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Contribution from the Departments of Chemistry, Southern Methodist University, Dallas, Texas 75275,
and University of Texas at Austin, Austin, Texas 78712

Synthesis, Spectral Properties, and Geometry of a Metallophosphorane

M. LATTMAN,*[1a] S. A. MORSE,[1a] A. H. COWLEY,[1b] J. G. LASCH,[1b] and N. C. NORMAN[1b]

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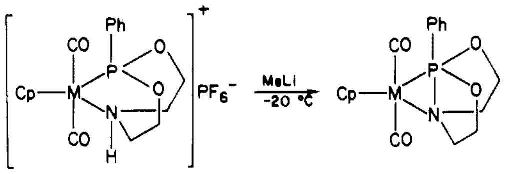
1 has been synthesized according to the following reaction at −78 °C in THF: $(o\text{-}\overline{OC_6H_4O})_2PCl + Na^+Co(CO)_3PPh_3^- \rightarrow (o\text{-}\overline{OC_6H_4O})_2PCo(CO)_3PPh_3$ (**1**) + NaCl. The X-ray crystal structure of **1** has been determined and reveals two trigonal-bipyramidal (TBP) geometries connected at the axial position of the Co and equatorial position of the five-coordinate phosphorus. Due to the instability of the derivative, a structure of low precision was obtained; however, the overall geometry of the molecule is clearly established. The phosphorane P–Co bond is ca. 0.025 Å longer than the phoshine P–Co bond. The geometry about the five-coordinate phosphorus is close to that in TBP. The crystal is monoclinic with a space group $P2_1/n$. The unit cell parameters are a = 10.527 (3) Å, b = 18.824 (4) Å, c = 18.546 (3) Å, β = 105.87 (2)°, and Z = 4. This is the first structural characterization of a monodentate pentacoordinate phosphorus–metal derviative.

Introduction

Metalated derivatives of the pentacoordinate group 15[16] elements are rare. Riess and co-workers[2] have synthesized bidentate, polycyclic systems by proton abstraction from a coordinated nitrogen atom, as illustrated in reaction 1. Malisch and co-workers[3] succeeded in obtaining monodentate arsenic and antimony derivatives according to reaction 2. However, only the antimony compound was stable enough to be isolated and structurally characterized.



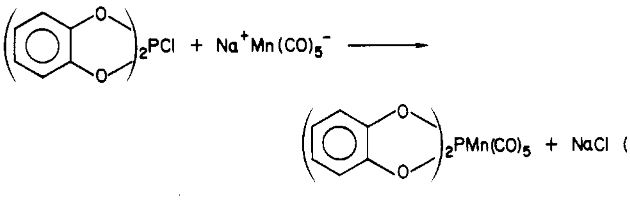
(1)

M=Mo, W; Ph=phenyl; Cp=η^5-C_5H_5

$$Cp(CO)(Me_3P)FeEMe_2 + 2RPhPCl \xrightarrow[-(RPhP)_2]{} Cp(CO)(Me_3P)FeEMe_2Cl_2 \quad (2)$$

R = Ph, Me; E = As, Sb

The first monodentate phosphorus derivative was synthesized by Lattman and co-workers[4] by nucleophilic attack of a transition-metal anion on a pentacoordinate phosphorus (reaction 3).



(3)

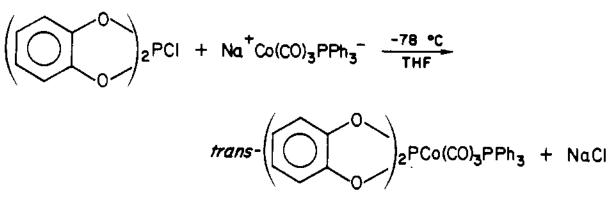
Subsequently, Ebsworth and co-workers[5] reported another monodentate metallophosphorane, obtained by oxidatively adding Cl_2 to a metallosubstituted phosphine (reaction 4).

$$Cl_2(CO)(Et_3P)_2IrPCl_2 + Cl_2 \rightarrow Cl_2(CO)(Et_3P)_2IrPCl_4 \quad (4)$$

The chemistry of pentacoordinate group 15 elements and, in particular, pentacoordinate phosphorus has been an area of extensive investigation.[6] Attachment of a transition metal opens up a new facet to the chemistry of these species, one of the most fundamental of which is structure. The only structurally characterized metallophosphoranes so far have been the bidentate molecules as illustrated in reaction 1. The bridging nature of these species hinders reliable conclusions as to the effect of the metal on the phosphorus structure or even the metal–phosphorus bond itself. This paper describes the synthesis, spectral properties, and structure of a new monodentate metallophosphorane.

Results and Discussion

Tricarbonyl(triphenylphosphine)[spirobi(1,3,2-benzodioxaphosphol-2-yl)]cobalt (**1**) is synthesized according to (5).



(5)

1

1 is a yellow-orange, crystalline compound that decomposes slowly in solution at room temperature. PP coupling is observed in the $^{31}P\{^1H\}$ spectrum (ether solution), which shows an AB pattern with chemical shifts at δ 47 and 56, J_{PCoP} = 258 Hz. Because of the small difference in chemical shifts, a reliable assignment cannot be made. However, with either assignment this does represent an upfield shift for the pentacoordinate phosphorus compared to the related molecule $(C_6H_4O_2)_2PMn(CO)_5$ (reaction 3), with δ 67.[4a] The J_{PMP} (M = transition metal) value is relatively large compared to trans-disubstituted octahedral complexes of the first transition series[7] but is comparable to the isoelectronic and isostructural (considering the metal) *trans*-$LFe(CO)_3L'$ [L = L′ = $P(NMe_2)_3$, $P(OCH_2)_3CEt$; L = $P(NMe_2)_3$, L′ = $P(OCH_2)_3C$-*n*-Pr] species where J_{PFeP} values span the range from ca. 65 to 300 Hz.[7] The $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution) shows the expected[4a] three signals due to the catecholate groups at δ 110.3 (J_{POCC} = 9.1 Hz), 120.8, and 145.3, while the carbonyls appear as a low-intensity, broad peak at δ 194. The observation that J_{POCC} is larger than J_{POC} (the latter of which is too small to be observed in **1**) is consistent with the observed ^{13}C spectrum of $(C_6H_4O_2)_2PMn(CO)_5$ and related copounds.[4a,c] The IR spectrum (ether solution) of **1** shows ν_{CO} bands at 2060 (s), 2003 (vs), and 1992 (vs) cm^{-1}. The splitting of the e band (formal C_3 symmetry about the cobalt) most likely arises from the unsymmetrical nature of the $(C_6H_4O_2)_2P$ group.

The structure of **1** was determined by X-ray diffraction and is illustrated in Figure 1 (along with selected bond distances and angles). The cobalt adopts a trigonal-bipyramidal (TBP) geom-

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(1) (a) Southern Methodist University. (b) University of Texas at Austin.

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(7) See: Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1 and references therein.

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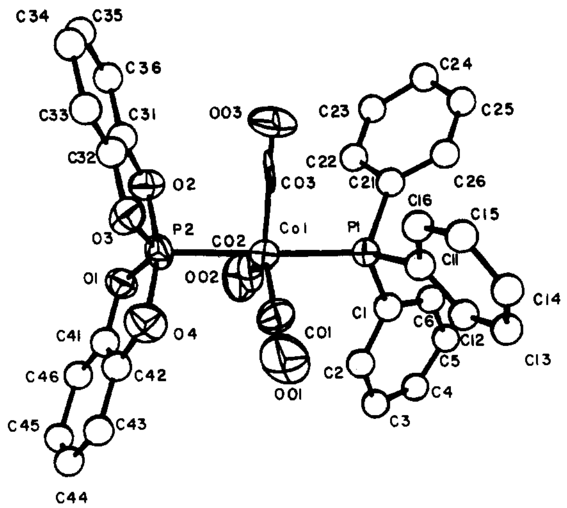

Figure 1. ORTEP drawing of $(C_6H_4O_2)_2PCo(CO)_3PPh_3$ (1). Selected interatomic distances (Å): Co(1)–P(1) = 2.230 (4); Co(1)–P(2) = 2.257 (4); P(2)–O(1) = 1.649 (9); P(2)–O(2) = 1.723 (9); P(2)–O(3) = 1.656 (10); P(2)–O(4) = 1.752 (9); Co(1)–C(01) = 1.77 (2); Co(1)–C(02) = 1.73 (2); Co(1)–C(03) = 1.84 (2). Angles (deg): P(1)–Co(1)–P(2) = 176.8 (2); P(1)–Co(1)–C(01) = 89.9 (5); P(1)–Co(1)–C(02) = 91.1 (5); P(1)–Co(1)–C(03) = 88.8 (4); P(2)–Co(1)–C(01) = 93.2 (5); P(2)–Co(1)–C(02) = 87.0 (5); P(2)–Co(1)–C(03) = 90.0 (4); Co(1)–P(2)–O(1) = 116.4 (4); Co(1)–P(2)–O(2) = 98.0 (3); Co(1)–P(2)–O(3) = 116.8 (4); Co(1)–P(2)–O(4) = 99.9 (4); O(1)–P(2)–O(2) = 84.1 (4); O(1)–P(2)–O(3) = 126.9 (5); O(1)–P(2)–O(4) = 88.1 (5); O(2)–P(2)–O(3) = 88.5 (5); O(2)–P(2)–O(4) = 162.1 (5); O(3)–P(2)–O(4) = 83.2 (5).

etry, with three carbonyls in equatorial positions and one axial site occupied by the PPh_3 ligand. The remaining axial site contains the $(C_6H_4O_2)_2P$ group. The geometry around the five-coordinate phosphorus, P(2), is distorted TBP with the cobalt in an equatorial position. Each of the catecholate ligands spans axial/equatorial positions to complete the pentacoordinate geometry. The remaining phosphorus, P(1), is distorted tetrahedral.

Both P–Co bonds are within the normal range of known P–Co bond lengths. A priori, it is difficult to predict the relative bond lengths of metal–P(V) and metal–P(III) linkages. Previous data[8] on complexes containing phosphonate, $(RO)_2P(O)$–, and phosphite ligands have shown the metal–P(V) bond to be from ca. 0.05 to 0.09 Å longer than the metal–P(III) bond. This difference is expected to decrease if a phosphine is substituted for the phosphite since metal–P bonds in phosphine complexes are usually longer than in phosphite complexes.[9] In the present case, the phosphorane P–Co bond length is ca. 0.025 Å longer than the phosphine P–Co bond.

Turning now to the geometry around P(2), many structures of the type $(C_6H_4O_2)_2PR$ (R = main-group moiety) have been reported,[10] and geometries close to those of pure TBP and pure rectangular pyramidal (RP), as well as in between, have been found. The best method for determining distortions from TBP to RP has been developed by Holmes et al.[6a,11] This method used the dihedral angle differences between the ideal and observed structures to obtain a percent value that indicates how far along the Berry coordinate the geometry lies (with low percentages indicating structures close to TBP and high percentages close to RP). If this method is applied to **1**, a value of 28%, from observed bond distances, is obtained (the percentage rises to 36% if unit bond distances are used).[6a,11] Thus, the observed position of $Co(CO)_3PPh_3$ is expected since large steric bulk, low electronegativity (relative to axial substituents), and π donation favor equatorial substitution in a TBP.[6,12]

Table I. Positional Parameters and Their Estimated Standard Deviations for $[(C_6H_4O_2)_2PCo(CO)_3PPh_3]$ (1)

atom	x	y	z	B,[a] A^2
Co(1)	0.1840 (3)	0.1370 (1)	0.3231 (1)	3.08 (6)
P(1)	0.1131 (5)	0.2487 (3)	0.3225 (3)	3.3 (1)
P(2)	0.2628 (6)	0.0249 (3)	0.3302 (3)	3.5 (1)
O(1)	0.218 (1)	−0.0287 (6)	0.3894 (6)	3.8 (3)
O(01)	−0.011 (2)	0.1133 (9)	0.1797 (8)	8.2 (5)
O(001)	0.509 (2)	0.087 (1)	0.094 (1)	10.1 (6)*
O(02)	0.129 (2)	0.1092 (8)	0.4657 (8)	6.8 (5)
O(2)	0.403 (1)	0.0375 (7)	0.4033 (6)	3.9 (3)
O(03)	−0.557 (1)	0.1917 (9)	0.322 (1)	8.6 (6)
O(3)	0.359 (1)	0.0052 (7)	0.2759 (7)	4.2 (4)
O(4)	0.141 (1)	−0.0147 (8)	0.2578 (7)	5.1 (4)
C(01)	0.066 (2)	0.122 (1)	0.236 (1)	4.7 (6)
C(1)	−0.028 (2)	0.260 (1)	0.359 (1)	3.8 (5)*
C(001)	0.445 (3)	0.143 (2)	0.126 (2)	9.7 (9)*
C(2)	−0.126 (2)	0.207 (1)	0.344 (1)	6.0 (6)*
C(02)	0.145 (2)	0.120 (1)	0.406 (1)	4.5 (6)
C(002)	0.297 (3)	0.121 (2)	0.111 (2)	12 (1)*
C(3)	−0.238 (2)	0.213 (1)	0.370 (1)	6.7 (7)*
C(03)	0.347 (2)	0.1714 (9)	0.322 (1)	4.9 (6)
C(003)	0.643 (3)	0.096 (2)	0.104 (2)	12 (1)*
C(004)	0.693 (3)	0.031 (2)	0.074 (2)	12 (1)*
C(4)	−0.248 (3)	0.271 (1)	0.411 (1)	8.3 (8)*
C(5)	−0.165 (2)	0.327 (1)	0.421 (1)	6.9 (7)*
C(6)	−0.055 (2)	0.318 (1)	0.396 (1)	6.7 (6)*
C(11)	0.068 (2)	0.2896 (9)	0.2294 (9)	2.8 (4)*
C(12)	−0.054 (2)	0.316 (1)	0.198 (1)	4.7 (5)*
C(13)	−0.090 (2)	0.342 (1)	0.124 (1)	4.5 (5)*
C(14)	−0.002 (2)	0.345 (1)	0.086 (1)	5.1 (5)*
C(15)	0.122 (2)	0.320 (1)	0.114 (1)	5.0 (5)*
C(16)	0.155 (2)	0.292 (1)	0.188 (1)	5.1 (5)*
C(21)	0.234 (2)	0.3081 (9)	0.3795 (9)	2.7 (4)*
C(22)	0.307 (2)	0.285 (1)	0.447 (1)	4.2 (5)*
C(23)	0.397 (2)	0.331 (1)	0.493 (1)	6.4 (6)*
C(24)	0.425 (2)	0.398 (1)	0.469 (1)	5.7 (6)*
C(25)	0.350 (2)	0.420 (1)	0.402 (1)	5.4 (6)*
C(26)	0.257 (2)	0.375 (1)	0.357 (1)	4.4 (5)*
C(31)	0.514 (2)	0.029 (1)	0.382 (1)	3.5 (4)*
C(32)	0.490 (2)	0.013 (1)	0.310 (1)	3.6 (5)*
C(33)	0.587 (2)	0.003 (1)	0.276 (1)	5.4 (6)*
C(34)	0.717 (2)	0.011 (1)	0.321 (1)	5.8 (6)*
C(35)	0.743 (2)	0.024 (1)	0.395 (1)	6.6 (6)*
C(36)	0.645 (2)	0.037 (1)	0.430 (1)	5.1 (5)*
C(41)	0.113 (2)	−0.069 (1)	0.356 (1)	4.1 (5)*
C(42)	0.068 (2)	−0.063 (1)	0.285 (1)	4.2 (5)*
C(43)	−0.036 (2)	−0.104 (1)	0.238 (1)	5.5 (6)*
C(44)	−0.091 (2)	−0.150 (1)	0.280 (1)	7.2 (7)*
C(45)	−0.055 (2)	−0.158 (1)	0.350 (1)	7.0 (7)*
C(46)	0.054 (2)	−0.115 (1)	0.399 (1)	6.1 (6)*

[a] Starred values indicate atoms refined isotropically.

Experimental Section

Synthesis. All procedure were carried out in an inert atmosphere. Solvents were rigorously dried over an appropriate drying agent and distilled and degassed prior to use. In a typical preparation, 3.84 g (4.74 mmol) of $[Co(CO)_3PPh_3]_2$ was reduced by the Na/Hg method.[13] After the excess amalgam was removed, the resulting mixture was added dropwise to a stirred solution of 2.63 g (9.29 mmol) of $(C_6H_4O_2)_2PCl$[14]

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Table II. Pertinent Crystallographic and Intensity Data Collection Parameters for $[(C_6H_4O_2)_2PCo(CO)_3PPh_3]$ (1)

formula	$CoC_{33}H_{23}O_7P_2\cdot OC_4H_{10}$
fw	726.45
cryst syst	monoclinic
space gp	$P2_1/n$
a/Å	10.527 (3)
b/Å	18.824 (4)
c/Å	18.546 (3)
β/deg	105.87 (2)
V/Å^3	3534.9 (2.1)
Z	4
ρ(calcd)/g cm^{-3}	1.226
μ(Mo Kα)/cm^{-1}	6.1
λ(Mo Kα)/Å	0.710 69
cryst size/mm	0.5 × 0.4 × 0.3
ω scan angle/deg	$0.8 + 0.35 \tan\theta$
2θ limits/deg	$2.0 \leq 2\theta \leq 40.0$
total no. of unique measd data	3185
no. of obsd data	1734
data omission factor	$I > 1.5\sigma(I)$
no. of variables	258
R	0.0864
R_w	0.1326

in 50 mL of THF held at −78 °C. After the addition was complete, the mixture was warmed slowly to 0 °C and the THF removed in vacuo. The resulting solid was washed repeatedly with cyclohexane until the washings were almost colorless. Subsequently, the solid was washed repeatedly with diethyl ether until the washings were almost colorless. The ether solution was quickly concentrated to yield crystals of **1** (3.26 g (48%)).

Spectral Measurements. NMR spectra were recorded on an IBM WP200SY multinuclear NMR spectrometer resonating at frequencies of 50.327 (^{13}C) and 81.026 (^{31}P) MHz. ^{13}C spectra were calibrated relative to solvent peaks referenced to external Me_4Si. ^{31}P spectra were run with an 8-mm NMR tube (containing the sample) inserted into a 10-mm NMR tube containing D_2O as a lock solvent. Peaks were referenced to external H_3PO_4. IR spectra were recorded on a Perkin-Elmer Model 283 spectrometer.

X-ray Structure Determination. A suitable single crystal of **1** was sealed under nitrogen in a Lindemann capillary prior to mounting on an Enraf-Nonius CAD-4F diffractometer. Unit cell parameters were deduced from a least-squares fit to 25, accurately centered, reflections and subsequently refined with higher angle data. These indicated a monoclinic lattice. Intensity data were collected at room temperature for one independent quadrant, $+h,+k,\pm l$ with ω–2θ scans. The final scan time for each reflection was deduced from an initial prescan, 10° min^{-1} and varied from 2–10° min^{-1}, depending on the net intensity gathered. Two check reflections were monitored every 30 min throughout data collection and showed an approximate 40% decrease in intensity over the 30-h data collection time.

Data were corrected for Lorentz, polarization, and decay effects but not for absorption. The position of the cobalt atom was deduced from a Patterson map. Successive difference Fourier maps and full-matrix least-squares refinement allowed location of all non-hydrogen atoms. Due to inferior crystal quality and the effects of crystal decay, only a relatively small number of reflections, 1734$I > 1.5\sigma(I)$, were considered observed. As a consequence, the carbon atoms in the aryl rings, C(1)–C(6), C(11)–C(16), C(21)–C(26), C(31)–C(36), and C(41)–C(46), were refined with isotropic thermal parameters. All other atoms were refined anisotropically. Hydrogen atoms were neither located nor refined but were placed in calculated positions 0.95 Å from their resepective carbon atom and included in the structure factor calculation. One molecule of diethyl ether was observed per asymmetric unit. This was ordered and refined successfully with isotropic thermal parameters. Final refinement converged smoothly, with no chemically significant peaks present in the final difference Fourier map. Certain aspects of refinement leave much to be desired as a result of poor crystal quality[15] and insufficient data. Nevertheless, we feel the structure of **1** is adequately determined in this experiment.

Atomic positional parameters are listed in Table I, and pertinent crystallographic data are summarized in Table II.

Acknowledgment. The generous financial support of the Robert A. Welch Foundation (M.L. and A.H.C.), the Research Corp. (M.L.), and SMU (Seed Grant, M.L.) is gratefully acknowledged. The authors thank Professor R. R. Holmes and Dr. R. O. Day for determining the percent distortion values.

Registry No. **1**, 95420-10-3; $[Co(CO)_3PPh_3]_2$, 24212-54-2; $(C_6H_4O_2)_2PCl$, 6857-81-4.

Supplementary Material Available: Listings of bond distances, bond angles, calculated hydrogen positions, thermal parameters, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(15) Because the crystals had to be grown quickly due to the sensitivity of **1** in solution, crystals were of generally poor quality. Five crystals were mounted before one suitable for data collection was obtained.

(16) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.