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PHOSPHORUS CHEMISTRY AND THE COORDINATION CHEMIST

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Abstract - (1) σ- and π-metal-phosphorus interactions are discussed using Pt-P bond distances and coupling constants $^1J(^{195}Pt,^{31}P)$ and $^1J(^{195}Pt,^{15}N)$. It is shown that the data lend themselves to more than one interpretation. (2) Some Ni(0), Rh(I), Ir(I), Pd(II) and Pt(II) complexes of Ph_2PCH_2CN, $PhP(CH_2CN)_2$ and $P(CH_2CN)_3$ are described and it is shown that "unexpected" behaviour is observed when large numbers of cyanomethyl groups are placed in close proximity. (3) The coordination chemistry of the chelating phosphines 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene, (XIV), is described and it is shown that distortions of the coordination polyhedron are often accompanied significant distortions of the organic ligand framework.

INTRODUCTION

The most significant difference between the 'classical' and "contemporary" periods of coordination chemistry resides in the type of donor atoms which have received, or are receiving, most attention from the practitioners of this art. Thus, nitrogen and oxygen donors played a dominant role during the 'Alfred Werner' and 'post classical' periods. Since the early fifties, however, there has been an explosive growth in research activity in the area of phosphorus coordination chemistry. It is noteworthy that while the first monograph largely devoted to this topic (1) appeared in 1973, this was followed in 1979 by an up-dated version (2) which covers two volumes.
The reasons for this rapid development are many and varied and range from the interest generated by the preparation of many novel types of compounds containing phosphorus donors, to their often unusual physico-chemical properties and to the numerous reactions, of actual or potential interest, in which complexes with phosphorus donors act either as catalysts or as catalyst precursors.
During the first part of this talk brief mention will be made of some general aspects of phosphine coordination chemistry and the remainder of the time will be devoted to the description of some studies of the coordinating properties of two types of recently synthesized phosphine ligands.

RANGE OF COMPLEXES WITH PHOSPHORUS DONORS

Practically all compounds having a lone pair of electrons on the phosphorus atom give smaller or greater numbers of coordination compounds. Both 'inorganic' and 'organic' phosphorus compounds, simple and complex, bind to few or many transition metal and non-transition metal centres. It is, therefore, not surprising that the great majority of the elements are known to form at least a few complexes with phosphorus donors as can be seen from Fig. 1.
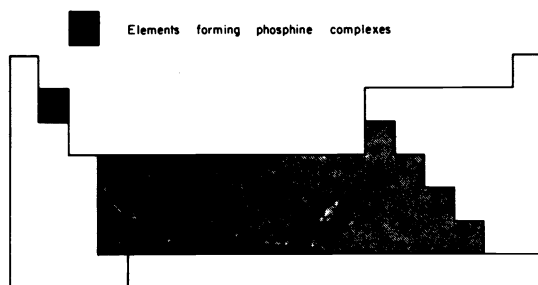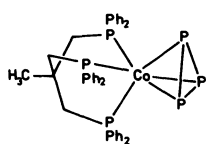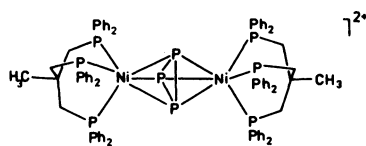

Fig. 1. Elements known to form complexes with phosphorus donors.

Phosphorus-containing moieties, which are 'unstable' in the free state, can also give well-characterised compounds as is the case of the P_3-fragment in the complexes (I) and (II) (3).
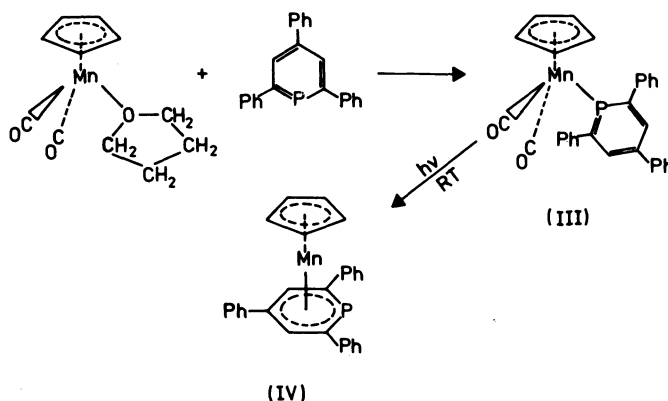

(I)   (II)

It has recently become apparent that molecules containing phosphorus σ-donor and multiple bonded π-donor functions may prefer to coordinate to metal centres through the latter system. The latest example of this type of behaviour is provided by the phosphorins and shown by the easy formation of (IV) from (III) (4).

(III)

(IV)

The range of complexes that can be produced by phosphorus donors is unparalleled in coordination chemistry. Thus, the appropriate choice of ligands, e.g., exploiting their different steric requirements, allows the preparation of sets of complexes, with the same metal centre, having different coordination numbers. One series of compounds showing this effect is shown in Table 1.

TABLE 1. Tertiary phosphine palladium(0) complexes (5)

| Ligand (L)	Complexes formed	Ligand (L)	Complexes formed
PMe_3	PdL_4	PPh_3	PdL_4, PdL_3
PMe_2Ph	PdL_4	PBz_3	PdL_3
$PMePh_2$	PdL_4	PPr_3^i	PdL_3, PdL_2
PEt_3	PdL_4, PdL_3	$P(cyclohexyl)_3$	PdL_2
PBu_3^n	PdL_4, PdL_3	PBu_2^tPh	PdL_2

Phosphorus donors are also capable of stabilising both very high and very low oxidation states and can give ranges of complexes with the same metal centre in several oxidation states. Two sets of compounds showing this behaviour are reproduced in Table 2.

TABLE 2. Range of oxidation states for phosphine complexes of manganese
   and nickel (6)

|			
Mn(-1)	$Na[Mn(CO)_3(Ph_3P)_2]$		
Mn(0)	$[Mn_2(CO)_8(Ph_3P)_2]$	Ni(0)	$[Ni(Ph_3P)_4]$
Mn(I)	$[MnCl(CO)_3(Ph_3P)_2]$	Ni(I)	$[NiCl(Ph_3P)_3]$
Mn(II)	$[MnCl_2(P{\sim}P)_2]$	Ni(II)	$[NiCl_2(Ph_3P)_2]$
Mn(III)	$[MnCl_2(P{\sim}P)_2]^+$	Ni(III)	$[NiCl_2(P{\sim}P)_2]^+$
Mn(IV)	$[MnCl_2(P{\sim}P)_2]^{2+}$	Ni(IV)	$[NiCl_2(P{\sim}P)_2]^{2+}$

$(P{\sim}P) =$
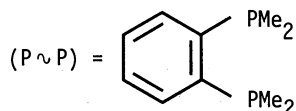
The use of slightly different phosphorus ligands allows the preparation of complexes of a
given metal centre, in one oxidation state, having the same stoicheiometry and differing in
their molecular geometry as is found for $[NiCl_2(Ph_3P)_2]$, which is pseudo-tetrahedral, and for
$[NiCl_2(Et_3P)2]$ which is trans-square planar (1). Indeed, with suitable phosphines, e.g.,
$BzPh_2P$, both forms can be obtained both in the solid state and in solution (1).
'Tailor made' phosphine ligands have been used to obtain coordination compounds with unusual
geometries, e.g., tripod-like ligands such as V and VI $(L'L_3)$ have been used to obtain five-
coordinate complexes with trigonal bipyramidal structure of the types $[MX(L'L_3)]$ (M = Co, Rh
and Ir) and $[MX(L'L_3)]^+$ (M = Ni, Pd and Pt) (VII).

$P(CH_2CH_2PR_2)_3$
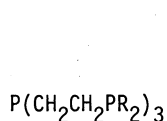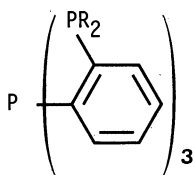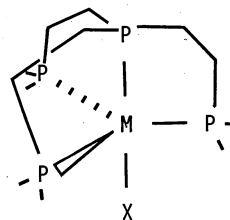
(V)   (VI)   VII

The appropriate design of phosphorus ligands, taking advantage of their wide range of donor
capacity and exploiting steric effects caused by different substituents on the phospho-
rus atom, can produce an extremely rich coordination chemistry. The most striking example
of the selectivity that can be achieved is provided by the use of chiral phosphines for
homogeneous hydrogenation (1).

TYPE OF BONDING IN PHOSPHINE COMPLEXES

The origin of the marked differences in coordinating properties between analogous nitrogen
and phosphorus donors has been much discussed for the last thirty years. The availability
of the phosphorus 3d-orbitals and their ability to overlap with metal d-orbitals in what is
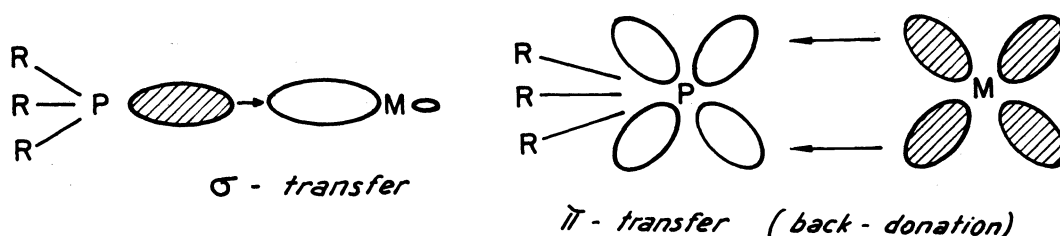commonly referred to as d_π-d_π-back bonding (see Fig. 2), have been extensively used since

Fig. 2. Schematic representation of σ- and π-M-P interactions

1950 (7) to account for most of the observed chemical and physico-chemical phenomena relating to phosphorus coordination chemistry. While the group-theoretical aspects of this interaction are self-evident, its quantitative aspects in various types of compounds and the extent to which it is reflected by various chemical and physico-chemical properties is a subject which is still open for discussion. Let me illustrate the nature of the problems that arise when one is trying to correlate changes in bond type with observable physical parameters using two examples, one taken from structural chemistry and the other from molecular spectroscopy. There is now a very substantial amount of structural information on transition metal complexes with phosphorus donors. [A recent sampling of the structural information contained in the Cambridge Structural Data File produced a list of 253 structures of complexes containing Pt-P bonds!]. In a recent paper Caldwell et al. (8) pointed out that there is a good linear relationship between the Pt-P bond length and the electron attracting or releasing power of the R-groups attached to phosphorus as measured by Tolman's $\sum x_i$ parameter (9) (see Fig. 3).
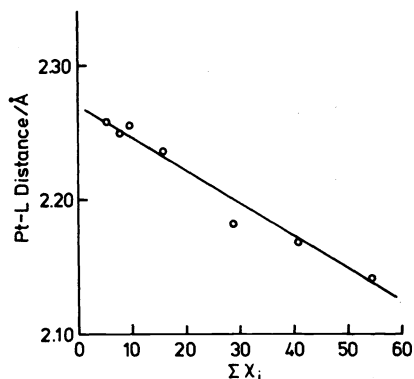

Fig. 3. Selected bond lengths in platinum(II) complexes of the type cis-[PtCl$_2$(R$_3$P)$_2$] (data from Ref. 8)

As can be seen, the shorter Pt-P bonds occur in complexes with those phosphines having the more electron attracting substituents. Caldwell et al. rightly point out that this relationship could arise either from:
1. "Electron withdrawing by phosphorus substituents [which] would be expected to favour d_π-d_π back donation from platinum to phosphorus, leading to a shortening of the Pt-P bond" or from
2. "... σ-bonding effects. Electron withdrawal at phosphorus would then be expected to contract the phosphorus σ-donor orbital. A contraction of the platinum acceptor orbitals, arising from the higher formal charge of the metal, when attached to a less basic phosphine, may be anticipated."

The second example is based on the use of spectroscopic data as means to assess the electronic nature of the metal-phosphorus interaction. Most forms of spectroscopy have been used for this purpose and the particular example chosen here is taken from nmr data. It is found (10) that there is a good linear relationship between the $^1J(^{195}Pt-^{15}N)$ values for amine complexes and the $^1J(^{195}Pt-^{31}P)$ values for the corresponding phosphine complexes (see Fig. 4).

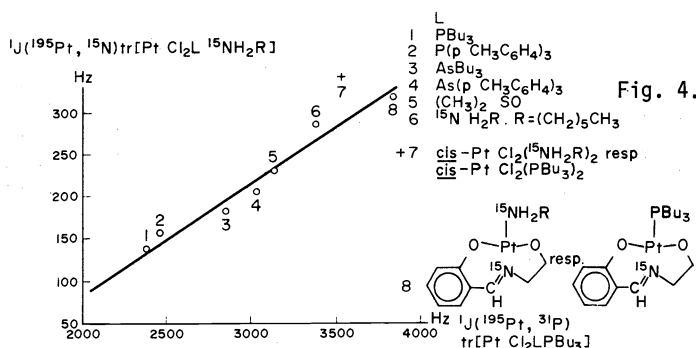Fig. 4. Relationship between $^1J(^{195}Pt\text{-}^{15}N)$ for amine complexes and of $^1J(^{195}Pt\text{-}^{31}P)$ for corresbonding phosphine complexes.

One-bond M-L coupling constants are often adequately expressed by an approximate equation of the type shown below (11). It has also been empirically (11) established that, for square

$$J(Pt\text{-}N) \; \propto \; \gamma_{Pt}\gamma_N(\Delta E)^{-1}\alpha_{Pt}^2\alpha_X^2[\Psi_{Pt(6s)}(0)]^2[\Psi_{X(ns)}(0)]^2$$

γ_{Pt} and γ_X = Magnetogyric ratios for the nuclei ^{195}Pt and ^yX respectively ($^yX = ^{15}N$ or ^{31}P).

ΔE = Mean singlet to triplet excitation energy in the complexes.

α_X = s-character of the hybrid used by donor atom X in the platinum-X bond.

$[\Psi_{X(ns)}]^2$ = Electron density of the indicated orbital evaluated at the parent nucleus.

planar platinum(II) complexes, the α^2 term is likely to be dominant and, consequently, changes in J-values should reflect primarily changes in s-character in the Pt-donor atom bond. As it is accepted that the π-contribution in a Pt-N bond, in complexes of primary amines, is insignificant and as the observed changes in J(Pt-N) are linearly related to the J(Pt-P) changes in the corresponding complexes with tertiary phosphines (see Fig. 4), one must conclude that either there is no significant π-contribution in the Pt-P bond in the complexes examined or that changes in π-contribution, over a wide range complexes of platinum(II), are linearly related to the corresponding changes in σ-contribution. Thus, the question of the nature and significance of bond type in phosphine complexes is still, and is likely to be for some considerable time, in a state where opinions may be sold as hard currency.


THE COORDINATING PROPERTIES OF SOME CYANOMETHYL PHOSPHINES

I should like now to proceed to give you a practical illustration of how a coordination chemist proceeds to study the donor capacity of a new phosphine ligand. The first screening is generally done by estimating two empirical ligand parameters, as defined by C. A. Tolman (9), one relating to the steric properties of the ligand, the cone angle Θ, and the other to the electronic or donor properties of the phosphorus atom as expressed by the electronic parameter ν.
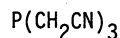The ligands chosen as examples were recently prepared by O. Dahl (12) and are shown below.

$$Ph_2PCH_2CN \qquad\qquad PhP(CH_2CN)_2 \qquad\qquad P(CH_2CN)_3$$
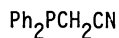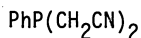
$$(VIII) \qquad\qquad\qquad (IX) \qquad\qquad\qquad (X)$$

Much can be learnt about phosphines by measuring their ^{31}P-nmr spectra. Thus, it is found that ^{31}P-nmr chemical shifts are particularly sensitive to changes of C-P-C bond angles. These, in turn, are strongly affected by the bulk of the substituents attached to the phosphorus atom which also determine the overall size of the phosphine and therefore there should be some relationship between the ^{31}P-nmr and the cone angles of the phosphines (9). The cone angles, calculated by Tolman's method, and the phosphorus chemical shift values of the cyanomethylphosphines are:(VIII):Θ = 139°, $\delta^{31}P$ = - 18.0 ppm; (IX): Θ = 129.5°, $\delta^{31}P$ = - 28.9 ppm; (X): Θ = 128°, $\delta^{31}P$ = - 33.1 ppm (12). The relationship between these values and those for related phosphines are shown in Fig. 5 and, as can be seen from this point of view,
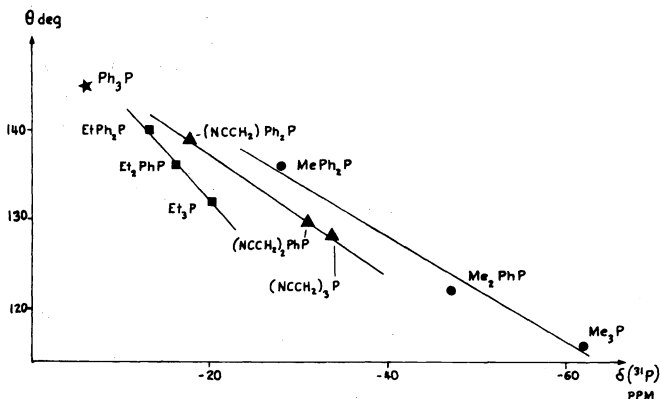
the ligands (VIII), (IX) and (X) are 'normal'.

Fig. 5. Relationship between $\delta^{31}P$ and cone angle Θ of some phosphines.

Furthermore, as pointed out by Tolman (12), many chemical and physicochemical properties of transition metal complexes are strongly influenced by the steric requirements of the coordinated phosphorus ligands as estimated by their cone angles. In the case of phosphines (VIII), (IX) and (X) these angles are intermediate between those of the corresponding Ph_nPMe_{3-n} and Ph_nPEt_{3-n} and almost identical with those of the related phosphites Ph_2POPh, XI, (Θ = 139°); $PhP(OPh)_2$, XII, (Θ = 134°) and $P(OPh)_3$, XIII, (Θ = 128°). Thus, from a steric points of view, the new phosphines are expected to behave similarly to the corresponding phosphites. The donor capacity of phosphines is frequently expressed, albeit semiquantitatively, in terms of Tolman's electronic parameter, ν. The values of this parameter for compounds (VIII) to (X) and for some related phosphines are shown in Table 3. Thus, even from this point of view, ligands (VIII), (IX) and (X) should behave like the corresponding phosphites, (XI), (XII) and (XIII).

TABLE 3. Measure of electronic effects in phosphine complexes

	ν	$\chi^{(*)}$		ν	χ
Et_3P	2061.7	1.8	$(EtO)_3P$	2077.0	6.8
Et_2PhP	2063.7		$(PhO)_2PhP$	2079.8	
Me_3P	2064.1	2.6	$(NCCH_2)_2PhP^*$	2084.2	
$EtPh_2P$	2066.4		$(PhO)_3P$	2085.3	9.7
Ph_3P	2068.9	4.3	$(NCCH_2)_3P^*$	2092.7	12
$(NCCH_2)Ph_2P^*$	2076.2		$(NC-\bigcirc -O)_3P$	2092.8	12.2
$(PhO)Ph_2P$	2074.6		F_3P	2110.8	18.2

(*) Obtained from ν_{CO} (A_1) in $[Ni(CO)_3L]$ (9)

(Definition of phosphine substituent contribution X_i from ν_{CO} for $PX_1X_2X_3$: $\nu = 2056.1 + \sum_{i=1}^{3} X_i$)

As also from an electronic point of view the new phosphines should show donor capacities close to those of the corresponding phosphites, the initial investigation of the cyanomethyl-phosphines was directed at establishing the extent to which the complexes of ligands (VIII) to (X) are similar to those of ligands (XI) to (XIII). For this purpose several sets of complexes were prepared and a representative selection is shown in Table 4. An easy assessment as to

TABLE 4. Some complexes of cyanomethyl phosphines

Compound	decomp. pt.	$\delta^{31}P$ [1] (ppm)	$^{1}J(M,P)$ (Hz)	Δ_{CS} (obs.)	Δ_{CS} (calc.)	ν_{CO} (cm^{-1})
<u>trans</u>-[PdCl$_2$(VIII)]	> 205°	13.4	-	31.4	34.5	-
<u>trans</u>-[PdCl$_2$(IX)]	> 202°	8.8	-	37.7	38.4	-
<u>trans</u>-[PdCl$_2$(X)]	> 228°	7.6	-	40.7	39.9	-
<u>cis</u>-[PtCl$_2$(VIII)]	> 230°	5.1	3691	23.1	24.7	-
<u>cis</u>-[PtCl$_2$(IX)]	> 228°	- 2.3	3650	26.6	28.3	-
<u>trans</u>-[PtCl$_2$(X)]	> 245°	3.6	2876	36.7	40.3	-
<u>trans</u>-[RhCl(CO)(VIII)]	> 150°	22.3	194	40.3	41.9	1975
<u>trans</u>-[RhCl(CO)(IX)]	> 150°	17.5	137	46.4	45.6	2015
<u>trans</u>-[RhCl(CO)(XI)]	> 205	16.0	141	49.1	47.0	1995
<u>trans</u>-[IrCl(CO)(VIII)]	> 135°	15.7	-	33.7	35.5	2040
<u>trans</u>-[IrCl(CO)(IX)]	> 215°	10.9	-	39.8	39.4	1970
<u>trans</u>-[IrCl(CO)(X)] [2]	> 145°	- 14.0	-	19.0	40.9	2020
[Ni(CO)$_2$(VIII)$_2$]	> 150°	22.3	-	40.3	41.6	2246, 2243(sh)
[Ni(CO)$_3$(IX)]	> 75°	16.4	-	46.3	-	2249, 2244(sh)
[Ni(CO)$_2$(IX)$_2$]	> 92°	15.4	-	44.3	42.5	2247, 2243(sh)
[Ni(CO)(IX)$_3$]	> 143°	12.2	-	41.1	-	2244(sh), 2241
[Ni(CO)$_2$(X)$_2$]	> 110	12.4	-	45.5	42.9	2249, 2245(sh)

[1] Measured in CD$_3$COCD$_3$. $\delta^{31}P$ values of free ligands (in ppm): (VIII) = - 18.0; (IX) = - 28.9; (X) = - 33.1. Shifts are given relative to H$_3$PO$_4$ with a positive value indicating a shift to lower field.

[2] The analytical data fits the composition [IrCl(CO)(X)].CH$_3$CN but in view of the large difference between $\Delta_{CS(obs.)}$ and $\Delta_{CS(calc.)}$ this compound is unlikely to be the acetonitrile solvate of the expected compound.

whether the new complexes are 'normal' representatives of their respective class of compounds is provided by the value of their ^{31}P-nmr chemical shifts. It has been established (14) that, for each type of compound, there is direct relationship between the coordination chemical shift, Δ_{CS}, defined as $\delta_{free\ lig.} - \delta_{compl.}$, and $\delta_{free\ lig.}$ of the type:

$$\Delta_{CS(calc.)} = A \times \delta_{free\ lig.} + B$$

where A and B are constants for each type of complex. As can be seen from the data given in Table 4, all but one of the complexes listed there are 'well behaved' and the 'problem' with <u>trans</u>-[IrCl(CO)(X)] is still under investigation.
It is also found that the coordination chemical shifts, Δ_{CS}, of the rhodium(I) complexes correlate well with the cone angles, Θ, of the corresponding ligands and that this correlation is a general one (see Fig. 6). What differences in coordinating behaviour between corresponding cyanomethyl and phenoxy compounds have we observed up to date ? The first
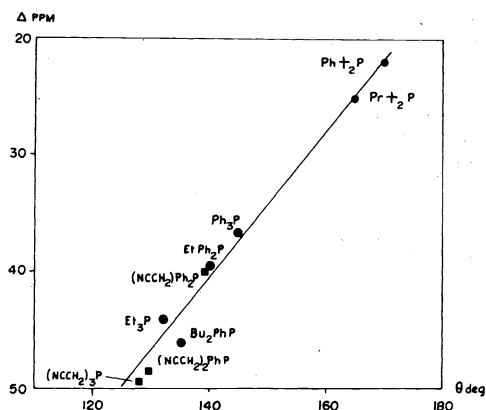
Fig. 6.   Relationship between coordination chemical shift, Δ_{CS}, and ligand cone angle Θ in complexes trans-[RhCl(CO)(L$_2$]

relates to one of the platinum complexes and the other to the nickel(0) complexes. Thus, while the three ligands Ph$_n$P(OPh)$_{3-n}$ give complexes of the type cis-[PtCl$_2$L$_2$], complexes of this geometry are obtained only for ligands Ph$_2$PCH$_2$CN, (VIII), and PhP(CH$_2$CN), (IX). *The ligand P(CH$_2$CN)$_3$, (X), however, gives* trans-[PtCl$_2$(X)$_2$]. The formation of cis-isomeric species in complexes of ligands (XI) to (XIII) has been attributed to the formation of d$_\pi$-d$_\pi$ bonding (1) but, as we have seen earlier, it could also be explained in terms of σ-interactions. Our unexpected result does not appear to be accountable in terms of π-bonding effects.

Nickel(0) readily forms phosphine and phosphite complexes of the type [NiL$_4$]. These four-coordinate species, when L is a triaryl phosphite such as (p-Cl.C$_6$H$_4$.O)$_3$P, are only slightly dissociated in solution (15). The complex [Ni{P(CH$_2$CN)$_3$}$_4$], however, is extensively dissociated in solution although, on the basis of steric and electronic arguments, one would expect it to behave like the corresponding phosphite complex. The configuration change cis → trans in the platinum(II) complex and the easy dissociation of the nickel(0) species with the ligand P(CH$_2$CN)$_3$ suggest that the close proximity of many polar CN-groups might be responsible for the 'unconventional' behaviour. Thus, we can conclude that the parametrization of the coordination behaviour of phosphines, as suggested by Tolman, has sound predictive value as long as the new ligand does not contain features which are not accounted for by values of the parameters.

THE COORDINATING PROPERTIES OF A CHELATING DIPHOSPHINE

Let me now turn, for the last part of my talk, to another aspect of phosphorus chemistry, namely that in which phosphorus ligands are used to prepare complexes with very specific molecular geometries which can be exploited for the regio- and stereo-selective synthesis of organic compounds (16). An essential part of the strategy here is to know how the molecular structure of the phosphine affects the geometry and reactivity of the complex. I shall illustrate some aspects of this relationship using a chelating ditertiary phosphine, (XIV).
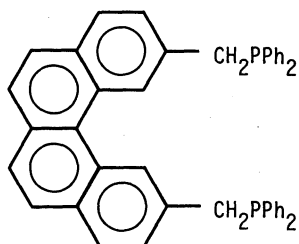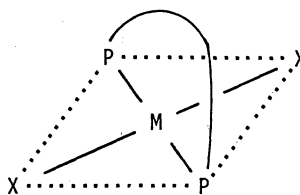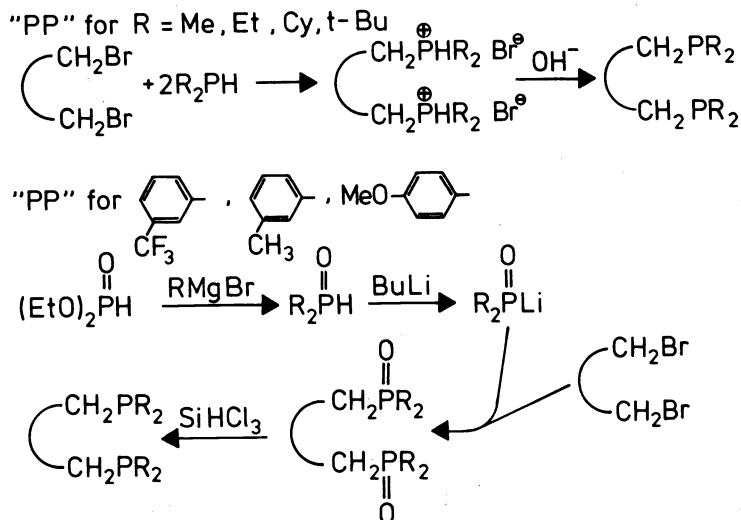

(XIV)   (XV)

This compound is one of a range of related ligands prepared in our group (17) using the synthetic routes shown in Scheme 1. The original scope of the work was to prepare a wide range of square planar complexes of type (XV) as examination of molecular models had shown that

SCHEME 1. Synthetic routes for chelating ligand "PP"

"PP" for R = Me, Et, Cy, t-Bu

$$\text{(ring)}\langle^{CH_2Br}_{CH_2Br} + 2R_2PH \longrightarrow \text{(ring)}\langle^{CH_2\overset{\oplus}{P}HR_2\ Br^{\ominus}}_{CH_2\overset{\oplus}{P}HR_2\ Br^{\ominus}} \xrightarrow{OH^-} \text{(ring)}\langle^{CH_2PR_2}_{CH_2PR_2}$$

"PP" for (phenyl)-CF₃ , (phenyl)-CH₃ , MeO-(phenyl)-

$$(EtO)_2\overset{O}{\underset{\|}{P}}H \xrightarrow{RMgBr} R_2\overset{O}{\underset{\|}{P}}H \xrightarrow{BuLi} R_2\overset{O}{\underset{\|}{P}}Li$$

$$\text{(ring)}\langle^{CH_2Br}_{CH_2Br}$$

$$\text{(ring)}\langle^{CH_2PR_2}_{CH_2PR_2} \xleftarrow{SiHCl_3} \text{(ring)}\langle^{CH_2PR_2}_{CH_2\underset{\|}{\underset{O}{P}}R_2}$$

ligands such as (XIV) should impart a preference for the formation of complexes of type (XV). Ligand (XIV) did indeed give a range of conventional complexes of this type as shown by the examples reported in Table 5.

TABLE 5. Some square-planar complexes formed by ligand (XIV) and by Ph₂PCH₂Ph (XIV)

Compound	Colour	$\delta^{31}P$ (ppm)	Δ_{CS} (obs.)	Δ_{CS} (calc.)	$^1J(M,P)$ (Hz)	$\nu_{CO}(cm^{-1})$
trans-[Ni(NCS)₂(XIV)]	orange red	14.9	23.6			
trans-[Ni(NCS)₂(XVI)₂]	orange red	14.1	22.8			
trans-[PdCl₂(XIV)]	deep yellow	19.7	28.4	31.1		
trans-[PdCl₂(XVI)₂]	deep yellow	20.1	28.8	31.8		
trans-[PtCl₂(XIV)]	yellow	18.6	27.3	25.6	2602	
trans-[PtCl₂(XVI)₂]	yellow	15.6	24.3	26.4	2585	
trans-[RhCl(CO)(XIV)]	pale yellow	28.2	36.9	38.0	124	1980
trans-[RhCl(CO)(XVI)₂]	yellow	29.5	38.2	39.4	118	1970
trans-[IrCl(CO)(XIV)]	yellow	21.7	30.4	32.2		1965
trans-[IrCl(CO)(XVI)₂]	yellow	21.8	30.5	32.8		1965

These complexes had the expected physico-chemical properties and the steric and electronic effects at the phosphorus sites, as measured by their infrared and nmr parameters, were very similar to those of the corresponding complexes with diphenylbenzylphosphine, XVI, (see Table 5).

Attempts to obtain square planar complexes with metal centres with electrons configurations other than d^8 soon convinced us that it was mainly the metal centre and not the organic ligand which determines the molecular geometry of the complex. Thus the complex [CoCl₂(XIV)] was readily obtained by ligand exchange from [CoCl₂(Ph₃P)₂] (18). Its high magnetic moment, μ_{eff} = 4.68 BM, and its electronic spectrum, however, showed that its coordination geometry was distorted tetrahedral as found for [CoCl₂(Ph₃P)₂] (19).

This observation started a series of investigations to establish whether ligand (XIV) did impart any preference at all for the formation of square planar complexes. The most informative set of results was obtained from the study of the three-coordinate complexes of the type [MX(XIV)] (M = Cu(I), Ag(I) and Au(I); X = anionic ligand) (20). A selection of these complexes and some of their properties are given in Table 6. The X-ray crystal structures

TABLE 6.   Some three-coordinate complexes of ligand (XIV)

Compound	$\Lambda_M(CH_3CN)$ [1]	$\Lambda_M(CH_3NO_2)$ [1]	$\delta^{31}P$ (ppm)	$^1J(^{109}Ag,^{31}P)$ (Hz)
[CuCl(XIV)]	insolv.	7.2	- 4.54 [2]	
[Cu(NO$_3$)(XIV)]	130.6	-	- 4.50 [2]	
[AgCl(XIV)]	18.4	10.3	+ 6.25 [3]	474
[Ag(NO$_3$)(XIV)]	117.2	insolv.	+ 7.98 [4]	536
[Ag(BF$_4$)(XIV)]	133.9	85.0	+ 12.06 [4]	593
[AuCl(XIV)]	83.0	66.5	+ 40.91 [4]	
[Au(NO$_3$)(XIV)]	133.8	81.3	+ 42.98 [4]	

[1]   Values of the molar conductivity, (in $ohm^{-1}cm^2mol^{-1}$), for ca. 10^{-3} M solutions at 25°. Under these conditions the normal range of Λ_M values for 1:1-electrolytes is 120-160 (CH$_3$CN) and 75-95 (CH$_3$NO$_2$) ohm^{-1} $cm^{-2}mol^{-1}$.
[2]   Measured in CH$_2$D$_2$ solution at 173° k.   [3]   Measured in CDCl$_3$ solution at 250°k.   [4]   Measured in CDCl$_3$ at 273°k.

of the three chloro-complexes were determined and their salient features are reproduced in Table 7.

TABLE 7.   Some structural data on complexes [MCl(XIV)] (M = Cu, Ag, and Au)

Complex	d(P$_1$-M)(Å)	d(P$_2$-M)(Å)	d(M-Cl)(Å)	α (P$_1$MP$_2$)	α (P$_1$MC)	α (P$_2$MCl)
[CuCl(XIV)]	2.258(2)	2.217(4)	2.222(2)	131.9(1)°	104.8(1)°	123.3(1)°
[AgCl(XIV)]	2.458(3)	2.411(3)	2.514(2)	140.7(1)°	98.2(1)°	120.9(1)°
[AgCl(XIV)]	2.307(2)	2.310(2)	2.818(3)	175.7(1)°	90.4(1)°	93.4(1)°

It is, thus, apparent that ligand (XIV) does impart a certain preference for the formation of linear P-M-P units and, therefore, also for the formation of square planar complexes, but it is also apparent that this effect is small compared with the energy required to change the coordination geometry from, say, tetrahedral to square planar in a transition metal complex.

We have also learnt how a metal centre brings about changes in P-M-P bond angles in complexes of ligand (XIV) without imposing too much overall strain on the organic molecular framework. The crystal structure of ligand (XIV) (22) is shown in Fig. 7. As can be seen, the two -CH$_2$-P vectors are eclipsed giving rise to a pseudo-boat type of ring conformation. This conformation is retained in all the square planar complexes in which the P-M-P bond angle is greater than 170° (23). An example of a structure of this type, that of
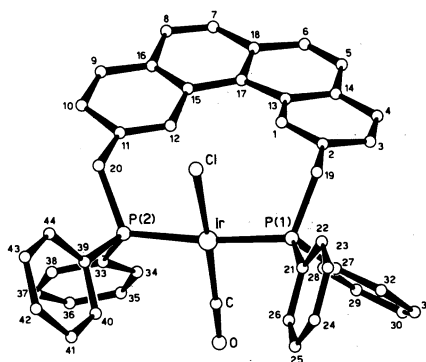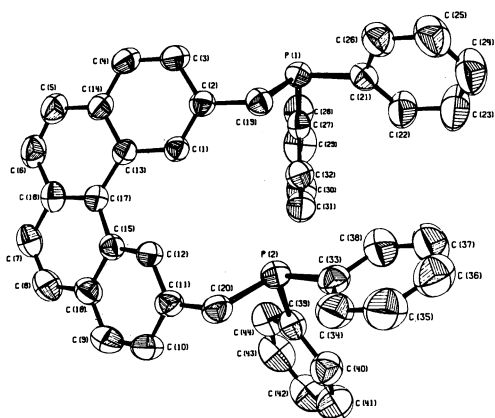
Fig. 7.   The crystal structure of ligand IX

Fig. 8.   The crystal structure of <u>trans</u>-[IrCl(CO)(XIV)]

<u>trans</u>-[IrCl(CO)(XIV)], is shown in Fig. 8.   The approximately linear P-M-P arrangement and pseudo-boat ring conformation are even retained in complexes of ligand (XIV) which are either five-coordinate, e.g., [RuCl(CO)(NO)(XIV)], (24) or six-coordinate, e.g., [IrCl$_3$(CO)(XIV)] (25) as shown in Figs. 9 and 10 respectively. The ring conformation, however, changes when
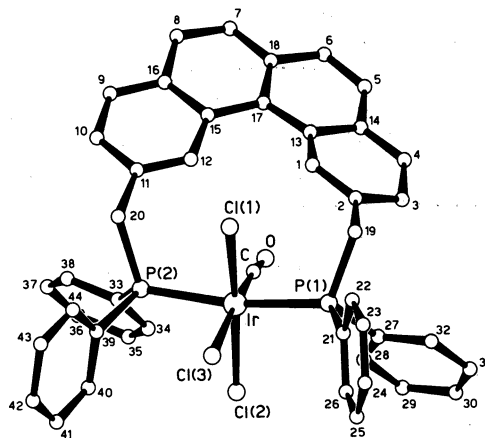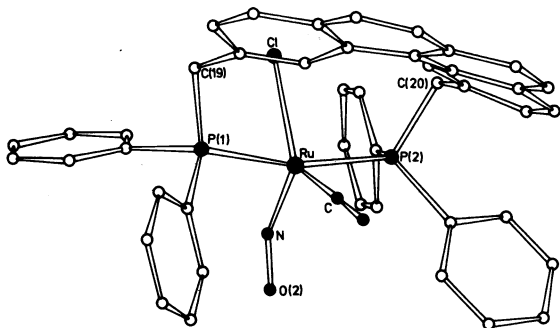

Fig. 9.   The crystal structure of [RuCl(CO)(NO)(XIV)]

Fig. 10.   The crystal structure of [IrCl$_3$(CO)(XIV)]

the P-M-P bond angle becomes smaller than 150°. The -CH$_2$-P vectors in these complexes become staggered as shown in Fig. 11 (21) for the complex [AgCl(XIV)].
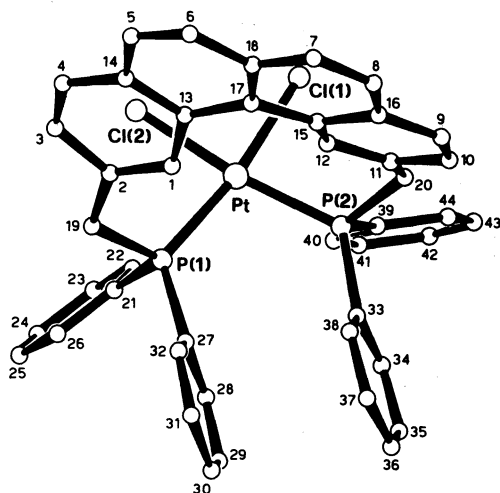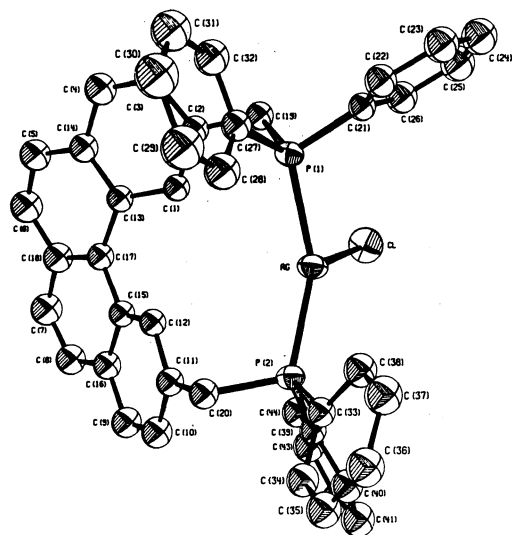

Fig. 11. The crystal structure of [AgCl(XIV)].

Fig. 12. The crystal structure of cis-[PtCl$_2$(XIV)]

It has also recently been shown (26) that ligand (XIV) can be coordinated to a metal atom in a very severely distorted form as found in cis-[PtCl$_2$(XIV)]. The crystal structure of this compound is shown in Fig. 12. Here most bond angles in the vicinity of the metal centre have been significantly distorted. The resulting structure, however, is stabilized by strong graphite-like interactions between two terminal phenyl groups. The implication of this observation is clear: apparently rigid organic molecules can be tied into proverbial knots upon coordination, particularly if the two donor atoms are separated by many carbon atoms or, in other words, the organic backbone is 'softer' than the coordination polyhedron in transition metal complexes. This is a factor that will have to be taken into account by chemists planning regio- and stereospecific organic syntheses using transition metal complexes of chelating phosphine ligands as is the case for effective asymmetric catalytic hydrogenation (27).

During the course of this talk I have tried to present to you the types of problems that confront a practising phosphine coordination chemist. My co-workers and I have enjoyed doing this work and I hope I have been able to communicate to you our sense of excitement during the development of the chemistry described in this talk.

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