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X-ray Crystallographic Study of the Complexes $Cr(PCl_3)(CO)_5$, $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$, $W(PBr_3)(CO)_5$ and $Mo(PMe_3)(CO)_5$: Insight into π-Acceptance by Phosphorus

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X-ray crystal structures are reported for $Cr(PCl_3)(CO)_5$, monoclinic $P2_1/c$, $Z = 4$, $a = 6.664(3)$ Å, $b = 12.886(4)$ Å, $c = 12.824(3)$ Å, $\beta = 91.71(3)°$, $V = 1100.8(6)$ Å^3, R (R_w) = 0.0378 (0.040) using 1623 unique data with $I > 2.5\sigma(I)$ at 180 K;$W(PCl_3)(CO)_5$; monoclinic $P2_1/c$, $Z = 4$, $a = 6.774(2)$ Å, $b = 13.022(2)$ Å, $c = 12.975(2)$ Å, $\beta = 91.48(2)°$, $V = 1144.2(4)$ Å^3, R (R_w) = 0.0449 (0.0493) using 1304 unique data with $I > 2.0\sigma(I)$ at 130 K; $Cr(PBr_3)(CO)_5$, triclinic, $P\bar{1}$, Z = 2, $a = 6.573(1)$ Å, $b = 6.688(2)$ Å, $c = 13.394(2)$ Å, $\alpha = 88.34(2)°$, $\beta = 86.94(1)°$, $\gamma = 87.53(3)°$, $V = 587.2(2)$ Å^3, R (R_w) = 0.0511 (0.0641) using 2057 unique data with $I > 2.0\sigma(I)$ at 130 K; $W(PBr_3)(CO)_5$, monoclinic $P2_1/c$, $Z = 4$, $a = 6.811(1)$ Å, $b = 13.419(2)$ Å, $c = 13.203(4)$ Å, $\beta = 92.54(2)°$, $V = 1205(4)$ Å^3, R (R_w) = 0.0397 (0.0460) using 1958 unique data with $I > 2.0\sigma(I)$ at 130 K; and $Mo(PMe_3)(CO)_5$, monoclinic $P2_1/c$, $Z = 4$, $a = 7.009(2)$ Å, $b = 11.703(2)$ Å, $c = 15.179(3)$ Å, $\beta = 103.25(2)°$, $V = 1211.9(5)$ Å^3, R (R_w) = 0.0205 (0.0265) using 1974 unique data with $I > 2.0\sigma(I)$ at 130 K. The compounds $Cr(PCl_3)(CO)_5$, $W(PCl_3)(CO)_5$, and $W(PBr_3)(CO)_5$ are isomorphous. Bond dimensions are interpreted in relation to the π-acceptor ability of the phosphorus ligand. The disposition of the PY_3 moiety is determined with reference to the near planar $M(CO)_4$ group for each of the complexes studied. The results are rationalized in terms of the steric and electronic properties of the substituents on the phosphorus. The P−Y bond lengths in the $PY_3M(CO)_5$ complexes are compared with those of the uncomplexed PY_3 ligand to probe the role of P−Y σ^* antibonding orbitals in the π-acceptor behavior of the phosphorus ligand.

Introduction

The study of metal−ligand interactions is important owing to the great diversity of properties which different ligands can confer on metal complexes.[1−12] It is known that the behavior of complexes can be modulated by the modification of ligands. Tertiary phosphines, for example, are widely used in organometallic and catalytic systems since their steric and electronic characteristics often can be tailored to control the reactivity and the geometric course of reactions involving complexes with these ligands.[4−15]

Some assessment of ligand steric effects in the case of phosphines and related ligands is available from Tolman's "cone angles" which are related to the dimensions of space filling models for the free ligands.[5] More detailed study of such effects has emerged from a series of papers by Brown and his coworkers applying molecular mechanics methods.[16−21] However, the electronic factor in metal−phosphorus interactions remains contentious. The magnitude and even the existence of a metal−phosphorus π- interaction, additional to M−P σ-bonding, has long been a subject of controversy. Depending on the electronic nature of the Y substituent in coordinated PY_3, the phosphorus (III) ligands have variously been classified as pure σ- donors,[6−8,22−25] σ-donors/π-acceptors and σ-donors/π-donors.[6,7,25]

Even where metal to phosphorus π-backbonding is invoked, the nature of the phosphorus acceptor orbital is uncertain. The traditional Dewar−Chatt model[26,27]of electron drift from metal

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(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley-Interscience: New York, 1988; pp 65−68.

(2) Huheey, J. E. *Inorganic Chemistry*; 3rd ed.; Harper and Row: New York, 1983; pp 432−441.

(3) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; pp 71−74.

(4) Xiao, S. X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033.

(5) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(6) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

(7) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

(8) Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758.

(9) Orpen, A. G. *Chem. Soc. Rev.* **1993**, 191.

(10) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206.

(11) Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

(12) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391.

(13) Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1992**, 641.

(14) Garner, S. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 533.

(15) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653.

(16) Caffery, M. L.; Brown, T. L. *Inorg. Chem.* **1991**, *30*, 3907.

(17) Lee, K. J.; Brown, T. L. *Inorg. Chem.* **1992**, *31*, 289.

(18) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89.

(19) Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 1548.

(20) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286.

(21) Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 5603.

(22) Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(23) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

(24) Carty, A. J.; Taylor, N. J.; Coleman, A. W.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 639.

(25) Rahman, M. M.; Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

(26) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.

0020-1669/95/1334-0330$09.00/0

Table 1. Crystal Data, Experimental Conditions and Refinements for the Complexes

	$Cr(PCl_3)(CO)_5$	$W(PCl_3)(CO)_5$	$Cr(PBr_3)(CO)_5$	$W(PBr_3)/(CO)_5$	$Mo(PMe_3)(CO)_5$
formula	$C_5O_5Cl_3CrP$	$C_5O_5Cl_3PW$	$C_5O_5Br_3CrP$	$C_5O_5Br_3PW$	$C_8H_9O_5MoP$
fw	329.38	461.22	462.75	594.60	312.06
cryst color	yellow	yellow	orange	gold	colorless
cryst size, mm	0.39 × 0.28 × 0.09	0.60 × 0.46 × 0.20	0.72 × 0.44 × 0.28	0.44 × 0.40 × 0.10	0.60 × 0.36 × 0.24
cryst habit	plates	prism	prism	plates	prism
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	P_21/c	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	6.664(3)	6.774(2)	6.573(1)	6.811(1)	7.009(2)
b, Å	12.886(4)	13.022(2)	6.688(2)	13.419(2)	11.703(2)
c, Å	12.824(3)	12.975(2)	13.394(2)	13.203(4)	15.179(3)
α, deg	90	90	88.34(2)	90	90
β, deg	91.71(3)	91.48(2)	86.94(1)	92.54(2)	103.25(2)
γ, deg	90	90	87.53(3)	90	90
V, Å^3	1100.8(6)	1144.2(4)	587.2(2)	1205.5(4)	1211.9(5)
Z	4	4	2	4	4
T, K	180	130(2)	130(2)	130(2)	130(2)
D_{calc}, g cm^{-3}	1.993	2.678	2.617	3.276	1.710
μ, cm^{-1}	18.90	109.30	113.11	196.53	12.11
R^a	0.0378	0.0449	0.0511	0.0397	0.0205
$R_w{}^b$	0.040	0.0493	0.0641	0.0460	0.0265
weighting					
g_1	8.827	0.0941	0.0805	0.0282	0.0841
$g_2{}^c$	4.7×10^{-5}	0	0	0.4875	6.3685

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(w||F_o| - |F_c||^2)/\sum(w|F_o|^2)]^{1/2}$. [c] The different refinement packages used at the two laboratories use different weighting schemes. For $Cr(PCl_3)(CO)_5$ the weighting scheme is $w = g_1/[\sigma^2|F_o| + g_2|F_o|^2]$. For the remaining compounds the weighting scheme is $w = 1/[\sigma^2|F_o|^2 + ({}_{g1}P)^2 + g_2P]$ where $P = (|F_o|^2 + 2|F_c|^2)/3$.

d orbitals into empty phosphorus 3d orbitals is being challenged by theories which suggest that coordinated PY_3 ligands accept electrons from M into phosphorus p, or P−Y σ^* receptor orbitals,[4,10-12,14,15,28-30] or the latter in combination with phosphorus d orbitals.[12]

The present work is part of a continuing program of study of M−L bonding interactions in complexes of the general form $ML(CO)_5$, where L is a tertiary amine, phosphine, phosphite, arsine or stibine and M is a chromium triad metal.[31-36] Earlier papers in this series have examined such complexes using dielectric, electro-optic, crystallographic and spectroscopic techniques. The results to date provide strong evidence for an important π- component in M−P (and M-As) bonding in the $ML(CO)_5$ complexes.

X-ray crystal structures are now reported for $Cr(PCl_3)(CO)_5$, $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$, $W(PBr_3)(CO)_5$ and $Mo(PMe_3)(CO)_5$. A comparative study is made of the structural parameters of these and other related complexes and of the uncoordinated PY_3 ligands. Evidence is sought in regard to L−M π-bonding for the $ML(CO)_5$ complexes.

Experimental Section

The preparation and characterisation of $M(PX_3)(CO)_5$ (X = Cl or Br; M = Cr or W) and $M(PMe_3)(CO)_5$ (M = Cr, Mo or W) have previously been described.[33] Complexes $Mo(PCl_3)(CO)_5$ and $Mo(PBr_3)(CO)_5$ were not examined due to their lower stability.[37] Crystals of the $M(PX_3)(CO)_5$ complexes were grown by vacuum sublimation (313 K, 0.1 mmHg) onto a water-cooled finger and those of $Mo(PMe_3)(CO)_5$ were grown from hexane solution at *ca.* 273 K over a period of several days.

X-ray Experimental Section

Crystal data and experimental details are given in Table 1. X-ray data for $Cr(PCl_3)(CO)_5$ were collected at the University of Sydney on a Enraf-Nonius CAD4-F diffractometer[38] with graphite monochromated Mo Kα (λ = 0.71069 Å) radiation at 180 K. Data for $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$, $W(PBr_3)(CO)_5$ and $Mo(PMe_3)(CO)_5$ were collected at the University of Canterbury on a Nicolet/Siemens P4 diffractometer[39] using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 130 K.

X-ray Study of $Cr(PCl_3)(CO)_5$

A yellow crystal measuring 0.39 × 0.28 × 0.09 mm was mounted onto a glass fiber and fixed into position by freezing water around it. Unit cell parameters were defined by the least-squares refinement of the setting parameters of 25 independent reflections. Data were collected using the $\omega-{}^3/_4\theta$ scan mode in the range $2° \leq 2\theta \leq 50°$ with index ranges $-6 \leq h \leq 6$, $0 \leq k$, $l \leq 12$. A total of 2058 reflections were collected of which 1790 were independent. A numerical absorption correction was applied, transmission ranged from 0.502 to 0.858. The structure was solved with SHELXS-86[40] with full-matrix least-squares refinement using SHELXS-76.[41] Scattering factors and anomalous dispersion terms for Cr were taken from ref 42, and all others were those supplied in SHELXS-76. All atoms were refined

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(27) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(28) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064.

(29) Rappe, A. K.; Colwell, K. S.; Casewit, C. J. *Inorg. Chem.* **1993**, *32*, 3438.

(30) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

(31) Aroney, M. J.; Cooper, M. K.; Pierens, R. K.; Pratten, S. J. *J. Organomet. Chem.* **1986**, *309*, 293.

(32) Aroney, M. J.; Clarkson, R. M.; Hambley, T. W.; Pierens, R. K. *J. Organomet. Chem.* **1992**, *426*, 331.

(33) Davies, M. S.; Pierens, R. K.; Aroney, M. J. *J. Organomet. Chem.* **1993**, *458*, 141.

(34) Aroney, M. J.; Davies, M. S.; Hambley, T. W.; Pierens, R. K. *J. Chem. Soc., Dalton Trans.* **1994**, 91.

(35) Aroney, M. J.; Buys, I. E.; Davies, M. S.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1994**, in press.

(36) Davies, M. S.; Allen, G. W.; Aroney, M. J.; Hambley, T. W.; Pierens, R. K. *J. Mol. Struct.*, **1994**, *326*, 81.

(37) Lang, H.; Huttner, G.; Zsolnai, L.; Mohr, G.; Sigwarth, B.; Weber, U.; Orama, O.; Jibril, I. *J. Organomet. Chem.* **1986**, *304*, 157.

(38) Enraf-Nonius Structure Determination Package. Enraf Nonius, Delft, Holland, 1985.

(39) Sheldrick, G. M. *SHELXTL PC, An Integrated System for Data Collection, Processing, and Structure Solution and Refinement*; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(40) Sheldrick, G. M. *SHELXS-86, A program for the solution of crystal structures from diffraction data*; University of Gottingen: Gottingen, Germany, 1986.

(41) Sheldrick, G. M. *SHELXS-76, A Program for X-ray Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(42) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Table 2. Fractional Atomic Coordinates for $Cr(PCl_3)(CO)_5$ and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	x	y	z	U_{eq}[a]
Cr(1)	0.7113(1)	0.7009(1)	0.1068(1)	16
P(1)	0.6895(2)	0.8651(1)	0.1633(1)	19
Cl(1)	0.4208(2)	0.9191(1)	0.2101(1)	35
Cl(2)	0.7595(2)	0.9791(1)	0.0623(1)	32
Cl(3)	0.8676(2)	0.9071(1)	0.2877(1)	31
C(1)	0.9612(6)	0.7376(3)	0.0491(3)	25
C(2)	0.8377(6)	0.6597(3)	0.2361(4)	22
C(3)	0.4585(6)	0.6669(3)	0.1637(3)	22
C(4)	0.5798(6)	0.7411(3)	−0.0213(3)	22
C(5)	0.7373(6)	0.5630(3)	0.0570(3)	23
O(1)	1.1088(4)	0.7610(3)	0.0138(3)	37
O(2)	0.9067(5)	0.6354(3)	0.3141(3)	31
O(3)	0.3090(4)	0.6471(2)	0.1982(3)	29
O(4)	0.5042(5)	0.7651(3)	−0.0976(3)	32
O(5)	0.7544(5)	0.4798(2)	0.0283(3)	40

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j \mathbf{U}_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 3. Fractional Atomic Coordinates for $W(PCl_3)(CO)_5$ and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	x	y	z	U_{eq}[a]
W(1)	0.7141(1)	0.6995(1)	0.1042(1)	11(1)
P(1)	0.6891(5)	0.8716(3)	0.1638(2)	14(1)
Cl(1)	0.4240(5)	0.9242(3)	0.2115(3)	29(1)
Cl(2)	0.7575(5)	0.9845(3)	0.0642(2)	25(1)
Cl(3)	0.8647(5)	0.9117(3)	0.2866(2)	27(1)
C(1)	0.9773(20)	0.7403(11)	0.0446(9)	14(1)
C(2)	0.8445(18)	0.6583(12)	0.2426(10)	17(3)
C(3)	0.4480(21)	0.6660(11)	0.1621(9)	16(3)
C(4)	0.5767(19)	0.7400(13)	−0.0305(11)	24(3)
C(5)	0.7427(20)	0.5538(12)	0.0535(10)	22(3)
O(1)	1.1258(13)	0.7663(9)	0.0113(8)	30(2)
O(2)	0.9102(13)	0.6368(8)	0.3203(7)	26(2)
O(3)	0.2955(13)	0.6485(8)	0.1985(7)	25(2)
O(4)	0.5035(13)	0.7654(9)	−0.1075(7)	29(3)
O(5)	0.7622(15)	0.4694(8)	0.0259(7)	31(2)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j \mathbf{U}_{ij} a_i^* a_j^* a_i a_j$.

Table 4. Fractional Atomic Coordinates for $Cr(PBr_3)(CO)_5$ and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	x	y	z	U_{eq}[a]
Br(1)	0.0951(1)	0.3862(1)	0.1252(1)	22(1)
Br(2)	−0.0907(1)	0.8690(1)	0.1257(1)	19(1)
Br(3)	0.3931(1)	0.7614(2)	0.0463(1)	25(1)
P(1)	0.1763(3)	0.6835(3)	0.1714(2)	12(1)
Cr(1)	0.2795(2)	0.7193(2)	0.3272(1)	12(1)
C(1)	0.0298(14)	0.8546(12)	0.3687(6)	21(2)
C(2)	0.1614(12)	0.4763(13)	0.3726(6)	18(2)
C(3)	0.5273(13)	0.5778(13)	0.2934(6)	17(2)
C(4)	0.3967(13)	0.9643(13)	0.2812(6)	18(2)
C(5)	0.3816(12)	0.7510(13)	0.4552(7)	19(2)
O(1)	−0.1222(10)	0.9279(10)	0.3939(5)	32(2)
O(2)	0.0896(10)	0.3343(10)	0.4013(5)	28(2)
O(3)	0.6811(10)	0.4962(10)	0.2772(5)	31(2)
O(4)	0.4669(10)	1.1092(9)	0.2540(5)	28(2)
O(5)	0.4514(11)	0.7644(10)	0.5301(5)	31(2)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j \mathbf{U}_{ij}\ a_i^* a_j^* a_i \cdot a_j$.

Table 5. Fractional Atomic Coordinates for $W(PBr_3)(CO)_5$ and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	x	y	z	U_{eq}[a]
W(1)	0.7120(1)	0.6970(1)	0.1061(1)	14(1)
P(1)	0.6879(3)	0.8644(2)	0.1645(2)	15(1)
Br(1)	0.4000(1)	0.9187(1)	0.2119(1)	26(1)
Br(2)	0.7631(1)	0.9824(1)	0.0580(1)	25(1)
Br(3)	0.8787(1)	0.9072(1)	0.2973(1)	24(1)
C(1)	0.9733(12)	0.7343(8)	0.0478(7)	20(2)
C(2)	0.8459(12)	0.6579(7)	0.2420(7)	16(2)
C(3)	0.4463(13)	0.6611(8)	0.1654(7)	20(2)
C(4)	0.5743(11)	0.7394(7)	−0.0287(7)	19(2)
C(5)	0.7380(11)	0.5547(8)	0.0547(6)	19(2)
O(1)	1.1190(9)	0.7583(7)	0.0147(6)	20(2)
O(2)	0.9126(9)	0.6380(6)	0.3195(5)	28(2)
O(3)	0.3022(9)	0.6440(6)	0.1988(5)	34(2)
O(4)	0.4990(9)	0.7636(6)	−0.1021(5)	28(2)
O(5)	0.7544(11)	0.4748(6)	0.0273(6)	34(2)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j \mathbf{U}_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 6. Fractional Atomic Coordinates for $Mo(PMe_3)(CO)_5$ and Equivalent Isotropic Displacement Parameters (10^3 Å^2)

	x	y	z	U_{eq}[a]
Mo(1)	0.2761(1)	0.1435(1)	0.2931(1)	16(1)
P(1)	0.2733(1)	0.2823(1)	0.4187(1)	19(1)
O(1)	−0.1658(3)	0.2108(2)	0.2081(1)	43(1)
O(2)	0.1348(4)	−0.0579(2)	0.4092(2)	48(1)
O(3)	0.7191(3)	0.0810(2)	0.3815(2)	43(1)
O(4)	0.4222(3)	0.3446(2)	0.1856(1)	39(1)
O(5)	0.2806(3)	−0.0269(2)	0.1342(1)	36(1)
C(1)	−0.0073(4)	0.1870(2)	0.2387(2)	26(1)
C(2)	0.1849(4)	0.0151(2)	0.3646(2)	26(1)
C(3)	0.5603(4)	0.1032(2)	0.3503(2)	27(1)
C(4)	0.3693(4)	0.2727(2)	0.2241(2)	24(1)
C(5)	0.2787(4)	0.0354(2)	0.1927(2)	24(1)
C(6)	0.4990(4)	0.2963(2)	0.5041(2)	27(1)
C(7)	0.2220(4)	0.4290(2)	0.3824(2)	31(1)
C(8)	0.0918(4)	0.2561(3)	0.4842(2)	34(1)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j \mathbf{U}_{ij} a_i^* a_j^* a_i \cdot a_j$.

anisotropically. Final agreement factors listed in Table 1 were determined from 1623 reflections with $I > 2.5\sigma(I)$ considered observed.

X-ray Crystal Structures of $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$, $W(PBr_3)(CO)_5$, and $Mo(PMe_3)(CO)_5$

Crystals were suspended in polyfluorinated polyether (Hoechst) and mounted onto a glass fiber, transferred to the diffractometer where there was immediate cooling. The space groups were determined by systematic absences and the cell parameters obtained from 25 automatically centred reflections; crystal and instrument stabilities were monitored using three standard reflections every 97 scans (no deterioration for any of the compounds was observed); Lorentz and polarisation corrections were included and an absorption correction based on ψ scans was applied. The structures were solved using SHELXS-86 [40] followed by full-matrix least-squares refinement using SHELXL-93.[39] All non-hydrogen atoms were refined anisotropically, the hydrogen atoms in $Mo(PMe_3)(CO)_5$ were generated in calculated positions (C-H = 0.96 Å) with isotropic thermal parameters. Scattering factor coefficients and anomalous dispersion terms were taken from ref 42.

Fractional atomic coordinates, average bond lengths and angles are listed in Tables 2–7. Figures 1 and 2 show ORTEP[43] plots of $W(PCl_3)(CO)_5$ and $Mo(PMe_3)(CO)_5$ with atomic numbering. Bond distances, bond angles, anisotropic thermal parameters, hydrogen atomic coordinates with isotropic thermal parameters, and torsion angles are submitted as supplementary material.

Discussion

The X-ray crystal structures of $Cr(PCl_3)(CO)_5$ and $W(PCl_3)(CO)_5$ reported here are the first for phosphorus trichloride complexes of the group VI transition metals. The structure of $Mo(PF_3)(CO)_5$ has been examined by gas phase electron diffraction[44] and an earlier X-ray crystal structure analysis has been reported for $Cr(PBr_3)(CO)_5$.[45] The $M(PX_3)(CO)_5$ (X = halogen) complexes have low melting points and consequently X-ray study at room temperature is impractical. In our work, data for $W(PBr_3)(CO)_5$ (which has the highest melting point of the compounds studied) at 294 K were found to be unsatisfactory. In order to confirm the reliability of results earlier obtained by Paine and coworkers for $Cr(PBr_3)(CO)_5$;[45] where it is stated

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(43) Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.

Table 7. Average Bond Lengths (Å) and Average Bond Angles (deg) of the $M(PY_3)(CO)_5$ Complexes[a]

complex	M−P	$M-C_{ax}$	$M-C_{eq}$(av)	$C-O_{ax}$	$C-O_{eq}$(av)	P−Y(av)
$Cr(PCl_3)(CO)_5$	2.245(1)	1.900(4)	1.905(4)	1.141(5)	1.130(4)	2.025
$Cr(PBr_3)(CO)_5$	2.250(2)	1.896(9)	1.902(9)	1.133(11)	1.134(11)	2.203
$Cr(PMe_3)(CO)_5$	2.3664(5)	1.850(2)	1.893(5)	1.153(2)	1.134(3)	1.814
$Mo(PMe_3)(CO)_5$	2.5082(7)	1.984(3)	2.036(5)	1.152(3)	1.134(3)	1.811
$W(PCl_3)(CO)_5$	2.378(2)	2.02(2)	2.03(2)	1.17(2)	1.15(2)	2.028
$W(PBr_3)(CO)_5$	2.382(2)	2.037(11)	2.048(12)	1.139(13)	1.131(13)	2.205
$W(PMe_3)(CO_5)$	2.516(2)	2.00(1)	2.01(2)	1.15(1)	1.15(4)	1.85

	$C_{ax}-M-C_{eq}$	$P-M-C_{ax}$	$P-M-C_{eq}$	M−P−Y	Y−P−Y
$Cr(PCl_3)(CO)_5$	90.2	178.2(1)	89.8	118.1	99.6
$Cr(PBr_3)(CO)_5$	89.4	176.8(3)	90.6	117.9	99.88
$Cr(PMe_3)(CO)_5$	90.6	178.2	89.4	115.8	102.4
$Mo(PMe_3)(CO)_5$	90.6	179.26(8)	89.23	115.7	102.7
$W(PCl_3)(CO)_5$	90.7	178.6(4)	89.3	117.8	100.0
W(PCl3)$(CO)_5$	90.7	178.6(4)	89.3	117.8	100.0
$W(PBr_3)(CO)_5$	90.5	178.8(2)	89.5	117.5	100.4
$W(PMe_3)(CO)_5$	90.2	179.3	89.8	115.6	102.7

[a] Errors specified for single value parameters are the standard deviation on the value, and for average values the range is specified.

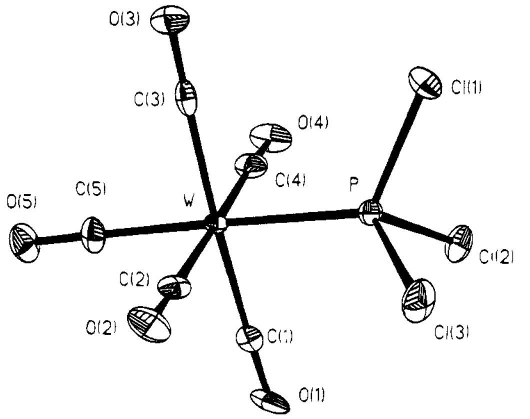

Figure 1. ORTEP picture of $W(PCl_3)(CO)_5$. Each atom is represented by a 30% thermal ellipsoid of vibration. The atomic numbering scheme given above applies also to $Cr(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$ and $W(PBr_3)(CO)_5$.

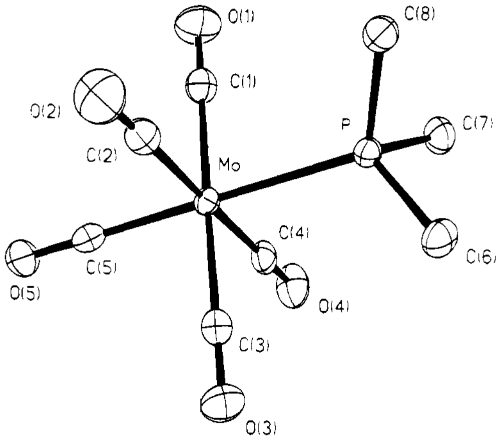

Figure 2. ORTEP picture of $Mo(PMe_3)(CO)_5$ showing atomic numbering scheme. All non-hydrogen atoms are represented by 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

that rapid crystal decay necessitated the use of two crystals, the crystal structure analysis of $Cr(PBr_3)(CO)_5$ as well as theother $M(PX_3)(CO)_5$ complexes was carried out at low temperature.

The results now found for $Cr(PBr_3)(CO)_5$ are in good agreement with those of Paine and coworkers.[45] Small differences in the unit cell parameters and bond lengths between the two data sets are due to variance in the temperature between the two experiments. The differences in the bond lengths are less than 1% and the cell parameters differ by less than 2%; the cell volume and density change accordingly.

The M−P bond lengths in $Cr(PCl_3)(CO)_5$, $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$ and $W(PBr_3)(CO)_5$ are the shortest yet reported for a $M(PY_3)(CO)_5$ type complex of the same M.[36] This is consistent with the widely held view that the phosphorus trihalides are very strong π-acceptor ligands, though it is known that ligand steric factors as well as electronic properties can affect the M−P bond dimensions.[35]

The X-ray structure now determined for $Mo(PMe_3)(CO)_5$ completes the triad of $M(PMe_3)(CO)_5$ complexes (M = Cr, Mo or W).[17,46] Comparison of analogous $M(PMe_3)(CO)_5$ and $M(PCl_3)(CO)_5$ compounds is valuable in that the PMe_3 and PCl_3 ligands are sterically similar; the Tolman cone angle for PMe_3 is 118° while that of PCl_3 is 124°.[5] Thus differences in the M−P bond dimensions between corresponding pairs of complexes can be attributed principally to the different electronic properties of the phosphorus ligands.

From the data summarised in Table 7 it is seen that the $M(PCl_3)(CO)_5$ complexes have much shorter M−P bonds than the corresponding $M(PMe_3)(CO)_5$ complexes (0.121 Å for Cr and 0.138 Å for W[47]) despite the fact that PMe_3 itself has been shown to exhibit π-acid behavior in such complexes.[12,31,33,48] The C−P−C angles in $M(PMe_3)(CO)_5$ complexes are found to be 102.7 ± 0.3° while the Cl−P−Cl angles in $M(PCl_3)(CO)_5$ have values 100.0 ± 0.5°. Hybridization arguments[24,49–55] have been used to suggest that M−P bonds would be shorter in the PCl_3 complexes because of the greater s-character of the P lone

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(44) Bridges, D. M.; Holywell, G. C.; Rankin, D. W. H.; Freeman, J. M. *J. Organomet. Chem.* **1971**, *32*, 87.

(45) Jelinek-Fink, H.; Duesler, E. N.; Paine, R. T. *Acta Crystallogr.* **1987**, *C43*, 635.

(46) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 4440.

(47) The difference for the tungsten complexes is a little enhanced because the structure of $PMe_3W(CO)_5$ was determined at room temperature while that of $PCl_3W(CO)_5$ was determined at 130 K.

(48) Wang, S. P.; Richmond, M. G.; Schwartz, M. *J. Am. Chem. Soc.* **1992**, *114*, 7595.

(49) Grim, S. O.; Plastas, H. J.; Huheey, C. L.; Huheey, J. E. *Phosphorus* **1971**, *1*, 61.

(50) Bennett, M. J.; Cotton, F. A.; LaPrade, M. D. *Acta Crystallogr.* **1971**, *B27*, 1899.

(51) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(52) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616.

(53) Bent, H. A. *J. Chem. Phys.* **1960**, *33*, 1258.

(54) Bent, H. A. *J. Chem. Phys.* **1960**, *33*, 1259.

(55) Bent, H. A. *J. Chem. Phys.* **1960**, *33*, 1260.

pair electrons, but differences only of the order of ±0.05 Å would be expected for a change in angle of this magnitude.[56] It has been shown from a recent study of a large range of ML(CO)$_5$ complexes that such rationalizations are in general not valid.[35]

Further support for a strong π-component in Cr(PX$_3$)(CO)$_5$ comes from comparison of Cr−P bond lengths in these complexes (2.245−2.250 Å) with that for Cr−N (2.249 Å) in Cr(quinuclidine)(CO)$_5$.[32] The Cr−P and Cr−N bond distances are virtually identical in these complexes yet the covalent radius for single-bonded N is known to be *ca.* 0.4 Å smaller than for P.[50,57,58] It is clear that Cr−P in Cr(PX$_3$)(CO)$_5$ is far shorter than expected for a purely σ-bonded system.

The M−C bond distances in M(PX$_3$)(CO)$_5$ (X = Cl or Br) are longer than those for the corresponding M(PMe$_3$)(CO)$_5$. This accords with the greater π-acid character of PX$_3$, relative to PMe$_3$, resulting in enhanced electron drift towards P from the π^* molecular orbitals of the CO ligands. Differences between M−C$_{ax}$ and average M−C$_{eq}$ for each M(PX$_3$)(CO)$_5$ complex are small. With the weaker π-acceptor PMe$_3$, M−C$_{ax}$ becomes shorter than the M−C$_{eq}$ bonds within the M(CO)$_4$ grouping. Change in the σ-basicity of the phosphorus ligands appears not to be an important factor from recent theoretical work by Pacchioni and Bagus.[12] Differences between the M−C$_{ax}$ and M−C$_{eq}$ bonds are not observed in the case of W(PMe$_3$)(CO)$_5$ where the resolution is relatively low due to high thermal motion in the crystal lattice at the higher temperature (294 K) of data collection.[46]

The CO bond lengths are generally insensitive to small changes in CO bond order in these complexes.[59,60] In Cr(PMe$_3$)(CO)$_5$ and Mo(PMe$_3$)(CO)$_5$, CO$_{ax}$ is longer than the average CO$_{eq}$ value, a reversal of the order found for the analogous M−C bond distances. This accords with the weaker π-acceptor behavior of PMe$_3$ relative to PX$_3$; the electronic response is more evident in the *trans* MCO grouping.

Bond angles about M for the five complexes examined are all similar with only small deviations from ideal octahedral geometry. The equatorial MCO groupings tend to be inclined slightly towards the phosphorus ligand except for Cr(PBr$_3$)(CO)$_5$ where very small deflections away from PBr$_3$ are seen. Steric interactions between the PY$_3$ and M(CO)$_5$ groupings appear not to be large. A small degree of tilting of the phosphine ligand is observed relative to M(CO)$_5$; the C$_{ax}$−M−P bond angles deviate by less than 2° from linearity apart from Cr(PBr$_3$)(CO)$_5$ where this angle is 176.8°. Little variation occurs in the M−P−X bond angles for the four M(PX$_3$)(CO)$_5$ complexes, all of which are *ca.* 118°. The M−P−C angles in the M(PMe$_3$)(CO)$_5$ complexes are *ca.* 116°.

The M(PBr$_3$)(CO)$_5$ complexes exhibit weak Br−Br nonbonded interactions where the Br−Br distances between molecules are 3.6−3.8 Å (see Figures 3 and 4). The chromium complex also has Br−CO close contacts. There is a change in crystal system as the metal is varied. The crystal of W(PBr$_3$)(CO)$_5$ is monoclinic $P2_1/c$, while Cr(PBr$_3$)(CO)$_5$ is triclinic $P\bar{1}$. The M(PCl$_3$)(CO)$_5$ and W(PBr$_3$)(CO)$_5$ complexes are isomorphous. The M(PMe$_3$)(CO)$_5$ complexes all have the monoclinic crystal symmetry but are not isomorphous with the M(PCl$_3$)(CO)$_5$ compounds.[61] The change observed for Cr(PBr$_3$)(CO)$_5$may result from increased Br−Br interactions associated with the smaller chromium complex molecule and the longer P−Br bond distances. Isomorphism is observed for the other ML(CO)$_5$ complexes with common L for which structures of more than one metal in the Cr triad are known.

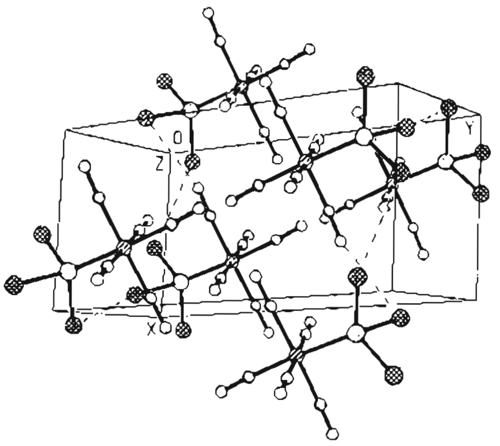

Figure 3. Unit cell picture of Cr(PBr$_3$)(CO)$_5$ showing unit cell axes. Dashed lines indicate close nonbonded contacts between atoms.

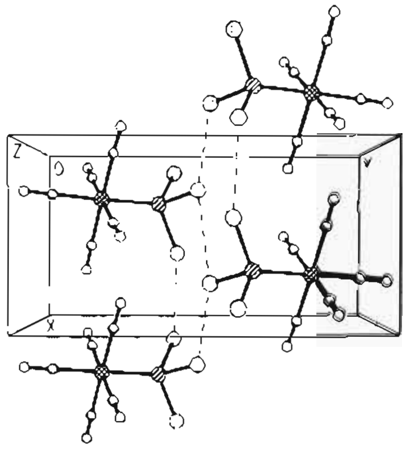

Figure 4. Unit cell picture of W(PBr$_3$)(CO)$_5$ showing unit cell axes. The dashed lines indicate nonbonded close contacts.

The disposition of coordinated PX$_3$ (X = Cl or Br) relative to M(CO)$_4$, about rotation axis M−P, is described by the torsion angles ω shown in Figure 5. The mutual orientation of these two groups is similar for all four M(PX$_3$)(CO)$_5$ complexes studied; one P−X is staggered with respect to two vicinal M−CO groups (ω_1 ~ 45°) while the other two P−X bonds have ω_2, ω_3 values of *ca.* ±15°. The M(PMe$_3$)(CO)$_5$ complexes have a different geometric arrangement in that one P−C eclipses a M−C$_{eq}$ bond (ω_1 ~ 0) and the other two P−C bonds have ω_2, ω_3 torsion angles of *ca.* ±30° (see Figure 6) to the adjacent M−C.

Such differences between the M(PCl$_3$)(CO)$_5$ and M(PMe$_3$)(CO)$_5$ species are surprising inasmuch as the methyl and chloro substituents are similar in size and the PCl$_3$ and PMe$_3$ ligands have cone angles which are close in value. However, it would be expected that steric repulsions between PCl$_3$ and equatorial M(CO)$_4$ would be exacerbated because of the shorter M−P bond

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[56] By analogy with Carty *et al.*[24] a Y−P−Y bond angle change of 4° resulted in a shortening of Cr−E in Cr(EPh$_3$)(CO)$_5$ of 0.077 Å. The Y−P−Y angle difference between M(PMe$_3$)(CO)$_5$ and M(PCl$_3$)(CO)$_5$ here is *ca.* 2.8° for a given metal M. On this basis a bond shortening of *ca.* 0.05 Å is expected.

[57] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Permagon Press: Oxford, England, 1984; p 567.

[58] For example, N−N in N$_2$H$_4$ is 1.46 Å while P-P in P$_2$H$_4$ is 2.22 Å; the covalent radius of N can reasonably be regarded to be substantially smaller than that of P.

[59] Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 314.

[60] Elschenbroich, C.; Salzer, A. *Organometallics*; VCH Publishers: Weinheim, Germany, 1989; pp 220−231.

[61] Cotton *et al.*[46] reported W(PMe$_3$)(CO)$_5$ in $P2_1/n$. Our results, and their own preliminary results, show that all three M(PMe$_3$)(CO)$_5$ compounds are isomorphous. The choice of space group is an arbitrary one.

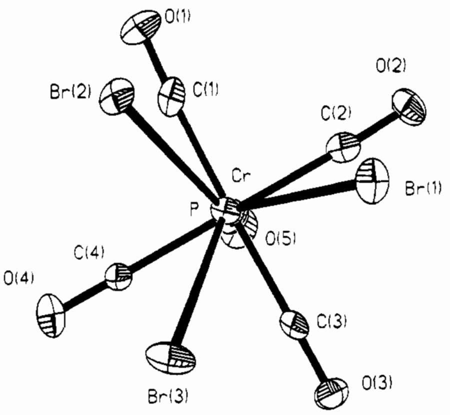

Figure 5. ORTEP picture of $Cr(PBr_3)(CO)_5$ viewed down the P−M−CO_{ax} axis showing the staggered arrangement of PBr_3 in relation to equatorial $Cr(CO)_4$.

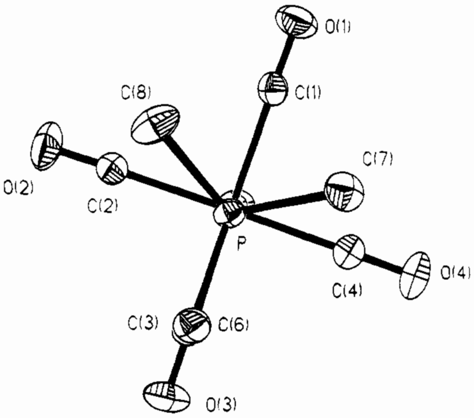

Figure 6. ORTEP picture of $Mo(PMe_3)(CO)_5$ viewed down the P−Mo−CO_{ax} axis showing the eclipsed orientation of PMe_3 with respect to equatorial $Mo(CO)_4$. Hydrogen atoms have been omitted for clarity.

in $M(PCl_3)(CO)_5$. The preference for staggered rather than eclipsed P−Cl (and P−Br) with M−CO may also be largely due to electrostatic repulsions between the electron rich halogen and CO groups. The absence of such strong electrostatic effects in the $M(PMe_3)(CO)_5$ complexes allows the eclipsed form in Figure 6. If the steric bulk of the phosphorus ligand is greater as in the $M(PPh_3)(CO)_5$ complexes, then M−P elongation ensues and staggered configurations with $\omega_1 \sim 45°$ and $\omega_2, \omega_3 \sim \pm 15°$ are found.[35,62−64]

A staggered configuration is also found for complexes with bulky ligands such as $M\{P(CH_2CH_2CN)_3\}(CO)_5$,[62] Cr{P(*o*-tolyl)$_3$}$(CO)_5$[65,66] and $Mo(P_4S_3)(CO)_5$[67] and for the caged phosphite complex $Mo\{P(OCH_2)_3CCH_3\}(CO)_5$[34] which, though the phosphite ligand is sterically undemanding, has negative charge centres on the O atoms bonded to P.[68] These results suggest that both steric and electronic effects determine the preferred ligand orientation in relation to the $M(CO)_4$ moiety.

Recent theoretical and crystallographic studies have proposed that the π-acceptor orbital in M−P π-backbonding is a P−Y σ^* molecular orbital,[9−15,28−30] or this in combination with phosphorus d orbitals.[12] Orpen and his coworkers[9−14] deduced from geometry variations of an extensive range of transition metal complexes with PY_3 ligands that "metal−phosphorus bond lengths increase on oxidising the metal, consistent with the presence of an important element of M−P π-backbonding". They found that reduction of M−P π-bonding in the MPY_3 systems causes a decrease in P−Y bond lengths, in accord with the PY_3 π-acceptor orbital having P−Y σ^* character, as well as a broadening of the Y−P−Y angles.

The $M(PY_3)(CO)_5$ complexes of this study are relatively unaffected by geometric distortions since the PY_3 fragments have low steric bulk. As such they are good models for studying π-behavior in M−PY_3 systems. Problems with disorder and librational motion reported for other PMe_3 complexes in refs 69−72 are not observed.

The average P−Cl and P−Br bond distances in these complexes are 2.027 Å and 2.204 Å, respectively. The analogous bond lengths in the free gas phase PCl_3 and PBr_3 molecules are 2.039−2.043 Å (P−Cl)[73−75] and 2.220 Å (P−Br),[75] *i.e.* the length of the phosphorus−halogen bond may decrease slightly upon complexation to $M(CO)_5$, but in view of the errors in these parameters the trend is of marginal significance. Bridges *et al.*[44] reported P−F bond shortening for coordinated PF_3. In the free PF_3 molecule this distance is 1.569(1) Å and this compares to 1.561(5) Å in $(PF_3)_4Ni$, 1.557(4) Å in $Mo(PF_3)(CO)_5$, and 1.51 ± 0.015 Å in $PF_3B(BF_2)_3$. Comparison of the P−F bond lengths in $PF_3B(BF_2)_3$ and $Mo(PF_3)(CO)_5$ shows a relative bond elongation in the molybdenum complex. This is suggestive of π-acceptance into the P−F σ^* orbitals in $Mo(PF_3)(CO)_5$. A commensurate F−P−F bond angle widening is observed as P−F shortens.[44] Broadening of the X−P−X bond angle is not obvious for PCl_3 and PBr_3 upon coordination to $M(CO)_5$. Such comparisons present a consistent picture but with the reservation that the data for the free and complexed PX_3 species were acquired in different physical states.

More meaningful is the comparison of average P−C bond lengths and average C−P−C bond angles of PMe_3 (1.846 Å, 98.7°),[76] PMe_3BH_3 (1.819 Å, 105.0°)[77] and the range of average values for the $M(PMe_3)(CO)_5$ complexes (1.811−1.85[78] Å, 102.5 - 102.7°). The C−P−C angle in PMe_3 widens by 6.3° following σ-bond formation with BH_3. Coordination with $M(CO)_5$ leads to a lesser widening of 3.8° since in $M(PMe_3)(CO)_5$ the σ-electron displacement away from P is partly offset

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(62) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 578.

(63) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *J. Am. Chem. Soc.* **1969**, *91*, 4326.

(64) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

(65) Howell, J. A. S.; Yates, P. C.; Palin, M. G.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *J. Chem. Soc., Dalton Trans.* **1993**, 2775.

(66) Howell, J. A. S.; Palin, M. G.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *Inorg. Chem.* **1991**, *30*, 4685.

(67) Cordes, A. W.; Joyner, R. D.; Shores, R. D.; Dill, E. D. *Inorg. Chem.* **1974**, *13*, 132.

(68) The cone angle[5] of PPh_3 (145°) is larger than PMe_3 (118°) and it could reasonably be that steric effects dominate in these complexes. The cone angle of $P(OCH_2)_3CCH_3$ is 101°.

(69) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661.

(70) Cloke, F. N. G.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393.

(71) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M. *J. Chem. Soc., Dalton Trans* **1985**, 423.

(72) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

(73) Shell, R.; Steele, D.; Gates, P. N. *J. Chem. Phys.* **1987**, *87*, 2893.

(74) Ruoff, A.; Bürger, H.; Biedermann, S.; Cichon, J. *Spectrochim. Acta* **1972**, *28A*, 953.

(75) Clark, R. J. H.; Rippon, D. M. *J. Mol. Spectrosc.* **1974**, *52*, 58.

(76) Bryan, P. S.; Kuczkowski, R. L. *J. Chem. Phys.* **1971**, *55*, 3049.

(77) Bryan, P. S.; Kuczkowski, R. L. *Inorg. Chem.* **1972**, *11*, 553.

(78) The average P−C bond length of $W(PMe_3)(CO)_5$[46] is longer than in the analogous Cr and Mo complexes for which data were collected at low temperature. Appreciable crystal decay was reported for the $W(PMe_3)(CO)_5$ structure determination which may result in a lowering of the resolution of bond parameters.

by metal to phosphorus π-electron drift. The trend accords with that predicted by Orpen.[9-14] The P−C bond lengths in PMe_3BH_3 and $M(PMe_3)(CO)_5$ have greater s-character than in PMe_3 and are seen to be appreciably shorter. It is observed that the P−C bond in the $M(PMe_3)(CO)_5$ complexes is not elongated relative to that in PMe_3BH_3 as would be expected if metal to phosphorus π-acceptance strongly involved P−C σ^* antibonding orbitals. In this regard, Krueger and coworkers[30] have shown that oxidation of Mo(III) in $Mo(PMe_3)_2CpCl_2$ to Mo(IV) appreciably increases the Mo-P bond lengths but results in very little decrease in the P−CH_3 bond; from this they infer that there is only a small involvement of P−CH_3 σ^* orbitals in the π-back-donation mechanism.

Overall, the relative bond distances M−P and M−C in the $M(PY_3)(CO)_5$ complexes examined in the present work provides evidence consistent with the notion of metal−phosphorus back-π-bonding, but convincing evidence is not found for the involvement of P−X and P-CH_3 σ^* antibonding orbitals in the π-back donation mechanism.

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Supplementary Material Available: For each of the five structures, tables of complete crystal data and structure refinement parameters, positional parameters, interatomic distances and angles, anisotropic thermal parameters, and torsion angles (27 pages). See any current masthead page for ordering information.