ORGANOPLATINUM:

SOME REACTION MODES

THESIS

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Slainte Mhath!

For my Folks then ~

for Rosie now.

"It is a cardinal error, Watson, to theorise
with insufficient data......."

Sherlock Holmes.

ABSTRACT

The thermal decomposition of organoplatinum(II) complexes of the type cis-L_2PtAr_2 and $(biL)PtAr_2$ [$Ar = C_6H_5$, 4-Me-C_6H_4; $L = Ph_3P$, $(4\text{-Me-}C_6H_4)_3P$, Ph_2MeP; biL = $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PC_2H_4PPh_2$ (dpe), $Me_2PC_2H_4PMe_2$ (dmpe)] has been studied.

In the condensed phase, the thermolyses have been examined by thermal analytical techniques (DSC and simultaneous TGA/DTA) and by product analysis (GLC). The results indicate that the complexes undergo thermal disruption via a predominant primary route which involves concerted reductive elimination of the platinum-bound aryl ligands as biaryl. This process is intramolecular, and no intermolecular exchange of aryls occurs prior to, or during, decomposition. Secondary reactions which produce quantities of arene and biaryl originating from the arylphosphine ligands, and whose operation is concurrent with, but essentially independent of, the primary reductive elimination, are also observed. These data are interpreted in terms of slower reactions (subsequent to the primary process) of the species L_2Pt^0 or $(biL)Pt^0$, involving aryl- or hydride-transfer to platinum, by oxidative insertion into P-C or C-H bonds, and ultimate reductive eliminations. Although their identities remain uncertain, analysis of the glassy, red-brown decomposition residues provides more evidence for these propositions.

In the presence of an added equimolar amount of the appropriate phosphine*, primary concerted reductive elimination

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*Normally identical to that already present in the complex.

of biaryl is facilitated. The effect is most marked for complexes of dpm in presence of free ligand. This general observation is in qualitative agreement with previous predictions and is discussed in terms of nucleophilic attack at Pt(II) by a phosphorus donor. Secondary reactions are largely, if not altogether suppressed, and this is attributable to the diminished tendency of Pt(0) to undergo the oxidative insertion sequences in higher coordination number phosphine complexes. An exception is $(dpm)_2Pt(0)$ which appears to decompose under the conditions of its formation. In this case, an additional secondary process involves rupture of the P-C-P bridge, presumably again by oxidative insertion of Pt(0) into P-C (the first such example with P-alkyl). When a phosphine different to that already present is added, there is some evidence that exchange may occur prior to the Pt-C scission processes.

The thermal decomposition of these systems was, additionally, followed in toluene solution. Product analyses served to corroborate the mechanistic conclusions drawn from the condensed-phase data. Primary, concerted, intramolecular reductive elimination is followed by the same slower secondary processes. Kinetic studies showed that the primary elimination is first-order in platinum complex and that, again, reductive elimination is facilitated by the presence of free phosphine.

Only the complexes <u>cis</u>-$(Ph_3P)_2PtAr_2$ displayed sufficient lability to be extensively studied under these conditions. Such activation parameters as were determined for these systems suggested that the enhanced lability of the 4-tolylplatinum species compared with its phenyl-analogue, and that of either system in the presence of Ph_3P (relative to the complex alone) may be largely due to entropy effects, interpretations of which are discussed.

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Introduction - Part I

CHAPTER ONE

Preamble In any introductory remarks to whatever aspect of organotransition-metal chemistry, some reference to the remarkable efflorescence of this field of investigation is considered mandatory. This is for no better reason than that it is a perfectly accurate assessment, as might well be judged from the expansion of specialist literature on the subject. The growing interest seems to stem not only from the vast scope of the subject - the novelty and variety of the compounds it embraces - but also from a general concern for the insight which it may yield into important related branches of the discipline.

The prominent position occupied by organometallics as a whole in various fields of organic synthesis has long been established. Organometals are widely employed as stoichiometric synthetic reagents or are implicated as intermediates in catalytic cycles. However, the inability to rationalise a given situation has not generally proved an inhibition to its exploitation, this being perhaps especially true of synthetic chemistry. It is, of course, recognised that the metal-influenced course of a given reaction is likely to be crucially determined by the reaction sequences which are peculiarly available to the participating organometal. There remains, however, a fundamental scarcity of information concerning the most basic features of the operation of many of these processes. This is a void which we can increasingly ill-afford to overlook, in view of forecasts of dwindling organic resources. If constructive reappraisal of current methods is to be made to allow more efficient exploitation of remaining supplies, then more and clearer insight is desirable.

The problem is particularly acute where d-block transition-metals are concerned. As well as their involvement in a variety of routine preparative schemes, organic derivatives of transition-metals are clearly implicated in a number of our more important industrial synthetic processes. For example, organotitanium intermediates are considered to contribute to Ziegler-Natta-type polymerisation of olefins[1]; organocobalt is an important intermediate in the hydroformylation of olefins, catalysed by $HCo(CO)_4$[2] (OXO process); organopalladium species play a crucial role in the oxidation of ethylene to acetaldehyde, catalysed by Pd(II)[2] (Wacker Process). Nevertheless, in spite of the significance of organo-transition-metal species in these and other examples the essential controlling influences on their reactions and reactivities are not well understood.

Central to understanding such systems lies the question of the operative modes whereby transition-metal-carbon bonds are created or broken, particularly when supplied only with thermal energy. The organometals which are cited as intermediates in the above (and related) examples are metastable and generally non-isolable. An increasing amount of investigative energy, however, is now being diverted into the exploration of isolable systems which contain the transition-metal-carbon bond, on the reasonable assumption that these may serve as models for general patterns of organo-transition-metal reactivity. After all, normal conditions of temperature and pressure are accidental and rather arbitrary impositions, and one environment's stable system may be another's transient intermediate. Before progressing to discussion of the major themes of this thesis - the processes associated with dislocation of the metal-carbon-bond - we might profitably trace the development of the underlying chemistry.

Historical Although organometallic chemistry, particularly that of the d-block elements, has undergone an exponential growth only over the past twenty-five years, the foundations were laid as long ago as the early and mid-19th Century. It was in 1827 that the Danish pharmacist Zeise succeeded in preparing a potassium salt whose anion had the composition $(C_2H_4PtCl_3)^-$[3]. This is now recognised as being the earliest organo-metallic compound, containing as it does a metal-olefin bond. The first contemporarily recognised organometals were, however, the simple alkyls of zinc prepared by Frankland. It was he who, in 1849, although attempting to isolate ethyl radicals, correctly recognised the product of the reaction of ethyl iodide with metallic zinc to be diethylzinc[4]. Frankland's work is notable in that not only did it provide a springboard for the development of organometallic chemistry, but it also led directly to the first tentative statement on the idea of valency - that each element has a limiting capacity for chemical combination[5].

Progress in the field thereafter was, as is normal, derivative of what had gone before. The work of Grignard on the organomagnesium halides which bear his name[6], and the studies of Schlenk and Ziegler on organic derivatives of the alkali metals[7] and on lithium alkyls[8] in particular, established organometallic chemistry, not merely as an individual and respectable discipline, but as an integral part of organic synthesis, a position which it continues to maintain.

Conspicuous throughout the development of metallo-organic chemistry, even as late as the middle of this century, was the lack of success, (and probable resultant lack of faith) in the area of the transition elements. A few advances had been achieved, of course. Apart from Zeise's anion, which seems to have been disregarded until its structure was better understood, organoplatinum chemistry gained an early start with the synthesis of methyl derivatives of Pt(IV) in 1907 by Pope and Peachy[9]. It now seems certain that simple organo-derivatives of Pt(II) were also prepared about this time[10], but their true identity was not recognised until much later[11]. Gibson et al., in the 1930's, were responsible for a fairly extensive development of the organic chemistry of Au(III)[12] In addition, during the previous decade, Hein reported polyphenyl derivatives of chromium[13]. Although it emerged that these were indeed true organochromium species, they were eventually demonstrated to belong to the family of 'sandwich' complexes[14], a class of compound whose contribution to the field will presently be discussed.

Perhaps it was the apparent inaccessibility of simple alkyl derivatives of transition elements which caused the seeming atrophication of this limb of organometallic chemistry. As is now clear, the stability of such compounds depends on somewhat subtle structural and electronic features of organic ligand and metal complex, and not entirely unsurprisingly, suitable stable combinations were seldom employed. In any case, whatever the reason, by 1950, when organometallic chemistry was more than a century old, the transition-metal branch was still considered to be something of an eccentric backwater.

The event that is generally credited as having galvanised the renaissance of this field was the discovery of the biscyclopentadienyl iron complex, more commonly called Ferrocene[15]. This discovery, and the subsequent elucidation of its novel sandwich structure[16], constituted an injection of adrenalin from which organotransition-metal chemistry has not looked back. The nonconformity and unexpectedness of the compound opened up new possibilities of structure and bonding, and created renewed interest in the organic chemistry of transition-metals.

So far, organotransition-metals have been discussed in broad terms, but clearly two general categories are evident, characterised by the nature of the metal-carbon bond. The first of these may be classified as π-organometals. Here an unsaturated organic moiety is coordinated to the metal <u>via</u> donation of its available π-electrons. These species have an extensive and richly varied chemistry[17] and they particularly epitomise the quintessential duality which is an attractive feature of all organometallic chemistry, inasmuch as both metal and hydrocarbon may induce behavioural modifications, one on the other, in subtle and often unique ways. This class of compounds includes complexes of alkenes - the descendants of Zeise's anion - and an absorbing lineage of pentahaptocyclopentadienylmetals - offspring of ferrocene. Also included are a number of organic systems which do not survive as free entities, but which may be stabilised by complexation. Examples of such are the cyclobutadienyl dianion[18] $(C_4H_4)^{2-}$ and the pentalenyl dianion[19] $(C_8H_6)^{2-}$.

In juxtaposition is the ever-expanding family of σ-organotransition-metals, characterised by the presence of a localised metal-carbon σ-bond. Broadly speaking, these originate in two ways. The first is via formal two-electron donation from carbon, and this class includes the metal-carbonyls, -cyanides, -isocyanides and -carbenes. In the second, the ligand group has, basically, a hydrocarbon skeleton. Since it is with the latter that the focus of interest in this thesis lies, it will be convenient at this point to declare an allegiance, and proceed to a more detailed discussion of their nature. It must be recognised, of course, that both π- and σ-coordination schemes are crucial, even when considering species which, superficially, contain either one or the other metal-carbon interaction. The two are often readily interconvertible under a variety of conditions, and in fact such σ-π rearrangements[20] frequently emerge as a critical control on the reaction of either type in specific instances. The significance of this will, in due course, become apparent.

Transition-Metal-Carbon σ-Bonds Since we will be primarily concerned with reactions which result in fission of the metal-carbon link, a brief consideration of the development of ideas on transition-metal-carbon bond-stabilities is appropriate at this stage.

At the time of the discovery of ferrocene, σ-organo-transition-metals were almost unknown. In addition to the alkyl-derivatives of Pt(IV)[9] and Au(III)[12] already mentioned, some recent work had produced stable titanium-carbon bonds,[21] and the intermediacy of a variety organotransition-metals was inferred from reaction products[22]. Nevertheless, the overall scarcity of examples seemed to confirm contemporary pessimism that the transition-metal-carbon bond was likely to be, by nature, weak[23], and as such was likely to continue to present severe problems to the synthetic chemist. The notion that such bonds are inherently unstable has persisted[17, 24], albeit with certain qualification.

'Stability', of course, continues to be one of the more ill-defined, and consequently, one suspects, frequently used - and abused - terms in chemical discussion. Thus it has been that the disruptive influence with respect to which a given organometal is deemed to be unstable - whether it be, for instance solvolysis, air oxidation or thermolysis - has not always been clearly defined. Ad hoc impressions of stability have been inferred from the relative ease of preparation of compounds, or from their destructive potential in terms of laboratory equipment (and personnel) when mistreated. Thus, 'dry dimethylmanganese explodes on impact'[25, 24]. Moreover, in any consideration of metal-carbon-bond stability, the distinction between thermodynamic and kinetic contributions is of fundamental importance.

The idea of inherent weakness centred mainly on thermodynamic aspects. Organotransition-metals, it is accepted, are thermodynamically unstable, i.e. there is a favourable free-energy change ($-\Delta G$) on decomposition by spontaneous molecular disruption. A considerable contribution comes, of course, from the rearrangement energies of initial fragments. However, the metal-carbon bond itself, it was concluded[23], would be weak, by consideration of the equilibrium thermodynamics of binding. Mulliken, in advancing his 'magic formula'[26] argued that the bond dissociation energy D_o (uncorrected for zero-point vibration energy) is the sum of the covalent bond energy X_{ij} and the ionic resonance energy. E_r, and that X_{ij} is quantitatively related to the appropriate overlap integral S_{ij} and the mean of ionisation potentials $\bar{I}$ by the relationship.

$$X_{ij} = \frac{AS_{ij}\,\bar{I}_{ij}}{1 + S_{ij}} \qquad (A = \text{constant})$$

According to Pauling[27], the resonance energy is dependant on the electronegativity differences:

$$E_r = (\chi_a - \chi_b)^2$$

Jaffé and Doak took these considerations and applied them to a series of hypothetical individual metal-carbon σ-bonds, including those of the first-row transition elements[23a]. Their conclusion was that both X_{ij} and E_r were diminished in the case of a

σ-organotransition-metal, and that the correspondingly low value of D_0 might explain their apparent inaccessibility. (Any extra resonance energy resulting from the case when the metal-carbon bond was to an aryl ligand was not considered.)

A number of further consequences were outlined. It was demonstrated that overlap integrals - and hence bond energies - generally decrease with increasing atomic weight in any periodic sub-group. (The orbitals of the lighter metal are less diffuse). This ought to be reflected in a trend of decreasing stability on descending such a group[23b]. In addition, it was shown that overlap integrals, valence-state ionisation potentials and electronegativity difference (and hence ionic resonance energy) are all increased by heightening the s-character of the bound carbon, and thus the general increase in both covalent and ionic contributions should result in enhanced interaction[23b]. In other words, stronger metal carbon bonds should be formed to sp^2 or sp ligands - aryl, vinyl or ethynyl. Furthermore, it is noted that by these arguments, bond strength should be increased by any agent which increases the electronegativity difference between metal and carbon.

Examples may, of course, be found in at least superficial agreement with all of the above observations. It may well be, for example, that the last proposition goes some way in explaining the generally observed relative stability (in the broadest sense) of σ-fluorocarbon derivatives of transition-metals over their hydrocarbon analogues[28]. However, these effects are likely to be no more than contributive (to a greater or lesser degree) to an overall picture of organotransition-metal stability which is, as will emerge, considerably more complex.

As the numbers of isolable σ-organotransition metals began to grow[29], the emphasis naturally shifted to become one of explaining the apparent stability of these species in spite of their assumed thermodynamic unfavourability. Binary alkyls (or aryls) were not recorded at the early stages. All the known examples had other co-ordinated ligands in addition to organic groups. Quite reasonably, therefore, attention began to be directed toward these other ligands as harbingers of enhanced thermal (or other) stability. In view of contemporary opinion, this stability was necessarily kinetic in origin, and the crystallisation of ideas about the nature of ligand — imparted thermal stability is perhaps best exemplified by the formulation of Chatt and Shaw[30]. Their hypothesis holds particular significance for the subject of this thesis, since, although it was intended to be general, the theory was largely based on their own definitive work on the very organic derivatives of divalent platinum which form the experimental basis for this monograph. (For this reason, illustration will, arbitrarily, be limited to the case of square-planar d^8 configurations, as characterised by the nickel triad in the divalent state).

Essentially, these authors' notable proposition was based on the premise that the activation energy E_a for spontaneous thermal decomposition of the organometal as represented in Figure 1.1, could be equated with the promotion energy required to transfer an electron from the highest occupied (HOMO) to the lowest

Figure 1.1

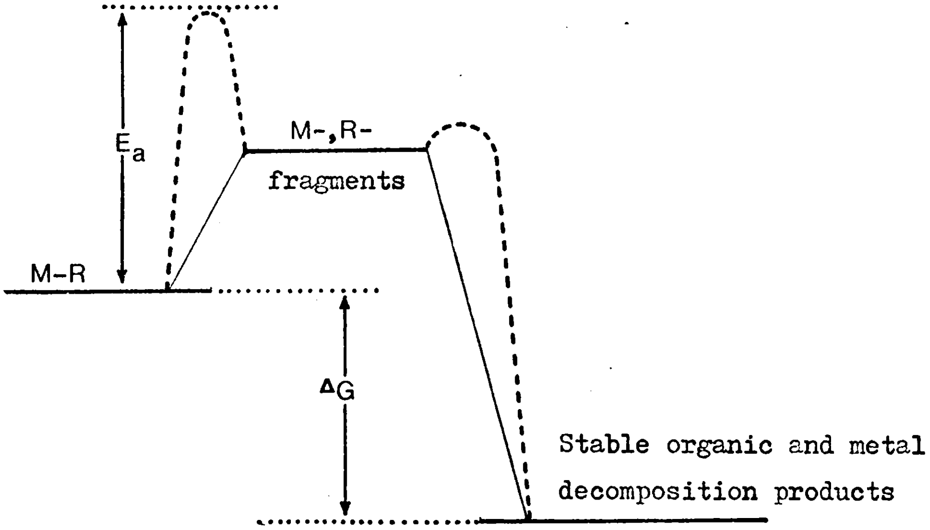
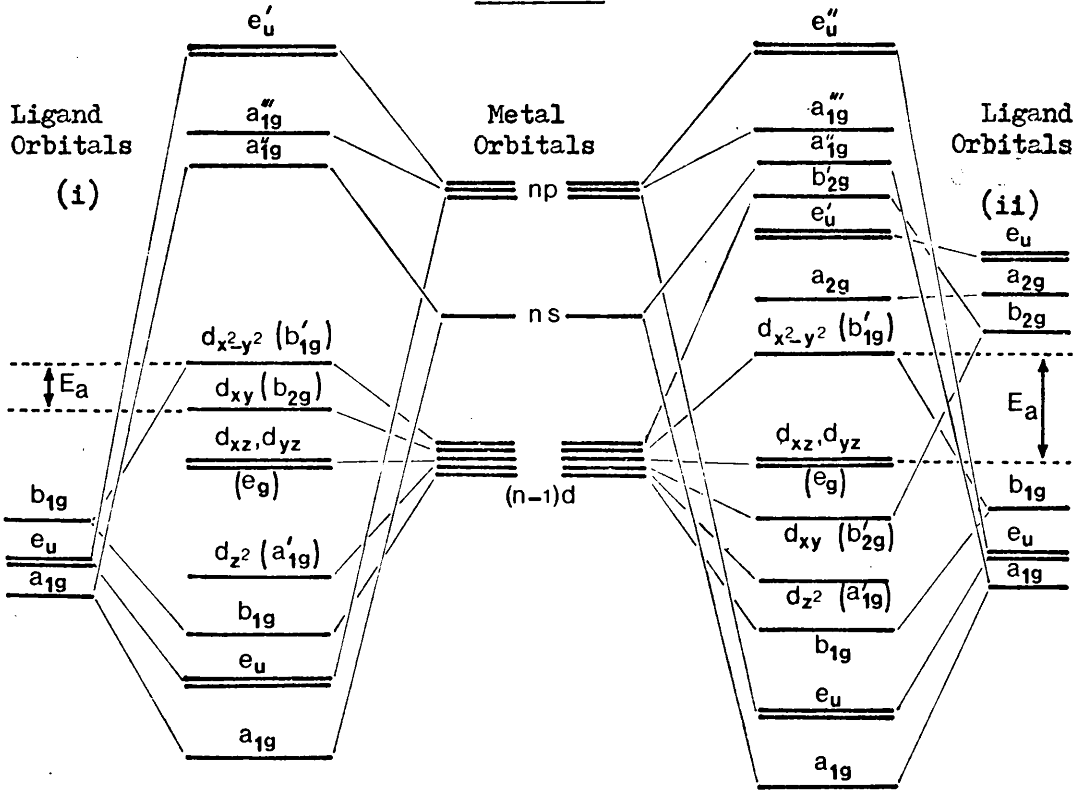


Figure 1.2



M.O. Diagram for L_2PtR_2 (i) in absence of (ii) in presence of Ligands capable of π-bonding in the xy-plane.

unoccupied molecular orbital (LUMO). For transition metals, with vacancies in the d-shell, the HOMO and LUMO are invariably closer in energy than in the case of main group organo-derivatives, against whose relative thermal stability the apparently labile organotransition-metals had to be considered. For early members of the transition period, the transfer was envisaged to be from a σ-bonding to a non-bonding orbital, whereas for later elements - such as the Ni-triad - whose d-shells are more that half-filled, the promotion would occur from a non-bonding to a σ-antibonding level. In either case the overall effect is that of weakening the σ-bond framework, and the requisite energy is directly dependant on the magnitude of the ligand-field splitting. The supporting ligands which seemed to be a prerequisite for stable metal-carbon bonds were so, according to the argument, due to special innate properties, which maximised ligand-field splitting and, by so increasing the activation energy for σ-bond scission, conferred general kinetic stability on the complex. One ligand-property which is capable of inducing such an effect is the capacity to participate in π-bonding (in addition to σ-bonding) with the metal. A powerful illustration of the relative enhancement of E_a in the presence of a ligand with a suitable orbital disposition appears in figure 1.2.

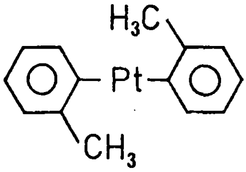
Certainly, the observed stabilities of the organo-platinum and organonickel species produced by Chatt and Shaw, employing, as they did, π-acidic tertiary organophosphines as supporting ligands, were well in accord with the theory. Other notable and empirically reinforced aspects of the argument were:

(i) The theory indicated the reverse trend in stability to that predicted on thermodynamic grounds alone (vide supra); heavier elements should form the more stable organic compounds[30a] - ligand field splitting in corresponding complexes is larger for heavier metal homologues.

(ii) Most stable organometals would possess orthogonal symmetries (octahedral or square-planar) since π-bonding is most favoured by these geometries[30a].

(iii) Generally, unsaturated carbon should be capable of forming the least labile linkage, through the capacity to π-bond with the metal, thus lending stability on both thermodynamic and kinetic grounds[30a]; on one hand, the metal carbon bond order is simply increased - on the other, the ligand field splitting is reinforced. One interesting specific extension of this argument was that applied to the unusually stable bis(*o*-tolyl) complexes. The steric demand of the *ortho*-methyl substituents was envisaged to dictate a preferential conformation in which the plane of the aryl was perpendicular to that of the complex. This maximised interaction of available ligand π-orbitals with the crucial d_{xy} orbital, at once both reducing its energy, and creating an intrisically stronger M-C bond. (d_{xy} is HOMO in the absence of π-bonding; see Fig. 1.2) Chatt and Shaw also recognised the significance of kinetic stability with respect of externally-induced decomposition, since they proposed that these same methyl groups, projecting above and below the metal coordination plane (see Fig. 1.3), will discourage any nucleophilic approach to the metal, thus accounting for the observed hydrolytic and oxidative stability of these complexes.

Figure 1.3



These simple, yet elegant propositions proved very attractive and gained wide acceptance among practitioners and authors[17, 32]. Similar hypothesis were advanced to rationalise the effect of other 'stabilising' ligands[31] (e.g. $C_5H_5^-$). Interpretation of the arguments in terms solely of homolytic scission[17, 32] may well have contributed to the enduring conviction that free-radical pathways predominate in thermal decompositions of organotransition-metals [24, 32, 45]. Nevertheless, the general influence was beneficial, and a fruitful era ensued. More recently however, a new change in emphasis has emerged, stemming from a number of directions.

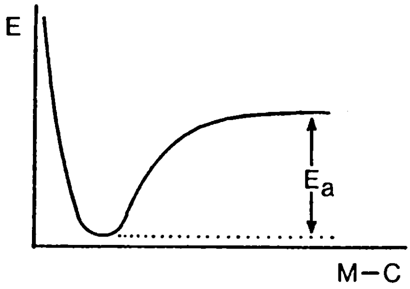
To begin with, the fundamental belief that transition metal carbon bonds are innately weak has come into question[33, 34]. Appropriate bond-dissociation energy data (as distinct from mean bond-energy[36, 27]) are very scarce, but such that are available (272 KJ.mole^{-1} for Pt-C in trans-$(Et_3P)_2PtPh_2$[35a]; 164 KJ.mole^{-1} for Pt-CH_3 in $(\eta^5\text{-}C_5H_5)PtCH_3$[35b]; ca. 250 KJ.mole^{-1} for Ti-CH_3 and ca. 350 KJ.mole^{-1} for Ti-Ph in $(\eta^5\text{-}C_6H_5)_2TiR_2$[35c]) are not indicative of relatively fragile metal carbon bonds[34].) Correlations of available bond-length or force-constant data which may be seen to reflect the equilibrium thermodynamics of the transition-metal-carbon bond, also support the view that these are not unusually weak[33, 34]. In fact, there seems little justification for suspecting that transition-metals form fundamentally weaker links to carbon than they do, for example, to hydrogen, nitrogen or oxygen, nor indeed that such bonding is substantially less effective than in main-group analogues[33, 34].

In addition to this, latter advances in the field have produced organotransition-metals which either (i) possess additional ligands which do not obviously fulfil the Chatt-Shaw criteria for stability - e.g. $(EtRu(NH_3)_5)^{2+}$ (Ref. 37), $(PhCH_2Cr(OH_2)_5)^{2+}$ (Ref. 38) - or increasingly (ii) contain no 'supporting' ligands at all*, - e.g. MMe_6(M=W[39], Re[40]), TiR_4 (R=methyl, benzyl[42], 1-adamantyl[43], 1-norbornyl[44]). Moreover, the likelihood that the type of mechanism advanced by Chatt and Shaw would be universally favoured for transition metal-carbon σ-bond scission has been challenged.

Braterman and Cross have carefully evaluated possible pathways whereby metal-carbon bond cleavage may occur[33]. These processes may be broadly classified as being concerted - in which more than a single metal coordination site is involved - or non-concerted. The latter may be further subdivided into the categories of promotional or non-promotional paths. A promotional operation is characterised by a change in electronic configuration along the reaction coordinate. The authors argue that, whereas promotional processes may well operate in systems where the metal has five or less d-electrons,

*for a review of homoleptic (binary) metal alkyls, see Ref. 86.

they are unlikely to be the most favourable option for thermal fragmentation of organometals in the second-half of the transition-block. Specifically, it is demonstrated that the scheme proposed by Chatt and Shaw - which is promotional - is an improbability for the thermal disruption (although its implication in photolysis is possible[33]) of square-planar systems with the metal in a d^8 configuration, whether such non-concerted cleavage yields an organic anion, radical or cation. If non-concerted ligand loss occurs at all, it will more resemble the non-promotional operation likely to occur for organic derivatives of main-group elements. In this case, the activation energy for unimolecular thermal bond rupture is that required to mechanically extend the internuclear distance beyond that required for bonding interaction (Fig. 1.4.)



As it seems now unlikely (vide supra) that transition-metal- and main-group-metal-carbon bonds differ greatly in respect of this parameter, it does not seem realistic to expect that it is this same process which governs their evidently different relative stabilities. The inference was that, for this area of the Periodic Table at least, concerted processes, of which there are several, probably dominate as determinants of thermal reactivity. They must do so in a kinetic sense, by permitting reaction in a direction of lower activation energy and it is their more ready availability to organotransition-metals, with their higher propensity for variable coordination and oxidation state, which is responsible for the ubiquitous lability of these species. In effect, then, the traditional explanatory roles of kinetic and thermodynamic factors have, in this case, become inverted.

The possible influence of metal electronic configuration on transition-metal-carbon bond dissociation retains some attraction, however, and a new role for d-d transitions has been proposed[45]. It was argued that the activation energy for M-C homolysis (in MMe_6) might be determined by the availability of low-lying electronically excited states of suitable symmetry. Mixing of one of these into the ground state might facilitate the necessary bond-weakening electronic redistributions, and so ease passage to the activated state. Notable consequences of this theory should be simultaneous dissociation of two <u>trans</u>-alkyls (in d^2, d^4 and d^5 configurations) or assymmetric dissociation of only one (for d^1, d^3 and d^6). However, it has been pointed out[46] that agreement with the behaviour of certain organometallic systems (of which d^8-square planar is one) is poor, and, further that expected spectroscopic consequences of the proposals are either absent or negligible.

Although there remains a lack of comprehensive and correlatable data on transition-metal-carbon σ-bond scission[47], it seems that concerted electron-pair processes do, as suspected[33, 48], operate widely in organotransition-metal chemistry. Indeed their function is manifestly not limited to the latter half of the d-block[47] (nor, perhaps, solely to transition elements). Certainly a great variety of reactions whose intimate natures are yet to be established, and for which rationalisations have previously been sought in other directions, may be explained in these terms[48].

The role of additional ligands - which cannot altogether be disregarded - may be understood in terms of their effective blocking of coordination sites which might otherwise be utilised in a concerted operation. Both σ- and π-bonding abilities may be important, both inasmuch as they will affect the tenacity of occupation of the site, and also in that they may influence the electron availability at the metal[23, 48]. For example, it has been suggested that good electron donors, whether in a π- (e.g. $C_5H_5^-$) or a σ-sense (e.g. phosphines), might inhibit metal-carbon homolysis, since, by decreasing the electron demand of the metal, they may thus, in some cases, discourage reductive electron-transfer[33].

Concerted, paired-electron processes which may be responsible for metal-carbon bond fission include amongst their number, α- and β-eliminations, mononuclear reductive elimination and binuclear elimination. During the course of this project, a considerable amount of investigation in this area has been simultaneously in progress elsewhere. Accordingly, these processes and the salients of current opinion on each will be surveyed in more detail in the course of Part II of this Introduction.

Platinum-Carbon σ-Bonds

Carbon is known to form σ-bonds to both the (formally) divalent[50] and tetravalent[51] metal. Platinum-carbon bonds are not considered to be atypical among σ-organotransition-metals, and, since they are of premier practical interest in this treatise, a summary consideration of their nature will serve to illustrate the fundamental aspects of the broader subject. First, however, a brief account of organoplatinum chemistry, specifically that of the formally divalent state, would be appropriate. The organic chemistry of platinum, in its various oxidation states (0, +2,+4) has been extensively reviewed[49-53], and is now well documented in specialist texts[32, 54].

Historical

Although the first divalent platinum compound which unequivocally contained a Pt-C σ-bond was not documented until 1957[55], it now seems certain that such a bond was in fact effected as early as the first decade of this century[10]. The first 'phosphine-stabilised' dialkylplatinum(II) complex appears to have been prepared in 1954 by Chatt and Foss[56]. It was however, the collaboration of Chatt and Shaw[30a] - already noted- which dramatically opened up the subsequent rapid development of organoplatinum(II)[50, 54].

Structural

In common with classical coordination complexes of Pt(II) the organic derivatives display a preference for tetracoordination and basically square-planar geometry. (The incidence of three- or five-coordination will be discussed as encountered.) Thus, cis/trans geometrical isomerism is a prominent feature of their physical chemistry. The ultimate configuration adopted by a given combination of ligands about the platinum atom is governed by the dictates of thermodynamic and kinetic trans-effects, to which platinum, of all its triad, appears most sensitive[56]. As a result, where neutral ligands are, for example, a pair of tertiary organic phosphines, cis-geometry is generally favoured if both anionic ligands are hydrocarbyls; whereas if one is replaced by a (less trans-labilising) halide, to give the mono-organo-derivative, then the trans-configuration usually results.

Stability

The stabilities of organic derivatives - including their thermal stabilities - cannot be summarily encompassed by a few brief statements. The panorama of organoplatinum(II), unremarkably, reflects a great diversity of reactivity. Platinum is, however, generally regarded as forming the most robust metal-carbon σ-bond of the Ni-triad[50], the order being:

$$Pt > Pd > Ni$$

This tendency is a probable partial explanation of the relative lack of current commercial or laboratory synthetic application for platinum, compared with Pd[2,57] and Ni[2, 58]. After all, if it is important that a metal-carbon bond be established in a catalytic or synthetic intermediate, it is no less critical (and arguably more so) that it be readily broken.

Of further note, perhaps, is that, on the whole, aryl derivatives display greater thermal stabilities than do alkyls.

Chatt and Shaw, in fact, advanced a series of decreasing stabilities depending on organic ligands[30a]:

o-substituted phenyl > PhC≡C > p-substituted phenyl ~ phenyl > alkyl > HC≡C

(Stabilities amongst alkyl derivatives decreased in the sequence:

$$\mathrm{Me} > \mathrm{Et} > \mathrm{Pr}^n > \mathrm{Bu}^n > \mathrm{PhCH_2}$$ [30a])

Explanations of these observations probably involve both thermodynamic and kinetic considerations, as will emerge in subsequent discussion.

Bonding

The bond formed between square-planar platinum(II) and a hydrocarbyl ligand is regarded as a normal, localised 2-electron covalent σ-bond, in which the carbon is a 1-electron donor. (In oxidation state formalism, both electrons of the bond are formally assigned to the ligand - which is seen as anionic, via 1-electron oxidation of the metal). In valence-bond terms, the bonding scheme requires overlap of sp^3, sp^2 or sp hybrid orbitals of the ligand, with a dsp^2 combination on the metal[59]. The molecular orbital representation of bonding, depicted in Fig. 1.2, employs the same metal-orbitals for bonding.

There also exists the possibility of metal-carbon π-bonding This would arise if the carbon atom possessed residual orbitals of π-symmetry, i.e., if the bound atom were sp^2 (e.g. phenyl, vinyl) or sp (e.g. ethynyl) hybridised. The mechanistics of the interaction are reckoned to involve back-donation of electrons from filled metal orbitals (valence-bond formalism) to vacant (antibonding) orbitals on carbon, and are schematically represented in Fig. 1.5. for Pt:

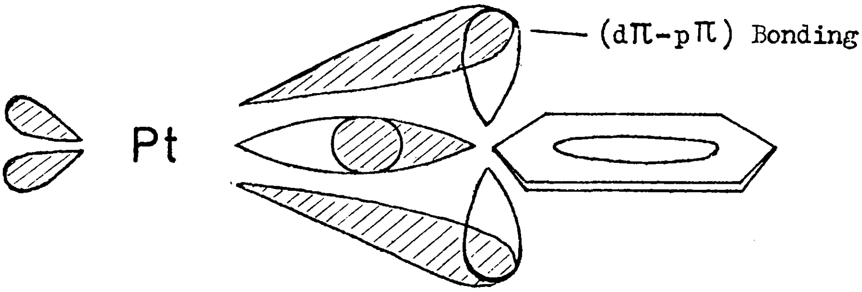


Figure 1.5

The relative contribution of π-bonding effects to overall transition-metal-carbon bonding is not a subject about which there is universal consensus[60]. Much attention has focussed on aryl complexes, and the Ni-triad has featured prominently. Chatt and Shaw, who considered M-C π-bonding to be an important contribution to stability, inferred from dipole measurements on analogous alkyl and aryl complexes (e.g. <u>cis</u>- $(Et_3P)_2PtMe_2$ has μ=5.65D; <u>cis</u>$(Et_3P)_2PtPh_2$ has μ=7.2D) that there was a significant mesomeric drift of electrons into the aryl ring, ostensibly by a π-interaction[30a]. This opinion seemed to be confirmed by Parshall,[61] who, from an investigation of ^{19}F parameters in $(Et_3P)_2Pt(Ar)X$ (where Ar = 2- or A-fluorophenyl) concluded that the $L_2(X)Pt$ moiety, when bound to fluorobenzene, was an electron donor in both inductive (σ) and resonance (π) senses. A parallel study including Pt- and Pd-, in addition to Ni-analogues, has more recently led to the tentative suggestion that Ni is the most effective π-donor[62]. However, in a broader investigation (which included the same fluorophenylplatinum(II) systems), Stewart and Treichel found [60] little variation in the quantity upon which π-bonding was assessed (the Taft resonance parameter,σ_r^{o}) in spite of wide variation of the appended metal-moiety. They therefore concluded that, although metal-carbon π-donation undoubtedly occurs, its significance is small, and its contribution to metal-aryl bonding is secondary alongside σ-bonding effects[60]. Similar conclusions have been drawn[63] from consideration of ^{13}C nmr parameters of phenylplatinum(II) derivatives of type trans-$[(C_6H_5)Pt(AsMe_3)_2L]^+PF_6^-$. Further support for these arguments, in the case of Ni, is provided by a recent proposition, based on x-ray photoelectron binding-energy measurements, that Ni-C π-bonding is unimportant in aryl- and alkenyl- (and alkyl-) nickel derivatives, although it seems to be significant for alkynyls[64]. Notwithstanding, and in general contrast, another recent publication suggests, on the basis of comparing electronic spectra of complexes of the type (2,2'-bipyridine)PtR_2 (R=alkyl, aryl), that π-bonding may be an important consideration in the phenyl-platinum[65] bond. X-ray structure determinations also fail to resolve any general agreement about the relative significance of M-C π-bonding in arylmetals[66].

Such π-bonding tendencies would not normally be expected in metal alkyls, where presumably suitable carbon orbitals are either involved in bonding to hydrogens or to other carbons, or are unfavourably high in energy. However, there is nmr evidence to suggest that metal-to-ligand π-donation may be operating even for a Pt-Me bond[67].

The writer does not presume to draw conclusions from this diversity of facts, which serve rather to illustrate that metal-carbon π-bonding must advisedly be invoked with due caution.

CHAPTER TWO

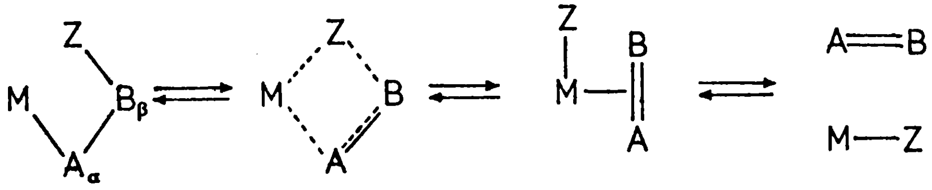
Introduction - Part II

CHAPTER TWO

Metal-carbon bond-scission need not occur primarily; its ultimate incidence and nature may be dictated by a prior sequence of favourable chemical events. A brief summary of currently established modes of reaction which are commonly encountered in organo-transition-metal chemistry, or which may be interpolated from 'inorganic' analogues, is therefore in order. Important implications are indicated, with due reference to Pt(II). In these considerations, organic derivatives of the Group IB metals (Cu, Ag, Au) have been included. Although these do not exactly satisfy the precise definition of 'transition-elements' in that, even in the unipositive state, they have filled d-shells, they do nevertheless, have access to higher oxidation states which justify their inclusion [Au(III) in particular, which is isoelectronic with Pt(II), forms many stable σ-organic compounds[69]]. Their general chemistry, moreover, reflects a broad similarity to that of other transition elements[68].

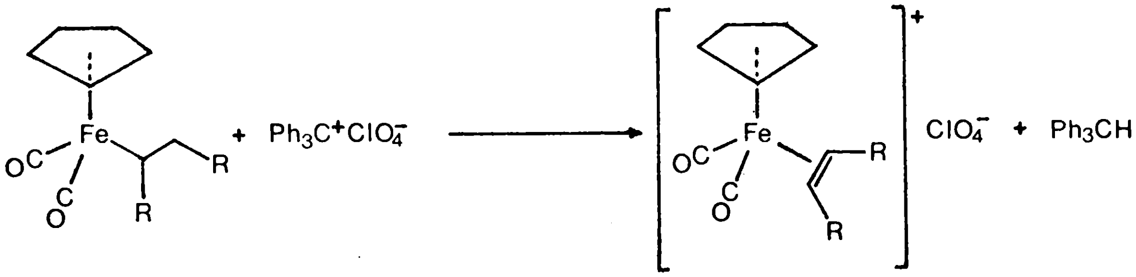
(i) β-ELIMINATION

General This process is generally considered to be a concerted electron-pair operation whereby an element—metal bond is broken via a $\sigma-\pi$ re-arrangement, with concomitant transfer of a β-substituent from ligand to metal:



The scheme depicts the most general case, and theoretically A, B, and Z might represent any suitable atoms, although Z is usually hydrogen. For example were A an oxygen and B a carbon atom, the representation is that of decomposition of a metal alkoxide to yield a metal hydride and an aldehyde[70]. (As such it may be operative in the Wacker process.) For our purposes, however, the β-atom will be carbon, and the implication of the process as a primary route to metal-carbon scission will be realised. The importance of this operation to the chemistry of alkylmetals - in which case the products are metal-hydride and alkene - has, in fact, been recognised for some time[71].

It was clear at a fairly early stage, however, that there was some interaction between transition metal and β-atom (or substituent). Among the first indications of the operation of a β-elimination mechanism was the discovery that reaction of an alkyl-iron(II) complex with the triphenylmethyl cation led to hydride abstraction and generation of an alkene-iron species:[73]



It is, of course, not clear that hydride transfer to metal was (or is) involved. However, it was soon reported that pyrolysis of an ethylplatinum(II) compound gave rise to ethylene, and a hydridoplatimum complex[74]:

$$\underline{\text{trans}}\text{-}[(Et_3P)_2Pt(C_2H_5)Cl] \underset{\text{high press.}}{\overset{180^{\circ}\text{C}}{\rightleftarrows}} \underline{\text{trans}}\text{-}[(Et_3P)_2Pt(H)Cl] + C_2H_4$$

By analogy with the previous example, it was suggested that the β-hydrogen probably migrated as a hydride ion. The scheme was subsequently shown to be reversible <u>via</u> olefin insertion (q.v.) into the Pt-H bond - to such an extent, in fact, that the resultant scrambling of hydrogen atoms was so rapid in relation to alkene loss that specific deuterium labelling could not unequivocally assign the origin of the abstracted hydrogen to the β-carbon[75]. This pattern of rapid reversibility has emerged as a common characteristic of β-elimination reactions (<u>vide infra</u>). It is interesting to note in passing that perhaps the earliest observation of β-elimination may have been that of Wanklyn and Carius, more than a century earlier. In a remarkable report[76], they outline the interaction of ethereal Et_2Zn and FeI_2 which produced ethylene and 'a hydride of iron'. An intermediate ethyliron species seems probable.

As the relevance of β-elimination has become increasingly evident, investigations associated with it have, broadly speaking, adopted two parallel paths. The first has been concerned with applications of its principles to synthetic organometallic chemistry, mainly by limiting the kinetic option of

β-elimination and thus fortifying the metal-carbon link. The second has comprised elegant studies, aimed at understanding the intimate nature of the process. After all, in some important systems, it is vital that selective β-elimination does occur.

Synthetic Aspects

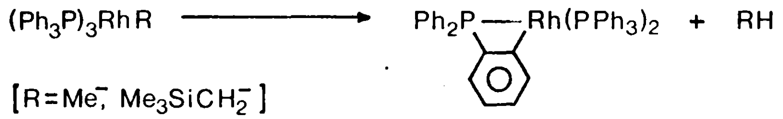
The first approach has, as is the nature of novel synthetic chemistry, had more immediate impact. Apart from the obvious requirement of a vacant (or potentially vacant) metal coordination site, the two underlying principles of the operation of β-elimination as applied to σ-bound metal-carbon systems are[71]:

(a) that the β-atom must be capable of forming a double-bond to carbon (or generally of comfortably increasing its existing bond-order to the metal-bound carbon).

(b) that the β-atom must possess a substituent that is readily transferrable to the metal atom (as, evidently, is hydrogen).

Clearly, there is a potentially great number of structural modifications in the ligand whereby one or both of the above criteria might be frustrated. The simplest hydrocarbyl ligand to which β-elimination is denied is undoubtedly the methyl group, which effectively lacks a β-atom. (An α-elimination (q.v.) pathway may, however, be accessible). This is probably predominantly responsible for the oft-observed enhanced thermal stability of methyltransition-metals compared with their higher-alkyl homologues. Such a powerful consideration is this, that several organometals are now known with methyl groups as the sole ligands. These include neutral Me_4Ti[41], Me_4Zr[77], Me_5Ta[78], Me_6W[39] and Me_6Re[40], and anionic ($ZrMe_6^{2-}$)[79] and ($Mo_2Me_8^{4-}$)[80] with its remarkable quadruply-bonded Mo_2^{4+} skeleton. (Me_4Cr has also been reported[81, 82]; it is highly unstable, decomposing at ca.-60°C[82]. Me_5Nb was too unstable to be characterised in the absence of other coordinating ligands[78] Dimethylmanganese is probably polymeric[82]) In addition to methyl, a wide variety of other σ-carbon ligands which, for one or other or both reasons, inhibit β-elimination. Among these are the cage-hydrocarbons for whom olefin formation is unfavourable - 1-adamantyl[43], 1-norbornyl and 1-or4-camphyl[44] - and ligands with unfavourable β-atoms and/or no transferrable β-substituents - e.g. benzyl[42, 83] or the monodentate and bidentate phosphonium ylides, $Me_3PCH_2^-$ [84] and $Me_2P(CH_2)_2^{2-}$ [84, 85]. Of particular note amongst this category are the neopentyl family of ligands (tertiary β-carbon or unfavourable other Group IVA β-atom) especially the widely-used $Me_3SiCH_2^-$ group[34, 86].

All these species have been successfully incorporated into a wide diversity of organotransition metals of notable stability, often as the only coordinated ligand. Additional stability no doubt derives both from their (frequent) coordinative saturation of the metal, and the great bulk of some of the groups themselves (some binary alkylmetals owe their stability ostensibly to ligand-bulk alone[81]), thereby insulating the metal from external attack. These homoleptic (or binary) organometals have been reviewed in some detail[34, 86-89], particularly derivatives of the neopentyl class[34, 86]. This broad type of organotransition-metal has been dubbed 'elimination-stabilised', but, as has been pointed out[86], this is a less-than-universal view. The only form of labilising elimination to which it may be claimed they are more stable is β-elimination. Certain aspects of certain ligands - e.g. great steric demand - may render them relatively more susceptible to other disruptive eliminations. Thus $(Ph_3P)_3Rh(CH_2SiMe_3)$ is less thermally stable than $(Ph_3P)_3RhMe$ presumably since the greater bulk of the former alkyl favours its decomposition according to[90]:

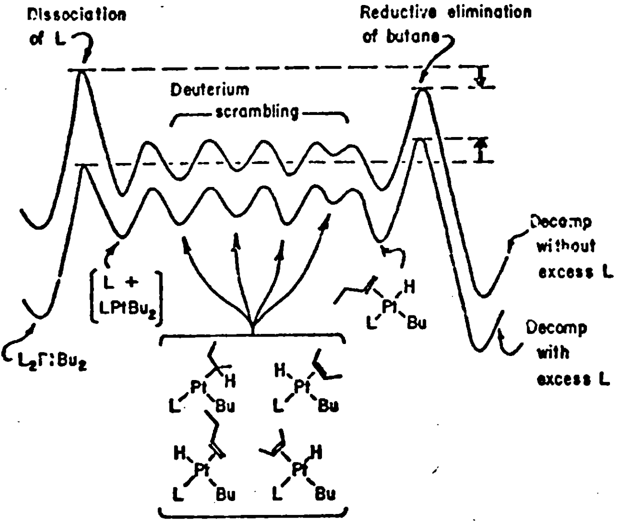


[This scheme invokes <u>ortho</u>-metallation and reductive elimination (q.v. both)].

Phenylmetals too, might be considered to be stabilised toward β-elimination, since their decomposition by this route would require a hydridometal-benzyne intermediate. This, however, will be discussed later in direct relation to decomposition of phenylplatinum(II) complexes. The kinetic stability of many alkynylmetals may be in part attributed to the unavailability of a β-elimination pathway to M-C fission, as well as to their M-C π-bonding capacity.

Mechanistic Aspects

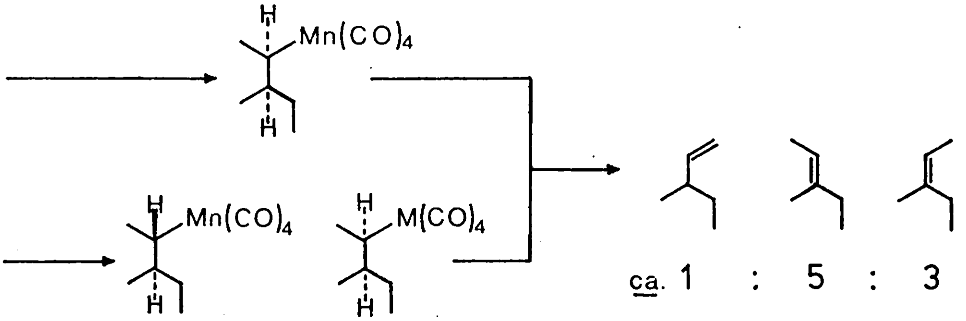
Investigation of the thermal decomposition of $(Bu^n_3P)Cu(n-C_4H_6)$, in ether solution, has established that the 1:1 mixture of 1-butene and n-butane which is produced is not the result of reactions of intermediate free radicals. Instead, 1-butene derives from the elimination of $(Bu^n_3P)CuH$ from the alkylcopper[91]. Butane results from reduction by the hydridocopper species of further n-butylcopper (again without free-radical production[92]) Dihydrogen is also generated, presumably through self-reaction of the hydride complex. (The last two schemes may be rationalised in terms of binuclear elimination (q.v.)). Specific deuteration of the initial alkylcopper (at the 2-carbon) establishes the stereochemical course of the decomposition as primary β-elimination of the copper hydride[91]. Similarly, examination of the thermal disruption of <u>cis</u>$(Ph_3P)_2Pt(n-C_4H_6)_2$ in solution has indicated that a primary alkene elimination, followed by an intramolecular reductive elimination of alkane from the alkylplatinum(II) hydride intermediate is responsible for the generation of the 1:1 product mixture of 1-butene and <u>n</u>-butane. Any appreciable free radical participation is again ruled out. Closer scrutiny of the reaction, however, highlights several notable features. Under normal circumstances, the rate-determining step appears to be loss of a coordinated phosphine, ostensibly to make way for the coordinative expansion required by migration of a hydride. In the presence of free phosphine, the reaction is greatly inhibited, and there is good evidence that the rate-limiting process is now the production of organic products. A second feature is one that is an important consideration in many incidences of β-elimination. The initial hydride elimination is rapidly reversible <u>via</u> non-regiospecific insertion(q.v.) of coordinated alkene into the Pt-H bond. This can be adjudged from the facts that deuterium originally present at C_1 or C_2 of the σ-butyl ligand is extensively scrambled along the length of product 1-butene, and that the hydrogen atom incorporated in the butane product may arise with equal probability from either C_1 or C_2 of the ligand. (Contributions from α-elimination (q.v.) are possible, but less likely). No kinetic deuterium isotope effect was noted, nor was there exchange with 1-butene free in solution[93]. The conclusion is that activation energy barriers between intermediates involved in scrambling are small in comparison to those associated with preliminary ligand loss, or final loss of organic groups from the coordination sphere



Reaction Coordinate Describing Thermal Decomposition of $(Ph_3P)_2PtBu_2^n$

(From Ref. 93)

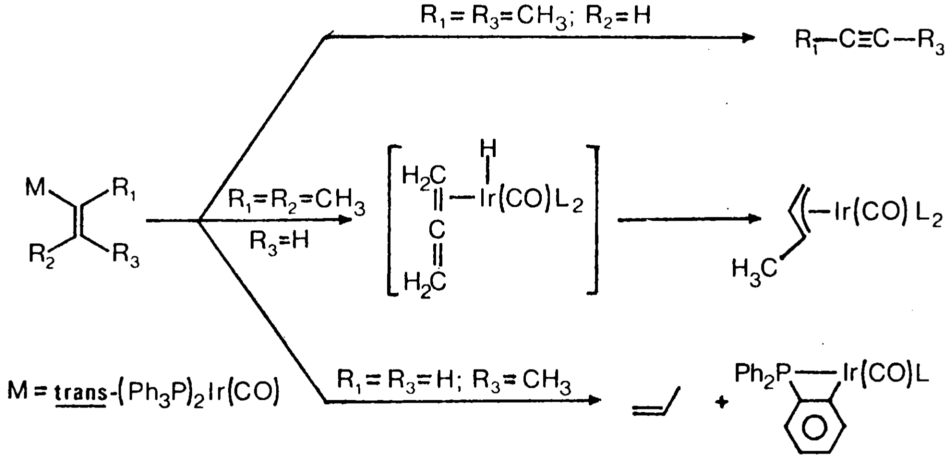
A predisposition to rapid reversibility was also manifest in the sequence leading to thermal decomposition of erythro-(2,3-dimethylpentyl) tetracarbonylmanganese(I) (thermally generated <u>in situ</u> from the corresponding acylpentacarbonylmanganese species) which yielded the same mixture of <u>cis</u>-and <u>trans</u>-3-methyl-2-pentene and 3-methyl-1-pentene as did a mixture of erythro- and threo-alkylmanganese isomers:



The alkenes themselves were not found to isomerise under the prevalent conditions. These workers concluded that the liberation of coordinated alkenes constituted the major exit from a manifold of rapidly equilibrating $RMn(CO)_4$ and $(alkene)Mn(CO)_4H$ fragments. (These observations, incidentally, frustrated the original goal of the study, which was to validate the assumption that β-elimination is a <u>cis</u>-elimination). However, a rapid elimination/insertion chain which scrambles hydrogen and carbon atoms relative to each other or the metal, does not invariably develop. This was true for the butylcopper reaction discussed above, and a parallel situation is to be found in organoiridium(I) chemistry. Thus, the observation that thermal decomposition of an ether solution of <u>trans</u>-$(Ph_3P)_2Ir(CO)(n\text{-}octyl\text{-}2,2\text{-}d_2)$ leads to simultaneous production only of octene-d_1 and octane-d_3, is consistent with primary β-elimination[95]; re-insertion must be absent unless it is totally regiospecific, which seems unlikely in view of the behaviour of isoelectronic alkylplatinum(II). β-elimination is, in this case, apparently involved in the rate-determining step[96], and a kinetic deuterium isotope effect of $K_H/K_D = 2.28 \pm 0.2$ is reported. There is, furthermore, good evidence that octane is produced by a rapid bimolecular reaction of $HIr(CO)(Ph_3P)_2$ with the unreacted alkyl complex, possibly via binuclear elimination[95] (q.v.).

β-elimination has been implicated as a metal-carbon scission route in a variety of other studies[47], but it is not always the sole operative pathway. For example both mono- and trialkylchromium(III) species may undergo β-elimination to an extent, in decomposition sequences that also seem to implicate α-elimination and one-electron-transfer reactions[97]. β-elimination appears also to be the primary tendency of suitable dialkylmanganese(II) compounds[98]. Organonickel(II), too, has shown some disposition to β-eliminate[99], but here again other primary decomposition modes may compete[100].

β-elimination is also, in theory, available to η^1-vinyl metals, from which alkynes would result as decomposition products. This is, to date, a rarely-observed occurrence, but organoiridium(I) once more provides a good example. Thus substituted vinylic derivatives trans-$(Ph_3P)_2(CO)Ir(Vy)$, which possess a cis vinylic hydrogen, preferentially undergo β-elimination of this atom, even where an eliminable allylic hydrogen is available. Where there is lack of a cis vinylic hydrogen, the β-elimination of allylic hydride will proceed, although more slowly, to yield a π-allene complex which then rearranges to an η^3-crotyliridium(I) species[101] (See Scheme) Absence of both eliminable β-hydrogens leads to decomposition by <u>ortho</u>-metallation and reductive elimination of propene.



The generation of a significant amount of acetylene from the thermal decomposition of $(\eta^1\text{-}C_2H_3)TiCl_3$[102] may also reflect a contribution by this mechanism. β-elimination of aryne from an aryl-metal - although intuitively unfavourable - has been reported, but will be discussed later.

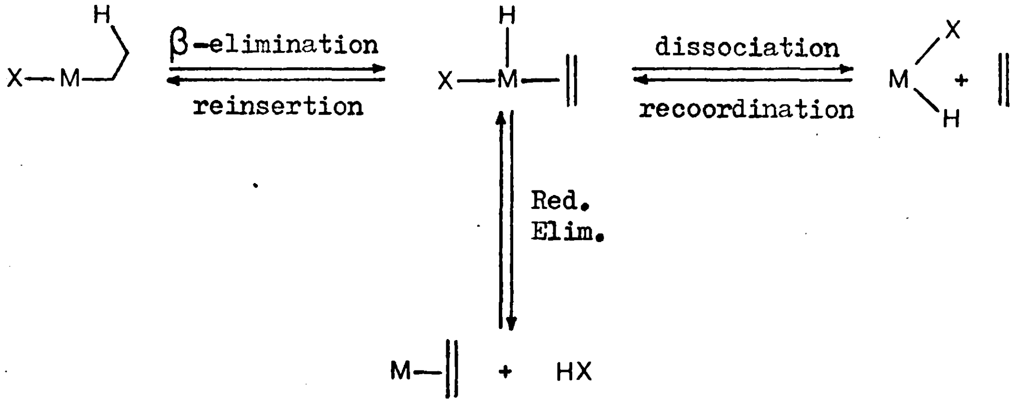
Even where it is not a primary route to irreversible metal-carbon bond fission, the β-interaction has proved to be of great significance in reactions of alkyl metals. It has, for instance, been invoked to explain σ-alkyl isomerisations in organo- Ni(II)[103], Pd(II)[104], and Au(III)[105] species, prior to their thermal decomposition by another route. (Reductive elimination (q.v.))

Further Implications

Controlling influences on paired-electron processes in organotransition-metals as a whole will be analysed in a subsequent section. Such factors as may be specific to β-elimination deserve some comment.

The hydride-transfer step is, in effect, an intramolecular oxidative addition (q.v.)[48, 96]. The precise nature of the transition-state is not known, but naively, the reaction should be facilitated where the C-H entity in question can most readily approach the metal[106]. This might explain, for example, the readier β-elimination from n-octyl- rather than vinyl-derivatives of Ir(I)[95, 101], or that from n-alkylplatinum(II) rather than metallocyclic analogues[93, 107]. It has also been suggested that some correlation may exist between the facility of these reactions, and the compatibility of products or reactants in terms of 'hard' and 'soft' interactions, [a concept that has been recently criticised[109]] the rational being, briefly, that the elimination would proceed (or not) so that maximum compatibility between ligand and metal was attained in these terms[108].

In spite of the elegance of many studies, however, some aspects of the internal energetics of β-elimination and its accompanying processes are far from well understood. For example, in the alkylplatinum(II) investigations, the role of free ligand is not entirely unequivocal; in one case, phosphine-loss is rate-limiting, and free ligand strongly inhibits the decomposition[93]; in another, added ligand accelerates the process[107]. Another feature of these reactions which deserves further investigation is the aspect of reversibility. The observation of products which arise from this operation is, in fact, determined by two reversible processes: (i) reversible insertion of alkene, while in the metal coordination sphere (ii) reversible exit of alkene from coordination. The incidence of scrambling by (i) is likely to depend on the relative activation energies for (ii) or for whatever other process may be responsible for removal of metal hydride from the system. (e.g. reductive elimination)



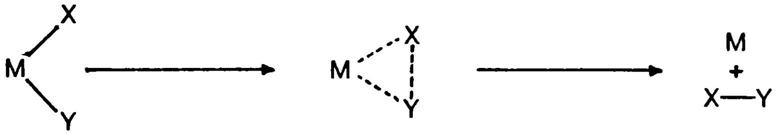
Thus, speculatively, the alkylcopper(I)[91] and alkyliridium(I)[95] systems may represent cases where alkenes, once formed, are irreversibly lost from the metal: perhaps because the activation energy for elimination is low, and this operation is thermodynamically favoured. (Reverse activation is higher-energy demanding). Hence, hydrogen scrambling occurs in neither case[91, 95, 96]. Furthermore, LCuH, an operative intermediate, does not react with free alkenes[92]. On the other hand, the alkylmanganese(I)[94] and alkylplatinum(II) species may well, by the same token, represent the opposite case. Here, non-regiospecific insertion/elimination chains are readily set up, presumably due to low activation energy barriers for (i) in both directions. Expulsion of alkenes must present a high energy barrier, since neither organometallic system shows any inclination to interact with product alkene, free in solution[93, 94]. (The platinum system interacts with 1,5-hexadiene, but only when the latter is used as solvent).

The di(n-butyl)platinum(II) species displays further mystifying features, particularly regarding the ultimate liberation of organic products. During the rapid Pt-H addition and elimination reactions, there is, as noted, no exchange with 1-butene free in solution. This would seem to indicate a significant activation energy barrier to alkene dissociation. Alkene loss must, however, be connected with reductive elimination of n-butane (to which high activation energy is ascribed), since butane and butene appear in equal amounts, irrespective of the extent of decomposition of dialkylplatinum[93]. The alkene, in turn, seems to exert a curious influence on the reductive elimination step. This is manifest in the apparent reluctance of the hydridoalkylplatinum intermediate to reductively eliminate while the coordinated alkene is a 2-butene - which is a necessary implication in the scrambling chain; 2-butenes are absent from the product distribution[93].

Even with a lack, to date, of detailed data, it is evident that the β-elimination mechanism is a most important consideration throughout organotransition-metal chemistry. If nothing else, the general stability of 'elimination-stabilised' organometals from various parts of the d-block implies this. It seems likely that many reaction schemes in which transient alkyltransition metals have been invoked, and which produce inter alia, alkenes, may be examples of β-elimination[109,110]. Indeed, it is interesting to note that the route may not even be limited to transition metal derivatives. For example, the thermal isomerisation of α-branched trialkylboranes[111] and the elimination of fluoroethylene from 2,2-difluoroethylsilanes[112] (by fluoride-transfer) have been assigned intramolecular β-elimination mechanisms.

(ii) REDUCTIVE ELIMINATION (Mononuclear)

Reductive elimination is, for our purposes, the synchronous loss of two ligands from a metal coordination sphere in such a way that they are ultimately united by a chemical bond; both metal coordination and formal oxidation state are reduced by two:



The process as depicted is concerted; bond-breaking is accompanied by bond-making. Processes which achieve the same end, but which proceed via free-living high-energy intermediates, will be discussed in a separate section.

Concerted reductive elimination - in common with the remaining metal-carbon scission modes which will be discussed - is, in comparison with β-elimination, a relatively unexplored phenomenon. A summary of salient aspects will, accordingly, be more brief.

Theoretically any two adjacent ligating atoms whose incipient mutual bonding is thermodynamically favourable might be united by reductive elimination. Reductive elimination leading to a variety of covalent bonds has, indeed, been reported, including inter alia H-H[113], H-Cl[114] and RS-SR[115]. Several examples of C-H elimination have been cited; some have been noted already, others will be encountered in connection with other reaction modes. Unequivocal reductive elimination of C-C remains relatively unstudied. (This might be considered unusual, since a reaction which leads, stereoselectively, to generation of a C-C bond is of obvious synthetic import). Correspondingly, no analogous 'elimination stabilised' organometallic chemistry has arisen around reductive elimination. This is basically because of the almost total lack of understanding of the factors which influence the kinetic threshold for this process. (That powerful kinetic influences are associated with this reaction is demonstrated by the vast abundance of transition-metal complexes which possess thermodynamically compatible adjacent ligands, but which show great (or total) disinclination to fulfil their potential for reductive elimination).

Mechanistic studies which establish reductive elimination of a carbon-carbon bond as a concerted intramolecular process are, as yet, scarce, and have tended to focus on only a few metal systems. Most of these results have appeared since the start of our own investigations.

Some time ago, it was reported that tetravalent platinum complexes of the type ($R_xPtX_{4-x}L_2$) (R=organic group; X=halide,

$x = 1-3$; L =tertiary phosphine or arsine) underwent smooth pyrolytic elimination of two anionic ligands to yield divalent platinum species. The organic groups (R) were mainly methyl although one acetyl group was occasionally present. The organic products of decomposition were predominantly ethane (or acetone) with, under special circumstances, some methyl halide. No attempt was made to define the mechanism[116]. Because of the ready characterisability of both organic and organometallic products, these reactions have proved very suitable for subsequent study.

It was recently demonstrated by selective deuteration and kinetic studies, that one of these complexes *fac*-($Me_3Pt(I)(PhMe_2P)_2$) undergoes intramolecular concerted reductive elimination of ethane[117]. Clark *et al.* have made an extensive study of these and related systems and some tentative conclusions have emerged. It appears that cationic species of type $(Me_3PtL_2Q)^+$ (L = tertiary phosphine, Q = solvent or other neutral donor) more readily eliminate ethane than the neutral species from which they are formed (by treatment with $AgPF_6$ and Q)[118, 119]. The *trans* labilising effects of L and Q are considered to be very important, and reductive elimination from trimethylplatinum(IV) cations generally occurs only (a) when two of the three methyl groups are *trans* to ligands of high *trans*-influence, and (b) when all three methyls are *not* chemically equivalent in the molecule[118, 119]. It seems likely that condition (a) can be extended to neutral complexes also[117].

However, selective introduction of different organic groups has illustrated that the neutral ligands do not exert an absolute control on the course of reductive elimination. Individual organic groups display distinct preferences for participation in reductive elimination. Clark et al. have advanced a preferential 'leaving-group order':

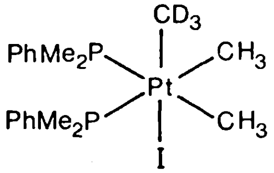
acetyl > methyl > phenyl >> trifluoromethyl[119]

A more recent study of pyrolysis of $[(PhCH_2)Me_2Pt(Br)(PMe_2Ph)_2]$ found that the yield of ethylbenzene was far from statistical, and hence that the benzyl group - in spite of a position <u>trans</u> to phosphine - was more reluctant than methyl to reductively eliminate[120]. (Decomposition was, nevertheless, more ready than in the <u>fac</u>-trimethyl analogue). Even perdeuteriomethyl ligands display a sufficient reluctance compared with their methyl relatives for a significant secondary kinetic isotope effect to be observed[117, 118].

$(K_{CH_3}/K_{CD_3} = 1.10 \pm 0.05)$[117]

However, much speculation will surround these reactions prior to the aquisition of more information. One interesting interpretive dichotomy has arisen from studies of $CD_3Me_2Pt(PMe_2Ph)_2I$ (A)

(A)



Clark <u>et al.</u> have suggested that the non-statistical distribution of ethanes (CH_3CD_3 60%; C_2H_6 40%) is a reflection, predominantly, of intramolecular exchange of methyl groups immediately prior to reductive elimination[118]. Conversely, Puddephatt <u>et al.</u> have ascribed the same observation to cooperative effects of <u>trans</u>-ligand influence and individual inclinations to reductively eliminate among the organic groups, claiming that no intramolecular scrambling takes place[117].

It is important to note that, among these organoplatinum(IV) species, reductive elimination has only been observed to operate where the organic ligand is 'β-elimination stabilised'. In the case of $[Et_2MePt(PMe_2Ph)_2I]$, thermal disruption apparently proceeds predominantly via β-elimination of ethylene (with prior phosphine dissociation) and subsequent reductive elimination of ethane and methane[120]. The small amount of butane and total absence of propane resulting from competitive primary reductive elimination might tend to suggest that alkylplatinum(IV) species preferentially undergo β-elimination, even where both possibilities are open. Both are certainly apparent contributors to the decomposition of the less straightforward trimethyleneplatinum(IV) complexes which give rise to quantities of propene and cyclopropane; the ascendancy of one or other, it is suggested, is sensitive to the nature of the <u>trans</u>-ligands[121]. (β-elimination here is also likely to be stereochemically unfavourable[107] and may be of an unusual type - <u>via</u> a π-allylmetal intermediate).

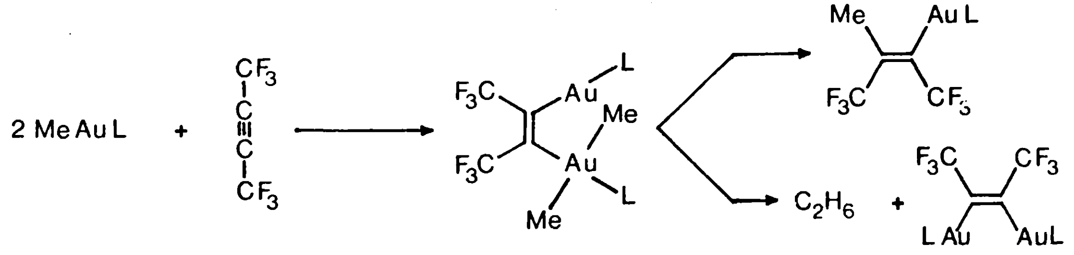
In another early study, this time of trialkylgold(III) complexes, it was found that $(Ph_3P)AuMe_3$ gave, on thermal decomposition, only ethane as organic product[122]. More recently it was demonstrated that reaction of methylgold(I) complexes with iodomethane also yielded ethane[123]:

$$LAuMe + MeI \longrightarrow LAuI + C_2H_6$$

(L = tertiary phosphine)

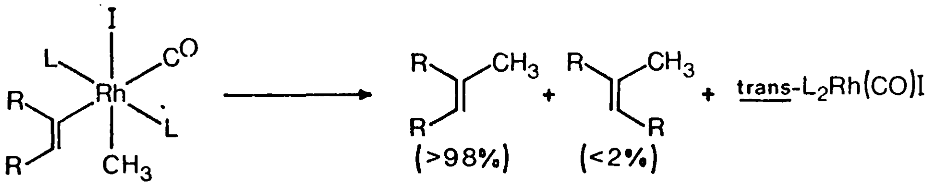
It was subsequently discovered that, when L=Ph_3P, the reaction proceeded through the same trimethylgold(III) species as had been studied earlier[124]. These observations have led to fruitful developments in investigations of the thermal behaviour of alkylgold(III) species.

Solution thermolysis of (Me_3AuPPh_3) leads to reductive elimination of ethane. The virtual absence of hydrogen abstraction product and of CH_3CD_3 upon thermolysis of a mixture of trimethyl- and tris-(trideuteriomethyl)-analogues, is strongly indicative of the concerted intramolecular nature of the reaction[125a]. Moreover, trans-($Me_2RAuPPh_3$) yields only MeR, as coupling product, whereas cis-($Me_2RAuPPh_3$) eliminates both C_2H_6 and MeR (R = ethyl, n-propyl, isopropyl). These observations are in accord with specific cis-stereochemistry for elimination[125]. The overall process is markedly inhibited by the presence of free Ph_3P, however, which led to the postulate that preliminary phosphine loss, leaving a (non-symmetrical) trialkylgold fragment from which reductive elimination occurs.[125] Reductive elimination of ethane has, in addition, been noted from the cationic trivalent gold species, $Me_2Au(MPh_3)_2^+$ (M = P, As, Sb). Here, the encroachment of the bulky ligands is considered to be conducive to the reductive elimination.[126] The same reaction mode has also been invoked to explain the unusual reaction of hexafluorobut-2-yne with MeAuL[127a,b] (L = tertiary phosphine), which proceeds via a curious alkene-bridged mixed-oxidation state species:[127c]



The direction of the final reaction is dictated by several environmental factors, but both products are rationalised by reductive elimination from Au(III)[127c]. It is notable that trialkylgold(III) compounds exhibit a strong preference for decomposition by reductive coupling rather than by β-elimination when both possibilities are open[125b], although the latter pathway may be employed for alkyl-ligand isomerisation[125a].

Concerted reductive elimination has also been established for alkyl(vinyl)rhodium(III) compounds[128]:



[R = ·CO_2Me; L = Ph_3P]

The absence of hydrogen abstraction product (dimethylfumarate) and lack of cis/trans-isomerisation of product alkene was sufficient evidence to discount radical precursors[128].

In more general terms, reductive elimination is almost certainly implicated in: the thermal disruption of fluorophenyl derivatives of Ni(II) and Pd(II)[62]; the selective cross-coupling of aryl- and vinyl-halides with Grignard reagents, catalysed by L_2NiX_2[103,129] and similar synthetic sequences involving Pd(II)[104] and Rh(I)[130]. In fact, perhaps owing to suspicion regarding transition-metal-carbon homolysis, reductive elimination has, of late, been inferred as a contributor to a plethora of chemical reactions too expansive to be catalogued here (See, for example, refs. 48, 58, 131-135).

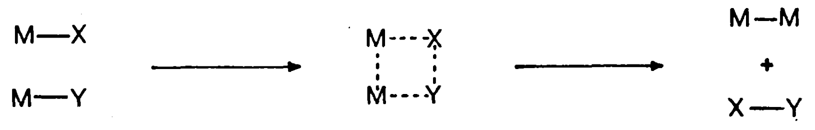
It is in spite of this growing awareness, then, that the current lack of understanding persists.

General Implications

In view of contemporary unfamiliarity with the intimate mechanism, only the most naïve, commonsense theses may be advanced concerning the influential factors specific to concerted mononuclear reductive elimination. One is certainly the ready availability to the metal of a stable oxidation state lower by two than that prior to elimination; the Pt(IV), Au(III) and Rh(III) examples discussed above provide good illustration. Another favourable influence is, intuitively, cis-coordination-site occupation by the incipient leaving groups. Concerted union of the two will require increasingly closer juxtaposition as the reaction coordinate is traversed, and this operation should be more readily initiated if the ligands occupy adjacent sites. The importance, in some cases, of the presence of an excess of strongly coordinating species has been noted[136], but this will be discussed under a subsequent heading.

(iii) BINUCLEAR ELIMINATION

This and the previous operation are related in that the binuclear process is, essentially also a reductive elimination. In this case, however, metal coordination and formal oxidation state are both reduced by one; the pathway may be invoked to describe the concerted conjunction of two ligands, initially bound to different metal atoms. One representation is:



The metals may be held in proximity by an existing metal-metal bond, or by bridging groups. This simple representation conceals the fact, however, that even where such a concerted bimolecular process is established to occur, there remains, as will be seen, considerable ambiguity concerning the precise machinery of transfer. For the sake of brevity, the discussion will be limited to the unequivocal establishment of C-C and C-H bonds by this route, of which there are notably few examples.

Mechanistic Aspects

In contrast to its Cu(I) analogue, whose decomposition by β-elimination has been discussed, $Bu^n_3PAg(n\text{-}C_4H_9)$ yields n-octane, almost quantitatively, on thermolysis. It has been established that this conversion is achieved predominantly by a process involving concerted silver-carbon scission and carbon-carbon formation without production of intermediate n-butyl radicals[137]. Analogous η^1-vinylic derivatives of both Cu(I) and Ag(I) were also shown to generate the appropriate 1, 4-dienes in the course of thermal decomposition. Complete retention of olefin stereochemistry was sufficient to demonstrate that this too was a concerted process which did not involve transient alkene radicals[138]. The stepwise displacement of biaryl from arylcopper polymers also appears to be a non-radical procedure[139]:

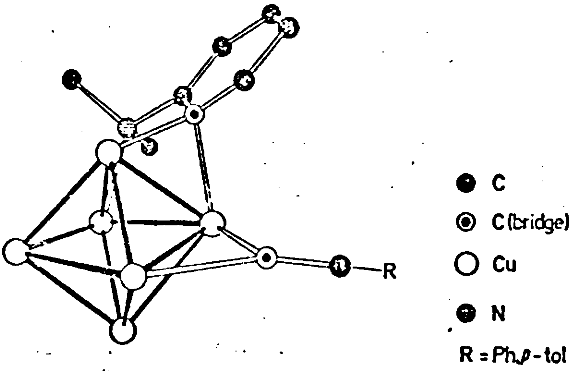
$$R_8Cu_8 \xrightarrow[k = 55{\cdot}0\times10^{-5}\ sec^{-1}]{-R_2} R_6Cu_8 \xrightarrow[k = 1{\cdot}9\times10^{-5}\ sec^{-1}]{-R_2} R_4Cu_8$$

Examples of C-H formation by a concerted bimolecular process include: the reaction of Bu^n_3PCuH with $Bu^n_3PBu^n_3PCu(I)$[92], particularly $Bu^n_3PCuBu^n$ as the step subsequent to β-elimination in the thermolysis of the latter;[91] the production of octane <u>via</u> interaction of $HIr(CO)L_2$ and $(octyl)Ir(CO)L_2$ subsequent to β-elimination of octene from the latter[95]; the production of alkene and carbonylmetal dimer through reaction of $(\eta^1$-vinylic$)Mn(CO)_5$ with $HMn(CO)_5$[140]. Binuclear elimination of H-H from <u>cis</u>-$H_2Os(CO)_4$ has also been observed[141].

<u>General Implications</u>

A favourable prerequisite for binuclear elimination is likely to be the propensity of the metal to undergo a one-electron reduction. However, this may not be the whole truth, and only reflects an over-simplistic interpretation of the nature of the process. The overall mechanistic picture may be viewed in a number of ways[48, 138]. A four-centre transition state (<u>vide supra</u>) is, of course, plausible. Also possible is intermetal disproportionation. For example, oxidative insertion of a C-Cu(I) fragment into a Cu(I)-C bond effectively generates a $Cu(0)-Cu(II)C_2$ species to which mononuclear reductive elimination is available[48]. Thus Whitesides <u>et al</u>., although convinced of the concertedness of coupling, felt unable to favour any one of the several mechanistic possibilities[138].

An inclination towards binuclear elimination might be expected to be exhibited by metals capable of forming metal-metal bonds, or whose organic derivatives favour an aggregate or cluster structure with existing juxtaposition of metal atoms. This latter predisposition is widely encountered among organic derivatives of the Group IB metals (Cu, Ag, Au), and in this context, an interesting concerted selective binuclear elimination has been reported, which may be an important clue as to the nature of the process in general. Thermolysis of the organocopper(I) hexamer $Ar_4Cu_6R_2$ (Ar = $\underline{o}$-$Me_2NC_6H_4$; R = $C{\equiv}CC_6H_4Y$) generates <u>only</u> Ar-R. This is understood in terms of the molecular structure of the hexamer.



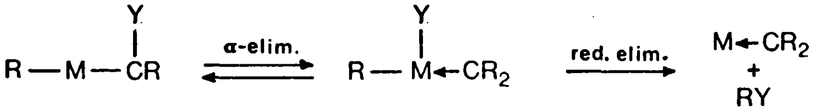
(From Ref. 142)

The template effect of the face of the octahedron is considered to be important, since there is only one aryl and one alkynyl group per face. However, it is also notable that each ligand is in a bridging position participating in 2-electron-3-centre bonding with two metal atoms, one of which is shared. It may be that this type of structure is of wide importance to binuclear elimination. It is certainly well established for Group IB organometals[143]. Bridging hydride ligands are, of course, encountered in many transition metal complexes[144].

It is very possible that binuclear eliminations are implicated in a wide variety of coupling reactions which involve transition-metals[57, 109, 145]. Some understanding of the mechanism, or mechanisms, and the influential factors, presents a stiff challenge to the mechanistic organometallic chemist.

(iv) α-ELIMINATION

This process is, to date, rarely encountered, and provides an indirect means of concerted metal-carbon scission. A metal substituent and a substituent from an α-carbon of a σ-organic ligand are eliminated together; hence 1,2-elimination is, perhaps, a better description[48]. One representation involves a metal-carbenoid intermediate:



$$\mathrm{R-M-\overset{\overset{Y}{|}}{C}R \; \xrightleftharpoons{\alpha\text{-elim.}} \; R-\overset{\overset{Y}{|}}{M}\leftarrow CR_2 \; \xrightarrow{\text{red. elim.}} \; M\leftarrow CR_2 + RY}$$

Carbene complexes of transition metals are recognised both as stable entities and as transient intermediates[146].

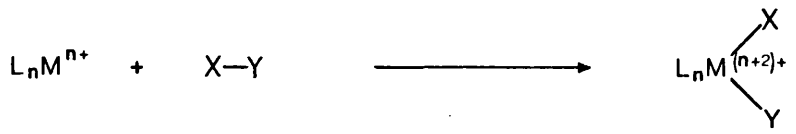
α-elimination will not feature in subsequent discussions of the mechanism of disruption of platinum-aryl bonds, since aryl ligands are denied this option by their lack of α-substituents. Reference to the few established examples is, then, largely academic.

The relative absence of CD_3H from thermolysis of $(CD_3)_4Ti$ in hexane establishes α-hydride-elimination as a predominant decomposition route with only minor contribution from homolysis[147]. α-elimination also results during the attempted preparation of $Ta^{V}(\text{neopentyl})_5$, which yields instead $Ta^{III}(CH_2CMe_3)_3(:CHCMe_3)$ in addition to one mole of neopentane[148]. A novel, reversible α-elimination to generate a transient methylenetungsten species[149] has been described, and production of a stable iron-carbene complex by α-hydride abstraction has also been reported, although whether *via* a hydridometal is not clear[150]. This same mechanism appears to contribute largely to the thermal disruption of (dpe)$_2$FeMe$_2$[151] (dpe = 1, 2-bis(diphenylphosphino)ethane) and to varying lesser extents to the decomposition of a number of other organometals[47].

Intuitive predictions of inducements to undergo 1, 2-eliminations - steric crowding and/or high-oxidation-state metal with empty d-orbitals[48] - seem, in the main, in agreement with observations to date.

(v) OXIDATIVE ADDITION

The most generally observed format for oxidative addition is the macroscopic reverse of reductive elimination, whereby a (usually low-valent) metal is effectively inserted into an element-element bond, thus increasing its own coordination and formal oxidation state by two:



$$L_nM^{n+} + X\text{—}Y \longrightarrow L_nM^{(n+2)+}(X)(Y)$$

The breadth of this field of chemistry is enormous, in that a wide diversity of metals and oxidation states, and even wider variations of X and Y have been so employed. The process is expansively documented and has been the subject of several reviews[49, 52, 152, 154] (and in view of rapid recent advances, is likely to be so again). To attempt a review here would be superfluous, and indeed, outside the scope of this dissertation. However, a brief consideration of oxidative addition in relation to metal carbon σ-bond scission is necessary on two counts.

First of all, oxidative addition at a metal which already bears a metal-carbon linkage may lead to a situation which favours fission of that bond by another route - e.g. reductive elimination Interestingly, the metal of central interest in this treatise - namely platinum - readily undergoes oxidative addition in both the zerovalent (d^{10})[49] and divalent (d^{8})[50] states. However, this aspect will, more conveniently, be expanded in the following section.

The other feature which bears some scrutiny is more fundamental. The mechanistics of oxidative addition might, by invoking the principle of microscopic reversibility, be extended into the area of reductive eliminations.

Most mechanistic studies have centred on the addition of alkyl- or acyl-halides to low valent metals, mainly Ir(I) and zerovalent-Ni, Pd and Pt. The reaction has been envisaged to proceed by three possible routes[155]: via a 3-centre transition state (the microreverse of the previously illustrated concerted reductive elimination) which should result in retention of configuration at carbon; via an S_N2 attack of the metal at carbon, and subsequent re-entry of the displaced anion into the metal coordination sphere - which achieves inversion of configuration at carbon; via halide-capture by the metal, and electron-transfer, liberating free organic radicals - which may be directly detectable, or inferrable through racemisation at carbon. In fact good evidence for the various operation of the concerted process[156], the S_N2 process[157-160], and both chain and non-chain radical schemes[161-164] has been presented. In addition, the weight of evidence seems to indicate a general tendency to trans-addition[165]. However, it must be recognised that the disruption of the carbon-halide link in this way is hardly likely to serve as an ideal model for the microreverse of formation of the C-C bond. However, the indications are that oxidative addition of a symmetrical bond such as H-H[166] or S-S[167], proceeds in a concerted fashion via a 3-centre transition-state. Oxidative insertion by a metal into a C-C bond is not widely encountered. Most examples involve insertion into strained-ring hydrocarbons to yield a metallocycle[168], (often as an intermediate in a metal-catalysed reaction[169]) and as such it might be said that the ultimate metal stereochemistry is restricted. Oxidative insertion of zerovalent-Ni, -Pd and -Pt into the C-C linkage of cyanogen has been reported[170], but no mechanistic or stereochemical details are available.

The intrinsic effects of oxidative addition on the incipient operation of concerted processes will be discussed subsequently as part of a general consideration of reaction controls.

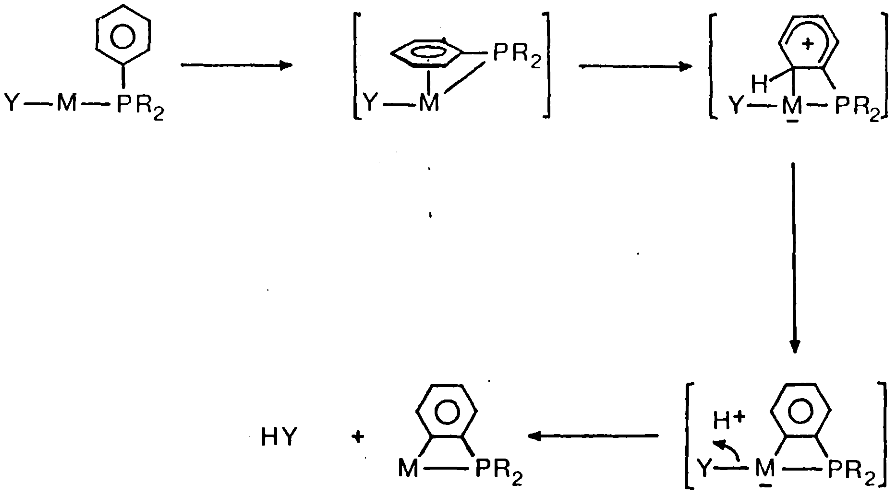
(vi) INTERNAL METALLATION : ortho-METALLATION

The formation of a bond between a transition metal and a carbon atom incorporated in an organic substituent of a coordinated ligand, constitutes an internal metallation. The reaction is, in effect, a substitution of metal for (almost invariable) a hydrogen atom. This operation is now firmly ensconced among the reaction patterns of transition metals. Metallations at aliphatic, olefinic and aromatic carbon have all been established, and phosphorous, arsenic, nitrogen, sulphur, oxygen or carbon donor ligands may be employed. The impressive array of metals which display this tendency serves to underline its widespread influence. However, a comprehensive review of observed occurrences of this process would no better serve to illustrate its implications for metal-carbon bond scission than would a few significant examples which illustrate basic features and specific involvement[171]. For present purposes, discussion may be further limited to one particular class of reaction, namely *ortho*-metallation of an arylphosphine.

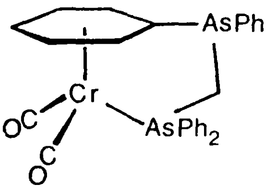
Mechanistic Implications

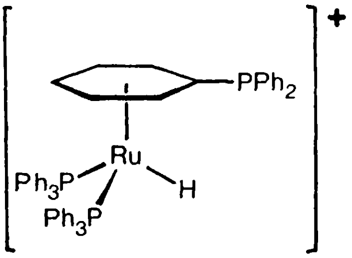
Parshall reviewed the subject in 1969 [172], and although such *ortho*-metallated compounds have continued to proliferate since then[173], the intimate machinery of the reaction is still in some doubt. Indeed, it is not obvious that one mechanism need fully account for the observed panorama of *ortho*-metallation.

It is possible to envisage two different routes in terms of established chemical theory, each of which can account for the overall effect. One is electrophilic substitution at carbon, perhaps *via* a metal-arene π-complex[172] and benzenium ion[174] intermediates:



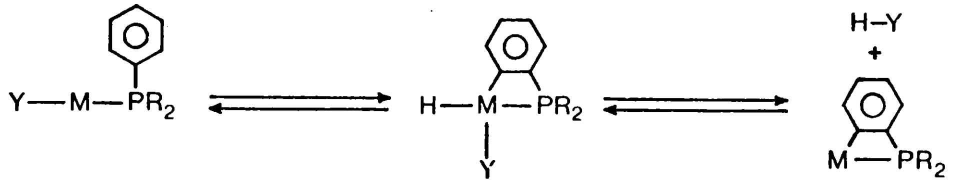
For triaryl phosphines, the substitution is sensitive to ring substituents[175a], which might lend support to this proposition. In addition, a number of transition metal complexes are known in which a ligand aryl substituent is π-bonded to the metal, e.g. those of Cr[176] and Ru[177]:



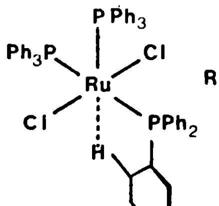


Notably, a suitable σ–π conversion is parallelled by the tautomerism exhibited by a naphthalene complex of ruthenium, whose chemical properties are consistent with the π-arene structure I[178], but whose solid-state structure has been demonstrated to be the hydrido-species II[179]:

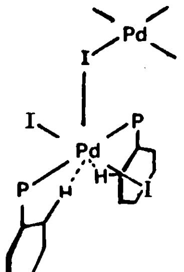
However, these last observations do not necessarily exclude an alternative metallation mechanism, that of primary oxidative addition of C–H to the metal:



This too might be expected to be facilitated by π-complex formation[172] (though less critically so) which might render it sensitive to ring substituent effects[175a]. Furthermore, the very small deuterium isotope effect observed in substiution of o-deuteriotriphenylphosphine has formed the basis for postulation of a 3-centre intermediate for the hydrogen transfer[175a]. Structural support for this argument may be drawn from several complexes in which there is close approach of requisite ortho-hydrogen atoms to the metal, e.g. those of Ru[180a] and Pd[181b].

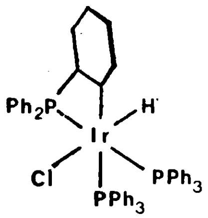


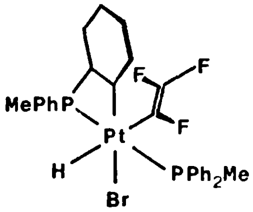
Ru-H = 2·59 Å



Pd-H = 2·8 Å

It may be, of course that there is no sharp division between the two mechanisms; apparent aberrations in behaviour may reflect a gradation, rather than a distinction, in preference for either. Whatever the general picture, there is reasonable evidence that for metallation of aryl phosphines in complexes related to those in which we are most interested, the oxidative addition description is certainly adequate. For example, refluxing the Ir(I) complex $(Ph_3P)_3IrCl$ - which is isoelectronic and isostructural with the Pt(II) complexes L_2PtR_2 - yields, by *cis*-addition, a hydridoiridium(III) species[175a]; A similar complex of platinum(II) has also been reported[175b]:

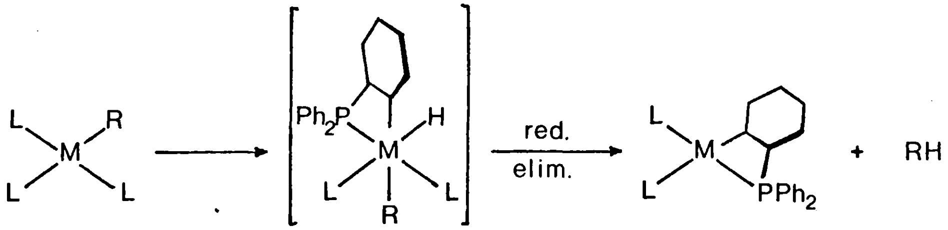




Such a scheme may often be readily reversible. This facet has been ingeniously exploited in the selective *ortho*-deuteriation of Ph_3P, catalysed by $(Ph_3P)_3Ru(H)Cl$[181]. This complex may undergo reversible ortho-metallation, reversible reductive elimination of H_2 (and D_2) and phosphine exchange. Operation of all these, in presence of an excess of Ph_3P under a D_2 atmosphere, leads to systematic replacement of *ortho*-protons by deuterons to an extent of 99%.

Contribution to Metal-Carbon Scission

Primary ortho-metallation is predominantly responsible for thermal metal-carbon cleavage in several square-planar (d^8) complexes of univalent iridium and rhodium (where the hydrocarbyls lack a β-atom), ostensibly via intermediates similar to the hydridoiridium(III) species illustrated above:



($L = Ph_3P$; $M = Ir$, $R = Me$[182], alkenyl[101] (no cis-β-hydrogen), CH_2SiMe_3[90]: $M = Rh$, $R = Me$[183])

A similar mechanism (though not strictly an aryl ortho-metallation) has been found to operate for a number of dimethylplatinum(II) complexes[184].

General Implications

The driving force for ortho-metallation is not immediately apparent. Thermodynamic compensation may arise from the generation of elimination products, or from a general 'tightening-up' of coordination around the metal. In the latter sense, thermodynamic considerations are, doubtless, partially responsible for the general preference for formation of 5-membered, rather than 4- or 6-membered rings, by metallation, as exemplified by the range of ortho-metallated arylphosphite ligands[185] and ortho-methyl-metallated 2-tolylphosphine species[186]. Less-favourable ring-strain and conformational torsion effects are likely to be present in tetracycles and hexacycles, respectively. Kinetic controls, too, of course, are likely to be of importance. For example, the tendency to 5-, in preference to 4-membered rings, perhaps partly reflects the less easily attainable transition state when approaching the latter.

Suffice it to say that the subtle interplay of factors which determines, in a given instance, the position of metallation in the hierarchy of decomposition pathways (relative, say, to primary β-elimination or reductive elimination) cannot be assessed at present. Clearly, though, ligand-metallation must be given due consideration as a potential concerted hydrogen-transfer source* during the thermal disruption of organotransition-metals.

(vii) INSERTION

The propensity of transition-metal-element bonds to undergo molecular insertion reactions has long been recognised. Linkages which have been found to engage in such processes include, inter alia, metal-hydrogen, metal-carbon, metal-oxygen, metal-halide and metal-metal; some of the more common inserting entities being, alkenes, alkynes, CO and SO_2. However, these widely assorted reactions and their import in synthetic and catalytic chemistry have been comprehensively reviewed, both generally and specifically[188-194].

Metallations by abstraction of atoms other than H are rare, but see Ref. 187.

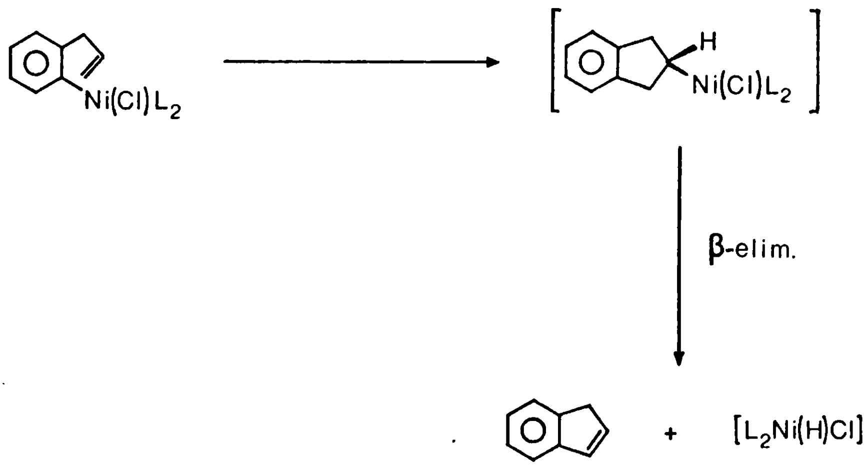
The discussion here can be limited to insertion by unsaturated hydrocarbon species.

Alkene (or alkyne) insertion into a metal-hydride bond is the reverse of β-elimination, and its significance has already been emphasised. Clearly, on the other hand, insertion of some such unsaturated species into a transition-metal-carbon bond prior to its rupture will greatly affect the nature of the products, creating, as it does, a new metal-carbon link to a modified organic ligand. Since unsaturated hydrocarbons may be primarily generated in thermolyses of σ-hydrocarbylmetals (vide supra) it may prove of some value to reflect briefly on the established chemistry of such species when in the presence of transition-metal-carbon σ-bonds.

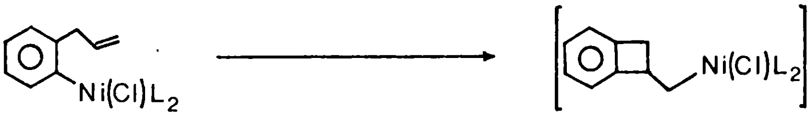
Detailed information, alas, is scant. Some investigations have featured polyunsaturated systems - 1,3 dienes and allene. What investigation has been undertaken on simple mono-unsaturated functions has centred on fluoroalkene and fluoroalkyne species, because of the isolabitily of the resultant fluoralkyl or fluorvinyl derivatives. Much of this work has, conveniently, employed platinum as the host-metal.

Insertion occurs from the coordination-sphere of the metal - reminiscent of the schemes envisaged for the rapid insertion/elimination sequences accompanying β-hydride elimination. Clark et al., in an investigation of insertion of tetrafluoroethylene and hexaflorobut-2-yne into platinum-carbon bonds in complexes of the type trans-(L_2PtMeX) and cis-(L_2PtMe_2) (L = tertiary phosphine or arsine: X = halide), deduced that the reaction proceeded via preliminary coordination of the unsaturated fluorocarbon. The stability of the intermediate π-complex, and the relative extent to which the multiple C-C bond was weakened, were proposed to be the critical controls on the rate of insertion[195]. Such 5-coordinate species were, in some cases, isolable[196]. More recently it has become apparent that insertion into Pt-C[197] (or Pt-H[198]) bonds proceeds in many cases by substitution of the ligand <u>trans</u> to alkyl (or hydride) and subsequent rearrangement of the resulting tetracoordinate cationic species to yield finally, the product of insertion. Certainly C_4F_6 inserts more readily from a four-coordinate than a five-coordinate geometry - the resultant fluoroalkene having the <u>cis</u>-configuration expected from collapse of the (intuitive) four-centre transition state[199]. Surprisingly, though, on the basis of nmr data, the unsaturated 'ligands' are more exchange labile when held in the site <u>cis</u> to the methyl group (which is naively the stereochemistry adopted immediately prior to insertion), than they are when in a <u>trans</u>-position [199]. It is perhaps too early for wide-ranging conclusions, but present evidence suggests that the propensity to undergo insertion is affected at least as much by the electronic properties of the other metal-bound ligands and of the substituents on the potential inserting molecule as it is by the attainment of the superficially favourable <u>cis</u>-geometry [199]. Also interesting is the fact that the cationic hydridoplatinum species are more susceptible to insertion than their methyl analogues, reflecting it has been suggested, to some extent the relative thermodynamics of Pt-H and Pt-C bonds[197]. The factors governing the regiospecificity (or lack thereof) of these insertion reactions, are not well understood.

A notable illustration of the profound effect which the insertion capability may have on the thermal decomposition of a σ-organotransition-metal is to be found in the case of trans-[(Et$_2$P)$_2$Ni(2-allylphenyl)Cl]. Thermolysis of this species in C_2Cl_4 affords indene as the major hydrocarbon product. This is rationalised in terms of an intramolecular insertion by the terminal alkene substituent of the aryl into the aryl-nickel bond as the first step, generating an indanylnickel intermediate. β-elimination yields the observed products[200] (The other minor organic and organometallic products are also in accord with the scheme).

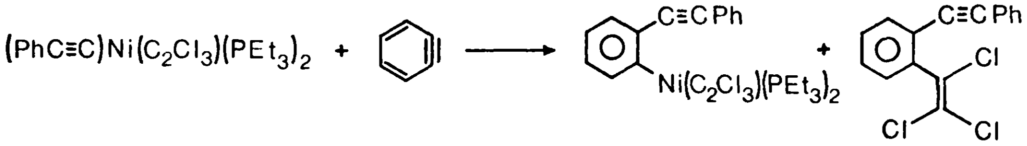


The insertion is apparently highly regiospecific in this case. This may be largely due to the fact that the alternative mode of insertion would generate the highly strained cyclobutene species:



(Failure to observe any decomposition products directly attributable to this precursor does not, of course, altogether rule out its participation. Conceivably, spontaneous isomerisation either of the organometallic intermediate, or of its elimination product might ultimately yield indene).

A further significant example of insertion-influenced decomposition is to be found in organonickel(II) chemistry. Thermal decomposition of benzenediazonium-2-carboxylate (a benzyne precursor[202]) in the presence of trans-(phenylethynyl)(trichorovinyl)bis(triethylphosphine)nickel(II) led to products arising from 1,2-metal-carbon-addition to a coordinated benzyne, and subsequent decomposition of the resulting new σ-organometal[201]:



THE IMPLICATION OF FREE RADICALS IN ORGANOTRANSITION-METAL CHEMISTRY

It would be remarkable indeed if single-electron transfer reactions were entirely absent from the chemistry of organotransition-metals. An established characteristic of many transition-metals is, after all, the ability to undergo facile one-electron redox reactions, and presumably in the absence of lower energy fragmentation pathways, these would also generally operate for organic derivatives. An interesting role for electron-transfer mechanisms in several reactions of organotransition-metals has recently been advanced[203]. It is suggested, for example, that radical mechanisms may conceivably contribute to β-elimination or alkene insertion reactions. The substance of these propositions remains to be empirically probed, an undertaking which serves to highlight the current emphasis in this topic. Whereas photolysis of σ-organotransition metals might be expected to lead to homolytic scission of the M-C bond[33], unequivocal generation of free radicals by thermal cleavage of transition-metal-carbon bonds is a rare occurrence. (Compare the thermolysis of alkylsilver(I), which results in concerted coupling, with the alkyl radical production on photolytic treatment[137]) Radical-production (or its absence) from such processes must therefore be unambiguously demonstrated. This is not straightforward, particularly on the positive side, since, with a few exceptions, free radicals have a tendency to very transient existences. Several indirect techniques, both directly observational and deductive, have been successfully applied to these investigations, and a brief consideration of these methods and their possible pitfalls, will serve to illustrate the major areas of occurrrence of radical pathways in organotransition-metal chemistry.

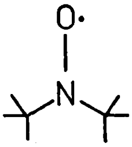
A: Observational Methods

(i) Spin Trapping/Radical Scavenging

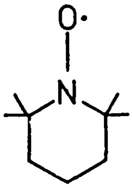
An essential feature of free radical pathways is that they give rise to paramagnetic fragments - i.e. possessing unpaired spins. All too often, these are not sufficiently long-lived to be themselves observed. So chemical agents are introduced which capture the paramagnetic species in such a way that their original nature may be characterised. This has been done in two main ways. One involves the introduction of a species, itself diamagnetic, which readily undergoes radical addition, to yield a paramagnetic species of appreciable longevity. This unpaired spin may then be examined directly by electron spin resonance spectroscopy. This approach may be truly termed 'spin-trapping'[204]. A popular choice in this category has been the species nitroso-tert-butane, Bu^tNO, which undergoes addition of radical R• to yield a stable nitroxyl radical species, whose hyperfine coupling parameters may be used to identify the original fragment:

This procedure has been employed to demonstrate the participation of free alkyl radicals both in the oxidative addition of alkyl halides to zerovalent platinum[162], and in the thermal scission of platinum-carbon bonds in R_2PtL_2 systems ($R = Me$, CD_3Et, $L_2 = 22^1$ bipyridyl; $R = Me$, $L_2 = 1, 10$ phenanthroline) in the presence of alkenes[205]. However, it is becoming clear that use of this reagent must be approached with caution, since it may itself induce M–C homolysis. The very readiness of its spin-trapping capability possibly reflects its potential as a one-electron reductant, and it may conceivably function as such from a coordinating position. It has been demonstrated, for example, that a benzene solution of $(Ph_3P)_2Pd(CH_2Ph)Cl$ gives rise, in the presence of Bu^tNO, to the radical fragment $\mathrm{Bu^{t}N(\dot{O})CH_2Ph}$[160]

A related approach with related difficulties is the use of selective radical scavengers which are themselves stable paramagnetic species and which yield, on combination with reaction-generated radicals, diamagnetic species which may be readily characterised. Such systems are the stable nitroxyl species di-*tert*-butylnitroxyl (DTBNO) and 2,2,6,6,-tetramethylpiperidine-*N*-oxyl (TMPO):



DTNBNO



TMPO

Here again, due caution must be exercised; DTBNO is known to coordinate to transition metals[206], and the presence of radical species in significant amounts may initiate bimolecular homolytic substitution (S_H2) reactions, which are established in main-group organometallic chemistry[208], and which have been found to operate for square-planar organoplatinum(II)[209]. In fact, TMPO displaces n-butyl radicals from $\mathrm{Bu^n_3PAgBu^n}$, which is itself not ordinarily a thermal source of butyl radicals[137]. Initiation of M-C homolysis by these scavenging radicals, and by the previously considered spin-trap (which is, after all, a precursor for the former type of agent) may obviously be closely related.

(ii) Chemically induced Dynamic Nuclear Polarisation (CIDNP)

The CIDNP phenomenon is a magnetic resonance effect; its origin is fairly complex and has been comprehensively discussed elsewhere.[210] The experimental manifestation may be observed in the proton magnetic resonance spectrum of the species present during the course of the reaction. Where the process involves encounter of free radicals, this may lead to enhanced absorption and/or emission in the n.m.r. spectrum. The technique has found little application as yet in the investigation of transition-metal-carbon bonds, although it has been employed to unequivocally demonstrate the intermediacy of alkyl radicals in oxidative addition of alkyl halides to Pt(0) and Pd(0)[164]. It has also been brought to bear in showing that Co(II)-catalysed reactions of Grignard reagents involve organic radicals[211]. Its great potential utility in this field lies in the fact that no (potentially interfering) internal agent is necessary. It has the drawback, however, that absence of CIDNP effects does not necessarily imply non-participation of free radicals.

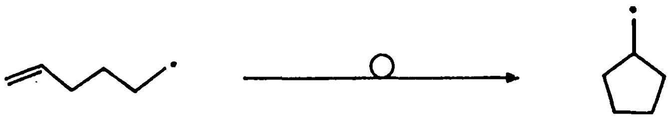
B: Deductive Methods

(i) Product Distribution Analysis

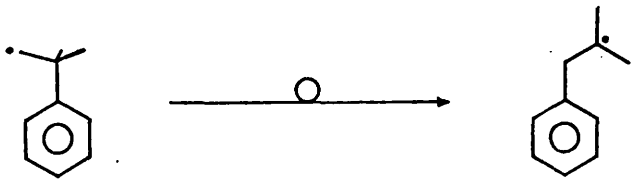
The participation of free radicals may be evaluated by careful consideration of the distribution of products. If this displays an unrealistic comparison with predictions based on the relative affinities for radical termination reactions - coupling, hydrogen (or other) atom abstractions, disproportionation[212] - then radicals may be discounted as predominant participants. This is the general emphasis of this approach. If, on the other hand, it suggests the possibility of free radicals, confirmation would be required via another technique. This scheme has been employed, for example, to rule out radical participation in the thermal decompositions of both $Bu^n_3PCuBu^n$ and $(Ph_3P)_2PtBu^n_2$, since the products in both cases - 1:1 n-butane: but-1-ene - would require an unreasonably high ratio of rate constants for disproportionation and coupling, respectively, of n-butyl radicals.

(ii) Molecular Rearrangements

This refinement of product distribution analysis exploits the known tendency for some radicals to undergo internal rearrangement at rates comparable with their termination by one or other route[213]. Two pertinent examples which have proved useful to evaluation of M-C fission paths, are the 5-hexenyl and the neophyl entities. The former radical undergoes a characteristic cyclisation to yield the cyclopentyl carbinyl radical[214]:



The neophyl radical is recognised to parent the benzyldimethylcarbinyl radical via a 1,2 phenyl shift[215].

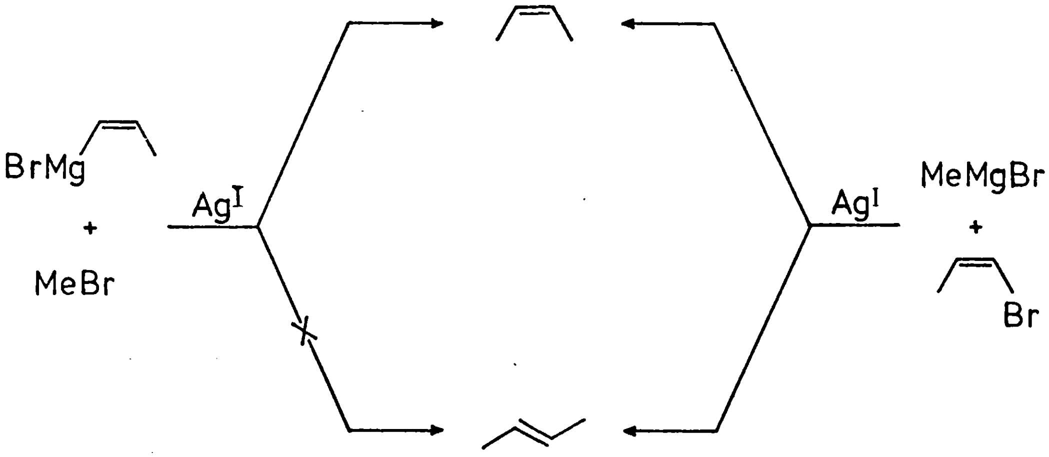


Therefore, should thermal disruption of 5-hexenyl- or neophylmetal derivatives proceed by M-C homolysis, the product distribution should show products derived from the rearranged radicals. Use of this knowledge has both proved and disproved radical participation in thermal metal-carbon bond cleavage. For example, thermolysis of (5-hexenyl)Cu(PBu^n_3) generated 1:1 1-hexene/1,5 hexadiene, elegantly discounting any significant contribution by homolysis to decomposition[91]. Use of the property of the neophyl radical was, in contrast, able to clearly establish that the thermal decomposition of (Neophyl)Cu(PBu^n_3) in ether - and almost certainly that of its Ag-analogue - proceeds largely by metal-carbon homolysis, followed by competing 1,2-phenyl migration, coupling, and hydrogen atom abstraction involving the resultant neophyl radical[215]. A cautionary note must be sounded here however. Care is required to establish that rearrangement does not occur prior to decomposition. For instance, (5-hexenyl)Ag(PBu^n_3) was found unsuitable for study, since it underwent rearrangement to (cyclopentylcarbinyl)Ag(PBu^n_3) at a rate competitive with its liberation of hydrocarbons[137].

(iii) Configurational Instability

A further sophistication is the employment of organic groups whose derived radicals isomerise or epimerise at competitive rates with termination modes. One hydrocarbyl ligand which has been so exploited is the cis- or trans-1-propenyl group. Propenyl radicals, if formed, would lose configurational specificity at a rate comparable with coupling[138]. Retention of stereochemistry has been sufficient to establish that thermal decompositions of vinylic derivatives of

Cu(I), Ag(I)[138] and Rh(III)[128] proceed without free radical participation It has also neatly shown that organic radicals arise specifically from the alkyl halide, but not from the Grignard reagent, in the Ag^I-catalysed cross-coupling of alkylhalides with Grignard reagents[203] viz:



(This does not necessarily imply M-C homolysis, however). The same caveat applies to these techniques however. For example, (cis-1-propenyl)Cu(PBu^n_3) was itself found to be configurationally unstable under decomposition conditions, and was therefore excluded[138].

The 2-norbornyl group has also been employed in this way; for example the reaction of (endo-2-norbornyl)Cu(PBu^n_3) to yield only endo-2-deuterio-norbornane shows that free norbonyl radicals - which would lead to loss of stereochemistry - were not involved[92]. Use of this phenomenon had earlier been made to support the proposition that alkyl radicals are intermediates in the metal-hydride reduction of alkylmercury compounds[217]. Nevertheless, here again, the approach proved inadequate to evaluation of radical intermediacy in thermolysis of silver(I) analogues, when (endo-2-norbornyl)Ag(PBu^n_3) was discovered to epimerise at a rate comparable to that of its thermal decompsotion[137].

Free radicals, then, do have an established position in the chemistry of organotransition-metals[47, 48] - a role that must now be critically evaluated. It must be said, however, that their implication specifically as a result of metal-carbon cleavage is comparatively rarely encountered, and further, must not be invoked without rigorous investigation, since concerted and non-concerted processes may display only the subtlest of visible differences. For example, the production of methane in the decomposition of methyltitanium(IV) compounds may or may not reflect a homolytic operation. Only the precise determination of the origin of the abstracted hydrogen (by deuterium labelling) ultimately demonstrates the contribution of concerted processes[147, 218]. Homolysis seems, as suspected[33], to occupy an energetically unfavourable place in the hierarchy of thermal decomposition modes - certainly in comparision to, say, β-elimination. What determines its operation in isolated cases - for example, the neophylcopper and -silver examples - is a matter for some conjecture and further exploration.

REACTIVITY CONTROLS

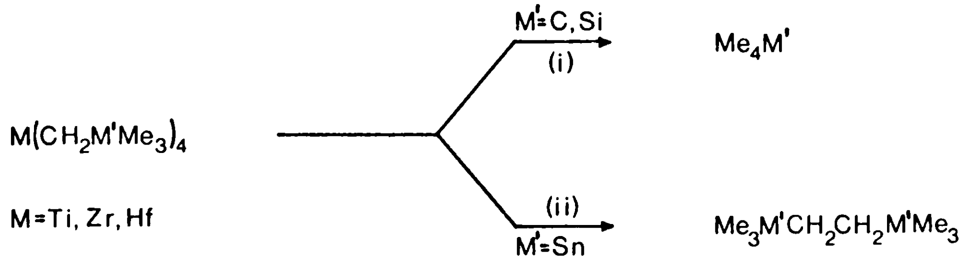
One apparent underlying common influence on the reactions of organotransition-metals is the favourability of 18- or 16-valence-electron occupation at the metal. The long recognised[219] '18-electron rule' describes the tendency of transition metals to form complexes corresponding in valence configuration to the next higher inert gas. This requires maximal population of all nine of the metal-derived orbitals - one s-type, three p-type and five d-type - leading to a full electron count of 18. However, the d-orbital energies decrease on traversing the transition series from left to right. The consequent increasing (n-1)d ⟶ np promotion energies make higher orbital occuption - and hence 18-electron configurations - less favourable as a period is traversed, and by Group (VIII), stable 16-electron complexes are increasingly encountered[17, 48] (for the coinage metals (Cu, Ag, Au) 14-electron environments are not unusual).

The significance of 18- and 16-electron configurations was appreciated by Tolman in a review[220]. Two fundamental postulates were advanced. First of all, diamagnetic organotransition-metals may only exist in (kinetically or spectroscopically) significant concentrations if they possess a 16- or 18-electron configuration. Secondly, and following on, the reaction pathways of organotransition metals - including those of catalytic cycles - would be dominated by the availability of 16- and 18-valence-electron intermediates. Supportive examples were drawn from the categories of oxidative addition/reductive elimination, Lewis base association/dissociation and insertion/deinsertion reactions, and illustration featured several catalytic cycles (including hydroformylation and hydrogenation of olefins).

These ideas have also featured prominently in a broader appraisal, by Braterman and Cross, of the common controlling influences on transition-metal-carbon bond stability[48]. It emerges that several superficially distinct bond-breaking modes may in fact be analagous - e.g. ligand dissociation and reductive elimination, and the interstitial case of olefin de-coordination. (A reverse relationship - that between oxidative addition and donor coordination, - has been empirically demonstrated in certain Ir(I) complexes[221]). It is also suggested that electron availability at the metal, more than the formal oxidation state, is a crucial determinant of whether ligands are likely to be expelled from the complex. Specifically, where a complex possesses an unfavourably high metal electron count (say, in metals at the end of the transition series), then elimination (of some description) is likely, in order to relieve this situation. For example, oxidative addition at Pt(II) yields 18-electron Pt(IV) species which, as we have seen, frequently undergo reductive elimination to regenerate Pt(II) complexes, which almost invariably have the more favourable 16-electron configuration. In the same vein, it is interesting to observe the relative effects on descending a particular sub-group. As a consequence of the Lanthanide contraction, the trend to increasing (n-1)d$\rightarrow$np promotion energies as the group is descended is not regular. For the Ni-triad, in fact, the order is: Ni>Pt>Pd. This in turn means that it is the second-row transition elements - in this case Pd - which show the greatest resistance to higher orbital occupation. This may, in part, account for the general lability of organic derivatives of palladium compared with those of platinum, in particular those of the tetravalent metal, of which only one stable example has so far been characterised, the pentafluorophenyl complex $((Ph_3P)_2Pd(C_6F_5)_2Cl_2)$[222].

It cannot be pretended, however, that a universal understanding is, as yet, apparent. The complexity of the problem confronting the exploratory chemist/theoretician in this field is indeed vast. Some fundamental apparent inconsistencies await rationalisation, but pitfalls await the unwary investigator who is over-dependent on analogy. For example, over-enthusiastic extension of observations from one metal to another - even in the same periodic sub-group - must be avoided, in the absence of empirical facts. One pertinent example is that of the n-butylcopper and -silver analogues; both of which undergo concerted metal-carbon cleavage, the former by β-elimination[91], the latter by binuclear coupling[137].

Just as varying the central metal may influence the direction of decomposition, so too, differences in organic ligand may produce marked alteration in mechanistic preference, even for the same metal. Compare, for instance, the decomposition pathways of n-butyl-, vinyl- and neophyl-derivatives of $Cu(PBu^n_3)$; the first displays a β-elimination tendency[91] (which is unfavourable or inaccessible to the others); the second undergoes concerted organo-coupling[138]; the third decomposes <u>via</u> metal carbon homolysis[215] (as, apparently does the CH_2SiMe_3 analogue[223]) Again, varying the metal (Ti, Zr or Hf) in neopentyl-type derivatives of Group (VI)B merely affect the relative ease of thermal disruption. Varying the β-atom, however, completely alters the decomposition mechanism[224].



Reaction (ii) is apparently a concerted reductive elimination, whereas (i) may involve homolysis (or α-elimination).

The issue is further complicated by the observation that several available modes may compete, especially under vigorous conditions. An example is decomposition of trimethyleneplatinum(IV) where, depending on local conditions, both β-elimination and reductive elimination are noted[121]. It may be then, that activation energies for the various options are of comparable magnitude, and the final determination of preference in a particular case is dependent upon a subtle interplay of, as yet, individually unassessable localised molecular conditions.

MISCELLANEOUS

Other modes of metal-carbon bond scission - for example, displacement of the metal by direct attack at the α-carbon - are recognised[225], but are considered outside the scope of this report. Other widely encountered aspects of general transition-metal chemistry which may have relevance - for instance, nucleophilic substitution or cis/trans isomerisation in square planar complexes - will be expanded as necessary during the discussion. However, there is one singular feature of the chemistry of square-planar species - particularly those of Pt(II) - which merits some amplification at this point. This is the susceptibility of the behaviour of a coordinated ligand to the nature of the ligand trans to it in the square-plane. Two broadly based series of phenomena, one kinetic and one thermodynamic, are observed.

trans-Effect and trans-Influence (Square-Planar Complexes)

The *trans*-effect is a kinetic phenomenon of valuable synthetic application in the chemistry of square-planar complexes, and describes the effect of a given ligand on the rate of substitution of the *trans* substituent[268]. The overall effect is therefore dependent to an appreciable extent on the nature of the transition state in the substitution reaction. A distinction has been drawn between this and the general ability of a ligand to detectably weaken the ligand-metal bond *trans* to itself in the equilibrium (ground) state of the complex. This thermodynamic consideration has been christened *trans*-influence [269] and this nomenclature has gained wide, if not quite universal, acceptance. The general features of *trans* (and *cis*) effects have been appraised by Hartley[270], while the significance of *trans*-influence, and its measurement, have been comprehensively reviewed by Clark *et al.*[271]

Uncertainties as to the nature of, and the relationship between these phenomena, have fuelled considerable debate in recent years. It might seem reasonable to suppose that the operation of the ground-state *trans*-influence would contribute significantly to the overall manifestation of the *trans*-effect. This is, indeed, undoubtedly true in some cases at least, but serious discrepancies between *trans*-influence and -effect observed for certain ligands have provoked much argument.

An aspect around which appreciable speculation has centred has been the relative contributions from σ- and π-bonding in the metal ligand skeleton. The formulation of more recent theories reveals a trend away from the previously ascendant propositions which envisaged π-acceptor properties of the ligand to be of premier importance[272]. These accounted for the observably high trans-effects of π-acids such as CO and C_2H_4, but did not explain the powerful trans-effects of H^- or CH_3^- which have little (if any) π-acceptor ability[273]. The preference of $(R_3P)_2PtX_2$ for cis-geometry[274] was not initially ascribed to the general bond-weakening ability of trans-phosphine ligands, but to their competition for the same metal orbital for π-bonding, in the trans-complex [275]. Pidcock et al., however, ultimately postulated that their observations were more consistent with a powerful σ-inductive effect of the phosphine [269] and, in fact, much of the recently acquired data is interpretable in these terms. The currently popular view is that powerful σ-donors exert high trans-influence (irrespective of their relative π-acidity) by engaging in highly efficient covalent bonding with the metal. The resultant rehybridisation of metal-ligand bonding orbitals is at the expense of the bond to the ligand trans to that of superior σ-bonding ability. The importance of metal-ligand sigma overlap-integrals has, accordingly, been stressed[276, 277]. Nevertheless, there is no general agreement over the particular type of metal orbital which is concentrated, by powerful σ-induction, in the metal-ligand bond, to the disadvantage of the trans-bond [271].

Interestingly, it has recently been suggested that the role played by π-bonding in determining trans-influence cannot be neglected. The inductive phenomenon may be largely transmitted via the metal d-orbitals (causing variations in electrostatic repulsion of the trans-ligand - in this case the more ionic Cl^-), and thus the ability of a (π-acceptor) ligand to remove dπ-electron density from the region of the trans-ligand may have a profound effect on the ultimate magnitude of its observed trans-influence [278].

Current opinion on the origin of trans-directing properties might be summarised:

σ-bonding is recognised to be important to both trans-influence and trans-effect. Strong σ-inductive effects modify the metal-trans-ligand bond in both the ground and transition states.

π-bonding is certainly of significance in determining trans-effect; π-acceptor ligands with low trans-influence (CO, C_2H_4) display kinetic trans-substituent labilising capability, ascribable to their π-stabilisation of the transition state. The relative role of π-bonding as a factor in trans-influence, although perhaps less important than previously imagined, is not, at present, certain.

A major reason for the dubiety surrounding the nature of trans-influence is the variety in methods by which it has been quantified[271]. Different techniques have differing sensitivities to specific features of metal-ligand bonding. For example, n.m.r. spin-spin coupling parameters - if the assumption that they are dominated by the Fermi contact term is correct[269] - will display sensitivity only to changes in the σ-bonding framework. X-ray crystallographic determinations, on the other hand, would be expected to depend on both σ- and π-effects, as would vibrational data. This diversity of techniques with particular sensitivities to different aspects of the trans-influence inevitably leads to difficulty in construction of a 'universal' gradation of ligands according to their *trans*-influence. Allen and Sze[279] have compiled a series according to $^1J(^{195}Pt-^{31}P)$ measurements (from several sources), which reflects a decreasing tendency of the ligand to concentrate metal 6s-character in its bond with Pt(at the expense of the diametrically opposed Pt-P bond) and hence decreasing *trans*-influence:

$SiMePh_2^- > Ph^- > Me^- \gg PEt_3\ PBu^n_3, PMe_2Ph > Ph_3P > P(OPh)_3$, CN >

$AsEt_3 > NO_2^- > \underline{p}MeC_6H_4NH_2 > EtNH_3 > py$, N_3^-, NCO^-, $NCS^- > Cl^-, Br^- I^- > ONO_2$

A series of structural trans-influence has been deduced from x-ray data[271]:

$R_3S:^- \simeq \sigma\text{-}C \simeq H^- \geqslant \text{carbenes} \simeq PR_3 \geqslant AsR_3 > CO \simeq RNC \simeq C{=}C \simeq Cl^- \simeq NH_3 > O$ (in acac).

CHAPTER THREE

Condensed-Phase Thermal Decomposition of Diarylplatinum(II) Complexes

CHAPTER THREE

Preamble: Value of the Platinum(II) Model

The choice of organoplatinum(II) as a suitable model has several advantages. Platinum has other stable accessible formal oxidation states, each differing by two from that chosen. Furthermore, the metal exhibits a tendency to form diamagnetic complexes with even electron population (18, 16 and occasionally 14 electrons). These properties might be envisaged to be conducive to the operation of paired-electron processes (zerovalent platinum has, however, been shown to be capable of acting as a single-electron transfer agent[226], and, as we have seen, free radicals may be implicated in oxidative addition reactions at the zerovalent metal[162-164]). Organoplatinum(II) is readily synthetically accessible, with sufficient stability to survive, in adequate yield, the rigorous purification which is required prior to accurate studies. Additionally, square-planar diorganoplatinum has a general preference for cis geometry, which intuitively would be a favourable prerequisite for incipient bond-formation between substituents. In an attempt to guarantee this configuration as far as possible throughout the decomposition, a number of bidentate tertiary phosphine ligands were introduced, as well as more conventional monodentate phosphine donors.

Aryl substituents were employed as the metal-bound organic ligands in the expectation that the β-elimination option would be suppressed. It may not be altogether disregarded as a possibility, however, and the probable consequences of its operation will be discussed.

These general features of the selected organometallic systems in addition to the fact that paramagnetic intermediates have only rarely been unambiguously implicated in reactions of organoplatinum(II) - and then in special circumstances[205, 209] - combined to form a hopeful basis for an investigative programme aimed at less-understood concerted processes.

Experimental Techniques (for full details, see Chapter 6)

Diarylplatinum(II) complexes were prepared via the established route of transmetallation[30a]. Treatment of the appropriate dichloro-compound with a solution of aryllithium was found to give superior results to use of the corresponding arylmagnesium halide. The materials were purified by (at least) three recrystallisations prior to thermolytic study. Satisfactory carbon and hydrogen microanalyses were obtained for all complexes. The generally colourless crystalline diarylplatinum(II) compounds displayed sufficient oxidative and hydrolytic stability to allow their storage in air. All were protected from light as a precautionary measure, since $(Ph_3P)_2PtAr_2$ was observed to become progressively greenish-yellow on exposure. The cis-configuration of monotertiary phosphine complexes was confirmed from $^1J(^{195}Pt-^{31}P)$ values. The dipole moment of the representative complex cis-$(Ph_3P)_2PtPh_2$ in benzene was measured to be 7.2D, in good agreement with the previously established value (7.0D)[30a].

The thermal behaviour of these complexes was examined instrumentally by simultaneous thermal gravimetry and differential thermal analysis (TGA/DTA) and additionally by differential scanning calorimetry (DSC). The universal thermolytic behaviour pattern, was a preliminary sharp endotherm as the complex melted - accompanied by the onset of weight-loss - which was then rapidly overwhelmed by an (overlapping) exotherm which characterised the accelerating decomposition:

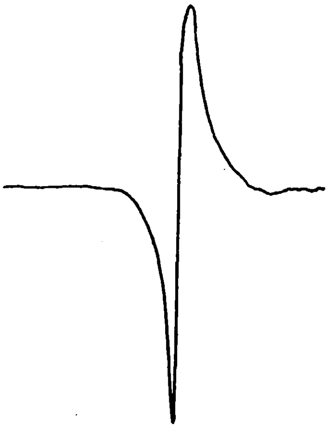


Fig. 3A

Representative DSC profile for decomposition of L_2PtAr_2

The complexes were thermolysed under an inert atmosphere (nitrogen or argon) at a temperature ca. 10° above decomposition onset (indicated by DSC or DTA exotherm) in a specifically designed pyrex apparatus (see experimental section). The volatile products were subsequently trapped at 77K under high vacuum (10^{-3}torr.) and decomposition undoubtedly continued throughout transfer. At the lower thermolysis temperatures employed for some complexes, transfer of higher-boiling components was inefficient. Accordingly, a higher temperature was required for the transfer stage - see Table 3.1. Product analysis was by quantitative gas liquid-phase chromatography (GLC) using an accurately introduced, suitable internal standard. The results displayed in Table 3.1 represent the only volatile products evolved. Screening for lower - boiling product fractions (methane, ethane, ethylene) was effected independently by thermolysis in vacuo and analysis of gaseous effluent by gas-phase i.r. spectroscopy. Dihydrogen alone would have escaped detection by these combined techniques.

Calibration experiments established that the error in product quantification was ±2% for biaryls and ±4% for arenes. Each thermolysis was performed at least twice to test reproducibility.

Nomenclature

The terms 'monotertiary phosphine' and 'ditertiary phosphine' refer to monodentate and bidentate tertiary phosphines respectively. The arbitrary abbreviations for the ditertiary phosphine ligands are: dpm - bis-(diphenylphosphino)methane; dpe-1,2-bis-(diphenylphosphino)ethane.

Results and Discussion

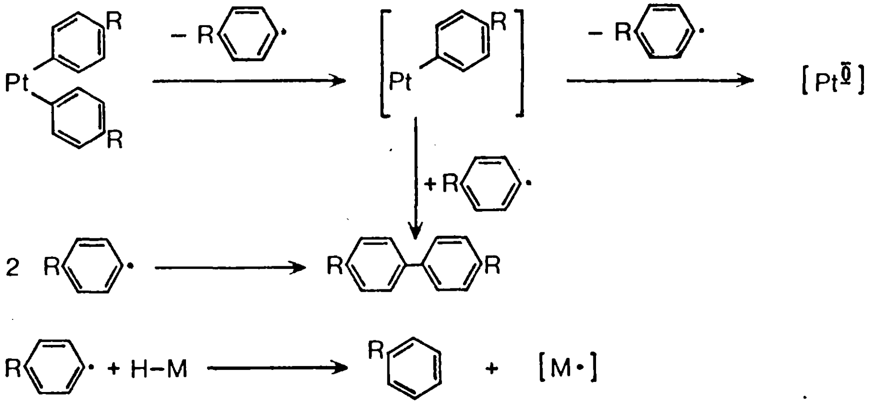
In discussion of thermal decomposition of these (arylphosphine)-arylplatinum(II) species, it is important to distinguish between primary and secondary processes. Primary processes are those rearrangements which occur in or from the intact complex molecule. Secondary processes, are those which occur in the modified molecular fragment, subsequent to a primary process. As it had been the intention to investigate certain propositions concerning transition-metal to carbon σ-bonding, the unambiguous assignment of the primary process has been a principal objective. This proved not to be straightforward as it was soon evident that primary and secondary reactions may result in coincident products. Before proceeding to interpretation of observations, however, it would be instructive to consider in more detail, the available primary options for molecular disruption associated with the Pt-C bonds, with particular reference to the distribution of organic products which each may generate. (Ancillary ligands are omitted for clarity).

Scheme 3.1 (i) depicts the pathways associated with primary homolysis of a platinum-carbon bond. The resultant free aryl radicals would be capable of undergoing coupling reactions on radical encounter, and perhaps also by aryl abstraction from intact or partially fragmented molecules. Additionally, hydrogen atom abstraction would be expected. (Here, M does not necessarily represent a metal atom, but a suitable molecular fragment with an accessible, abstractable hydrogen atom). The product distribution would thus be anticipated to include both arene and biaryl derived from the platinum-bound aryls. A lack of information concerning the stereochemical stability of substituted aryl radicals precludes any discussion as to whether these would be likely to isomerise (by H-shifts) at a rate competitive with coupling. It is safest to assume that the symmetrical, unisomerised coupling product would predominate.

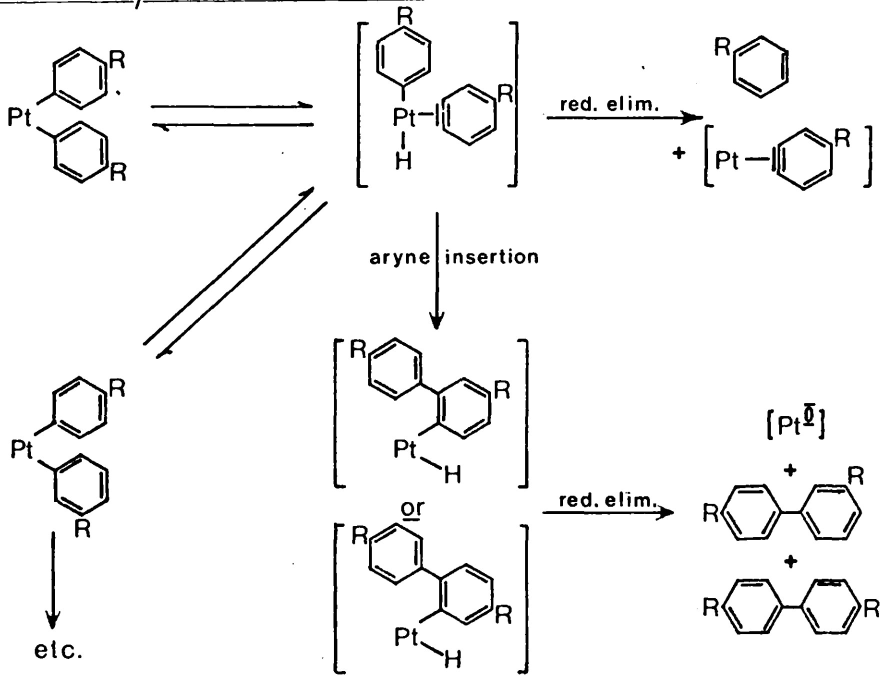
Scheme 3.1 (ii) outlines the various consquences if primary β-elimination is an operative mode. This might be considered to be an unfavourably energy-demanding process, creating as it does, a hydridometal-aryne complex as a key intermediate. However, just such a scheme appears to be a major contributor to the thermal decomposition of $(\eta^5-C_5H_5)TiAr_2$ complexes (Ar = Ph-, o-tolyl, p-tolyl) which yield arene quantitatively[227] (other hydrogen atoms are trans-

Options for M-C Bond Scission in cis-L_2PtAr_2

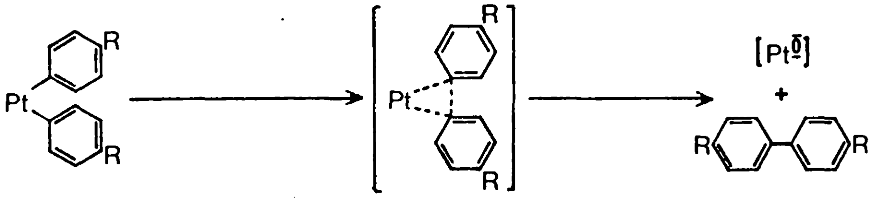
(i) Primary Homolysis



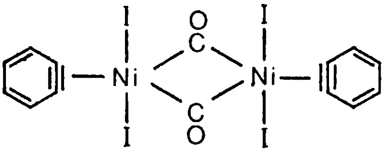
(ii) Primary β-Hydride Elimination



(iii) Primary Concerted Reductive Elimination



ferred, in an intramolecular fashion, from the cyclopentadienyl ligands). Aryne-metal complexes are not unknown in their own right, notably those involving trigonal metal clusters[228]. Of particular interest here is a benzyne-nickel species to which structure 3B has been assigned on spectroscopic evidence.[229]



3B

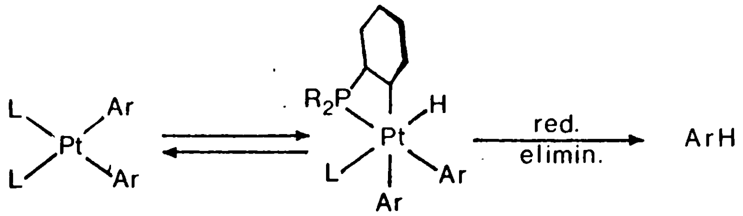
Several products might then arise from the benzyne-platinum intermediate (see scheme). Spontaneous reductive elimination would lead to the production of arene. This has the parallel of butane generation from $(Ph_3P)_2PtBu^n_2$ [93] Coupling products might also be expected from this mechanistic format, via insertion of the coordinated aryne into the remaining Pt-C σ-bond and subsequent reductive elimination. Notably, unless this insertion were entirely regiospecific - which would seem unlikely - a mixture of isomeric biaryls ought to result (see scheme).

It may be recalled that such a scheme was advanced to explain the reductive coupling products from a diorganonickel(II) decomposition in the presence of a benzyne precursor[201]. Against this, it must be noted that the organotitanium system did not display this predisposition[227], nor were coupling products - via an analagous route - significantly present during the decomposition of $(Ph_3P)_2PtBu^n_2$ [93]. This might reflect the preferential insertion by an unsaturated hydrocarbon into a metal-hydrogen rather than a metal-carbon bond, where the choice is available[197]. On the other hand, this in itself raises important stereochemical consequences for the ultimate product distribution. This reinsertion simply reverses the initial β-elimination. Unless it too is wholly regiospecific - which again, by analogy[93], seems unlikely - then the ensuing manifold of elimination/insertion will effectively scramble the positions of aryl carbon and hydrogen atoms relative to the metal (and each other). The result would be that any coupling products, whether by this or any other mechanism, should display considerable isomer distribution - potentially all possible substitution combinations - if a β-elimination process operates to any extent.

The superficially simplest process, perhaps - that of primary reductive elimination of the adjacent aryl groups - is illustrated in scheme 3.1 (iii). The reaction as portrayed is concerted - bond-making accompanies bond-breaking - and thus isomer-specific. The only anticipated organic product is the symmetrical biaryl.

The possibility of primary ortho-metallation must also be considered at this stage. Although not in itself a metal-carbon scission operation, it may ultimately achieve this result[90,101,182,183] as demonstrated in scheme 3.1(vi) Were such a sequence to occur as a primary route in a diarylplatinum(II) molecule, then metal-derived arene would be a predominant product, *via* a hydridodiarylplatinum(IV) intermediate.

Scheme 3.1(iv) Primary ortho-Metallation

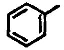
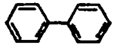
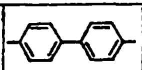
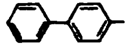


INTERPRETATION OF PRODUCT DISTRIBUTIONS

Examination of the volatile product distributions from the thermal decomposition of the phenylplatinum(II) complexes, (dpm)$PtPh_2$, (dpe)$PtPh_2$ and cis-$(Ph_3P)_2PtPh_2$, immediately reveals two striking common features. First of all, an appreciable amount of benzene is evolved by each. Secondly, a greater quantity of product - indeed of biaryl - is generated by each system than can be accounted for solely in terms of the excision of aryl groups originally bound to platinum. Clearly, a proportion of the products owe their origin to aryl groups initially incorporated in the phosphine ligands. This evident multiplicity of reaction pathways completely precludes any mechanistic interpretation. The various primary decomposition possibilities discussed above might only be distinguished if the origin of the organic products could be unambiguously assigned to the initial aryl substituents of the metal atom. Since in these three complexes the substituents of both platinum and phosphorous are identical, the crucial assignment of origin cannot be made. The stereoselective introduction of a suitable substituent 'handle' on either the phosphorous-or platinum-bound aryl will, however, allow the necessary differentiation of the ultimate fate of each. It will in addition, allow the stereochemical integrity of the observed processes to be tested and, hence, clear mechanistic distinctions may, hopefully, be drawn.

Thus, thermolysis of cis-$(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ yields 4,4'-bitolyl (0.97 mole) but no toluene (see Table 3.1), illustrating that, within experimental error, the originally

Table 3.1

SYSTEM	decomp. onset (T_d K)	thermol. temp. (T_t K)	thermol. time (hr)	PRODUCTS: mole.[mole Pt]$^{-1}$					
									R_3P; P⌒P
(dpm)PtPh_2	503	508	2·0	0·29	*	1·19	*	*	a
(dpe)PtPh_2	516	523	2·0	0·20	*	1·13	*	*	a
cis-[$(Ph_3P)_2PtPh_2$]	419	(i) 433 (ii) 523	1·0 1·0	0·35	*	1·12	*	*	0·14
(dpm)Pt(4-Me-C_6H_4)$_2$	516	518	2·0	0·13	0·15	0·09	0·89	0·08	a
cis-[$(Ph_3P)_2$Pt(4-Me-C_6H_4)$_2$]	380	(i) 403 (ii) 528	1·0 7·0	0·30	-	0·29	0·97	t	0·15
cis-[{(4-Me-C_6H_4)$_3$P}$_2$PtPh_2]	418	518	5·0	-	0·59	1·01	0·29	≤0·01	0·06
1:1 (dpm)PtR_2^{b}	502	508	1·8	0·29 (0·21)	0·09 (0·08)	0·60 (0·64)	0·45 (0·45)	0·03 (0·04)	a
1:1 *cis*-[$(R_3P)_2PtPh_2$]^b	418	(i) 433 (ii) 523	1·0 1·0	0·15	0·13	1·02	0·03	0·08	c

[a] Not detectable by technique employed. [b] R=Ph; 4-Me-C_6H_4-. [c] Both phosphines detected but not quantified.

[t] Trace detected (<10^{-3} mole)

metal-bound aryl groups generate only σ-coupled dimer, quantitatively and without isomerisation. The absence of arene originating from these ligands is a potent indication that neither free aryl radicals (tolyl species are good hydrogen atom sources[230]) nor primary β-elimination are responsible for the products of platinum-carbon cleavage. (Schemes 3.1(i) and 3.1(ii); R = CH_3) Any contribution by primary ortho-metallation may also be discounted.

The operation of a β-elimination mechanism at any stage is an untenable proposition on two further counts. First of all, in the unlikely event of coupling being the only result of primary β-elimination, or in the more plausible contingency that β-elimination/insertion accompanies the coupling reaction, some loss of isomer specificity would be expected (see Scheme 3.1(ii)) In fact, only one isomer - the symmetrical 4,4'-bitolyl - is observed. Second, since the β-elimination mechanism requires an additional coordination site, the presence of a strongly ligating nucleophile might be expected to effect an inhibition on the overall decomposition reaction - if by this route - analagous to that found with $(Ph_3P)_2PtBu^n_2$, for which a primary β-elimination process is established to operate[93]. In fact, as will be discussed subsequently, precisely the opposite effect is noted throughout this series of arylplatinum complexes, and decomposition is consistently facilitated by the presence of tertiary phosphine.

It seems evident, then, that the selective coupling of aryl groups - as a result only of thermal rupture of the metal-carbon bonds - is effected by primary, concerted reductive elimination.

In addition to 4,4'-bitolyl, quantities of benzene and biphenyl are also produced during the thermolysis of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ - self-evidently originating from the coordinated arylphosphine. This is as might be expected by strict analogy with the thermolytic behaviour of $(Ph_3P)_2PtPh_2$. It is thus demonstrated that both arene and excess biaryl (in the latter case indistinguishable from the reductive elimination product) may be attributed to some secondary process (or processes) involving the arylphosphineplatinum skeleton, most probably subsequent to the reductive elimination step. Significantly, no detectable amount of the cross-coupled biaryl, 4-methylbiphenyl, was observed, suggesting that the process responsible for coupling of aryl substituents linked originally to platinum occurs independently of that generating biaryl from initially phosphorus-bonded groups. That the latter is authentically a secondary process may be gauged from the observation that further prolonged thermolysis of the platinum-bearing residue from thermolysis of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ after removal of the 1 molar equivalent of 4,4(-bitolyl yielded only further quantities of biphenyl and benzene (vide infra)

The absence of 4-methylbiphenyl from the volatile product distribution might, tentatively, also lend support to the proposition that platinum-carbon homolysis is not primarily involved. Bimolecular homolytic substitution at phosphorus[231] by the resultant 4-tolyl radicals would, potentially, liberate phenyl radicals, leading ultimately to the crossed product.

Examination of the thermal decomposition products of cis-$[(4\text{-Me-}C_6H_4)_3P]_2PtPh_2$ effectively substantiates the above findings. (See Table 3.1.) Topologically, conversion from the previous complex involves only transposition of phenyl and 4-tolyl groups and here it is biphenyl that appears quantitatively (1.01 mole) as primary reductive elimination product, with corresponding absence of benzene. Secondary products are (analogous to $(Ph_3P)_2Pt(4\text{-Me-}C_6H_4)_2$) toluene and 4,4'-bitolyl. Notably, the last of these observations distinguishes the secondary coupling process also as occurring with complete preservation of isomer specificity. 4-methylbiphenyl, although detectable in this case, is still an extremely minor product ($\leqslant$1 mole %)

The proposed mechanistic scheme of primary concerted reductive elimination of biaryl, followed by secondary processes which may give rise to both biaryl and arene, appears to have general applicability to the family of complexes which have two monodentate triarylphosphine ligands coordinated to the diarylplatinum fragment. Extension, by analogy, to the species bearing a bidentate, ditertiary phosphine is not at first sight, straightforward, as demonstrated by analysis of the thermolytic behaviour of $(dpm)Pt(4\text{-Me-}C_6H_4)_2$. The predominant product is, indeed, that expected from primary reductive elimination - namely 4,4'-bitolyl (0.89 mole). However, in addition to quantities of benzene and biphenyl anticipated by analogy with the monophosphine derivatives, appreciable amounts of toluene and 4-methylbiphenyl are also produced. (See Table 3.1) This might be superficially construed as being indicative of some significant alteration in mechanism, but this need not be the case. The possible nature of the secondary processes, and reasons why dpm complexes may be more susceptible to undergoing these reactions will be discussed at greater length presently. In the meantime, however, one important fact must not be overlooked. The decomposition onset temperatures and hence the initial thermolysis temperatures for (diphosphine)arylplatinum complexes are higher than those for monophosphine analogues by ca.80–120K (Table 3.1) (This does not necessarily represent a direct measure of relative thermal stabilities, as it takes no account of, for example, lattice energy differences). At these relatively elevated temperatures, the thermal agitation within the molecule must be considerable before the disruptive processes begin to operate. A reasonable conclusion is that, although reductive elimination continues to predominate as the primary process, what were formerly discrete secondary processes are now no longer purely so, but (given, perhaps, the high-energetic conditions of elevated temperature) begin effectively to compete with metal-carbon bond scission. (The yield of 4-methylbiphenyl from $[(4\text{-Me-}C_6H_4)_3P]_2PtPh_2$ can, for example, be observed to rise – to a maximum of 0.01 mole – on increasing the initial thermolysis temperature). Thus, the machinery of coupling by reductive elimination from the metal no longer operates quite independently of the coupling and hydrogen atom transfer processes which are evidently inherent in the secondary pathways. In fact, as will emerge, in the presence of free phosphine, which both allows decomposition under less vigorous conditions and also effectively (though not completely) suppresses secondary reaction (either in the condensed phase or in solution), there is no evidence of mechanistic competition. In fairness, nevertheless, it must be said that, under these conditions, some contribution by platinum-carbon homolysis to the overall decomposition scheme cannot be altogether discounted*, on this evidence.

The effect may be reasonably assumed to operate for (dpm)$PtPh_2$, but whether it might also be extended to (dpe)$PtPh_2$ (which has a comparable decomposition-onset temperature) remains a matter for conjecture, as the substituent-labelled derivative (dpe)$Pt(4\text{-}Me\text{-}C_6H_4)_2$ could not be prepared and purified in sufficient yield to allow study.

That the primary reductive elimination step is indeed intramolecular, and that binuclear eliminations play no part, is confirmed by scrutiny of the thermolysis product distribution from an equimolar homogeneous mixture of (dpm)$PtPh_2$ and (dpm)$Pt(4\text{-}Me\text{-}C_6H_4)_2$ (prepared by freeze-drying an appropriate benzene-solution mixture). It can be seen (Table 3.1) that the distribution does not significantly deviate from that expected from parallel independent decomposition of the two systems (Quantities in parentheses). The ultimate fate of unequivocally metal-bound aryls is essentially unaffected by the presence of other, different metal-bound aryl groups. Of particular relevance is the detected yield of 4-methylbiphenyl. The operation to any extent of a primary binuclear coupling process would, in the presence of both σ-phenyl and σ-4-tolyl substituents on platinum, be reflected in an increase in production of the cross-coupled biaryl. No such variation is noted. It is worth noting that this argument applies both to concerted and non-concerted types of binuclear coupling; since the encounter reactions of free aryl radicals, if formed, would not be expected to be restricted to those between aryls

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*Lead-phenyl bonds, for example, undergo homolysis in the condensed phase at 525K (Ref. 232) from the same platinum parent, the non-increase in production of 4-methylbiphenyl supports the proposition that primary platinum-carbon bond homolysis is not responsible for the product distribution in this case (nor, indeed, generally). This single datum also effectively demonstrates that no process involving intermolecular exchange of metal-bound aryl groups can be occurring in these systems prior to or during their thermal decomposition. It is, however, emphasised that, although any contribution by intermolecular action may, on the basis of these distribution data, be discounted from the predominant primary reaction, there is no such implication for the auxilliary pathways. The ancillary phosphine ligand is invariant throughout the mixture, i.e. each molecule has identical aryl substituents on the ligand. Relative contributions by inter- or intramolecular processes which invclve these particular aryl groups, would obviously not be expected to induce changes in product distribution relative to the parallel, individual cases.

During the course of our investigations there have appeared a number of descriptions of thermal decompositions in related systems, which may be rationalised in terms of primary reductive elimination of organic groups from the metal atom. It is envisaged to be responsible for the production of ArR from complexes of type $(Et_3P)_2MRAr$[62] (M = Ni, Pd). This concerted route also seems implicit in the quantitative formation of metal-derived biaryl during the pyrolysis of $(Ph_3P)_2PtAr_2$[233] (Ar = m-FC_6H_4, p-FC_6H_4, Ph). These results, together with observation of coupling products from, for example, $(Et_3P)_2PdMe_2$[234], $(Me_3P)_2NiMe_2$[235] and $(Et_2P)_2NiPh_2$[30b] would appear to indicate that reductive elimination from 16-electron square-planar complexes of this general type, is an attractive thermal option. It is over the ultimate fate of the resultant 14-electron species that confusion and some contradictions have arisen.

The Nature of Secondary Processes

Reductive elimination of hydrocarbyl ligands from the 4-coordinate entity L_2PtR_2 might be expected to yield the bicoordinate zerovalent species $L_2Pt(0)$. Such coordinatively unsaturated and electron deficient molecules are likely to be very reactive[220] and, in fact, no such species bearing any of the phosphine ligands employed in this study has, as yet, proved isolable. Nevertheless, $(Ph_3P)_2Pt(0)$ has been shown to be present as a low-concentration (but important) dissociation product in solutions of $(Ph_3P)_3Pt(0)$[163, 236]. In addition, several isoelectronic and isomorphous palladium species $L_2Pd(0)$ - which L is an organophosphine of high steric demand - have recently been structurally characterised [237]. In view of these, and of the fact, as will emerge, that available extra phosphine is observed to stabilise the zerovalent state subsequent to elimination, it is not unreasonable to suppose that $L_2Pt(0)$ is a general decomposition intermediate. The observed secondary products may in each case be attributed to reactions of this species.

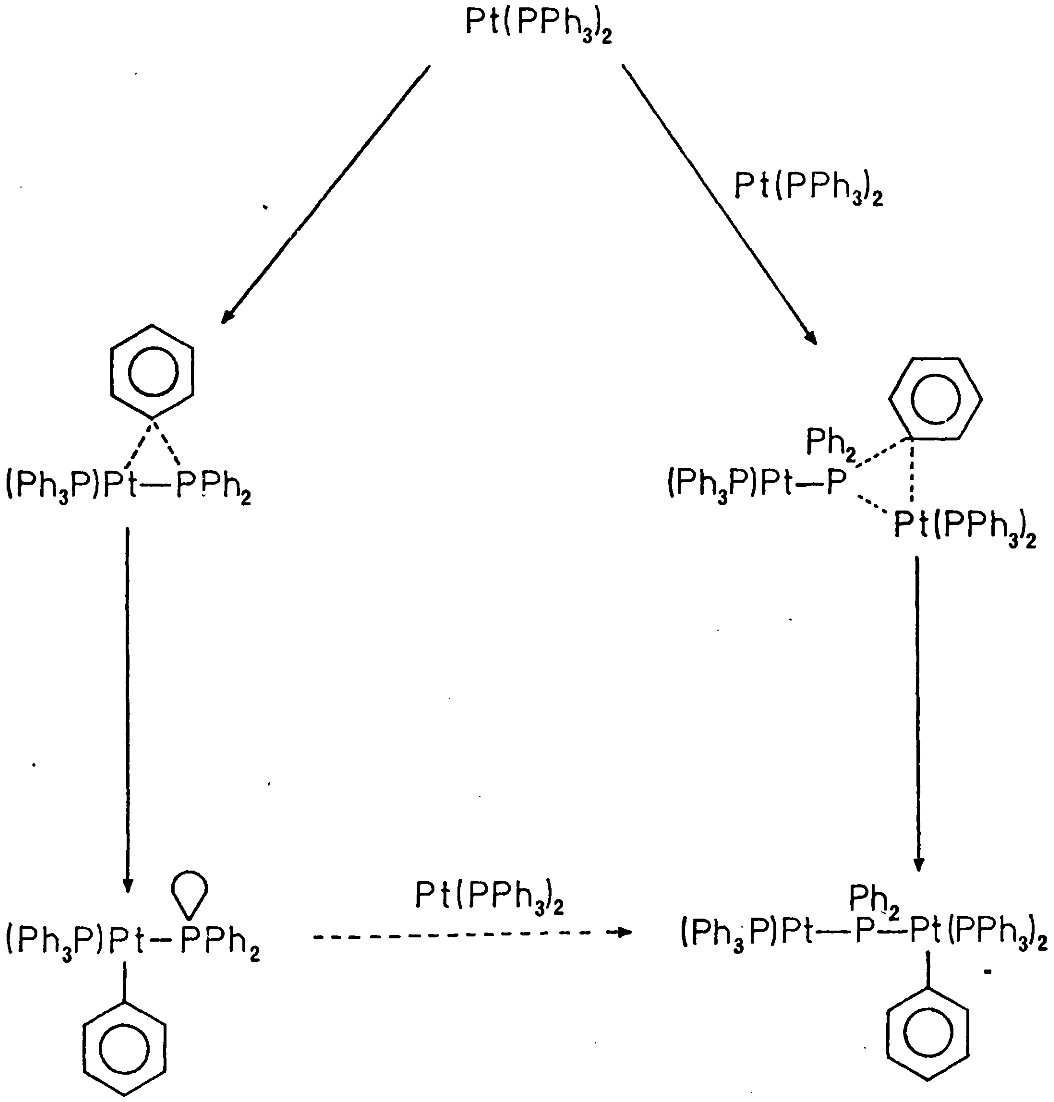
Such 14-electron intermediates have already been invoked as a consequence of thermal elimination from organoplatinum(II). In particular, Whitesides et al. deduced that $(Ph_3P)_2Pt(0)$ was produced as a result of the β-elimination/reductive elimination sequences that are responsible for the molecular disintegration of

$(Ph_3P)_2PtBu^n_2$, although no further decomposition products of the zerovalent fragment were reported[93]. The same species was envisaged by Glockling et al., during the course of our own investigations, to be the immediate product subsequent to reductive coupling of the aryl ligands of $(Ph_3P)_2PtAr_2$[233]. In this case, further decomposition of the intermediate reportedly generated 1 mole of (ligand-derived) benzene. Benzene is also a product of the thermolysis of $(Ph_2MeP)_2PtEt_2$ in solution, ostensibly by the similar decomposition of $(Ph_2MeP)_2Pt(0)$[120].

The present findings are, to some extent, at variance with the foregoing observations. Ligand-derived arene, it is true, is an ultimate product, but this is invariably accompanied by an appreciable quantity of biaryl originating from the phosphine aryl substituents. In fact, comparable quantities of ligand aryls ultimately appear in both products (See Table 3.1).

A number of significant observations may be made. The stereospecificity of coupling is continued in the secondary reactions. Representative phosphorous(V) analogues (Ph_3PO or Ph_3PS) do not display this decomposition pattern under the same conditions. These facts, in conjunction with the evidence that both primary and secondary processes occur under the same conditions, either independently or (occasionally) in limited (but isomer-specific) competition, render an explanation in terms of ligand to metal aryl-transfer an attractive one. This scheme is a plausible first step in the sequences that ultimately produce both arene and biaryl. The reaction may be envisaged to proceed via oxidative insertion of the now electrophilic metal into a phosphorus-carbon bond, in either an inter- or intramolecular fashion, as illustrated for $(Ph_3P)_2Pt(0)$ in scheme 3.2:

Scheme 3.2



This operation, in either case, would produce a monoarylplatinum(II) species, and the tenaciously bridging diphenylphosphido group. Notably, the operation of a succession of such steps might be expected to lead to oligomeric or polymeric organometallic products; in accord with our present empirical observations (vide infra). The retention of the substitution pattern in the coupling products suggests the transfer is effected via attack of the metal at the phosphorus linked carbon, and that preliminary ortho-metallation plays no part in the migration.

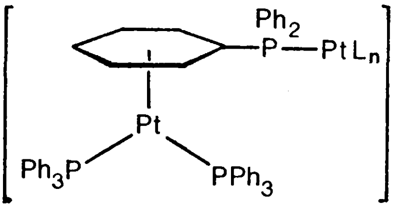
These proposals are not without precedent. A similar (ostensibly intramolecular) aryl-transfer mechanism has been advanced to explain the elimination of all three possible biaryl combinations in the thermal decomposition of trans-$(Ar_3P)_2Ni(Br)Ar'$.[238]

Once a σ-aryl substituent is established on the metal atom, alternative subsequent steps may account for the observed product generation. Prior or subsequent ortho-metallation of a further phosphine substituent creates a hydridoarylplatinum(IV) species, from which arene may readily be eliminated. Precisely such an explanation was advanced by Glockling et al. for their results[233]. On the other hand, migration of a further aryl group to the same platinum atom would generate a diarylplatinum(II) fragment. Stereospecific reductive coupling from this species would certainly be in accord with the observed biaryl production.

Binuclear elimination cannot be discounted as being responsible for product generation. It would, it is true, initially leave the metal in its rarely encountered, formally univalent state[239].

Electronic disproportionation, or metal-metal bonding schemes would be required to explain the observed diamagnetism of the residual material in all cases. Nevertheless, recent structural characterisation of thermal decomposition products of $(Ph_3P)_3Pt(0)$ would appear to establish the plausibility of formation of Pt-Pt bonds in a scheme that also implicates ligand to metal aryl transfer and diphenylphosphido bridge formation[240]

A conceivable common intermediate in these processes may be an η^6-(phosphino)areneplatinum species such as 3C:



3C

Such a species has some structural precedent in $[(Ph_3P)_3RuH]^+$, discussed previously in connection with ortho-metallation.[177]
This hexahapto aryl group would be suitably placed for H or Ar transfer to platinum, and might be formed synchronously with, or immediately subsequent to primary reductive elimination.

In an attempt to establish the molecularity of the aryl-transfer, an equimolar mixture of $(Ph_3P)_2PtPh_2$ and $[(4\text{-}Me\text{-}C_6H_4)_3P]_2PtPh_2$ was examined thermolytically. The operation to any appreciable extent of intermolecular modes will necessarily increase the yield of 4-methylbiphenyl relative to that in the individual cases. (neither produced more than trace amounts of this product; see table 3.1) The statistical limit for the ascendancy of cross-coupled biaryl is the production of biphenyl, 4-methylbiphenyl and 4,4'-bitolyl in a ratio of 1:2:1, (assuming minimal substituent effect by the *para*-methyl group on the transfer-controlling step), which might be interpreted as indicative of predominantly intermolecular operation. In effect, the product distribution shows a greatly enhanced yield of 4-methylbiphenyl and, moreover, the ratio of the three biaryls (excluding the assumedly quantitative yield of primarily produced biphenyl) is, optimistically, close to the theoretical statistical distribution. Certain reservations must accompany any interpretation, however. Intermolecular phosphine exchange prior to transfer or elimination would be an alternative explanation. Although ^{31}P n.m.r. studies conclusively demonstrated that such scrambling does not occur in benzene solution during preparation of the homogeneous mixture, its occurrence prior to or during decomposition in the vigorous conditions of the melt cannot be unequivocally ruled out. Nevertheless, the operation of intermolecular aryl transfer must be considered a strong possibility. These data cannot, of course, differentiate between mononuclear and binuclear eliminations of products.

The interpretation of possible secondary reaction mechanisms has been limited to the terms of concerted processes. In view of the established role of free organic radicals in some oxidative addition reactions[161-4], it would be unrealistic to conclude that aryl radicals may not be implicated - at least to some extent - in the secondary processes. The product distribution data for secondary decomposition in no way excludes this possibility. However, the general insensitivity (and often, indeed, complete independence) of primary product distributions, in spite of the concurrent operation of secondary decomposition modes, indicate that the contribution by secondarily produced radicals must, at best, be small. (Significant variation in product ratios, as a result of competitive bimolecular homolytic attack, would otherwise be expected).

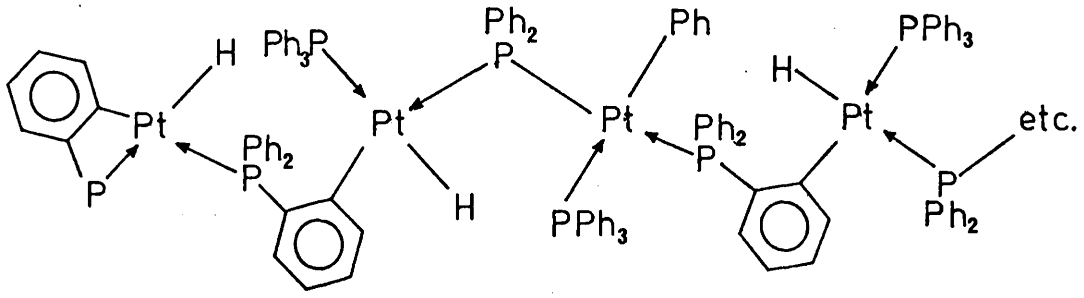
The secondary processes, although viable under the same reaction conditions as are primary steps, undoubtedly evolve products more sluggishly. Thermogravimetric curves reveal a steady, slow weight-loss over many hours at atmospheric pressure, and $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_4H_4)_2$, for example, continued to evolve C_6H_4 and Ph_2 after ten hours at 528K in vacuo. (The primary processes, by comparison, are apparently complete in a few minutes, on DTA or DSC evidence - although primary product recovery is not necessarily as rapid). The amounts of arene and ligand derived biaryl are, therefore, to an extent dependent on the time (and, relatedly, the temperature) of thermolysis. Furthermore, although the product distribution data are essentially reproducible, given the same conditions, they do not conform to any recognisable stoichiometry. Some phosphine is also liberated by the monophosphine complexes. (This may also apply to the diphosphine complexes: the free ligand would neither have been wholly transferred nor detected). Explanations for this puzzling behaviour do not come readily to mind. One may be that whilst aryl or hydrogen transfer to the metal (generating the Pt(II) species), occur readily and perhaps reversibly, the conditions which allow irreversible formation of ultimate products are likely to be more exacting. For example a cis-diarylplatinum(IV) fragment or a suitable alignment of eliminable substituents on adjacent metal atoms might be required. In short, the attainment of the requisite molecular configuration for elimination might conceivably exert the ultimate control on the reactions. On the other hand, the overall reaction, including the initial transfer, might simply be a slow process. This would imply the survival of the secondary precursor, $L_2Pt(0)$ in significant amounts. Clearly, a closer consideration of the nature of the residual materials must preface any further interpretation. Interestingly, an attempt to stabilise the bicoordinate zerovalent intermediate, by introduction of a suitable bulky phosphine, was baulked at the preparative stage. Treatment of trans-$(Cy_3P)_2PtCl_2$ (Cy = cyclohexyl) with PhLi in ether, either at reflux or at ambient temperature, let to no production of a phenylplatinum species even after four days. Starting complex was recovered quantitatively. Unfavourable stereochemical constraints either in products or intermediates probably account for this failure.

Nature of Thermolysis Residues

Apart from slight variations in colour, from dark red-brown to dark brown, these substances are generally very similar. They have a glassy consistency and exhibit limited solubility in organic solvents (e.g. methylene chloride, toluene) to give solutions varying in colour from deep amber to intense cherry red. Attempts at recrystallisation proved fruitless, however, irrespective of foregoing thermolysis time and ultimately led to recovery of the initial apparently amorphous material. Attempts to resolve components (if a mixture) by T.L.C. on alumina likewise met with unsatisfactory results. None displayed a defined melting point (DSC). These observations (and, additionally, the plasticity of the residues in the presence of organic solvents) would seem to indicate that these substances have a polymeric constitution. Their inertness in air, as solids or in solution, are more characteristic of higher-valent platinum that of zerovalent derivatives. The polynuclear platinum-cluster species which were reported to predominate in the residues from $(Ph_2P)_2PtAr_2$, subsequent to unimolar benzene elimination[233], could not be identified. Elemental microanalysis of residues from thermolysis carried out under a nitrogen atmosphere, demonstrated that such species as L_2PtN_2 were not produced. This is in accord with evidence that, whereas such species may be formed by Ni, where $L = Et_3P$, the Pd and Pt analogues are not accessible[241].

All these facts are in accord with the secondary modes which have been proposed, but seem to belie the survival of appreciable quantities of the zerovalent intermediates in spite of - on the basis of product extent - a relatively small amount of full secondary decomposition. Figure 3D portrays the local functions that might be thus expected to be present in the residual material from a triphenylphosphine derivative:

3D



ortho-metallated-, σ-phenyl- and perhaps hydrido-platinum derivatives would all be anticipated.

Toluene solutions of the various residues were treated with conc. aqueous HCl [standard experiments had demonstrated that platinum aryls quantitatively generate arene under these conditions] and the resulting solutions analysed by quantitative GLC (using n-decane as internal standard). The results of these experiments are summarised in Table 3.2. These data demonstrate that in every expected case, phenyl groups are present as platinum substituents in the residue. No phenylplatinum species are present in the residue from $[(4\text{-Me-}C_6H_4)_3P]_2PtPh_2$, and, notably, no σ-bound biaryl species were detected in any incidence (or alternatively any remaining untransferred biaryl). The data do reveal a singular anomaly, however. The residue from (dpe)$PtPh_2$ consistently contains a higher assay of σ-phenylplatinum entities than any other (three separate measurements on different residues which varied only within a range of 0.04 mole, demonstrated that this result is not spurious). This observation is borne out be i.r. evidence. The phenylplatinum oomplexes are characterised by a sharp absorption of fair intensity at 1565 cm^{-1} (This band is absent in the spectra of tolyl analogues, or of $(dpe)_2Pt(0)$). In the i.r. spectra of residues, this band is witnessed almost to vanish. However, the spectrum of the residue from (dpe)$PtPh_2$ retains this absorption, albeit at <u>ca.</u> $\frac{1}{3}$ original intensity. This relative abundance of metal-bound phenyl subsituents must be judged alongside the fact that (dpe)$PtPh_2$ does not give rise in comparison to the others, to an anomalous secondary product yield. These findings are not in themselves inconsistent if it is in fact the case that the second stage in the reaction - i.e. the

Table 3.2

Residual σ-Phenylplatinum Assay

Parent Complex	mole PhH per mole resid. Pt
(dpm)PtPh$_2$	0.082
(dpm)Pt(4-Me-C$_6$H$_4$)$_2$	0.074
(dpe)PtPh$_2$	0.460 [a]
cis-(Ph$_3$P)$_2$PtPh$_2$	0.082
cis-(Ph$_3$P)$_2$Pt(4-Me-C$_6$H$_4$)$_2$	0.067
cis-(4-tolyl$_3$P)$_2$PtPh$_2$	0.000

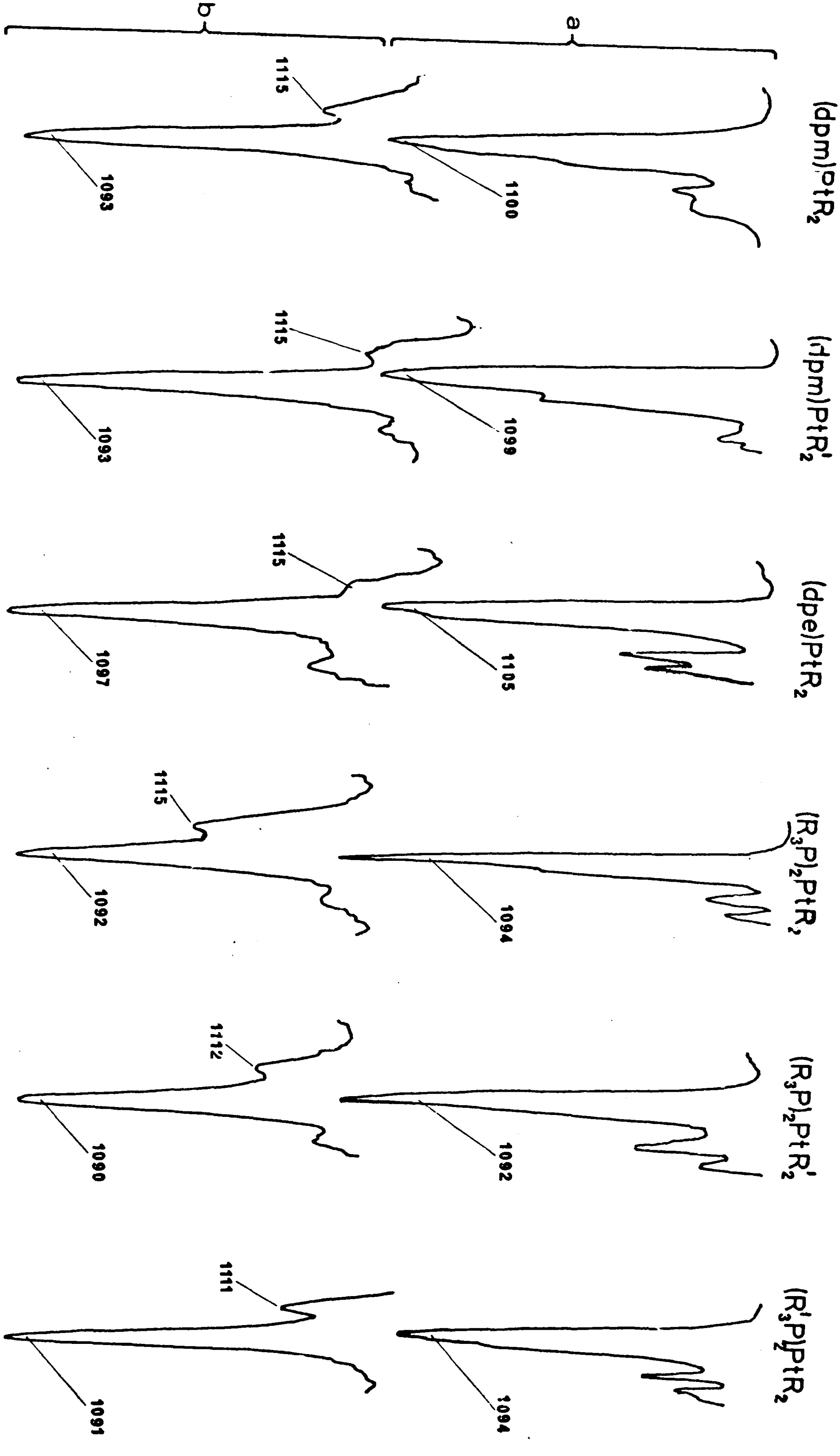
[a] Mean of data for 3 individual residues (values were within 0.04mole)

attainment of a suitable molecular configuration followed by elimination - controls the rate of evolution of products. An abundance of transferred aryls would not intrinsically guarantee suitable configurations. The reason for the apparently higher incidence of permanent aryl-transfer in this case is not, however, clear. It is likely to be stereochemical in origin, but a convincing rationalisation is not apparent.

Several workers have presented i.r. spectroscopic evidence for the assignment of <u>ortho</u>-metallated structures. Unfortunately, the region of the infrared spectrum generally associated with characteristic absorptions of 1,2-disubstituted aromatics (770-735cm^{-1} [242]) is too complex in the parent compounds to allow safe diagnostic use. All the triaryl and diarylphosphine complexes, however, (including dichloroplatinum derivatives) display reasonably intense absorption at <u>ca.</u>1100cm^{-1}. In every case, examination of the spectrum of the corresponding thermolysis residue reveals the appearance of a new band at ca 1110-1115cm^{-1}. The incidence of bands in this region has previously been considered indicative of <u>ortho</u>-metallation of arylphosphines[243, 244]. The bands near 800cm^{-1} which often accompany these absorptions are not immediately evident, but may be obscured. Only in the dpm complexes can new bands (at 775cm^{-1}) be unabiguously said to appear in this region on thermolysis. (See Fig. 3.1)

From the i.r. spectra, there is no evidence for Pt-H containing fragments[50]. (The GLC analysis would not have quantified H_2) However, the <u>ortho</u>-metallation reaction is often reversible, and it may be that, in the absence of an eliminable substrate, the

Figure 3.1



Characteristic IR Absorption for Arylphosphines of L_2PtAr_2 (a) Before (b) After Thermolysis [$R = Ph$; $R' = 4\text{-}Me\text{-}C_6H_4$]

equilibrium may lie to the unmetallated side.

It is perhaps not surprising, but is nevertheless worth noting, that the residues from complexes possessing the same ancillary phosphi ligand, have identical i.r. spectra, irrespective of the original platinum-bonded aryl groups.

Further Implications

The above experimental observations are not inconsistent with the schemes which are proposed to be inherent in secondary decomposition of these molecular systems. The limited competitive interference of these processes with preliminary reductive elimination from (dpm)$PtAr_2$ deserves some further enlargement. As was implied earlier, it may be that the higher energetic conditions required for the thermolysis may mean that the threshold for the oxidative insertion of Pt(II) species (as opposed to Pt(0)) into P-C or C-H bonds - which is envisaged to be a plausible step immediately prior to secondary product elimination - may already have been surpassed before any decomposition sets in. On the other hand, the small bight of the dpm ligand[245] (P-Pt-P angle of only 73°) may render the Pt-atom in the parent complex more susceptible to this type of attack. The absence of data for (dpe)$Pt(4\text{-}Me\text{-}C_6H_4)_2$ precludes satisfactory resolution of this argument. There are indications, however, that further explanations may be involved, and that further reaction options may come into play at these more energetic conditions. Most relevant to this question may be that of substituent exchange between platinum and phosphorus during, or prior to primary reductive elimination.

It may be that such a transfer mechanism explains the production of Ph_2MeP (as well as Ph_3P) during the pyrolysis of $(Ph_3P)_2PtMe_2$[246]. Also of significance may be an observation made from the GLC characterisation of $(4\text{-}Me\text{-}C_6H_4)_3P$ recovered from the high temperature thermolysis of $[(4\text{-}Me\text{-}C_6H_4)_3P]_2PtPh_2$: two small overlapping peaks were observed - combined weight $<1\%$ of total effluent yield. These components could not be unambiguously identified, but their retention times are intermediate between those of Ph_3P and $(4\text{-}Me\text{-}C_6H_4)_3P$. Their observation would not be inconsistent with the production of small amounts of the mixed-substituent phosphines.

Additional Note

Thermodynamic parameters relating to these processes could not be extracted by the differential thermal techniques (DTA or DSC) This was because fusion and decomposition of the complexes, which have opposing thermal characteristics, were found to be concurrent in every case. The extent to which endotherm and exotherm overlapped could not be assessed, and thus enthalpy correlations were rendered impossible.

CHAPTER FOUR

The Effect of Added Phosphine on the Thermal Decomposition of Diarylplatinum(II) Complexes

CHAPTER FOUR

Preamble

Concerted reductive elimination from a metal centre spontaneously reduces by two the formal oxidation state, the coordination number, and the electron enumeration at the metal atom. It has been reasoned that the process should be more facile where the metal has a high coordination number and an unfavourably high level of orbital population[48]. The tendency of platinum (and its triad) is towards lower orbital occupation than the bulk of elements to its left in the Periodic Table. In accordance with this, hexacoordinate, 18-electron platinum (IV) species readily undergo reductive elimination reactions, yielding square-planar, 16-electron divalent species[116-121, 48].

More generally, it is argued that agents which effectively increase the electron occupation at the central metal, should encourage reactions which, in turn, relax this situation. This may certainly be said to occur for, say, loss of a coordinated monodentate donor or olefin, but should also apply generally to other paired-electron processes, including reductive elimination, which relieve an unfavourably high orbital occupation.[48].

Oxidative addition is one scheme whereby the metal electron availability is raised (by two), and oxidative additions are frequently observed to precede reductive eliminations. The organoplatinum (IV) system, for example, on which rigorous study of reductive elimination has focused, are generated by oxidative addition to platinum (II) species[116-121].

The introduction of 2-electron donors, capable of ready nucleophilic attack on the metal, should be expected to produce an analogous effect, at least for metals which are coordinatively unsaturated. Indeed, it has been noted that ligand loss by reductive elimination often seems to be accelerated by the presence of strongly coordinating species[99, 247]. Square-planar complexes, with their coordination vacancies, would be expected to show some susceptibility to this particular kind of labilisation, and several examples are to be found in the organic chemistry of nickel(II). Examples of Lewis base induced coupling include:

$$[(2\text{-biphenylyl-O})_3P]_2NiMe_2 + 2Ph_3P \longrightarrow C_2H_6 + [(2\text{-biphenylyl-O})_3P]_2Ni(Ph_3P)_2 \quad \text{(Ref. 248)}$$

$$(bipy)NiEt_2 + 2CH_2{=}CHCN \longrightarrow \text{butane} + (bipy)Ni(CH_2{=}CHCN)_2 \quad \text{(Ref. 249)}$$

$$\begin{tikzcd}
(Me_3P)_2NiMe_2 \arrow[r, "PMe_3"] & (Me_3P)_3NiMe_2 \arrow[r, "Ph_3P"] \arrow[d] & C_2H_6 + (PMe_3)_3NiPPh_3 \\
 & C_2H_6 + Ni + 3PMe_3 & \text{(Ref. 235)}
\end{tikzcd}$$

The establishment of 5-coordinate species such as $(Et_3P)_3Ni(C{\equiv}CPh)_2$[30b] $(Me_3P)_3NiMe_2$[235] and $(bipy)Ni(olefin)Et_2$[249] on treatment of the organonickel parent with the appropriate donor species, seems to indicate that the nucleophile may play an active role along the reaction coordinate rather than functioning solely as an agent for stabilising the low-valent metal product. It may be argued, of course, that the effect of these ligating agents is, to some extent steric. Its most important stereochemical implications are likely to be the inhibition of other available elimination modes, for example β-elimination, by blocking the necessary extra coordination site[93], and binuclear elimination, by similarly discouraging metal-metal interactions[95]. This may in some cases lead to a relative enhancement of reductive elimination, but need not necessarily do so[93].

The fact remains, nevertheless, that the role of the nucleophile has seldom been critically evaluated by examination of a system which unequivocally undergoes reductive elimination in the absence of donor species. It has already been established that the series of bis(phosphine)diarylplatinum(II) complexes under examination thermally decompose <u>via</u> primary concerted reductive elimination of the metal-bound aryl ligands. These coordinatively unsaturated systems provide an ideal opportunity to test the hypothesis of nucleophilic facilitation of this process. Tertiary organic phosphines were chosen as nucleophiles for their potency towards Pt(II) substrates[250], and also, since several tris-and tetrakis-phosphine complexes of zerovalent platinum are known[49], in the hope of stabilising the metal product subsequent to reductive elimination. Generally, the same phosphine as that already present was introduced, to circumvent the complications of possible ligand exchange, either prior to or subsequent to the elimination step.

<u>Experimental Techniques*</u>

The same thermolytic and product-analysis techniques as for the complexes alone were employed here on intimate mixtures of L_2PtAr_2 and L.

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*For full details, see Chapter 6

This mixing was achieved by freeze-drying of appropriate benzene solutions or, where the solution stability of the system was insufficient - as for the $(Ph_3P)_2PtAr_2$ species - by grinding together in an agate mortar.

The known zerovalent platinum species $(dpe)_2Pt(0)$[251] and $(Ph_3P)_3Pt(0)$[252] were characterised by their elemental analysis, and by comparison of ir, mass spectrometric and D.S.C. parameters with those of an authentic sample, or with available reported data[251, 252]. The more labile species $(dpm)_2Pt(0)$ was indentified as a residual component by mass spectrometry.

As was the case with the pure complexes, a general pattern of thermal behaviour was revealed by the instrumental methods. A single sharp endotherm was observed first, attributable to fusion of the free ligand, and concomitant solvation of the complex. This was followed (though not, generally, immediately) by an irreversible exothermic process, accompanied by the onset of weight loss. This decomposition exotherm was inavariably less sharp than that observed for the complex alone.. (See Figs. 4.1 and 4.2).

Results and Discussion

Two notable effects of the presence of free phosphine on the thermolytic behaviour of the complexes are apparent. Firstly, decomposition is facilitated in every case. This is shown by DTA and/or DSC measurement of relative decomposition onset temperatures (Table 4.1) The effect is most marked for the complexes of dpm., when an equimolar quantity of dpm is present; the onset of decomposition for these systems is ca. 105° below the decomposition

Table 4.1

SYSTEM	decomp. onset (±2K)		δT_N
	T_1	T_2	
(dpm)PtPh$_2$	503	398	-105
(dpm)Pt(4-Me-C$_6$H$_4$)$_2$	516	410	-106
(dpe)PtPh$_2$	516	481	-35
cis-[(Ph$_3$P)$_2$PtPh$_2$]	419	380	-39
cis-[(Ph$_3$P)$_2$Pt(4-Me-C$_6$H$_4$)$_2$]	380	365	-15

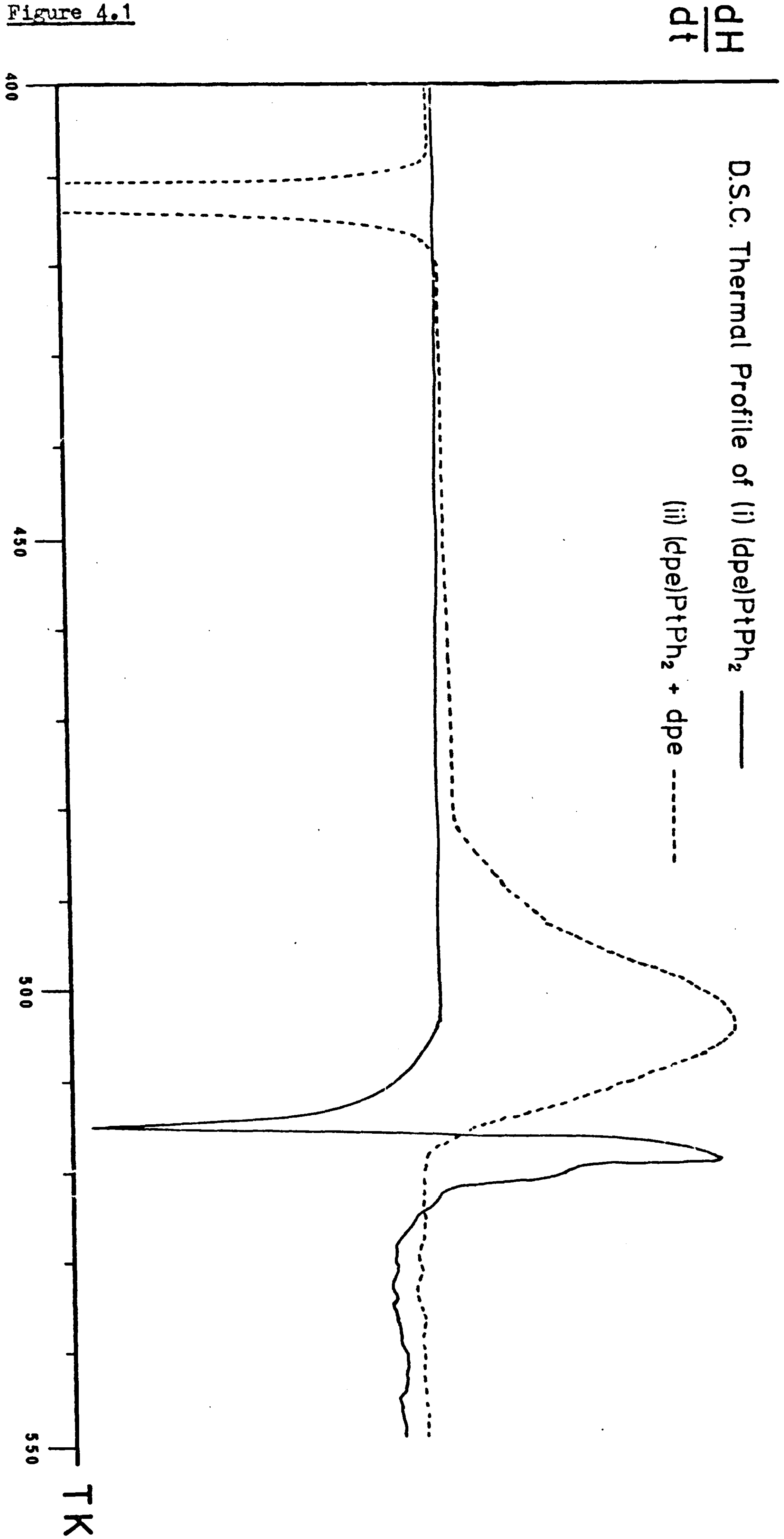
T_1: free ligand absent; T_2: free ligand present.

onset for pure (dpm)$PtAr_2$. Even where the effect is less pronounced, however, such as in the case of the (dpe)$PtPh_2$, comparison of DSC data (Fig. 4.1) reveals that decomposition in the presence of free dpe is well accomplished appreciably in advance of the onset of thermal disruption of the complex by itself. The reasons for individual variations in the magnitude of this effect are not obvious, and probably arise from a complicated interaction of separately unassessable parameters, but the qualitative implications are clear.

That the effect is truly attributable to electron-donation, and is not merely a result of solvation is, of course, a matter of some import. This question, in a sense, can never be wholly resolved, since it is generally observed that media with more electron-donor propensity provide the better solvents for these species. However, prolonged thermolysis (4-6hr) of a saturated solution of (dpm)Pt$(4\text{-}Me\text{-}C_6H_4)_2$ in perhydrotriphenylene (a fused cyclohexane system to which low nucleophilicity is ascribed) at 413K - at which temperature, decomposition occurs spontaneously in the presence of free dpm - consistently produced no detectable indication of decomposition. We therefore conclude that the electron-donor capability of the added phosphine has a major contributory role in the facilitation of thermal decomposition. (Further conclusive evidence that this is the case has arisen from studies of the kinetics of decomposition of various complexes <u>in the same solvent</u> (toluene) both in the presence and absence of free ligand; this will be presented in Chapter 5.)

Secondly, and in juxtaposition, analyses of the thermolysis products confirm that the decomposition process is indeed that of primary

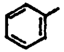
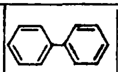
Figure 4.1



D.S.C. Thermal Profile of (i) (dpe)PtPh$_2$ ——

(ii) (dpe)PtPh$_2$ + dpe ------

Table 4.2

SYSTEM	decomp onset (T_d K)	thermol. temp. (T_t K)	thermol. time (hr)	PRODUCTS: mole.[mole Pt]$^{-1}$							
									L	other	residues
(dpm)PtPh$_2$ + dpm	398	403	2·0	0·09	*	0·98	*	*	0·18	Ph$_3$P 0·04 Ph$_2$MeP 0·14	contain (dpm)$_2$Pt$^{\overline{0}}$
(dpm)Pt(4-Me-C$_6$H$_4$)$_2$ + dpm	410	413	2·0	0·02	-	-	0·98	-	0·20	Ph$_3$P 0·03 Ph$_2$MeP 0·21	contain (dpm)$_2$Pt$^{\overline{0}}$
(dpe)PtPh$_2$ + dpe	481	488	2·0	-	*	1·01	*	*	-	-	(dpe)$_2$Pt$^{\overline{0}}$
cis-[(Ph$_3$P)$_2$PtPh$_2$] + Ph$_3$P	380	385	4·0	0·03	*	0·99	*	*	0·08	-	largely (Ph$_3$P)$_3$Pt$^{\overline{0}}$
cis-[(Ph$_3$P)$_2$Pt(4-Me-C$_6$H$_4$)$_2$] + 2Ph$_3$P	365	393	4·0	0·06	-	0·05	1·02	-	0·58	-	largely (Ph$_3$P)$_3$Pt$^{\overline{0}}$

reductive elimination of biaryl from platinum. This reaction is quantitative in every case (Table 4.2) including that of $(dpm)Pt(4\text{-}Me\text{-}C_6H_4)_2$ for which - in the absence of free ligand - it could be demonstrated that other processes compete to a limited but significant extent with biaryl elimination. Indeed, it is evident that generation of secondary aryl-derived products is generally suppressed, relative to analogous treatment in the absence of phosphine. In the case of $(dpe)PtPh_2$, the presence of dpe during the thermolysis prevents any secondary reaction whatsoever.

These observations are in accord with the expected stabilisation, by additional available coordinating species, of the zerovalent state of the metal. That this is in fact the correct explanation is demonstrated by the formation of $(dpe)_2Pt(0)$ as the only residual species - subsequent to quantitative elimination of biphenyl only (Table 4.2) - from the thermal reaction of dpe with $(dpe)PtPh_2$:

$$(dpe)PtPh_2 + dpe \xrightarrow{490K} (dpe)_2Pt(0) + Ph_2$$

The explanation for the apparent uniqueness of this system seems to be that $(dpe)_2Pt(0)$, alone among the zerovalent platinum species that may be analogously formed in this series of reactions, is thermally stable under the prevalent conditions of its formation (ca. 490K) DSC studies reveal that it undergoes independent thermal decomposition from Ca. 573K (vide infra)

Thermal decomposition of $(dpm)PtAr_2$ in the presence of equimolar quantities of dpm is not quite so straightforward. Quantitative 4,4-bitolyl and no toluene or 4-methylbiphenyl are produced when Ar= $4\text{-}Me\text{-}C_6H_4$ (Table 4.2) indicating an uncomplicated primary reductive elimination of biaryl is operative, analogous to the dpe example. However, although the mass spectra (at 250°C) of the residues unequivocally indicated the presence of $(dpm)_2Pt(0)$*, this species appears to decompose further, even under the relatively mild conditions of its formation. The i.r. spectra of residues reveal the appearance of new bands at 1112 cm^{-1} and at 780 cm^{-1}, possibly indicative of the presence of ortho-metallated species, in accord with the small quantities of benzene produced (Table 4.2) The incidence of other products from this secondary decomposition, and further analogies with the dpe-containing system, will be discussed presently.

Interestingly, attempts to independently synthesise $(dpm)_2Pt(0)$ by conventional routes[251, 252] met with failure. This can be attributed to the evident instability of the monomeric species in even warm solution, rendering its purification and isolation peculiarly difficult. Both the Ni(o)[253] and Pd(o)[254] analogues have been reported. A brief report[255] of the isolation by an indirect route of a yellow crystalline complex corresponding (microanalytically) to $(dpm)_2Pt(0)$, has appeared, but such few details as are presented (namely a melting point, with decomposition, in excess of 573K) are somewhat inconsistent with our findings.

The hypothesis that the more restricted secondary reactions in this series of decompositions can be legitimately attributed to thermal decomposition modes of the expected zerovalent platinum species seems readily extendable to the examples involving monodentate phosphines.

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*The molecular ion was a minor peak in a spectrum dominated by the fragmentation patterns of decomposition products - notably Ph_2MeP, Ph_3P and dpm.

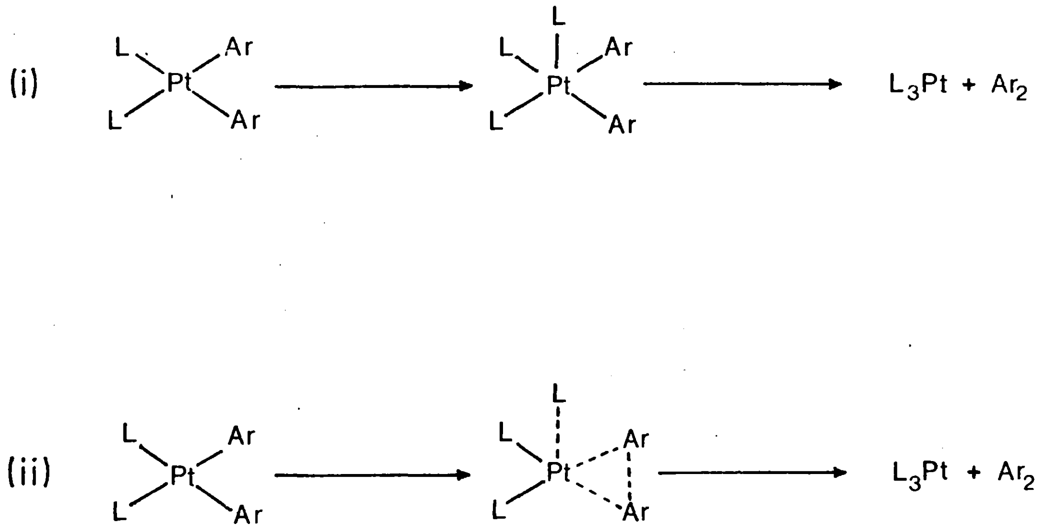
The product distribution data for thermolysis of $(Ph_3P)_2PtAr_2$ (Table 4.2) again reflect a quantitative concerted reductive elimination of metal-derived biaryl, accompanied by limited effusion of secondary products. The residual materials from the thermolyses with one or two equivalents of Ph_3P appear to be largely (though not purely) composed of $(Ph_3P)_3Pt(0)$. This species has been noted to show a certain tendency toward thermal ligand loss[163, 236] - perhaps thus accounting for the quantities of liberated Ph_3P* (Table 4.2) - and this species decomposes in a manner that would account for the nature of secondary products (See previous chapter) The appearance of an i.r. absorption at 1115 cm^{-1} - suggestive of ortho-metallation - strengthens this conviction.

The precise mechanism of nucleophilic labilisation of these organoplatinum complexes deserves some comment. It seems clear that the ultimate metal product is reached via formation of the anticipated polyphosphine zerovalent platinum species, which may or may not further decompose. Inevitably, the route to this point, with concomitant assistance of elimination, involves interaction of the (additional) phosphorus donor orbital with the metal atom. The exact nature of this interaction, along with the reaction coordinate, may, however, only be guessed. Two extreme views are conceivable (Schemes 4.1) The platinum atom may expand its coordination, by full ligation of phosphine - yielding a true metastable intermediate prior to biaryl elimination - thus maximising the transient electron population (eighteen) at the metal (Scheme 4.1(i)). Five-coordinate derivatives

*At the low temperatures employed, transfer of Ph_3P prior to estimation may well have been incomplete.

of platinum (II) have adequate precedent, both as stable entities[256b, 257] and as reaction intermediates[256b, 258]. Alternatively, the reaction may pursue a course related to classical nucleophilic substitution at carbon[259], in which an initially weak donor-acceptor interaction is progressively strengthened while concurrent scission of metal-carbon bonds proceeds. This format (Scheme 4.1 (ii)) ensures the minimum increase in the metal electron-occupation as the reaction coordinate is traversed.

Schemes 4.1



It is of interest that, whereas (dpm)PtPh$_2$ shows a very marked instability in the presence of free dpm (indicated by the relative onset points of decomposition exotherms in the DSC thermal profiles – Fig. 4.2), the same complex, in the presence of dpe, decomposed at a temperature comparable with those of (dpe)PtPh$_2$ in the presence either of free dpe or dpm. (The decomposition onset temperatures, in fact lie within a range of 10°). An attractive implication is that the

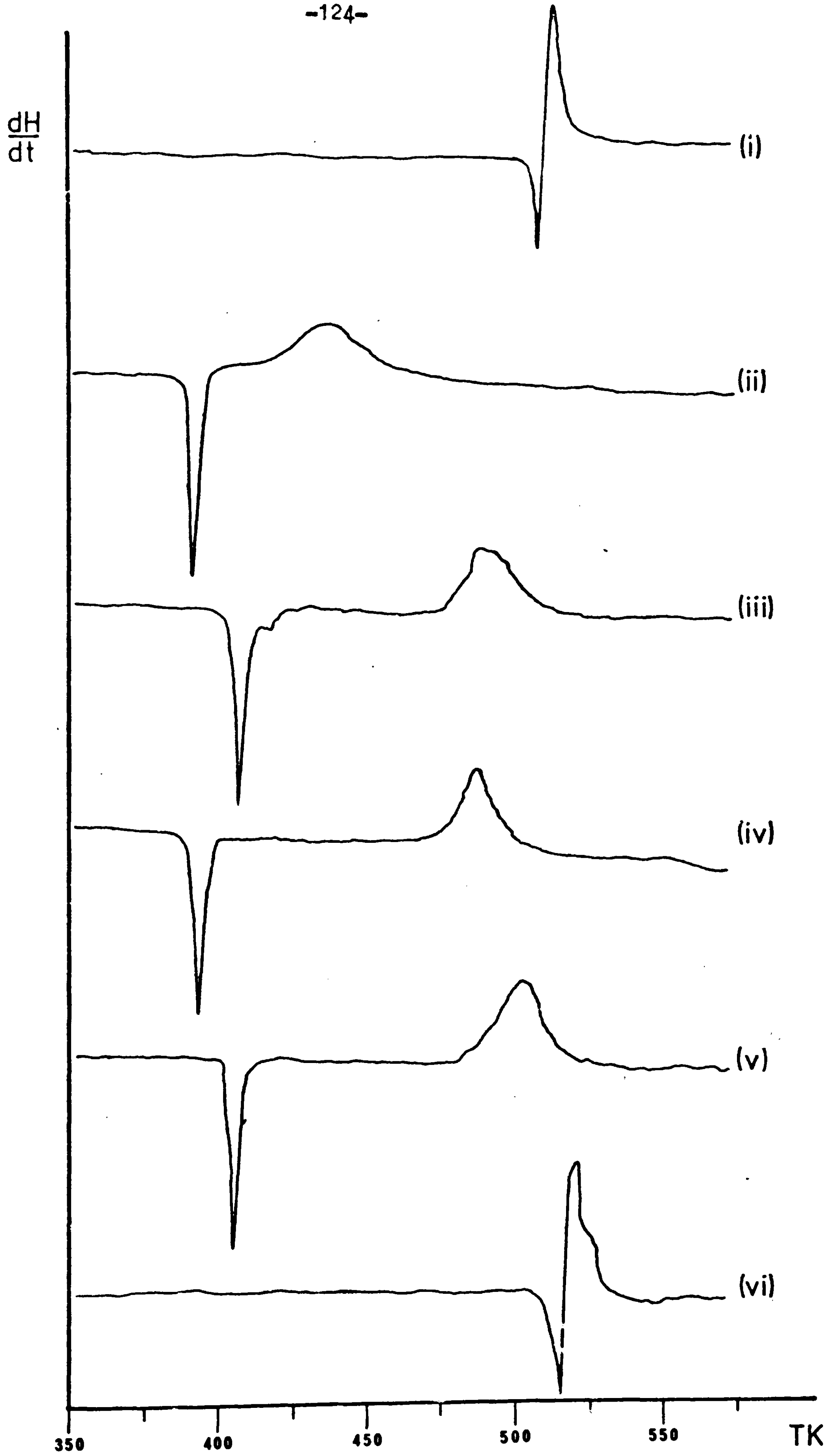


Figure 4.2 Comparative DSC Thermal Profiles for (i) (dpm)$PtPh_2$ (ii) (dpm)$PtPh_2$ + dpm (iii) (dpm)$PtPh_2$ + dpe (iv) (dpe)$PtPh_2$ + dpm (v) (dpe)$PtPh_2$ + dpe (vi) (dpe)$PtPh_2$

observed exotherms of profiles (iii), (iv) and (v) (Fig. 4.2) reflect the disruption of closely similar species - for example, that depicted in Fig. 4.3. (no significance in broken-line bonds):

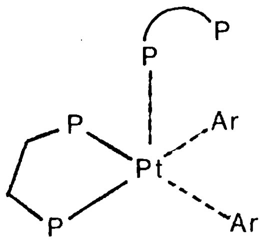


Fig. 4.3

The inference may be drawn that dpe replaces dpm as the bidentate ligating species at a rate which is appreciably greater than that of the (presumably rate-determining) reductive elimination of biaryl. This might reasonably be expected to occur in view of the consequent relief of the 4-membered ring strain inherent in the dpm parent-complex[245]. It seems probable that (iii) and (iv) of Fig. 4.2 are the decomposition profiles of identical intermediates, while the transient species of (v) will differ only in the substituent chain-length of the monodentate attacking phosphine.

These similar decomposition onset data in spite of the bridge length of the attacking species favour an explanation in terms of a 5-coordinate intermediate over the potential hexacoordinate species - which would in any case require the unrealistic total population at platinum of twenty electrons. These data do not, however, delineate which of Schemes 4.1 the overall reaction resembles more closely, nor does the pentacoordination interpretation suggest any convincing reason for the anomalous instability imparted to (dpm)PtAr$_2$ by free dpm only.

Incidence of Secondary Reaction.

The general restriction of secondary product generation relative to that from the pure complexes, may be ascribed to the higher coordination and lowered electrophilicity of the central metal when additional ligand molecules are available for complexation. The metal is thereby rendered less exposed and, probably, less inclined to the metal arene interactions and subsequent insertion reactions that are envisaged to characterise the secondary processes. The accuracy of this contention is reflected in the relatively lowered assays of transferred phenyl groups* in the residues from the phosphine-aided decompositions of (dpm)PtAr$_2$ (0.018 mole/molePt) and (Ph$_3$P)$_2$PtAr$_2$ (0.01mole/mole Pt) and from thermolysis of (dpe)$_2$Pt(0) (0.02mole/mole Pt). Given suitable energetic conditions, however, secondary processes which generate ligand derived arene and biaryl, do come into play (Table 4.2). Analogous mechanistic routes to those proposed for the pure complexes may be invoked to account for these products, possibly involving thermal ligand loss as a preliminary step. (More phosphine is generally liberated than can be satisfactorily accounted for by an initial excess of free ligand in the mixture). Perhaps more interesting is the evidence that additional secondary options, that do not appear to operate in the absence of free ligand, are available to the systems which contain bidentate phosphines.

*Obtained, as in the previous chapter, by HCl quenching of a toluene solution, and quantitative GLC analysis.

Thermal decomposition of (dpm)PtAr_2 (Ar = Ph or 4-Me-C_6H_4) leads - evidently via $(dpm)_2Pt(0)$ - to appreciable amounts of Ph_2MeP and (to a lesser degree) Ph_3P, in addition to more conventional secondary hydrocarbon products (Table 4.2) Although $(dpe)_2Pt(0)$ is more thermally robust, it ultimately decomposes at 590K to yield, somewhat analogously, $Ph_2P(CH{=}CH_2)$ and (less) Ph_3P in addition to benzene, a smaller quantity of biphenyl, trace amounts of ethylene and of four other less volatile species whose character was not determined, but whose GLC retention characteristics implied tertiary phosphines (No Ph_2EtP, Ph_2MeP, methane or ethane was detected).

These observations indicate the operation, in both cases, of processes which result in inter alia, severance of a P-C bond in the alkylene bridge. Nevertheless, no mechanistic innovations need be introduced in order to explain the intrusion of such pathways into the secondary reaction manifold. Phosphorus-carbon cleavage has, after all, been implicit in the more universal secondary reaction schemes. In this case, however, the low-valent metal appears to have the further option of direct insertion into a phosphorus-alkyl bond in the ligand bridge. In the dpe case, decomposition of the resultant phosphinoethylplatinum fragment via β-elimination, adequately explaines the production of Ph_2P $(CH{=}CH_2)$. (This mode will, in addition, supplement ortho-metallation as a hydrogen-transfer route). The phosphinomethylplatinum species which would result from analogous insertion in the dpm complex does not have access to this Pt-C scission route. The alternative, however, is via hydrogen transfer, most plausibly by an <u>ortho</u>-mechanism, ultimately to yield Ph_2MeP. The lesser yield of Ph_3P in both reactions is explicable in terms of reductive coupling of a remaining diphenylphosphido group with a phenyl ligand (subsequent to its transfer to platinum by the conventional route.) This, to an extent, substantiates the previous proposition that the oxidative insertion of Pt into a P-C bond of (particularly) Ph_3P is to some degree reversible. No Ph_2PCH_2Ph was detected from thermolysis of the dpm system (unless its GLC retention time was coincident with that of another component). This is also the case for Ph_2PH. The latter, and $Ph_2PCH_2CH_2Ph$ may conceivably have been among the unidentified minor fractions from the thermolysis of $(dpe)_2Pt(0)$. These products are those expected from reductive elimination of either of the phosphinoalkylplatinum substituents with a transferred phenyl or hydride group. Whether this reflects a genuine preference of platinum alkyls for Pt-C scission options other than reductive elimination of C-C bonds, or whether the relative absence of these products is due in some way to specialised local molecular conditions, cannot be legitimately argued on present evidence.

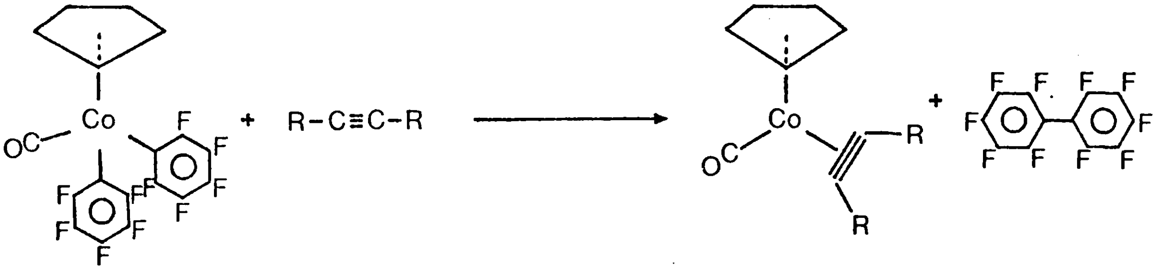
Although the incidence of insertion of low valent metals into aliphatic carbon-phosphorus bonds is undoubtedly rarer than that of similar insertions into aromatic carbon-phosphorus[228b, 244] (and carbon-hydrogen[243, 244]) bonds, there seems no reason to suppose that, given appropriate conditions, it should not occur. The rationalisation of its occurrence in these cases may be stereochemical in origin. Reductive elimination of the metal substituents in the absence of additional phosphine leaves a bicoordinate (and, in the case of chelating phosphines, possibly non-linear), electron-starved metal fragment. The exposed electrophilic metal would thus be expected to attack the more accessible phosphine substituents - the aryl groups - possibly *via* a metal-arene π-complex and probably in an intermolecular fashion. However, when extra phosphine ligands are available to increase the coordinative saturation of the zerovalent species, these intermolecular tendencies will be reduced. Intramolecular attack on the arylphosphine substituents may be restricted by the constraints of the cross-linked molecular skeleton, and hence, attack on the alkylene bridge may be rendered comparably favourable. The highly-strained 4-membered metallocycle of the dpm complexes may provide an explanation of why the bridge-cleavage option - which effectively relaxes the molecular tension - proceeds under such relatively mild conditions for $(dpm)_2Pt(0)$.

Such reactions are not without precedent. An example of formation of $Ph_2P(CH{=}CH_2)$ from a dpe complex of Cu(I) has already been reported[260]. It is not clear, however, whether this reaction is mechanistically analogous to those that are proposed here.

General Implications

The facilitation of disruptive eliminations by increasing the electron availability at the metal may have widespread import in the determination of reaction patterns of organotransition-metals. The fact that many solvents may be ascribed some nucleophilic capacity may, indeed, in some part explain the often enhanced lability of organotransition-metals in solution.

Mononuclear, <u>cis</u>-reductive elimination from a coordinatively-unsaturated complex might be expected to display particular sensitivity to this kind of labilisation, which resembles, in certain respects, classical nucleophilic substitution at a metal centre. (These have been especially well-documented[261] for square-planar complexes of Pt(II)) Apart from the examples alluded to in the preliminary part of this chapter[235, 248. 249], a similar format may explain such observations as the alkyne-induced coupling of perfluoroaryl ligands from Co(III)[262]:



Although substitution reactions at hexacoordinate metals are generally dissociative in character[264], reaction <u>via</u> a more electronically saturated species may also explain the reductive elimination of H_2 from $[OsH_2(CO)(NO(Ph_3P)_2]^+$ in the presence of Ph_3P or CO (to yield $[Os(CO)(NO)(Ph_3P)_2L)^+]$[265] since there is evidence that in dihydride complexes of this type, there is considerable distortion from octahedral geometry. In $FeH_2\ [PPh(OEt)_2]_4$, for example, the spatial distribution of the larger ligands approaches a tetrahedral arrangement[266]. The more open pseudotetrahedral structure (which is considered to be of general importance in reactions of H_2ML_4 species[267]) would be expected to render the metal more accessible to external attack.

Where other elimination mechanisms dominate the molecular disruption, however, other factors may be important. The inhibition by tertiary phosphines of the decompositions of $(Ph_3P)_2PtBu^n_2$ [93] and $(Ph_3P)_2Pt(CH_2)_4$[107] is explicable in terms of the β-elimination process which governs the reactions. Phosphine-dissociation, which is necessary to provide an extra coordination site as a (rate-limiting) prerequisite for β-elimination, is effectively suppressed [93, 107]. Interestingly, reductive coupling of carbon atoms still remains less energetically favourable, at least where the ancillary ligands is Ph_3P*.

There are however, two serious counter-examples which cannot easily be rationalised in the light of the present findings. Thermolysis of L_2PtR_2 (R=Me, Et: L_2 = 2,2' bipyridyl, or 1,10-phenanthroline) in the presence of certain alkenes (diethyl fumarate, diethyl maleate) and the spin-trap Bu^tNO, apparently gives rise to alkyl radicals[205]. It must, however, be borne in mind that Bu^tNO has been shown to induce M-C homolysis[160], and some cooperative reaction of alkene and nitroxyl - perhaps from within the metal coordination sphere - cannot be discounted.

The more direct contrast to our results is presented by the thermal behaviour of the phosphinotrialkylgold(III) complexes $LAuR_2R^1$ ($L=Ph_3P$: R_1R^1 = various alkyls). These species undergo reductive elimination of bialkyl on thermal decomposition in solution[125].

*Some carbon-carbon coupling is evident in the thermal reductive elimination of significant amounts of cyclobutane from $(Et_3P)_2Pt(CH_2)_4$[268]

The coupling is stereospecifically between <u>cis</u>-ligands, and occurs in preference to α- or β-elimination. The process is, however, significantly inhibited by added phosphine. It is proposed that reductive elimination takes place from a tricoordinate alkylgold fragment subsequent to phosphine loss. Trigonal geometry is ruled out, however, to account for the retained <u>cis</u>-specificity of coupling in mixed alkyl complexes.

A convincing explanation for the contrast between the decomposition behaviour of these alkylgold(III) complexes and the isoelectronic (and isostructural) arylplatinum(II) species, and indeed, of why a lower-coordinate, 14-electron intermediate should be a prerequisite for reductive elimination, cannot be offered. This apparent dichotomy serves only to highlight the continuing inadequacy of current understanding in this field, and the need for more extensive correlations.

CHAPTER FIVE

Mechanism and Kinetics of Thermal Decomposition of Diarylplatinum(II) Complexes in Solution.

CHAPTER FIVE

Having established the patterns of thermal behaviour of cis-L_2PtAr_2 complexes in the condensed phase, we now turn to a parallel investigation of the same organometallic systems in homogeneous solution. Such an examination, it was considered, might be profitable for a number of reasons. First of all, it was desirable to verify the proposition that if a single unimolecular decomposition mode predominates in the vigorous and congested conditions of the condensed phase, then it will be likely to do likewise in solution, where the complex molecules are more isolated from each other. This consideration - viz. that intermolecular action should be reduced by solvation - in addition to the milder conditions possible for solution thermolysis, might well have some influence on the operation of secondary processes, relative to the condensed-phase results. Judicious choice of solvent may also provide additional indication as to the participation (or not) of certain types of reaction intermediate (vide infra). However, perhaps most important is the consideration that a variety of systems may be studied under the same (or accurately variable) control conditions, and the kinetics of decomposition may be quantitatively evaluated. This should allow legitimate correlation of the reaction propensities of different organoplatinum complexes. In addition, the labilising effect of free phosphine may be verified and, hopefully, quantified.

The choice of toluene as the solvent for this programme of studies combined the desirable features of sufficiently high boiling point, reasonable solvent ability for the materials involved, and apparent inertness towards either reactants or products. This hydrocarbon is also recognised as an efficient source of abstractable hydrogen atoms for free aryl radicals[280]. Toluene does have the disadvantage that arene generated by this route from the (potential) homolytic scission of 4-tolyl-platinum bonds cannot be monitored. However, the advent of this reaction can be evaluated for the phenylplatinum complexes (by quantification of metal-derived benzene) and in either case the products of subsequent reaction of the resultant 1-benzyl radicals - namely 1,2-diphenylethane and diphenylmethane (or 4-benzyltoluene) - can be readily identified.

<u>Experimental Techniques</u> (See Ch.6 for full details)

For the kinetic studies, toluene solutions of the organoplatinum complexes (typically 2×10^{-3}M) containing an accurately introduced quantity of n-dodecane as internal standard, were prepared and decomposed under an atmosphere of dried nitrogen. Accurate ($\pm 0.25^{\circ}$) uniform temperatures (50°, 60° or 70°C) were maintained by immersion of the specifically designed decomposition vessel in a thermostatically controlled water-bath. Homogeneity in the solution was ensured by continuous agitation via a flexible-drive magnetic stirrer. (See Ch. 6)

Toluene for these studies was purified by rigorous distillation using a 40cm stainless-steel spinning-band column.

In order to monitor the kinetics of decomposition, aliquots (0.5ml) were withdrawn from solution by syringe at intervals, and quenched by injection into septum-capped pyrex tubes containing conc. aqueous HCl (1.0ml). These were stored at -5°C for (minimum) 18 days prior to quantitative analysis by GLC. (Calibration experiments established these as optimum conditions for 100% cleavage of Pt-C bonds by HCl only without further decomposition by another route). A correction factor allowing for cubical expansion of solvent was introduced into the calculation of rate constants since, although concentrations both of initial complex and of decomposition product were determined at room temperature, the actual concentrations in the vessel at the moment of sampling would be significantly different due to the volume expansion of toluene.

For the phenylplatinum complexes, benzene production was evaluated by trap-to-trap vacuum distillation (273K/77K; 10^{-3}torr.) of a sample of unquenched residual solution (since benzene is a quenching product.) A second internal standard (n-decane) was accurately added to the distillate, and quantitative analysis effected by GLC. Calibration experiments indicated that benzene transfer under these conditions was 98% effected.

For non-kinetic investigations, a saturated solution of the organoplatinum complex (containing internal standard) was maintained at 333K in a pyrex tube, under nitrogen, for at least 24hr. One aliquot was now acid-quenched and another vacuum-distilled prior to determination of products by quantitative GLC.

The errors in quantification by this technique were as before ±2% for biaryl and ±4% for benzene.

Results and Discussion.

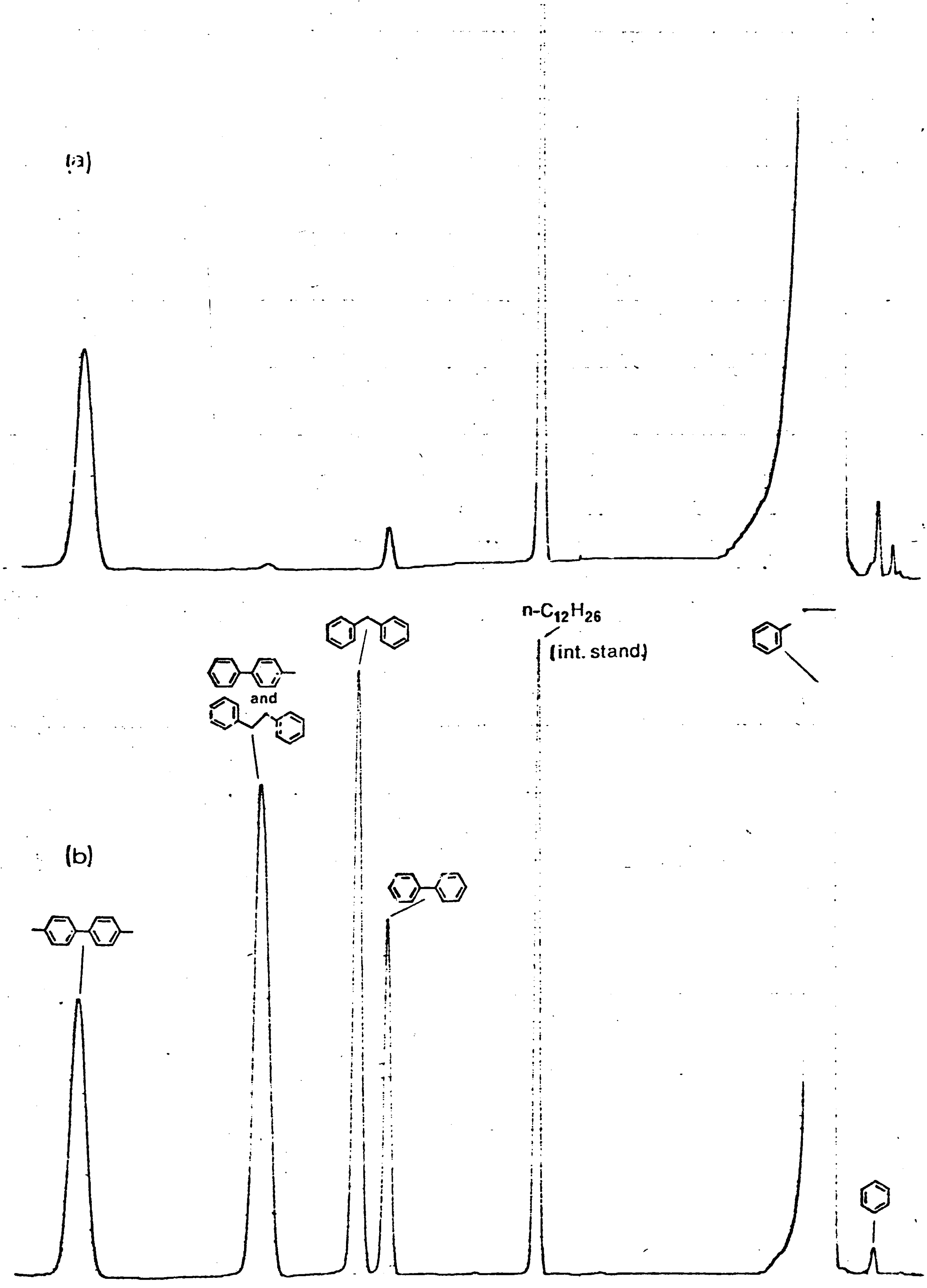
A. Complexes Containing Ph_3P

This family of complexes was found most suitable for more

Fig. 5.1: Comparative GLC Profiles

(a) Products of thermal decomposition of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in toluene at 60 C; >95% primary decomp.

(b) Standard separation pattern.

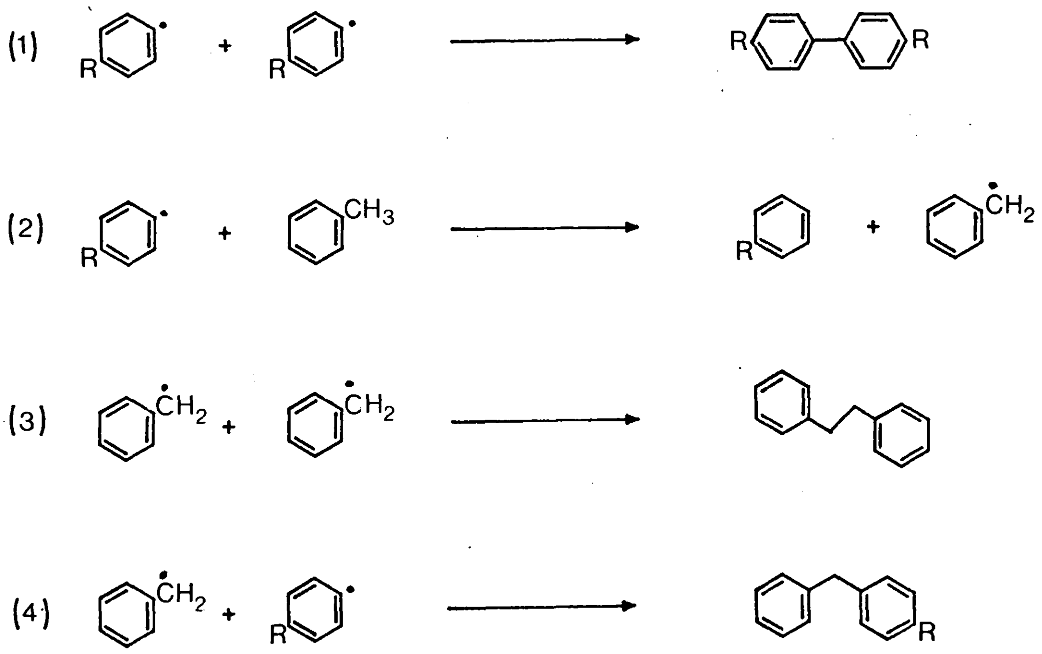


to a maximum extent of less than 1.0 mole%, and, in fact, was detectable at all only after decomposition was 85% complete. No other biaryl isomers were detected (See Fig. 5.1)

Care was exercised that higher boiling species which might arise in consquence of aryl radical attack on toluene, should not escape detection. Hydrogen-atom abstraction from a toluene molecule preferentially occurs from the α-carbon to generate the moderately stable benzyl radical[281]. This species may decay either by self-reaction to yield 1,2-diphenylethane (bibenzyl)[282], or by combination with further phenyl or 4-tolyl radicals - which hypothetically initiated the radical sequence - to yield diphenylmethane or 4-benzyltoluene, respectively [Schemes 5.1; (3) and (4).]

Schemes 5.1

Consequences of Primary Pt-C Homolysis from L_2PtAr_2 in Toluene



Bibenzyl, in fact, has the same GLC retention characteristic (on the column employed) as 4-methylbiphenyl. The former should, however, arise irrespective of whether a phenyl- or tolylplatinum species is decomposing, on the reasonable assumption that, if a platinum-carbon homolytic route predominates for one, then it will also operate extensively for the other. Since no such component was detected among the decomposition products from $(Ph_3P)_2PtPh_2$, it seems safe to deduce that the incidence of a product from $(Ph_3P)_2Pt(4\text{-Me-}C_6H_4)_2$ with the requisite GLC retention time, may be attributed to the generation of 4-methylbiphenyl (This fraction, in any case, amounted to <1mole %). The other radical-derived hydrocarbons were unequivocally absent from the respective product distributions. The formation of methylbiphenyls by direct bimolecular homolytic substitution at toluene is not considered a likely possibility. Experiments suggest that reactivities of aromatics towards (at least) phenyl radicals are not great enough that aromatic arylation can efficiently compete with hydrogen abstraction from alkyl ring-substituents[283, 284].

The intermediacy, to any appreciable extent, of free aryl radicals in these organoplatinum decompositions, may further be firmly discounted by consideration of the expected modes and relative rates of termination of the metal-derived radicals - viz. combination [scheme 5.1(1)] and hydrogen-atom abstraction from solvent [scheme 5.1(2)] It is true that the product of (1) is that observed - namely biaryl. However, it has been demonstrated that when phenyl radicals are generated at 60°C in cyclohexane (by <u>in situ</u> thermal decomposition of phenylazotriphenylmethane (P.A.T)[283]) hydrogen-abstraction competes so favourably with coupling that biphenyl generation is totally suppressed and only benzene is produced (82% based on P.A.T)[285]. The hydrogen donor efficacy of toluene towards phenyl radicals is about one quarter that of cyclohexane[284] (their relative reactivities per aliphatic C-H bond are closely similar), and so it might be expected that, at least, ca.20% of phenyl radicals liberated by whatever means in toluene would ultimately appear as benzene. In fact, it was independently recorded that thermal decomposition of P.A.T. in toluene produced a 50% yield of benzene[283] (the pseudo-first-order rate constant for equation 5.1(2) was estimated to be 10^5 sec^{-1}). If primary metal-carbon homolysis was the predominant decomposition mode of, say, $(Ph_3P)_2PtPh_2$, then benzene production of the order of 100 mole% might be anticipated (since each complex molecule possesses two incipient primary aryl radicals). Clearly though, differences in, for example, relative radical 'caging' properties[286] of L_2PtAr_2 and P.AT., might effectively truncate this estimate, but not, in all likelihood, by two orders of magnitude. The insignificant quantities of metal-derived arene produced during the thermal disruption of $[(4\text{-}Me\text{-}C_6H_4)_3P]_2PtPh_2$ and, by inference, $(Ph_3P)_2PtPh_2$ and $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$, are manifestly inconsistent with the appreciable operation of a primary platinum-carbon homolytic step in the decomposition sequence.

The (virtual) absence of metal-derived arene, and of substitution-isomers among the biaryl products from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ effectively excludes the operation of a β-hydride elimination mechanism (See Chapter 3).

The fate of the metal-bound aryl ligands here as in the condensed phase, is, essentially, the exclusive formation of biaryl. Thermal decomposition of an equimolar mixture of $(Ph_3P)_2PtPh_2$ and $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in toluene yielded, in addition to biphenyl and 4,4'-bitolyl (and benzene), less than 2.0 mole% of 4-methylbiphenyl, when decomposition was 90% complete. This at once demonstrates both that coupling is all but totally intramolecular and that virtually no intermolecular aryl exchange occurs prior to or during the coupling step. (This datum additionally excludes free radical intermediates). The foregoing evidence firmly establishes that no primary mode of molecular disruption other than concerted, unimolecular reductive elimination, makes any significant contribution to the thermal decomposition of $(Ph_3P)_2PtAr_2$ in toluene solution. The predominance of this mechanism in solution serves to consolidate the previous conclusions from studies of the condensed phase behaviour of the same systems.

Incidence of Secondary Reactions

It is evident that secondary processes which generate further organic products, are operational in the solution decomposition of $(Ph_3P)PtAr_2$. Even although the conditions are milder, these reactions function - as in the condensed phase - under the same conditions as the primary biaryl generation, but essentially independent of it. From thermolysis of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in toluene, it is clear that the minor products - benzene (12.9 mole%)* and biphenyl (7.7 mole%)* - correspond to those formed as a result of secondary operations in the condensed phase. There is no evidence to suggest that the mechanistic

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*After 95% primary decomposition at 60°C schemes postulated formerly (Chapter 3) are not valid. The total absence of products of decomposition of benzyl radicals would seem to underpin the original contention that the secondary processes too, do not involve free radicals to any significant degree. It appears, then, that the hypothetical fragment $(Ph_3P)_2Pt(0)$ is not greatly stabilised by solvation and milder conditions, and, ostensibly, continues to undergo decomposition by the oxidative insertions of low-valent platinum into P-C and C-H bonds, followed by reductive eliminations, that have been previously outlined (chapter 3)

It may of course, be said that the quantity of benzene obtained by distillation from the residual solution from decomposition of $(Ph_3P)_2PtPh_2$ may have been artificially enhanced by the distillation process itself, since, as the residual involatile material was progressively concentrated, intermolecular reactions akin to those suspected in the condensed phase would grow increasingly likely. (Indeed, the ultimate solid residue, although contaminated by white crystalline organic decomposition products, was strikingly reminiscent in its colour and glassy consistency, of the residues from condensed phase thermolyses. It displayed the new i.r. absorption at 1115cm^{-1} suggestive of <u>ortho</u>-metallation). However, this argument is contradicted by the observation that the yield of benzene from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$, which can be monitored directly throughout decomposition (since benzene is not a quenching product) is comparable.

An alternative route to secondary benzene in these instances is that of transfer hydrogenolysis of coordinated triphenylphosphine by solvent. This has been observed to occur for a number of Ph_3P complexes of transition metals (including $(Ph_3P)_2PtCl_2$) on heating in a variety of organic solvents, notably amines[287]. The precise mechanism of these hydrogen-transfer reactions is not known. (They may, for example, involve similar addition/elimination sequences as those already suggested to account for our secondary products.) Although they cannot be altogether discounted as contributing to the secondary processes in the present case, their involvement is considered to be relatively unlikely; toluene is not renowned for its hydrogen donating ability, except to high-energy intermediates (vide supra), and, in fact, xylene was found not to exhibit this ability [287]. In any case, the reaction would be likely to produce α-substituted benzylic products, whose absence has already been noted.

The minute quantity of 4-methylbiphenyl (1 mole %) which becomes evident only in the latter stages of decomposition may arise from limited competition of secondary-type processes with primary metal-carbon scission. The indications are that the secondary reactions proceed at a slower rate - in solution, as in the condensed phase. As has been argued, the secondary machinery may well be intermolecular (and may involve a rate-limiting product-liberation step). In the solution, then, as the absolute rate of the primary reductive elimination progressively diminishes (with precursor concentration) there may remain an increasingly large concentration of secondary intermediate species capable of attacking unreacted tolylplatinum(II) molecules. There is an additional (but perhaps less likely) possibility that new tolylplatinum fragments might be created by ring-metallation of solvent arene[288]. There was, however, no corresponding appearance of 4-methylbiphenyl among the products from $(Ph_3P)_2PtPh_2$. In any event, the very minor incidence of crossed-biaryl product underlines the fact that such reactions, if they occur, do so to a comparatively insignificant extent. (Only trace amounts of crossed-product were detectable from the condensed phase thermolysis).

Kinetic Studies

Turning first to the thermolysis of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in homogeneous toluene solution, the primary decomposition, monitored by observing the production of 4,4'-bitolyl, can be shown to obey the first-order rate law:

$$- d[L_2PtR_2]/dt = k[L_2PtR_2]$$

There is close adherence to first-order kinetic behaviour for at least two half-lives (Fig. 5.2) The first-order rate constants ($k\ sec^{-1}$) obtained at 50°, 60° and 70°C are presented in Table 5.1.

These parameters were found to be in good linear agreement with the Arrhenius relationship which may be expressed logarithmically:

$$\ln k = \ln A - Ea/RT$$

Accordingly, plotting $\ln k$ against $1/T$ yielded the empirical activation energy for the reductive elimination of bitolyl of $E_a = 76.3 \pm 3.9$ KJ. mole^{-1}. (Fig 5.3)

Similar observation of the generation of biphenyl during thermal decompositions of $(Ph_3P)_2PtPh_2$ in toluene medium demonstrated that this elimination also proceeds in accordance with first order kinetics

Table 5.1

Thermal Decomposition of $(Ph_3P)_2PtAr_2$ – Kinetic Parameters

Complex	T(°C)	k (sec^{-1}) × 10^{-5}	$t_{\frac{1}{2}}$ (hr.)
$(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$	50	4.95 ± 0.25	3.89
"	60	12 34 ± 0.61	1.56
"	70	26.04 ± 0.82	0.74
$(Ph_3P)_2PtPh_2$	50	3.38 ± 0.26	5.70
"	60	7.60 ± 0.78	2.53
"	70	35.71 ± 0.97	0.54

Table 5.2

Thermal Decomposition of $(Ph_3P)_2PtAr_2$ with Added Ph_3P – Kinetic Parameters

Complex	Ph_3P (mol. equiv.)	T(°C)	k (sec^{-1}) × 10^{-5}	$t_{\frac{1}{2}}$ (hr.)
$(Ph_3P)_2PtPh_2$	1.01	60	9.13 ± 0.42	2.11
"	8.62	60	9.64 ± 0.37	2.00
$(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$	8.80	60	15.26 ± 0.43	1.26
"	9.22	50	6.48 ± 0.31	2.97

Figure 5.2 First-order Plots for Thermal Decomposition of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in Toluene

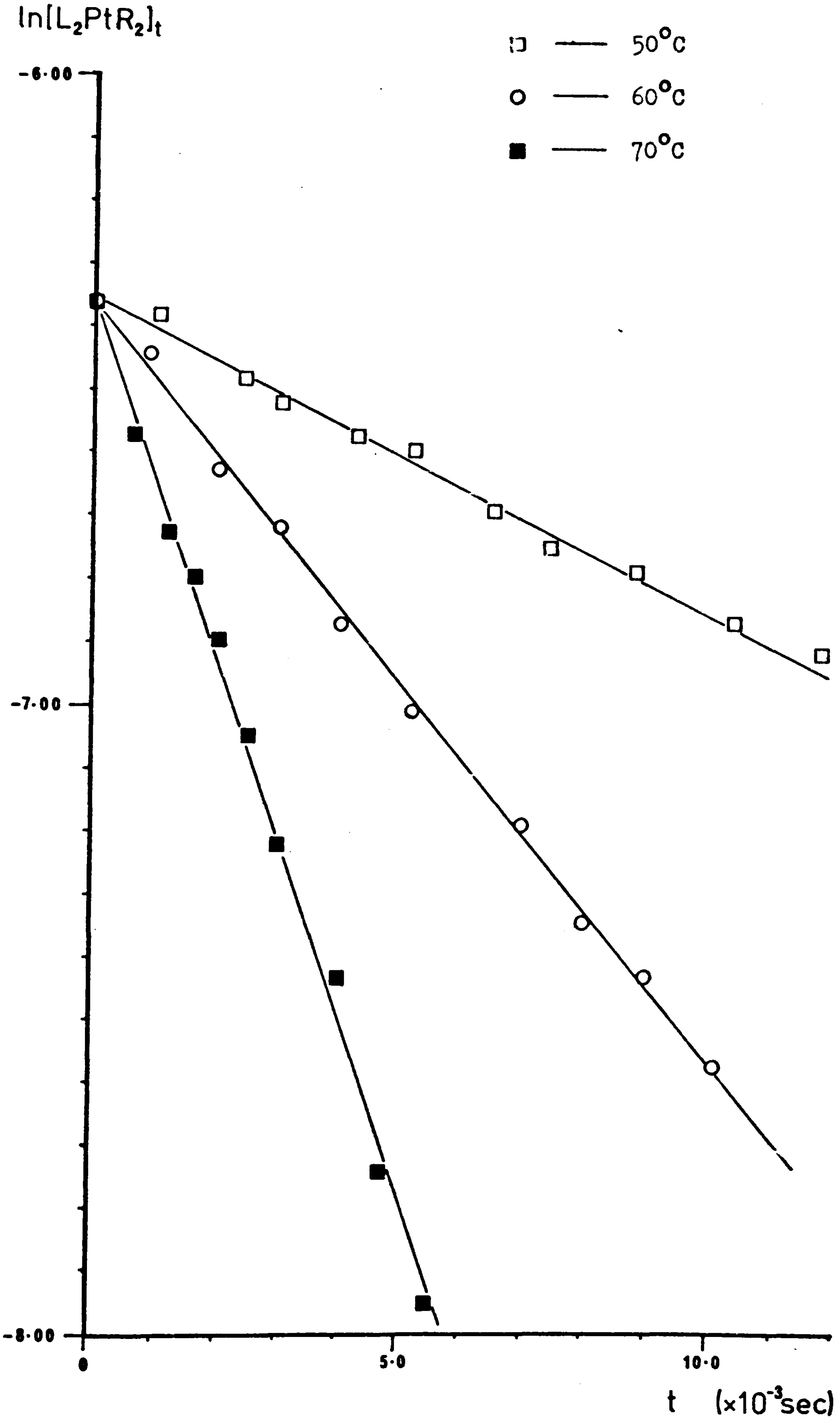


Figure 5.3 Arrhenius Plots for Thermal Decompositions of Systems Containing $(Ph_3P)_2PtAr_2$ in Toluene

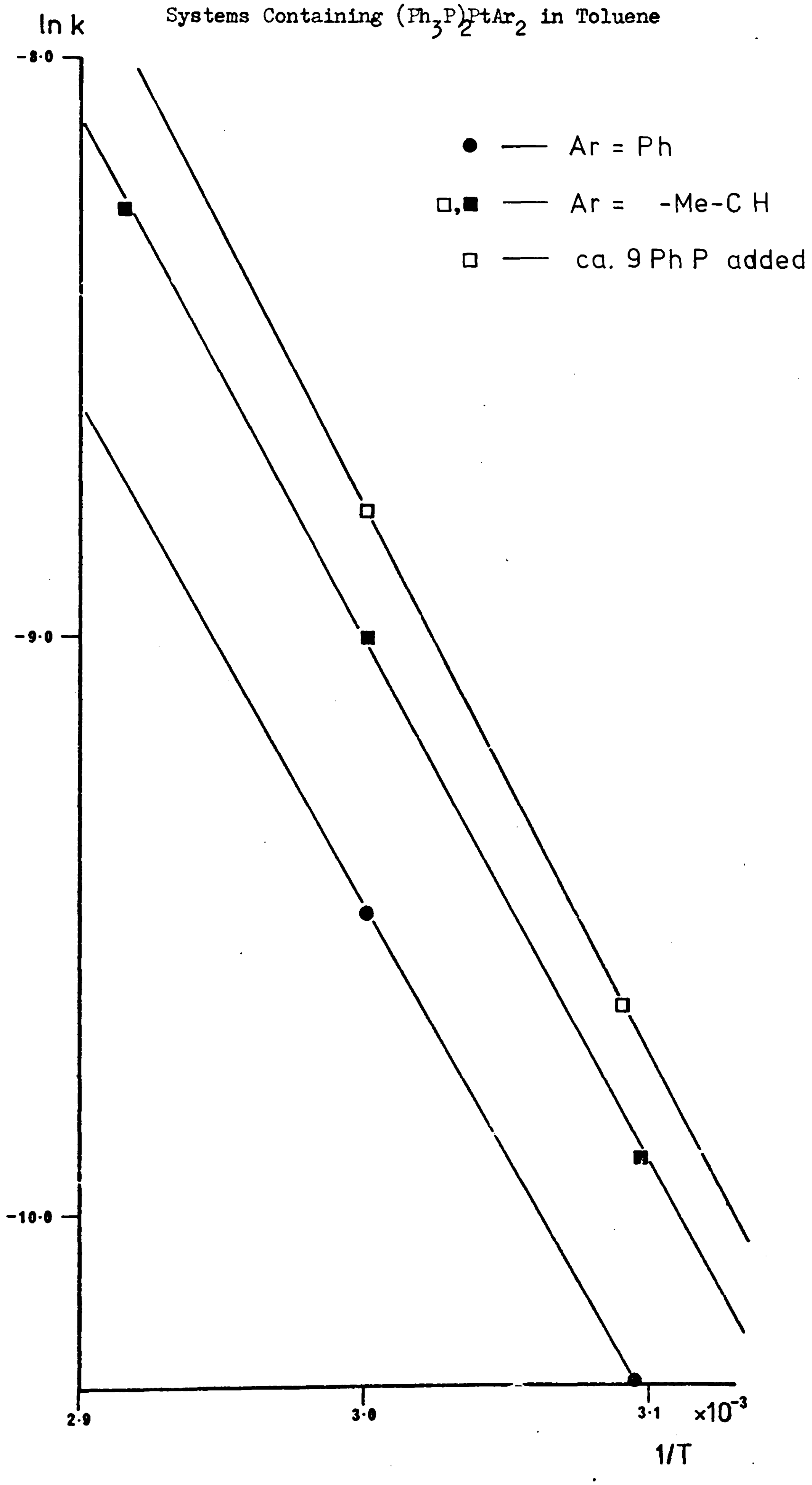
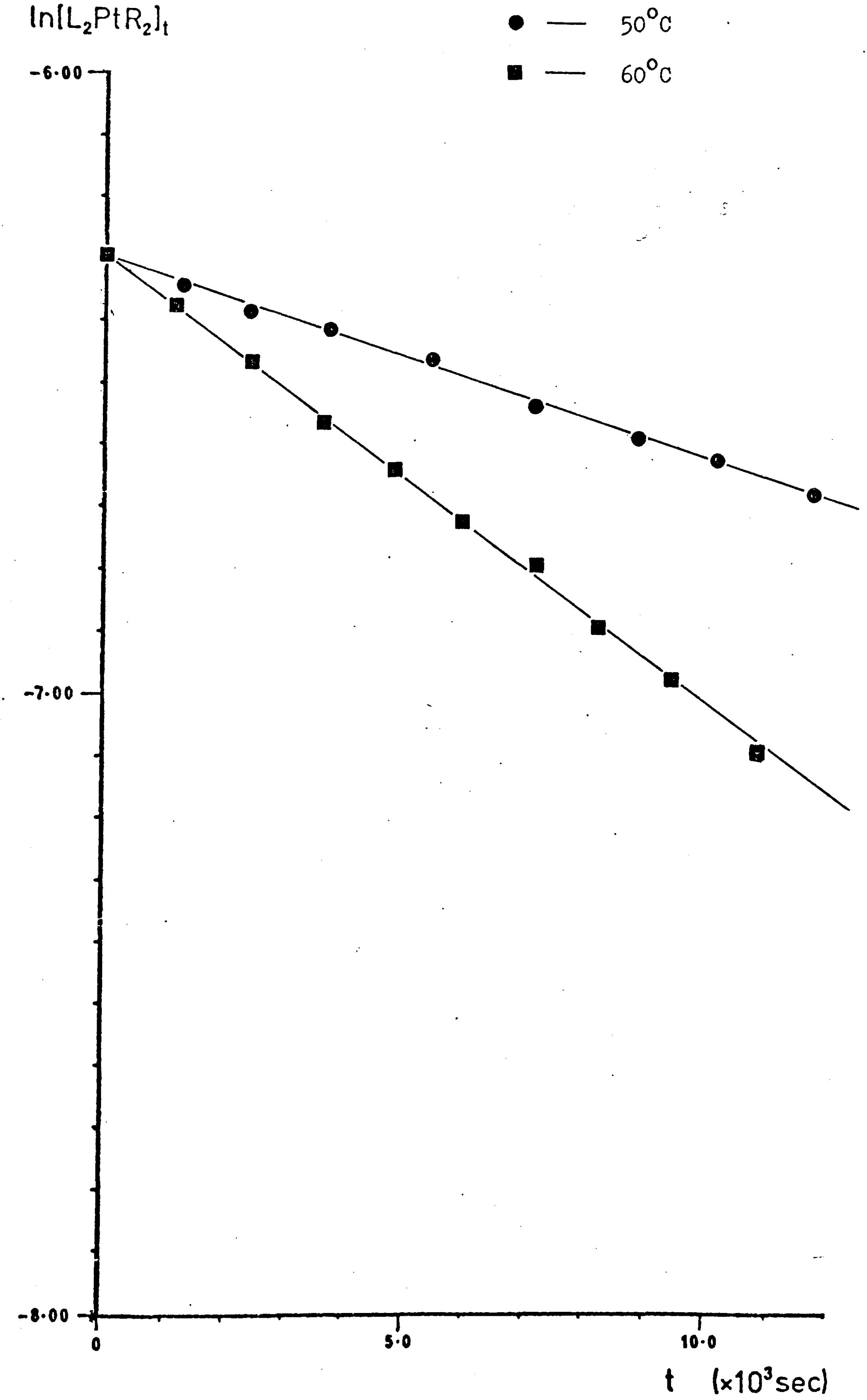


Figure 5.4 First-order Plots for Thermal Decomposition of $(Ph_3P)_2PtPh_2$ in Toluene



to a comparable extent of decomposition (see Fig. 5.4.) Rate constants obtained at 50° and 60°C appear in Table 5.1. Repetition of these two determinations established their reproducibility (within 3-4%).

Observation of this reaction at 70°C yielded a first-order rate constant $k = 35.71 \pm 2.84 \times 10^{-5}$ sec^{-1}. This result is quite inconsistent with all other data obtained for the $(Ph_3P)_2PtAr_2$ system. It is also at variance with the dictates of normal Arrhenius parameters (which, ordinarily, are expected to lead to a two- or threefold increase in rate for a 10° rise in temperature), particularly in view of the satisfactory Arrhenius correspondence for the ditolylplatinum decompositions. In the absence of a convincing rationalisation this result is, in the meantime, to be regarded as adventitious, presumably through the accelerating effect of some undetected impurity. Time, unfortunately, has not yet permitted a repetition of this determination.

There is obviously, a systematic error in determination of the concentration of unreacted $(Ph_3P)_2PtPh_2$ at a given time (by monitoring biaryl production) due to the secondary production of biphenyl which presumably parallels that observed for $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$. In fact, thermolysis of the latter had given rise (at 60°C) to only ca. 2 mole % of biphenyl after one primary half-life. A similar reaction by $(Ph_3P)_2PtPh_2$ would lead to an overall rate constant little more than 5% too high, which is, in any case, of the order of the experimental uncertainty of the technique. (It could not, however, be responsible for the anomalous k-value for

$(Ph_3P)_2PtPh_2$ at 70°C, as the secondary biphenyl production from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ at this temperature is little more extensive). Accordingly, this will not affect the quantitative comparisons to be discussed in due course.

Application of the Arrhenius relationship to the two authentic k-values leads to an estimate of E_a for biphenyl elimination of 71.0 KJ mole^{-1} (error estimated as ± 4KJ.mole^{-1}), which, within the bounds of experimental uncertainty, corresponds very closely to that for reductive elimination of bitolyl from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$. The implications of the comparative kinetic and activation parameters for the parallel biaryl elimination reactions will be discussed at more length presently.

The secondary decompositions could not be kinetically quantified. Their extent was limited in the time required to extract satisfactory primary reaction parameters, and the progressive increments in secondary products were too close to the level of experimental uncertainty for them to be reliably analysed.

Effect of Added Ph_3P

a) Mechanistic

Thermal decomposition of $(Ph_3P)_2PtAr_2$ in toluene in the presence of amounts of free phosphine yields metal-derived biaryl which, by the previously employed criteria, may be attributed wholly to primary concerted reductive elimination from platinum. After 2-3 half-lives, the colour of the solution becomes bright yellow, indicative[289] of the formation of zerovalent species $Pt(Ph_3P)_n$ (n = 3 or 4). In accord with this hypothesis, only trace amounts of the secondary products, benzene and [from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$] biphenyl, could be detected. On the occasion of more prolonged thermolysis, the yellow colouration gave way to a rich cherry-red (an observation noted during the thermolysis of $(Ph_3P)_nPt(0)$ in solution[240, 290]) and a limited quantity of benzene was detected. $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ was not so treated.

In effect, then, the presence of free Ph_3P, as in the condensed phase, does not materially affect the operation of the primary reductive elimination from Pt(II) but does tend to stabilise the resulting zerovalent species, probably by bestowing greater coordinative and electonic saturation on the metal atom and thus rendering it less susceptible to secondary attack.

b) Kinetic

Time has not allowed the fulfilment of as comprehensive an investigation as might be desired. Several of the more critical facts have, however, emerged.

Biaryl production from $(Ph_3P)_2PtAr_2$ in the presence of a 8- to 10-fold excess of Ph_3P is kinetically first-order in platinum complex (Figs. 5.5 and 5.6) The rates, however, are consistently enhanced in relation to those displayed by the complex alone. At 60° for example, the phosphine-induced increases in rate constants for $(Ph_3P)_2PtPh_2$ and $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ correspond closely - 26.8% and 25.7% respectively (See Table 5.2)

However, decomposition of $(Ph_3P)_2PtPh_2$, at 60°C, in the presence of only 1 molar equivalent of Ph_3P also follows apparent first-order kinetics, at least for one half-life, and with a rate constant only 5.3% lower than that effected by 9 molar equivalents (Table 5.2) This is a rather

Figure 5.5 First-order Plots for Thermal Decomposition of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in Presence of Excess Ph_3P in Toluene

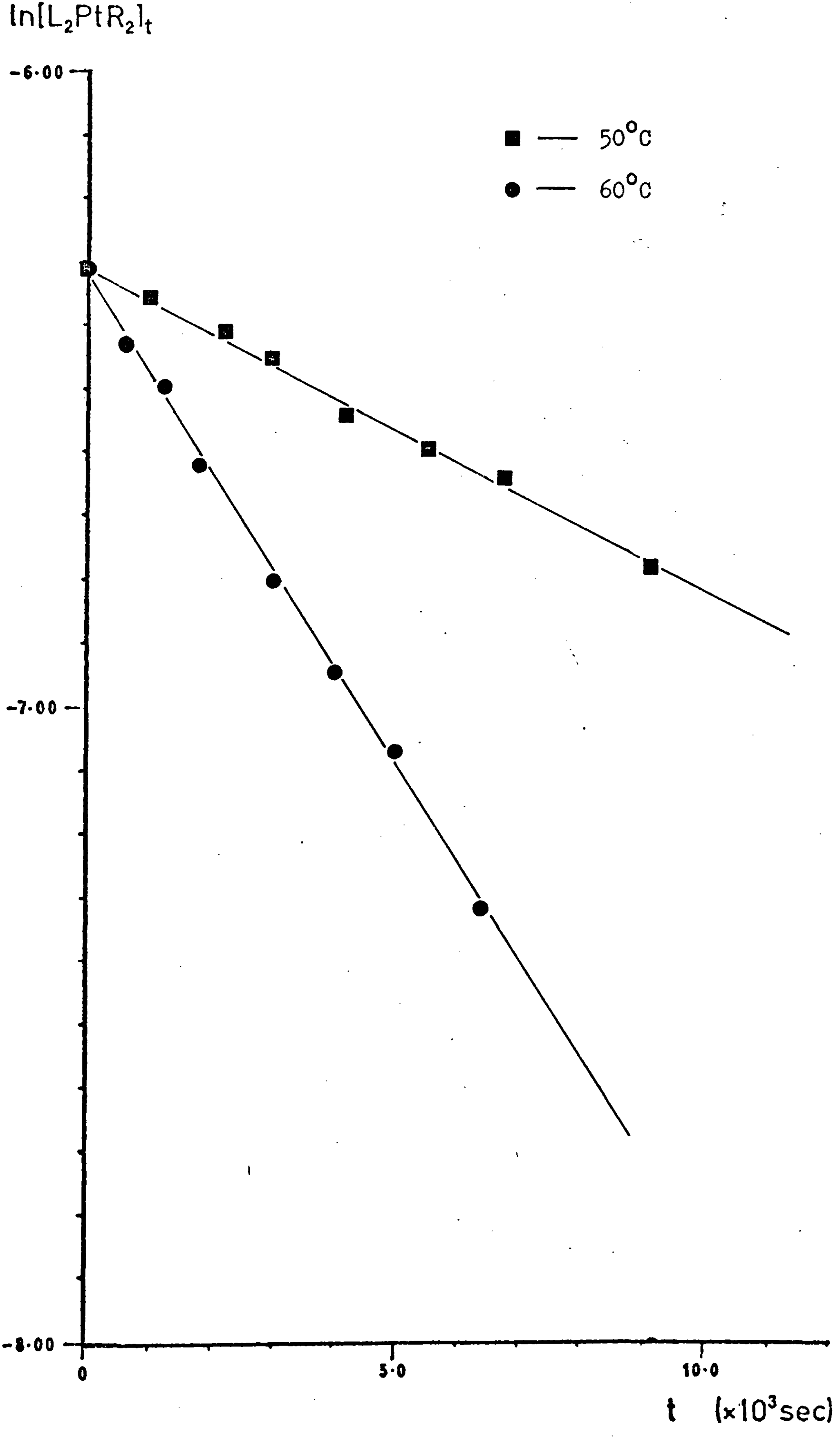
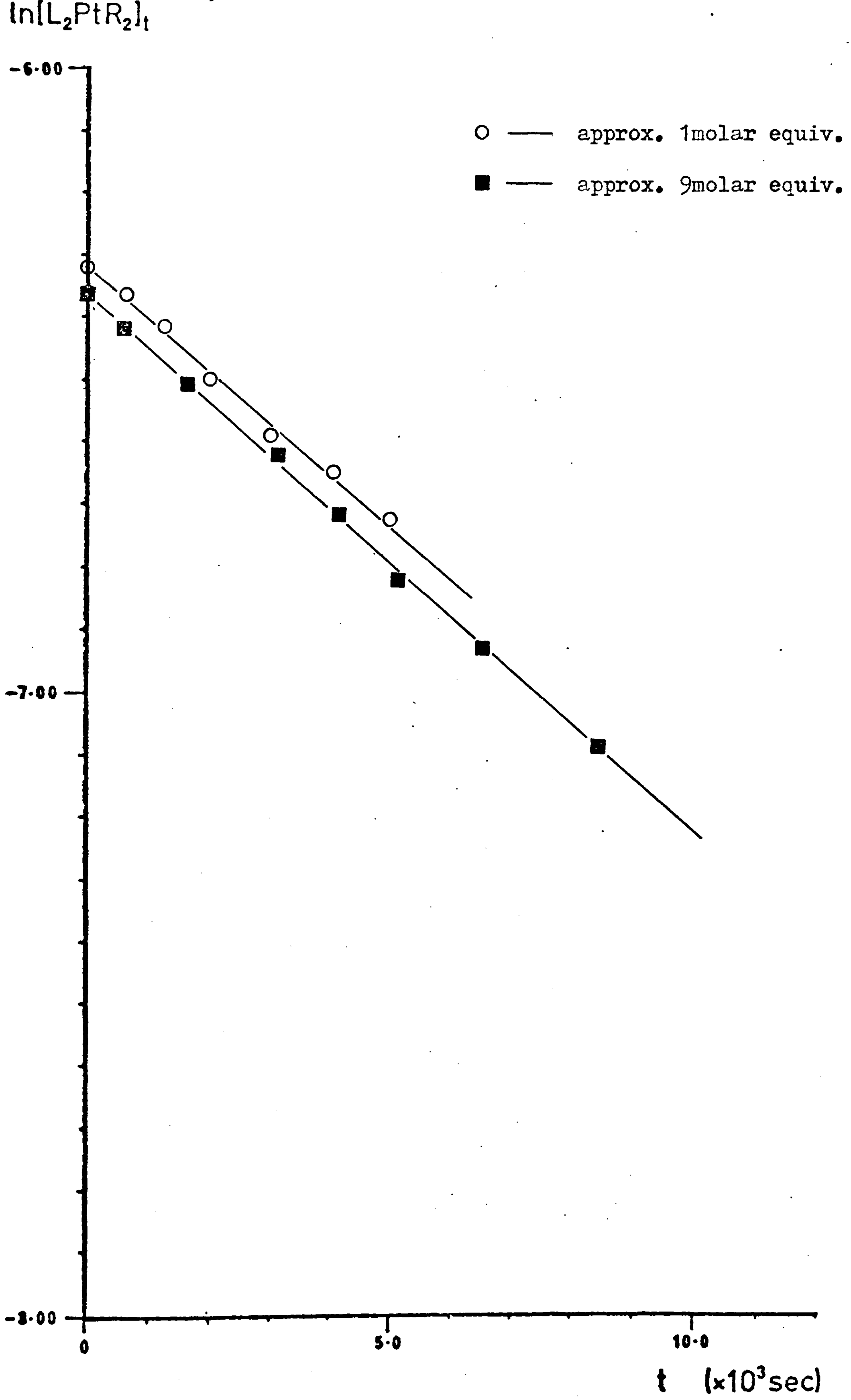


Figure 5.6 First-order Plots for Thermal Decomposition of $(Ph_3P)_2PtPh_2$ in Presence of Differing Amounts of Ph_3P in Toluene Solution



singular observation. Although pseudo-first-order agreement is to be expected in the presence of a large excess of free ligand (since there is an effective steady-state concentration of phosphine throughout the reaction), as this concentration is reduced, a ligand-concentration dependence - certainly a rate reduction, and perhaps an approach to a second-order rate law - might be anticipated, by analogy, say, with nucleophilic substitution at platinum[291]. [In fact, the kinetic dependence on Ph_3P had been foreseen as potentially even more complicated, since it was envisaged that further controls might be exercised by the development of equilibria[236b, 290]:

$$(Ph_3P)_2Pt(0) \underset{-Ph_3P}{\overset{+Ph_3P}{\rightleftharpoons}} (Ph_3P)_3Pt(0) \underset{-Ph_3P}{\overset{+Ph_3P}{\rightleftharpoons}} (Ph_3P)_4Pt(0) \quad]$$

The consistent enhancement of decomposition by free ligand, alongside the relative insensitivity of the rate to its concentration and the apparent adherence to first order kinetics, would seem to suggest that whilst some interaction of phosphine and complex facilitates reductive elimination, this association is not part of the rate-limiting process. This would be consistent with a rapid pre-equilibration to form an associative intermediate, from which (rate-determining) reductive elimination may then occur: e.g.

$$Ph_3P + (Ph_3P)_2PtAr_2 \overset{K}{\rightleftharpoons} (Ph_3P)_3PtAr_2 \longrightarrow \text{etc.}$$

In order to explain the observed result, the value of the equilibrium constant K would require to be sufficiently large that the equilibrium would still lie predominantly to the right (as written) even at equimolar concentrations of Ph_3P and $(Ph_3P)_2PtR_2$. Such pentacoordinate species have adequate precedent as intermediates in 'classical' ligand substitution at square-planar Pt(II) complexes[291], and also in the phosphine-catalysed <u>cis/trans</u> isomerisation reactions of L_2MX_2[292] (L = tertiary phosphine or phosphite; M = Pt, Pd; X = halide).

In an attempt to verify this proposal, the ^{31}P nmr spectrum of a mixture of $(Ph_3P)_2PtPh_2$ and excess Ph_3P (in toluene-d_8 under nitrogen) was examined. The 1:4:1 pattern characteristic of $(Ph_3P)_2PtPh_2$ (centred 19.2ppm*) remained unaffected, however, although there was no sign of a signal directly attributable to Ph_3P (normally at 5.1ppm) This latter observation can be rationalised. The limited solubility of $(Ph_3P)_2PtPh_2$ in toluene necessitated spectrum accumulation by the pulse Fourier-transform technique. Accumulation time was 12 hours, and some decomposition at the operating temperature (35°C), leading to $(Ph_3P)_nPt(0)$ was inevitable. A signal at 24.4ppm was attributed to rapid-exchange time-averaging of the signals of $(Ph_3P)_nPt(0)$ and free Ph_3P. The spectrum of $(Ph_3P)_2PtPh_2$ in chloroform-d_1 (which could be recorded more rapidly, due to greatly enhanced solubility) also remained unaffected by the presence of 1 molar equivalent of Ph_3P: similar results had been obtained for $(Ph_3P)_2PtBu^n_2$[93] and $(Ph_3P)Au\ Me_3$[125] in halocarbon solvents. The analogous complex of Ph_2MeP (although, as emerged, it is much less susceptible to reductive

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*positive shifts downfield relative to H_3PO_4

elimination) was also employed to investigate the possibility of extensive preformation of L_3PtR_2. The ^1H nmr signals associated with the methyl protons of Ph_2MeP are sensitive to coordination to platinum[293], and $(Ph_2MeP)_2PtCl_2$ has been shown by this technique to undergo rapid phosphine exchange with Ph_2MeP free in solution[294]. Nevertheless, introduction of Ph_2MeP, over a range of concentrations, to chloroform-d_1 or benzene-d_6 solution of $(Ph_2MeP)_2PtPh_2$ produced no change in the spectra of free or complexed phosphine, indicating neither rapid exchange nor further direct ligation.

It is not easy to reconcile these observations with the kinetic result. It may only be speculated that the initial association between free-ligand and complex takes place in an unusual fashion, to which these spectroscopic techniques are not sensitive. Perhaps an 'outer-sphere' coordination is involved in the pre-equilibrium step, since (from the unaffected $^1J(^{195}Pt-^{31}P)$-values) there does not appear to be appreciable disturbance of the σ-bond electron density around the platinum atom. Outer-sphere complexes involving phosphorus donors and organotransition-metals have previously be postulated as reaction intermediates[308].

It is evident that the qualitative prediction that neutral nucleophiles may facilitate reductive elimination[48] is broadly borne out in the case of $(Ph_3P)_2PtAr_2$. Clearly, though, an extensive programme of further investigation will be required to establish the intimate mechanics of the effect.

Although the overall reaction may be electronically analagous, the procedure is not directly comparable with (normal) nucleophilic ligand substitution reactions of the type that have been extensively studied in Pt(II) chemistry[256, 263]. If it were, it is likely that the enhancing effect of free phosphine would be greater (by orders of magnitude) than has been observed.

Ligand-substitution at square-planar Pt(II) is recognised to be an associative interchange process (designated I_a[263]) occurring via a 5-coordinate (most probably trigonal bipyramidal[291]) active intermediate.[291] Under pseudo-first-order conditions (excess y), displacement of X by Y proceeds according to a two-term rate law:

$$-d[A_3PtX]/dt = k_1[A_3PtX] + k_2[A_3PtX][Y]$$

where K_1 and K_2 are respectively first and second-order rate constants. The observed pseudo-first-order rate constant k_{obs} may therefore be expressed:

$$k_{obs} = k_1 + k_2[Y]$$

(Thus k_1 and k_2 may be obtained by plotting k_{obs} against Y) A two-term rate law indicates a two-path mechanism for the reaction. The route represented by k_1 is the 'solvent' path, in which the rate-determining step is the displacement of X by a solvent molecule which is then more rapidly replaced by Y. The pathway associated with k_2 is direct displacement of X by Y. k_1 and k_2 could, then, be designated k_s and k_y. For these reactions, good agreement was found with the linear free-energy relationship[291]:

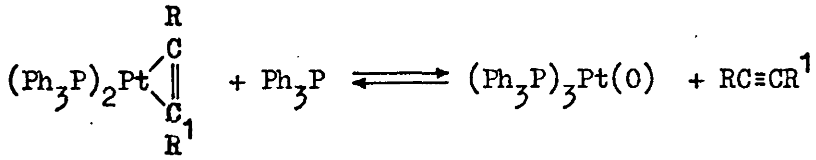
$$\log\left(\frac{k_y}{k_s}\right) = s\, n^o_{Pt}$$

The constant s depends on the sensitivity of the platinum substrate to nucleophiles and is termed 'nucleophilic discrimination factor'; n^{o}_{Pt}, defined by the equation, is the 'nucleophilic reactivity constant' of Y (towards the Pt-substrate) in solvent S. A considerable number of such constants, for reactions in methanol, have been collated[291].

Returning now to the reductive elimination reactions, they can be seen to differ kinetically from I_a substitution reactions in several ways. For one thing, irreversible reductive elimination takes place reasonably readily in the presence of solvent only. For another, while Ph_3P measurably accelerates the reaction, its effect is not spectacular (relative to toluene alone) and seems to be quite insensitive to free-ligand concentration, which might suggest a continued predominance of 'solvent only' kinetics (if the reaction was mechanistically analogous to I_a substitution). There would be alternative inferences (in I_a terms) from these data. Either the value of n^{o}_{Pt} for Ph_3P in toluene is extremely low, or the s-value for $(Ph_3P)PtAr_2$ is small. The former proposition would, in effect, require that toluene (at 60°C) is a more efficient nucleophile than methanol (at 30°C) by at least a factor of 10^8; Ph_3P in methanol is among the most potent of nucleophiles (towards <u>trans</u>-$(pyridine)_2PtCl_2$), having $n^{o}_{Pt} = 8.79$[291]. Since aniline and thiophenol are no better than, respectively, 10^3 and 10^4 times more effective (at 30°C) than methanol, this seems an insupportable tenet. The second alternative is no more reasonable, since even if the rate constants obtained for phosphine-assisted biaryl elimination were to correspond to a predominance of 'ligand only' displacement, an s-value of the order of 0.01 would be required -

even allowing (unreasonably) toluene a nucleophilicity approaching that of aniline. Tertiary phosphine (and arsine) complexes were found to have generally higher s-values among Pt(II) species: the range spanned 0.5 to 1.4[291].. It must be conceded, of course, that the substrates in question were halidoplatinum species, and the (intuitively) lesser charge separation in the organoplatinum analagues might produce a dulling of substrate sensitivity to the nature of the nucleophile that such an effect would amount to more than two orders of magnitude is, it is felt, unreasonable.

An interesting and perhaps indicative comparison may be found in the kinetics of the equilibrium between the zerovalent platinum species, $(Ph_3P)_3Pt(0)$ and $(Ph_3P)_2Pt(alkyne)$ in benzene solution at 25°C:



$$(Ph_3P)_2Pt\left(\begin{matrix} C\text{-}R \\ \| \\ C\text{-}R^1 \end{matrix}\right) + Ph_3P \rightleftharpoons (Ph_3P)_3Pt(0) + RC{\equiv}CR^1$$

$R = Me; R^1 = Ph$

(The metallocycloalkene extreme is, perhaps unjustly, represented to accentuate the possible analogy with reductive elimination).

The forward reaction (as written) proceeds, in excess of Ph_3P, predominantly by an associative pathway, i.e. by direct attack by Ph_3P on the substrate. The kinetics of the reverse process (in excess of $RC{\equiv}CR^1$) are, by contrast, in accord with the predominance of a stepwide, dissociative route, via the 14-electron $(Ph_3P)_2Pt(0)$ intermediate[236b]. These observations may be naively interpreted as indicating appreciable discrimination, by the (albeit, d^{10}) metal, between the various nucleophiles - Ph_3P, alkyne and, presumably, benzene. In fact, the mechanics of this system - which displays a concentration dependence on both substrate and nucleophile - are evidently more closely akin to those of I_a ligand substitution than they are to reductive elimination.

From present data, then, it may only be concluded that for reductive elimination of biaryl from $(Ph_3P)_2PtAr_2$, although the rate-determining-step may be influenced by the presence of coordinating nucleophile, its energetics are dominated by other considerations. Interestingly, application of the Arrhenius relationship to the rate data obtained for thermal decomposition of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ in the presence of Ph_3P (9 mol. equiv.) at 50° and 60°C led to the estimated value of $E_a = 75.5$ K.J. mole^{-1} which is in remarkably close agreement with the values obtained for $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ and $(Ph_3P)_2PtPh_2$ (Fig. 5 and Table 5.3) The significance of this will be discussed presently in relation to the nature of reductive elimination. Meanwhile, the true essence of nucleophilic assistance of these reactions remains a manifestly complex problem, and not one that may be presently resolved by further speculation on the meagre data which is available. More comprehensive assessment of concentration dependency (e.g. at nucleophile concentrations less than that of the substrate) and judicious variation in nucleophile and solvent are necessary extensions.

B. Other Complexes

Without exception, all the other diarylplatinum systems which were investigated were considerably more reluctant to undergo thermal decomposition than those containing Ph_3P as ancillary ligands.

To those complexes which could be induced to decompose under these conditions, a primary mechanism of concerted reductive elimination of biaryl could be unequivocally assigned, on the previous criteria.

i) Complexes Containing dpe or dmpe*

The complex (dpe)$PtPh_2$ consistently showed no inclination to decompose thermally over a 12 day period at 60°C under dry nitrogen in homogeneous toluene solution, either alone or in the presence of excess dpe (6 mol. euiv.)

Similarly, neither of the complexes (dmpe)$PtAr_2$ (Ar = Ph, 4-Me-C_6H_4) produced any indication of thermal decomposition when thermolysed alone, in toluene, over a 12-day period.

ii) Complexes Containing dpm

Neither (dpm)$PtPh_2$ nor (dpm)Pt(4-Me-C_6H_4)$_2$ showed any detectable sign of decomposition after 12 days in solution at 60°C. Both, however, were found to decompose slowly via concerted reductive elimination of biaryl, when an excess of free dpm was introduced (ca. 10 mol. equiv). The first order rate constant for decomposition at 60°C, of (dpm)Pt(4-Me-C_6H_4)$_2$ by this route was measured to be $1.07 \pm 0.03 \times 10^{-6}$ sec^{-1} ($t_{\frac{1}{2}}$ = 180±5 hours), (see Fig. 5.7)

This notable labilisation by the addition of free phosphine parallels that observed in the condensed phase studies of these complexes. There was no appearance of secondary products. The reaction, however, has proceeded to an extent of only 35% in the 5-days over which it was monitored. (Benzene and biphenyl would have been detected; Ph_2MeP and Ph_3P, which were products of the condensed phase thermolyses, would not have survived the quenching treatment

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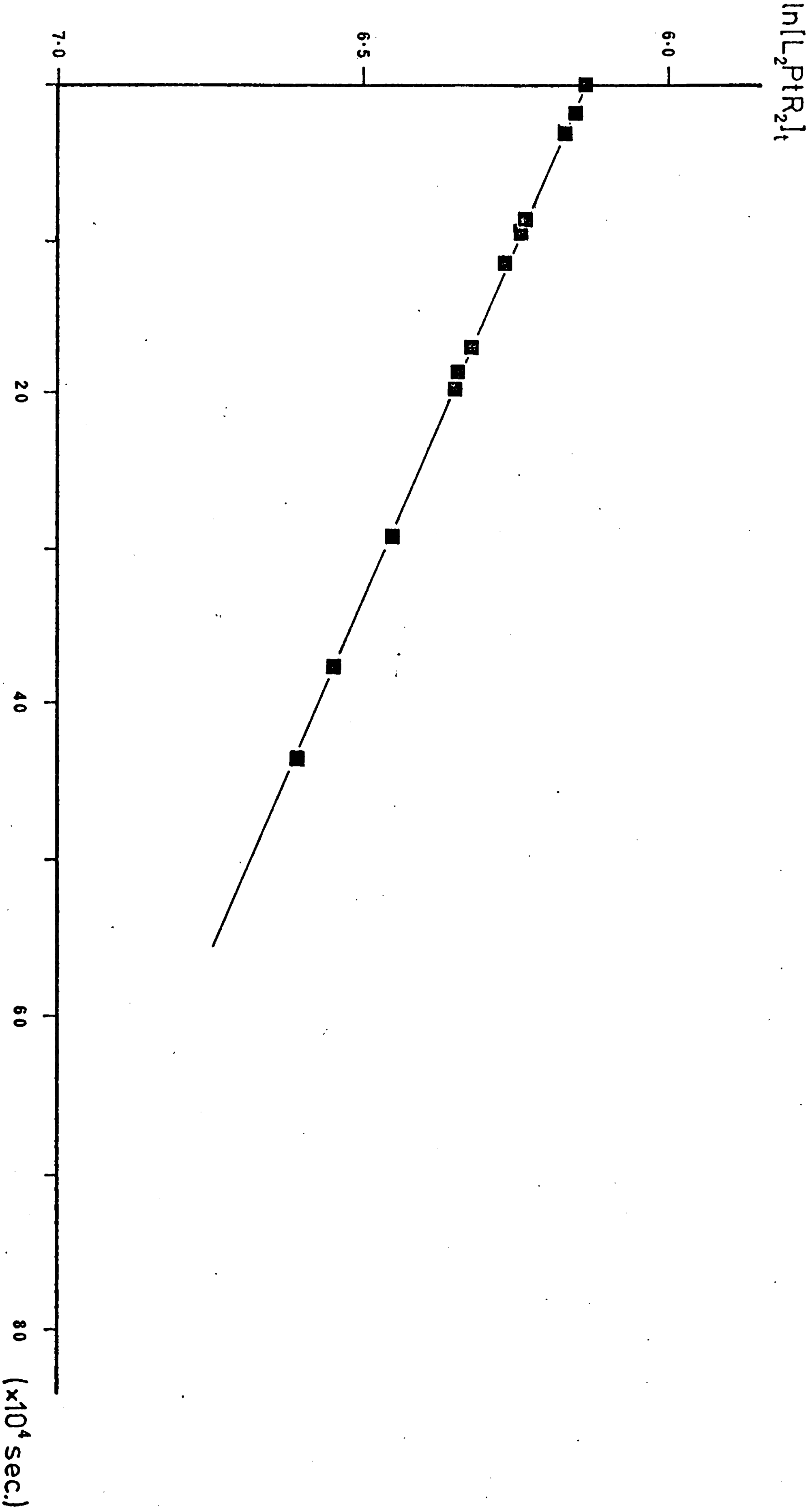
* 1,2-bis(dimethylphosphino)ethane.

Figure 5.7 First-order Plot for Thermal Decomposition of $(dpm)Pt(4\text{-}Me\text{-}C_6H_4)_2$ in Presence of Excess dpm in Toluene Solution



with HCl). The lemon-yellow solution was not analysed further.

4,4'-bitolyl was also produced over several days by a solution of (dpm)Pt(4-Me-$C_6H_4)_2$ to which an excess (ca. 10 mol. equiv.) of Ph_2MeP had been added. The precise identity of the decomposing diarylplatinum species cannot, however, be certain (see e.g. next section) due to the possibility of ligand exchange.

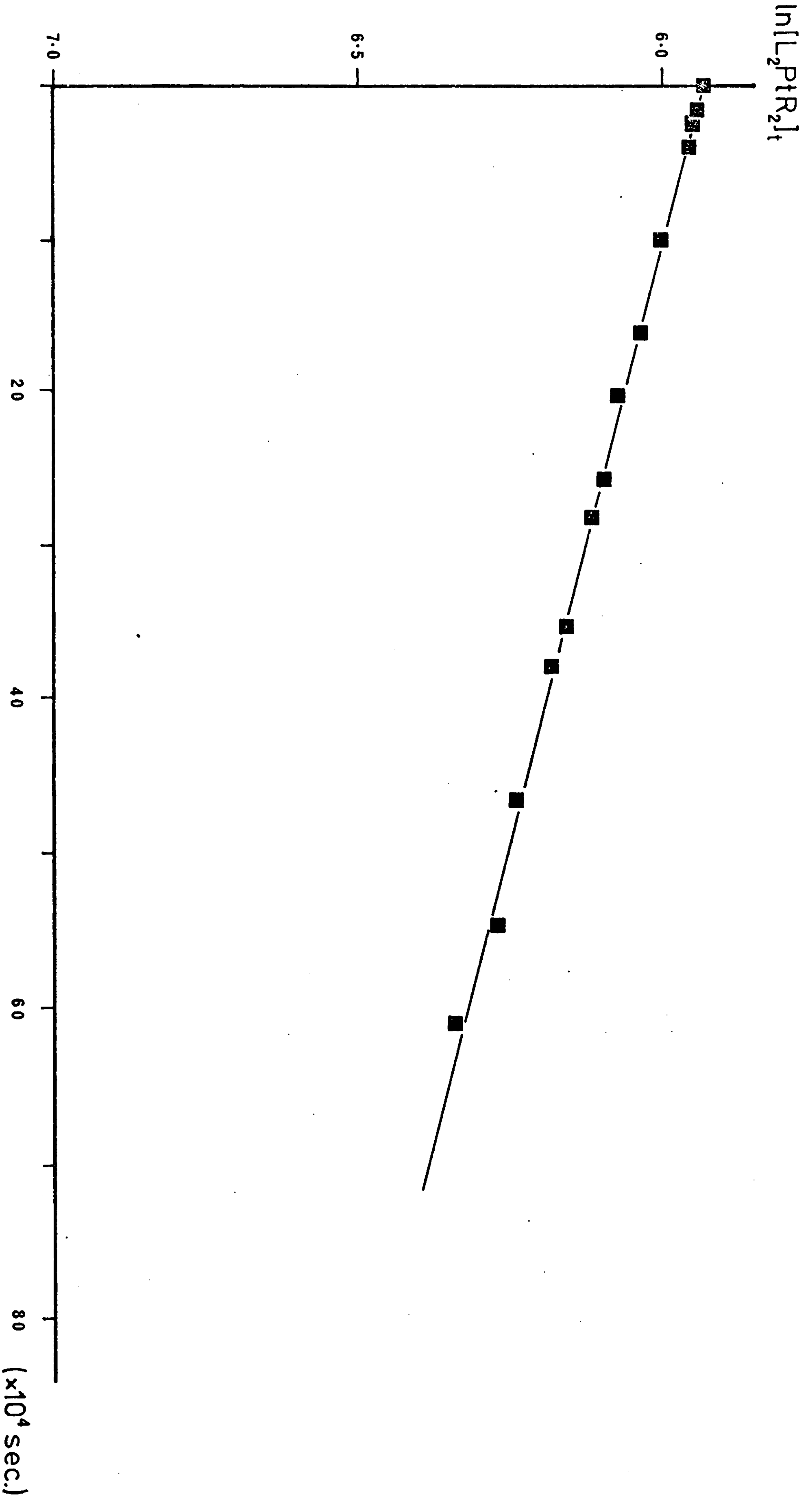
iii. Complexes Containing Ph_2MeP

Disinclination to undergo thermal decomposition is not altogether a function of bidenticity of the ancillary ligand. Complexes cis-$(Ph_2MeP)_2PtAr_2$ (Ar = Ph, 4-Me-C_6H_4) underwent concerted reductive elimination of biaryl only very slowly in toluene at 60°C. The first-order rate constant for this process was determined, for $(Ph_2MeP)_2PtPh_2$, to be $6.66 \pm 0.12 \times 10^{-7}$ sec^{-1} ($t_{\frac{1}{2}}$ = 290±6hr). (See Fig. 5.8) Decomposition of $(Ph_3P)_2PtPh_2$ under identical conditions gave $k = 7.6 \times 10^{-5}$ sec^{-1} (Table 5.1). Only a small quantity of secondary benzene was generated during the time that decomposition of $(Ph_2MeP)_2PtAr_2$ was observed (ca. 2 mole% after 37% primary reaction). Methane would have escaped detection.

General Implications

The data from parts A and B, such as they are, serve to demonstrate a general mechanistic preference among complexes of the type cis-L_2PtAr_2 underlines that this process may be facilitated by the introduction of free phosphine. Indeed, the results obtained from the solution decompositions display remarkable similarity to those which arose from condensed phase studies, even as far as the operation of secondary decomposition modes, and the suppression of these by the presence of excess phosphine.

Figure 5.8 First-order Plot for Thermal Decomposition of $(Ph_2MeP)_2PtPh_2$ in Toluene Solution



The notable individual variations in stability towards reductive elimination, and in particular the singularly higher rates of decomposition for complexes of Ph_3P relative to any other system (whether phosphine-assisted or not) cannot be easily rationalised. Consideration of relative $^1J(^{195}Pt-^{31}P)$ values does not betray any apparent gross electronic disparities in the various phosphine-platinum donor-bonds, which could reasonably account for an increase of at least 100-fold in the rate of decomposition of $(Ph_3P)_2PtAr_2$ compared with its Ph_2MeP or dpe analogues, which might, intuitively, be expected to display electronic similarity (See Table 5.3) - [The anomalously low coupling constants for $(dpm)PtAr_2$ are evidently due to the severe constriction of bond-angles in the 4-membered metallocycle[245]; the Pt-P and Pt-C bonds are otherwise normal. In any case, $(dpm)PtAr_2$ complexes are themselves more stable than $(Ph_2MeP)_2PtAr_2$].

A steric explanation is also difficult to discover. It certainly cannot be argued that chelation is not contributive, but bidenticity of phosphine ligand is not the sole consideration, for there remains the enhanced thermal stability [relative to $(Ph_3P)_2PtAr_2$] of $(Ph_2MeP)_2PtAr_2$. The only superficial difference between the latter two systems is that the less stable has a bulkier, more complex substituent on each of the coordinated phosphorus atoms. Could it be then, that the greater the tendency of the adjacent phosphines to be mutually repelled, the greater is the general disposition to undergo reductive elimination? This would be consistent with the even more marked elimination stability of the chelate phosphine complexes, in which the donor atoms are held in juxtaposition. Another way of viewing this argument is that as the total number of molecular degrees of freedom (vibrational, rotational) - available at least to the platinum-phosphine skeleton - becomes more restricted, then the tendency to reductively eliminate is decreased. If this were so, it would lead to the tentative prediction of actual complex-stability towards reductive elimination increasing in the order:

$(Ph_3P)_2PtAr_2 < (Ph_2MeP)_2PtAr_2 < (dpe)PtAr_2 <$

$(dpm)PtAr_2 \overset{?}{<} (dmpe)PtAr_2$

Present data are not inconsistent with this order, but a suitable solvent system which would allow direct decomposition comparisons will be required to investigate the authenticity of these propositions.

These arguments are obviously related to molecular entropy contributions, and, as will emerge, it appears that entropy effects are of major significance in the thermal reductive elimination reactions of these complexes (vide infra).

C. On the Possible Nature of Reductive Elimination from cis-L_2PtAr_2

A perusal of the literature reveals that in a large number of examples of carbon-carbon coupling via transition-metal-carbon scission, one or both of the bound carbon atoms is sp^2 or sp hybridised, i.e.
been found to behave in this way include η^1-aryl
has gands which have
-vinyl[128, 129, 138], -alkynyl[142], -cyano[297] and [142, 235, 295-297]
been found to behave in this way include η-aryl
-vinyl[128, 129, 138], -alkynyl[142], -cyano[297] and -acyl[116,296] substituents; acetyl groups, in particular, have been cited for their favourability towards reductive elimination from Pt(IV)[119]. A possible explanation

of this tendency might be that the availability of a polarisable electron density - arising from the π-framework of one (or both) of the ligands - between adjacent metal-bound groups might be conducive to incipient bond formation between them. In other words, the electron density which contributes to the embryo (ligand-ligand) σ-bond might be derived, in part, from the ligand π-orbitals. Turning specifically to diarylplatinum (II) species, such an interaction, in its extreme form, may be portrayed as in Fig. 5.9 (Ancillary ligands are omitted for clarity).

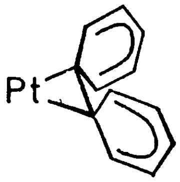
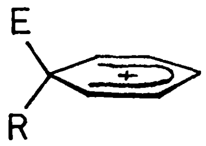


Figure 5.9

Such a structure may represent a hypothetical transition-state for reductive elimination of biaryl. A contributive consideration might be the extent to which metal-aryl (dπ-pπ) back-bonding would tend to restrict the mutual orientation of the aryl rings. The most favourable conformation for the transition state would involve both rings perpendicular to the complexation plane, with π-orbitals directed at each other; this orientation has been considered to be one which is favoured by π-back-bonding[30a]. (Back-bonding in this case might additionally be seen to actively increase the electron density between the two α-carbon atoms). These considerations are, in effect, an attempt to assess the extent to which the stable state of cis-L_2PtAr_2 is likely to approach an activated state such as 5.9

. An extension of this hypothesis, and one which can be empirically tested, is the possible influence which a substituent R might have on the stability (or instability) of a species such as 5.9. Ring-substituent effects on reactivity patterns in electrophilic aromatic reactions may be interpreted in terms of the relative stabilities conferred by substituent properties on benzenium intermediates[174] (Fig. 5.10) which are clearly related to 5.9.

Figure 5.10



Attempts to quantitatively correlatate reactivities and substituent effects - particularly on aromatic species - have been made using the linear free-energy relationship employed by Hammett[298-300] which may be expressed:

$$\log\left(\frac{k}{k_o}\right) = \sigma\rho$$

(where k and k_o are the rate constants for substituted and unsubstituted species respectively, ρ is the reaction constant at a given temperature, and σ is a measure of the substituent effect, generally in terms of electron donating or accepting propensity; several scales of σ-values are available, depending upon the degree to which the substituent action is considered to be inductive or mesomeric[299,300])

Crude application of the relationship to the rate data obtained for reductive elimination from $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ and $(Ph_3P)_2PtPh_2$ yielded a reaction constant (at 60°C) of $\rho=-1.2$ (or -0.6, if both 4-methyl substituents are individually assessed) assuming a substituent constant for the 4-methyl group of $\sigma=-0.17$[299]. Such a negative value of ρ might be seen to reflect a moderately electrophilic progress to the transition-state[298] (the para-methyl group is electron-donating) and as such would be in accord with a reaction proceeding via 5.9. However, it is emphasised that application of the Hammett equation here is quite arbitrary, and it is not obvious that this example should necessarily conform to the relationship, nor, indeed, that the chosen σ-value is likely to be the one appropriate to this reaction. Many studies in which the ring substituents and substitution patterns were carefully varied would be required to verify any applicability of the equation. In any case, closer scrutiny of kinetic and activation data suggest that these ideas are a gross oversimplification of complex factors. Seeking an explanation solely in terms of the Hammett equation leads, as will become evident, to serious interpretational difficulties and possibly to wrong conclusions.

The empirical activation energy E_a may be estimated graphically from the logarithmic form of the Arrhenius equation (vide supra) The additional activation parameters, enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation may be estimated from the relationships (for 25°C):

$$\Delta H^{\ddagger} = E_a\text{-}RT \text{ KJ.mole}^{-1} \text{(Ref. 301)}$$

$$\Delta S^{\ddagger} = 19.155(\log_{16}A\text{-}13.23) \text{ J. mole}^{-1}.\text{deg}^{-1} \text{ (Ref. 302)}$$

Comparative values for activation parameters are presented in Table 5.4. With particular reference first to $(Ph_3P)_2PtAr_2$ alone, a striking feature is the appreciable negative entropy of activation. The more unequivocal value for disruption of $(Ph_3P)_2Pt(4\text{-Me-}C_6H_4)_2$ of -99.4 J. deg^{-1}.mole^{-1} is, in fact, more pronounced than those that characterise concerted intramolecular multicentre rearrangements in organic chemistry (e.g. Cope and Claisen rearrangements[303]), and is indicative of a considerable loss of conformational freedom on proceeding to the transition state. In other words, appreciable new bonding has been effected during the attainment of the transition state, which is consistent with the formation of a species resembling 5.9 (and firmly underlines the concertedness of the process). The estimated $\Delta S^{\ddagger}$ for decomposition of $(Ph_3P)_2PtPh_2$ (and, indeed, for that of $(Ph_3P)_2Pt(4\text{-Me-}C_6H_4)_2$ in the presence of excess phosphine) is of the same order of magnitude, underlining the generality of this contention.

Notably, however, the enthalpy of activation appears, within experimental error, to be virtually unaffected by a methyl group as _para_-aryl-substituent. It is here that interpretations in terms of Hammett formalism are found to be rather inadequate. The conventional explanations of Hammett parameters in terms of electronic donation (or acceptance) by substituents - whether they be inductive or mesomeric in nature - would be expected to be reflected more in enthalpy contributions to activation. Here, if the data are to be believed, the control on activation is largely, if not wholly, entropy determined. Although the Hammett equation strictly represents a linear free-energy relationship, and should ideally reflect both enthalpy and entropy considerations, no clear theory has emerged which describes contributions to substituent effects by entropy properties. The successful operation of the relationship appears to depend on significant contributions by enthalpy effects to substituent-influenced activation[304].

There remains to be explained, then, the appreciable and apparently entropy-determined facilitation of biaryl elimination when the aryl group bears a 4-methyl substituent. It may be assumed that contributions to entropy changes on approaching the transition state, arising from the platinum-phosphine skeleton are the same in both phenyl- and 4-tolylplatinum systems (and probably minimal). The disparity in $\Delta S^{\ddagger}$-values therefore reflects only the difference in ease of restriction of rotational and/or vibrational degrees of freedom associated with the platinum-aryl part of the molecule; in order to achieve 5.9 it is evident that rotation about the Pt-C bonds will have to be effectively and, selectively (with respect to ring-orientation) stopped. That this is evidently more facile for the tolylplatinum species is consistent with its having a lower, aryl-associated entropy, in the ground-state, thus allowing easier passage into the transition state. The alternative explanation is that the ground-state entropies for both complexes are essentially equal, but the transition-state entropy for the tolyl complex is higher. This latter explanation may seem superficially attractive since the tolylplatinum transition state will have extra vibrational (and rotational) degrees of freedom associated with the methyl substituents; the ground-state of this complex, however, will have equivalent contributions so that the overall contribution to $\Delta S^\ddagger$ should be negligible. It seems likely, then, that the former proposition is more nearly accurate. The precise machinery by which the 4-methyl group effects a critical lowering of entropy can only be guessed. Electron-donation might conceivably induce polarisation effects in the aromatic π-orbitals[305], which might lead to rotational restriction by mutual interaction of the rings. This, however is more likely to be related to ground-state contributions from structures akin to 5.9, and would thus be expected to produce detectable enthalpy effects also. The origin of the entropy effect may, perhaps more plausibly, be steric - the more bulky substituent merely presenting a physical impediment to rotation; some contribution by relative solvation effects cannot be discounted in this context.

As noted, the virtual absence of relative activation enthalpy effects with variation of aryl substituent, would appear to belie any significantly differing contributions by extreme valence-bond structures of the type represented in Fig 5.9 to the ground state configurations of the complexes. A similar inference might be drawn from the comparison of $^1J(^{195}Pt-^{31}P)$ values for phenyl and 4-tolylplatinum complexes with various ancillary phosphines (Table 5.3) Any appreciable rehybridisation at carbon of the type implicit in 5.9 (approach to sp^3) would be expected to promote, by σ-induction, a corresponding significant change in the Pt-P bond trans to itself, and hence in the appropriate coupling constant (as extreme examples cis-$(Ph_3P)_2PtMe_2$ has $^1J(Pt-P)$ = 1886.0 HZ, while the dmpe analogue has $^1J(Pt-P)$ = 1705.9)

Table 5.3

Comparative $^{1}J(^{195}Pt - ^{31}P)$ Values (Hz.) for Diarylplatinum Analogues

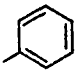
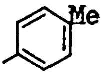
Ar / Complex		
$(dpm)PtAr_2$	1391.8	1390.4
$(dpe)PtAr_2$	1668.7	—
$(dmpe)PtAr_2$	1642.1	1642.7
cis-$(Ph_2MeP)_2PtAr_2$	1762.7	1758.7
cis-$(Ph_3P)_2PtAr_2$	1748.4	1742.4

Table 5.4

Thermal Decomposition of $(Ph_3P)_2PtAr_2$ - Estimated Activation Param.

Decomposing System	$E_a \pm 4.0$ (KJ.mole^{-1})	$\Delta H^{\ddagger}$ [25°C] (KJ.mole^{-1})	$\Delta S^{\ddagger}$ [25°C] (J.mole^{-1}.deg.$^{-1}$)
$(Ph_3P)_2PtPh_2$	71.0	68.5	-115.4
$(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$	76.3	73.8	-99.4
" + ca. $9Ph_3P$	75.5	73.0	-96.2

No such significant difference between analagous phenyl and 4-tolyl species is evident. Unfortunately, ${}^{1}J({}^{195}Pt-{}^{13}C)$ values, which would have provided a more sensitive evaluation of the hybridisation at the α-carbon, were inaccessible, due to the limited solubility of the materials and the very low n.m.r. sensitivity of the ${}^{13}C$-nucleus.

The relative activation energetics estimated from the rate data for the phosphine assisted decomposition of $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$, in common with other aspects of this reaction so far discussed, are somewhat mystifying. Here, too, there is no appreciable difference in $\Delta H^{\ddagger}$ relative to parallel decomposition of the complex alone, nor, indeed, to that of $(Ph_3P)_2PtPh_2$. Once more, if the estimate is accurate, ease of passage to the transition-state is dominated by entropy considerations. (Table 5.4 and Fig. 5.3) This is not entirely unreasonable. If the apparent preequilibrium formation of an associated species is a genuine effect, entropy contributions from the association will not figure in $\Delta S^{\ddagger}$, and the activation process will reflect the unimolecular decomposition of this new species. The energetic requirements of this process might, in the absence of spectroscopically detectable electronic effects, be anticipated to be broadly similar to that for L_2PtAr_2. Outer-sphere association of free ligand, particularly in the vicinity of the aryl ligands, might, for example, be expected to restrict ring rotation, thus lowering the effective entropy loss which is required in order to attain the transition-state. Once again it might be argued that the transition-state itself may have lower overall entropy than in the absence of phosphine, but correspondingly, this may be answered by the argument that if entropy contributions from the preassociation may be initially ignored, they may only be so if they remain relatively invariant along the reaction coordinate, at least as far as the activated complex. These data shed no further light on the seemingly unusual mechanism of phosphine-assisted elimination, save perhaps to underline that the operative process is essentially similar to the concerted decomposition route which operates in the absence of phosphine.

Although the estimated differences in $\Delta S^{\ddagger}$ on which these conjectures are based may appear comparatively small, they are certainly sufficient to account for differences in rate of the order noted; the dependence of the rate constant k on $\Delta S^{\ddagger}$ is exponential and relatively minor variations in $\Delta S^{\ddagger}$ might be expected to produce significant changes in rate[306].

In the light of these conclusions, some further speculation on the enhanced (reductive) elimination stability of other diarylplatinum species relative to those containing Ph_3P, seems in order. It was previously suggested that stability seemed to increase with increasing (potential) rigidity of the P-Pt-P framework. At first sight, this might appear contradictory, since it ought to contribute to an overall decrease in molecular entropy, thus, ostensibly, destabilising the complex with respect to its transition state. This, however, may be a misleading view; entropy associated with the platinum-phosphine skeleton may not contribute directly to the energetics of attainment of the activated-state. It may, on the other hand, exert an indirect influence. Potentially greater restriction on the movement of the phosphine ligands may correspondingly allow greater freedom of rotation and vibration to the aryl ligands in the opposite 'molecular hemisphere'. It might be fairly reasonably assumed that entropy changes originating from the phosphine ligands, during progress to a transition-state resembling 5.8, are comparatively small, since the metal atom remains, essentially, 4-coordinate (See Fig. 5.11) This may certainly be assumed in the case of bidentate phosphines - unless bridge-coordination contributes significantly during reaction - where the relative positions of atoms in ligating groups are held more-or-less rigidly. Given that this is the case, then the all-important $\Delta S^\ddagger$ is dominated by the energetics of removing degrees of rotational and vibrational freedom from the arylplatinum framework. Where these motions are (hypothetically) accentuated by a more restricted, rigid ancillary skeleton, then the entropy change for activation becomes more negative, and the molecule is thus entropy stabilised. The veracity of this speculative proposal remains, of course, to be explored.

CONCLUSIONS AND PROJECTIONS

The evidence which has accrued from the investigation of thermal disruption of organoplatinum(II) complexes of the general type cis-L_2PtAr_2 indicates that the primary tendency of these species is metal-carbon cleavage via unimolecular, concerted reductive elimination of biaryl. This is generally followed, under the same conditions, by secondary decomposition which may be best understood in terms of ligand-to-metal aryl- and hydrogen-transfer steps in the unstable 14-electron fragment (which is the primary product) and further reductive elimination reactions (generating ligand-derived biaryl and arene). Product distribution analysis from both condensed-phase and solution decompositions has verified the molecularity of the primary reaction, and has demonstrated that free-living paramagnetic fragments are not active participants to a significant extent. These conclusions are confirmed by kinetic evaluation of decomposition in solution. Primary disintegration is inevitably first-order in (only) organoplatinum parent, and the pronounced negative entropies of activation suggest a transition-state in which appreciable new bonding has occurred, with a concomitant loss of conformational freedom - in accord with a concerted unimolecular process whose reaction profile may be represented as in Fig. 5.11.

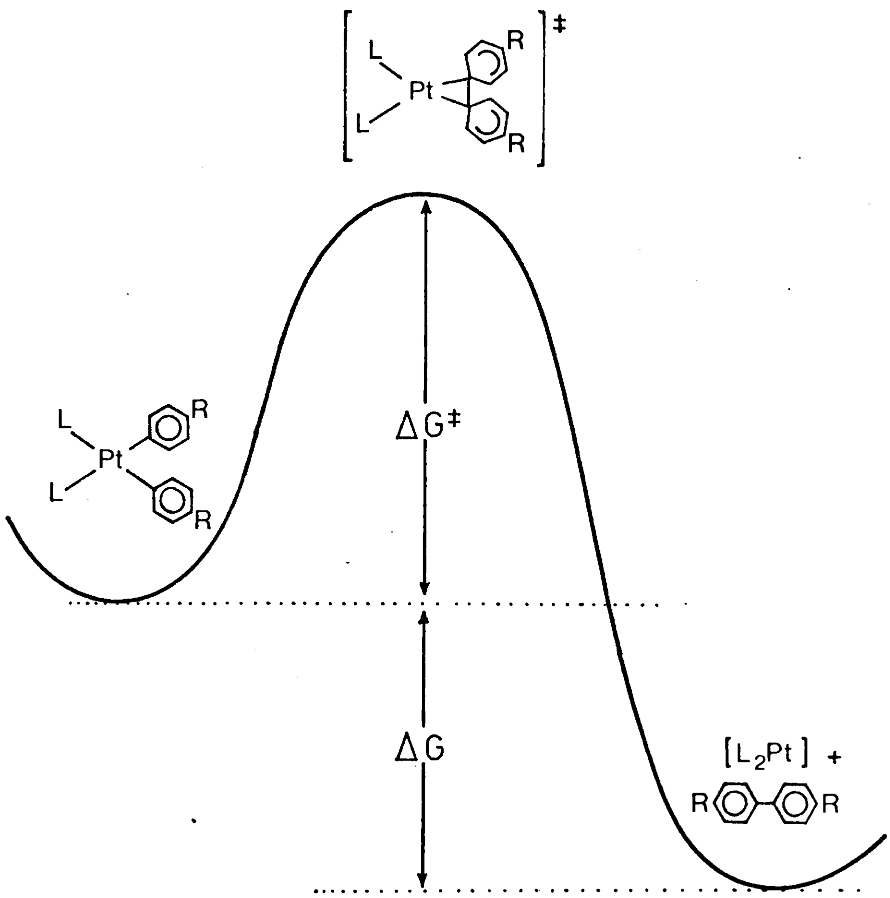


Figure 5.11

Comparison of estimated activation parameters on varying the 4-aryl-substituent suggests that entropy requirements for activation exert a dominant influence on reaction control (at least in solution) the enthalpy demand for attainment of the activated complex being relatively insensitive to para-substitution. Conventional interpretations of aryl-substituent effects cannot be readily invoked and their relative influence on local entropy may only be speculatively assessed. Clearly, this facet might be further investigated by variation of substituent groups and substitution configurations of the metal-bound aryl ligands. Appendages which more appreciably restrict the orientational freedom of adjacent aryls - such as

2-methyl substituents[30a] - are one obvious extension. Another might be the introduction of groups recognisedly capable of powerful direct resonance π-electronic interaction with the α-carbon; such might include 4-NO_2 or 4-CN[299]. More pronounced enthalpy contributions to activation might thereby be expected.

Entropy considerations might also, conceivably, dictate the differing tendencies of diarylplatinum complexes bearing other ancillary phosphine ligands. This proposal would be best verified by a rigorous comparative investigation in which the decomposition of each could be followed under identical conditions. This would probably entail higher temperatures and/or and alternative solvent. 1,1,2,2-tetrachloroethane might be an excellent candidate, since it combines more efficient solvation ability (for these complexes) than toluene with a comparably high boiling-point. This medium, however, as commercially supplied, would require even more stringent purification than did the toluene which was employed. Enhanced solvation might also allow an alternative method for monitoring decomposition kinetics, at least for tolyl complexes. $(Ph_3P)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$ was shown to undergo full decomposition over 4 days at ambient temperature in chloroform-d_1 (and anaerobic conditions) by monitoring the appearance of the 'H-nmr signal due to the methyl protons of 4,4'-bitolyl at the expense of the absorption attributable to the 4-methyl group of the coordinated aryl. (Circumstances have not, at the time of writing, permitted quantitative evaluations to be performed). This complex is particularly suited to this approach since it is most soluble, and the methyl chemical shift for the complex (1.84ppm) is sufficiently separated from that of the product (2.34ppm). However, other complexes to which this method might be applied - provided satisfactory signal/noise characteristics can be established - are (dpm)Pt(4-Me-$C_6H_4)_2$ 2.18ppm , (dmpe)Pt(4-Me-$C_6H_4)_2$ 2.00ppm and cis-($Ph_2MeP)_2$Pt(4-Me-$C_6H_4)_2$ 2.00ppm . Chloroform-d_1 is probably too low-boiling to serve as a suitable universal solvent for these comparative studies. Although sym-tetrachloroethane-d_2 is not available, the normal solvent could be employed, as its characteristic ^{1}H-nmr absorption is sufficiently shifted relative to those of 4,4'-bitolyl or any of the complexes.

An inherent and useful spin-off from these studies, would, of course, be some indication of the solvent dependency of the decomposition kinetics. On the other hand, diversification into the field of chlorocarbon media would widen the extent of requisite preliminary screening of decomposition products, in order to establish the contribution (if any) of reaction modes other than reductive elimination. Tetrachloroethylene, for example, attacks the metal directly during thermolysis of trans-[($Et_3P)_2$Ni(2-allylphenyl)Cl] in that solvent[200] . Indications are, however, that, $(Ph_3P)_2PtCl_2$ is not a significant product of decomposition of $(Ph_3P)_2$Pt(4-Me-$C_6H_4)_2$ in chloroform-d_1, although this contention is subject to quantitative analytical proof.

The secondary decomposition reactions also deserve further investigation, although such a programme is likely to be extensive enough to furnish a separate research project. If general, these processes may account for the broad non-isolability (on the gram scale) of electron deficient species of the type $L_2Pt(0)$. Indeed, they may ultimately find a place among the, as yet, relatively unexplored reactivity patterns of phosphine complexes of zerovalent metals as a whole, among which they might be most aptly studied. The contribution by ortho-metallation to the ultimate generation of secondary product (arene) could be established by selective ortho-deuteriation of the phosphorus-borne aryl groups. This has been described for Ph_3P[181] (vide supra, ch. 2) and dpm and dpe may be prepared from Ph_3P[307]. The incidence of arene-d_1 components among the decomposition products is assessible by gas liquid-phase chromatography in conjunction with mass spectrometry (GC-MS). The more exacting side to such an investigation, however, would entail more intensive attempts to establish the structural nature of the metal-bearing product, perhaps by chromatographic techniques of greater sophistication.

As had been predicted[48], the presence of quantities of free phosphine (generally identical to that already incorporated in the molecule) during the thermal decomposition of cis-L_2PtAr_2 significantly facilitates the concerted reductive elimination of biaryl. This effect is particularly pronounced for $(dpm)PtAr_2$ complexes when dpm is introduced. Nevertheless, such limited kinetic and activation parameters as have been extracted suggest that, at least for complexes containing Ph_3P, decomposing in solution, the electronic machinery on which the prediction was based, is not operatively responsible for the enhancement of platinum-carbon scission. The estimated enthalpy of activation is, again, closely similar to that for the unaided elimination The crucial considerations for relative reactivity once more appear to be those of entropy during the activation stage. From the kinetics, it appears that the phosphine-induced elimination is relatively insensitive to ligand concentration at least down to equimolar amount, which would seem to indicate a favourable preassociation of ligand and complex prior to the rate-limiting step. On the other hand, this association evidently does not cause sufficient electronic perturbation at the metal to be spectroscopically detectable. It can be broadly concluded that reductive elimination is, in this context, not mechanistically analogous to conventional two-electron donor loss, except in the superficial sense of formal electron-counting. More substantial conclusions must await a more extensive study of the effect of excess ligand than has been possible here. A thorough evaluation of concentration dependence is primarily necessary, as well as expansion to the organoplatinum systems which were not examined or for which examination was qualitative. Diversification of nucleophile and of solvent would add interesting additional dimensions to the understanding of an effect that has previously attracted little more than passing mention[99, 131].

A prominent aspect of this work has been to establish the concerted nature of the Pt-C scission mode which is favoured under thermal conditions. It would, of course, be of great interest to investigate the possiblity that the metal-aryl bonds might be induced to undergo homolytic scission by photochemical excitation of the type originally envisaged to be responsible for thermal disruption in these complexes. Unfortunately the all-important d-d bands in arylphosphine complexes are all but masked by intense absorbtions (in the ultra-violet) associated with the arylphosphine ligands. This may be partially offset by the utilisation of alkylphosphine ligands such as dmpe. Sadly, however, no comparative thermal data for such complexes has so far been accessible. Chlorocarbon solvents might again provide useful media for irradiation, particularly CCl_4, in view of the fact that termination reactions of aryl radicals in this solvent have been extensively documented[283, 284]. Thorough screening of the thermal behaviour of the organometallic system in the ultimately chosen solvent medium would, obviously, be a prerequisite.

CHAPTER SIX

Experimental

CHAPTER SIX

Section A: Preparative

In general, all preparative schemes were undertaken in oven-dried glassware under dried, inert-gas atmospheres, since many of the reagents and/or intermediates, and perhaps, additionally, products were thought likely to be oxidatively or hydrolytically unstable in solution. For the same reason, hydrocarbon solvents (benzene, toluene, diethyl ether) were dried by storage over extruded sodium wire, chlorocarbon solvents (chloroform, methylene chloride, *sym*-tetrachloroethane) were distilled and stored over activated Linde 5A molecular sieves and tetrahydrofuran (T.H.F.) was refluxed (under a dried nitrogen atmosphere) with potassium chips and benzophenone until the advent of blue colouration (arising from the formation of the ketyl radical-anion[309]) indicated the destruction of residual water. The ether was now distilled (under nitrogen) and stored over Linde 5A molecular sieves. Oxygen-free nitrogen and argon were used as inert atmospheres, and were dried by passage through 48" x 1" diam. columns packed with activated 5A molecular sieves (a short section of silica -gel blue in mid-column served as a deactivation indicator).

Dichloroplatinum(II) Complexes

The generally white and notably insoluble bis(phosphine)-dichloroplatinum(II) precursors for the arylplatinum species were most successfully synthesised *via* a common route - viz. by methathetical displacement of PhCN from *cis*-$(PhCN)PtCl_2$ by the appropriate phosphine.

Since all the complexes were prepared in this way, only one representative synthesis need be described in full.

Preparation of bis(benzonitrile)dichloroplatinum(II)[310]

$PtCl_2$ (7.9g, 29.8 m.mole) was suspended in benzonitrile (250 ml) in a 500 cm^3 conical flask (no inert atmosphere necessary in this case). The mixture was heated to 110°C and vigorous stirring was continued at this temperature (under a fume-hood) for 8 hours. The mixture was then filtered hot (using a preheated receptacle flask, funnel and fluted paper) and the rich amber liquors allowed to cool. Upon standing overnight glistening golden yellow crystals of $(PhCN)_2PtCl_2$ formed. These were recovered by vacuum filtration and dried under high vacuum (7.2g). Addition of a 5-fold excess of light petroleum (40-60°) to the filtrate yielded a further crop of finer, pale-yellow crystals of the same material, which were similarly treated (6.6g). Analyses: Found - C,35.69%, H, 2.09%, calcd. for $C_{14}H_{10}N_2Cl_2Pt$-C, 35.60%, H, 2.13%; total recovery 13.8g, 98% based on Pt; m.pt., 220°C.(lit. 220°C).[310]

Preparation of bis(diphenylphosphino)methane dichloroplatinum(II)

Bis(diphenylphosphino)methane (3.75g; 9.76 m.mole) and bis(benzonitrile)dichloroplatinum(II) (4.30g; 9.11 m.mole) were stirred in suspension in benzene (150 ml) under a nitrogen atmosphere for 16 hours at ambient temperature. The initially golden-yellow liquors were by this time virtually colourless. The resultant chalk-white precipitate was removed and washed for 1 hour in refluxing benzene to remove any trace of unreacted starting material. The product was now thoroughly dried *in vacuo* and analysed by i.r. and

^{1}H-nmr techniques, which confirmed a cis-dichloroplatinum configuration Strong absorption bands in the i.r. at 287 and 308 wavenumbers, forming a roughly symmetrical doublet - modes characteristic of a cis-dichloroplatinum configuration) and coordination of the ditertiary phosphine to platinum through both phosphorous atoms (^{1}H nmr absorption due to methylene protons at 4.42 ppm shows 1:2:1 triplet character arising from coupling to two magnetically equivalent ^{31}P nuclei and characteristic satellite triplets of $\frac{1}{4}$ relative intensity, indicative of coupling to the 33.7% abundant isotope ^{195}Pt, which has nuclear spin $I = \frac{1}{2}$; $^3J(^1H-^{195}Pt) = 70.0$ Hz). The fine white powder form of (dpm)PtCl$_2$ so obtained was generally used in further synthetic procedures without additional purification (owing mainly to its poor solubility; even the ^{1}H nmr data required pulse-Fourier-transfer analysis) Analyses: found - C, 46.69%, H, 3.51%; calcd. for $C_{25}H_{22}P_2Cl_2Pt$ - C, 46.16%, H, 3.41%; Recovery 5.80g, 97.9%; m.pt.,>300°C Delicate, colourless needles could, however, be obtained from boiling sym-tetrachloroethane.

Similarly prepared and characterised were:

1,2-bis(diphenylphosphino)ethane dichloroplatinum(II) - (dpe)PtCl$_2$

Analyses: found - C, 47.18%, H, 3.61%; calcd. for $C_{26}H_{24}P_2Cl_2Pt$ - C, 46.93%, H, 3.64%; m.pt., >300°C.

1,2-bis(dimethylphosphino)ethane dichloroplatinum(II) - (dmpe)PtCl$_2$

Caution must be exercised in the handling of dmpe (a straw-coloured liquid). The spontaneous aerial oxidation of this alkylphosphine is exothermic enough to ignite benzene. The phosphine was added to the reaction mixture <u>via</u> a hypodermic syringe against a counter-current of nitrogen (which is, of course, the essential atmosphere for this synthesis). The white product (dmpe)$PtCl_2$ is particularly insoluble in all common solvents. Analyses: found - C, 16.91%, H, 3.41%; calcd. for $C_6H_{16}P_2Cl_2Pt$ - C, 17.31%, H, 3.88%; m.pt., >300°C.

cis-bis(triphenylphospine)dichloroplatinum(II) - $(Ph_3P)_2PtCl_2$

Analyses: found - C, 53.70%, H, 3.79%; calcd. for $C_{36}H_{30}P_2Cl_2Pt$ - C, 54.69%, H, 3.83%; m.pt >300°C.

cis-bis(tri-4-tolylphosphine)dichloroplatinum - $(4\text{-}Me\text{-}C_6H_4)_3P\ _2PtCl_2$

Analyses: found - C, 58.33%, H, 4.83%; calcd. for $C_{42}H_{42}P_2Cl_2Pt$ - C; 57.27%, H, 4.81%; m.pt >300°C.

cis-bis-(diphenylmethylphosphine)dichloroplatinum(II) - $(Ph_2MeP)_2PtCl_2$

Analyses: found - C, 46.27%, H, 3.87%,; calcd. for $C_{26}H_{26}P_2Cl_2Pt$ - C, 46.85%, H, 3.93%; m.pt., >300°C.
Fine colourless plates could be obtained from boiling ethanol.

trans-bis-(tricyclohexylphosphine)dichloroplatinum(II) - $(Cy_3P)_2PtCl_2$

Analyses: found - C, 53.17%, H, 8.13%; calcd. for C H P_2Cl_2Pt - C, 52.29%, H, 8.05%; m.pt., >300°C.

bis(diphenylphosphino)methylamine dichloroplatinum(II) - (dpma)$PtCl_2$

Analyses : found - C, 44.33%, H, 3.41%; calcd. for $C_{25}H_{23}P_2NCl_2Pt$ - C, 45.12%, H, 3.48%; m.pt., >300°C.

The primarily obtained materials varied in colour from chalk-white to pale ivory, probably due to varying small amounts of residual $(PhCN)_2PtCl_2$. All the complexes assigned <u>cis-</u>geometry

Table 6.1

Pt-Cl Infrared Stretching Frequencies in L_2PtCl_2 (cm.$^{-1}$)

Complex	ν(Pt-Cl)	
(dpm)$PtCl_2$	289	308
(dpe)$PtCl_2$	292	312
(dmpe)$PtCl_2$	280	303
(dpma)$PtCl_2$	295	318
cis-$(Ph_3P)_2PtCl_2$	300	323
cis-$(4\text{-}tol_3P)_2PtCl_2$	298	320
cis-$(Ph_2MeP)_2PtCl_2$	290	312
trans-$(Cy_3P)_2PtCl_2$	341	

had the characteristic twin infra-red absorptions (attributed to symmetrical and antisymmetrical Pt-Cl stretching modes; in trans-complexes only the asymmetrical mode is i.r. active). Solid state infra-red data for dichloroplatinum complexes is displayed in Table 6.1. Configuration in solution was subsequently verified by ^{31}P nmr spectroscopy.

$(Ph_2MeP)_2PtCl_2$ could, alternatively, be prepared directly by refluxing $PtCl_2$ with (2 mol. equiv) Ph_2MeP in absolute ethanol. An attempt to synthesise $(dpm)PtCl_2$ analogously led to precipitation of amounts of fine black powder and to deposition of greenish-white crystals. A pungent odour reminiscent of paraldehyde was noted from the liquors The black material did not melt within the measurable range and is assumed to have been metallic Pt. The crystalline material displayed no Pt-Cl absorption in its infra-red spectrum, but elemental analysis and ^1H nmr data were strongly suggestive of the ionic species $[(dpm)_2Pt^{2+}]Cl_2^-$ (The ^1H nmr spectrum in chloroform-d_1 is not quite first-order, but broadly approximates to a 1:4:1 triplet of 1:4:6:4:1 quintets, expected by Pt-H and (virtual) P-H spin-spin coupling: $^2J(P\text{-}H) = 4Hz$, $^3J(Pt\text{-}H)=47Hz$. Subsequently $^1J(Pt\text{-}P)$ was determined to be 2043 Hz which would accord with mutually <u>trans</u> phosphorous ligands).

Phosphine Ligands.

With two exceptions, phosphine ligands were used as supplied by B.D.H. (Ph_3P) and Strem Chemicals (dpm, Ph_2MeP, $(4\text{-}Me\text{-}C_6H_4)_3P$, Cy_3P). Phosphines used in decomposition studies were purified by recrystallisation from propan-2-ol. Additionally, dpe and dmpe were synthesised in the laboratory. (dpma was prepared independently by Dr. R. Keat).

Preparation of 1,2-bis(diphenylphosphino)ethane - dpe[307]

Chopped lithium wire (1.02g, 147.8 m.g-atom) was added to a solution of Ph_3P (13.066g, 49.8 m.mole) in dried T.H.F. ($75cm^3$), under argon. The mixture was allowed to stir at ambient temperature for 3 hours. Within 5 minutes the solution had become opaque and deep-red in colour, (due to formation of $Li^+PPh_2^-$). A solution of 1,2-dichloroethane ($3.0\ cm^3$, 37.95 m.mole) in T.H.F. ($10cm^3$) was now stirred in slowly. After 30 minutes stirring, methanol ($25cm^3$) was cautiously added (with vigorous agitation) until the colouration was neutralised, and the whole poured into distilled water ($500cm^3$). A thick crust of off-white solid was formed. This was recovered by filtration, washed with water and then with methanol. Recrystallisation from boiling propan-2-ol gave fine white needles of dpe.

Analysis: found - C, 78.69%, H, 6.16% calcd. for $C_{26}H_{24}P_2$ - C, 78.38% H, 6.07%; recovery - 12.7g, 84% based on $C_2H_4Cl_2$; m.pt., 135°C lit. 136°C[307]

Preparation of 1,2-bis(dimethylphosphino)ethane - dmpe[312]

Ethylene (ca. 3g, 0.1 mole) was condensed into a steel bomb containing $Me_2P(S)\cdot P(S)Me_2$* (7.8g, 0.042 mole) and KI (0.2g). The bomb was maintained at 280° for 48 hours in an autoclave. Recrystallisation of the yellowish solid product - by hot filtration from boiling ethanol - gave ivory $Me_2P(S)CH_2P(S)Me_2$ (5.0g, 56%; m.pt 263°C) This was now added to Bu^n_3P (20 ml) and heated, under nitrogen, to 240°C in a 100ml flask. The fraction distilling at ca. 170° was collected as a pale straw-coloured liquid. $Me_2PCH_2CH_2PMe_2$ oxidises very readily on exposure to air, and was, therefore, stored in a sealed ampoule under nitrogen (Recovery - 2.1g, 33%).

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* Which had previously been prepared from $SPCl_3$ and MeMgBr [312b]

Aryllithium Reagents

Dichloroplatinum complexes were converted to arylplatinum analogues by treatment with the requisite aryllithium reagent.

Phenyllithium in Diethyl Ether[313]

Lithium metal (1.73g, 250.7m.g-atom) was extruded as a wire into hydrocarbon oil, and subsequently, chopped into small pellets (ca.5mm), in a stream of argon and allowed to fall into anhydrous diethyl ether (250ml) under an atmosphere of dried argon. To this suspension was cautiously added (at ambient temperature) with vigorous agitation, a solution of distilled bromobenzene (14.10g, 89.80 m.mole) in diethyl ether (30ml). The mixture was brought to gentle reflux and was so maintained, with stirring, for 16 hours. At this stage, all remaining lithium metal displayed a clean metallic surface, and the application of Gilman I test (vide infra) indicated the formation of organolithium in solution. The reaction mixture was now allowed to stand for sufficient time at room temperature to permit sedimentation of the brown solid suspension and the solution was finally decanted through dried glass-wool into a nitrogen-filled, calibrated, pressure equilibrating reservoir-funnel for determination, storage and subsequent use. Safe destruction of all unreacted metallic lithium was effected by rapid quenching by a large volume (ca. 150ml) of methanol.

4-lithiotoluene (p-tolyllithium) in Diethyl Ether

A solution of purified 4-bromotoluene (15.69g, 91.73 m.mole) in anhydrous diethyl ether (30ml) was dropwise added to a stirred dispersion of finely chopped extruded lithium metal (1.6g, 231.9 m.g-atom) obtained as previously described in anhydrous ether (250ml) under an atmosphere of dried argon. The mixture was stirred at gentle reflux for five hours, until a bright metallic lustre was exposed on the surface of the lithium pellets. Gilman I test indicated the presence of organolithium. After being allowed sufficient time at ambient temperature for sedimentation of suspended solids, the solution was decanted through dried glass wool into a nitrogen-filled, calibrated, pressure-equilibrating reservoir-funnel for determination, storage and subsequent use. Unreacted metallic lithium was destroyed by rapid addition of a large volume (ca.150ml) of methanol.

Determination of Organolithium Solutions

A modification of the Gilman double-titration technique[314] was used to obtain accurate determinations (reproducible to within 2%) of the effective concentration of aryllithium in its ether solution. Into one 25ml conical flask was placed ca.10ml distilled water, while into another was placed ca. 5ml pure* 1;2 dibromoethane. Both flasks were fitted with rubber septum caps and thoroughly purged with dried nitrogen (via hypodermic needles). Meanwhile a 2ml. hypodermic syringe was flushed with nitrogen, and used to accurately extract 1ml of aryllithium solution, which was injected directly into the distilled water and the mixture vigorously shaken. The resultant solution was then carefully titrated against 0.1M HCl using bromothymol blue (3 drops) as indicator, to determine the overall hydroxide ion concentration after hydrolysis of the organolithium. A further 1 ml aliquot of aryllithium was now accurately withdrawn and injected directly into the dibromoethane, thus effectively quenching the organolithium without the production of free hydroxide. After thorough

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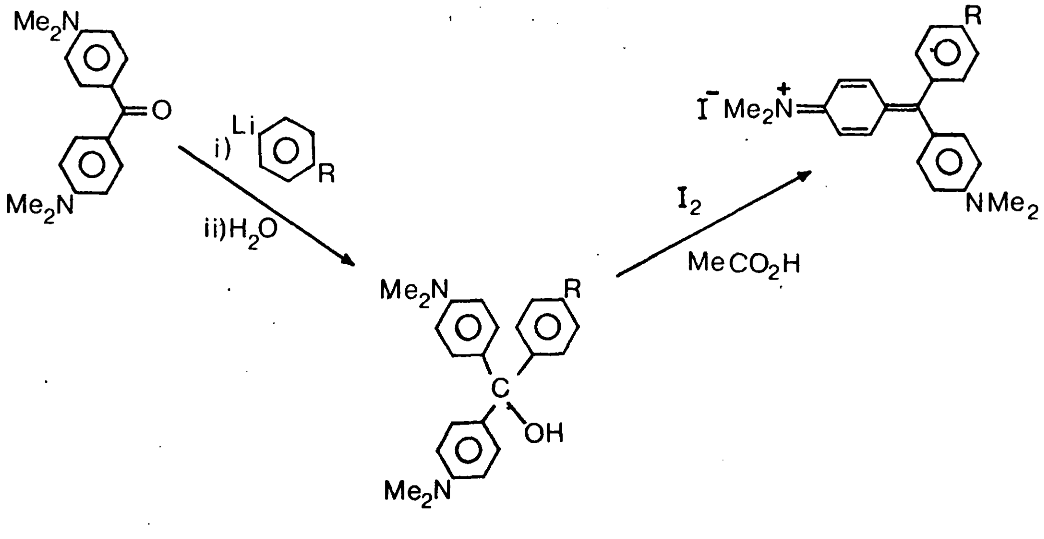
*Purified by passage down a short alumina column mixing, ca 10ml of distilled water was introduced, and the whole shaken vigorously for five minutes, to ensure efficient transfer of all residual base to the aqueous phase. This was now similarly titrated to determine the 'background' concentration of base in the diethyl ether solvent. Subtraction of this latter residual base determination (typically 0.05 M) from the former, total base determination (typically 0.4 M) yielded the free hydroxide concentration arising from organolithium hydrolysis alone, and hence the concentration of aryllithium itself.

Gilman I Colour Test[315]

Two test solutions were prepared: (a) 1% (by weight) of 4,4'-tetramethyldiaminobenzophenone (Michler's Ketone) in benzene; (b) 0.2% (b/w) iodine in glacial acetic acid. The test procedure was as follows:

To ca. 1cm^3 of solution (a) was added an equivalent volume of organolithium solution. After shaking, a further 2cm^3 (approx.) of water were added and the mixture thoroughly agitated. Finally, 1-2 cm^3 of solution (b) were added - persistence of intense green/blue colouration indicates the presence of organolithium in solution.

The essential features of the reaction may be represented:



Diarylplatinum (II) Complexes

Most satisfactory results were obtained using the established transmetallation route[30], with only slight modification - namely, that no benzene was used as co-solvent with diethyl ether. The technique employed was identical for all complexes, at least prior to final purification, and so a representative preparation is described in full.

Preparation of 1,2-bis(diphenylphosphino)ethane diphenylplatinum(II)- (dpe)PtPh$_2$ Ref. 317b

A 0.42 M solution of phenyllithium in diethyl ether (60ml; 25.2 m. mole) was dropwise added to a stirred suspension of 1,2-bis(diphenylphosphino)ethane dichloroplatinum(II) (4.00g; 6.02 m.mole) in anhydrous diethyl ether (100ml) at 0°C, under an atmosphere of dried nitrogen. On addition, the ivory suspension became pale orange. Stirring was maintained overnight (16 hr.) at ambient temperature (ca. 18°C). Gilman I Test at this stage indicated the survival of excess phenyllithium. This was destroyed by the cautious addition of 100 ml. ice-water, after the temperature of the reaction mixture had been lowered to 0°C. The yellow solid was isolated from the liquid phases by filtration, and infra-red analysis on a dried sample gave no indication of Pt-Cl containing species remaining. The aqueous and ether fractions were now separated and the aqueous fraction was washed with 3 x 50ml. aliquots of fresh ether. The combined ether portions were decolourised with activated charcoal, dried over anhydrous magnesium sulphate, and evaporated to small volume. Addition of an excess of 40-60 petroleum yielded further yellow solid.

Recrystallisation was best effected from hot ethanol by dissolving the maximum amount of solid in a volume of hot 1:1 ethanol/acetone, filtering through preheated apparatus and allowing the acetone to evaporate from the hot liquors. Two recrystallisations gave fine white crystals of 1,2-bis(diphenylphosphino)ethane diphenylplatinum(II) Analysis: Found - C, 61.15%, H, 4.68%; calcd. for $C_{38}H_{34}P_2Pt$ C, 61.04% H, 4.58%; recovery - 9.1g, 42.5% based on Pt; m.pt 243°C.

Prepared according to the same procedure were:

bis(diphenylphosphino)methane diphenylplatinum(II) - (dpm)$PtPh_2$[317b]

From the yellowish-white solid obtained from the reaction of (dpm)$PtCl_2$ with ethereal PhLi, fine white crystals could be obtained from boiling 1:1 ethanol/benzene, employing the hot-filtration technique. The solid is suspended in (typically 100ml) of solvent mixture, and the whole heated, with vigourous stirring. As soon as light reflux is attained, the mixture is filtered through preheated funnel and paper and collected in a preheated flask. This was generally allowed to stand overnight (protected from adventitious dust) to allow full sedimentation of crystals. Crystals of (dpm)$PtPh_2$ for crystallographic analysis were prepared by Soxhelet extraction into refluxing ethanol. (Analysis: found - C,60.63%, H, 4.38%; calcd. for $C_{37}H_{32}P_2Pt$ - C, 60.57%, H, 4.40% ; Recovery - 48%; m.pt 234°C).

bis(diphenylphosphino)methane di(4-tolyl)platinum(II) - (dpm)Pt(4-Me-$C_6H_4)_2$

The yellow crude material from the arylation reaction gave, after three recrystallisations (by hot filtration) from 3:1 ethanol/benzene fine cubic crystals, translucent with a faint yellow tinge.
Analysis: found - C,61.56%, H, 4.83%: calcd. for $C_{39}H_{36}P_2Pt$ - C, 61.49%, H, 4.76%; recovery - 42%; m.pt 224-5°C.

1,2-bis(dimethylphosphino)ethane diphenylplatinum(II) - (dmpe)$PtPh_2$

Successful recrystallisation from the ivory arylation product could be achieved (by hot filtration) employing either 3:1 ethanol/benzene or 1:1 ethanol/acetone mixtures. Fine, glistening white needles were obtained. Analyses: found - C, 43.21%, H, 5.27%; calcd. for $C_{18}H_{26}P_2Pt$ - C, 43.29%, H, 5.25%; recovery 34%; decomp. from 245°C.

cis-bis(triphenylphosphine)diphenylplatinum(II) - $(Ph_3P)_2PtPh_2$[30a]

Fine white needles could be obtained by successive hot-filtration purification of the initial ivory precipitate using 3:1 ethanol/benzene These were observed to adopt a greenish tinge on prolonged exposure to light, and were thus stored in the dark.
Analyses: found - C, 66.05%, H, 4.58% calcd. for $C_{48}H_{40}P_2Pt$ - C, 65.97%, H, 4.61%; recovery 57%; m.pt 143-4°C, dec., lit.144-160°C, dec.[30]

cis-bis(triphenylphosphine)di(4-tolyl)platinum(II) - Ph$_3$P)$_2$Pt(4-Me-C$_6$H$_4$)$_2$[316]

Use of 3:1 ethanol/benzene as recrystallisation solvent for the ivory-yellow crude material led to inclusion of benzene which could not be removed by sustained pumping. Consequently, 1:1 ethanol/acetone was employed to give the ultimate fine white needles. These displayed a light sensitivity paralleling that of the phenyl analogue, necessitating dark-storage.

Analyses: found - C, 66.62%, H, 4.97%; cald. for $C_{50}H_{44}P_2Pt$ - C, 66.58%, H, 4.92%; recovery - 61%; m.pt 106-7°C*

cis-bis(diphenylmethylphosphine)diphenylplatinum(II)-(Ph$_2$MeP)$_2$PtPh$_2$

Here, no initial precipitation occurred during the arylation reaction. The ether fraction, after drying and decolouration, was reduced to ca. 30ml. and a white solid was precipitated by the addition of 40-60° light petroleum. Recrystallisation, by hot filtration, from boiling ethanol gave fine white crystals. More careful recrystallisation in a lagged vessel under a slow current of nitrogen resulted in translucent rectangular cuboids.

Analyses: found - C, 60.40%, H, 4.78%; calcd. for $C_{38}H_{36}P_2Pt$ - C, 60.87%, H, 4.84%; recovery - 43%; m.pt. 163°C, dec.

cis-bis(diphenylmethylphosphine)di(4-tolyl)platinum(II) - (Ph$_2$MeP)$_2$Pt(4-MeC$_6$H$_4$)

The grey-white solid isolated from the arylation yielded, after successive recrystallisations from 1:1 ethanol/acetone, pale grey crystals of $(Ph_2MeP)_2Pt(4\text{-}Me\text{-}C_6H_4)_2$. The grey colour was attributed to

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*The reported decomposition point of 160-61°C is at variance with these observations - Ref. 316

slight contamination by persistent colloidal platinum which had survived from the preparation of $(Ph_2MeP)_2PtCl_2$ by the direct method ($PtCl_2$ + Ph_2MeP in refluxing ethanol).

Analyses: found - C, 60.53%, H, 5.01%; calcd. for $C_{40}H_{40}P_2Pt$ - C, 61.61%, H, 5.17%; Recovery - 38%; m.pt. 187-88°C, dec.

cis-bis(tri-4-tolylphosphine)diphenylplatinum (II) - $[(4\text{-}Me\text{-}C_6H_4)_3P]_2PtPh_2$

The initially ivory precipitate could be refined by successive hot filtrations using 1:1 ethanol/acetone solvent mixtures, to yield, ultimately fine white granular crystals

Analyses: found - C, 67.78%, H, 5.55%: calcd. for $C_{54}H_{52}P_2Pt$ - C, 67.69%, H, 5.47%; recovery - 35%; m.pt. 157°C, dec.

Attempted preparations by this route were:

bis-(tricyclohexylphosphine)diphenylplatinum (II)- $(Cy_3P)_2PtPh_2$

Starting material, trans-$(Cy_3P)_2PtCl_2$, was recovered unchanged (quantitatively) after four days treatment with 50% molar excess of ethereal PhLi at ambient temperature and at reflux.

1,2-bis(diphenylphosphino)ethane di(4-tolyl)Platintum(II) - $(dpe)Pt(4\text{-}Me\text{-}C_6H_4)$

Treatment of $(dpe)PtCl_2$ with ethereal 4-tolyllithium as described above for the phenyl analogue led to the isolation of an ivory solid. The i.r. spectrum of this material, however, indicated that it contained a relatively small amount of tolylplatinum species (These all display a characteristic sharp intense absorption at $800\pm5cm^{-1}$). Attempts at recrystallisation from a variety of solvent combinations apparently resulted in decomposition (dark brown colouration) and produced quantities of material insufficient to justify further purification for decomposition studies. A repetition of the procedure gave no improvement. The anomalous inaccessibility of this compound by this route remains unexplained.

Additional

Bis(diphenylphosphino)methylamine di(4-tolyl)platinum(II) - (dpma)Pt(4-Me-C_6H_4) - was prepared analogously, but has not yet been purified.

Bis[(diphenylarsino)methane]diphenylplatinum(II) - (dam)$PtPh_2$ - has also been obtained in an impure state (*via* the corresponding dichloride by the general route).

Zerovalent Platinum Complexes

Preparation of Bis-[1,2-bis(diphenylphosphino)ethane]platinum(0)[251]

(dpe)$PtCl_2$ (2.09g, 3.14 m.mole) was added to a stirred suspension of dpe (2.80g, 7.03 m.mole) in 2:1 ethanol/water (100ml) under a nitrogen atmosphere. The mixture was refluxed for one hour, by which time most of the solid material had dissolved, yielding a pale yellow-green solution. A saturated aqueous solution of $NaBH_4$ (20ml) was now cautiously added. From the first addition, immediate precipitation of a dense lemon-yellow solid took place. This was recovered by filtration and thoroughly dried *in vacuo*. Subsequent recrystallisation from 4:3 benzene/methanol, under nitrogen yielded glistening golden-orange plates of $(dpe)_2Pt(0)$.

Analyses: - C, 63.35%. H, 4.93%; calcd. for $C_{52}H_{48}P_4Pt$ - C, 62.96%, H, 4.88%; recovery - 71%; m.pt 251-3°C

Attempted Preparation of Bis(diphenylphosphino)methane platinum(0)

Attempts to prepare $(dpm)_2Pt(0)$ by the above route consistently led to precipitation of a rust brown solid material which could not be recrystallised. Its identity was not established, save that Ph_2MeP was a product of its thermolysis. However, treatment of $(dpm)PtCl_2$ and an excess (in ethanol) of dpm with theanolic KOH, according to the method of Ugo *et al*[252] resulted in the precipitation of a lemon-yellow solid. The solubility of this material was not good, and recrystallisation attempts from benzene, ethanol, methanol, acetone (and various combinations of these) did not lead to materials with satisfactory analyses for $(dpm)_2Pt(0)$ in significant amounts. In addition, a faint odour, ascribable to Ph_2MeP accompanied recrystallisation attempts from hot solvents.

General

The infra-red, n.m.r. and mass spectrometric characteristics of all complexes were recorded as a matter of course. Full mass spectrometric parameters for many of these species have been collated elsewhere[317].

Section B: Instrumental

Melting points were measured on a Koffler hot-stage, and are uncorrected.

^1H n.m.r. parameters were recorded on JEOL C-60HL or Varian HA100 instruments, and for more insoluble compounds by pulse-Fourier-transform accumulation using a Varian XL100 instrument. This latter was also employed for collection of ^{31}P data.

Mass spectrometric measurements were performed on an AEI MS12 instrument at 70 eV.

Infra-red spectra of solid complexes dispersed in KBr discs were obtained on a Perkin-Elmer 225 spectrophotmeter. Gas-phase analyses were carried out on a Perkin-Elmer 577 instrument using a 50mm path gas-cell with KBr windows.

Gas chromatographic determinations were performed by a Pye Series 104 gas - chromatograph equipped with heated injection and flame ionisation detection facilities and a linear oven-temperature programmer.

Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-1B instrument at $16^{o}.min^{-1}$ and simultaneous thermal gravimetry and differential thermal analysis were effected on Stanton-Redcroft equipment, at a heating rate of $4^{o}.min^{-1}$. Both instruments employed nitrogen atmospheres.

Section C: Decomposition

Part I - Condensed Phase Studies

Intimate solid mixtures both of complexes and of complexes and phosphines were prepared by freeze drying of appropriate benzene solution mixtures. Where instability in solution precluded this (such as mixtures of $(Ph_3P)_2PtAr_2$ and Ph_3P) mixtures were prepared by grinding together in an agate mortar.

a) Instrumental Methods

Differential thermal techniques revealed a general trend for the pure complexes; viz. a preliminary melting endotherm which was rapidly overwhelmed by an overlapping sharp decomposition exotherm. These irreversible procedures were accompanied by an accelerating weight loss (TGA) which slowly diminished after 40-60 min to a continuing gradual effusion. At the higher heating rate used in DSC studies, the initial endotherm for the complexes cis-$(Ph_3P)_2PtAr_2$ (R = Ph; 4-Me-C_6H_4) is swamped by the decomposition exotherm. The onset of the exotherm is, however, markedly less rapid, and with R = Me-C_6H_4, displays a small transient endothermic inflection.

TGA showed no demarcation between primary and secondary processes; since TGA depends on the volatilisation, at atmospheric pressure, of decomposition products, some of which were initially produced below their standard vaporisation temperatures, the observed gravimetric profiles will be somewhat distorted from the true decomposition pattern of product loss.

Differential thermal techniques demonstrated that for the complexes in the presence of phosphine, the preliminary thermal effect is endothermic - attributable to fusion of the phosphine, and dissolution of complex in the melt. This is followed, but not, generally, immediately, by an exothermic effect which is accompanied by the onset of weight loss - and, by inference, decomposition.

b. Product Analyses

Thermolyses were carried out under an atmosphere of pure nitrogen (or argon) in the pyrex apparatus portrayed in Fig. 6.1. The thermolysis

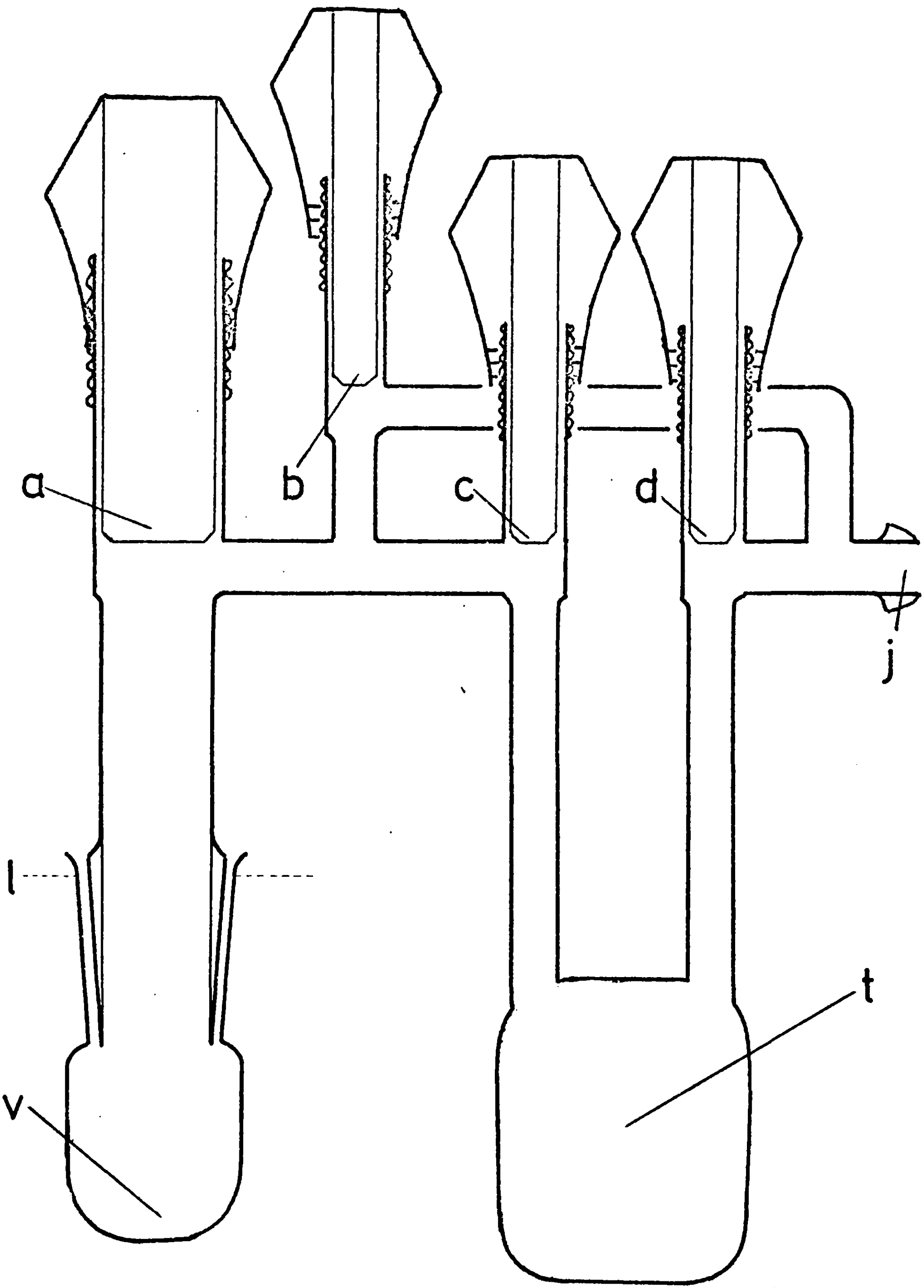

Figure 6.1

Apparatus employed for product recovery from condensed-phase thermolyses of L_2PtAr_2

temperature was selected slightly in excess of that at which decomposition onsets (from DSC or DTA data.) After an appropriate time (by which TGA results suggested that major weight loss would be complete), the volatile products were recovered by trapping at 77K at high vacuum ($\leqslant 10^{-3}$torr.)

The following procedure was adopted (consult Fig. 6.1.) The complex (or mixture) was weighed (typically 100-150mg) in the vessel V This was attached to the main skeleton of the apparatus - as shown- which was itself incorporated into an (alternatively) inert-atmosphere/ high-vacuum via ball-joint j. The system was thoroughly evacuated, isolated from the pumping system, and then carefully filled to one atmosphere with dried nitrogen (or argon). Nitrogen, for this purpose, was additionally dried by passing through a spiral trap at 77K. Trap t was immersed in liquified nitrogen. All valves, except bypass b, remained open to ensure pressure equilibration. Decomposition was initiated by immersion of V to level 1, in a rapidly-stirred silicone oil bath at a pre-equilibrated temperature. After the appropriate period, the system was isolated from the constant-pressure gas system, and cautiously re-evacuated (to obviate violent bubbling from the molten residues and consequent loss of sample from V. All exposed glass surface between 1 and c was maintained at high temperature (ca. 100°C) throughout the transfer, by heating tape.

When transfer had been effected, all valves were closed and heating sources were removed. Inert atmosphere was reintroduced; first, via valves b and a to the decomposition vessel V which was detached for weighing and recovery of residual materials; second (after sealing a) via b and c into the cold-trap t The temperature in the trap was next raised to 273K by immersion in ice water. Valve-core c was removed from its housing and replaced by a rubber septum. (A slightly positive inert gas pressure in the system ensured the exclusion of atmospheric contaminants during this procedure.) A quantity of n-decane, as a GLC internal standard, was accurately introduced, and the entire contents of t were dissolved in (2-3ml) diethyl ether. The solution was withdrawn by syringe and injected into a septum-sealed and nitrogen flushed ampoule, which was stored at -5°C prior to analysis by GLC.

1.0ml aliquots (minimum of 5) were analysed, and peak areas of product fractions were compared with that of the quantitatively-known internal standard to determine precise product yields (2% for biaryls, 4% for arenes). Calibration experiments demonstrated that product peak areas were proportional to concentrations (in mg.ml.$^{-1}$). The detector sensitivity of the instrument was the same (to within 2%) for arenes, biaryls and standard, but lower for arylphosphines (correction factor 1.34) Peaks could be integrated by triangulation or by excision from the chart[318] and weighing. Use of both techniques on the same sample led to results that differed by no more than 2%. The latter (peak-weight) technique was found to be less time-consuming, and was generally employed. Agreement was good between weight-losses observed directly (from the residual weight) and those determined from GLC observations. Elemental analyses of the residues, although indicative of no (apparent) regular stoichiometry, also corresponded with estimations from GLC measurements of molar losses.

Chromatographic separation and quantification of aryl-derived products were carried out on a 5-foot, 8% Apiezon L/Gas-Chrom Q (100-120 mesh) glass column. Temperature programme: isothermal at

60^{o} for 60 sec.; maximum 200^{o}, linearly at 15^{o}. min^{-1}; isothermal at 200^{o} for 10 min. Monotertiary phosphine products were monitored using a 5-foot, 2% OV-1/Gas-Chrom Q (100-120 mesh) column, again with internal n-decane as standard. Temperature programme: isothermal at 60^{o} for 60 sec.; maximum 250^{o}, linearly at 15^{o}. min^{-1}.

Attempts to assign the nature of the glassy, red brown residues from the decomposed pure complexes were, as previously described, less than conclusive. Infra-red analysis (of the solids) leading to indications of <u>ortho</u>-metallation have already been outlined (Chapter 3). ^{1}H n.m.r. spectra displayed complicated, unresolved absorptions, predominantly in the aromatic region. Solutions of the residues in benzene or chloroform were spotted on to 6" thin-layer (alumina) chromatographic plates, and eluted accordingly. Development of the plates show no resolution of components; a continuous smear resulted. Careful attempts at crystallisation, both by gradual evaporation under nitrogen (from toluene or chloroform) or by slow cooling (again under nitrogen) of toluene solutions to 193K produced, apparently unchanged, glassy solids. For estimation of residual, metal-bound phenyl groups, the following procedure was adopted. An amount (typically 8-10mg) of residue was dissolved in (3.0ml) benzene-free toluene (see Part II) in a septum-capped ampoule. To the solution, an appropriate amount of n-decane (2.0 μl) was added as internal standard. The solutions were now quenched by addition of conc. aqueous hydrochloric acid (3 ml.), and stored for 14 days at -5^{o}C (See part II). Benzene was determined by GLC analysis.

Column: 5-foot, 8% Apiezon L/Gas-Chrom Q (100-120 mesh); temperature programme: isothermal at 80° for 60 sec.; maximum 150° linearly at 15° min^{-1}.

The identity of residues from phosphine-aided decompositions could be established by more conventional means. The most stable, $(dpe)_2Pt(0)$ was identified by its elemental analysis (found - C, 62.47%, H, 4.96%; calcd. for $C_{52}H_{48}P_2Pt$ - C, 62.96%, H, 4.88%). The melting point (252°C; lit. 253°C), DSC profile i.r. spectrum and mass spectrum (which shows a strong molecular ion, M+, and characteristic doubly charged M^{2+} ion) from decomposition residue (an orange solid, bright yellow when powdered) were all identical to those of an independently synthesised sample. The dpm analogue was apparently too thermally unstable to survive in high quantity, but the mass spectrum of the appropriate decomposition residues displayed a weak ion centred at mass 963 (calcd. for $(dpm)_2Pt = 963$) with characteristic platinum-isotope pattern. (The remainder of the mass spectrum was dominated by fragmentation patterns of dpm, Ph_3P and Ph_2MeP). $(Ph_3P)_3Pt(0)$ was not the sole intact product of decomposition of $(Ph_3P)_2PtAr_2$ in the presence of Ph_3P; elemental analysis reflected the limited decomposition observed (by volatile product analysis). However, dissolution of the residue in acetone and addition of <u>iso</u>-pentane precipitated a flocculent yellow solid which, after recovery (80%) and drying, analysed satisfactorily for $(Ph_3P)_3Pt(0)$ (found - C, 65.89%, H, 4.53%; calcd. for $C_{54}H_{45}P_3Pt$ - C, 66.05%, H, 4.62%) The i.r. spectrum corresponded with that reported[252].

Part II - Solution Studies

(a) Solvent purification and Solution Preparation

Commercially supplied toluene (AnalaR) contains up to 1% (b/w) benzene (in addition to xylenes). Such a quantity is significant compared with the possible concentrations of toluene-solution decomposition products of L_2PtAr_2 systems, and since benzene may, peradventure, be included among these, it was necessary that its presence as a solvent impurity be rendered insignificant. This was achieved by careful distillation of toluene, employing a 40cm stainless steel spinning-band distillation column, equipped with a column heater. Toluene was first dried over sodium wire, and, during distillation, was stored over activated 5A molecular sieves. The distillation column itself was open to the atmosphere via a 6" x ½" diameter column packed with silica-gel blue. From 80ml. toluene, gradual distillation of the initial 30ml. reduced the concentration of benzene below the detectable level at the instrument sensitivity required for the GLC analyses of ultimate products. The next 40ml of distillate was essentially impurity-free.

Solutions were accurately prepared in volumetric glassware which was thoroughly washed, and dried in a vacuum desiccator. The solubility of $(Ph_3P)_2PtPh_2$ was determined to be 2·1 $mg.ml^{-1}$ at 25°C. Accordingly, the resulting concentration (ca. $2 \times 10^{-3}M$) was used throughout the study for comparative purposes.

For preparation of decomposition samples, a standard procedure was invariably followed. A quantity of organoplatinum complex (40-50mg) was accurately weighed into a 25ml volumetric flask (followed, if required, by an appropriate amount of excess phosphine). A teflon-coated magnetic stirrer bar (8mm) was introduced. The flask was now fitted with a rubber septum, and encased in aluminium foil (to exclude light). A minimum period of 8 hours purging with dried nitrogen (<u>via</u> 1 mm. hypodermic needles) now ensued. After purging, the nitrogen outlet needle was removed and 23-24ml of purified toluene was injected (taking care to exclude air bubbles), and stirring was continued for 16 hours (overnight) to ensure full dissolution. (The extent of decomposition during this operation was generally insignificant). The septum cap was removed, and the magnetic stirrer bar withdrawn, with careful rinsing. A microsyringe was employed to accurately introduce n-dodecane as internal standard (10 μl) and the solution was made up to the calibration. A glass stopper was fitted and the solution thoroughly shaken. A 50ml syringe was used to inject the contents of the flask into the decomposition vessel (Fig. 6.2 - see section b.)

(b) Thermal Decomposition and Analysis Procedures

Solution thermolyses were carried out in the pyrex apparatus stylised in Figure 6.2. This was first thoroughly purged with dried nitrogen for 16 hours, <u>via</u> inlet needle <u>i</u> and with taps $\underline{t}_1$ and $\underline{t}_2$ (greaseless, teflon barrel type: 2mm aperture) both open. (Outlet <u>o</u> was connected to a gas bubbler). When purging was completed, $\underline{t}_2$ was closed, and nitrogen in the supply line was exhausted through a further bubbler to maintain a slight positive pressure of gas in the vessel. The solution was now injected <u>via</u> septum port <u>s</u>. On withdrawal of the needle, $\underline{t}_1$ was closed, $\underline{t}_2$ was opened, and the vessel

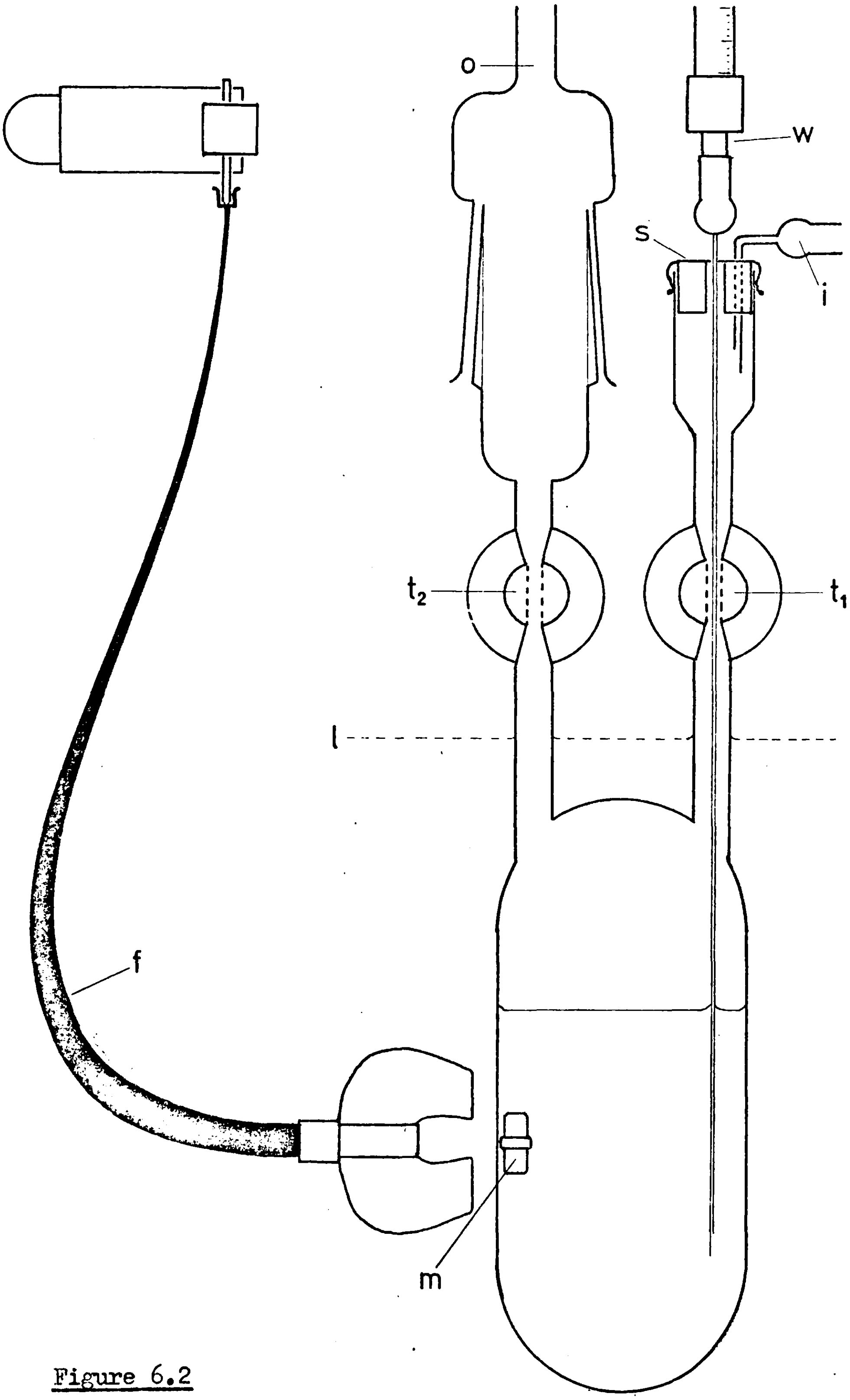

Figure 6.2

Apparatus employed for thermal decomposition of L_2PtAr_2 in solution immersed (to level l) in the thermostatically controlled water bath, from which light was excluded. Vigorous stirring, to ensure homogeneity was commenced *via* the flexible-drive stirring apparatus f (incorporating electric motor, automobile speedometer cable, and a small horseshoe magnet) and the 10mm teflon-coated internal magnet m. Timing, by digital electric chronometer (Schuco), was commenced when exhaustion of expanding nitrogen (through the outlet bubbler) ceased - indicating temperature equilibration in the vessel. Tap t_2 was then closed. Tap t_1 was momentarily opened to allow reequilibration of nitrogen pressure in the supply line and vessel, and resealed. This was the normal status of the apparatus during decomposition, except during sampling.

For sampling, a 1.0ml capacity hypodermic syring w, fitted with a 6" fine-bore needle was thoroughly rinsed with pure toluene and dried with compressed air. It was then inserted *via* the septum into the injection lock, filled with nitrogen, withdrawn and exhausted. This operation was repeated twice to ensure that no adventitious oxygen be introduced into the main vessel. The needle was now reinserted, tap t_1 was opened, and the needle passed through the bore into the solution. At this stage, the chronometer reading was noted and, simultaneously, a portion of solution (0.5ml) was drawn into the syringe w. This was withdrawn and injected directly into *ca.* 1ml. of conc. aqueous hydrochloric acid in a 9.5 x 1.0cm (diameter) pyrex test tube, which was sealed with a rubber septum (Tap t_1 is meanwhile closed). The quenched sample was immediately consigned to storage at -5°C to await GLC analysis. The entire operation, from withdrawal to quench, requires 18±2 seconds; there is, hence, a 10 second uncertainty in sampling time. The midpoint of this procedural period is the time used when plotting. The syringe was now prepared for the next withdrawal.

Calibration experiments showed that products could be quantified by this method with an error of 2% for biaryls and 4% for arene (benzene, only, here). Separation was achieved using a 5-foot, 8% Apiezon L/Gas-Chrom Q (100-120 mesh); Temperature programme: isothermal at 80° for 60 sec.; maximum 190°, linearly at 15° min^{-1}; isothermal at 190° for 12 min. (Where biphenyl is the highest-boiling component, a final isothermal period of only 6 min. is necessary).

Optimum conditions for quenching were also established by calibration experiments. The HCl cleavage of platinum-aryl bonds to yield arene and the dichloroplatinum species, is sluggish in the latter stages by this route (since it depends, for one thing, on the partition of HCl between the two solvents), not being complete even after 8 hours at room temperature. In order to prevent quenching being accompanied by a significant amount of further reductive elimination, each sample was refrigerated (-5°C). This effectively suppressed decomposition by the primary route, but 100% quenching required 16-18 days (minimum) storage.

Since benzene is a quenching product from phenylplatinum complexes, the (secondary) production of benzene during their thermal decomposition had to be investigated by a different technique. This was achieved by trap-to-trap vacuum distillation, using an apparatus that was essentially identical with that displayed in Figure 6.1, with vessel v replaced by a pyrex test-tube with a suitable joint. Into this was placed a measured quantity (5ml) of unquenched residual solution. After connection to the vacuum line, this was cooled to 273K, and the low-boiling fractions carefully distilled under high vacuum into the cold-trap at 77K. Calibration experiments showed that >98% of benzene present in solution could be transferred, under these conditions, along with solvent toluene. A further internal standard (n-decane) was now accurately added (10μl), the precise volume of transferred liquid was determined, and the concentration of transferred benzene (and hence of original, residual benzene) was computed by quantitative GLC analysis, as before. (The transfer and recovery techniques are essentially those described for the condensed phase thermolytic studies - vide supra)

The amber or red (or, occasionally, where free phosphine is present, yellow) residual solutions, have not, as yet, received extensive attention. The amorphous solids which remained after distillations were generally not analysed further, save by i.r. spectroscopy in the cases alluded to in the text. The amounts recovered were small (5-10mg) and will be appreciably contaminated by higher-boiling fractions (biaryls and n-dodecane).

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