SOME STERIC, CONFORMATIONAL AND ENTROPY EFFECTS OF TERTIARY PHOSPHINE LIGANDS

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Early in 1969 we set out to generate unusual transition metal chemistry using sterically demanding tertiary phosphine ligands. Up to that time tertiary phosphine-transition metal chemistry had developed rapidly but it was generally not possible to estimate the relative importance of the electronic and steric effects of a tertiary phosphine on the chemistry of its complexes [1]. We hoped to learn more about steric effects and make them dominant over electronic effects simply by using very bulky tertiary phosphines. In this way we also expected to generate and stabilize unusual species. Bulky groups have of course been widely used to stabilize unusual organic compounds, obvious examples being free radicals.

We first chose to study tertiary t-butylphosphines not only because the t-butyl group is bulky but also because we envisaged that the ^{1}H NMR pattern of the t-butyl hydrogens would be very useful in studying the complexes. In 1963 we had discovered a new method of determining the stereochemistry of transition metal-tertiary phosphine complexes [2], particularly methylphosphine complexes, due to the occurrence of a 1 : 2 : 1 methyl triplet pattern if the phosphines are complexed mutually *trans* (an example of "virtual coupling" as it was known in those days) but a doublet pattern(s) for other arrangements. The number of triplets or doublets also depended on the presence (or absence) of a plane of symmetry through the metal—phosphorus bond. This method has been used thousands of times since then by ourselves and many other researchers. We anticipated that it could be similarly used to determine the stereochemistry of and generally to characterize tertiary t-butylphosphine-metal complexes.

Some of the results we have obtained in this work have been far more interesting than we could possibly have hoped for. Particularly interesting and satisfying to me are the subtle ways in which sterically demanding substituents stabilize and promote ring formation e.g. in cyclometallation reactions and in the formation of large chelate rings.

What I have done in this paper is to survey the more important results of our research. Others have of course developed some very interesting chemistry using bulky tertiary phosphine ligands and I apologise for giving this chemistry

only a brief (or no) mention. I have written the survey in the form of a series of generalizations (i—ix) on the effects of sterically demanding tertiary phosphine ligands, with examples.

(i) *Very bulky tertiary phosphines such as those of type PBu$_2^t$R (R = alkyl or aryl) will not coordinate in mutually cis-positions.* Less sterically demanding tertiary phosphines (PMe$_3$, PEt$_3$, PPh$_3$, etc.) will generally coordinate in either mutually *cis-* or *trans*-positions but ligands such as PBu$_3^t$ or PBu$_2^t$R will almost always go mutually *trans*, hence 1 : 2 : 1 triplet ^{1}H NMR {-C(CH$_3$)$_3$} patterns are observed. Such ligands have very large cone angles [3,4]. Only under special circumstances can PBu$_2^t$R ligands be made to coordinate mutually *cis*. Thus if R = H the normal product with for example platinous chloride is *trans*-[PtCl$_2$(PBu$_2^t$H)$_2$] but the corresponding *cis*-isomer can be prepared photochemically [5]. Also the diphosphine *cis*-1,2-{Bu$_2^t$PCH$_2$}$_2$C$_6$H$_4$ gives chelates of type *cis*-[PtX$_2$-^{1},2-{Bu$_2^t$PCH$_2$}$_2$C$_6$H$_4$] (X = H or Cl). Presumably the seven-membered chelate ring allows the bulky PBu$_2^t$ groups to stay sufficiently far apart [6].

(ii) *There is strong non-bonding interaction between a bulky tertiary phosphine and other ligands e.g. Cl, Br, CO, alkyl etc. on the metal.* The best evidence for this comes from variable temperature ^{31}P NMR spectroscopy. Thus at room temperature the ^{31}P-{^{1}H} NMR spectrum of *trans*-[RhCl(CO)(PBu$_2^t$Et)$_2$] is broad but on cooling down to —60°C three sharp patterns (two A$_2$X and one ABX) result. These corresponds to the three rotamers (I, II and III) [7].

$$(I) \qquad\qquad (II) \qquad\qquad (III)$$
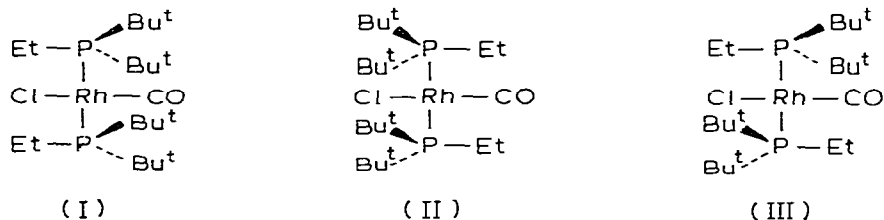
There is a high energy barrier to the eclipsing of a P—Bu^t and an Rh—Cl or Rh—CO bond and rotation around the P—Rh bond becomes very slow or ceases at low temperatures. With complexes of PBu$_2^t$R where R is less sterically demanding than methyl, ethyl, or phenyl, e.g. if R = H or C≡CPh, the energy barrier is even higher and sharp resonances due to the rotamers are observed at room temperature [5,8]. As discussed later restricted rotation around the metal—phosphorus bonds with the associated effects on internal rotational entropy is important in large chelate ring formation and cyclometallation.

(iii) *In order to reduce steric strain coordinatively unsaturated complexes are often formed.* The first examples we found were with rhodium(III) and iridium(III). These two valency states, with d^6-electron configurations, usually favour octahedral coordination e.g. their trichlorides with PEt$_3$ give complexes of type [MCl$_3$(PEt$_3$)$_3$]. However, RhCl$_3$ when treated with PBu$_2^t$R or PBu^{t}R$_2$


$$(IV)$$
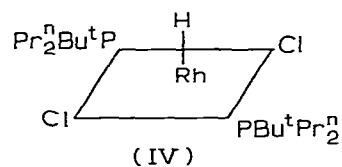
(R = alkyl) gives five coordinate hydrides [RhHCl$_2$L$_2$] [9,10]. The crystal structure of [RhHCl$_2$](PBu^{t}Pr$_2^n$)$_2$ shows it to be square pyramidal (IV) [9]. Iridium behaves similarly. Complexes of type [IrHCl$_2$L$_2$] (L = PBu$_2^t$R) are particularly interesting since they are highly coloured (purple) and the ^{1}H NMR shift of the hydride is the largest yet observed (>60τ) [11,12]. The intense colour is probably due to electronic excitations to a low lying vacant orbital. One of the theories to explain the high field shift of transition metal hydrides requires the "mixing in" of an excited state into a ground state [13,14]. The presence of an unusually low-lying vacant orbital presumably allows the mixing in to an exceptional degree. The absence of a *trans*-ligand probably results in an unusually short iridium—hydrogen bond which will also give a high τ-value [12]. Such five-coordinate iridium(III) complexes react rapidly with small rod-like molecules such as CO or RNC to give colourless six-coordinate adducts for which the hydride resonance has dropped to about 20τ [15]. Several other research groups have used bulky PR$_3$ ligands to stabilize rhodium(III) and rhodium(I) systems with low coordination numbers [16,17] and also complexes of types M(PR$_3$)$_x$ M = Ni, Pd, Pt; x = 2 or 3 [3,18—22].

(iv) *The other associated ligands are preferably small.* Bulky tertiary phosphines are very sterically demanding and if the other ligands are small then steric strain is reduced. Hydride is the smallest ligand and hydride formation and stabilization is particularly widely occurring with bulky PR$_3$ ligands. Thus replacement of a chloride ligand by hydride reduces the steric strain and leads to stabilization. Hydride formation and coordinative unsaturation often occur together. As discussed under (iii) above, treatment of rhodium(III) or iridium(III) trichlorides with PBu$_2^t$R (R = Me, Et, etc.) gives coordinatively unsaturated monohydrides [MHCl$_2$(PBu$_2^t$R)] [9,10]. With even more bulky phosphines PBu$_2^t$Ph or PBu$_3^t$ under similar conditions, coordinatively unsaturated dihydrides [MH$_2$Cl(PBu$_2^t$R)$_2$] (R = Bu^t or Ph) form [23]. Bulky tertiary phosphines can also cause kinetic stabilization. Thus many monohydrides of platinum(II) of type *trans*-[PtHXL$_2$] (X = anionic ligand, L = PR$_3$ or AsR$_3$) are known but attempts at further reduction to a dihydride usually lead to decomposition. However, if L is a bulky tertiary phosphine, PBu$_2^t$R, P(cyclohexyl)$_3$ etc. stable dihydrides *trans*-[PtH$_2$(PBu$_2^t$R)$_2$] etc. are readily prepared [24]. Moreover, by the sodium borohydride reduction of *cis*-[PtCl$_2$1,2-{Bu$_2^t$PCH$_2$}$_2$-C$_6$H$_4$] the first *cis*-dihydride of platinum (II) was prepared [6].

Recently Bu$_2^t$P(CH$_2$)$_3$PBu$_2^t$ [25] has been used to prepare *cis*-platinum dihydrides. Another example of kinetic stabilization is with iridium pentahydrides, [IrH$_5$L$_2$]. With L = PMe$_3$, PEt$_3$ or PMe$_2$Ph they are rather labile but with L = PBu$_3^t$, PBu$_2^t$Ph or PBu$_2^t$(*p*-tolyl) they are particularly robust and easily handled [23].

(v) *The kinetic stabilization of intermediates.* There are many examples in organic chemistry where bulky substituents have been used to stabilize (trap) intermediates. Not surprisingly therefore we have found several examples where bulky tertiary phosphine ligands stabilize compounds of a type which are not observed but might have a transient existence with smaller tertiary phosphines. Thus a common method of converting a tertiary phosphine-transition metal chloride complex to the corresponding hydride is by sodium borohydride reduction. An intermediate transition metal-borohydride complex is not usu-

ally detected. However, when a five coordinate iridium(III) hydride [IrHCl$_2$(PBu$_2^t$Me)$_2$] (V) is treated with sodium borohydride the dihydrido tetrahydroborate complex [IrH$_2$(BH$_4$)(PBu$_2^t$Me)$_2$] (VI) is formed. This slowly decomposes even in benzene to give the iridium pentahydride [IrH$_5$(PBu$_2^t$Me)$_2$]. The corresponding complex [IrH$_2$(BH$_4$)(PBu$_3^t$)$_2$] shows no tendency to decompose in benzene solution [23,26].
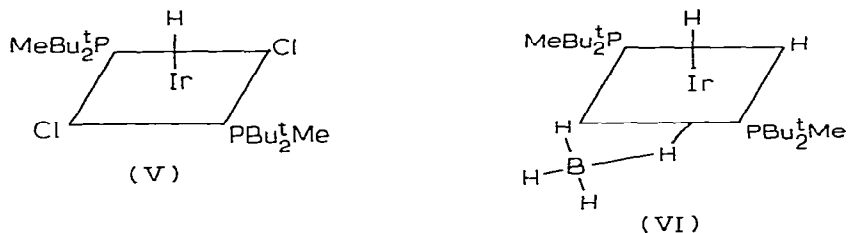
One can also trap or stabilize unusual valency states. Thus when a bulky phosphine such as PBu$_2^t$Et is added to an ethanolic RhCl$_3$ solution at ca. 0°C the rhodium(II) species *trans*-[RhCl$_2$(PBu$_2^t$Et)$_2$] forms rapidly. Under more vigorous conditions (heating) this rhodium(II) species is converted into the square pyramidal rhodium(III) hydride [RhHCl$_2$(PBu$_2^t$Et)$_2$][10]. The first examples of mononuclear iridium(II) complexes were also prepared [27—29]. Carbonylation of a sodium chloroiridate solution followed by heating with PBu$_2^t$-(2-methoxyphenyl) causes demethylation and gives the yellow iridium(I) carbonyl complex VII. This in air, and after an induction period, is converted into the blood-red iridium(II) complex VIII with loss of carbon dioxide [27—28]. Alternatively, treatment of iridium trichloride with PBu$_2^t$(2-methoxyphenyl) gives the purple five coordinate iridium(III) hydride IX which in air
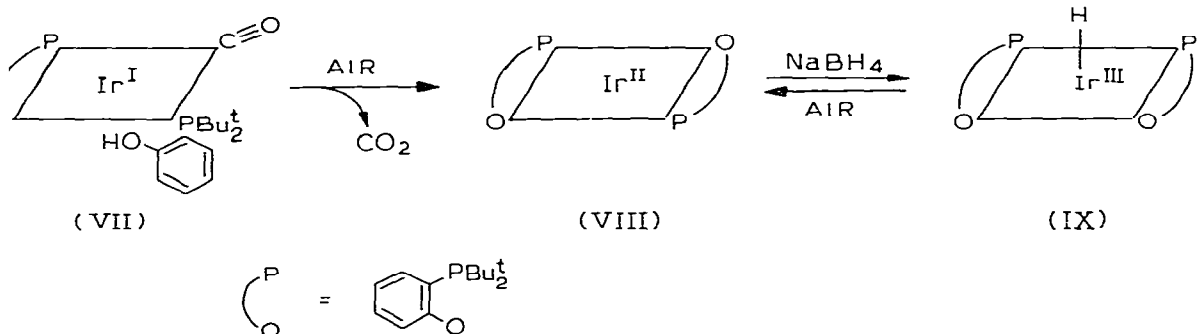

is "oxidized" to the iridium(II) complex VIII [27—29]. The iridium(II) complex VIII is a reversible carrier of dioxygen. However, the dioxygen complex is slowly converted into a new iridium(III) complex in which one of the t-butyl groups has been metallated [28,29]. These and other reactions illustrate some of the very unusual chemistry caused by bulky tertiary phosphine ligands.

(vi) *The decarbonylation of alcohols*. In 1961 Chatt and I showed that alcohols were a convenient source of hydrogen and of carbon monoxide, for the synthesis of transition metal hydrides, metal carbonyls and metal carbonyl hydrides [30,31]. Many of these reactions were promoted by bases, e.g., the ethoxide ion. Such reactions are common with metal complexes containing bulky tertiary phosphine ligands. Thus complexes of type [RhHCl$_2$(PBu$_2^t$R)$_2$]

react in seconds with methoxide ion in methanol at $20°C$ to give *trans*-[$RhCl(CO)(PBu_2^tR)_2$] [10]. Also, the five coordinate hydrides [$IrHCl_2(PBu_2^tR)_2$] react with boiling 2-methoxyethanol to give *trans*-[$IrCl(CO)(PBu_2^tR)_2$] [12]. Ruthenium trichloride reacts with PBu_2^tR or $P(cyclohexyl)_3$ (L) in 2-methoxyethanol to give the five coordinate carbonyl hydrides [$RuHCl(CO)L_2$] [32,33]. I suggest that two factors are involved in these reactions, (1) the presence of a vacant coordination site facilitates attack by the primary alcohol (or alkoxide), (2) decarbonylation, etc., invariably results in a decrease of interligand steric repulsion when these bulky phosphine ligands are present.

(vii) *Metal—metal bond formation.* This was an effect which we certainly did not expect. When an alcoholic ruthenium(III) chloride solution is carbonylated and a ligand such as PEt_3, PPh_3, PBu_2^tEt (L) is added to the resultant solution then six-coordinate ruthenium(II) complexes [$RuCl_2(CO)_2L_2$] are formed. However, if the very bulky ligands PBu_2^tPh, $PBu_2^t(CH_2Bu^t)$ or PBu_3^t (Q) are added then only one tertiary phosphine per ruthenium is complexed and binuclear ruthenium(I) complexes [$Ru_2Cl_2(CO)_4(Q)_2$] (X) with a ruthenium—ruthenium bond are formed [34,35].
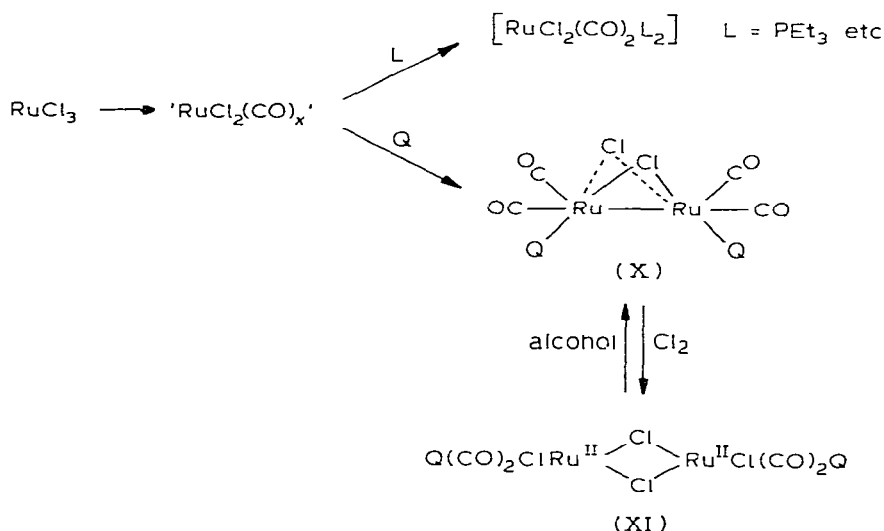

The ruthenium—ruthenium bond may be broken by treatment with chlorine, giving the ruthenium(II) species XI but such is the tendency to reduce steric strain that XI reacts with alcohols to give back the ruthenium(I) species X.

(viii) *Cyclometallation.* Metallation on carbon is a reaction where the hydrogen of a C—H bond is replaced by a metal. In a cyclometallation reaction of say a nitrogen-, phosphorus- or arsenic-donor ligand a carbon atom on an organic group attached to the donor atom is metallated: hence a chelate system is formed [36,37]. We originally found that in the cyclometallation of a tertiary phosphine ligand the steric requirements of the substituents on phosphorus played a dominant role [38]. Thus the ease with which the hydrogen was displaced by the metal from the carbon atom shown in XII was enormously influenced by the size of R_1 and R_2. If R_1, R_2 are small, metallation would usually

not occur, if R_1, R_2 are larger, e.g., phenyls, it would sometimes occur and

(XII)

sometimes not, but if R_1, R_2 were very bulky, e.g., Bu^t, then metallation often occurs readily and rapidly. In all cases so far examined the tendency to metallate is increased in the order (R_1 or R_2) Me < Ph < Bu^t and clearly steric effects are dominant over electronic effects. We have in this way been able to cyclometallate many different kinds of groups including phenyl, p-tolyl, naphthyl, anthryl; methyl-, ethyl- or isopropyl-groups in the 2-position of a phenyl group; purely aliphatic groups such as n-propyl, isobutyl and neopentyl [39], the carbon of an OCH_2 (ether) group [40], the β-CH_2 group of -CH_2CH_2-COOEt [41], pentamethylene and hexamethylene chains [42] and many others.

One example, the platination of PBu^t(o-tolyl)$_2$, illustrates the stereospecificity of such cyclometallation reactions [43]. Recently we have shown that $Bu_2^tP(CH_2)_5PBu_2^t$ reacts with rhodium trichloride to give the five coordinate hydride [RhHCl{$Bu_2^tPCH_2CH_2\dot{C}HCH_2CH_2PBu_2^t$}]: this is fluxional on the NMR time scale, corresponding to the rapid reversible interconversion of XIII

(XIII)   (XIV)

and XIV with fission of a C—H bond [44,45]. The corresponding iridium complex [IrHCl{$Bu_2^tPCH_2CH_2\dot{C}HCH_2CH_2PBu_2^t$}] dehydrogenates on heating to give the very unusual iridium-carbene or -ylide complex [IrCl{$Bu_2^tPCH_2CH_2\dot{C}$-$CH_2CH_2PBu_2^t$}] [45]. We went on to show that O-metallation is similarly promoted by steric effects. Thus when a ligand of type PR$_2$(2-methoxyphenyl) is treated with platinous chloride, if R = Me then a complex [PtCl(PMe$_2$C$_6$H$_4$-OMe-2)$_2$] is formed which shows no tendency to O-metallate even on prolonged boiling in high boiling alcohols. With R = Ph, cis-[PtCl$_2$(PPh$_2$C$_6$H$_4$-OMe-2)$_2$] can be isolated but in boiling 2-methoxyethanol it evolves methyl chloride and gives the bis-chelate [Pt(PPh$_2$C$_6$H$_4$O)$_2$]. With R = Bu^t O-metallation occurs much more readily than with R = Ph, giving [Pt(PBu$_2^t$C$_6$H$_4$O)$_2$] [40]. Moreover phosphines containing the very bulky 2,6-dimethoxyphenyl group are O-metallated much more readily than the corresponding phosphine with the 2-methoxyphenyl group. Thus, for example, PBu$_2^t${C$_6$H$_3$(OMe)$_2$-2,6} with iridium trichloride gives the purple 5-coordinate hydride [IrH{PBu$_2^t$C$_6$H$_3$(OMe)O}$_2$] which in air gives the red iridium(II) species

$[\overline{Ir\{PBu_2^tC_6H_3(OMe)O\}}_2$ and its corresponding purple dioxygen adduct $[IrO_2\{PBu_2^tC_6H_3(OMe)\dot{O}\}_2]$. This dioxygen adduct slowly C-metallates to give the five coordinated complex $[\overline{Ir\{PBu_2^tC_6H_3(OMe)O\}}\ \{PBu^t(CMe_2\dot{C}H_2)C_6H_3\text{-}}$ $(OMe)\dot{O}\}]$ containing a tridentate, dimetallated, ligand [47].

When it became apparent that steric effects were dominant in these cyclisation (cyclometallation) reactions it was realized that there was a close analogy between what we had found and what had been known by organic chemists for many years, namely the Thorpe-Ingold or *gem*-dialkyl effect. Thorpe and Ingold were interested in the formation of small rings and found that replacement of a CH_2 by CMe_2 invariably increased the stability of a ring (and/or the yield of the cyclised product) and also increased the rate at which it was formed. Thus Ingold wrote in 1921 [48] - "The reality of the phenomenon cannot be doubted" and pointed out that there are numerous examples of synthetic experiments in which the effect of the *gem*-dialkyl group on ring closure is clearly manifested. He also pointed out that in essential oils wherever a cyclopropane or cyclobutane ring was present then in all cases it carried a *gem*-group (such as a *gem*-dimethyl); i.e., the *gem*-dialkyl effect was used in nature. Work done since then has further illustrated how general the phenomenon is in carbocyclic chemistry and there appear to be no exceptions [49,50,51]. Two factors are responsible for the effect - (a) An entropy component, first suggested by Hammond [52], who pointed out that a *gem*-dimethyl grouping would reduce the loss of internal rotational entropy which occurs on cyclisation and (b) an enthalpy effect, as suggested by Allinger and Zalkow [53], who showed that a *gem*-dialkyl substituent would reduce the number of extra *gauche* interactions which are introduced on cyclisation. Sometimes the *gem*-dialkyl effect can be large, for example XV cyclises (lactonises) faster than XVI by a factor of 2×10^{10} [54,55]. The equilibrium constant for lactone ring formation is also very much higher with XV than with XVI but was too high to measure accurately.
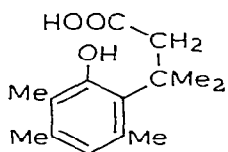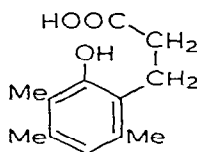

(XV)   (XVI)

Although methyl groups can have a large effect in carbon chemistry they are probably not sufficiently bulky to have a significant effect with the larger atom phosphorus, hence the need for the t-butyl group "a *gem*-t-butyl effect" [56]. One can in this way explain why cyclometallation reactions are promoted by steric effects. Thus, O-metallation occurs readily when $PBu_2^t(2,6\text{-dimethoxy-}$ phenyl) is treated with platinous chloride. As discussed above (in ii) a PBu_2^t group interacts with a *trans* Cl—Pt—Cl moiety so that there is a large energy barrier to rotation around the P—Pt bond and the preferred conformation will be as shown (XVII). Moreover, the ^1H NMR spectrum of the free phosphine shows non-equivalent OMe groups caused by restricted rotation around the P—C bond. Hence, the preferred conformation around the Pt—P and P—C bonds will be as shown in XVIII with one OMe group forced close to the chlorine, and metallation occurs readily. Moreover, since rotation around the P—Pt

and C—P bonds is restricted the loss of internal rotational entropy on cyclisa-
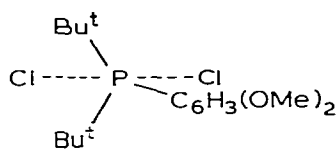

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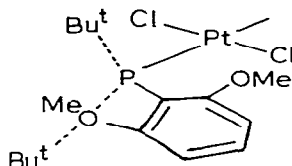
(XVIII)

tion will be small. Similar arguments can be used to explain the other cyclomet-allation reactions of tertiary phosphines (or tertiary arsines). Since *gem*-dimethyl groups have quite a marked effect on cyclisations when they are bonded to carbon one would expect them to have a marked effect when bonded to nitrogen, which is smaller than carbon. Hence there is a ready explanation for the observation by Cope and coworkers [57] that dimethylbenzylamine cyclopalladates very readily whereas benzylamine will not cyclopalladate [56].

(ix) *Large chelate ring formation.* Until recently large chelate rings (>8-membered) were thought to be unstable with respect to open-chain (polymeric) structures. This is generally true but in the past few years we and other workers have successfully made large chelate rings (12- to 72-membered) [42,58]. Some of the compounds prepared by other workers have been formed under conditions of kinetic control; e.g., the large chelate ring complexes of Co^{III} with $\alpha\omega$-diamines [59]. Others require high-dilution; e.g., complexes of type *trans*-$[PtCl_2\{CH_2=CH(CH_2)_mCO_2(CH_2)_nC_5H_2Me_2N\}]$ which undergo slow polymerization when concentrated [60]. Other large ring chelates dissociate in solution, e.g. $[Rh_2Cl_2(CO)_2\{Ph_2PCH_2CH_2OCH_2CH_2PPh_2\}_2]$ [61,62]. For most of the large ring chelates reported by others there is little or no information as to their stability in solution. However, we have shown that a variety of long chain diphosphines (and more recently diamines [63,64] and disulphides [65]), with sterically demanding substituents on the donor atoms, form large ring chelates (12- to 72-membered), e.g., ligands of type $Bu_2^tP(CH_2)_nPBu_2^t$ (n = 5—10 and 12), $Bu_2^tP(CH_2)_4C\equiv C(CH_2)_4PBu_2^t$, $Bu_2^tPC\equiv C(CH_2)_nC\equiv PBu_2^t$ (n = 4 or 5) whereas $Me_2P(CH_2)_{12}PMe_2$, $PPh_2(CH_2)_{10}PPh_2$ gave intractable polymeric material. Using these diphosphines with the sterically demanding PBu_2^t end groups we have made large ring chelates of Pt^{II}, Pd^{II}, Rh^I, Rh^{III}, Ir^I, Ir^{III}, Ru^{II} with halides, carbonyl halides, hydrido halides, methyls, etc. One advantage of using phosphorus-donors is that one can study species in solution using ^{31}P NMR spectroscopy. Thus we find that in solution these large ring chelates are stable indefinitely, showing no tendency to give open-chain polymers; i.e., the large ring chelates are more thermodynamically stable then open-chain precursors or polymeric species. The causes of this large ring stabilization are almost certainly an extension of the factors which promote cyclometallation; i.e., non-bonding interactions between sterically demanding groups (PBu_2^t, NMe_2) which give (a) a favourable conformational effect and (b) a favourable entropy effect. One grouping might have quite a small effect on the ΔH and $T\Delta S$ components of ring formation but several such sterically demanding groupings, suitably positioned, will have a cumulative effect. A good illustrative example is the stable 20-atom ring compound formed in high yield from $Bu_2^tP(CH_2)_7PBu_2^t$ and $[PdCl_2(PhCN)_2]$. The complex *trans*-$[Pd_2Cl_4\{Bu_2^tP(CH_2)_7PBu_2^t\}_2]$ has the

crystal structure shown in Figure 1 and ^{31}P NMR spectroscopy shows the ring to be stable in solution, as is the corresponding platinum complex. Consideration of space-filling molecular models suggests that the preferred torsion angle for the arrangement $PdCl_2$—PBu_2^t—CH_2—CH_2 is 60° i.e. as in the Newman projection XIX. Additionally the Cl—Pd—Cl moieties in XIX are arranged as dis-

(XIX)
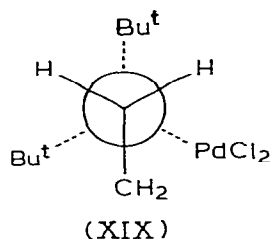
cussed in Section viii. Thus the torsion angles in the structure shown in Fig. 1 are all preferred torsion angles and no torsional strain is introduced on cyclisation. This would not be the case with small end groups on phosphorus. The immediate precursor to the 20-atom ring compound trans-[PdCl$_2$ $\{$Bu$_2^t$P(CH$_2$)$_7$-PBu$_2^t\}_2$] will be an open-chain compound such as PdCl$_2\{$Bu$_2^t$P(CH$_2$)$_7$PBu$_2^t\}$-PdCl$_2\{$Bu$_2^t$P(CH$_2$)$_7$PBu$_2^t\}$ which will have preferred torsion angles closely similar to those observed in the 20-atom ring (Figure 1). Moreover, because of restricted rotation around the Pd—PBu$_2^t$ and P—C bonds caused by the Bu^t groups, the loss of rotational entropy on cyclisation in several of the bonds will be less than with less sterically demanding phosphines; i.e., there will
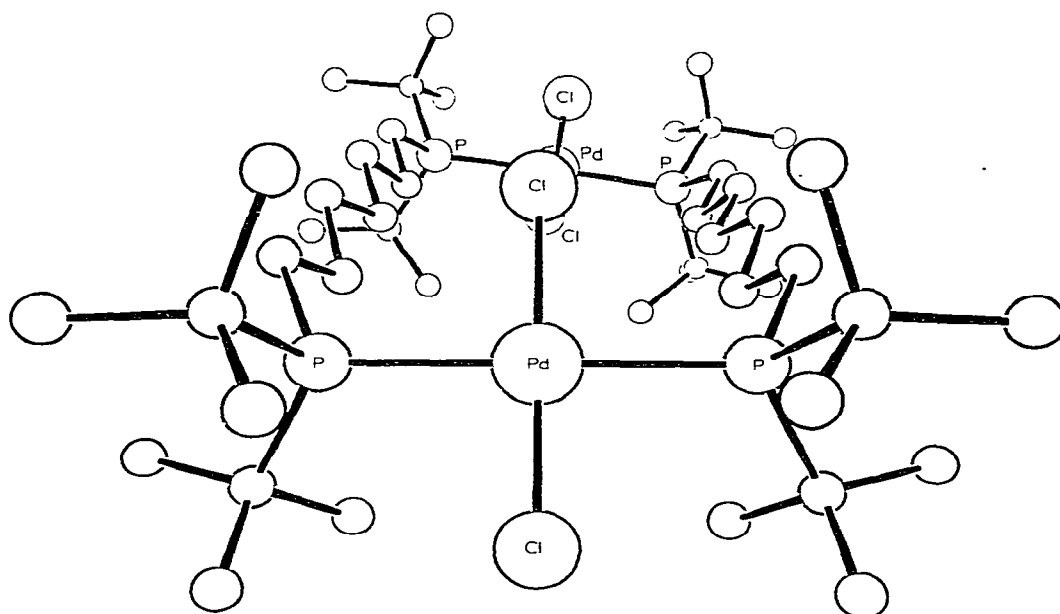

Fig. 1. ORTEP drawing of the structure of the 20-atom ring complex [Pd$_2$Cl$_4\{$Bu$_2^t$P(CH$_2$)$_7$PBu$_2^t\}_2$] kindly supplied by Dr. W.S. McDonald of this department. A small packing effect causes one P—Pd—P to be inclined 9° to the other. (Reproduced from ref. 42 with the permission of The Chemical Society.)

also be a cumulative $T\Delta S$ effect [42]. Similar arguments can be used to explain the stability of the other large ring chelates we have made [42]. Approximately twelve of these have had their crystal structures determined by X-ray diffraction. A feature common to all these large ring chelates (12- to 26-membered rings) is that the sterically demanding groups (PBu_2^t, NMe_2, SBu^t) always occupy "corner" positions i.e. where there are $\sim 60°$ torsion angles in the ring.

As was pointed out by Ingold the *gem*-dialkyl effect is used in nature to form small carbocyclic rings. A feature common to all the macrolide antibiotics including cyclic peptides and depsipeptides is the presence of large numbers of sterically demanding substituents around the large rings (10- to 38-membered) [42,66,67]. About 200 of these macrolides are now known. Thus it would appear that the beneficial effects of sterically demanding substituents that we have found for large chelate ring formation are used extensively in nature to stabilize and promote the formation of the large macrolide rings.

Conclusion and possible developments

Our simple approach of using bulky or sterically demanding tertiary phosphine ligands to generate unusual chemistry, to stabilize unusual intermediates, coordinatively unsaturated species, hydrides etc. was successful. However, the effect of sterically demanding substituents in promoting cyclometallation and large ring formation was not expected. To me the most satisfying result to come out of this work is the way that non-bonding interactions can be important especially when they are cumulative. This has not been realized by many chemists in the past. Since these interactions are a function of atomic sizes, bond lengths, bond angles and torsion angles one should be able to use them widely in chemistry. With space-filling molecular models or even chemical common-sense and a knowledge of bond lengths etc. the enthalpy effects of substituents on a conformation can be predicted qualitatively. However, one should also not ignore the effects of substituents on internal rotational entropy changes. These $T\Delta S$ effects can be at least as important as ΔH effects. Often in chemistry ΔH and $T\Delta S$ effects oppose each other but in this instance they reinforce each other. In conclusion therefore I should like to suggest that sterically demanding substituents could be used to generate interesting effects in areas other than purely organic chemistry or metal-ligand chemistry of the kind discussed in our research.

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References

1 C.A. McAuliffe (Ed.), Transition Metal Complexes of Phosphorus, Arsenic and Antomony Ligands, Macmillan, London and Basingstoke, 1973.
2 J.M. Jenkins and B.L. Shaw, Proc. Chem. Soc., (1963) 279.
3 C.A. Tolman, Chem. Rev., 77 (1977) 313.

4   C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
5   A. Bright, B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, J. Chem. Soc. (A), (1971) 1826.
6   C.J. Moulton and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1976) 365.
7   B.E. Mann, C. Masters, B.L. Shaw and R.E. Stainbank, J. Chem. Soc. Chem. Commun., (1971) 1103.
8   H.D. Empsall, E.M. Hyde, E. Mentzer and B.L. Shaw, J. Chem. Soc. Dalton, (1977) 2285.
9   C. Masters, W.S. McDonald, G. Raper and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1971) 210.
10 C. Masters and B.L. Shaw, J. Chem. Soc. A, (1971) 3679.
11 C. Masters, B.L. Shaw and R.E. Stainbank, J. Chem. Soc. Chem. Commun., (1971) 209.
12 C. Masters, B.L. Shaw and R.E. Stainbank, J. Chem. Soc. Dalton, (1972) 664.
13 A.D. Buckingham and P.J. Stephens, J. Chem. Soc., (1964) 2747.
14 P.W. Atkins, J.C. Green and M.L.H. Green, J. Chem. Soc. A, (1968) 2275.
15 B.L. Shaw and R.E. Stainbank, J. Chem. Soc. Dalton, (1972) 2108.
16 H.L.M. van Gaal and F.L.A. van den Bekerom, J. Organometal. Chem., 134 (1977) 237.
17 T. Yoshida, T. Okano, D.L. Thorn, T.H. Tulip, S. Otsuka and J.A. Ibers, J. Organometal. Chem., 181 (1979) 183.
18 W. Kuran and A. Musco, J. Chem. Soc. Dalton, (1975) 1673.
19 M. Green, J.A. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1975) 3.
20 A. Immirzi, A. Musco, P. Zambelli and G. Carturan, Inorg. Chem. Acta, 13 (1975) L13.
21 M. Matsumoto, H. Yoshiska, K. Nakatsu, T. Yoshida and S. Otsuka, J. Amer. Chem. Soc., 96 (1974) 3323.
22 S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, J. Amer. Chem. Soc., 98 (1976) 5850.
23 H.D. Empsall, E.M. Hyde, E. Mentzer, B.L. Shaw and M.F. Uttley, J. Chem. Soc. Dalton, (1976) 2069.
24 B.L. Shaw and M.F. Uttley, J. Chem. Soc. Chem. Commun., (1974) 918.
25 T. Yoshida, T. Yamagata, T.H. Tulip, J.A. Ibers and S. Otsuka, J. Amer. Chem. Soc., 100 (1978) 2063.
26 H.D. Empsall, E. Mentzer and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1975) 861.
27 R. Mason, K.M. Thomas, H.D. Empsall, S.R. Fletcher, P.N. Heys, E.M. Hyde, C.E. Jones and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1974) 612.
28 B.L. Shaw, J. Organometal. Chem., 94 (1975) 251.
29 H.D. Empsall, E.M. Hyde and B.L. Shaw, J. Chem. Soc. Dalton, (1975) 1690.
30 J. Chatt and B.L. Shaw, Chem. and Ind., (1960) 931.
31 J. Chatt and B.L. Shaw, Chem. and Ind., (1961) 290.
32 F.G. Moers and J.P. Langhart, Rec. Trav. Chim. Pays-Bas, 91 (1972) 591.
33 D.F. Gill and B.L. Shaw, Inorg. Chem. Acta, 32 (1979) 19.
34 R. Mason, K.M. Thomas, D.F. Gill and B.L. Shaw, J. Organometal. Chem., 40 (1972) C67.
35 D.F. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc. Dalton, (1973) 311.
36 M.I. Bruce, Angew. Chem. Internat. Ed., 16 (1977) 73.
37 J. Dehand and M. Pfeffer, Coord. Chem. Rev., 18 (1976) 327.
38 A.J. Cheney, B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc. Chem. Commun., (1970) 1176.
39 R. Mason, M. Textor, N.A. Al-Salem and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1976) 292.
40 C.E. Jones, B.L. Shaw and B.L. Turtle, J. Chem. Soc. Dalton, (1974) 992.
41 H.D. Empsall, E.M. Hyde, D. Pawson and B.L. Shaw, J. Chem. Soc. Dalton, (1977) 1292.
42 N.A. Al-Salem, H.D. Empsall, R. Markham, B.L. Shaw and B. Weeks, J. Chem. Soc. Dalton, (1979) 1972.
43 A.J. Cheney, W.S. McDonald, K.H.P. O'Flynn, B.L. Shaw and B.L. Turtle, J. Chem. Soc. Chem. Commun., (1973) 128.
44 C. Crocker, R.J. Errington, W.S. McDonald, K.J. Odell, B.L. Shaw and R.J. Goodfellow, J. Chem. Soc. Chem. Commun., (1979) 498.
45 C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell and B.L. Shaw, J. Amer. Chem. Soc., in press.
46 H.D. Empsall, E.M. Hyde, R. Markham, W.S. McDonald, M.C. Norton, B.L. Shaw and B. Weeks, J. Chem. Soc. Chem. Commun., (1977) 589.
47 H.D. Empsall, P.N. Heys and B.L. Shaw, J. Chem. Soc. Dalton, (1978) 257.
48 C.K. Ingold, J. Chem. Soc., (1921) 305, 951.
49 E.L. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York, 1962.
50 E.L. Eliel, N.L. Allinger, S.J. Angyll and G.A. Morrison, Conformational Analysis, Interscience, New York, 1965.
51 B. Capon and S.P. McManus, Neighbouring Group Participation, Volume 1, Plenum Press, New York and London, 1976.
52 G.S. Hammond in M.S. Newman (Ed.), Steric Effects in Organic Chemistry, Wiley, New York, 1956, p. 468.
53 N.L. Allinger and V. Zalkow, J. Org. Chem., 25 (1960) 701.

54 S. Miltstein and L.A. Cohen, Proc. Natl. Acad. Sci. U.S.A., 67 (1970) 1143.

55 S. Milstein and L.A. Cohen, J. Amer. Chem. Soc., 94 (1972) 9158.

56 B.L. Shaw, J. Amer. Chem. Soc., 97 (1975) 3856.

57 A.C. Cope and E.C. Friedrich, J. Amer. Chem. Soc., 90 (1968) 909.

58 A.J. Pryde, B.L. Shaw and B. Weeks, J. Chem. Soc. Chem. Commun., (1973) 947.

59 H. Ogino and J. Fujita, Bull. Chem. Soc. Japan, 48 (1975) 1836.

60 J.C. Chottard, E. Mulliez, J.P. Girault and D. Munsay, J. Chem. Soc. Chem. Commun., (1974) 780.

61 N.W. Alcock, J.M. Brown and J.C. Jeffery, J. Chem. Soc. Dalton, (1976) 583.

62 N.W. Alcock, J.M. Brown and J.C. Jeffery, J. Chem. Soc. Dalton, (1977) 588.

63 A.G. Constable, W.S. McDonald and B.L. Shaw, J. Chem. Soc. Dalton, (1979) 496.

64 A.G. Constable, W.S. McDonald and B.L. Shaw, J. Chem. Soc. Dalton, (1979) 1109.

65 R.J. Errington, W.S. McDonald and B.L. Shaw, in press.

66 S. Masamune, G.S. Bates and J.W. Corcoran, Angew. Chem. Internat. Ed., 16 (1977) 585.

67 S. Masamune, personal communication.