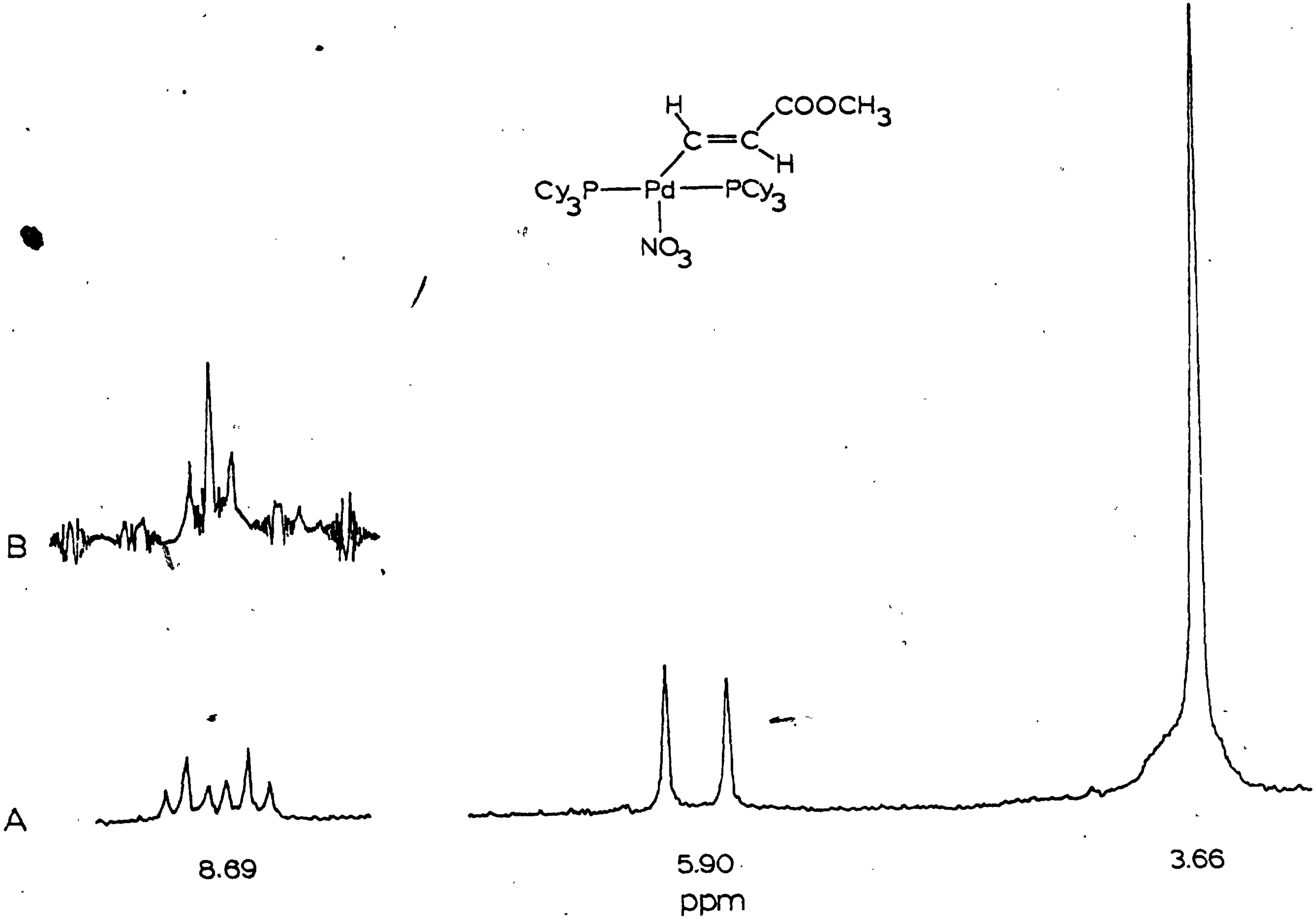
X	R^1	R^2	δH	Other Resonances
NO_3	CH_3	$COOCH_3$	6.07	$\delta(CH_3)$ 2.67, $\delta(COOCH_3)$ 3.60
NO_3	Ph	$COOCH_3$	5.78	$\delta(COOCH_3)$ 3.53
NO_3	Ph	CF_3	5.94 J(F-H)=10	$\delta(CF_3)$ 54.16 J(P-F)=5.1
NO_3	H	$COOCH_3$	5.90 J(H-H)=16	δ(H) 8.69 J(P-H)=6.0, $\delta(COOCH_3)$ 3.66
NO_3	CF_3	CF_3	5.72 J(F^2-H)=9.5	$\delta(CF_3{}^1)$ 42.51 ($CF_3{}^2$) 51.00 J(F^1-F^2) 12.2
Cl	CH_3	$COOCH_3$	6.11	$\delta(CH_3)$ 2.68, $\delta(COOCH_3)$ 3.60
Cl	Ph	$COOCH_3$	5.81	$\delta(COOCH_3)$ 3.68
Cl	Ph	CF_3	5.83 J(F-H)=10	$\delta(CF_3)$ 54.35 J(P-F)=4.2
Cl	H	$COOCH_3$	5.91 J(H-H)=15.8	δ(H) 8.60 J(P-H)=6.1, $\delta(COOCH_3)$ 3.66
Cl	CF_3	CF_3	5.85 J(F^2-H)=9.2	$\delta(CF_3{}^1)$ 49.62, $\delta(CF_3{}^2)$ 58.59 J(F^1-F^2)=12.1

[a] Spectra obtained in $CDCl_3$; ^{1}H chemical shifts are in positive ppm downfield from TMS: coupling constants are in Hz.

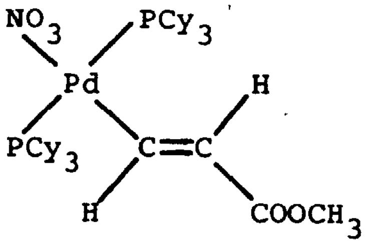
Figure IV-1. ^1H nmr spectrum of trans-$PdNO_3[HC{=}CCOOCH_3$-(H)]$(PCy_3)_2$.

A. Spectrum run at 1000 Hz sweepwidth in $CDCl_3$. Spectrum also contained broad resonances between 1 and 3 ppm due to the cyclohexyl protons.

B. Appearance of the signal at 8.69 ppm while irradiating the signal at 5.90 ppm.


H
COOCH3
C=C
H
Cy3P—Pd—PCy3
NO3
B
A
8.69
5.90
ppm
3.66

the two vinylic hydrogens having a trans disposition about the double bond.[14] The triplet appearance of the low field resonance is due to coupling to the mutually trans phosphorus atoms and implies that it is due to the hydrogen atom on the carbon atom α to the palladium atom. Such a low chemical shift for a vinylic proton on the carbon in the α position of a metal-bonded alkenyl derivative has been observed previously.[15] Thus the structure of this alkenyl derivative is unambiguously determined as VIII in which cis addition has occurred and the hydride atom has added to the carbon containing the electron-withdrawing group.



VIII

The vinylic hydrogen resonance of the product derived from insertion of the acetylene $CF_3C{\equiv}CPh$, appears as a 1:3:3:1 quartet due to coupling to the fluorine atoms of the trifluoromethyl group [J(F-H)=10 Hz]. The magnitude of this coupling requires the hydrogen to be on the same carbon as the trifluoromethyl group[16] but the disposition of the palladium atom or the phenyl group about the double bond with respect to the vinylic hydrogen cannot be determined.

The insertion product derived from the acetylene

$CF_3C{\equiv}CCF_3$ shows in its ^1H nmr spectrum one vinylic hydrogen resonance at 5.72 ppm which is a 1:3:3:1 quartet due to coupling to the fluorine atoms of one of the CF_3 groups [J(F-H)=10.0 Hz]. The ^{19}F nmr spectrum of this product displays two equally intense sets of signals. The low field resonance centred at 42.51 ppm is a 1:3:3:1 quartet due to coupling to the fluorine atoms of the other CF_3 group [J(F-F)=12.2 Hz]. The high field resonance centred at 51.00 ppm is a doublet of quartets due to coupling not only to the low field fluorine atoms but to the vinylic hydrogen atom. Noise decoupling of the proton region causes this signal to collapse to a quartet. The large value of J(F-F) implies that the two CF_3 groups are cis to one another about the alkenyl carbon-carbon bond.[16]

Compound VII formed by the reaction of the zero-valent acetylene complex $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ with HCl also has this cis disposition of the CF_3 groups.

The ^1H nmr spectra of the zero-valent compounds $Pd(RC{\equiv}CR)(PCy_3)_2$ ($R{=}CF_3$ or $COOCH_3$) show the broad resonance, between 1.00 and 2.5 ppm, of the cyclohexyl protons and in the case of $R{=}COOCH_3$ a singlet at 3.69 ppm due to the methyl ester protons. The ^{19}F nmr spectrum of $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ exhibits a broad resonance at 51.2 ppm, similar in shape to the analagous platinum compound. The appearance of this signal is due to the spectrum being an $A_3A'_3XX'$ type (X=P,A=F).

The infrared spectra of all the alkenyl products (Table IV-3) show a band between 1550 and 1620 cm^{-1} of

TABLE IV-3

Infrared Data for <u>Trans</u> bistricyclohexylphosphine Palladium Compounds[a,b]

Compound	ν(C=C)	ν(C=O)	ν(NO$_3$)	ν(CF$_3$)
$PdNO_3[CH_3C{=}C(COOCH_3)H]L_2$	1572	1702	1285	
$PdNO_3[PhC{=}C(COOCH_3)H]L_2$	1554	1717,1684	1284	
$PdNO_3[PhC{=}C(CF_3)H]L_2$	1576		1286	1243,1117
$PdNO_3[HC{=}C(COOCH_3)H]L_2$	1558	1712	1292	
$PdCl[CH_3C{=}C(COOCH_3)H]L_2$	1570	1699		
$PdCl[PhC{=}C(COOCH_3)H]L_2$	1565	1720		
$PdCl[PhC{=}C(CF_3)H]L_2$	1580			1242,1117
$PdCl[HC{=}C(COOCH_3)H]L_2$	1556	1710		
$PdCl[CF_3C{=}C(CF_3)H]L_2$	1611			1252,1109
$PdNO_3[CF_3C{=}C(CF_3)H]L_2$	1616		1285	1253,1111

[a] All values in cm^{-1}; spectra recorded as nujol mulls.

[b] $L = PCy_3$.

TABLE IV-4

Spectroscopic Data for Pd(Acetylene)(PCy$_3$)$_2$ Compounds[a]

Acetylene	NMR ppm.	Ir cm^{-1}
$CF_3C{\equiv}CCF_3$	δCF_3 51.29	$\nu(C{\equiv}C)$ 1762 $\nu(C\text{-}F)$ 1285,1245,1160,1115
$CH_3OOCC{\equiv}CCOOCH_3$	$\delta COOCH_3$ 3.69	$\nu(C{\equiv}C)$ 1813 $\nu(C{=}O)$ 1683

[a] NMR spectra recorded in CD_2Cl_2; Infrared spectra as Nujol mulls.

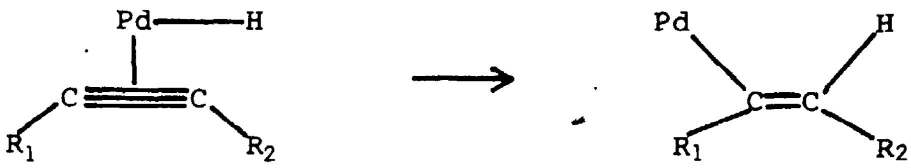
[b] Both compounds also showed a broad intense signal in the ^1H nmr spectrum between 1 and 3 ppm due to the cyclohexyl protons.

weak to medium intensity, which may be assigned to ν(C=C). For those products containing an ester group a band at around 1720 cm^{-1} due to ν(C=O) is observed and for those products containing CF_3 groups strong bands between 1100-1400 cm^{-1} due to ν(C-F) are observed.[17] The nitrato derivatives all contain a strong band at around 1285 cm^{-1} indicative of a coordinated nitrate anion.[18] The two zero-valent acetylene compounds $Pd(RC{\equiv}CR)(PCy_3)_2$ both show a sharp intense band, at 1813 cm^{-1} for $R{=}COOCH_3$ and at 1762 cm^{-1} for $R{=}CF_3$. This band is due to ν(C≡C) which is lowered in frequency upon coordination to the metal.[19]

Infrared and ^{19}F and ^{1}H nmr data for the two zero-valent compounds are contained in Table IV-4.

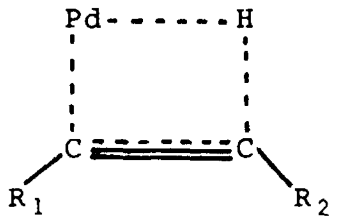
d) Discussion

In considering the nature of the insertion step, (equation 7), two models may be proposed which represent



(7)

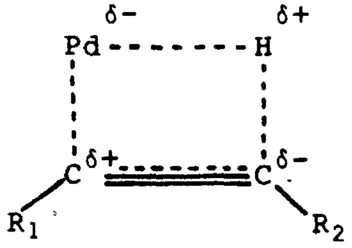
the extreme descriptions of the transition state. In the first model, the commonly held assumption is made that the Pd-H bond remains intact while the appropriate geometry of the transition state is attained. This suggests (but does not necessarily require) a four centred transition state, A.



A

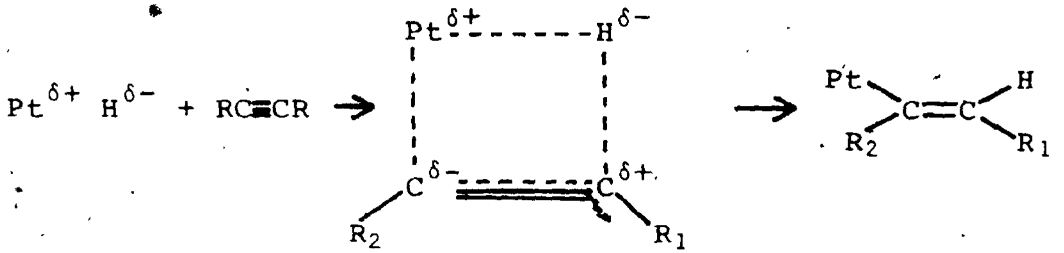
In the alkenyl products obtained here the disposition of the substituents on the double bond is such that it would appear that cis addition of the Pd-H fragment across the triple bond of the acetylene has occurred. This is confirmed for $R_1=R_2=CF_3$ by the large J(F-F) = 12.2 Hz and for $R_1=H$, $R_2=COOCH_3$ by the large J(H-H) = 16 Hz[16]. This is consistent with a four centred transition state, although not proof of it.

For a disubstituted acetylene inserting into palladium hydride bond via such a transition complex, the disposition of the acetylenic substituents with respect to the α and β positions of the alkenyl product would depend primarily on the polarity of the Pd-H bond. For $R_1=Ph$, $R_2=CF_3$ and $R_1=H$, $R_2=COOCH_3$ the electron-withdrawing substituent is unambiguously determined to be on the β-carbon of the alkenyl group. Thus the polarization of the transition state may be described as in B.



B

This contrasts with results obtained on acetylene insertion into Pt(II) systems. For the compounds trans-$PtX(H)(PEt_3)_2$ X=Cl,NO_3 the resulting alkenyl product always had the most electron-withdrawing substituent on the β-carbon[1] as is the case found here. However, for the cationic complex trans-$[Pt(H)(S)(PEt_3)_2]PF_6$ reversal of the substituents sometimes occurred to give a mixture of products.[1] In no case was this found for the products of the reaction of disubstituted acetylenes with the Pd hydrido-nitrate or the Pd hydrido-solvated cation. Moreover for the analagous platinum hydride cation trans-$[Pt(H)(S)(PCy_3)_2]PF_6$ the alkenyl group tended to have the stereochemistry with the more electron-withdrawing acetylenic substituent on the α-carbon. Thus, with $CF_3C{\equiv}CC_6H_5$ only a product with the CF_3 on the α-carbon is obtained[1]. To explain the difference between the two platinum hydrido-cations an argument based on the relative basicities of tricyclohexylphosphine and triethylphosphine was used. As tricyclohexylphosphine is more basic than triethylphosphine it will increase the electron density on platinum more so than triethylphosphine would.[20] Thus the charge difference between the platinum atom and the hydride could reverse leading to a transition state in which the platinum is more positively charged than is the hydride (equation 8). It appears that this increase in electron density on the metal when going from triethyl to tricyclohexylphosphine is not great enough in the case of palladium to cause the palladium atom to be positive in nature with respect to the hydridic hydrogen.



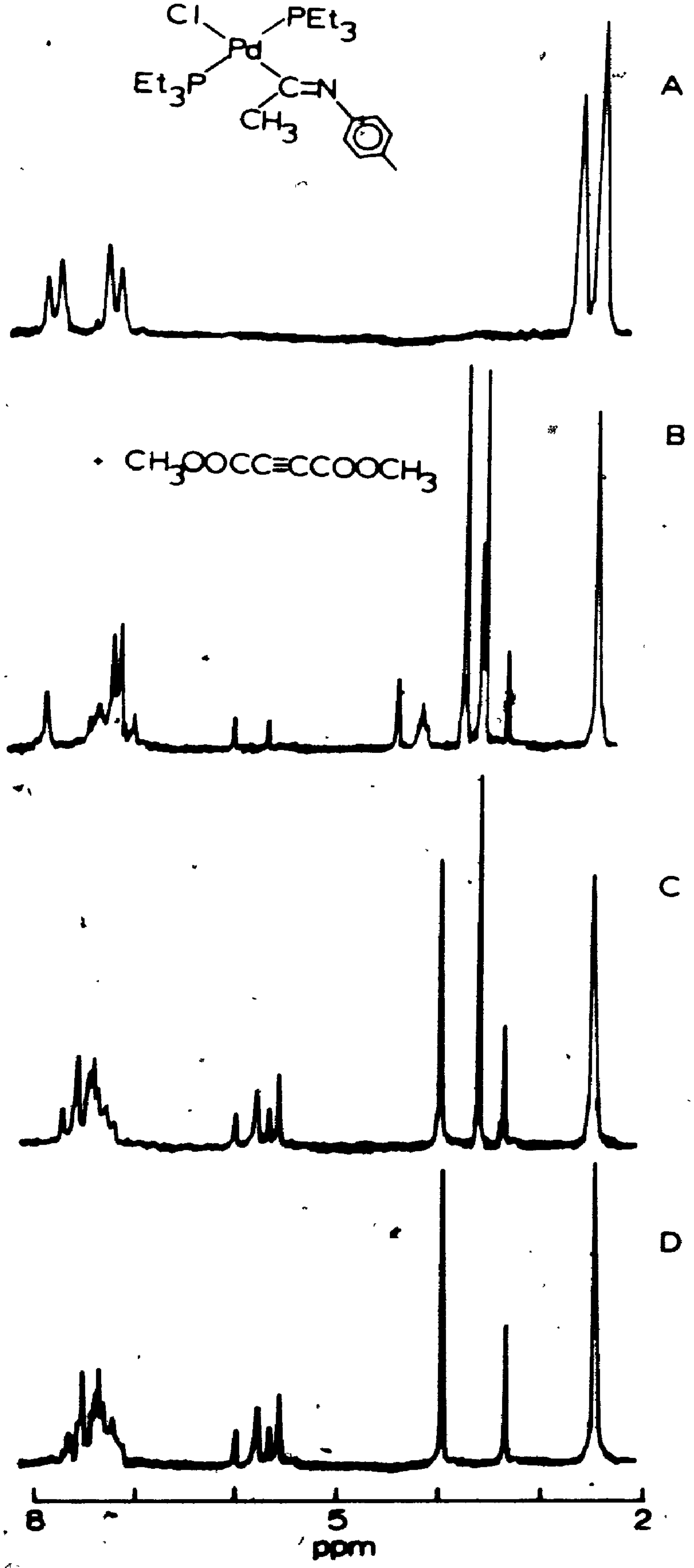
(8)

A second model for the insertion step involves actual migration of the hydridic hydrogen to the coordinated acetylene. In its extreme form, it could be regarded as a stepwise process involving prior cleavage of the Pd-H bond. Such cleavage might be heterolytic or homolytic.

That facile Pd-H cleavage may occur in the course of such reactions is readily demonstrated in the reaction of *trans*-$PdNO_3(H)(PCy_3)_2$ I with the acetylene $CF_3C{\equiv}CCF_3$ or DMA.

If a dichloromethane solution of the I is stirred under a one atmosphere pressure of $CF_3C{\equiv}CCF_3$ a reaction takes place which may be conveniently followed in the infrared spectrum. Over a period of a few hours the hydride band disappears and a new band due to the zero-valent complex $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ appears. Further reaction produces a band at 1616 cm^{-1} due to an alkenyl product.

These results could be explained if the insertion process occurs by a sequence of steps involving (a) reductive elimination of HPF_6 and formation of the zero-valent compound


Cl
PEt3
Pd
Et3P
C=N
CH3
A
B
+ CH3OOCC≡CCOOCH3
C
D
8
5
2
ppm

sponge$\cdot HNO_3$ salt precipitated. From the solution the zero-valent acetylene complex was isolated in high yields.

Thus, it appears that only for acetylenes containing two electron-withdrawing groups does an equilibrium between the Pd(II) hydride and the Pd(0) complex exist. The insertion "step" would then appear not to involve heterolytic cleavage of the Pd-H bond followed by protonation of the coordinated acetylene. For the acetylenes $RC{\equiv}CR$ ($R{=}CF_3$, $COOH_3$), the proton sponge drives the equilibrium (C) completely to the right. It is not surprising that only for the acetylenes $RC{\equiv}CR$ $R{=}CF_3$ or $COOCH_3$ do the equilibria between the Pd-hydride and the Pd(0) exist. The only Pd(0) acetylene complexes made so far, contain electron-withdrawing groups. The presence of the electron-withdrawing substituents assists in the stabilization of the zero-valent complex; attempts to prepare Pd(0) acetylene complexes using other acetylenes have resulted only in decomposition.

The zero-valent acetylene compound $Pd(RC{\equiv}CR)(PCy_3)_2$ reacted with HCl to form the alkenyl compound. Presumably, the addition of acid regenerates the palladium hydride which can then undergo insertion. Such protonation reactions to form alkenyl derivatives are quite common for the platinum zero-valent acetylene complexes $Pt(RC{\equiv}CR)(PR_3)_2$.[21]

The $\nu(C{\equiv}C)$ of $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ comes at 1762 cm^{-1} in the infrared spectrum, one of the lowest values for a Pd(0) acetylene complex. For a series of related metal π-

acetylene complexes the $\nu(C\equiv C)$ has an inverse relationship to the bend back angle of the substituents on the acetylene.[22] This bend back angle is caused either by an electronic factor or by a steric factor. In this case the large bulky phosphine ligands may sterically force the substituents on the acetylene away from linearity causing the low value of $\nu(C\equiv C)$. An X-ray study of this compound is in progress to determine such steric effects.[23]

e) Experimental

Palladium powder was obtained from Johnson Matthey Mallory Ltd. and $NaBH_4$ from Fisher Scientific. Tricyclohexylphosphine was purchased as the carbon disulphide adduct from Strem Chemicals Inc. and was decomposed to the free phosphine by refluxing in ethanol. $CH_3C\equiv CCOOCH_3$ was obtained by the methylation of tetrolic acid with methanol using sulphuric acid as a catalyst and was purified by distillation under vacuum. $CF_3C\equiv CPh$ was kindly provided by Dr. C.S. Wong.

All reactions involving palladium hydride complexes were carried out under an inert atmosphere using standard techniques.[24] Solvents were dried over molecular sieves and degassed by the freeze-thaw method prior to use.

i) Preparation of $Pd(NO_3)_2$[25]

Palladium powder (2.0 g) was dissolved in 5 ml. of concentrated nitric acid. The resulting deep red-brown solution was very carefully taken to dryness on a hot plate to give a dark brown crystalline mass. The crystals were transferred to a dessicator and stored therein.

ii) Preparation of trans-$Pd(NO_3)_2(PCy_3)_2$[12]

To a slurry of tricyclohexylphosphine (4.86 g) in 50 ml. of ethanol at -40°C was added solid $Pd(NO_3)_2$(2.00 g). The solution was stirred at -40°C for two hours and then warmed to room temperature. The bright yellow precipitate was filtered and washed with ether to give trans-$Pd(NO_3)_2$-$(PCy_3)_2$. Yield was 6.40 g (93%).

iii) Preparation of trans-$PdNO_3(H)(PCy_3)_2$[12]

Trans-$Pd(NO_3)_2(PCy_3)_2$ (5.00 g) was dissolved in a mixture of 150 ml. of benzene and 75 ml. of ethanol and the solution cooled to 0°C. $NaBH_4$(0.241 g) in ethanol (20 ml.) was added dropwise. The solution became dark brown and after the addition was complete the solution was stirred for 24 hours at room temperature.

The solution was then filtered and the solvents removed under vacuum to give a dark brown solid. This solid was placed on a frit and washed with 2 x 10 ml. portions of ice-cold degassed acetone to give a grey-white solid. Yield was 3.86 g (84%).

iv) Preparation of trans-$PdCl(H)(PCy_3)_2$.

Trans-$PdNO_3(H)(PCy_3)_2$ (3.00 g) and Et_4NCl (3.4 g) were dissolved in dichloromethane and stirred for an hour. The solvent was removed and the residue extracted with three 50 ml portions of benzene. The benzene extracts were reduced to a small volume and pentane added to induce crystallization. Yield was 2.19 g (76%).

v) Preparation of trans-$[Pd(H)CH_3CN(PCy_3)_2]PF_6$

To a suspension of trans-$PdCl(H)(PCy_3)_2$ (1.00 g) in acetonitrile (10 ml) was added $AgPF_6$(0.359 g) in 3 ml. of acetonitrile. The thick white precipitate of silver chloride was removed by centrifugation to give a clear solution. This solution was concentrated and dichloromethane (4 ml) added. After filtration through celite diethyl ether was added to the filtrate to produce white crystals. Yield was 0.96 g (79%).

vi) Preparation of trans-$PdNO_3[RC{=}C(R^1)H](PCy_3)_2$

Trans-$PdNO_3(H)(PCy_3)_2$ (0.250 g) was dissolved in dichloromethane (10 ml) and one equivalent of the appropriate acetylene was added. After 4 hours the solvent was removed and the residue taken up in benzene, and passed through a column containing florisil. Methanol was added to the filtrate to give white crystals of the vinylic product. In this way were prepared

trans-$PdNO_3[CH_3C{=}C(COOCH_3)H](PCy_3)_2$ (73% yield)
trans-$PdNO_3[PhC{=}C(COOCH_3)H](PCy_3)_2$ (71% yield)
trans-$PdNO_3[PhC{=}C(CF_3)H](PCy_3)_2$ (65% yield)
trans-$PdNO_3[HC{=}C(COOCH_3)H](PCy_3)_2$ (68% yield)

vii) Preparation of trans-$PdNO_3[CF_3C{=}C(CF_3)H](PCy_3)_2$

Trans-$PdNO_3(H)(PCy_3)_2$ (0.250 g) was dissolved in 0.5 ml. of CD_2Cl_2 and the solution transferred to a thick-walled nmr tube. A large excess of the acetylene $CF_3C{\equiv}CCF_3$ was condensed into the tube and the tube sealed. The ^1H nmr spectrum was monitored. The appearance of a

1:3:3:1 quartet in the region of 5-6 ppm indicated that a vinylic product was being formed. After 4 hours this signal ceased to gain in intensity. At this point the tube was opened and the contents chromatographed on a silica gel column. Elution with diethyl ether gave two bands. The second band contained the title compound in 45% yield. The first band contained too little material for identification.

viii) Preparation of $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$

a) Trans-$PdNO_3(H)(PCy_3)_2$ (0.250 g) in dichloromethane (10 ml.) was stirred under an atmosphere of $CF_3C{\equiv}CCF_3$. After 8 hours the solvent was removed and the residue recrystallized from benzene/methanol to give white crystals of the acetylene complex in 45% yield.

b) A benzene solution (10 ml.) of trans-$PdNO_3(H)$-$(PCy_3)_2$ (0.300 g) and proton sponge (.088 g) was stirred under one atmosphere pressure of hexafluoro-2-butyne. After several minutes a white precipitate, identified as the acid salt of the proton sponge, was apparent. This precipitate was filtered off and the filtrate passed through a column containing florisil. The eluent was taken to dryness and recrystallized from benzene/methanol to give white crystals of the title compound. Yield was 0.211 g (62%).

ix) Preparation of $Pd[CH_3OOCC{\equiv}CCOOCH_3](PCy_3)_2$

To a benzene solution (10 ml.) of trans-$PdNO_3(H)$-$(PCy_3)_2$ (0.300 g) and proton sponge (.088 g) was added

50 μl of $CH_3OOCC{\equiv}CCOOCH_3$. After several minutes a white precipitate, identified as the acid salt of the proton sponge, was apparent. This precipitate was filtered off and the filtrate passed through a column containing florisil. The eluent was taken to dryness and recrystallized from dichloromethane/methanol to give cream crystals of the title compound. Yield was 0.261 g (78%).

x) Preparation of trans-$PdCl[RC{=}C(R^1)H](PCy_3)_2$

To a solution of trans-$[Pd(H)(CH_3CN)(PCy_3)_2]PF_6$ (0.250 g) in 10 ml. of dichloromethane, acetonitrile or acetone was added one equivalent of acetylene. After 3 hours an excess of LiCl dissolved in methanol was added and the solvents then removed. The product was extracted from the residue with benzene and precipitated as white crystals upon the addition of methanol. In this way were prepared

trans-$PdCl[CH_3C{=}C(COOCH_3)H](PCy_3)_2$ (68% yield)
trans-$PdCl[PhC{=}C(COOCH_3)H](PCy_3)_2$ (65% yield)
trans-$PdCl[PhC{=}C(CF_3)H](PCy_3)_2$ (61% yield)
trans-$PdCl[HC{=}C(COOCH_3)H](PCy_3)_2$ (72% yield)

xi) Preparation of trans-$PdCl[CF_3C{=}C(CF_3)H](PCy_3)_2$

To a dichloromethane solution (10 ml) of $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ (0.200 g) was added acetyl chloride (17.2 μl) in methanol (5 ml.). The reaction mixture was stirred for 3 hours during which time the solution lightened in colour. Removal of the solvents followed by recrystallization of the residue afforded white crystals of the vinylic product. Yield was 0.120 g (57%).

(f)

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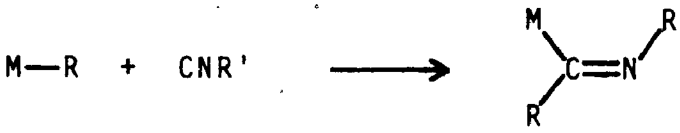
CHAPTER V

THE CHARACTERIZATION OF A PRODUCT DERIVED FROM THE REACTION OF A CARBON-BONDED METAL IMINE WITH DIMETHYLACETYLENEDICARBOXYLATE; EVIDENCE FOR KETIMINE-ENAMINE TAUTOMERISM IN A CARBON-BONDED METAL IMINE

a) Introduction

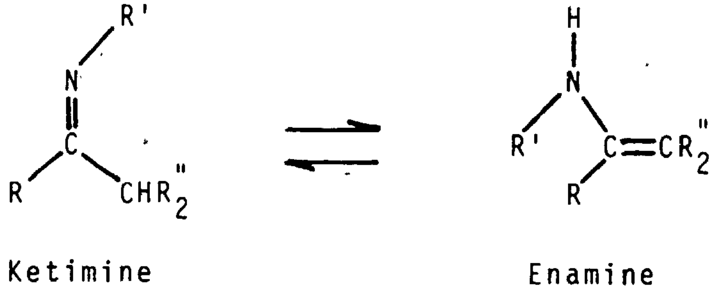
The reaction of isocyanide with an alkyl transition metal complex often results in migratory insertion of the isocyanide into the metal-carbon bond[1] to produce an imine, bonded to the metal via a carbon atom (equation 1).



(1)

Insertion into carbon-molybdenum[2], -iron[3], -cobalt[4], -platinum[5,6], -palladium[7,8,9] and -nickel[10] bonds has been reported.

A great deal of chemistry is associated with the imine function in organic chemistry.[11,12] In particular, if at least one of the substitutents on the α carbon of the imine is a hydrogen atom, tautomerism occurs between an enamine form and a ketimine form (equation 2).

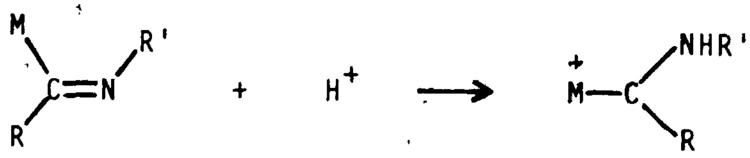


(2)

For organic imines the imine usually exists mostly in the ketimine form but can undergo reactions which are characteristic of an enamine or characteristic of a ketimine.

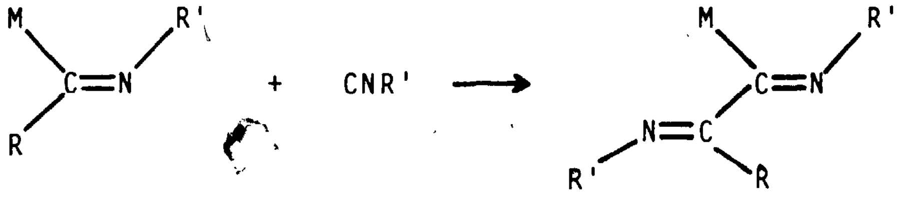
However, for transition metal carbon-bonded imine species, which possess α hydrogen atoms, ^1H nmr and infrared studies show only the presence of the ketimine form.[5-9] Reactions of transition metal carbon-bonded imine species are limited to two types, neither of which indicate the presence of an enamine tautomer.

Protonation or alkylation of the nitrogen atom of the imine results in formation of a carbene ligand.[13,14] (equation 3)



(3)

Addition of isocyanide sometimes results in further insertion to give a new imine species.[8,15] (equation 4)


(4)

During our work on the migratory insertion reactions of substituted acetylenes with palladium complexes containing a metal-carbon bond, we tried to react substituted acetylenes with the carbon-bonded imine, trans-PdCl[CH_3C=N p-tolyl]$(PEt_3)_2$. A rapid reaction occurred with the acetylene $CH_3OOCC{\equiv}CCOOCH_3$ or with the acetylene $CF_3C{\equiv}CCF_3$. However, the products obtained from these reactions were not those derived from insertion of the acetylene into the palladium-carbon bond. Rather their formation appeared to be a result of direct reaction of the acetylene with the imine function, the metal atom playing no role in the process. In particular, the nature of the products was such that their formation was best explained by a reaction sequence which had proceeded through the enamine tautomer of the imine.

This chapter deals with the characterization of the products of the reaction of the acetylenes $CH_3OOCC{\equiv}CCOOCH_3$ and $CF_3C{\equiv}CCF_3$ with the imine trans-PdCl(CH_3C=N ptolyl)-$(PEt_3)_2$ and with the elucidation of the reaction sequence of their formation.

b) Results and Discussion

The carbon-bonded imine complex trans-PdCl(CH_3C=NR)-

$(PEt_3)_2(I)$*, reacts readily, in chloroform, with the acetylene $CH_3OOCC{\equiv}CCOOCH_3$ (DMA) to eliminate methanol and form two new compounds II and III. The formation of II proceeds through an intermediate IIa, which is detectable by ^1H nmr and infrared spectroscopy and which has not yet eliminated methanol (equation 5).

$$\mathrm{I} + CH_3OOCC{\equiv}CCOOCH_3 \longrightarrow \mathrm{IIa} + \mathrm{III} \longrightarrow \mathrm{II} + \mathrm{III} + CH_3OH \qquad (5)$$

A set of ^1H nmr spectra showing the formation of and subsequent reaction of the intermediate IIa to give II is shown in Figure V-1.

Compounds II and III could be isolated by chromatography of the reaction mixture on silica gel to give orange and red crystals respectively. Both compounds were exceedingly stable both in solution and in the solid state.

The spectroscopic properties of compounds II and III are very similar. Each infrared spectrum (Table V-1) shows bands at 3040 cm^{-1} due to olefinic-type hydrogen stretching modes, a band at 1720 cm^{-1} due to an ester carbonyl group

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* R = *p*-tolyl

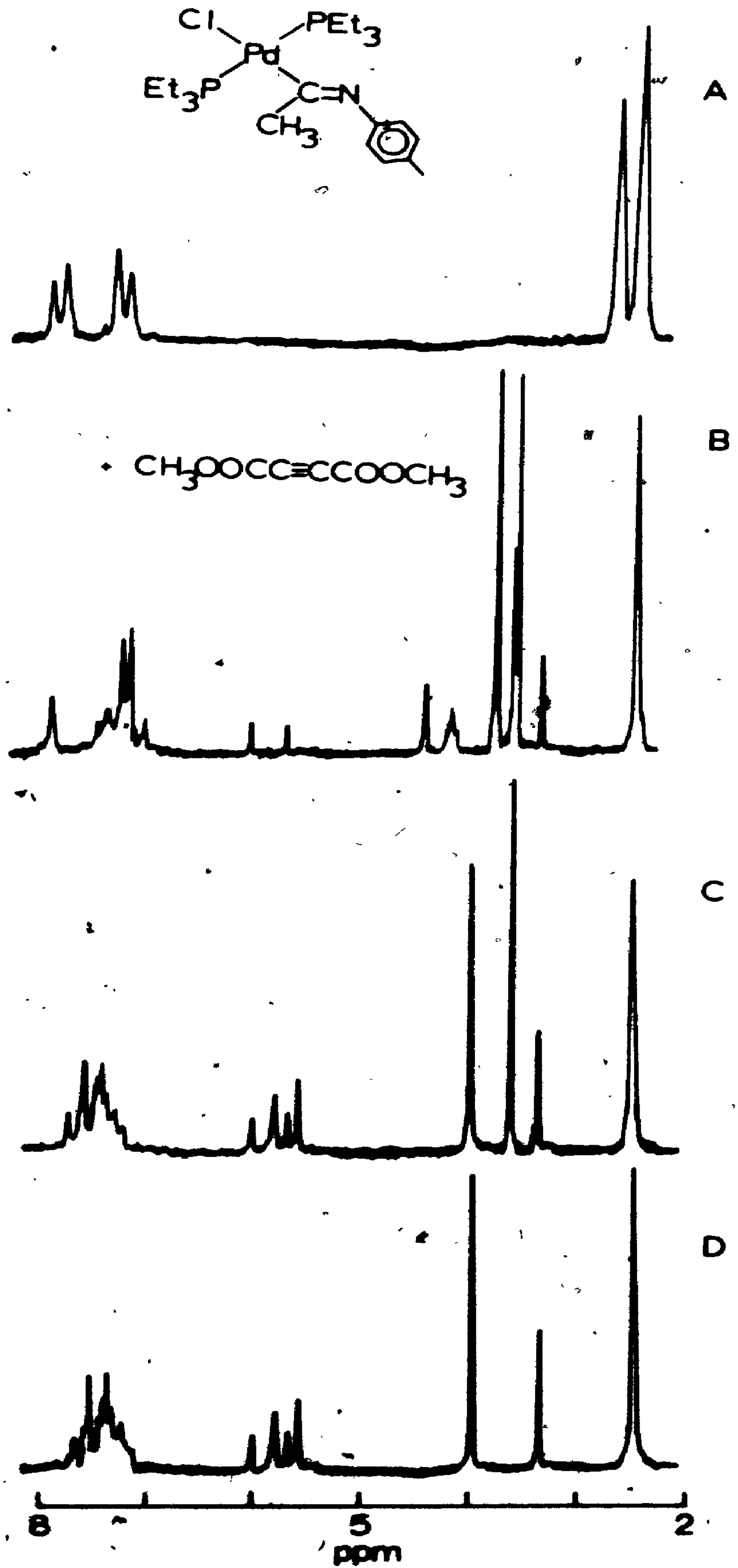
Figure V-1. An ^{1}H nmr study of the reaction of <u>trans</u>-Pd Cl[CH_3C=N<u>p</u>-tolyl]$(PEt_3)_2$ with DMA. All spectra also contain peaks between 1 and 2 ppm due to the phosphine ethyl hydrogens.

A. ^{1}H nmr spectrum of <u>trans</u>-PdCl[CH_3C=N<u>p</u>-tolyl]-$(PEt_3)_2$ (I)

B. ^{1}H nmr spectrum of I, ten minutes after the addition of DMA.

C. ^{1}H nmr spectrum of I, 24 hours after the addition of DMA.

D. ^{1}H nmr spectrum of the product obtained from C after the removal of all volatile products.


Cl
PEt$_3$
Pd
Et$_3$P
C=N
CH$_3$
A
B
CH$_3$OOCC≡CCOOCH$_3$
C
D
8
5
2
ppm

and at 1660 and 1625 cm^{-1} due to ketonic and carbon-carbon double bond stretching vibrations respectively.

In the ^1H nmr spectra (Table V-1), both compounds II and III have signals between 1-3 ppm due to mutually trans-triethylphosphine ligands, at 3.14 and 3.82 ppm respectively due to a methoxy ester group, as well as the characteristic peaks of a p-tolyl group. Two olefinic hydrogen resonances in the region of 5.4-5.9 ppm are observed for each product.

Possible structures for the compounds II and III are developed in Figure V-2. Structures IV-VI result from elimination of methanol at the nitrogen atom to form the six- and five-membered cyclic lactams, while structures VII-IX are formed by elimination of methanol at the carbon β to the palladium atom.

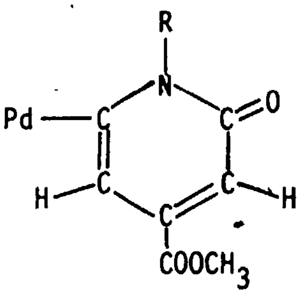
To assist in the determination of the correct structures the ^{13}C nmr spectrum was run for each of the products (Table V-2). The two spectra are very similar. Signals at 7.5 and 14.5 ppm can be assigned to the ethyl carbons of the triethylphosphine ligands at 20.7 ppm to the methyl carbon of the p-tolyl group, at 124, 130, 136 and 141 ppm to the p-tolyl aromatic carbons, at 52 ppm to a methoxy ester carbon, at 100 and 110 ppm to olefinic carbons each of which are bonded to one hydrogen, at 142 ppm to an olefinic carbon bearing no hydrogens and at 166 ppm to an ester carbonyl carbon.[16] Two resonances at 182 and 205 ppm remain. If the resonance at 205 ppm is assigned to the carbonyl carbon in the ring and the

TABLE V-1 Infrared and NMR Data for New Compounds[a]

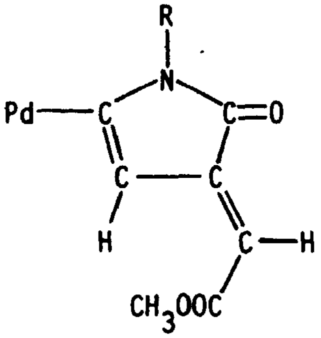
Complex	Ir Frequencies	^{1}H NMR Signals		^{19}F NMR Signals	
II	ν(C=O) 1728,1667	Me(tolyl)	2.34		
	ν(C=C) 1631	OMe	3.82		
		C=CH	5.43,5.65		
III	ν(C=O) 1716,1664	Me(tolyl)	2.34		
	ν(C=C) 1621	OMe	3.19		
		C=CH	5.53,5.85		
IIa	ν(C=O) 1731,1682	Me(tolyl)	2.35		
		OMe	3.43,3.60		
		C=CH$_2$	4.03,4.25		
		C=CH	7.73		
X		Me(tolyl)	2.25	CF$_3$^{2}	57.61,57.68
		C=CH$_2$	4.15,4.42	CF$_3$^{1}	58.35,58.45
		C=CH	6.32 J(F^1-H)=8.75		
XIa		Me(tolyl)	2.38		
		OMe	3.76,3.84		
		PdC(Me)	3.03 J(P-H)=2.0		
		C=CH	7.16		
XIb		Me(tolyl)	2.30		
		OMe	3.69,3.78		
		PdC(Me)	2.79 J(P-H)=2.0		
		C=CH	7.16		

[a] ^{1}H nmr signals in positive ppm downfield from TMS; coupling constants in Hz.

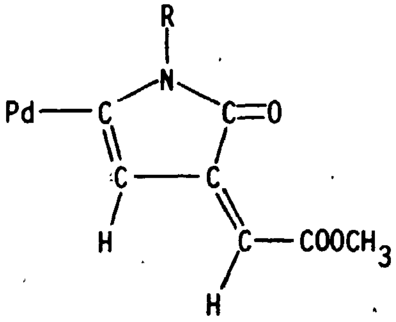
Figure V-2. Possible structures for compounds II and III. Other ligands on palladium have been omitted for the sake of clarity. R = *para*-tolyl.



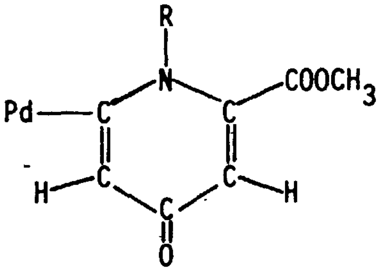
IV



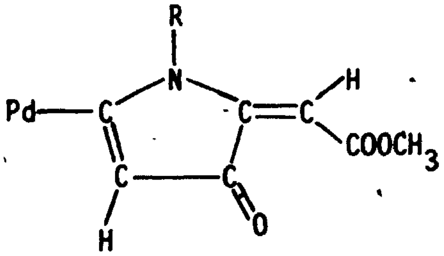
V



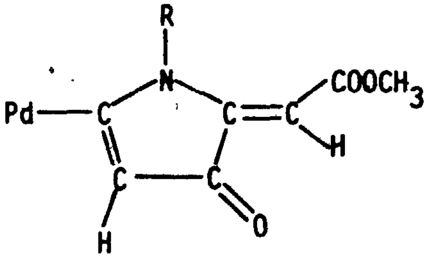
VI



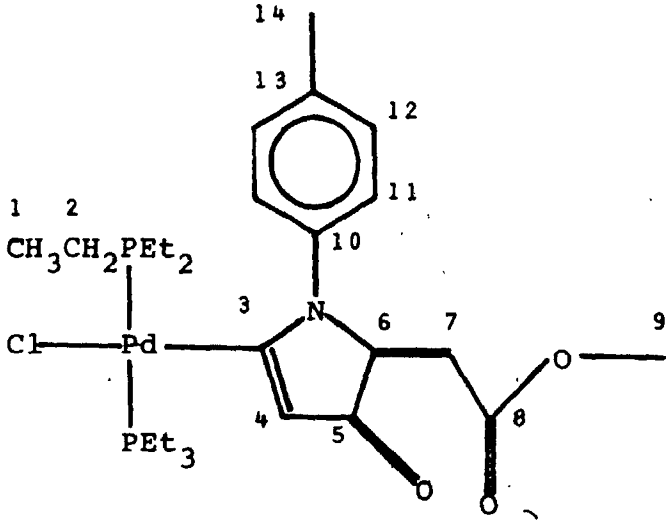
VII



VIII



IX



Numbering scheme for the ^{13}C nmr spectrum of II and III. For III the ester group is on the other side of the double bond between carbons 6 and 7.

TABLE V-2

^{13}C NMR Data for Compounds II and III[a,b,c]

Carbon	δ(III)	δ(II)
1	7.6 (q)	7.8 (q)
2	14.4[d] (t,t)	14.6[d] (t,t)
3	181.4	184.4
4	101.7 (d)	98.5 (d)
5	202.2[e]	205.1
6	141.7[f]	141.8[f]
7	109.6 (d)	110.5 (d)
8	166.8	165.6
9	52.0 (q)	51.3 (q)
10	138.2[f]	141.8[f]
11	124.2 (d)	123.7 (d)
12	129.7 (d)	129.5 (d)
13	136.5	135.9
14	20.6 (q)	20.8 (q)

[a] All chemical shifts in positive ppm downfield from TMS.

[b] Numbers in brackets refer to the appearance of the ^{13}C spectrum when not hydrogen decoupled; q = quartet, t = triplet, d = doublet.

[c] Numbering scheme is given on the facing page.

[d] Also coupled to phosphorus J(P-C) = 14.5 Hz.

[e] Coupled to ^{14}N J(N-C) = 6.3 Hz.

[f] These values may be reversed.

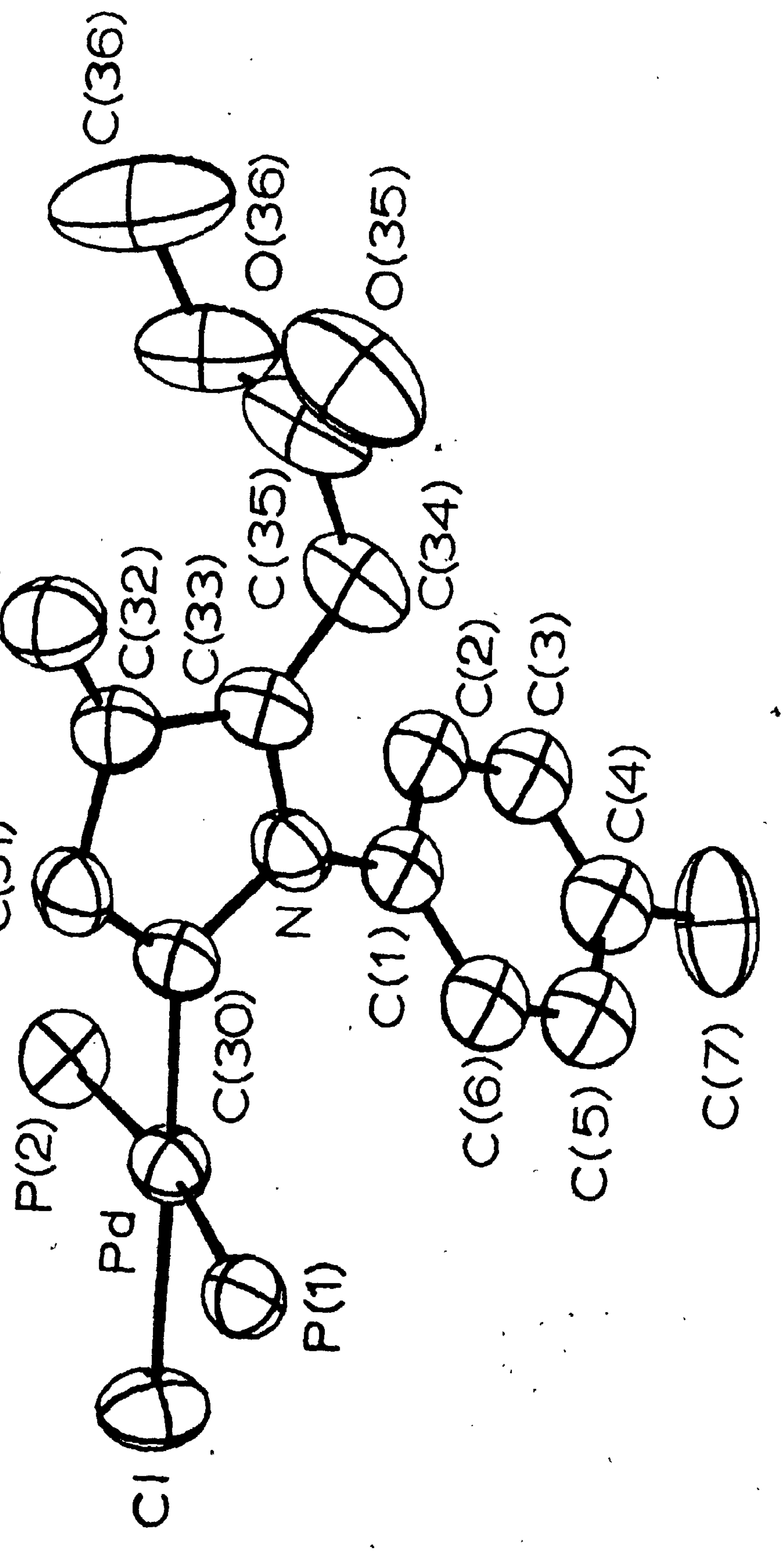
resonance at 182 ppm to the carbon bonded to the palladium, structures IV-VI are very unlikely to be correct as the carbonyl carbon of a lactam has a ^{13}C chemical shift of about 160 ppm. Of structures VII-IX, those of VIII and IX fit the given assignments quite well. For example, the β-carbon of the α-β unsaturated five-membered cyclic ketone 1-methylcyclopentene-3-one has a ^{13}C chemical shift of 179.4 ppm and the carbonyl carbon a shift of 208 ppm.[17] However, 1-methylcyclohexene-3-one which is analogous to structure VII has ^{13}C chemical shifts of 162.2 and 197 ppm for the β and carbonyl carbon atoms[17].

To confirm the identity of II an X-ray crystallographic study was undertaken (Chapter VI).

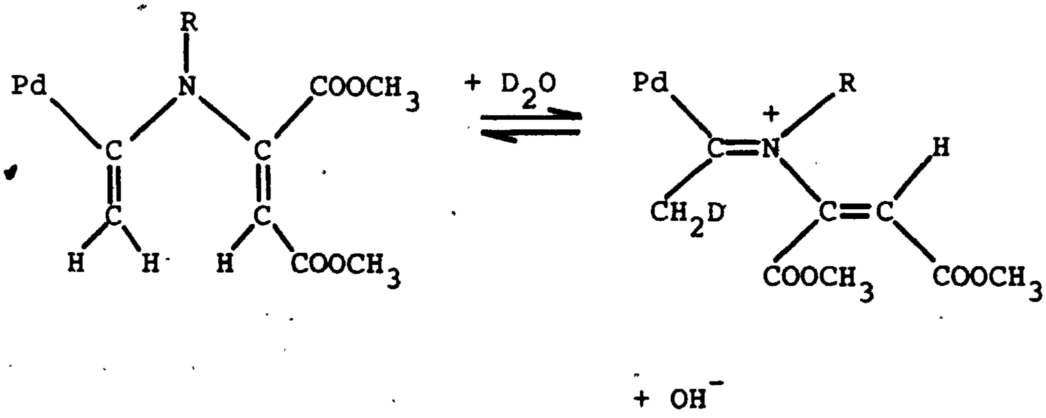
The result of this study showed the structure of II contained a five-membered ring in which MeOH had been eliminated at the carbon β to the palladium atom (structure VIII) and with the two carbonyl groups <u>cis</u> about the exocyclic double bond. An ORTEP drawing of the molecule is shown in Figure V-3.

A possible mechanism to account for the formation of II is one which involves the enamine form of the carbon-bonded metal imine(I). The N-H fragment of the enamine can add across the triple bond of the acetylene to give the intermediate IIa.[18] The original double bond of the enamine can now act as a nucleophile and attack one of the carbonyl carbon atoms to eliminate methanol to form II

Figure V-3. ORTEP drawing of the molecular structure of II.

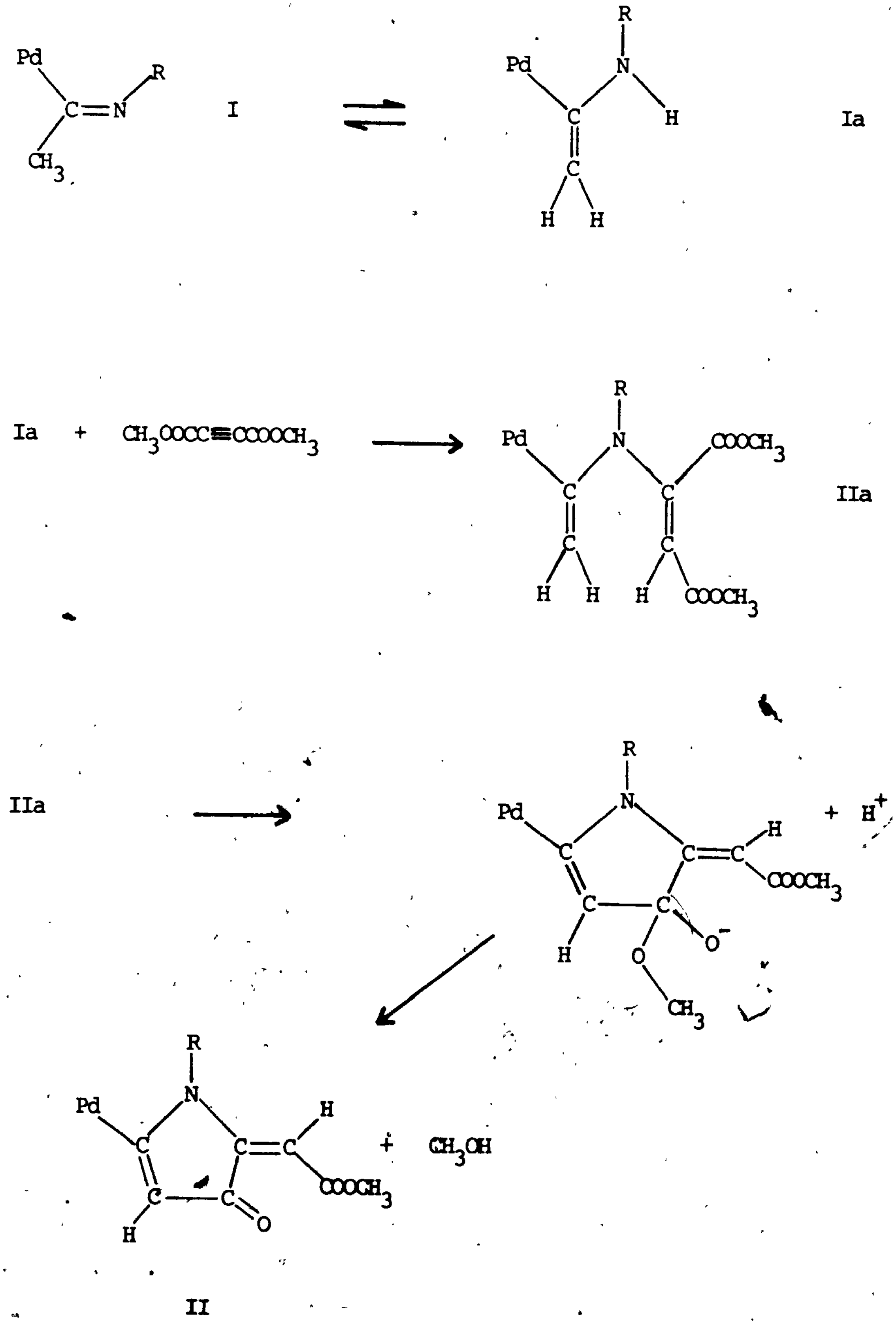

C(36)
O(36)
O(35)
C(35)
C(34)
O(32)
C(32)
C(33)
C(31)
N
C(2)
C(3)
C(4)
C(1)
C(30)
C(6)
C(5)
C(7)
P(2)
Pd
P(1)
Cl

(Figure V-4). Support for this mechanism is found in four experimental observations. Firstly, the protons of the methyl group on the imine(I) exchange with D_2O to give the deuterated species, $PdCl(CD_3C{=}N$ p-tolyl$)(PEt_3)_2$. This strongly implies the existence of the ketimine-, enamine tautomerism. Secondly the ^1H nmr and infrared data of the observed intermediate IIa (Table V-1) are consistent with the proposed intermediate. The ^1H nmr of IIa has in addition to resonances due to trans-triethylphosphine ligands and a p-tolyl group, two signals at 3.43 ppm and 3.60 ppm assigned to two sets of methoxy protons and three uncoupled resonances at 4.03, 4.25 and 7.73 ppm due to olefinic protons. The absence of an N-H stretch in the infrared precludes any of these being due to amino hydrogens. Furthermore the two protons at 4.03 and 4.25 ppm exchange with D_2O. The proposed intermediate also possesses two geminal protons which should readily exchange with D_2O through a mechanism involving a quaternary nitrogen atom (equation 6).



(6)

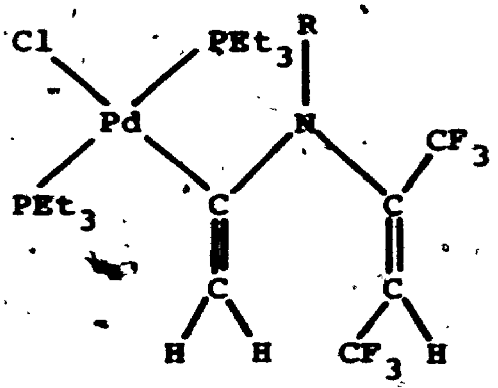
Figure V-4. Reaction scheme for the formation of II. Other ligands on palladium have omitted for the sake of clarity. R = <u>para</u>-tolyl.


Pd
C=N
R
CH3
I
Pd
R
N
H
C
C
H H
Ia
Ia + CH3OOCC≡CCOOCH3
Pd
R
N
COOCH3
H H H COOCH3
IIa
IIa
Pd
R
N
H
COOCH3
H
O-
O
CH3
+ H+
Pd
R
N
H
COOCH3
H
O
+ CH3OH
II

Thirdly, the starting imine(I) reacts with hexafluoro-2-butyne to give a rather unstable product (X) which can be characterized by its ^1H and ^{19}F nmr spectra (Table V-1). The ^1H nmr spectrum of this product has peaks between 1-3 ppm due to mutually <u>trans</u> triethylphosphine ligands, at 2.3 and 7.0 ppm due to a p-tolyl group as well as three signals at 4.15, 4.42 and 6.32 ppm due to olefinic protons. The latter resonance is a 1:3:3:1 quartet due to coupling to the fluorine atoms of a CF_3 group. The two high field olefinic protons exchange with D_2O. The ^{19}F nmr spectrum consists of two sets of resonances in the ratio of 1:4. The more intense set is comprised of two equally intense signals, a singlet at 57.51 ppm and a doublet at 58.35 ppm. The weaker set is also comprised of two equally intense signals, a singlet at 57.68 ppm and a doublet at 58.45 ppm. The doublet appearance of one of the signals in each set is due to the coupling to the olefinic hydrogen at 6.32 ppm. The lack of coupling between the CF_3 groups implies that the CF_3 groups are <u>trans</u> to each other about a double bond.[19] Each of these sets of signals is consistent with a structure similar to that of the intermediate IIa except that the addition of the enamine has been <u>trans</u> across the triple bond.

The presence of two sets of signals in the ^{19}F nmr spectrum can be explained if there is restricted rotation about the vinyl carbon-nitrogen bond or about the nitrogen-carbon bond of the carbon bonded to the palladium atom.

Either of these situations would create two geometrical isomers. The ^1H chemical shifts of the olefinic protons are not sensitive enough to determine a difference between these isomers, although it appears that the ^{19}F chemical shifts are.



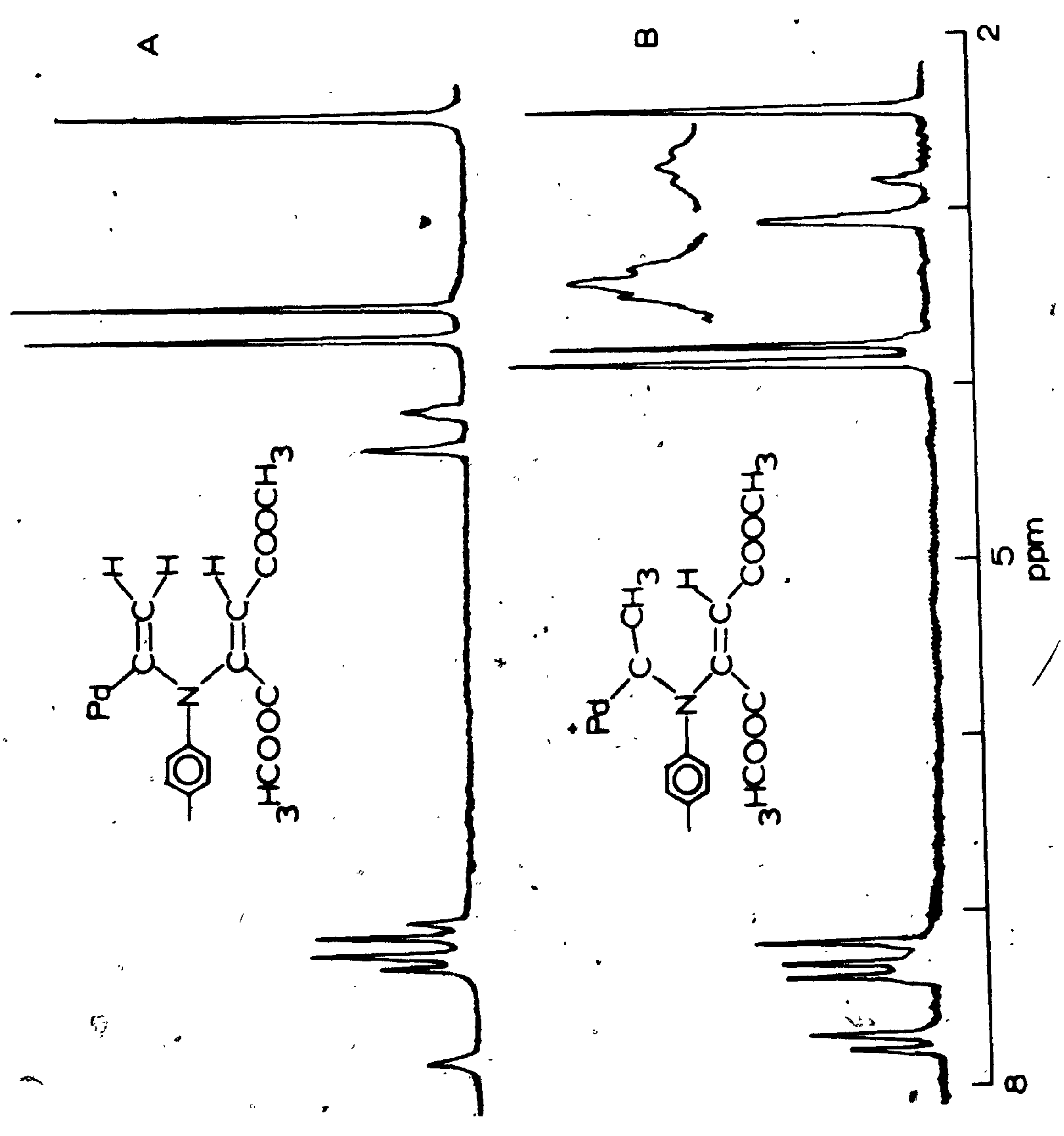
X

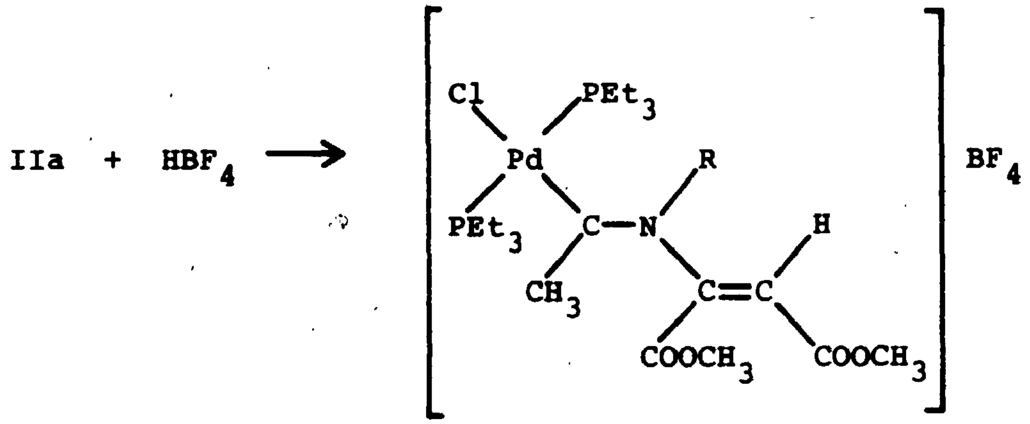
Fourthly, if a solution of the intermediate IIa in $CDCl_3$ is treated with HBF_4 the ^1H nmr spectrum changes. The original resonances of IIa are replaced by two new sets of signals XIa and XIb in the ratio of 4:1. The basic pattern is the same for each of these new sets as for the original set belonging to IIa, except that the signals for the two high field olefinic protons are absent (Table V-1). Instead, for each set a peak corresponding to an intensity of three protons at around 2.8 ppm is observed which is a 1:2:1 triplet due to coupling to the mutually trans phosphorus atoms (Figure V-5). This result is consistent with the proposed structure of the intermediate IIa. A proton of the acid adds to the geminal carbon of the olefin to form a carbene (equation 7).

Figure V-5. Reaction of the intermediate IIa with HBF_4.

A. ^1H nmr spectrum of IIa. Signals for the phosphine ethyl hydrogens and for III not shown.

B. ^1H nmr spectrum of IIa on addition of HBF_4.

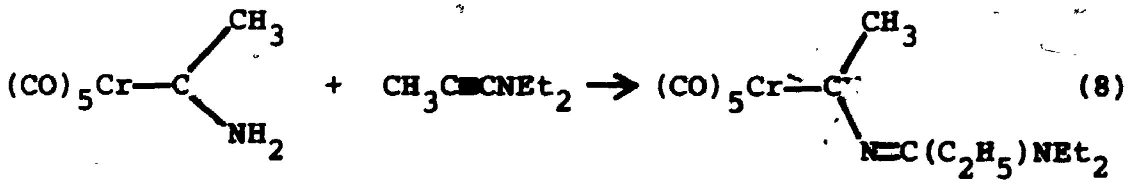

A
B
2
5
ppm
8



(7)

Two isomers are possible due to restricted rotation about the C-N bond of the carbene ligand, a phenomenon common to many carbene complexes of transition metals.[20]

Although addition of primary or secondary amines across the triple bonds of acetylenes is common in organic chemistry[18], reactions involving amines associated with transition metal complexes are few. Recently Dötz[21] observed the addition of the N-H_2 fragment of a chromium carbene complex across an acetylene (equation 8) to form



(8)

a new carbene substituted at the heteroatom of the carbene. It thus appears that the addition of N-H across unsaturated organic molecules may be useful in producing novel organometallic compounds. It is also interesting to note that the similar platinum-carbon bonded imine *trans*-PtCl($CH_3C=N$(*p*-tolyl))($PMe_2Ph)_2$, reacts with DMA to give analogous products. The methyl protons of this platinum imine also exchange in D_2O. However, the imine trans-PtCl($CH_3C=N$(p-tolyl))(PPh_3)$_2$ does not react with DMA and the methyl protons do not exchange in D_2O. This implies that a necessary criterion for the reaction of metal-carbon bonded imines with acetylenes to form heterocycles is the presence of exchangeable α-protons which allow the presence of a ketimine-enamine tautomerism to form the reactive enamine tautomer.

The identity of the minor species III is not certain, but in view of its very similar spectroscopic properties to those of II and the observation that if a solution of pure III or II in $CDCl_3$ is left to stand for a few days, small amounts of the other product are formed, it seems that it has structure VII in which the carbonyl groups are trans about the double bond. The same mechanism for the formation of III as for II is possible, except that the addition of the enamine across the triple bond has occurred in a trans-fashion as was observed for the reaction of I with hexafluoro-2-butyne.

c) Experimental

^{13}C spectra were recorded in $CDCl_3$ on an XL-100 spectrometer using TMS as an internal standard. Trans-PdCl($CH_3C=N$ p-tolyl)(PEt_3)$_2$ was prepared as in Chapter II.

i) Reaction of trans-PdCl($CH_3C=N$ p-tolyl)(PEt_3)$_2$ with dimethylacetylenedicarboxylate (DMA).

To 0.500 g of the imine (I) in $CDCl_3$ was added one equivalent of DMA and the reaction monitored by ^{1}H nmr. An immediate reaction occurred with the disappearance of the methyl resonance of the imine and of the methoxy ester resonance of the acetylene to give two distinct sets of new signals IIa and III. The less intense set, III, had signals at 2.34, 3.19, 3.30, 5.53 and 5.85 ppm in the relative ratios of 3:3:3:1:1, as well as peaks in the region of 1-3 ppm and 7 ppm characteristic of triethylphosphine ligands and the aromatic protons of the p-tolyl group. The more intense set, IIa, had signals at 2.35, 3.43, 3.60, 4.03, 4.25 and 7.73 ppm in the ratios of 3:3:3:1:1:1, along with peaks between 1-3 ppm and at 7 ppm due to trans triethylphosphine ligands and the aromatic protons of the p-tolyl group. Over a period of 24 hours the intensities and positions of the weaker set of signals III remained constant, while those of set IIa slowly vanished with the formation of a new set of resonances, II, at 2.34, 3.82, 5.43 and 5.65 ppm in the ratio of 3:3:1:1, as well as the peaks of an aromatic AB quartet at 7.21 ppm and peaks between 1-3 ppm indicative of trans phosphine ligands. A peak of intensity 3 also appeared at exactly the same chemical shift (3.30 ppm) as that of one of the peaks of the less intense set III. Upon removal of the solvent and redissolution in $CDCl_3$, the ^{1}H nmr spectrum was exactly the same except that the signal at 3.30 ppm was absent for both species. Addition of methanol regenerated this peak, and thus it was attributed to methanol which had been formed in the reaction. The solvent was removed and the dark red-orange product chromatographed on silica gel using diethyl ether as the eluent. Two bands were observed in the ratio of 1:4. The first band which contained the smaller product gave dark, red-orange crystals. Their ^1H nmr spectrum was identical to that of set III, except that the peak at 3.30 ppm ascribed to methanol was absent. M.p. 165° Anal. Calcd. for $C_{26}H_{42}ClNO_3P_2Pd$: C, 50.33; H, 6.82; N, 2.26. Found: C, 50.22; H, 6.68; N, 2.36. The second band which contained the major product gave yellow-orange crystals. Their ^1H nmr spectrum was identical to that of set II except that the peak at 3.30 ppm ascribed to methanol was missing. M.p. 176° Anal. Calcd. for $C_{26}H_{42}ClNO_3P_2Pd$: C, 50.33; H, 6.82; N, 2.26; Found: C, 50.06; H, 6.76; N: 2.31.

(ii) Reaction of the intermediate IIa with D_2O.

A mixture of the intermediate IIa and III in $CDCl_3$ solution was prepared as above. D_2O was added and the ^1H nmr spectrum monitored. After 2 hours the signals at 4.03 and 4.23 ppm belonging to the intermediate IIa had disappeared and a signal at 4.62 ppm due to DOH was observed. Further reaction occurred to produce IIa with deuterium incorporated only for the signal at 5.65 ppm.

(iii) Reaction of trans-$PdCl(CH_3C{=}N$ p-tolyl$)(PEt_3)_2$ with D_2O.

A solution of the imine in $CDCl_3$ together with a large excess of D_2O was shaken in an nmr tube and the ^1H nmr spectrum monitored. After two hours the methyl peak of the imine had vanished and a signal at 4.61 ppm due to DOH was observed.

iv) Reaction of trans-PdCl(CH_3C=N p-tolyl)(PEt_3)$_2$ with hexafluoro-2-butyne.

Hexafluoro-2-butyne was bubbled through a chloroform solution of I for several minutes. The solution was stirred for an additional 10 minutes and then stripped to dryness. The rather unstable product was characterized by its ^1H and ^{19}F nmr spectra.

(d)

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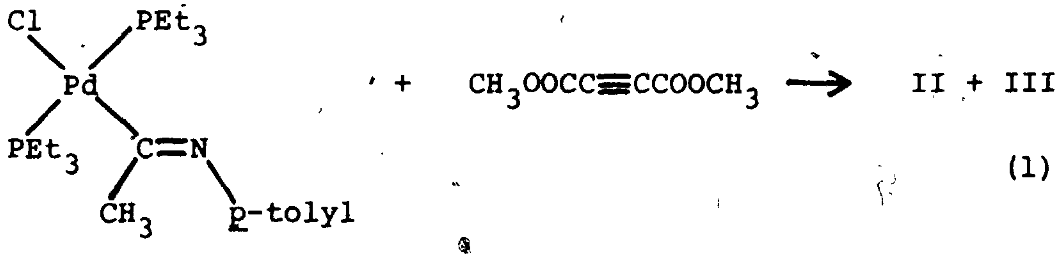
CHAPTER VI

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRANS-CHLORO(1-PARA-TOLYL-3-OXO-2-E-CARBOMETHOXYMETHYLIDENE 2,3 DIHYDRO-PYRROLE)BIS(TRIETHYLPHOSPHINE)PALLADIUM(II)

a) Introduction

The carbon-bonded imine trans-Pd[$CH_3C{=}N$-p-tolyl]Cl-$(PEt_3)_2$(I) reacted with the acetylene $CH_3OOCC{\equiv}CCOOCH_3$, with the elimination of methanol, to form two new crystalline products (equation 1).



(1)

Analysis of the ^{13}C nmr, ^1H nmr and infrared spectra of the compounds II and III failed to conclusively identify the structures. Therefore an X-ray, crystallographic study was undertaken on compound II to establish its molecular structure. Armed with this information, one could then design experiments which would elucidate the mechanism of the reaction outlined in equation 1.

This chapter deals with the solution and refinement of the structure of II while Chapter V describes the chemistry associated with II and III.

The author does not profess to be a crystallographer and does not intend to present a critique of the X-ray method. The general techniques and procedures involved in performing the X-ray experiment are well described in several texts.[1,2,3] For a knowledge of the experimental procedure followed here at Western the reader is urged to consult the Ph.D. thesis of Stepaniak[4] or of Davies[5].

b) Collection and Reduction of X-ray Data

Well developed orange crystals of $PdCl(P(C_2H_5)_3)_2(C_{14}H_{12}NO_3)$ with acicular habit were recrystallised from a mixture of toluene and hexane.

A preliminary photographic examination employing Weissenberg and precession techniques showed no systematic absences indicating that the crystals were triclinic with Laue symmetry $P\bar{1}$. Cell constants derived from the films were subjected to a cell reduction.[6] The density of the crystals was measured by flotation in an aqueous solution of zinc chloride. The observed density, 1.35(1) g cm^{-3}, agrees well with the calculated density, 1.343 g cm^{-3}, assuming two molecules per cell. $P\bar{1}$, (C_i^1, No.2)[6] was chosen as the space group, and later confirmed by a successful analysis. No symmetry constraints are imposed upon the molecule. The crystal data are presented in Table VI-1.

TABLE VI-1 Crystal Data for Trans-$PdCl[C_{14}H_{12}NO_3](PEt_3)_2$

$C_{26}H_{42}ClNO_3P_2Pd$	f.w. = 620.43
Analysis found (calculated)	C,50.06(50.33);H,6.76(6.82); N,2.31(2.26)
Crystal descriptions	orange-red prisms
Systematic absences	none
Laué symmetry	$\bar{1}$
Crystal system	triclinic
Space group	$P\bar{1}$
Equivalent positions	$x,y,z;\ \bar{x},\bar{y},\bar{z}$
Cell constants	a=10.960(2)Å α=99.90(1)° b=17.825(3)Å β=98.13(1)° c=8.235(2)Å γ=77.06(1)°
Cell volume	1535.7$Å^3$
Wavelength used for cell determination	1.54056Å
Temperature at which cell was determined	20°C
Method of density determination	flotation ($H_2O/ZnCl_2$)
Density (observed) (calculated)	1.35(1)g cm^{-3} 1.343 g cm^{-3}
Z	2
Symmetry constraints	none

A crystal of approximate dimensions 0.45 mm x 0.13 mm x 0.12 mm was chosen from which to record intensity data. It was mounted with the long dimension [001] offset from coincidence with the diffractometer ϕ axis by some 7 degrees.[7] Nine faces were identified by optical goniometry as (110), $(\bar{1}\bar{1}0)$, $(00\bar{1})$, $(11\bar{2})$, $(1\bar{1}\bar{2})$ and the forms {100} and {010}. After data collection the crystal dimensions were accurately measured on a microscope fitted with a filar eyepiece. A drawing of the data crystal is shown in Fig. VI-1.

Intensity data were recorded on a Picker FACS-1 automatic diffractometer. Cell constants and an orientation matrix were refined[8] using 27 carefully centered reflections with $32<\theta<65°$ covering the regions of reciprocal space from which data were to be collected. [illegible] check crystal quality ω scans of several intense, low angle reflections, were recorded with a take-off angle of 2.0° and a wide open counter. These had an average width at half-height of 0.108°.[9] The conditions of data collection are summarized in Table VI-2. During the collection of data, five standard reflections were examined for every 200 data recorded. Two showed only random fluctuations, while the remaining three increased in intensity, an effect attributed to an increase in crystal mosaicity resulting from the X-ray exposure. ω scans were recorded at the conclusion of the data collection run for these standards, but an average increase in width at half-height of only 0.01° was observed. No correction was made to the data for this effect.

Figure VI-1. Drawing of the data crystal.

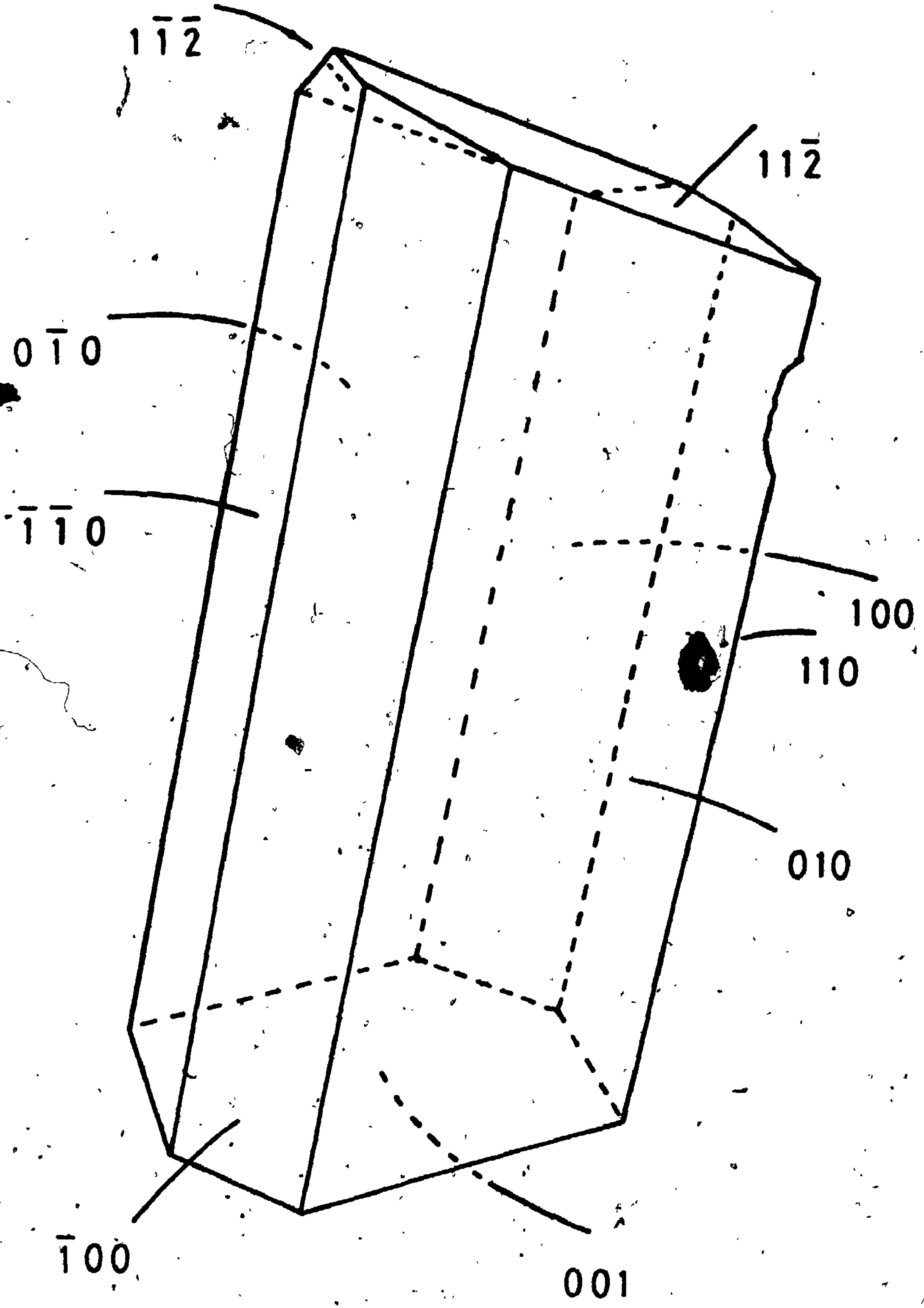

$1\bar{1}\bar{2}$
$11\bar{2}$
$0\bar{1}0$
$\bar{1}\bar{1}0$
100
110
010
$\bar{1}00$
001

TABLE VI-2 Experimental Conditions for Data Collection

Radiation	CuKα
Wavelength	1.54056 Å
Filter	pre-filtered, Ni foil (0.018 mm)
Mean W scan width at half height	0.108°
Scan rate	2.0° min^{-1}
Stationary background count time	10 sec.
% available Bragg intensity obtained for a given reflection	90%
Take-off angle	2.0°
Tube KV; MA	40; 14
Scan range	1.4°
Crystal aperture distance	33 cm.
Aperture dimensions	5 mm x 5 mm
2θ range	$2° \leq 2\theta \leq 130°$
Data collected	±h, ±k, l
No. of data collected	5761
p value	0.03
No. of reflections with $I > 3\sigma(I)$	5043
Crystal faces	(110), $(\bar{1}\bar{1}0)$, (001), $(11\bar{2})$, $(1\bar{1}\bar{2})$ (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$
Crystal dimensions	0.45 mm x 0.13 mm x 0.12 mm
Absorption Coefficient	$\mu = 66.22\ \text{cm}^{-1}$ (CuKα)
Transmission coefficients	0.187 to 0.342

Coincidence losses in counting for strong reflections were minimized by the use of copper foil attenuators.

A total of 5761 reflections was measured. The recorded intensities were corrected for Lorentz and polarization effects. A standard deviation $\sigma(I)$ was assigned to each intensity(I), where

$$(\sigma(I))^2 = C + \frac{1}{4}(tc/tb)^2(bl + bh) + (pI)^2 \quad \text{where } I = C = \frac{1}{2}(bl + bh)tc/tb,$$

C = total count measured in time tc, and bl and bh are background counts each measured in time tb. The ignorance factor, p, was chosen as 0.03.[10] Of the total number of reflections processed, 5043 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

c) Solution and Refinement of the Structure

The structure was solved by the heavy atom method, and refined by full-matrix least-squares techniques on F. Scattering factors for neutral non-hydrogen atoms were taken from Cromer and Waber,[11] while those for H were from Stewart, Davidson and Simpson.[12] The real and imaginary anomalous dispersion corrections of Cromer and Libermann[13] were included for the Pd, Cl and P atoms.

A three dimensional Patterson synthesis yielded positional parameters for the Pd atom. A least-squares cycle followed by a difference Fourier provided position parameters for the two phosphine P atoms and the Cl atom. The positions of these atoms and an overall scale factor were varied in a least-squares calculation. The positions of the remaining 30 non-hydrogen atoms were readily obtained from a difference Fourier synthesis.

Two cycles of refinement varying positional and isotropic thermal parameters for all 34 non-hydrogen atoms gave agreement factors

$$R_1 = \Sigma||F_o|-|Fc||/\Sigma|F_o| = 0.11 \text{ and } R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.15.$$

The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, and the weight w was calculated as $4F_o^2/\sigma^2(F_o^2)$. The data were then corrected for absorption effects by the analytical method.[8] Transmission coefficients varied from 0.187 to 0.342.

In further refinement cycles the phenyl ring was included as a rigid group (D_{6h}, C-C 1.392A).[14] All other atoms were assigned anisotropic thermal parameters. Two cycles of refinement (5043 observations, 265 variables) converged the model at $R_1 = 0.049$ and $R_2 = 0.074$. An inspection of the molecular geometry at this stage revealed only one unsatisfactory feature. One ethyl group of a triethylphosphine ligand contained a short C-C bond of 1.361(13)A, compared to the others, which averaged 1.537(8)Å.

Accordingly atoms C(22) and C(23) of this group were omitted, structure factors were computed after one cycle of refinement, and a difference Fourier synthesis examined. Atoms C(22) and C(23) were present as a poorly resolved region of electron density. Also apparent on the synthesis were 41 of the 42 hydrogen atoms. With this evidence to support the choice of space group, and the essential validity of the model, it was decided to include the C atoms of the ethyl group in ideal positions (C-C 1.54Å, P-C-C 109.8°). Idealized coordinates were also calculated for the 42 H atoms (C-H 1.00 Å). Thereafter the contributions from the ethyl group atoms and the H atoms were included in calculation of F_c, but no attempt was made to refine these atoms further.

After three cycles of refinement the fixed atom parameters were recalculated. Two final cycles (5043 observations with $F^2 > 3\sigma (F_o^2)$ and 247 variables) converged at agreement values $R_1 = 0.046$ and $R_2 = 0.0674$. In the final cycle the greatest shift, 1.95 e.s.d., was associated with the x coordinate of C(15), one of the ethyl group C atoms. Of the data for which $0 < F^2 < 3\sigma(F_o^2)$ no structure factor was in error by greater than 6σ.

A statistical analysis of R_2 over various ranges of $|F_o|$, $\lambda^{-1} \sin \theta$ and diffractometer setting angles χ and ϕ showed no abnormal trends. A comparison of F_o and F_c suggested extinction effects were minimal, and could be ignored. The error in an observation of unit weight is 2.98 electrons. A total difference Fourier synthesis computed from structure factors based upon the final model showed no features of chemical significance. The highest peak, of electron density 1.031 e $Å^{-3}$ at fractional coordinates (-0.4518, 0.2056, 0.3389) is of no chemical significance, and lies close to one of the phenyl ring C atoms.

Final positional and thermal parameters for the non-group atoms are given in Table VI-3. Parameters associated with the rigid group are presented in Table VI-4. Hydrogen atom parameters are given in Table VI-5. Structure amplitudes are listed in Appendix 1, as $10|F_o|$ and $10|F_c|$ in electrons.

d) Description of the Structure

The crystal structure consists of discrete molecules, for the closest intermolecular distance of approach is 2.38 Å between hydrogen atom H1C(36) and the same atom in the equivalent position 1-x, 1-y, 1-z. The shortest Pd-Pd distance of approach is 8.026(1) Å.

A perspective drawing of the molecule showing the atom numbering scheme is presented in Figure VI-2, while a stereoview of the molecule is given in Figure VI-3. Details of the cyclic ligand formed by reaction of the coordinated imine with the disubstituted acetylene are given in Figure VI-4 and selected bond distances and bond angles in Table VI-6. Some weighted least-squares planes are presented in Table VI-7.

The coordination geometry around the Pd atom is approximately square planar. A weighted least-squares plane through the Pd, the two P, the Cl and the C(30) atoms shows that the largest deviation from the plane is that of P(2) by 0.225(2)Å. The two phosphine ligands occupy mutually

TABLE VI-3.

POSITIONAL AND THERMAL PARAMETERS FOR NON-GROUP ATOMS

	x	y	[illegible]	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
[illegible]	657.8(3)	2160.4(2)	551.7(4)	519(2)	489(2)	570(2)	-128(1)	52(1)	145(1)
Cl	- 437.1(14)	1388.2(7)	1728(2)	966(9)	557(7)	1028(11)	-275(6)	382(8)	206(7)
P(1)	- 699.4(11)	3257.1(7)	1726(2)	484(6)	589(7)	565(7)	-116(5)	54(5)	124(5)
P(2)	1711.2(14)	1040.2(7)	- 551(2)	775(8)	520(7)	782(9)	- 73(6)	98(7)	95(6)
C(10)	- 614(5)	4238(3)	1453(7)	710(31)	609(28)	793(36)	- 65(24)	142(28)	195(26)
C(12)	- 708(5)	3291(3)	3940(7)	746(33)	898(38)	636(33)	-151(28)	105(27)	200(29)
C(14)	-2298(5)	3185(4)	829(8)	513(27)	934(40)	938(43)	-154(27)	52(28)	79(34)
C(11)	551(6)	4526(3)	2321(9)	901(39)	669(32)	1020(47)	-211(29)	209(36)	89(32)
C(13)	-1773(7)	3908(5)	4710(9)	916(45)	1557(66)	702(42)	- 31(45)	262(36)	33(43)
C(15)	-2442(8)	3122(6)	-1028(10)	670(38)	2345(103)	839(48)	- 91(52)	-206(36)	-207(58)
C(20)	2874(7)	1137(4)	-2218(10)	1012(47)	822(40)	1260(60)	-235(35)	485(45)	-169(40)
C(21)	3342(8)	434(5)	-3469(12)	1369(68)	1061(56)	1460(77)	-100(50)	639(62)	-154(54)
C(22)	2381	238	218	1393					
C(23)	3287	502	1702	1773					
C(24)	550(8)	588(4)	-2369(11)	1368(66)	859(44)	1323(67)	-529(45)	393(56)	-337(46)
C(25)	- 160(9)	1105(7)	-3627(14)	1354(76)	1995(105)	1573(92)	62(75)	-516(71)	-664(82)
C(30)	1487(4)	2791(2)	- 455(6)	441(21)	524(23)	621(28)	- 83(18)	76(20)	119(21)
C(31)	1048(4)	3133(3)	-1871(6)	495(23)	610(26)	575(27)	-140(20)	- 29(20)	180(22)
C(32)	1936(4)	3538(2)	-2241(6)	549(24)	511(24)	609(28)	- 76(19)	88(21)	166(21)
C(33)	2983(4)	3437(3)	- 862(7)	458(22)	528(24)	783(33)	- 84(19)	130(22)	149(23)
C(34)	3957(5)	3796(3)	- 591(8)	525(25)	636(29)	1093(46)	-159(22)	12(28)	228(30)
C(35)	4183(5)	4262(3)	-1860(10)	502(28)	750(37)	1520(66)	-175(26)	5(35)	518(41)
C(36)	4783(8)	4155(5)	-4492(14)	1341(68)	1539(75)	2091(103)	- 12(57)	790(70)	1123(75)
C(7)	6003(7)	1676(4)	5456(10)	1183(54)	977(48)	1032(52)	- 25(41)	-471(45)	127(40)
O(32)	1899(3)	3924(2)	-3358(5)	687(20)	728(21)	785(24)	-126(17)	121(18)	296(19)
O(35)	3996(4)	4956(2)	-1689(8)	947(31)	681(26)	1932(56)	-243(23)	- 64(34)	448(31)
O(36)	4623(4)	3776(3)	-3175(7)	779(25)	844(27)	1426(41)	- 27(21)	436(22)	536(28)
N	2672(3)	2871(2)	145(5)	423(17)	643(22)	597(23)	-141(16)	- 17(17)	175(18)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. All parameters have been multiplied by 10^4.

[b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)\text{Å}^2$. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

TABLE VI-4 Rigid Group Parameters

x_g^a	y_g	z_g	δ	ε	η
0.4301(2)	0.23217(12)	0.2742(3)	1.575(3)	-2.404(2)	-1.158(3)

Derived Group Atom Parameters

Atom	x	y	z	B(Å)^2
C(1)	3492(3)[b]	2643(2)	1465(4)	4.56(9)
C(2)	4737(3)	2299(2)	1222(3)	5.28(10)
C(3)	5547(2)	1978(2)	2500(4)	5.87(11)
C(4)	5111(3)	2001(2)	4020(4)	6.41(12)
C(5)	3866(3)	2345(2)	4262(3)	6.41(12)
C(6)	3056(2)	2666(2)	2984(4)	5.48(10)

[a] x_g, y_g and z_g are the fractional coordinates of the group origin; δ, ε and η (radians) are the group orientation angles. See ref.14.

[b] Derived group atom positional parameters have been multiplied by 10^4.

TABLE VI-5 Hydrogen Atom Parameters

Atom	x	y	z	B(Å)^2	Atom	x	y	z	B(Å)^2
H1C(2)[a]	5051[b]	2282	132	6.31	H1C(13)	-1673	4439	4573	9.62
H1C(3)	6442	1731	2329	6.87	H2C(13)	-2605	3816	4134	9.62
H1C(5)	3553	2361	5354	7.40	H3C(13)	-1732	3874	5915	9.62
H1C(6)	2161	2912	3158	6.51	H1C(15)	-2668	3653	-1341	12.06
H1C(31)	222	3098	-2542	5.38	H2C(15)	-1650	2926	-1458	12.06
H1C(34)	4539	3763	459	6.87	H3C(15)	-3149	2838	-1481	12.06
H1C(10)	-642	4249	236	6.51	H1C(21)	2619	307	-4256	11.38
H2C(10)	-1370	4604	1883	6.51	H2C(21)	3981	561	-4074	11.38
H1C(12)	-798	2771	4149	6.93	H3C(21)	3740	-16	-2861	11.38
H2C(12)	112	3404	4511	6.93	H1C(23)	3716	45	2269	15.00
H1C(14)	-2503	2711	1138	7.38	H2C(23)	3929	724	1297	15.00
H2C(14)	-2898	3656	1285	7.38	H3C(23)	2798	908	2496	15.00
H1C(20)	2500	1582	-2838	9.10	H1C(25)	-556	1616	-3028	15.59
H2C(20)	3621	1261	-1447	9.10	H2C(25)	435	1173	-4366	15.59
H1C(22)	1689	65	630	12.00	H3C(25)	-832	845	-4297	15.59
H2C(22)	2852	-206	-518	12.00	H1C(7)	6197	1100	5227	10.03
H1C(24)	993	90	-2978	10.22	H2C(7)	6801	1880	5562	10.03
H2C(24)	-69	475	-1708	10.22	H3C(7)	5595	1858	6503	10.03
H1C(11)	671	4444	3508	7.73	H1C(36)	5319	4552	-4032	13.08
H2C(11)	1307	4227	1763	7.73	H2C(36)	5208	3767	-5354	13.08
H3C(11)	444	5092	2252	7.73	H3C(36)	3942	4424	-4950	13.08

[a] H1C(2) is bonded to C(2), etc.

[b] Positional parameters have been multiplied by 10^4.

Figure VI-2. A view of the molecule, showing the atom numbering scheme. 50% probability thermal ellipsoids are shown. For the sake of clarity phosphine ethyl carbons are not shown.

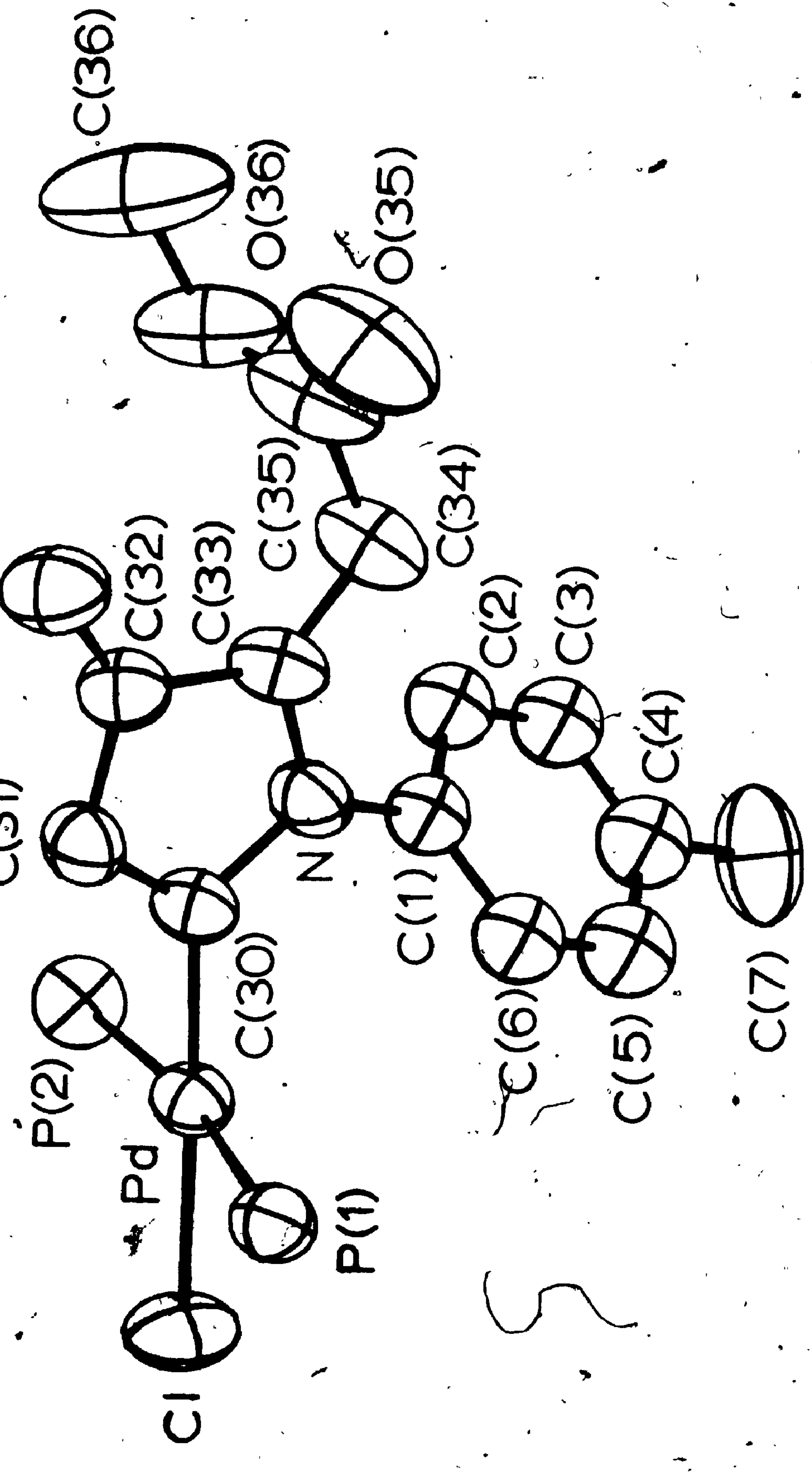
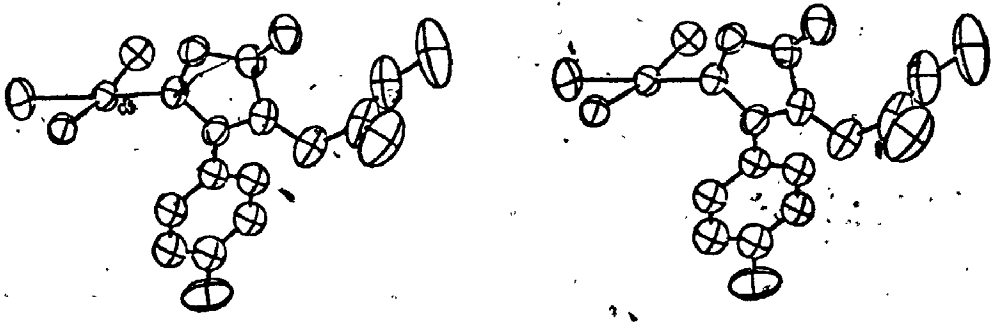

C(36)
O(36)
O(35)
C(35)
C(34)
O(32)
C(32)
C(33)
C(31)
N
C(2)
C(3)
C(4)
C(1)
C(7)
C(30)
C(6)
C(5)
P(2)
Pd
P(1)
Cl

Figure VI-3. A stereoview of the molecule. 50% probability thermal ellipsoids are shown and phosphine ethyl carbons are not included.



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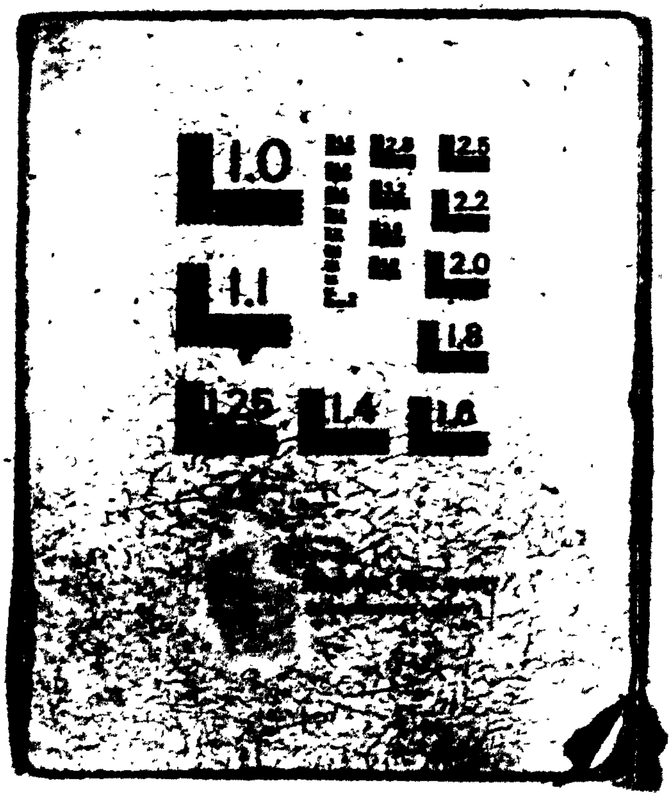

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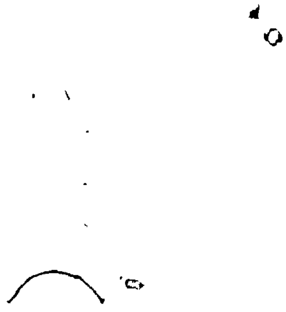


Figure VI-4. Interatomic dimensions in the pyrrole ligand.

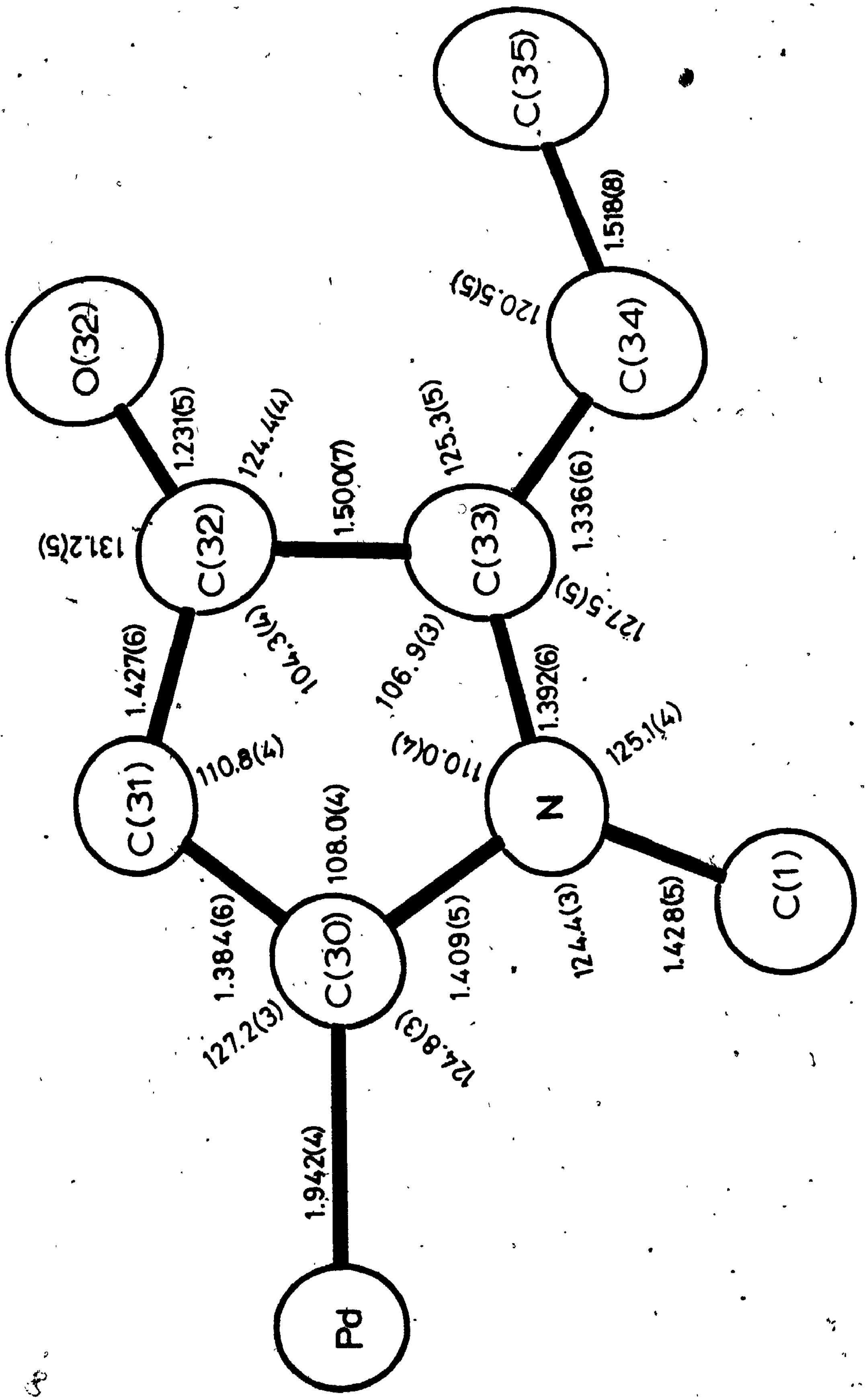

C(35)
1.518(8)
120.5(5)
C(34)
O(32)
1.231(5)
124.4(4)
125.3(5)
1.500(7)
1.336(6)
131.2(5)
C(32)
C(33)
127.5(5)
1.427(6)
104.3(4)
106.9(3)
1.392(6)
C(31)
110.8(4)
110.0(4)
125.1(4)
N
108.0(4)
C(1)
1.384(6)
C(30)
1.409(5)
124.4(3)
1.428(5)
127.2(3)
124.8(3)
1.942(4)
Pd

TABLE VI-6

Selected Intramolecular Bond Distances (Å) and Angles (deg)

Distances

Pd - C(30)	1.942(4)	N - C(1)	1.428(5)
Pd - Cl	2.408(1)	C(31) - C(32)	1.427(6)
Pd - P(1)	2.329(1)	C(32) - O(32)	1.231(5)
Pd - P(2)	2.318(1)	C(32) - C(33)	1.500(7)
P(1) - C(10)	1.825(5)	C(33) - N	1.392(6)
P(1) - C(12)	1.816(6)	C(33) - C(34)	1.336(6)
P(1) - C(14)	1.826(5)	C(34) - C(35)	1.518(8)
P(2) - C(20)	1.809(7)	C(35) - O(35)	1.195(7)
P(2) - C(24)	1.830(8)	C(35) - O(36)	1.343(8)
C(30) - C(31)	1.384(6)	O(36) - C(36)	1.418(8)
C(30) - N	1.409(5)		

Angles

P(1) - Pd - P(2)	170.1(1)	Pd - C(30) - C(31)	127.2(3)
C(30) - Pd - Cl	177.9(1)	C(30) - C(31) - C(32)	110.8(4)
C(30) - Pd - P(1)	91.7(1)	C(31) - C(32) - C(33)	104.3(4)
C(30) - Pd - P(2)	90.5(1)	C(31) - C(32) - C(32)	131.2(5)
Cl - Pd - P(1)	87.6(1)	C(33) - C(32) - O(32)	124.4(4)
Cl - Pd - P(2)	89.8(1)	C(32) - C(33) - N	106.9(3)
Pd - P(1) - C(10)	121.9(2)	C(32) - C(33) - C(34)	125.3(5)
Pd - P(1) - C(12)	112.7(2)	N - C(33) - C(34)	127.5(5)
Pd - P(1) - C(14)	107.4(2)	C(33) - N - C(30)	110.0(4)
Pd - P(2) - C(20)	117.9(2)	C(33) - N - C(1)	125.1(4)

cont'd

TABLE VI-6 cont'd

Pd - P(2) - C(24)	108.5(2)	C(30) - N - C(1)	124.4(3)
C(10) - P(1) - C(12)	105.4(3)	C(33) - C(34) - C(35)	120.5(5)
C(10) - P(1) - C(14)	102.9(3)	C(34) - C(35) - O(35)	124.5(8)
C(12) - P(1) - C(14)	105.1(3)	C(34) - C(35) - O(36)	109.7(5)
C(20) - P(2) - C(24)	105.9(4)	O(35) - C(35) - O(36)	125.8(7)
C(31) - C(30) - N	108.0(4)	C(35) - O(36) - C(36)	114.1(6)
Pd - C(30) - N	124.8(3)		

TABLE VI-7 Weighted Least-Squares Planes

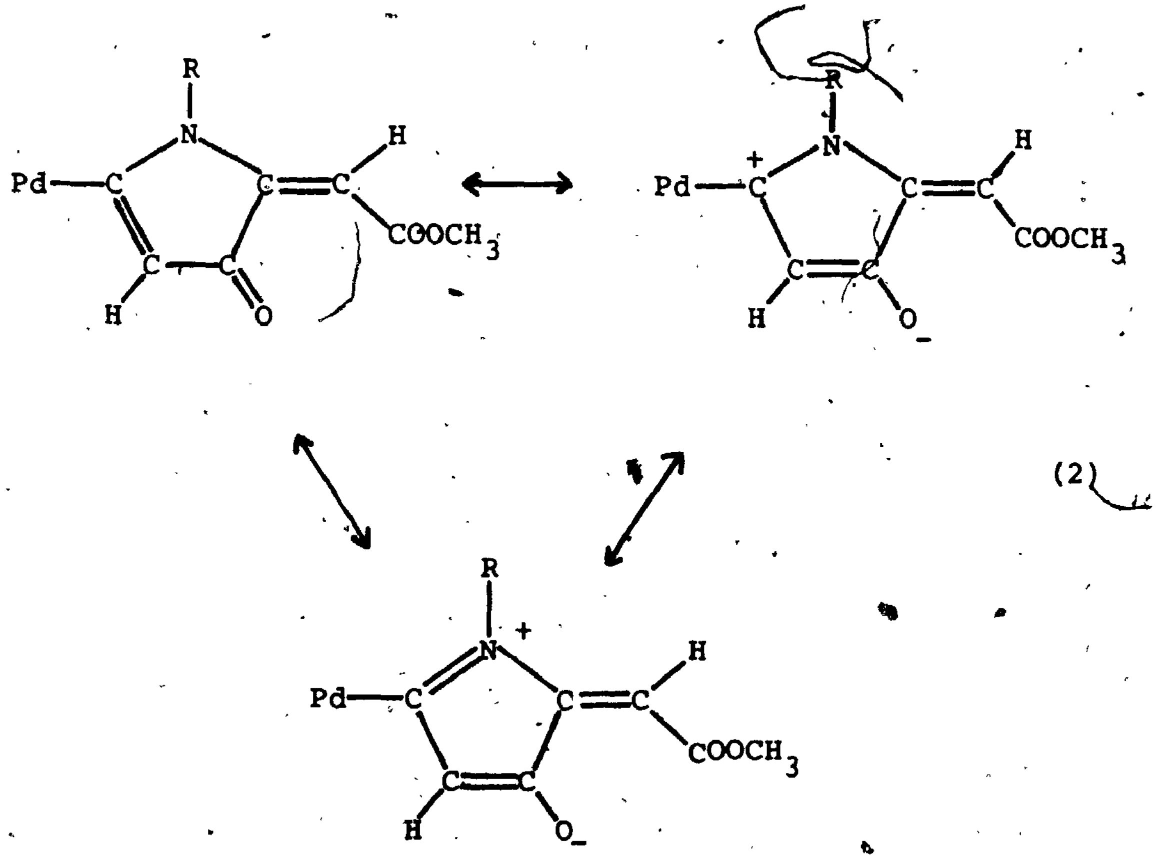
Atom	Dev from Plane Å	Atom	Dev from Plane Å
Atoms Included: Pd, P(1), P(2), C(30), Cl			
Equation of Plane $6.375x + 0.1862y + 5.954z = -0.7697$			
Pd	0.0184(3)	C(30)	-0.0408(46)
P(1)	-0.1273(12)	Cl	0.0061(17)
P(2)	-0.2254(15)		
Atoms Included: C(30), C(31), C(32), C(33), N, O(32)			
Equation of Plane $3.880x - 11.66y - 4.001z = 2.492$			
C(30)	-0.003(4)	C(33)	-0.013(5)
C(31)	-0.006(5)	N	0.007(4)
C(32)	0.015(5)	O(32)	-0.002(4)

trans coordination sites while the remaining two positions in the square plane are occupied by the chloride atom and the organic derivative formed by reaction of the coordinated imine with the disubstituted aceytylene.

The mean Pd-P distance is 2.323(6)Å. This is equivalent to the values of 2.308(4)Å obtained for trans-Pd(H)Cl$(Et_3P)_2$, and 2.306(5)Å for trans-Pd$(C_6H_4NNC_6H_5)$Cl-$(Et_3P)_2$.[16] The Pd-C(30) distance of 1.942(4)Å is comparable to other Pd-C distances found so far.[17,18] If the Pd-Cl distance of 2.408(1)Å is averaged over thermal motion, using a model in which the Cl atom is assumed to ride on the Pd atom, a valueof 2.427(1)Å is obtained. Both of these distances are significantly longer than the sum of the covalent radii which is 2.30 Å.[19] The normal length of a terminal Pd-Cl bond is between 2.30 - 2.33 Å.[20-21] This lengthening of the bond can be attributed to the strong trans influence of the sp^2 hybridized atom C(30). A similar lengthening of the Pd-Cl bond trans to a sp^2 carbon atom has been observed by Weaver.[16]

The five ethyl groups refined without constraints gave a mean P-C distance of 1.821(4)Å. Comparable means of 1.84(2)Å in Pd(H)Cl$(Et_3P)_2$[15] and 1.82(1)Å in $(C_6H_4NNC_6H_5)$-PdCl$(Et_3P)_2$[16] have been obtained. The mean Pd-P-C angle, excluding that formed by the fixed carbon atom C(22), is 113.7(28)°, and the mean C-P-C angle is 104.8(7)°. A similar distortion from tetrahedral geometry is observed for triethylphosphine ligands in other complexes.[15,16]

The organic group trans to the Cl atom is best formulated as a pyrrole derivative. The short distances between C(33) and C(34) of 1.336(6)Å, between C(32) and O(33) of 1.231(5)Å and between O(35) of 1.195(7)Å imply multiple bond character. Both the C(30) - C(31) bond length of 1.384(6)Å and the value for C(31) - C(32) of 1.427(6)Å are short. From chemical and spectroscopic considerations, the C(30) - C(31) bond may be assigned as a double bond with an H atom bonded to C(31), and the shortness of the C(31) - C(32) bond can be attributed to resonance structures of the type below (equation 2).



(2)

A least squares plane through O(32) and the five atoms of the ring shows the greatest deviation from planarity to be that of C(32) by 0.015(5)Å. The geometry about the N atom is essentially trigonal planar. The two keto groups are <u>cis</u> about the exocyclic double bond imposing the E configuration. These considerations lead to the organic group being formulated as 1-p-tolyl-3-oxo-2-E-carbomethoxymethylidene 2,3-dihydro-pyrrole.

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APPENDIX I

OBSERVED AND CALCULATED STRUCTURE FACTORS

($10|F_o|$ vs. $10|F_c|$ in electrons)

***** L = 0 *****

H	K	FO	FC
-12	-10	95	[illegible]
-12	-9	69	98
-12	-8	155	155
-12	-7	86	93
-12	-6	156	152
-12	-5	136	129
-12	-4	149	134
-12	-3	[illegible]	98
-12	-2	76	87
-12	-1	75	68
-12	0	53	56
-12	1	63	61
-12	2	132	128
-11	-13	162	165
-11	-11	176	173
-11	-10	47	102
-11	-9	46	57
-11	-8	96	96
-11	-7	87	83
-11	-6	121	116
-11	-5	137	120
-11	-4	219	211
-11	-3	65	67
-11	-2	129	133
-11	-1	69	76
-11	1	65	78
-11	2	156	152
-11	3	162	165
-11	4	87	121
-11	5	138	139
-11	6	44	48
-10	-15	71	72
-10	-14	33	22
-10	-13	203	208
-10	-12	35	34
-10	-11	263	265
-10	-10	38	56
-10	-9	136	129
-10	-8	132	177
-10	-7	99	101
-10	-6	234	151
-10	-5	56	47
-10	-4	253	246
-10	-2	302	297
-10	-1	117	122
-10	0	156	165
-10	1	237	237
-10	3	173	158
-10	4	37	43
-10	5	116	121
-10	6	82	75
-10	7	159	163
-10	8	135	132
-10	9	36	43
-9	-16	179	132
-9	-15	98	96
-9	-14	166	149
-9	-13	186	186
-9	-12	139	181
-9	-11	261	258
-9	-9	263	267
-9	-8	142	146
-9	-7	166	131
-9	-6	256	194
-9	-5	69	79
-9	-4	282	216
-9	-3	144	142
-9	-2	323	317
-9	-1	112	122
-9	0	456	426
-9	1	156	158
-9	2	82	89
-9	3	155	147
-9	4	99	95
-9	5	109	107
-9	6	46	52
-9	7	168	177
-9	8	43	77
-9	9	142	144
-9	10	109	122
-8	-18	118	112
-8	-17	120	123
-8	-16	236	211
-8	-14	142	145
-8	-13	115	115
-8	-12	53	62
-8	-11	207	202
-8	-10	55	60
-8	-9	256	252
-8	-8	113	116
-8	-7	278	274
-8	-6	191	196
-8	-5	257	250
-8	-4	153	151
-8	-3	136	106
-8	-2	364	353
-8	-1	73	32
-8	0	561	535
-8	2	106	105
-8	3	153	145
-8	4	116	116
-8	5	218	236
-8	6	40	52
-8	7	251	243
-8	9	253	236
-8	10	47	66
-8	11	113	115
-8	12	107	115
-7	-19	730	167
-7	-18	22	46
-7	-17	279	272
-7	-16	183	179
-7	-15	169	188
-7	-14	170	170
-7	-13	187	182
-7	-12	48	59
-7	-11	322	327
-7	-10	48	49
-7	-9	367	394
-7	-8	336	348
-7	-7	503	508
-7	-6	186	182
-7	-5	475	460
-7	-4	263	271
-7	-3	176	112
-7	-2	449	438
-7	-1	149	146
-7	0	559	535
-7	1	129	131
-7	2	351	372
-7	3	76	78
-7	4	156	153
-7	5	208	259
-7	6	75	79
-7	7	190	191
-7	8	48	28
-7	9	264	268
-7	10	70	58
-7	11	233	235
-7	12	105	126
-7	13	66	52
-7	14	66	71
-6	-19	123	126
-6	-17	255	242
-6	-16	76	87
-6	-15	141	131
-6	-14	272	264
-6	-12	165	112
-6	-11	183	186
-6	-10	134	131
-6	-9	256	252
-6	-8	662	646
-6	-7	349	345
-6	-6	760	776
-6	-5	600	609
-6	-4	75	78
-6	-3	322	313
-6	-2	226	233
-6	-1	155	147
-6	0	459	477
-6	1	163	177
-6	2	500	520
-6	3	191	197
-6	4	579	573
-6	5	87	88
-6	6	189	187
-6	7	149	140
-6	8	296	287
-6	10	58	44
-6	11	379	366
-6	12	52	40
-6	13	191	198
-6	14	82	88
-6	15	41	39
-5	-23	78	71
-5	-19	144	153
-5	-18	39	47
-5	-17	193	201
-5	-16	144	156
-5	-15	303	301
-5	-14	266	258
-5	-13	292	225
-5	-12	246	271
-5	-11	83	108
-5	-10	122	125
-5	-9	175	186
-5	-8	547	668
-5	-7	258	249
-5	-6	718	716
-5	-5	642	629
-5	-4	233	249
-5	-3	268	266
-5	-2	474	473
-5	-1	83	96
-5	0	219	218
-5	1	82	44
-5	2	484	507
-5	3	418	426
-5	4	726	813
-5	5	264	239
-5	6	536	503
-5	7	137	154
-5	8	48	55
-5	9	277	284
-5	10	82	71
-5	11	339	296
-5	12	56	51
-5	13	262	245
-5	14	37	25
-5	15	76	75
-5	16	36	38
-4	-20	141	149
-4	-19	185	119
-4	-18	35	29
-4	-17	214	211
-4	-15	167	164
-4	-14	71	22
-4	-13	438	425
-4	-12	37	26
-4	-11	339	338
-4	-10	185	184
-4	-9	275	256
-4	-8	436	422
-4	-7	186	187
-4	-6	610	593
-4	-5	723	785
-4	-4	226	233
-4	-3	1017	1049
-4	-2	544	576
-4	-1	224	233
-4	0	78	53
-4	1	361	341
-4	2	347	345
-4	3	762	742
-4	4	590	639
-4	5	611	644
-4	6	631	610
-4	7	252	231
-4	8	353	346
-4	9	186	187
-4	10	81	75
-4	11	171	163
-4	12	156	153
-4	13	248	239
-4	14	49	49
-4	15	185	139
-4	16	57	51
-4	17	82	32
-3	-20	189	198
-3	-19	111	113
-3	-18	116	142
-3	-17	186	97
-3	-15	95	84
-3	-14	41	37
-3	-13	166	176
-3	-12	149	159
-3	-11	594	603
-3	-10	454	455
-3	-9	279	255
-3	-8	484	509
-3	-7	279	253
-3	-6	525	612
-3	-5	955	976
-3	-4	929	1015
-3	-3	343	333
-3	-2	62	67
-3	-1	98	60
-3	0	362	315
-3	1	790	787
-3	2	222	219
-3	3	756	742
-3	4	258	272
-3	5	576	549
-3	6	787	816
-3	7	217	213
-3	8	477	499
-3	9	61	44
-3	10	96	83
-3	11	55	58
-3	12	285	193
-3	13	248	240
-3	14	250	255
-3	15	231	247
-3	17	159	164
-3	18	69	73
-2	-20	218	217
-2	-19	32	27
-2	-18	99	94
-2	-17	57	62
-2	-16	45	73
-2	-15	61	63
-2	-14	198	194
-2	-13	485	482
-2	-12	234	231
-2	-11	851	878
-2	-10	65	83
-2	-9	[illegible]	811
-2	-8	[illegible]	336
-2	-7	458	423
-2	-6	459	468
-2	-5	489	552
-2	-4	640	710
-2	-3	593	544
-2	-2	1111	1219
-2	-1	196	201
-2	0	843	859
-2	1	96	81
-2	2	235	243
-2	4	377	344
-2	5	867	872
-2	6	367	373
-2	7	464	462
-2	8	579	593
-2	9	96	181
-2	10	113	198
-2	12	135	139
-2	13	63	68
-2	14	362	338
-2	15	264	260
-2	16	98	93
-2	17	276	287
-2	19	66	71
-1	-20	121	119
-1	-19	61	83
-1	-18	166	156
-1	-17	31	16
-1	-16	139	139
-1	-14	193	199
-1	-13	244	270
-1	-12	376	376
-1	-11	745	753
-1	-10	81	68
-1	-9	654	730
-1	-8	44	43
-1	-7	281	265
-1	-6	239	241
-1	-5	841	872
-1	-4	422	365
-1	-3	253	274
-1	-2	915	929
-1	-1	517	595
-1	2	352	329
-1	3	101	72
-1	4	57	39
-1	5	351	377
-1	6	141	170
-1	7	476	519
-1	8	396	444
-1	9	739	776
-1	10	153	177
-1	11	136	159
-1	12	174	163
-1	13	50	37
-1	14	241	210
-1	15	218	270
-1	16	293	244
-1	17	244	256
-1	18	49	41
-1	19	129	127
0	-20	92	45
0	-19	137	137
0	-18	165	159
0	-17	186	138
0	-16	195	174
0	-15	48	48
0	-14	275	221
0	-12	262	324
0	-11	577	494
0	-10	345	344
0	-9	628	673
0	-7	646	623
0	-6	96	129
0	-5	335	339
0	-4	147	136
0	-3	93	176
0	-1	53	86
0	0	0	6456
0	1	52	46
0	3	94	174
0	4	249	236
0	5	332	335
0	6	96	129
0	7	456	473
0	9	617	673
0	10	752	744
0	11	571	595
0	12	379	376
0	13	46	43
0	14	271	271
0	16	142	176
0	17	188	188
0	18	166	168
0	19	174	177
0	20	60	65
1	-19	174	177
1	-18	67	51
1	-17	247	254
1	-16	249	244
1	-15	211	220
1	-14	243	213
1	-13	40	32
1	-12	179	143
1	-11	136	153
1	-10	119	177
1	-9	749	756
1	-8	349	444
1	-7	443	519
1	-6	344	329
1	-5	355	377
1	-4	55	39
1	-3	123	72
1	-2	351	309
1	1	539	505
1	2	597	905
1	3	253	236
1	4	416	375
1	5	841	872
1	6	235	241
1	7	251	265
1	8	64	40
1	9	633	736
1	10	96	60
1	11	773	753
1	12	391	378
1	13	776	778
1	14	193	199
1	16	136	130
1	17	150	156
1	19	43	93
1	20	123	119
2	-19	78	71
2	-17	277	247
2	-16	91	93
2	-15	247	248
2	-14	347	330
2	-13	42	48
2	-12	136	139
2	-10	117	100
2	-9	95	101
2	-8	585	593
2	-7	453	442
2	-6	351	373
2	-5	762	772
2	-4	388	344
2	-2	736	743
2	-1	95	81
2	0	867	855
2	1	193	221
2	2	1165	1219
2	3	594	544
2	4	630	710
2	5	491	552
2	6	487	459
2	7	686	627
2	8	348	356
2	9	773	811
2	10	93	93
2	11	646	677
2	12	233	231
2	13	604	602
2	14	197	196
2	15	54	43
2	16	36	23
2	17	57	42
2	18	100	94
2	19	37	27
2	20	268	217
3	-18	67	73
3	-17	193	164
3	-15	228	242
3	-14	258	255
3	-13	258	240
3	-12	281	193
3	-11	53	54
3	-10	94	83
3	-9	62	66
3	-8	442	459
3	-7	273	253
3	-6	749	914
3	-5	574	569
3	-4	257	222
3	-3	751	742
3	-2	221	219
3	-1	785	787
3	0	364	315
3	1	92	60
3	2	67	67
3	3	341	333
3	4	923	1015
3	5	952	996
3	6	484	637
3	7	267	253
3	8	492	509
3	9	278	255
3	10	454	455
3	11	597	603
3	12	150	159
3	13	347	376
3	14	47	37
3	15	99	84
3	17	182	97
3	18	114	102
3	19	155	113
3	20	179	198
4	-17	85	82
4	-16	56	51
4	-15	182	189
4	-14	41	49
4	-13	255	239
4	-12	157	153
4	-11	173	143
4	-10	75	75
4	-9	198	187
4	-8	359	346
4	-7	254	231
4	-6	643	638
4	-5	622	604
4	-4	612	595
4	-3	774	742
4	-2	351	345
4	-1	349	341
4	0	72	53
4	1	274	231
4	2	943	976
4	3	1815	1845
4	4	220	231
4	5	732	785
4	6	617	593
4	7	99	127
4	8	437	422
4	9	275	254
4	10	185	195
4	11	333	303
4	12	33	26
4	13	477	475
4	14	76	22
4	15	167	164
4	17	218	211
4	19	136	119
4	20	139	149
5	-16	46	38
5	-15	71	75
5	-14	38	25
5	-13	245	249
5	-12	57	51
5	-11	312	296
5	-10	86	71
5	-9	278	284
5	-8	55	55
5	-7	110	136
5	-6	518	523
5	-5	240	239
5	-4	418	413
5	-3	418	436
5	-2	491	537
5	-1	88	44
5	0	225	218
5	1	69	96
5	2	479	473
5	3	266	264
5	4	235	249
5	5	647	629
5	6	717	714
5	7	255	249
5	8	675	658
5	9	183	186
5	10	118	125
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4	11	175	114
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4	14	127	137
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4	16	107	106
4	17	46	33
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5	-15	76	65
5	-14	223	236
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5	-6	146	165
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6	-9	117	105
6	-8	58	66
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6	7	165	171
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6	14	176	169
6	15	67	55
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7	2	197	191
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7	5	223	229
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7	7	254	243
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7	9	154	151

H	K	FO	FC
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7	13	150	149
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8	5	77	61
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8	8	164	195
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8	10	117	111
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9	-6	160	157
9	-5	64	79
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9	-3	169	160
9	-1	266	183
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9	3	254	255
9	4	212	285
9	5	127	121
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9	8	191	190
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10	6	102	104
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11	1	104	108
11	2	43	51
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-10	6	58	66
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-9	-15	122	112
-9	-14	112	127
-9	-13	114	116
-9	-12	139	132
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-9	-6	164	152
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-9	0	140	149
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-9	2	227	227
-9	3	108	110
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-8	-16	93	90
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-8	-14	94	94
-8	-13	339	303
-8	-12	112	105
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-8	-8	259	250
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-7	-11	411	316
-7	-10	263	237
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-7	-7	143	166
-7	-6	275	277
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-7	-3	240	236
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-7	3	241	246
-7	4	211	247
-7	5	147	149
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-7	8	135	134
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-6	-10	372	371
-6	-9	254	253
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-6	-7	312	319
-6	-6	89	107
-6	-5	65	87
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-6	6	222	224
-6	7	153	99
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-5	-13	146	172
-5	-11	416	412
-5	-10	238	213
-5	-9	507	436
-5	-6	56	26
-5	-5	56	62
-5	-4	235	254
-5	-3	156	112
-5	-2	640	618
-5	-1	334	344
-5	0	540	650
-5	1	536	541
-5	2	126	147
-5	3	40	43
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-5	6	73	58
-5	7	165	161
-5	8	150	151
-5	9	149	151
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-5	12	34	101
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-4	-17	142	154
-4	-16	245	254
-4	-15	46	36
-4	-14	140	133
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-4	-12	120	126
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-4	-10	56	54
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-4	-7	470	250
-4	-6	43	161
-4	-5	231	227
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-4	9	190	186
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-4	11	144	152
-4	12	141	141
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-4	15	25	23
-3	-19	186	165
-3	-18	134	132
-3	-17	249	244
-3	-16	258	244
-3	-15	51	35
-3	-14	113	290
-3	-13	145	125
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-3	-11	144	179
-3	-10	153	122
-3	-9	443	432
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-3	-7	634	661
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-2	-15	273	215
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-2	-11	67	90

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-2	2	557	561
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-2	6	100	106
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-2	9	357	334
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-1	-18	59	51
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-1	-13	178	135
-1	-12	227	227
-1	-11	156	151
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-1	-7	564	564
-1	-6	635	640
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-1	6	590	590
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-1	14	85	86

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1	-10	176	136
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1	1	317	342

H	K	FO	FC
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2	12	152	144
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4	-5	162	163
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4	11	161	163

H	K	FO	FC
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4	14	119	116
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6	5	173	166

H	K	FO	FC
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6	9	246	242
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6	11	241	247
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6	15	73	67
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7	-7	161	173
7	-6	144	142
7	-5	253	262
7	-4	83	57
7	-3	244	239
7	-2	92	86
7	-1	251	262
7	1	121	123
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7	4	156	152
7	6	223	229
7	8	213	228
7	9	124	122
7	10	116	125
7	11	195	193
7	13	144	145
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8	-8	124	116
8	-7	67	60
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8	-2	136	130
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9	-7	41	45
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9	-5	75	75

H	K	FO	FC
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10	2	110	116
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-9	-10	133	134
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-8	-17	177	186
-8	-15	166	162
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-8	-12	69	57
-8	-11	189	203
-8	-10	41	26
-8	-9	96	95
-8	-8	253	249
-8	-7	129	123
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-8	-5	215	206
-8	-4	311	325
-8	-3	129	108
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-7	6	163	168
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-6	-17	50	63
-6	-16	80	78
-6	-15	96	79
-6	-14	224	229
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-6	-12	242	248
-6	-11	348	342
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-6	-8	249	243
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-6	-5	36	62
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-6	7	123	130
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-4	-11	365	359
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-4	-8	71	77
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-4	7	260	256
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-4	10	75	64
-4	11	56	54
-4	12	140	146
-3	-19	162	152
-3	-18	43	47
-3	-17	263	263
-3	-16	143	147
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-3	-8	265	256
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-3	6	42	54
-3	7	222	213
-3	8	136	147
-3	9	321	317
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-3	12	30	36
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-2	-18	37	44
-2	-17	342	345
-2	-16	144	153
-2	-15	330	336
-2	-14	94	102
-2	-13	126	122
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-1	2	341	346
-1	3	265	267
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-1	5	162	156
-1	6	152	139
-1	7	144	148
-1	8	212	216
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-1	10	147	159
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1	-9	249	254
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1	9	36	43
1	10	206	203
1	11	66	70
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1	14	114	119
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2	-9	146	203
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2	5	463	473

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H	K	FO	FC
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2	-14	138	139
2	-13	132	125
2	-12	135	176
2	-11	91	86
2	-10	156	183
2	-9	95	93
2	-7	211	246
2	-6	159	147
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2	-4	411	395
2	-3	154	171
2	-2	168	163
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2	1	43	65
2	2	235	244
2	3	347	348
2	4	166	155
2	5	339	339
2	6	53	63
2	7	232	199
2	9	90	98
2	10	88	74
2	11	17	29
2	12	152	149
3	-15	79	7
3	-14	143	150
3	-13	99	88
3	-12	185	199
3	-11	44	40
3	-10	174	157
3	-9	176	113
3	-7	259	248
3	-6	178	170
3	-5	391	143
3	-4	218	218
3	-3	141	147
3	-2	151	143

H	K	FO	FC
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3	0	98	91
3	1	167	160
3	2	175	164
3	3	114	113
3	4	132	123
3	5	249	250
3	6	52	47
3	7	142	156
3	9	127	136
3	11	92	89
3	12	69	64
3	13	43	41
4	-14	116	118
4	-12	184	170
4	-11	126	92
4	-10	194	238
4	-9	99	129
4	-8	224	249
4	-7	130	126
4	-6	175	128
4	-5	183	160
4	-3	198	177
4	-2	144	152
4	-1	197	158
4	0	182	181
4	1	159	173
4	2	213	215
4	3	41	35
4	4	261	279
4	5	236	194
4	6	113	117
4	7	199	219
4	8	50	53
4	9	178	134
4	10	63	73
4	11	82	75
4	12	55	67
5	-12	159	150
5	-10	176	187
5	-9	58	64
5	-8	168	176
5	-6	137	133
5	-5	76	83
5	-3	113	170
5	-2	151	157
5	-1	182	188
5	0	167	153
5	1	156	155
5	2	139	130
5	3	96	91
5	4	269	190
5	6	182	172
5	7	77	72
5	8	94	93

H	K	FO	FC
5	9	65	70
5	10	71	68
5	11	53	51
6	-11	63	68
6	-10	163	159
6	-9	49	41
6	-8	167	172
6	-6	122	113
6	-4	72	75
6	-3	172	176
6	-1	283	276
6	0	77	86
6	1	244	250
6	2	87	81
6	3	152	153
6	4	97	95
6	5	95	91
6	6	112	113
6	8	90	99
6	9	106	109
6	10	47	41
6	11	81	79
7	-8	135	139
7	-7	45	44
7	-6	89	99
7	-4	125	127
7	-3	48	92
7	-2	83	89
7	-1	167	172
7	1	197	204
7	3	131	134
7	4	68	61
7	5	82	83
7	8	111	106
7	9	59	54
8	-4	128	103
8	-2	97	104
8	-1	86	73
8	0	36	35
8	1	164	161
8	3	136	142
8	5	111	107
8	7	79	84

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-9	-12	86	89
-9	-11	79	76
-9	-10	108	114
-9	-9	66	86
-9	-8	133	123
-9	-7	66	70

H	K	FO	FC
-9	-6	115	113
-9	-5	41	41
-9	-4	61	70
-9	-3	56	68
-9	-2	36	44
-9	-1	186	197
-9	1	151	140
-8	-13	111	119
-8	-11	77	85
-8	-10	63	68
-8	-9	174	170
-8	-8	116	117
-8	-7	239	212
-8	-6	137	143
-8	-5	67	73
-8	-4	33	41
-8	-3	81	84
-8	-2	115	110
-8	-1	116	127
-8	0	107	127
-8	1	133	130
-8	2	35	38
-8	3	76	73
-7	-15	98	131
-7	-14	86	89
-7	-13	82	79
-7	-12	65	63
-7	-11	65	63
-7	-10	48	54
-7	-9	147	109
-7	-7	294	268
-7	-6	118	114
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-7	-4	107	107
-7	-2	117	119
-7	0	85	77
-7	1	107	98
-7	2	96	94
-7	3	135	178
-7	4	45	54
-7	5	76	76
-6	-16	145	157
-6	-15	68	58
-6	-14	142	146
-6	-13	46	63
-6	-12	103	99
-6	-11	95	91
-6	-10	95	88
-6	-9	161	162
-6	-8	53	36
-6	-7	304	300
-6	-6	125	139
-6	-5	283	282
-6	-4	182	185
-6	-3	36	16

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-6	1	39	39
-6	2	149	157
-6	3	146	139
-6	4	157	165
-6	5	122	114
-6	6	46	48
-6	7	66	70
-5	-16	123	114
-5	-15	51	49
-5	-14	112	154
-5	-12	178	183
-5	-11	45	46
-5	-10	197	203
-5	-9	127	129
-5	-8	154	150
-5	-7	248	258
-5	-5	273	270
-5	-4	150	144
-5	-3	150	154
-5	-2	86	85
-5	-1	126	122
-5	0	61	56
-5	2	179	178
-5	3	69	61
-5	4	223	230
-5	5	123	119
-5	6	79	70
-5	7	73	85
-4	-16	56	59
-4	-15	101	91
-4	-14	150	154
-4	-13	106	102
-4	-12	285	292
-4	-10	330	329
-4	-8	125	111
-4	-7	105	96
-4	-5	308	293
-4	-4	60	50
-4	-3	159	180
-4	-2	60	65
-4	-1	157	143
-4	0	99	87
-4	1	171	164
-4	2	137	132
-4	3	80	63
-4	4	191	185
-4	5	115	116
-4	6	135	141
-4	7	129	128
-4	8	51	51
-3	-16	135	143
-3	-14	49	46
-3	-13	215	227

H	K	FO	FC
-3	-12	230	294
-3	-11	162	170
-3	-10	213	209
-3	-9	77	75
-3	-8	86	82
-3	-7	59	60
-3	-6	60	69
-3	-5	136	291
-3	-4	61	75
-3	-3	308	312
-3	-2	66	62
-3	-1	343	343
-3	0	49	33
-3	1	250	244
-3	2	86	86
-3	3	117	116
-3	4	165	163
-3	6	172	173
-3	7	105	102
-3	8	79	79
-3	9	66	63
-3	10	[illegible]	60
-2	-16	[illegible]	86
-2	-15	83	87
-2	-13	282	288
-2	-12	142	146
-2	-11	143	126
-2	-10	259	260
-2	-8	146	170
-2	-7	111	102
-2	-6	93	79
-2	-5	185	185
-2	-4	276	259
-2	-3	255	236
-2	-2	167	169
-2	-1	346	327
-2	1	230	272
-2	3	114	123
-2	4	58	52
-2	5	60	61
-2	6	140	131
-2	7	41	36
-2	8	133	136
-2	9	61	57
-2	10	87	92
-1	-16	98	99
-1	-15	99	111
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-1	-11	217	220
-1	-10	186	198
-1	-9	115	106
-1	-8	295	285
-1	-7	72	77
-1	-6	268	270

H	K	FO	FC
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-1	-4	227	243
-1	-3	261	262
-1	-1	362	365
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-1	2	46	3
-1	3	71	78
-1	4	78	61
-1	6	117	112
-1	7	65	68
-1	8	176	175
-1	10	171	162
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0	-14	102	101
0	-13	115	120
0	-12	81	75
0	-11	139	173
0	-10	82	86
0	-9	102	142
0	-8	196	177
0	-7	227	217
0	-6	103	86
0	-5	153	152
0	-4	64	63
0	-2	263	170
0	-1	175	165
0	0	173	163
0	1	246	236
0	3	127	115
0	5	93	89
0	7	142	149
0	8	117	115
0	9	71	66
0	10	142	153
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1	-14	118	126
1	-13	52	63
1	-12	77	79
1	-11	74	76
1	-9	211	221
1	-8	83	61
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1	-6	157	150
1	-5	129	131
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1	-3	76	77
1	-2	276	277
1	0	269	216
1	1	247	242
1	2	178	179
1	3	243	247
1	4	93	89
1	5	132	127
1	6	60	56
1	7	147	144
1	8	99	102
1	10	114	116
2	-14	156	158
2	-12	96	172
2	-10	115	112
2	-9	170	115
2	-7	241	253
2	-6	176	172
2	-5	241	241
2	-4	147	154
2	-3	230	219
2	-2	116	111
2	-1	220	216
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2	2	121	119
2	3	117	112
2	4	149	153
2	5	44	79
2	6	95	111
2	7	136	155
2	8	55	52
2	9	106	104
2	10	65	43
2	11	57	56
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3	-7	142	135
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3	-3	214	205
3	-2	52	46
3	-1	155	155
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3	2	128	121
3	3	147	142
3	4	149	150
3	5	157	159
3	6	83	86
3	7	147	145
3	8	30	63
3	9	125	135
3	11	21	32
4	-12	126	123
4	-10	139	154
4	-9	91	34
4	-8	143	141
4	-7	46	91
4	-6	79	88
4	-5	283	219
4	-3	155	152
4	-1	136	94
4	0	33	33
4	1	105	107
4	2	131	176
4	4	259	214
4	5	62	54
4	6	179	195
4	7	83	87
4	8	142	145
4	9	51	42
4	10	86	89
5	-10	172	137
5	-9	56	52
5	-8	92	105
5	-6	153	176
5	-5	133	176
5	-4	70	84
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5	3	111	109
5	4	145	147
5	6	144	150
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6	-7	44	41
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6	-4	113	101
6	-3	101	105
6	-2	42	34
6	-1	152	159
6	1	127	137
6	3	129	129
6	4	43	40
6	5	77	76
6	6	57	122
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7	-2	42	44
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7	1	113	125
7	2	39	36
7	3	99	111

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-8	-4	55	57
-8	-2	112	174
-8	-1	74	75
-7	-12	44	44
-7	-10	47	37
-7	-9	126	116
-7	-6	196	176
-7	-5	121	129
-7	-4	61	38
-7	-2	95	107
-7	-1	60	60
-7	0	147	143
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-7	2	94	98
-6	-12	67	62
-6	-11	83	82
-6	-9	108	119
-6	-8	89	90
-6	-7	267	273
-6	-6	37	33
-6	-5	207	210
-6	-3	72	71
-6	-2	65	71
-6	0	116	115
-6	1	36	26
-6	2	149	150
-6	3	46	28
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-5	-10	103	105
-5	-9	53	44
-5	-8	165	166
-5	-7	210	219
-5	-6	133	137
-5	-5	107	190
-5	-2	87	78
-5	-1	44	33
-5	0	60	30
-5	2	156	163
-5	4	147	165
-4	-14	96	96
-4	-13	111	117
-4	-12	159	118
-4	-11	108	97
-4	-10	142	144
-4	-9	60	33
-4	-8	171	179
-4	-7	99	110
-4	-6	174	123
-4	-5	177	170
-4	-3	172	173
-4	-2	38	39
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-4	2	126	127
-4	3	59	60
-4	4	236	203
-4	6	108	113
-3	-13	161	146
-3	-12	114	113
-3	-11	156	162
-3	-10	161	161
-3	-9	118	127
-3	-8	109	107
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-3	-4	76	75
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-2	-8	70	83
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-1	6	97	102
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1	-10	69	43
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1	-7	235	292
1	-5	171	169
1	-3	106	119
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1	6	67	64
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1	8	29	10
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2	-9	99	90
2	-7	106	106
2	-6	39	21
2	-5	184	179
2	-3	163	158
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3	4	152	157
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3	6	127	126
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5	4	95	96

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-6	-2	66	67
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-5	-7	114	171
-5	-6	151	152
-5	-5	116	115
-5	-4	82	79
-5	-3	35	40
-5	0	32	42
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-4	-8	160	173
-4	-7	73	76
-4	-6	197	207
-4	-5	99	191
-4	-4	139	151
-4	-3	66	57
-4	-1	40	39
-4	0	61	44
-4	1	106	133
-4	2	87	87
-3	-9	25	91
-3	-8	91	104
-3	-6	143	164
-3	-5	56	55
-3	-4	159	156
-3	-3	79	76
-3	-2	59	66
-3	-1	62	44
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-3	1	70	66
-3	3	94	106
-2	-9	133	104
-2	-8	67	56
-2	-7	56	67
-2	-6	110	120
-2	-5	48	36
-2	-4	135	137
-2	-3	95	94
-2	-2	122	133
-2	-1	41	39
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-2	1	34	25
-2	3	106	130
-2	4	65	78
-1	-9	132	135
-1	-7	77	76
-1	-6	55	84
-1	-5	37	41
-1	-4	147	146
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-1	3	77	78
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0	-8	65	33
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0	-5	71	80
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0	-3	72	65
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0	0	117	131
0	2	116	116
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1	-7	92	91
1	-6	60	65
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1	-3	80	97
1	-2	111	115
1	-1	42	40
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1	2	118	132
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2	-6	92	89
2	-5	75	73
2	-4	46	51
2	-3	56	91
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2	-1	81	78
2	0	132	131
2	2	118	110
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3	-1	72	78