Structural systematics: the role of P-A .sigma.* orbitals in metal-phosphorus .pi.-bonding in redox-related pairs of M-PA3 complexes (A = R, Ar, OR; R = alkyl)

A. Guy Orpen, and Neil G. Connelly

Organometallics, **1990**, 9 (4), 1206-1210• DOI: 10.1021/om00118a048 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Structural Systematics: Role of P–A σ^* Orbitals in Metal–Phosphorus π-Bonding in Redox-Related Pairs of M–PA$_3$ Complexes (A = R, Ar, OR; R = Alkyl)

A. Guy Orpen* and Neil G. Connelly

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

Received November 1, 1989

The geometry variations in the M–PA$_3$ units of 24 transition metal–phosphine and –phosphite complexes whose crystal structures are known for multiple oxidation states of the complex are tabulated and discussed. Conclusions are drawn with regard to the effect of oxidation at the metal on M–P π-back-bonding and the consequent structural effects on the PA$_3$ ligand. Metal–phosphorus bond lengths increase on oxidizing the metal, consistent with the presence of an important element of M–P π-back-bonding. Reduction of M–P π bonding causes a decrease in the average P–A bond lengths, in accord with the PA$_3$ π-acceptor orbital having P–A σ^* character. A qualitative molecular orbital theory is described that allows rationalization of these changes and others in PA$_3$ geometry. In particular the effect of M–P π-bonding is to enhance the tendency for a pyramidal PA$_3$ structure, with A–P–A angles $\ll 120°$.

Introduction

The importance of tertiary phosphine and phosphite ligands in transition-metal coordination chemistry is well documented.[1,2] Such ligands are critical in tailoring the reactivity of metals in a wide range of catalytic and stoichiometric chemistry. As such the description of their interactions with metals has been the subject of a large body of research. The terms of the debate on the relative importance of "electronic" and "steric" factors, the bonding between phosphine and metal and its division into σ and π components, and the roles that these play in determining the physical and chemical properties of phosphine complexes were clearly described in a classic review by Tolman.[3] In this paper we present and analyze structural data that are germane to the question of the importance of π-bonding in transition metal–phosphine (and –phosphite) complexes.

In conventional descriptions of transition metal–phosphine (M–P) bonding, the electronic interaction is regarded as having σ and π components. The σ component involves donation of electrons from the ligand lone pair to an empty orbital, of σ pseudosymmetry, on the metal. The π component involves back-donation, from filled metal orbitals of π pseudosymmetry to empty orbitals of the same symmetry on the phosphine ligands. The π-acidity of phosphine ligands has often been ascribed[4] to the presence of "low-lying" and empty 3d orbitals on the phosphorus atom (see Figure 1). Aspects of this description have been challenged on numerous occasions and for varying reasons. The relative importance of the σ and π components has been assessed on the basis of a wide range of physical measurements and techniques of data analysis, with a correspondingly wide range of conclusions being drawn. For example, authors have variously inferred that the data were in accord with the complete absence of[5] or significant role for[6] metal–phosphine π-bonding in PPh$_3$ complexes. The variation in conclusions reflects, of course, the different questions asked by the techniques used, rather than a fundamental paradox. In recent years the nature of the π-acceptor function on the phosphine ligand has been reassessed in light of ab initio molecular orbital calculations on simple phosphines (PA$_3$, A = H, F, Me) and their complexes.[7] These calculations indicate that the phosphine LUMOs are a doubly degenerate pair of orbitals of π symmetry (e under the local C_{3v} symmetry of the PA$_3$ unit), which have P–A σ^* as well as phosphorus 3d character. This description is in accord with experimental observations by electron transmission spectroscopy.[8] The P–A σ interaction of e symmetry involves phosphorus 3p$_x$ and 3p$_y$ orbitals. In these LUMOs the σ^* orbitals mix into the phosphorus 3d leading to well-hybridized π-acceptor orbitals as illustrated in Figure 2. The degree of mixing and hence the degree of rehybridization depend on the relative energies of the σ^* and P 3d orbitals and the distribution of the σ^* orbital. Perturbation theory tells us that the lower the energy and the greater the concentration of the σ^* orbitals on phosphorus, the more effective will be the σ^*–P3d mixing and the π-acceptor function that results (in terms of both energy and potential for M–P overlap). The more electronegative the substituent A, the more phosphorus 3p character there is in the σ^* orbital, and the lower it is in energy. This description therefore places greater emphasis on the polarization of the P–A σ^* orbitals as the basis for the widely recognized enhancement in phosphine π-acidity in the sequence PR$_3$ < PAr$_3$ < P(OR)$_3$ < P(OAr)$_3$ < PF$_3$ (R = alkyl). In contrast, the "traditional" view emphasises the inductive effect of the substituents on the phosphorus 3d orbital energies.[4]

The prediction that metal–phosphine π-bonding occurs through orbitals that are partly P–A antibonding is one that may be tested by experiment. Thus, if it can be arranged for the amount of M–P π-bonding to vary, changes would be expected to follow in the geometry of the PA$_3$ ligand, with P–A bonds lengthened by increased M–P π-bonding. It is the results of such a test, in which the effect of oxidation at the metal on M–P and in-

---

[1] McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Pergamon: London, 1987; Vol. 2, pp 989-1066.

[2] *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C., Meek, D. W., Eds.; Advances in Chemistry Series 196; American Chemical Society: Washington, D.C., 1982. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983.

[3] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.

[4] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principals and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley CA, 1987; pp 69-70. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp 64-65.

[5] Rahman, Md. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1-7, and references therein.

[6] Wovkulich, M. J.; Atwood, J. L.; Canada, L.; Atwood, J. D. *Organometallics* **1985**, *4*, 867-871.

[7] Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033-7037. Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064-4065.

[8] Tossell, J. A.; Moore, J. H.; Giordan, J. C. *Inorg. Chem.* **1985**, *24*, 1100-1103. Giordan, J. C.; Moore, J. H.; Tossell, J. A. *Acc. Chem. Res.* **1986**, *19*, 281-286.

0276-7333/90/2309-1206$02.50/0

Table I

complex (no.)	charge	ref	R_{cryst}	M–P	M–Cl	M–CO	P–A	A–P–A
$[TaCl_4(dmpe)_2]$ (**1**)	+1	20	0.046	2.692 (5)	2.430 (3)		1.770[a]	102.7[a]
	0	20	0.041	2.653 (3)	2.506 (2)		1.843	103.4
trans-$[CrCl_2(dmpe)_2]$ (**2**)	+1	21b	0.057	2.445 (5)	2.293 (4)		1.813 (13)	104.5 (10)
	0	21a	0.055	2.369 (3)	2.348 (3)		1.831 (7)	101.8 (7)
trans-$[Cr(CO)_2(dmpe)_2]$ (**3**)	+1	21b	0.051	2.366 (3)		1.860 (7)	1.819 (7)	102.4 (3)
cis-$[Cr(CO)_2(dmpe)_2]$	0	22	0.046	2.278 (3)		1.812 (6)	1.830 (7)	100.7 (3)
$[\{Cr(CO)_2\}_2(\mu\text{-dppm})(\mu\text{-}\eta^6{:}\eta^{6'}\text{-biphenyl})]$ (**4**)	+1	23	0.069	2.373 (2)		1.845 (10)	1.854, 1.849	101.8
	0	23	0.057	2.321 (2)		1.826 (8)	1.848, 1.859	100.4
$[Mo(\eta\text{-}C_7H_7)(CCPh)(dppe)]$ (**5**)	+1	24	*b*	2.533 (1)			1.818 (9), 1.829 (9)	103.6 (4)
	0	24	*b*	2.472 (1)			1.838 (5), 1.845 (5)	102.2 (2)
trans-$[MoCl_2(dmpe)_2]$ (**6**)[a]	+1	25	0.030	2.537 (2)	2.404 (2)		1.810 (6)	104.5
	0	25	0.037	2.463 (1)	2.439 (1)		1.818 (4)	101.8
$[Mn(CO)(dppe)(\eta\text{-}C_6H_6Ph)]$ (**7**)	+1	26	0.035	2.338 (2)		1.803 (3)	1.829 (3), 1.821 (3)	104.6 (1)
	0	26	0.039	2.221 (3)		1.772 (3)	1.864 (2), 1.849 (3)	101.6 (1)
$[Mn(CO)_4\{PPh_2CC(O)N(Me)C(O)CPPh_2\}]$ (**8**)[c]	+1	27	0.056	2.325 (10)		1.808 (40)	1.80 (3), 1.83 (3)	*b*
	0	27	0.059	2.346 (2)		1.835 (10)	1.761 (7), 1.832 (11)	*b*
trans-$[MnCl_2\{o\text{-}(Me_2P)_2C_6H_4\}_2]$ (**9**)	+2	14	*b*	2.428 (1)	*b*		1.795 (5), 1.809 (4)	*b*
	+1	14	*b*	2.345 (1)	*b*		1.811 (8), 1.819 (6)	*b*
trans-$[TcCl_2(dppe)_2]$ (**10**)	+1	28	0.035	2.501 (1)	2.319 (1)		1.827, 1.839	103.2
	0	28	0.029	2.429 (1)	2.424 (1)		1.838, 1.850	101.5
$[Re_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-dppm})_2]$ (**11**)	+1	29b	0.051	2.524 (2)	2.356 (3)		1.818 (1), 1.84 (2)	103.7
	0	29a	0.036	2.475 (2)	2.388 (2)		1.828 (8), 1.842 (8)	103.0
$[Re_2Cl_4(PMe_2Ph)_4]$ (**12**)	+2	30	0.056	2.508 (7)	2.291 (7)		1.81 (1), 1.84 (1)	106.7
	+1	30	0.048	2.460 (5)	2.330 (4)		1.83 (1), 1.83 (1)	104.6
	0	30	0.028	2.418 (1)	2.387 (1)		1.828, 1.826	103.0
$[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ (**13**)	+1	31	0.045	2.261 (3)		1.818 (3)	1.578 (6)	104.9 (1)
	0	31	0.035	2.146 (1)		1.743 (3)	1.598 (3)	100.8 (1)
$[Fe\{P(OMe)_3\}_3(C_8H_{13})]$ (**14**)	+1	32b	0.075[d]	2.154 (2)			1.600 (2)	102.2 (2)
	0	32a	0.035	2.138 (1)			1.621 (1)	98.7 (2)
cis,trans-$[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$ (**15**)[c]	+1	33	0.047	2.429 (2)		1.899 (4)	1.826 (5)	105.3 (2)
	0	33	0.046	2.424 (2)		1.876 (5)	1.829 (5)	104.2 (2)
$[Co(PEt_3)_2(\eta\text{-}C_5H_5)]$ (**16**)	+1	34	0.045	2.230 (1)			1.829 (3)	103.5 (1)
	0	34	0.026	2.218 (1)			1.846 (3)	100.3 (1)
$[Co_4(\mu_3\text{-}PPh)_4(PPh_3)_4]$ (**17**)	+1	35	0.078	2.183			1.861	102.8
	0	35	0.066	2.156			1.841	101.3
$[Co(PEt_3)_2(\eta^5\text{-}2,4\text{-}C_5H_5Me_2)]$ (**18**)	+1	36b	0.038	2.204 (1), 2.292 (1)			1.832 (5)	102.2
	0	36a	0.038	2.149 (1), 2.180 (1)			1.848 (4)	99.6
$[Co_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-MeCCMe})]$ (**19**)	+1	37	0.053	2.231 (1)		1.780 (4)	1.832 (4), 1.833 (3)	102.7 (1)
	0	37	0.052	2.203 (1)		1.750 (4)	1.839 (4), 1.838 (4)	101.1 (1)
$[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$ (**20**)	+1	38	0.050	2.162 (4)			*b*	*b*
	0	38	0.044	2.138 (2)			*b*	*b*
$[\{Rh(CO)(PPh_3)(\mu\text{-RNNNR})\}_2]$ (R = *p*-tolyl) (**21**)	+1	39	0.068	2.335 (1)		1.859 (4)	1.825 (6)	104.6 (2)
	0	39	0.054	2.290 (5)		1.814 (20)	1.855 (13)	102.6 (4)
$[\{Rh(CO)(PPh_3)\}_2(\mu\text{-}\eta^5{:}\eta^{5'}\text{-}C_{10}H_8)]$ (**22**)	+2	10	0.048	2.322 (4)		1.821 (18)	1.813 (18)	104.2 (8)
	0	10	0.043	2.255 (1)		1.808 (7)	1.844 (5)	102.6 (2)
trans-$[IrCl_4(PMe_2Ph)_2]$ (**23**)	0	13	*b*	2.392 (5)	2.324 (5)		*b*	*b*
	−1	40	*b*	2.352 (2)	2.365 (1)		*b*	*b*
$[H_2Pt_4(PBu^t_3)_4]$ (**24**)	+2	41b	0.059	2.267 (7)			1.91 (3)	110 (2)
	0	41a	0.056	2.223 (7)			1.91 (3)	109 (2)

[a] Disordered atoms involved. [b] Data not available for this parameter. [c] Ligand-based oxidation. [d] Neutron data.

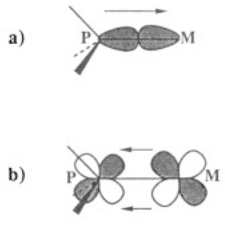

Figure 1. Schematic representation of the "traditional" view of the principal M–P bonding interactions in metal–phosphine complexes: (a) P to M σ donation; (b) M to P π back-donation by d_π–d_π overlap.

traphosphine geometry is examined, that are reported here. Aspects of this work have been presented in preliminary form.[9] Here we confirm those observations, against a larger set of data, and extend the discussion of the effect of variation in M–P π bonding on phosphine geometries to cover angular distortions. Finally we show how a qualitative molecular orbital treatment accounts for these observations.

Results

We[10] and others[11] have examined the molecular structures of pairs of complexes that form redox couples. The principal objective has been to establish the structural consequences of adding or removing an electron (or electrons) from a molecule or ion and thereby learn about the electronic structure of the species, in particular about its HOMO(s). In studies of this sort, in organometallic and coordination chemistry, phosphines have often been used to provide isolable, crystalline compounds for crystallographic analysis. However, the structures of these pairs of compounds also provide the means of testing the dual hypotheses that metal–phosphine π-bonding has observ-

---

[9] Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310–1311.

[10] See, e.g.: Freeman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2283–2289.

[11] For example: Kubat-Martin, K. A.; Spencer, B.; Dahl, L. F. *Organometallics* **1987**, *6*, 2580–2587, and references therein. See also ref 14 and 20–40.

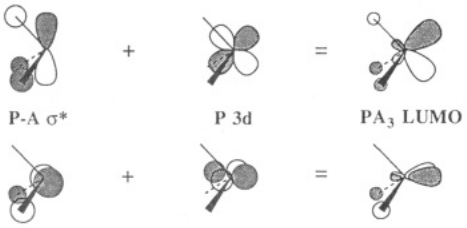

Figure 2. Mixing of phosphine P–A σ^* and P 3d orbitals leading to well-hybridized π-acceptor LUMOs on phosphorus.

able structural consequences and that it involves some P–A σ^* contribution.

The relevant complexes (**1**–**24**) whose structures have been determined in two (and for **12** in three) oxidation states are listed in Table I. It is particularly notable that the complexes in the table are drawn from transition metals from groups 5 to 10 inclusive, encompassing early, middle, and late transition metals with metal electron counts in the reduced species varying from d^1 to d^{10}. Furthermore the PA$_3$ ligands vary widely from trialkyl- to mixed arylalkyl- and triarylphosphines and trimethylphosphite. In all but two cases the primary site of oxidation is considered to be the transition metal (or metals for the polynuclear species **4**, **11**, **12**, **17**, **19**, **20**–**22**, and **24**). In the two other instances, **8** and **15**, oxidation occurs primarily at a redox-active ligand [$Ph_2PCC(O)N(Me)C(O)CPPh_2$ and o-$O_2C_6Cl_4$, respectively]. The evidence for these assignments of redox site (or HOMO location if you will) arises from ESR spectroscopy of radical species, theoretical calculations, and structural evidence. The metal orbitals depopulated are d$_\pi$-type (and not involved in M–L σ-bonding) for the mononuclear species **1**–**3**, **5**–**7**, **9**, **10**, **13**, **14**, **16**, **18**, and **23**. In the polynuclear complexes oxidation typically occurs from metal–metal antibonding orbitals. Thus, in the complexes that show metal-based oxidation, either the metal atom(s) suffer depopulation of the d$_\pi$ orbitals actually responsible for back-bonding to the phosphine or these orbitals are lowered in energy by virtue of the increase in the metal oxidation state. In any event the metal atom(s) become worse π-donors (and better σ-acceptors) on oxidation of these complexes. The structural consequences of oxidation on the gross geometries of these complexes is in general small with the following exceptions: in **1** there is a subtle but distinct change in coordination geometry from square antiprismatic to dodecahedral; in **3** there is a cis–trans isomerization on oxidation; in **22** in which there is 180° rotation about the central C–C bond of the μ-fulvalene ligand and formation of a Rh–Rh bond on double oxidation; and in **24** there are marked increases (from ca. 145° to near 180°) in Pt–Pt–P angles on oxidation. These cases are retained for completeness and show no aberrant behavior when compared with the other complexes in the table.

In summary, for the vast majority of cases in the table there is no change in the trans (or cis) influences on M–P bond length, in coordination number or geometry, spin state (all are low spin) or other factors that might affect the metal–phosphine bonding. Thus these pairs of structures allow comparison of metal–phosphine geometries in very similar environments, differing primarily in the ability of the metal to act as a π-base. The changes in M–L bond lengths and the ligand geometries on oxidation may therefore be ascribed to first order as a consequence of the loss of M–L π back-bonding. Table I lists the averaged M–L and P–A (A = C alkyl or aryl, or OMe in **13** and **14**) bond lengths and A–P–A angles for **1**–**24**. In all cases the averaging of bond lengths is over all chemically equivalent molecular dimensions. Where appropriate, the P–C(sp^3) and P–C(sp^2) bond lengths have been averaged separately. As a guide to the precision of the data in the table the crystallographic R indexes for the structure determinations are quoted, and the estimated standard deviations (esd's) of the individual parameters, where reported by the original authors, are given. For each of **1**–**24** the top line of data refers to the most oxidized form of the complex and the lower line(s) refer to the structures of the reduced form(s), with the charge on the complex being as listed. Where a parameter is unavailable, this is indicated in Table I. Where a parameter is not present because it is inappropriate for the complex in question, this is indicated by a space. For comparison of the effects of oxidation on M–L bond lengths for ligands that are primarily σ-donor and π-acceptor, respectively, the averaged M–Cl and M–C bond lengths for chloro and carbonyl ligands are given.

Of the 24 sets of structures, 22 show metal-based oxidations, giving 23 pairs of structures for comparison in evaluating the effects of reduced M–L π back-bonding (**12** yields two pairs, 0/+1 and +1/+2). In all 23 cases the M–P distance increases on oxidation, by between 0.012 (2) and 0.117 (4) Å. In one case, **1**, the phosphine ligand shows disorder, and its PA$_3$ geometry will be discounted, leaving 28 pairs of P–A bond lengths for comparison. Of these, 21 show a decrease on oxidation, 3 an increase, and 4 no change (within the number of digits published). All 19 pairs of averaged A–P–A bond angles show an increase on oxidation. All seven pairs of M–C(O) distances show an increase on oxidation. In contrast all eight pairs of M–Cl bond lengths show a decrease on oxidation. The statistical significance of the signs of these differences may be tested by the sign test.[12] In the one-tailed sign test the null hypothesis, that metal-based oxidation does not cause M–P bond lengths to increase, may be rejected at much better than the 99.9% confidence level. The equivalent null hypotheses for P–A bond lengths (that they do not decrease), A–P–A angles (that they do not increase), M–C(O) lengths (that they do not increase), and M–Cl lengths (that they do not decrease) may all be rejected at >99.9%, ≫99.9%, >99%, and >99.5% confidence levels, respectively. Complete exclusion of the four "exceptional" cases, in which some reorganization of the coordination geometry is caused by oxidation (see above), leads to no important changes in these statistics.

In the two cases where oxidation is ligand based, the M–P distance decreases on oxidation for **8** and increases for **15**, in neither case significantly. Changes in P–A bond lengths are also insignificant, and **15** shows a small increase in A–P–A angle. On oxidation **8** shows an insignificant decrease in M–C(O) length, while **15** shows a small increase.

Discussion

The implications of the results in Table I are clear. The changes in M–L distances are consistent with loss of M–L π back-bonding on oxidation of the metal. Hence the M–C(O) distances increase. In contrast the decrease in M–Cl distance is to be expected for a ligand that is primarily a σ-donor. The increase in M–P bond length is therefore in accord with an important role for M–P π-bonding in these species, a role disrupted by oxidation of the metal. Other structural evidence from series of complexes [*mer*-$MCl_3(PR_3)_3$] and [*trans*-$MCl_4(PR_3)_2$] (M = Re, Os, and *trans*-$[MCl_2\{o\text{-}(Me_2P)_2C_6H_4\}_2]^{n+}$ (M = Cr, Mn, Fe,

---

(12) Siegel, S. *Non-Parametric Statistics*; McGraw-Hill: New York, 1956; pp 68–75.

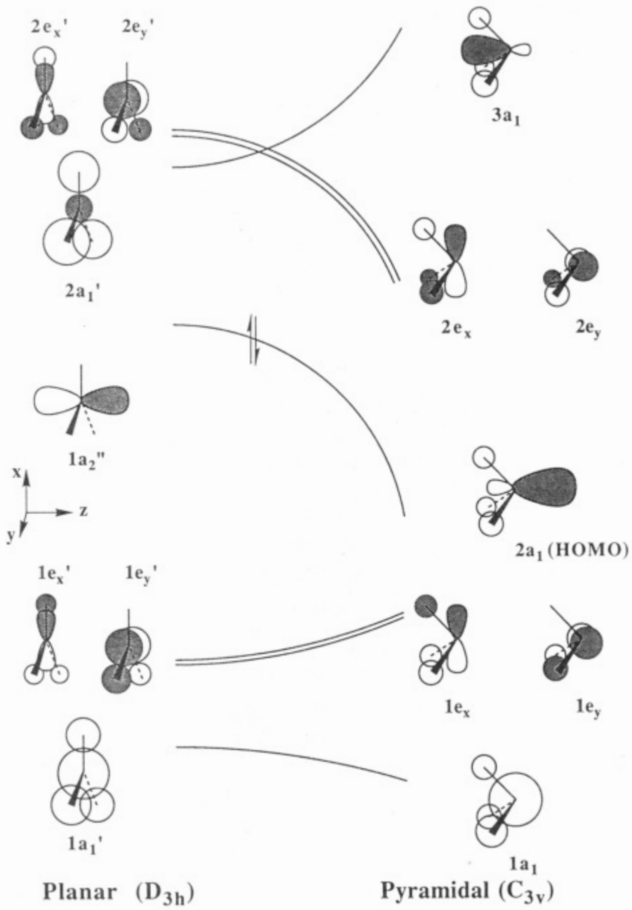

Figure 3. Walsh diagram for the pyramidalization of a PA_3 molecule. The planar (D_{3h}) molecule has A–P–A angle = 120°; for the pyramidal (C_{3v}) species A–P–A < 120°. The HOMO is $1a_2''$ ($2a_1$).

Co, Ni)[14] is consistent with this view. Thus in the first two series the M(IV)–P distance is longer than the M(III)–P for the same metal, while the variation in M–Cl length is reversed [M(IV)–Cl < M(III)–Cl]. From the data in the table one may also conclude that the increases in M–P distances are accompanied by decreases in P–A bond lengths and increases in the A–P–A angles. The first of these observations is clearly consistent with the view that the phosphine π acceptor functionality contains some P–A antibonding character—that when π donation from M to P is diminished, the P–A bonds are strengthened.

The variations in A–P–A angles, as well as the changes in P–A bond lengths, are readily understood in terms of qualitative molecular orbital arguments based on perturbation theory, as for instance described by Gimarc.[15,16] The shape of free tertiary phosphines, PA_3, is of course pyramidal, with A–P–A angles typically ca. 103°. This geometric preference may be traced to the eight valence electron count at phosphorus in PA_3 species.[15,16] Figure 3 shows a partial Walsh diagram for the deformation of a PA_3 molecule from planar (D_{3h} local symmetry) to pyramidal (C_{3v} local symmetry) qualitatively adapted from that in ref 15. Pyramidalization at phosphorus causes the HOMO ($2a_1$) to fall markedly in energy. This orbital is the phosphine lone pair, and its fall in energy is a consequence of mixing phosphorus 3s character (from the $3a_1$ MO) into the phosphorus $3p_z$ (of $2a_1$). The amount of mixing and hence the degree of pyramidality is dependent on the electronegativity of the substituents A. The more electronegative A, the greater the mixing and the more pyramidal the equilibrium PA_3 geometry (i.e., the smaller the A–P–A angle) that results. For highly pyramidal geometries the LUMOs are the 2e set of P–A σ^* orbitals. In this description, in accord with the ab initio calculations,[7] these are antibonding combinations of P $3p_x$ and $3p_y$ with A σ orbitals; in addition, they would have some P 3d character, as discussed above. The energy of the LUMOs falls rapidly as the phosphine becomes more pyramidal, as a consequence of reduced overlap between the P $3p_{x,y}$ and A σ orbitals as the A atoms move out of the xy plane. For the same reason the P–A σ orbitals are destabilized as A–P–A angles are reduced. Therefore this simplified picture of the electronic structure of phosphines is consistent with the ab initio calculations described above and may be tested against the geometric data of the table.

In this description the geometric consequences of coordinating a phosphine to a metal will mainly derive from depopulation of the HOMO, through P to M σ donation, and from population of the LUMOs, as a result of M to P π-back-bonding. In this study we focus on the effect of switching off the π-bonding by oxidation of the metal. The result of partially populating the 2e LUMOs will be to increase the P–A bond lengths and to increase the driving force for PA_3 pyramidalization. On reducing the amount of M–P π back bonding we should therefore expect decreased P–A distances and increased A–P–A bond angles. This is precisely what is observed in Table I.

The Walsh diagram of Figure 3 further suggests that if the geometry at phosphorus can be constrained to give small A–P–A angles, enhanced π-acceptor qualities should result as a consequence of lowered LUMO energy. Thus by this argument $P\{OCH_2\}_3CCH_3$ should be a better acceptor than $P(OEt)_3$, for example. This is difficult to test since small steric bulk is simultaneously conferred on the PA_3 ligand by this constraint, but it is in line with some measures of π-acceptor ability.[17] As discussed above the P–A σ^* orbitals are likely to play a more important role in M–P π bonding when A is more electronegative. More generally this mechanism of π-acidity would be expected to operate in ligands XA_3 (or XA_n, n = 1–3) where A is (much) more electronegative than X. Examples include silyls (SiA_3, A = R, halogen, etc.), $SnCl_3$, SO_3, and CF_3. In the latter case there are no low-lying d orbitals to augment the C–F σ^*. Furthermore, by this argument BF_3 and $AlCl_3$ should act as both σ- and π-acids. In all these cases and for PA_3, strongly π-basic metals would be expected to weaken the X–A bonds markedly and therefore ease their cleavage in the reaction chemistry of M–XA_3 complexes. Such chemistry is of course well-known.[18] Gladysz, Fenske, et al. have recently shown[19] that in related cir-

---

(13) Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1970**, 30–31.

(14) Bennett, M. A.; Robertson, G. B., private communication.

(15) Gimarc, B. M. *Molecular Structure and Bonding*; Academic Press: New York, 1979.

(16) Gimarc, B. M. *J. Am. Chem. Soc.* **1971**, *93*, 593–599.

(17) See ref 3 and: McEwen, G. K.; Rix, C. J.; Traynor, M. F.; Verkade, J. G. *Inorg. Chem.* **1974**, *13*, 2800–2802.

(18) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171–185.

(19) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1806–1810.

(20) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* **1983**, *22*, 770–774.

(21) (a) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339–1348. (b) Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1141–1154.

(22) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685–692.

(23) Van Order, N., Jr.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680–5690.

cumstances there is little evidence for a ground-state effect of this type being the cause of the enhanced R–I reactivity observed in iodoalkane complexes. In contrast it is the iodine 5d orbitals that are responsible, by stabilization of the transition state in R–I bond cleavage by nucleophiles. We note that the relative electronegativities of the contact atom (iodine) and its substituent atom (carbon) do not imply particularly large involvement of the I–C σ^* orbital in the ground state.

The effects of σ-bonding, which would be expected to reduce occupancy of the HOMO $2a_1$ and therefore the driving force for pyramidalization, cannot be tested effectively by the data of the table. Similarly there is insufficient evidence to establish the influence of varying the metal in determining phosphine geometry. In subsequent publications we will show how these aspects of the qualitative MO theory may be assessed by use of other crystallographic data, drawn from the Cambridge Structural Database.

Conclusion

Consideration of the geometry variations in 24 sets of transition metal–phosphine and –phosphite complexes, whose crystal structures are known for multiple oxidation states of the complexes, leads to the following conclusions:

Metal–phosphorus bond lengths increase on oxidizing the metal, consistent with there being an important element of M–P π back-bonding present in these species.

Reduction of M–P π-bonding causes a decrease in the P–A bond length, in accord with the PA_3 π acceptor orbital having P–A σ^* character.

Qualitative molecular orbital theory allows rationalization of these changes and also the angular deformations in PA_3 geometry that follow from oxidation of the metal. In particular the effect of M–P π bonding is to enhance the tendency for a pyramidal PA_3 structure with A–P–A angles $\ll 120°$. Conversely PA_3 ligands with small A–P–A angles should be better π-acceptors than those with larger A–P–A angles, other things being equal.

Acknowledgment. It is our pleasure to acknowledge the contributions made to this work by the chemists, synthetic and structural, who prepared and characterized the compounds discussed in this paper and to thank Drs. D. M. P. Mingos, G. B. Robertson, and M. W. Whiteley for providing us with their results prior to publication.

---

(24) Whiteley, M. W.; Beddows, R. L., private communication.

(25) Fong, L. K.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. *Inorg. Chem.* **1986**, *25*, 1880–1886.

(26) Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019–1026.

(27) Fenske, D. *Chem. Ber.* **1979**, *112*, 363–375.

(28) Libson, K.; Doyle, M. N.; Thomas, R. W.; Nelesnik, T.; Woods, M.; Sullivan, J. C.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3614–3619.

(29) (a) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882–2891. (b) Dunbar, K. R.; Powell, D.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2842–2846.

(30) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950–4954.

(31) Orpen, A. G.; Connelly, N. G.; Whiteley, M. W.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1989**, 1751–1757.

(32) (a) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496–7504. (b) Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981–987.

(33) Freeman, M. J.; Orpen, A. G.; Connelly, N. G. unpublished results.

(34) Harlow, R. L.; McKinney, R. J.; Whitney, J. F. *Organometallics* **1983**, *2*, 1839–1842.

(35) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160–162.

(36) (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422–1426; (b) **1986**, *5*, 635–644.

(37) Aggarwal, R. P.; Connelly, N. G.; Crespo, M. C.; Dunne, B. J.; Hopkins, P. M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 33–35.

(38) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *Polyhedron* **1986**, *5*, 2021–2031.

(39) Connelly, N. G.; Finn, C. J.; Freeman, M. J.; Orpen, A. G.; Stirling, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1025–1027.

(40) Mingos, D. M. P., private communication.

(41) (a) Frost, P. W.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G.; Gregson, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1104–1106. (b) Goodfellow, R. J.; Hamon, E. M.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1604–1606.