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LIGAND INTERACTIONS IN CROWDED MOLECULES

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A. INTRODUCTION

The chemistry of transition metal complexes containing tertiary phosphines as ligands is greatly influenced by the nature of the substituents on phosphorus. Such effects are generally attributed to some combination of the steric and electronic characteristics of the individual ligands. Certainly the σ-donor nature of the phosphorus ligand is largely determined by the substituents on phosphorus, which also influences the ability of the phosphine to act as a π-acceptor of electron density from the metal centre. Although it is generally accepted that such π-interaction occurs, the question of whether it is $(d\pi-d\pi)$, $(d\pi-p\pi)$ or $(d\pi-\sigma^*)$ is still the subject of some discussion [2]. While our understanding of the nature of the phosphine–transition metal bond is reasonably well developed, our level of understanding of ligand steric effects is much lower. Moreover, the clear separation of steric and electronic components of the ligand interaction with the metal is extremely difficult.

The first major attempt to describe the steric properties of a ligand was made by Tolman in 1970 [3]. Tolman defined the cone angle of a ligand as the angle subtended at the metal just large enough to enclose the van der Waals radii of the outermost atoms of the ligand. The cone angles were determined empirically using CPK models of phosphine molecules (assum-

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ing an M–P bond distance of 2.28 Å); where ligands had some flexibility, the substituents on phosphorus were folded back into as small a cone angle as possible while still retaining three-fold symmetry.

Trogler and Marzilli [4] developed an alternative approach through a study of the ^{1}H NMR spectra of a series of complexes of the type $[CoL(DH)_2(CH_3OH)]^+$, where L is a tertiary phosphine and DH is dimethylglyoximato. The chemical shift of the methanol methyl resonance was found to be sensitive to the steric bulk of L, and on the assumption that the DH ligands approach the methanol methyl group more closely with increasing size of L, cone angles for the different ligands L were calculated semi-empirically. These values are in quite good agreement with those obtained by Tolman.

It seems clear, on the basis of these and numerous subsequent studies, that the concept of cone angle provides a reasonable measure of relative ligand size. As Tolman realized at the outset, cone angle does not describe the absolute steric demand of a particular phosphine ligand, and it certainly takes no account whatsoever of the intermeshing of ligands when two or more are coordinated to the same metal centre. So, for example, the compounds $Pt^0(PPh_3)_4$ and $Pt^0(PCy_3)_3$ (Cy = cyclohexyl) would not be expected to exist based on the cone angles of 145° for PPh_3 and 170° for PCy_3 [5]. However, both are readily prepared, stable compounds and indeed an X-ray structural analysis of $Pt(PCy_3)_3$ [6] shows it to be a relatively unhindered molecule. The values of 145° for PPh_3 and 170° for PCy_3 thus describe the relative sizes of these ligands but do not describe how such ligands can be accommodated about the metal centre.

Several quantitative approaches to the problem of ligand intermeshing have been described. Stepaniak and Payne [7] used available crystallographic data for square planar complexes with *cis* geometry. In their calculations, the conical symmetry of the ligand was removed, and the maximum and minimum cone angles were determined by employing vector measurements between phosphine substituents with incremental rotation about the metal–phosphorus bond. Not surprisingly, a minimum value of the variable cone angle was obtained at the 0° rotation position for each phosphine ligand, reaffirming the fact that the least hindered orientation is indeed the one which is adopted in the solid state stereochemistry. In each case there is substantial variation in the cone angle value as rotation about the M–P bond is allowed to occur, with the measured maximum values being generally comparable to the cone angle as measured by Tolman, and the minimum value (e.g. for PCy_3 a minimum value of 113°) allowing the existence of species such as $Pt^0(PCy_3)_3$ to be rationalized.

Ferguson et al. [8–11] have also used crystallographic data to develop the concept of ligand profile, in which the semi-cone angle subtended at the

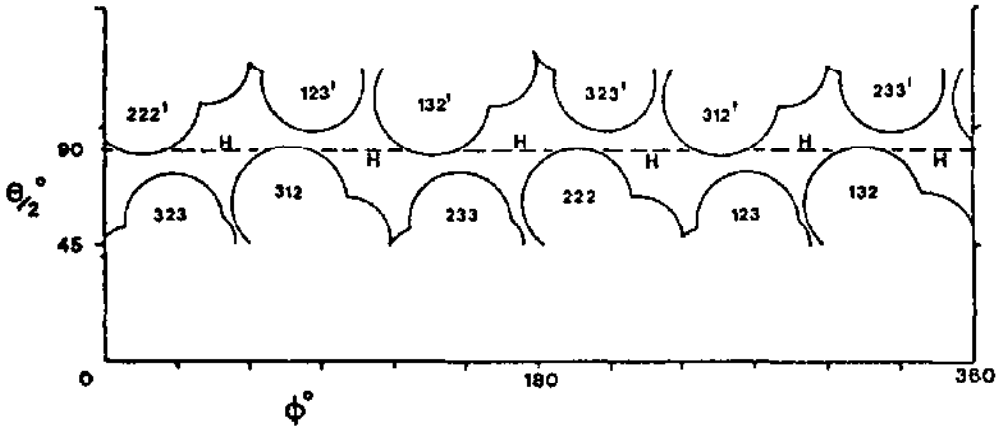


Fig. 1. Ligand profile of Pt–Bu_3 in *trans*-$H_2Pt(P^tBu_3)_2$.

metal between the M–P bond and the point of contact of the vector M → X from the metal to the van der Waals radius of the outermost ligand substituent is measured. As rotation is allowed to occur about the M–P bond, the ligand profile yields quantitative information about the spatial arrangement of the phosphine ligand substituents. For example, intermeshing of the ligands in the molecule *trans*-$H_2Pt(P^tBu_3)_2$ is immediately obvious [12] from the ligand profile diagram of the P^tBu_3 ligands (space group symmetry requires that the carbon atoms bonded to phosphorus are fully staggered about the P–Pt–P axis) (Fig. 1). Figure 1 also shows clearly that there are six sites, separated by 60°, which are essentially sterically equivalent, as a result of gaps between the "teeth" of the *t*-butyl "cogs". There are, therefore, three possible ways in which a pair of *trans*-hydrido atoms can be accommodated in the plane normal to the P–Pt–P axis. A similar approach to the calculation of ligand profiles has been taken by Smith and Oliver [13]. A different approach [14] has used the determination of the *cis : trans* ratios of the W(CO) L L′ complexes to evaluate the relative sizes of twelve phosphines (L′).

While these more recent approaches provide considerable information about ligand intermeshing, and provide reasonable correlations between what we know of ligand size and the actual chemistry of phosphine–metal complexes, a number of questions remain to be addressed. These include the following: (a) Does a phosphine ligand have the same "size" in all its complexes? (b) By what types of distortion does a phosphine ligand adjust to increasing steric crowding about the metal centre? (c) What correlations can be drawn between the solid state structure of a phosphine–metal complex, and its behaviour in solution where presumably free rotations about the M–P bonds can occur? To address such questions meaningfully, a sufficient

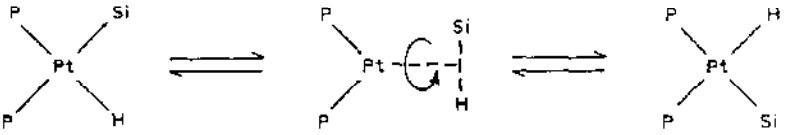
number of crystal structure determinations needs to be available for complexes of a particular phosphine with a particular metal. This is only now possible; for tricyclohexylphosphine complexes of platinum(II), the number of structures now known (approximately thirty) provides a sufficient database to address such questions, and the properties of tricyclohexylphosphine as a bulky ligand make it very suitable for the study of ligand interactions. The purpose of this article is, then, to review the unique chemistry of bulky phosphine complexes of platinum, with particular reference to the tricyclohexylphosphine complexes we have prepared and hence to increase our understanding of the ways in which such sterically demanding ligands are accommodated about a metal centre. Throughout this discussion, however, the extent to which electronic and steric effects of phosphine ligands are interwoven must be remembered. This is well illustrated, for example, by the comparison by Richardson and Payne [15] of $L_2Pt(C_4F_6)$ for $L = PPh_3$ and $L = PCy_3$.

B. THE CHEMICAL SIGNIFICANCE OF BULKY PHOSPHINE–METAL COMPLEXES

Since the first report [16,17] of phosphine complexes of zerovalent palladium and platinum, the major interest in the preparation of bulky phosphine complexes of transition metals has been to stabilize coordinatively unsaturated species, especially of low valent metals. The earlier molecular weight [18] and NMR [19] studies of the four-coordinate species, $Pt(PPh_3)_4$, established the formation in solution through loss of phosphine ligand, of the three- and two-coordinate species $Pt(PPh_3)_3$ and $Pt(PPh_3)_2$. However, using bulky phosphines, the two-coordinate platinum(0) complexes are sufficiently stable to be isolated and characterized. In particular, $Pt(PCy_3)_2$ [20], $Pd(PPh^tBu_2)_2$ [21], $Pt(P^tBu_3)_2$ [22] and $[Pt(^tBu_2P(CH_2)_3P^tBu_2)]_2$ [23] have been structurally characterized by X-ray diffraction methods. It then becomes possible to examine the chemistry of the otherwise inaccessible two-coordinate, 14-electron species, Pt^0L_2. One relatively simple comparison [24] of the chemistry of such species was that of $Pt(PCy_3)_2$ and $Pt(PEt_3)_3$ towards a series of molecules RH (where R = variously substituted phenyl) containing activated hydrogen, to form *trans*-$HRPt(PR_3)_2$. It was found that $Pt(PCy_3)_2$ was more reactive towards C–H, O–H, and N–H bond cleavage than $Pt(PEt_3)_3$, but was less reactive towards cleavage of the C–C bond of C_6H_5CN. It was also observed that $Pt(PCy_3)_2$ is more nucleophilic than $Pt(PCy_3)(C_2H_4)_2$.

Although members of the two-coordinate species PtL_2 should be highly reactive, the degree and nature of their reactivity can be regulated by the degree of steric overcrowding produced by L; this has recently been demonstrated nicely [25] in a series of platinum–silicon derivatives. The oxidative

addition of silanes to $Pt^0(PCy_3)_2$ in hexane solution led to isolation of the platinum(II) product *cis*-$H(R_3Si)Pt(PCy_3)_2$, which when dissolved in benzene solution exhibited two dynamic processes: namely, an intramolecular ligand position interchange which had been observed previously [26] for the

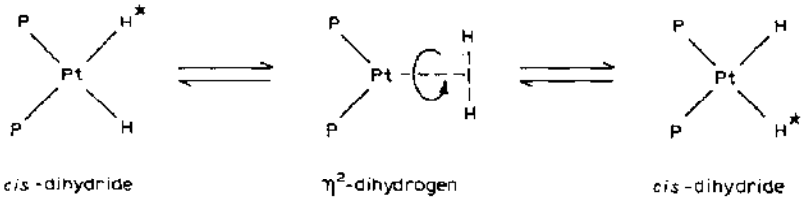


species *cis*-$H(R_3Si)Pt(PPh_3)_2$ and a readily reversible oxidative addition–reductive elimination equilibrium represented by the equation

cis-$H(R_3Si)Pt(PCy_3)_2 \rightleftharpoons Pt^0(PCy_3)_2 + HSiR_3$

The position of this delicately balanced equilibrium was found to be markedly dependent on the nature of the silicon substituent, with more electron withdrawing substituents causing displacement towards the platinum(II) complex. The existence of this oxidative addition–reductive elimination equilibrium is no doubt a combined effect of the steric and electronic properties of all the ligands involved, but since no such equilibrium is observed for the PPh_3 analogues, the acute inter-ligand repulsions which arise for $L = PCy_3$ must be largely responsible. This seems to be confirmed by the observation [27] that analogous chelating diphosphine complexes *cis*-$H(R_3Si)Pt(Cy_2P(CH_3)_nPCy_2)$ do not exhibit either of the above equilibria for $n = 2$, 3 or 4, and only for the case of $n = 7$ (where any chelate ring effect must be largely absent and the ligand resembles most closely two free PCy_3 ligands) is there any evidence for similar intramolecular ligand position exchange and oxidative addition–reductive elimination equilibria.

By employing the bulkiness of both tertiary phosphines and chelating diphosphine ligands, it is possible to examine the mechanism of activation of dihydrogen. *cis*-Dihydride species have been prepared previously [23] for a number of bulky chelating diphosphines (e.g. $^tBu_2P(CH_2)_nP^tBu_2$) and are stable towards air in both the solid state and solution. In our laboratory, we have recently studied [28] the species *cis*-$H_2Pt(Cy_2P(CH_2)_nPCy)$ which in solution are believed to undergo an intramolecular hydride ligand exchange process (on the NMR timescale) possibly via a platinum(0) η^2-dihydrogen intermediate.



The spin lattice relaxation time (T_1) of the hydride ligands (e.g. for *cis*-$H_2Pt(1,3\text{-}Cy_2P(CH_2)_3PCy_2)$ $T_1 = 350$ ms) is intermediate [29] between the values expected for a formal η-H_2 ligand (30–70 ms) and a terminal hydride ligand (700 ms–2 s [29–31]), and therefore consistent with formulation as an η^2-H_2 intermediate.

We have also observed the species *cis*-$H_2Pt(PCy_3)_2$ as an intermediate during the reaction of hydrogen gas with $Pt^0(PCy_3)_2$ at low temperatures, which spontaneously and irreversibly isomerizes to the *trans*-isomer at temperatures greater than $-50\,^\circ C$. In contrast, *cis*- and *trans*-bis(phosphine) platinum(II) dihydride complexes with less bulky phosphine ligands [32] exist in equilibrium in solution.

$$cis\text{-}H_2Pt(PEt_3)_2 \rightleftharpoons trans\text{-}H_2Pt(PEt_3)_2$$

The complex *cis*-$H_2Pt(PCy_3)_2$ also undergoes the same intramolecular hydride ligand exchange process as the chelating disphosphine analogues [33]. Thus, even with these sterically demanding phosphine ligands, oxidative addition of dihydrogen occurs to give a kinetic product of *cis*-geometry which then converts to the *trans*-analogue as the final thermodynamic product.

The greater stability of the dihydrides such as *trans*-$H_2Pt(PCy_3)_2$, obviously a consequence of the steric protection of the Pt–H bond provided by the very bulky phosphines, has allowed a detailed study of their chemistry. The *trans*-dihydrides, L_2PtH_2, (L = PPh^tBu_2, PCy_3, P^iPr_3) are stable to air in solution and do not require a hydrogen atmosphere to prevent decomposition [34]. The very hindered complex $Pt^0(P^tBu_3)_2$ does not add hydrogen or oxygen, or react with methanol at normal pressure. *trans*-$H_2Pt(PCy_3)_2$ reacts with activated acetylenes to give the corresponding hydrido(alkenyl) platinum(II) complexes [35], the remaining Pt–H bond being inert towards excess acetylene presumably for steric reasons.

$$trans\text{-}H_2Pt(PCy_3)_2 + RC{\equiv}CR' \rightarrow trans\text{-}H[RHC{=}C(R')\text{-}]Pt(PCy_3)_2$$

Kinetic studies provide evidence that these reactions proceed via an electron transfer process, and ESR studies are consistent with the formation of novel bis(phosphine)hydrido platinum(II) (π-acetylene) species in which the unpaired electron is delocalized over an unsaturated three-membered metallocyclic ring. This is of course relevant to the understanding of homogenous catalytic systems in which one of the key steps is insertion of the unsaturated molecules into the metal–hydrogen bond. Insertion of CO_2 [36] and CS_2 [37] into the Pt–H bond of *trans*-$H_2Pt(PCy_3)_2$ has also been described.

A further interesting consequence of the steric overcrowding produced by bulky phosphine ligands, is evident in the tendency to undergo orthometalla-

tion reactions which such complexes display (i.e. C–H bond activation). The very hindered dihydride, *trans*-$H_2Pt(P^tBu_3)_2$ undergoes a facile intramolecular metallation reaction in solution [38] to form a dinuclear hydride-bridged species according to the following equation

$$trans\text{-}H_2Pt(P^tBu_3)_2 \rightarrow [(^tBu_2PCMe_2CH_2)PtH]_2 + H_2 + P^tBu_3$$

whereas the species $HXPt(P^tBu_3)_2$ forms mononuclear metallated products [39]

$$trans\text{-}HXPt(P^tBu_3)_2 \rightarrow trans\text{-}[(^tBu_2PCMe_2CH_2)PtX(P^tBu_3)] + H_2$$

These examples illustrate the importance of the steric properties of phosphine ligands in determining the overall chemistry of platinum complexes. It is therefore highly desirable to develop a more detailed and sophisticated understanding of the nature of steric interactions between ligands in such complexes.

C. LIGAND INTERACTIONS IN TRICYCLOHEXYLPHOSPHINE–PLATINUM COMPLEXES

We will consider three different experimental methods of gathering information about ligand interactions in tricyclohexylphosphine–platinum complexes. X-ray crystal structure determination is, of course, by far the most important; it does, however, provide only static solid state information. We also describe the uses of ^{31}P solid state NMR spectroscopy, as well as ^1H NMR spectroscopic techniques, to correlate solid state information with the solution behaviour of tricyclohexylphosphine complexes.

There are now well over twenty reported crystal structures of mono-nuclear tricyclohexylphosphine complexes of platinum, and about twelve others of dimeric or cluster structures [40–49]. As is demonstrated below, they reveal that the steric overcrowding in such molecules is accommodated, progressively and in this order, by the following types of distortion: (a) lengthening of the Pt–P bond; (b) significant departures from square geometry at the Pt centre (but preserving planarity); (c) distortion of the Pt–P–C angles and of the phosphine ligand as a whole; (d) deviation from planar geometry.

Table 1 contains some data on the relevant structurally characterized derivatives. Those which contain only one PCy_3 ligand bonded to Pt can be used as a reference for the stereochemistry of the phosphine ligand in an uncrowded environment. In such a case (e.g. $(PCy_3)Pt(SnCl_3)$(Me-allyl)) the three Pt–P–C angle values typically lie in the range 110°, 114° and 112°, so that the phosphine ligand has retained its essential tetrahedral symmetry at phosphorus, the three cyclohexyl rings are each in the chair conformation,

TABLE 1

Compound	Ref.	P–Pt–P	Pt–P	Pt–P–C	Other
$Pt(PCy_3)(^tBuNCS_2)_2$	50	–	2.278(4)	109.6, 114.3, 111.8	Pt–S1 = 2.329(4) Pt–S4 = 2.326 Pt–S3 = 2.364(3)
$Pt(PCy_3)(C_2H_4)(C_2F_4)$	51	–	2.343(2)	109.9, 113.6, 111.8	
$Pt(PCy_3[(OC(CF_3))_2CH_2]_2$	52	–	2.230(4)		Pt–O1 = 2.79(1) Pt–O3 = 2.10(1) Pt–O2 = 1.99(1) Pt–O4 = 1.98(1)
$[Pt(PCy_3)(\mu\text{-}CO)]_3$	41	–	2.267(7) 2.282(9)		
$Pt_3(PCy_3)_4(\mu\text{-}CO)_3$	42	–	2.303(5) 2.285(5) 2.351(4) 2.349(4)		
$Pt(PCy_3)(SnCl_3)$(Me-allyl)	53	–	2.282(1)	109.9, 114.7, 11.4	Pt–Sn = 2.544(0) Pt–Sn–Cl = 113.3, 120.2, 128.0
trans-$Cl_2Pt(PCy_3)_2$	54	180	2.337(2)	111.2, 114.7, 111.4	
trans-$I_2Pt(PCy_3)_2$	55	180	2.371(2)	111.0, 113.8, 111.5	
trans-$H_2Pt(PCy_3)_2$	56	180	2.26(1)		
trans-$[Me(H_2O)Pt(PCy_3)_2]^+ PF_6^-$	57	176	2.340(2) 2.333(2)	110.1, 115.4, 113.0 110.3, 115.4, 110.7	Pt–C = 2.340(2)
trans-$H(O_2CH)Pt(PCy_3)_2$	36	168.0	2.289(3) 2.287(3)		Pt–O = 2.27(1)
trans-$H(OCO_2Me)Pt(PCy_3)_2$	36	166.1	2.290(3) 2.287(3)		Pt–O = 2.13(1)
trans-[H(3-Me-1,2-butadiene)$Pt(PCy_3)_2$	58	164	2.332(2) 2.329(2)	108.9, 115.3, 111.9 109.2, 115.9, 111.9	
trans-$H(S_2CH)Pt(PCy_3)_2$	37	161.1	2.274(5) 2.278(5)	103.6, 118.6, 114.8 106.3, 115.7, 113.6	Pt–S = 2.368(6)
trans-$H(OCH{=}CPh_2)Pt(PCy_3)_2$	59	167.9	2.287(4) 2.286(4)		Pt–O(A) = 2.12(2) Pt–O(B) = 2.17(2)

trans-H(OC=CHC(Me)(COOEt)OCO)-Pt(PCy_3)$_2$	60	166.4	2.287(7) 2.298(6)		Pt–O = 2.11(2)
trans-H(PhHC=C(CF_3))Pt(PCy_3)$_2$	61	159.7	2.296(2) 2.298(2)	109.0, 118.0, 111.4 110.6, 117.9, 111.3	Pt–C = 2.11(1)
trans-H(H_3Si)Pt(PCy_3)$_2$	62	166.2	2.280(2) 2.283(2)	110.3, 117.4, 111.5 109.8, 117.2, 110.6	Pt–Si = 2.382(3)
trans-H(Ph_3Sn)Pt(PCy_3)$_2$	63	160.2	2.294(2) 2.283(2)	110.2, 115.0, 115.4 110.2, 121.2, 111.6	Pt–Sn = 2.654(1) Pt–Sn–C = 123, 117, 117
trans-H(Cl_3Sn)Pt(PCy_3)$_2$	63	159.0	2.319(5) 2.302(5)	107.8, 119.9, 109.7 103.8, 109.2, 105.5	
trans-[H(Ph_3P)Pt(PCy_3)$_2$]$^+$ PF_6^-	64	155.2	2.325(3) 2.346(3)		Pt–P1 = 2.359(3)
trans-[H(Cy_2Ph)Pt(PCy_3)$_2$]$^+$ PF_6^-	57	142.7	2.346(3) 2.337(3)	104.9, 124.7, 110.7 105.5, 122.9, 111.5	Pt–P1 = 2.383 Pt–P–C = 116, 116, 115
trans-Cl($PhCl_2Si$)Pt(PCy_3)$_2$	65	167.8	2.350(1) 2.388(1)	106.6, 112.1, 112.5 104.8, 121.4, 113.4	Pt–Si = 2.280(1) Pt–Cl = 2.409(1) Si–Pt–Cl = 164.7
(PCy_3)$_2$Pt(C_2H_4)	33	116.3	2.284(1)		Pt–C = 2.137(7) C–C = 1.440(7) C–Pt–C = 39.4 Pt–C–C = 70.3
[(PCy_3)$_2$Pt(allyl)]$^+$ PF_6^-	13	111.2	2.335(3) 2.327(4)	107.3, 118.0, 115.8 107.2, 118.6, 113.8	
(PCy_3)$_2$Pt(C_4F_6)	15	110.2	2.309(2) 2.301(2)	109.5, 120.2, 109.6 105.2, 124.6, 110.5	
(PCy_3)$_2$Pt($O_2C_2(CO_2Me)_2$)	66	109.3	2.270(4) 2.276(4)	103.8, 121.5, 111.3 105.4, 121.9, 111.5	Pt–O1 = 2.05(1) Pt–O2 = 2.04(1) O1–Pt–O2 = 81.6
(PCy_3)$_2$Pt	20	160.5	2.231(4)	114.9, 120.7, 106.9	
(PCy_3)$_3$Pt	6	120	2.303(ave)		

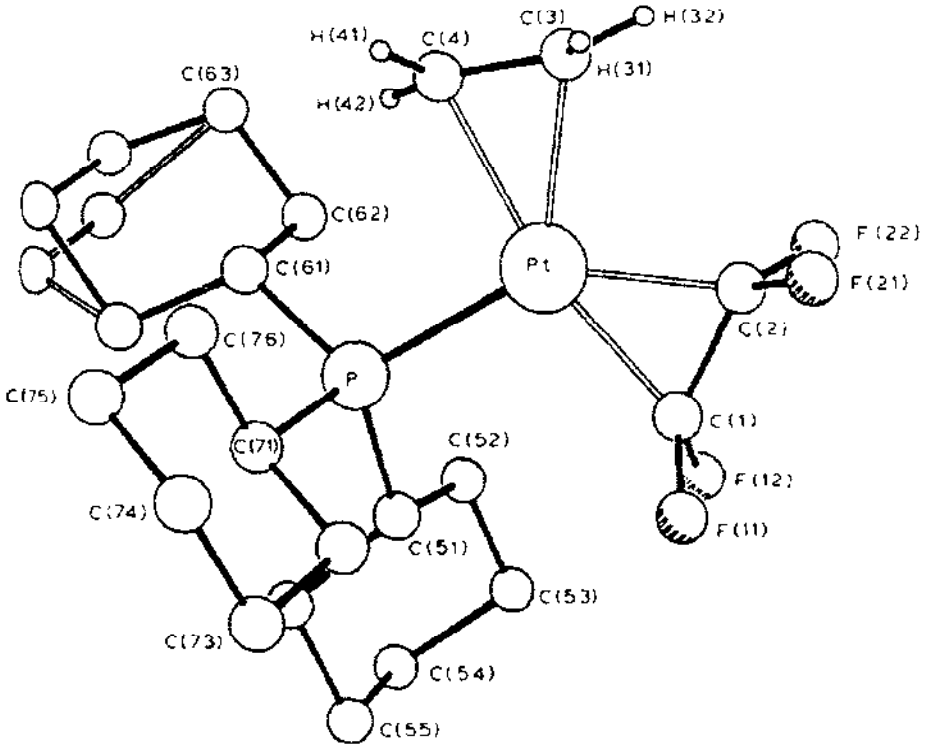


Fig. 2. The structure of $(Cy_3P)Pt(C_2H_4)(C_2F_4)$.

and the Pt–P bond length is 2.27–2.28 Å, with the exception of $(PCy_3)Pt(C_2H_4)(C_2F_4)$ (Figs. 2, 3). The increase, in the latter compound, of the Pt–P distance to 2.343(2) Å is clearly an electronic effect and reflects the strong competition by C_2F_4 with PCy_3 for the π-electron density from platinum. With this exception, therefore, the normal Pt–P distance can be regarded as approximately 2.28 Å. This is essentially the same as that observed in most other phosphine platinum complexes.

Mononuclear compounds containing more than one PCy_3 ligand can be subdivided into several classes.

(i) trans-*$XYPt(PCy_3)_2$*

(a) Where X = Y = Cl, I or H (Fig. 4)

The two compounds *trans*-$X_2Pt(PCy_3)_2$, X = Cl or I, are isostructural, have a staggered arrangement of cyclohexyl rings and a P–Pt–P angle of 180°. The Pt–P–C angles are all near normal, and although there are a number of relatively short intramolecular halogen–carbon distances, there is little evidence of overcrowding. However, a comparison of Pt–P distances with those observed in other platinum(II) *trans*-dihalides of less bulky

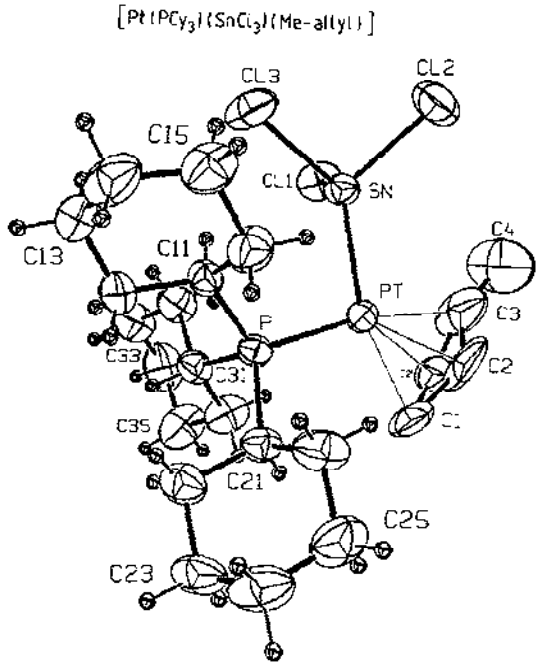


Fig. 3. The structure of $(Cy_3P)Pt(SnCl_3)$(Me-allyl).

phosphines, e.g. *trans*-$Br_2Pt(PEt_3)_2$ (Pt–P = 2.314 Å) [67] and *trans*-$I_2Pt(PMe_3)_2$ (Pt–P = 2.315 Å) [68], shows that the overcrowding has been minimized (i.e. ligand–ligand interactions minimized) by a significant lengthening of the Pt–P bond to 2.337(2) Å (X = Cl) and 2.371(2) Å (X = I). The shorter Pt–P bond length of 2.26(1) Å for *trans*-$H_2Pt(PCy_3)_2$ which contains the much smaller hydrido ligand, is also consistent with this. Although no longer centrosymmetric, the structure of $[Me(H_2O)Pt(PCy_3)_2]^+$

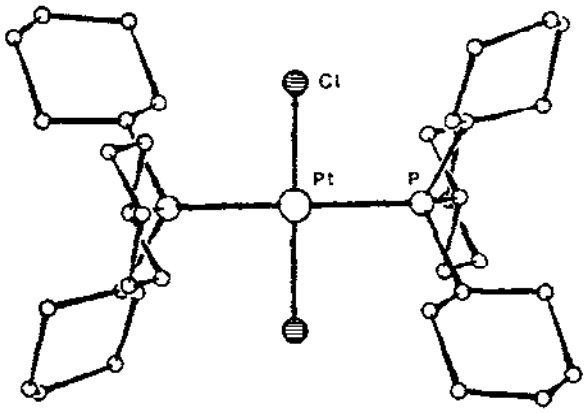


Fig. 4. The molecular structure of *trans*-$Cl_2Pt(PCy_3)_2$.

PF_6^- can be placed in this same category, with the larger methyl and water ligands being accommodated by an essentially staggered arrangement of the two trigonal phosphines and a lengthening of the Pt–P distances (2.330(2) and 2.340(2) Å) as in the dichloride or diiodide.

(b) trans-*HXPt(PCy$_3$)$_2$; X = planar ligand*

The second general type consists of those compounds which correspond to the stoichiometry *trans*-HXPt(PCy_3)$_2$ where X is generally a planar, unsymmetrically coordinated group (e.g. O_2CH). Although few published data are available for such compounds, it appears that the cyclohexyl rings adopt an almost eclipsed conformation. The P–Pt–P angles lie in the range 168–161°, being bent back over the hydride ligand to relieve the steric interaction between the cyclohexyl rings and the other ligand X. A closely-related case is that of the structure of *trans*-H[PhHC=C(CF_3)-]Pt(PCy_3)$_2$ in which the alkenyl group is in a plane perpendicular to the coordination plane, with the two trigonal PCy_3 ligands adopting the eclipsed conformation. In a different attempt to reduce the interactions between the cyclohexyl substituents and the ligand for the analogous compound with X = S_2CH, one Pt–P–C angle in each phosphine ligand is increased somewhat compared to the values of the diiodo and dichloro derivatives. Clearly, however, the major relief from overcrowding in these molecules is obtained by reduction of the P–Pt–P angle, readily allowable because of the small size of the hydride ligand. The somewhat unusual eclipsed conformation of the trigonal phosphines is presumably possible only because of the planar nature of X (Fig. 5).

(c) trans-*HXPt(CPy$_3$)$_2$; X = ER$_3$*

A third structural type corresponds to the compounds *trans*-H(R_3E)Pt(PCy_3)$_2$ where E = P, Sn or Si. Members of this class exhibit some of the most severe ligand interactions in stable complexes yet observed and are worth describing in detail. In some respects, *trans*-H(H_3Si)Pt(PCy_3)$_2$ belongs to the previous class of structural types; on the basis of the P–Pt–P angle, the Pt–P bond distances and the Pt–P–C bond angles. The Pt–P–C angles are largest (about 117°) for the cyclohexyl ligands closest to the silyl substituent, providing a protective envelope against attack by other substrates. The angles P–C–C between the carbon atoms within the rings are also large (up to 119.3°). The Pt–Si bond (2.382(3) Å) is significantly longer than similar Pt–Si bond lengths reported for other compounds [69], no doubt a combined result of the *trans*-influence of the hydride ligand and steric interaction of SiH_3 with the cyclohexyl rings. That the cyclohexyl rings have an almost eclipsed conformation is then perhaps surprising, although

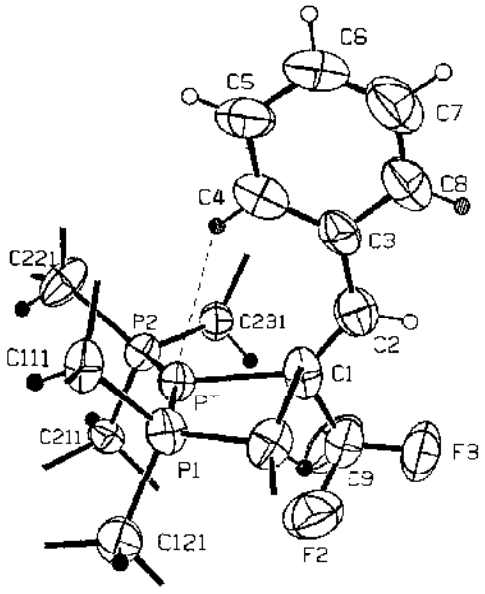


Fig. 5. The structure of *trans*-H[PhHC=C(CF_3)–]Pt(PCy_3)$_2$ (cyclohexyl rings omitted).

understandable if one views –SiH_3 as essentially spherical and substantially different in size from say, $SiCl_3$.

The other members of this class, where ER_3 = $SnPh_3$, $SnCl_3$, PPh_3 and PCy_2Ph clearly show a cog-wheel type of interaction evidenced by the staggered arrangement of all ligands which is a result of the combined bulk of the substituents. Presumably, in solution these ligands undergo concerted rotation about the Pt–P and Pt–E bonds (see below). For the derivative *trans*-H(Ph_3Sn)Pt(PCy_3)$_2$ (Fig. 6), greater interaction between the ligands is apparent from the larger Pt–P bond length (2.294(2) Å) and the larger Pt–P–C angles (up to 121.2°) compared to the complexes so far discussed. The P–Pt–P angle is not as small as might at first be expected and is offset, to some extent, by a long Pt–Sn bond. Also, some reduction in the interaction between the phenyl and cyclohexyl rings is achieved by a slight distortion from tetrahedral geometry about the tin atom. The P–C–C angles are also significantly distorted and lie between a minimum value of 111°, and 118°. Apart from these deviations the cyclohexyl rings all have chair conformations.

The structure of the species *trans*-H(Cl_3Sn)Pt(PCy_3)$_2$ is very similar. The P–Pt–P angle is very similar and if the Pt–Sn distance is considered to be the same, then it can be concluded that the "coordination volumes" required by the $SnCl_3$ and $SnPh_3$ ligands at the metal centre are comparable. The views of these two complexes, shown in Fig. 7, illustrate the staggered orientation that all the ligands attempt to adopt with respect to each other.

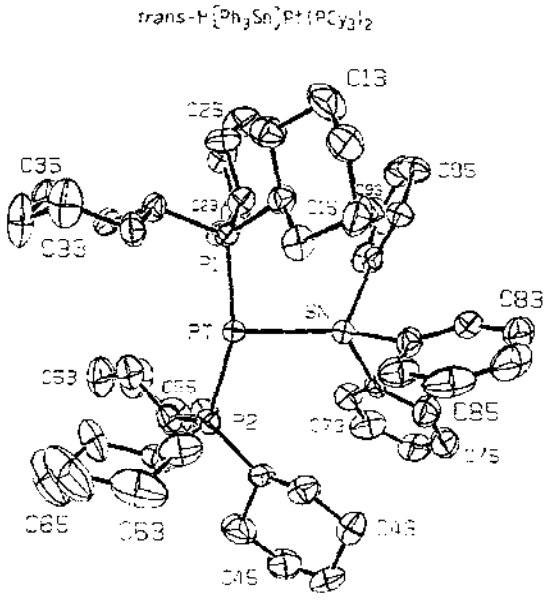


Fig. 6. The structure of *trans*-$H(Ph_3Sn)Pt(PCy_3)_2$.

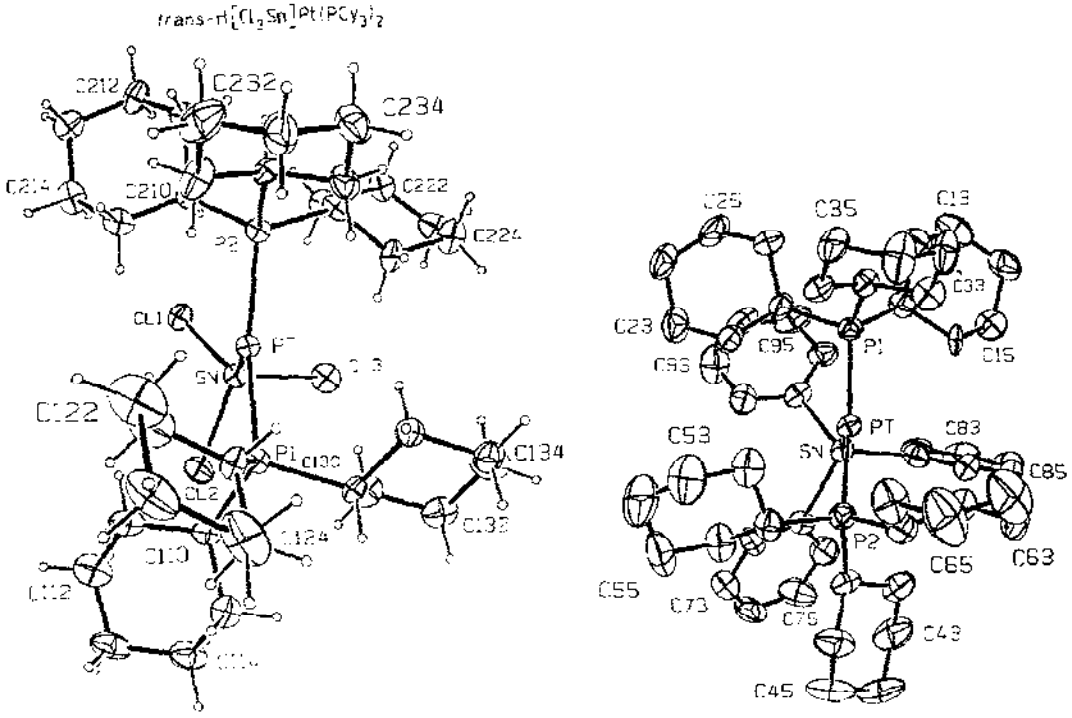


Fig. 7. A comparison of the structures of *trans*-$H(Ph_3Sn)Pt(PCy_3)_2$ and *trans*-$H(Cl_3Sn)Pt(PCy_3)_2$.

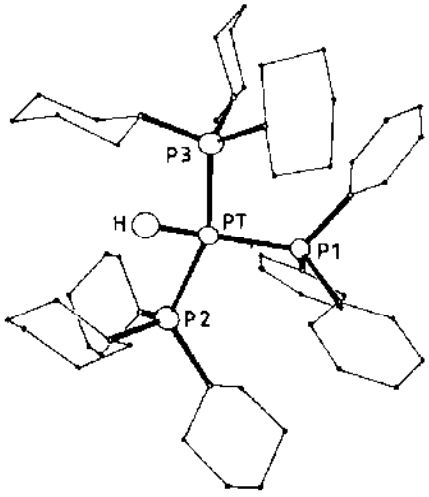


Fig. 8. The structure of the cation *trans*-$[H(Ph_3P)Pt(PCy_3)_2]^+$.

The compound *trans*-$[H(Ph_3P)Pt(PCy_3)_2]^+PF_6^-$ (Fig. 8) exhibits even greater distortion, probably due to the shorter Pt–P_1 bond length compared to the Pt–Sn distance of the isoelectronic tin analogue. As a result, the Pt–P_2 and Pt–P_3 bond lengths are longer and the P_2–Pt–P_3 angle is smaller than that observed for the analogous tin derivative. However, the relative orientations of the cyclohexyl and phenyl rings are virtually identical in the two compounds.

The molecule with the most severe intramolecular ligand interactions is that of the complex *trans*-$[H(Cy_2PhP)Pt(PCy_3)_2]^+PF_6^-$ (Fig. 9). Compared to the triphenylphosphine analogue above, the Pt–P_1 bond distance of 2.383 Å is even longer as are those of Pt–P_2 (2.346(3) Å) and Pt–P_3 (2.337(3) Å). Even so, this lengthening is not sufficient to accommodate the increased bulk of the PCy_2Ph ligand, and the P–Pt–P angle is reduced still further by over 12° to a remarkable 142.7°. All of the ligand substituents adopt a staggered conformation with respect to each other. The extreme crowding is also shown by the large Pt–P_2–C_{41} (125°) and Pt–P_3–C_{91} (123°) angles for the cyclohexyl rings of the PCy_3 ligands closest to the PCy_2Ph moiety, together with a concomitant reduction in other Pt–P–C angles (106 and 105°). The angles at some of the carbon atoms within the cyclohexyl rings are also somewhat enlarged, but the chair conformation is maintained in each case.

(d) trans-*$XYPt(PCy_3)_2$; X, Y = bulky ligands*

The fourth structural type comprises those compounds which have two different bulky substituents in a *trans* arrangement as well as two tricyclohexyl phosphine ligands. Only one compound of this type has been

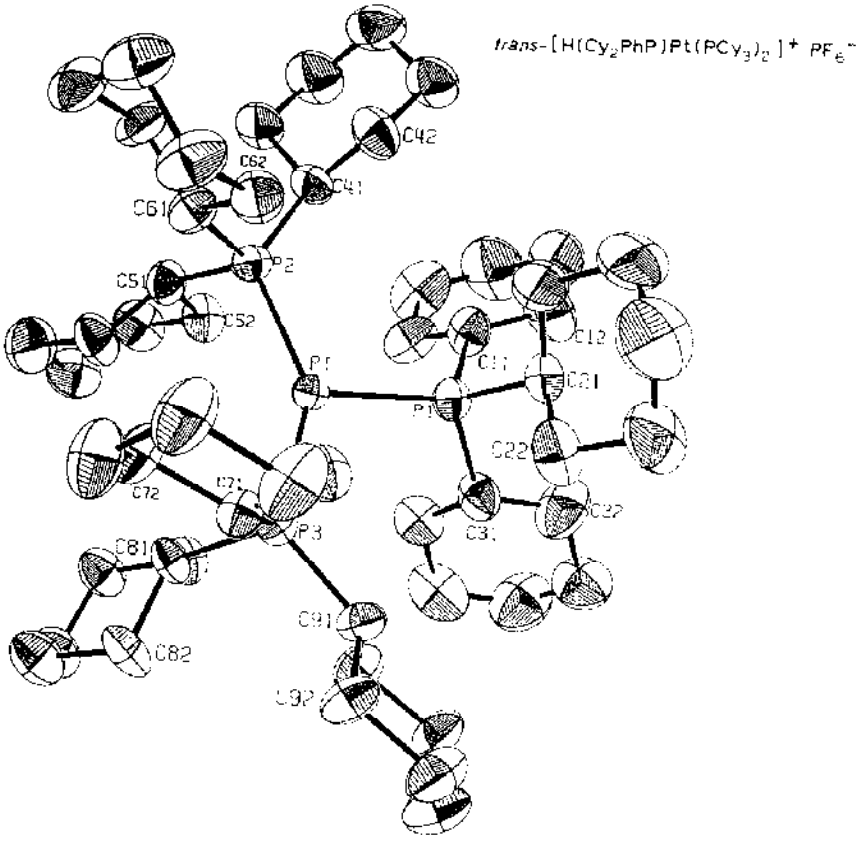


Fig. 9. The structure of *trans*-$[H(Cy_2PhP)Pt(PCy_3)_2]^+$.

structurally characterized, namely *trans*-$Cl(PhCl_2Si)Pt(PCy_3)_2$ (Fig. 10), prepared by the oxidative addition of the chlorosilane $PhSiCl_3$ to $Pt(PCy_3)_2$. In this species, the final method of reduction of steric overcrowding is apparent. The Pt–P bonds are now extremely long (2.350(1) Å, 2.388(1) Å); the P–Pt–P angle significantly reduced (167.8°); the Pt–P–C angles severely distorted (e.g. 121.4°, 106.6° and 104.8°), but now a distinct deviation from planar geometry is observed from the Cl–Pt–Si angle of 164.5°. An intramolecular H---Pt interaction is also apparent in this compound (see also Fig. 17).

(ii) cis-$XYPt(PCy_3)_2$

This structural type includes six compounds with a *cis*-bis-tricyclohexylphosphine stereochemistry which have been structurally characterized (Table 1).

$Pt(PCy_3)_3$ is a surprisingly uncrowded molecule which possesses a trigonal planar arrangement of the phosphine ligands about platinum. The inter-

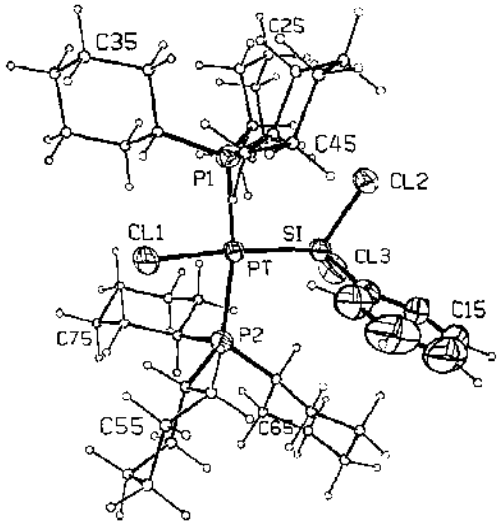


Fig. 10. The structure of *trans*-Cl($PhCl_2Si$)Pt(PCy_3)$_2$.

meshing of the cyclohexyl rings and the slightly longer Pt–P bonds (2.30 Å) minimize the interligand repulsions in this molecule.

(η^2-C_2H_4)Pt(PCy_3)$_2$ (Fig. 11) has a P–Pt–P angle of 116.3° with a Pt–P distance of 2.284(1) Å. In this case, however, there are some significant distortions from tetrahedral geometry at phosphorus, the Pt–P–C angles being 120.7°, 114.9° and 106.9° respectively.

The compound [(allyl)Pt(PCy_3)$_2$]$^+$ PF_6^- · C_7H_6 (Fig. 12) has a P–Pt–P angle of 111.2° which might be expected to impose large distortions on both

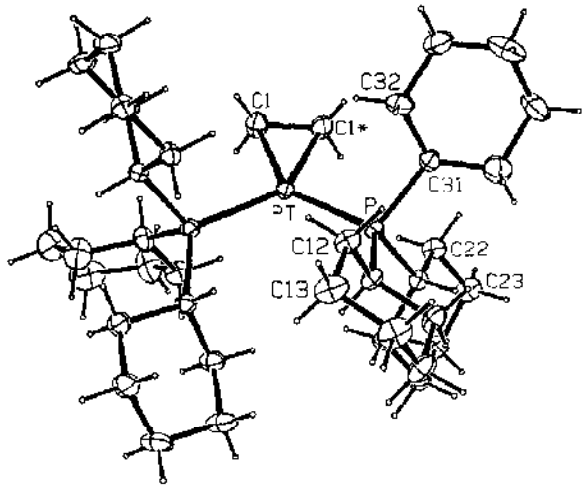


Fig. 11. The structure of (η^2-C_2H_4)Pt(PCy_3)$_2$.

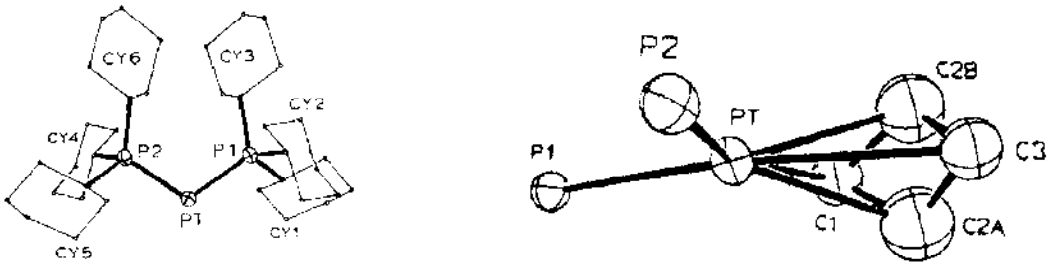


Fig. 12. Two views of the cation $[(allyl)Pt(PCy_3)_2]^+$ showing (i) the relative orientation of the phosphine ligands and (ii) the coordination of the allyl moiety.

phosphine ligands. However, the cyclohexyl substituents all adopt a chair conformation and have a staggered arrangement with respect to each other (see below). In this molecule, severe ligand interactions have been diminished by the significantly longer Pt–P bonds (2.335(3) Å, 2.327(4) Å) compared to $Pt(PCy_3)_3$ and $(\eta^2\text{-}C_2H_4)Pt(PCy_3)_2$ and to a much lesser extent by the variations in the Pt–P–C angles, in the range 107.2° to 118.6°.

For the compound $(C_4F_6)Pt(PCy_3)_2$ (Fig. 13) both the P–Pt–P angle and the Pt–P bond length are smaller than for the previous example. The smaller P–Pt–P angle may be interpreted in terms of greater interaction between the phosphine ligands and the unsaturated substituent. The C_1–C_2–C_3 and C_4–C_3–C_2 angles of 133.7 and 135.4° respectively (giving "bend-back" angles of 46.3 and 44.6°) are well removed from the linearity expected from the *sp*-hybridization of C_2 and C_3 and are significantly larger than in the triphenylphosphine analogue $(Ph_3P)_2Pt(C_4F_6)$ (39.9°, ave.). The origin of this effect can also be electronic since the PCy_3 ligand is more basic than

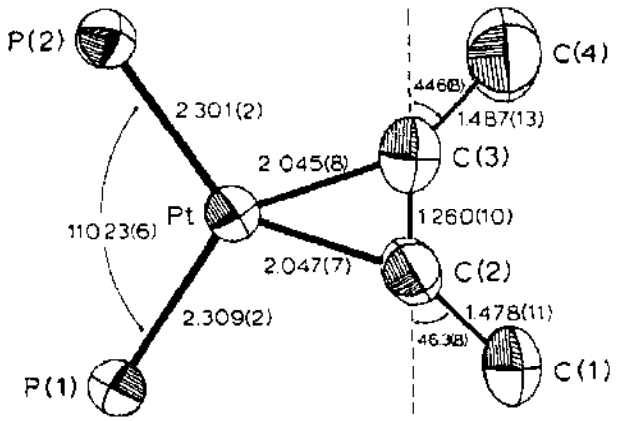


Fig. 13. The structure of $(C_4F_6)Pt(PCy_3)_2$.

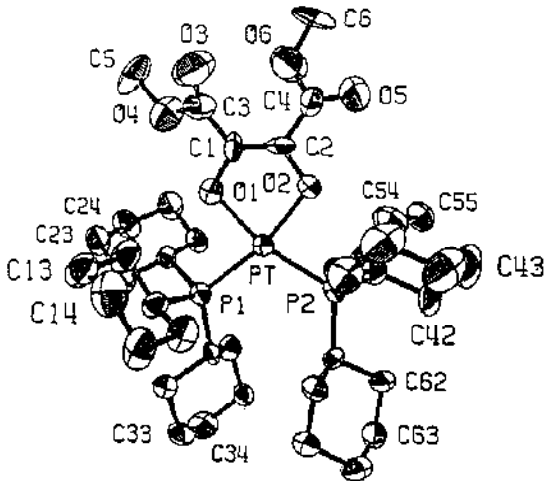


Fig. 14. The structure of $Pt(PCy_3)_2[O_2C_2(COOCH_3)_2]$.

PPh_3, although there is evidence for steric interaction between the cyclohexyl rings and the CF_3 substituents. Severe distortions in the phosphine ligand are apparent from the Pt–P–C angles which vary from 124.6° to 105.2°. However, it is clear that the shortening of the Pt–P bond (2.309(2) Å, 2.301(2) Å) for the more hindered molecule over its allyl analogue is a result of the electronic properties of the carbon ligands, since such shortening only serves to increase the steric interactions. Carbon ligands are known to have a high *trans*-influence [70], which is lowered by substitution with electronegative substituents (i.e. CF_3). Confirmation apparently comes from inspection of the crystal structure of the species $(Cy_3P)_2Pt[O_2C_2(COOCH_3)_2]$ (Fig. 14) in which both the P–Pt–P angle and the Pt–P bond lengths are further diminished. As a result there are some significant distortions in the cyclohexyl rings—the Pt–P–C angles vary from 121.9° to 103.8° although a chair conformation is still maintained. The presence of the oxo-ligands with their low *trans* influence results in shortening of the Pt–P bond (2.270(4) and 2.276(4) Å) even though this increases the steric interactions. Diminution of the P–Pt–P angle (109.3°) may be a result of the steric interaction of the phosphines with the oxo-ligands or, more likely, an attempt to increase the bonding orbital overlap between phosphorus and platinum. This argument does not make any allowance for the difference in oxidation state between $(C_4F_6)Pt(PCy_3)_2$ and $(PCy_3)_2Pt[O_2C_2(COOCH_3)_2]$, which is also expected to result in shortening of the Pt–P bond length (and probably a reduction in the P–Pt–P angle) in the platinum(II) complex. In this connection, it is interesting to note that the P–Pt–P angle of $Pt(PCy_3)_2$ itself, is not 180°, but only 160.5°.

These observations, together with inspection of the structure of $Pt(PCy_3)_3$,

indicate that when two tricyclohexylphosphine ligands are coordinated to platinum with a *cis*-geometry, there is less steric ligand interaction than when a PCy_3 ligand is *cis*- to a different bulky ligand (e.g. PCy_2Ph).

As an extension to their studies of ligand profile, Ferguson et al. [8] have measured the torsion angles M–P C–H for tricyclohexylphosphine ligands (and other ligands) in various environments. In an uncrowded environment, for monophosphine mercury compounds, for example, these torsion angles had similar values in the range of approximately 65, 173, 90°. However for "crowded" environments, e.g. in $(Cy_3P)_2PtI_2$ and $Pt(PCy_3)_3$, the torsion angles are significantly different and lie in the range 60, 175, −45°. In the more recently examined compounds, even more crowded tricyclohexylphosphine ligand environments have been structurally characterized and even larger deviations can be observed. For example, in the species *trans*-$H(Ph_3Sn)Pt(PCy_3)_2$, the Pt–P–C–H torsion angles [63] are 85, −82, −178° for P_1 and −60, −163, −158° for P_2 and these demonstrate the different local distortions at the two phosphorus ligands. Comparison of these torsion angles is particularly useful since it takes account of the relative orientations of the cyclohexyl rings.

In summary, this brief description of some of the known structures of tricyclohexylphosphine–platinum complexes, demonstrates clearly the "softness" of such species. Not only is the phosphine itself able to adjust by molecular distortion to a variety of crowded steric environments, but the metal centre contributes further by deviations from square geometry and, more reluctantly. Many of these structures also show, as a result of steric crowding, relatively short intramolecular metal–hydrogen distances which, as we will discuss elsewhere, have significance in terms of C–H bond activation.

An entirely different approach to the study of ligand interactions in tertiary phosphine complexes of platinum(II) employs the technique of solid state ^{31}P NMR spectroscopy. Some time ago, as part of a study of polymer immobilized phosphine ligands and their platinum complexes [71–73], we recorded the cross-polarization magic-angle-spinning (CP/MAS) ^{31}P NMR spectra of solid tertiary phosphines, tertiary phosphine oxides and tertiary phosphine complexes of Ni(II), Pd(II) and Pt(II). It was shown that solid-state effects can result in non-equivalence of ^{31}P shieldings in simple *cis*-$Cl_2Pt(PR_3)_2$ complexes; for example, *cis*-$Cl_2Pt(PPh_3)_2$ which in solution gives a high resolution ^{31}P NMR spectrum consisting of a single resonance with ^{195}Pt satellites ($\delta = 14.3$ ppm, $J_{P-Pt} = 3673$ Hz), in the solid state gives a two-line (with ^{195}Pt satellites) ^{31}P NMR spectrum ($\delta = 12.9$ ppm, $J_{P-Pt} = 3877$ Hz and $\delta = 8.6$ ppm, $J_{P-Pt} = 3623$ Hz) due to an inequivalence of the phosphine ligands in the solid. Such an effect may be caused by asymmetry induced by the solid state, which renders the two phosphorus nuclei within a

molecule inequivalent (i.e. an intramolecular effect). Alternatively, there may be two non-equivalent sites within the crystal lattice, each type of site resulting in a different resonance. The reported crystal structure of *cis*-$Cl_2Pt(PPh_3)_2$ [74] confirms the intramolecular origin of the solid state ^{31}P NMR spectrum. In the case of *trans*-$Cl_2Pt(PR_3)_2$ complexes, the CP/MAS ^{31}P NMR spectra show in each case a single resonance (with ^{195}Pt satellites) indicating the equivalence of the two phosphines in a centrosymmetric environment.

As an extension of this work, the solid state ^{31}P NMR spectra have now been obtained [65] for a series of complexes (*trans*-$XYPt(PCy_3)_2$) in which the two phosphine environments are known to be inequivalent (e.g. X = H, X = $SnPh_3$) from X-ray structural analysis. For these crowded molecules, an AB spectrum was observed in the solid state with the large $^2J_{P-Ptrans}$ coupling with two distinct $^1J_{P-Pt}$ coupling constants, confirming the non-equivalence of the phosphorus atom environments. Such inequivalence can only be caused, in a *trans* geometry, by different orientations of the cyclohexyl rings, although, unless the differences are quite large, it may be difficult to differentiate between the chemical shifts in the solid state ^{31}P NMR spectra. For example, in *trans*-$H(Ph_3Sn)Pt(PCy_3)_2$, the difference in the chemical shift is only 4 ppm. However, for the compounds *trans*-$Cl(R_3Si)Pt(PCy_3)_2$ where $R_3Si = Cl_3Si$, $PhCl_2Si$ or $MeCl_2Si$ for example, not only are the relative orientations of the cyclohexyl rings in the two PCy_3 ligands different, but also the proximity of each phosphorus nucleus to other electron-rich centres (e.g. chlorine nuclei) differs. This causes a substantial difference in the shielding of the two phosphorus nuclei: over 15 ppm in the case of *trans*-$Cl(PhCl_2Si)Pt(PCy_3)_2$. On cooling a dichloromethane solution of this compound, the single resonance observed at room temperature in the solution ^{31}P NMR spectrum, becomes at $-90\,^\circ C$ an AB spectrum virtually identical to that obtained by solid state ^{31}P NMR measurements (Fig. 15). The non-equivalence of these bulky phosphine ligands in Pt(II) complexes can thus be established on the basis of NMR studies alone, and can be attributed to different orientations of the two trigonal phosphines relative to each other and to the other ligands.

Finally, to explore further the correlation between solid state structure and solution behaviour of tricyclohexylphosphine–platinum complexes, we have extended the use of high resolution ^1H NMR spectroscopy. For such sterically-crowded molecules, the crystal structure evidence would suggest that the "free" rotation about the M–P bond of the phosphine ligands which is possible in solution can by no means be "free". An earlier report [75], demonstrating the occurrence of ligand interactions in such rotations, concerned the derivative $[(Cy_3P)_2Pt(allyl)]^+X^-$. Prepared by the reaction of *trans*-$[H(MeOH)Pt(PCy_3)_2]^+PF_6^-$ with allene, the resulting complexes ex-

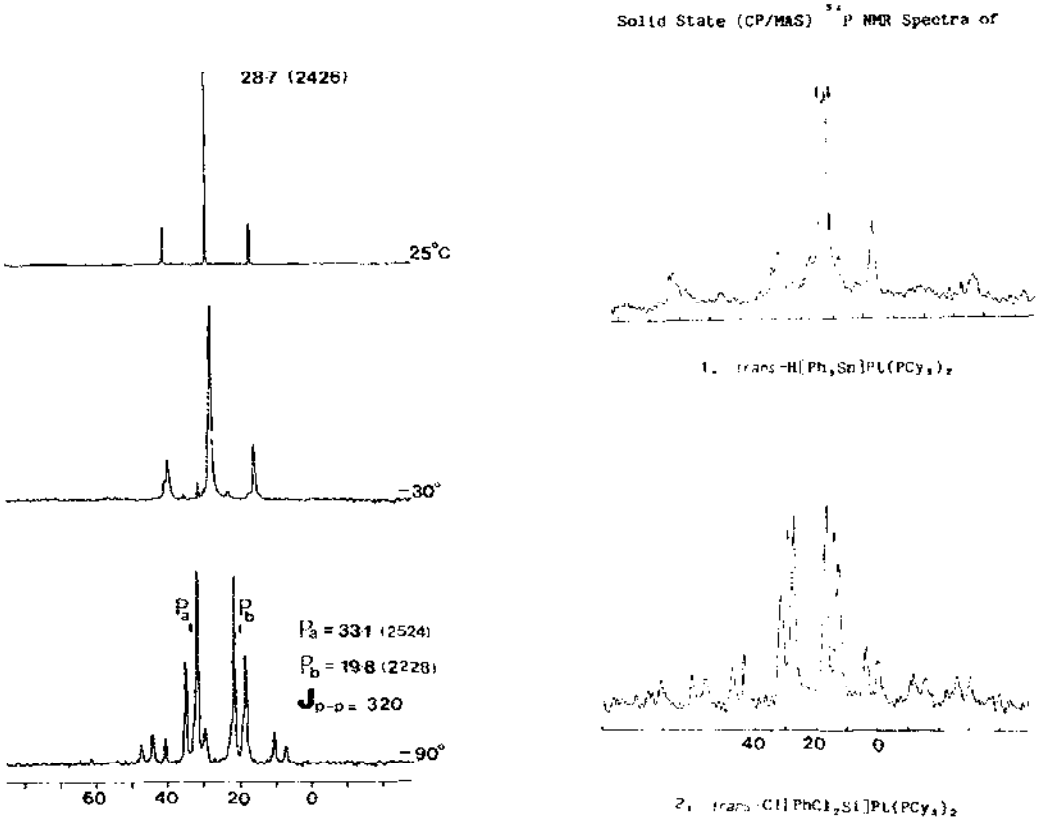
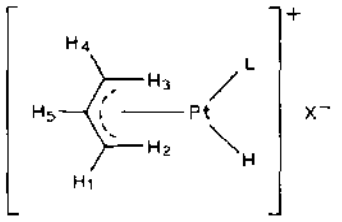


Fig. 15. VT solution ^{31}P NMR spectra of *trans*-Cl[$PhCl_2Si$]Pt(PCy_3)$_2$ (CD_2Cl_2).

hibited either a "static" or a "dynamic" behaviour depending on the nature of the anion. For the cases X = BF_4, PF_6, ClO_4, or NO_3, the allyl protons exhibited an AB_2C_2 pattern in the ^{1}H NMR spectrum. However, for X = Cl or Br, the allylic protons gave rise to an AX_4 spin system due to exchange of *syn* and *anti* protons. A "static" structure was obtained in these cases at lower temperature. This exchange process is believed to occur via a σ-allyl intermediate. In contrast, when the temperature of a solution of the "static" (at room temperature) compound $[(Cy_3P)_2Pt(allyl)]^+PF_6^-$ was lowered, non-equivalence of the *syn* protons, H_1 and H_4 was observed. This non-equivalence cannot be attributed to a σ-allyl structure, since a "static" structure was obtained at room temperature, and also the chemical shifts observed do not correspond to a σ-allyl arrangement. The non-equivalence of the two *syn* protons was therefore attributed to restricted rotation of the PCy_3 groups around the Pt–P bond. The angle between the phosphine ligands was later found [13] to be only 111° and it can be envisaged that in solution the cyclohexyl groups of the two phosphine ligands are meshed



tightly together in a cog-wheel type arrangement in which neither PCy_3 ligand can rotate independently of the other.

In extending these investigations relating the solid state and solution

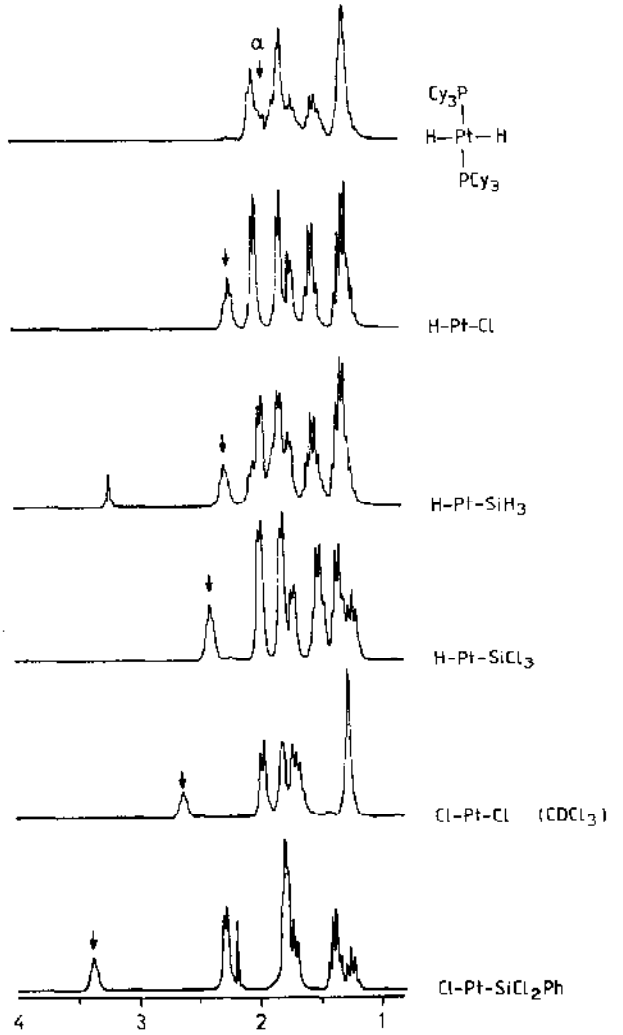


Fig. 16. ^{1}H NMR spectra of cyclohexyl region of *trans*-$XYPt(PCy_3)_2$ (C_6D_6).

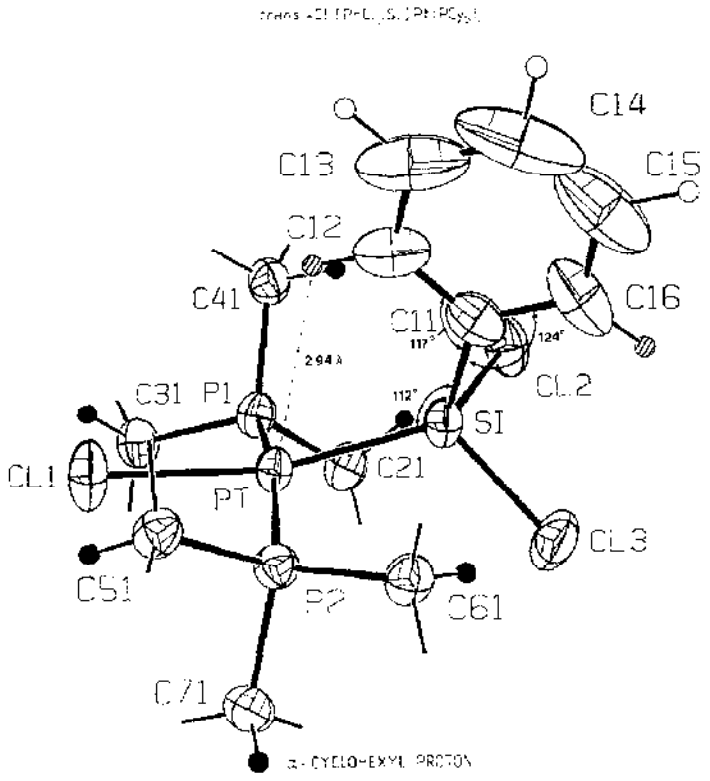


Fig. 17. Part of the structure of *trans*-Cl($PhCl_2Si$)Pt(PCy_3)$_2$.

structures, the assignment of all the cyclohexyl protons of PCy_3 in the ^1H NMR spectra has been studied [76], and is viable at a spectral frequency of 400 MHz in favourable cases. Preliminary results show that the proton bonded to the α-carbon of the cyclohexyl rings is particularly sensitive to the stereochemistry and the nature of the substituents at the platinum centre (Fig. 16). For example, there is a distinct difference in the shielding of the α-cyclohexyl protons in *cis*- and *trans*-$Cl_2Pt(PCy_3)_2$. In a much more interesting example, the resonance of the α-protons for *trans*-$HClPt(PCy_3)_2$ occurs at 2.34 ppm, but for *trans*-Cl($PhCl_2Si$)Pt(PCy_3)$_2$, where the hydride ligand has been replaced by the $SiCl_2Ph$ moiety, it occurs at 3.26 ppm (in the same solvent at the same temperature)—a shift of 0.92 ppm downfield. At $-90\,^\circ C$, when the cyclohexyl rings are inequivalent and ligand rotations have been frozen, six different environments for the α-protons are observed, the most deshielded resonance at a remarkable 4.26 ppm! Moreover, a careful examination of the crystal structure of this compound shows that there are indeed six different environments for the α-cyclohexyl protons (Fig. 17). While individual assignment of the six observed resonances is not yet possible, this method does show the ability to correlate impressively the

solution and solid state structures. It would seem very clear that in this very crowded molecule, the single resonance observed for the α-cyclohexyl protons at room temperature can only represent a time-averaged situation as the three ligands, $PhCl_2Si$– and both PCy_3 ligands, rotate in a concerted cog-wheel fashion. More detailed studies should begin to provide information about the energetics of such concerted rotational motions.

The objective of this brief article is to make clear that an understanding of ligand interactions in metal–phosphine complexes must be based on a sufficiently large number of crystal structure determinations on closely-related molecules. This number is now large enough for tricyclohexylphosphine complexes of platinum to enable us to begin understanding the types of distortion that such a ligand may accommodate. It is also possible through the use of several NMR techniques to develop substantially our understanding of the correlations between static, solid state structures and the solution behaviour of such complexes.

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