The Role of R_3P–M Bond Bending in Determining the Stereochemical Features of Tertiary Phosphine Complexes of Transition Metals

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For *cis*- and *trans*-$MXY(PR_3)_2$ 'planar' systems (M = Ni, Pd, Pt) the large deviations of $\angle$PMP bond angles from ideal {defined as α = ($\angle$PMP – 90°) *cis*; (180° – $\angle$PMP) *trans*} are shown to correlate linearly with the average R_3P tilt angle $\beta_{avg.}$ [β = (180° – $\angle C_TPM$) where C_T = the centroid of the (α-C)$_3$ unit of a R_3P ligand]: the data are best rationalised by assuming that unfavourable electron repulsions involving P(α-C≡)$_3$ units and neighbouring ligands are minimized by R_3P–M bond bending.

A continuing conundrum in co-ordination chemistry is the fact that the large distortions from ideal co-ordination geometries frequently observed in R_3P complexes show no correlation with the R_3P cone angle.[1,2] For example the $\angle$PPtP bond angle data for the five cations $PtH(PR_3)_3^+$ (Table 1)[3] are very similar even though the R_3P cone angles vary from 118° (PMe_3) to 170° (PCy_3). This observation is understandable if the major repulsion terms controlling $\angle$PPtP angles are ones involving the electrons associated with the P(α-C≡)$_3$ units† and those of neighbouring ligands and that such repulsions lead to R_3P–M bond bending, (Figure 1). Evidence of the influence of the P(α-C≡)$_3$ moiety on the magnitude of $\angle$PPtP is the general observation† that in *cis*-$PtXY(PR_3)_2$ complexes a staggered conformation of adjacent P(α-C≡)$_3$ groups [viewed down the PP axis, *e.g.* Figure 2a (cogwheel) and 2b] will usually give rise to $\angle$PPtP of *ca.* 98—103°, whilst eclipsed configurations of the type shown in Figure 2c and 2d have $\angle$PPtP values of *ca.* 106—110°. For example Pt(cycloheptyne)$(PPh_3)_2$ [$\angle$PPtP 102.58(3)°] has a distorted staggered conformation of P(α-C≡)$_3$ units whilst Pt(cyclohexyne)$(PPh_3)_2$ [$\angle$PPtP 109.54(5)°] has an 'almost eclipsed' conformation of P(α-C≡)$_3$'s.[4] Similarly for the two forms of complex (**1**) [$\angle$PPtP 97.73(5) and 106.2(1)°][5] the larger $\angle$PPtP is associated with an 'almost eclipsed' conformation of PMe_3 ligands (Figure 2d). Thus changes in $\angle$PPtP, which at first may be perceived as a consequence of changes in the steric bulk of PR_3 ligands, may in fact be more a consequence of a change in the conformation of adjacent P(α-C≡)$_3$ units. One such example is the pair of complexes $Pt(C_4F_6)(PPh_3)_2$, $\angle$PPtP 100.17(4)° [staggered (cogwheel) P(α-C≡)$_3$ units: Figure 2a] and $Pt(C_4F_6)(PCy_3)_2$, $\angle$PPtP 110.23(6)° [almost eclipsed P(α-C≡)$_3$: Figure 2d].[6]

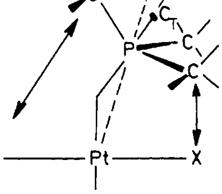

Figure 1. Electron repulsions influencing the co-ordination geometry of R_3P–Pt complexes. C_T = centroid of α-C_3.

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† The α-C≡ symbol implies the inclusion of electron density associated with CH and/or CC bonds. Structural features referred to in this communication were obtained by analysis of the relevant structural data taken 'as is' from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

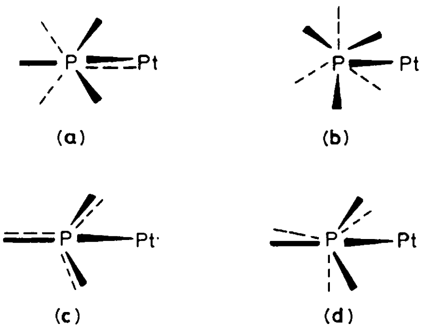
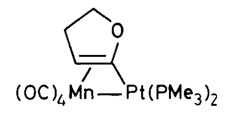


Figure 2. Examples of $P(\alpha\text{-}C\equiv)_3$ conformations in *cis*-$PtXY(PR_3)_2$: (a) and (b) 'staggered' (PPtP ≃ 98—103°); (c) eclipsed, and (d) 'almost' eclipsed, (∠PPtP ≃ 106—110°).



(A)

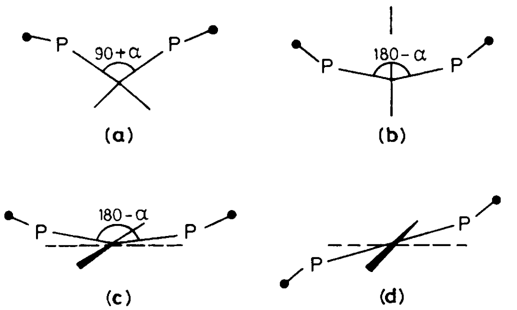


Figure 3. Examples of (a) and (b) in-plane '*xy*' tilting of R_3P; (c) and (d) out-of-plane '*z*' tilting of R_3P (*i.e.* relative orientations of $P\text{–}C_T$).

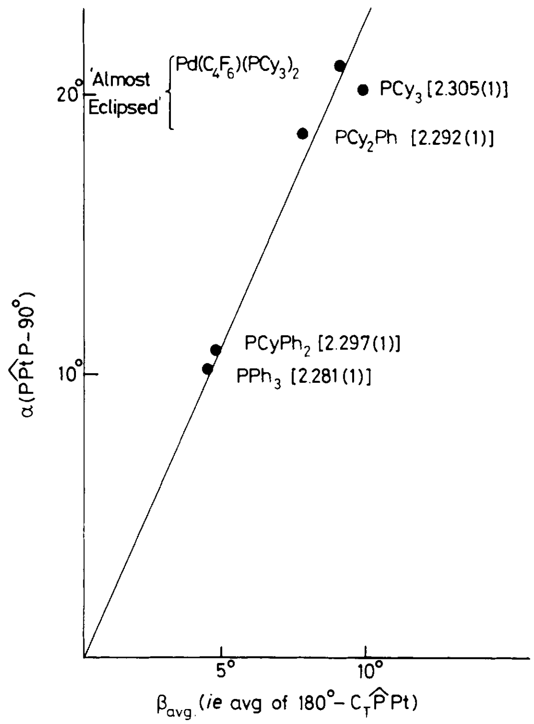


Figure 4. The α *vs*. β plot for the hexafluorobut-2-yne complexes $Pt(C_4F_6)(PR_3)_2$.[6] [P–Pt bond length in Å is given in brackets.]

Table 1. ∠PPtP Bond angle data (°) for $[PtH(PR_3)_3]^+$ cations.

	∠P^1PtP^2	∠P^2PtP^3	∠P^1PtP^3	Ref.
$PtH(PMe_3)_3^+$	100.6	100.7	156.8(1)	3a
$PtH(PEt_3)_3^{+a}$	100.1	101.5	158.4(2)	3b
$PtH(PEt_3)_3^{+a}$	101.2	103.6	155.2(2)	3b
$PtH(PPh_3)_3^+$	99.7	100.6	159.6(2)	3c
$PtH(PCy_3)_2(PPh_3)^{+b}$	101.9	102.8	155.2(2)	3d

[a] Two independent molecules in the unit cell. [b] Cy = cyclohexyl.

In R_3P complexes of Pt, Σ∠CPC and Σ∠PtPC are essentially unchanged by the degree of steric crowding[2] [*i.e.* $P(\alpha\text{-}C\equiv)_3$ is not easily compressed]. In contrast individual ∠CPC vary from *ca.* 100 to 108° and individual ∠PtPC from *ca.* 103 to 125°[2]† consistent with the concept of P–Pt bond bending. For in-plane (*xy*) P—Pt bond bending (Figure 3a,b) and out-of-plane (*z*) bending (Figure 3c) α, the deviation of ∠ PPtP from ideal for *cis*- and *trans*-$PtXY(PR_3)_2$ complexes, should correlate with the average tilt angle, $\beta_{avg.}$, per PR_3.‡ [β = 180° − ∠C_TPPt; (C_T = centroid of '$\alpha\text{-}C_3$') see Figure 1]. Figure 4 shows a plot of α, (∠PPtP − 90°), *vs*. $\beta_{avg.}$ for $M(C_4F_6)(PR_3)_2$. Similar linear correlations with respect to α *vs*. $\beta_{avg.}$ plots are observed for a large number of 'planar' complexes of Ni, Pd, and Pt of the type *cis*-$MX_2(PR_3)_2$ and *trans*-$MXY(PR_3)_2$ (X_2, XY = halides, sulphur donor chelate ligands, σ-bonded C ligands *etc.*). Some representative examples are given in Figure 5.§ R_3P–M bond bending can be in the *xy* sense [Figure 3a, *e.g.* $PtCl_2(PPh_3)_2$;[7] Figure 3b, *e.g.* $PtCl(PEt_3)_3^+$],[3b] the *xyz* sense [*e.g.* *cis*-$PtCl_2(PBu^t_2Ph)_2$],[8] or purely in the *z* sense [Figure 3c, *e.g.* $PdCl\{C_6H_4\text{-}o\text{-}C(Me){=}NNHPh\}(PEt_3)_2$,[9] $PtClMe(PMePh_2)_2$:[10] ∠PMCl is *ca.* 90°]. R_3P–M Bond bending in the $+z/-z$ sense (Figure 3d) occurs in *trans*-$MX_2(PR_3)_2$ systems (*e.g.* Figure 5). For complexes of the type $MXY(PR_3)_2$ the slope $\alpha/\beta_{avg.}$ is *ca.* 1.9 (XY = halides, sulphur donor chelates *etc.*: Figure 5) and *ca.* 2.2 for $M(C_4F_6)(PR_3)_2$ (Figure 4). For *cis* complexes where X and Y donor atoms are directly bonded to one another (*i.e.* ∠XMY = *ca.* 35—45°) and where X and Y do not have large in-plane substituents close to PR_3 the slope $\alpha/\beta_{avg.}$ is *ca.* 4.0. Examples are $MXY(PPh_3)_2$ (M = Ni, Pd, Pt; XY = η^2-alkenes, η^2-CS_2, η^2-quinone); $[\eta^2\text{-}MeSCH_2)Pd(PPh_3)_2]^+$; $(Ph_3P)_2\overline{Pt(\mu\text{-}S)P}t(CO)(PPh_3)$; and $[(\eta^3\text{- allyl})Pt(PCy_3)_2]^+$.†

This suggests that when the electron density associated with the M–X and M–Y bonds is drastically distorted (bent) from the 90° ideal and away from the PR_3 ligands (*n.b.*: ∠XMY is *ca.* 35—45°) the resulting increase in ∠PMP is accommodated in part by a net shift of the electron density close to M and associated with the P–M bonds, away from the 90° ideal position thereby necessitating less tilting of the PR_3 ligands. (*i.e.* the $\alpha/\beta_{avg.}$ ratio is determined at least in part by the

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‡ (a) The average 'bend angle' of R_3P about a 'pivotal point' on the 'ideal 90° axis' is 1/2 α + β_{avg}. (b) Intermeshing of substituents on neighbouring donor atoms tends to favour in-plane (*xy*) bending.

§ (a) The α,β data for $MX(PR_3)_3^+$ systems are for the '*trans*-$(PR_3)_2$ unit'. (b) In $PtXR(PR_3)_2$ systems *xy* bending is towards the halide X.

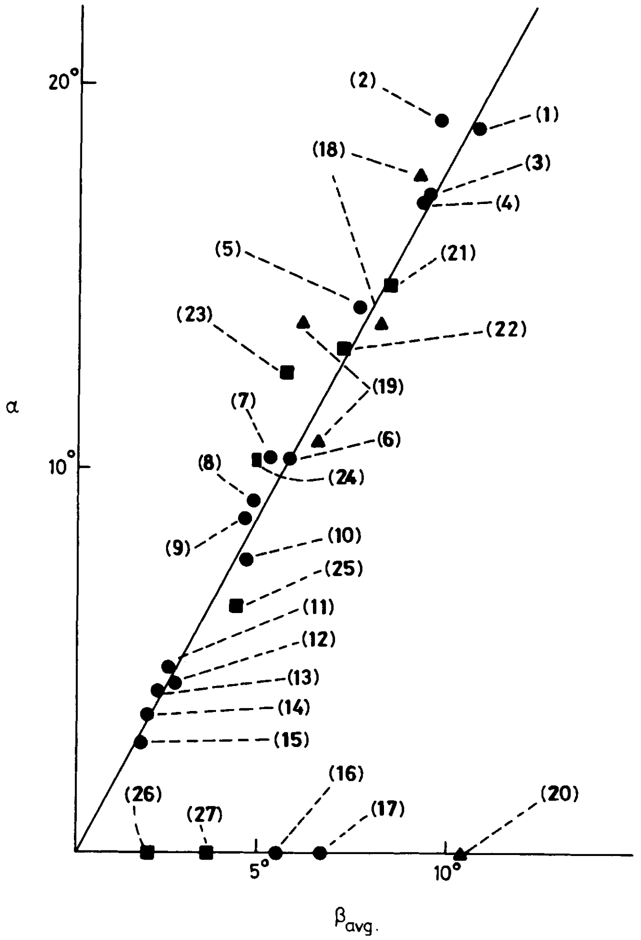

Figure 5. [*c* = *cis*; *t* = *trans*; ● = Pt; ▲ = Ni; ■ = Pd.] ●; (**1**) $PtCl(PMe_3)_3^+$, (**2**) *t*-$PtCl(MeNaphPhSi)(PMe_2Ph)_2$, (**3**) $PtCl(PEt_3)_3^+$, (**4**) *c*-$PtCl_2(PBu^t{}_2Ph)_2$, (**5**) $PtF(PEt_3)_3^+$, (**6**) *c*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$, (**7**) *t*-$PtClMe(PMePh_2)_2$, (**8**) $S(S)_3Pt(PPh_3)_2$, (**9**) $CH_2(CH_2)_3Pt(PPh_3)_2$, (**10**) *c*-$PtCl_2(PPh_3)_2$, (**11**) *c*-Pt(cyclopropyl)$_2(PMe_2Ph)_2$, (**12**) *t*-$PtIMe(PPh_3)_2$, (**13**) *t*-$PtClMe(PPh_3)_2$, (**14**) *t*-$PtCl(CH_2CN)(PPh_3)_2$, (**15**) *t*-$PtCl(MeCO)(PPh_3)_2$, (**16**) *t*-$PtI_2(PCy_3)_2$, (**17**) *t*-$PtCl_2(PCy_3)_2$, ▲; (**18**) *t*-$NiCl(CH_2SiMe_3)(PMe_3)_2$, (**19**) *t*-$NiCl(COSiMe_3)(PMe_3)_2$, (**20**) *t*-$NiCl_2(PCy_3)_2$, ■; (**21**) *t*-$PdCl[C_6H_4$-*o*-$C(Me)NNHPh](PPh_3)_2$, (**22**) $PdCl(PMe_2Ph)_3^+$, (**23**) *t*-$PdCl(CH_2CN)(PPh_3)_2\cdot$acetone, (**24**) *t*-$PdCl(CH_2CN)(PPh_3)_2\cdot MeCN$, (**25**) *t*-$PdCl(CH_2CN)(PPh_3)_2\cdot C_6H_6$, (**26**) *t*-$PdI_2(PPh_3)_2$, (**27**) *t*-$PdCl_2(PPh_3)_2$.

relative location of the 'net electron density' of neighbouring donor atoms). The rationalization of $\angle$PMP data in terms of R_3P–M bond bending without rehybridization of P (*cf.* Σ $\angle$CPC data) (i) suggests similar bending at S–M, Cl–M bonds *etc.*; (ii) accounts for the relative ease of formation of '$M(\mu\text{-}PR_2)M$' systems with $\angle$MPM of 70—80° yet with $\angle$RPR angles of *ca.* 102—108°, values typical of individual PR_3 ligands; (iii) explains the relative ease of formation of 4-membered chelate ring systems containing P(or S *etc.*) donor atoms; and (iv) is further evidence of the importance of repulsions between proximal electron clouds for the successful rationalization of molecular stereochemistry.[11]

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