# Structural Evidence for the Participation of P–X σ* Orbitals in Metal–$PX_3$ Bonding

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Examination of metal–phosphorus and phosphorus–substituent atom bond lengths in a series of reduction–oxidation related pairs of transition metal phosphine complexes yields evidence of the participation of P–substituent σ* orbitals in the π-acceptor function of the phosphine.

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Conventional descriptions[1] of metal–phosphine bonding ascribe the π-acceptor properties of the phosphine to empty phosphorus 3d orbitals. In contrast, recent theoretical studies of the frontier orbitals of $PX_3$ molecules[2] (X = H, $CH_3$, and F) and their interaction with metal atoms[3] have emphasised the importance of P–X σ* orbitals in the π-acidity of these ligands. The LUMO of the $PX_3$ molecule has been shown to contain substantial P–X σ* character (for each of X = H, $CH_3$, and F, although most clearly for X = F) in addition to some phosphorus 3d character; this permits understanding of the enhanced M–P π-bonding for electronegative X.[2,3] Indeed the π-acidity of $PH_3$ has been successfully modelled in *ab initio* calculations[3] without recourse to phosphorus 3d orbitals at all. Figure 1 illustrates how the combination of phosphorus 3d and P–X σ* orbitals of *e* symmetry leads to well hybridised π-acceptor orbitals. We should therefore expect that in complexes where π-donation of electron density from metal to phosphorus is important there should be concomitant weakening of the P–X bond. To test this hypothesis we have examined the results of a series of crystallographic studies on pairs of transition metal phosphine and phosphite complexes related by electron transfer reactions (*i.e.* differing only in the total number of electrons). These pairs provide ideal tests for this

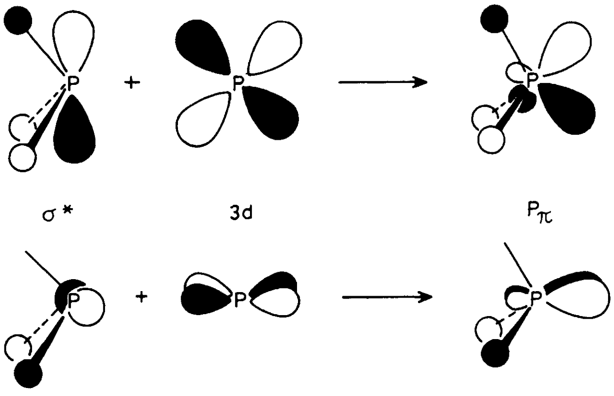

**Figure 1.** Doubly degenerate $PX_3$ LUMO ($C_{3v}$ local symmetry assumed).

**Table 1.** Metal–phosphorus and phosphorus–substituent distances.

| Complex | Ref. | Charge | Counter ion | M–P[a]/Å | P–X[a]/Å |
|---|---|---|---|---|---|
| $\mathrm{[Mn(CO)(Ph_2PCH_2CH_2PPh_2)(\eta^5\text{-}C_6H_6Ph)]}$ (**1**) | 4 | 0 | | 2.221(1) | 1.849(3)[Ph]; 1.864(2)[$\mathrm{CH_2}$] |
| | | 1 | $\mathrm{PF_6}$ | 2.339(2) | 1.821(3)[Ph]; 1.829(3)[$\mathrm{CH_2}$] |
| $\mathrm{[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]}$ (**2**) | 5 | 0 | | 2.146(1) | 1.598(3) |
| | | +1 | $\mathrm{BF_4}$ | 2.262(2) | 1.579(6) |
| $\mathrm{[\{Rh(CO)(PPh_3)\}_2(\eta^5,\eta'^5\text{-}fulvalene)]}$ (**3**) | 6 | 0 | | 2.255(2) | 1.844(5) |
| | | +2 | $\mathrm{PF_6}$ | 2.322(4) | 1.813(15) |
| $\mathrm{[\{Rh(CO)(PPh_3)\}_2\{\mu\text{-}N(tolyl)NN(tolyl)\}_2]}$ (**4**) | 7 | 0 | | 2.290(5) | 1.855(12) |
| | | +1 | $\mathrm{PF_6}$ | 2.335(1) | 1.825(5) |
| *cis,trans*-$\mathrm{[Ru(CO)_2(PPh_3)_2(\mathit{o}\text{-}O_2C_6Cl_4)]}$ (**5**) | 8 | 0 | | 2.424(2) | 1.829(5) |
| | | +1 | $\mathrm{PF_6}$ | 2.429(2) | 1.826(5) |
| $\mathrm{[Co(PEt_3)_2(\eta\text{-}C_5H_5)]}$ (**6**) | 9 | 0 | | 2.218(1) | 1.846(3) |
| | | +1 | $\mathrm{BF_4}$ | 2.230(1) | 1.829(3) |
| $\mathrm{[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]}$ (**7**) | 10 | 0 | | 2.138(1) | 1.621(1) |
| | | +1 | $\mathrm{BF_4}$ | 2.153(2) | 1.600(2) |
| $\mathrm{[Mn(CO)_4\{PPh_2C\overline{C(O)N(Me)C(O)C}PPh_2\}]}$ (**8**) | 11 | 0 | | 2.346(2) | 1.833(8)[Ph]; 1.760(7)[C=] |
| | | +1 | I | 2.33(1) | 1.83(3)[Ph]; 1.79(3)[C=] |
| $\mathrm{[Re_2Cl_4(\mu\text{-}Cl)_2(Ph_2PCH_2PPh_2)_2]}$ (**9**) | 12 | 0 | | 2.475(2) | 1.828(8)[Ph]; 1.843(8)[$\mathrm{CH_2}$] |
| | | +1 | $\mathrm{H_2PO_4H_3PO_4}$ | 2.524(3) | 1.82(1)[Ph]; 1.84(1)[$\mathrm{CH_2}$] |

[a] M–P and P–X distances are averaged over equivalent bonds, with the e.s.d.s in the least significant digit for *individual* bond lengths, as determined by least-squares, quoted in parentheses.

purpose since the M–P distances cannot be affected by, for example, changes in *trans*-ligand. They allow comparison of metal–phosphine bonding in very similar environments, differing principally in the degree of metal–$\mathrm{P_\pi}$ bonding.

Table 1 lists the M–P and P–X bond lengths derived from *X*-ray structural studies, by us, (**1**)—(**5**),[4—8] and others, (**6**)—(**9**),[9—12] on 9 redox-related pairs. Spectroscopic (e.s.r.), theoretical (extended Hückel calculation), and structural evidence indicates that the oxidations of (**1**)—(**4**), (**6**), and (**7**) are largely metal based, the HOMO of the neutral complex being of the '$t_{2g}$' type for (**1**)—(**3**) and (**6**), and metal–metal anti-bonding for (**4**). For (**5**) and (**8**) the oxidation is largely ligand-based [*i.e.* is associated with $o$-$\mathrm{O_2C_6Cl_4}$ for (**5**) and $\mathrm{Ph_2PC\overline{C(O)N(Me)C(O)C}PPh_2}$ for (**8**)], for example as indicated by the e.s.r. spectrum of (**5**). In each of the cases where oxidation is known to be primarily metal-based the metal–P distances *increase* markedly on oxidation while the P–X distances *decrease*. In the two cases where oxidation is known not to be metal-based there is no significant change in M–P *or* P–X distances. The variations in M–P lengths are those to be expected if the phosphorus–metal bond contains an important $\pi$-component. The loss of electrons from '$t_{2g}$' type orbitals [as in (**1**), (**2**), and (**3**)] leads to direct loss of $\pi$-back-donation. Electron loss from other metal orbitals [as in (**4**)] leads to contraction and lowering in energy of all metal orbitals, once again leading to reduced back-donation. Ligand-based oxidation, as in (**5**) and (**8**), has little or no effect on metal–phosphine $\pi$-bonding and hence on M–P distances.

The qualitative conclusions are clear. First the changes in M–P lengths are consistent with M–P bonding in these complexes containing an important $\pi$-component. Metal–ligand distances for pure $\sigma$-donors would be expected to decrease on metal-based oxidation owing to the contraction of metal orbitals. This conclusion is in accord with the variation in M–P and M–Cl distances in high oxidation state (+III and +IV) *mer*-$\mathrm{MCl_3(PR_3)_3}$ and *trans*-$\mathrm{MCl_4(PR_3)_3}$ complexes[13] (M = Re, Os, and Ir) in which the $\mathrm{M^{III}}$–P distances are shorter than $\mathrm{M^{IV}}$–P and $\mathrm{M^{III}}$–Cl longer than $\mathrm{M^{IV}}$–Cl. Secondly the decreases in P–X bond lengths, which accompany the increases in M–P distances, are in accord with theoretical predictions of the participation of P–X $\sigma^*$ orbitals in M–P $\pi$-bonding.

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