distances in selected acetato-bridged dimolybdenum compounds. From the table it is clear that a typical Mo–O distance is 2.10–2.11 Å. In **1**, however, the Mo–O distance is 2.155 Å (average). Although, it is impossible to generalize from only one structure, it appears possible that this increase in the Mo–O bond distance is a result of a trans labilization of the acetate ligand by the ambt ligand. Since this is the first trisubstituted mixed-ligand complex of the quadruply bonded system, there is no precedent for an observed trans effect in these bimetallic complexes. Attempts are now being made to prepare further mixed-ligand complexes.

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Registry No. **1**, 75534-39-3; **2**, 75534-41-7; **3**, 75534-43-9; dimolybdenum tetraacetate, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors for the three structures (25 pages). Ordering information is given on any current masthead page.

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π Acidity of Tris(2-cyanoethyl)phosphine. X-ray Structural Studies of $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo) and $Mo(CO)_5P(C_6H_5)_3$

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The X-ray crystal structures and IR spectra of the compounds $M(CO)_5P(CH_2CH_2CN)_3$, M = Cr (**1**) and Mo (**2**), and $Mo(CO)_5P(C_6H_5)_3$ (**3**) are reported. Compounds **1** and **2** are isomorphous and crystallize in the monoclinic space group $P2_1/n$ with unit cell parameters a = 16.913 (5) Å, 17.140 (2) Å, b = 6.538 (3) Å, 6.639 (1) Å, c = 17.402 (4) Å, 17.574 (2) Å, β = 117.91 (2)°, 118.09 (1)°, v = 1700 (2) Å^3, 1764.3 (9) Å^3, and Z = 4, 4, where the two figures for each parameter refer to the Cr and Mo compounds, respectively. Each molecule occupies a general position within the unit cell. The M–P distances are 2.364 (1) and 2.506 (1) Å for the Cr and Mo compounds, and the average M–CO$_{ax}$ and M–CO$_{eq}$ distances are 1.876 (4) and 1.891 (4) Å and 2.008 (4) and 2.044 (5) Å, respectively. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 9.653 (5) Å, b = 12.301 (5) Å, c = 9.503 (8) Å, α = 90.88 (5)°, β = 95.73 (5)°, γ = 74.89 (4)°, V = 1084 (2) Å^3, and Z = 2. Again, each molecule occupies a general position within the cell. The Mo–P distance is 2.560 (1) Å and the average Mo–CO$_{ax}$ and Mo–CO$_{eq}$ distances are 1.995 (3) and 2.046 (4) Å, respectively. On the basis of these structural data as well as ν(CO) infrared data, tris(2-cyanoethyl)phosphine can be described as a good π-acceptor ligand.

Introduction

Spectroscopic data (ν(CO) and ^{13}C NMR)[1,2] for low-valent metal carbonyl complexes containing trivalent phosphorus ligands strongly imply that the 2-cyanoethyl substituent on phosphorus is very electron withdrawing relative to the ethyl group. This is a somewhat surprising result since the CN substituent is separated from the phosphorus atom by two saturated carbon atoms. Concomitantly, the tris(2-cyanoethyl)phosphine is a much poorer base than is triethylphosphine, having a ΔHNP value of 679 relative to 111 for the latter phosphine.[3]

In general trivalent phosphorus ligands bearing good electron-withdrawing groups exhibit strong metal–phosphorus binding in low-valent organo–transition-metal derivatives.[4] In order to examine the bonding properties of this rather unique ligand, we have carried out X-ray structural investigations of the $M(CO)_5P(CH_2CH_2CN)_3$ species, where M = Cr and Mo. In addition the X-ray structure of $Mo(CO)_5P(C_6H_5)_3$ was determined for comparative purposes.

Experimental Section

Preparations. A procedure similar to that described by Connor et al.[5] was employed in the synthesis of the $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo) complexes. A methylene chloride solution of 0.54 g (1.2 mmol) of $[(C_2H_5)_4N][Mo(CO)_5Br]$, 0.25 g (1.3 mmol) of P-

Table I. Crystallographic Parameters

parameter	compd 1	 2	 3
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	16.913 (5)	17.140 (2)	9.653 (5)
b, Å	6.538 (3)	6.639 (1)	12.301 (5)
c, Å	17.402 (4)	17.574 (2)	9.503 (8)
α, deg	90.0	90.0	90.88 (5)
β, deg	117.91 (2)	118.09 (1)	95.73 (5)
γ, deg	90.0	90.0	74.89 (4)
V, Å^3	1700 (2)	1764.3 (9)	1084 (2)
Z	4	4	2
d_X, g/cm^3 (calcd)	1.505	1.616	1.527
fw	385.24	429.18	498.29
cryst size, mm	0.20 × 0.30 × 0.30	0.20 × 0.25 × 0.30	0.20 × 0.30 × 0.30
μ, cm^{-1}	8.250	8.518	7.027
2θ range, deg	0–45	0–45	0–50
no. of data	1532	2617	3199
$F_o^2 > 3\sigma(F_o^2)$	1433	1793	3081
no. of variables	269	269	331
R_1	0.027	0.026	0.024
R_2	0.038	0.034	0.035
esd	0.974	1.052	0.808
diffractometer	Syntex $P\bar{1}$	CAD-4F	Syntex $P\bar{1}$

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Table II. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for $Cr(CO)_5P(CH_2CH_2CN)_3$ (1)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.05751 (3)	0.21822 (8)	0.17098 (3)	2.78 (1)	2.47 (2)	2.83 (1)	0.04 (2)	1.57 (1)	0.12 (2)
P(1)	−0.02104 (4)	0.3152 (1)	0.24737 (4)	2.38 (2)	2.19 (3)	2.59 (2)	0.24 (2)	1.24 (2)	0.27 (2)
O(1)	−0.0438 (2)	−0.1817 (4)	0.1233 (2)	5.9 (1)	3.3 (1)	5.6 (1)	−1.0 (1)	2.06 (8)	−0.4 (1)
O(2)	0.2010 (2)	0.0309 (5)	0.3373 (1)	4.38 (9)	7.9 (2)	5.1 (1)	2.0 (1)	2.09 (7)	2.4 (1)
O(3)	0.1553 (1)	0.6240 (4)	0.2142 (2)	4.62 (9)	3.7 (1)	7.2 (1)	−1.23 (9)	3.03 (7)	−0.9 (1)
O(4)	−0.0843 (2)	0.4007 (4)	0.0024 (1)	4.7 (1)	6.4 (1)	3.90 (9)	−0.3 (1)	1.26 (7)	1.6 (1)
O(5)	0.1634 (2)	0.0744 (2)	0.0822 (1)	6.27 (9)	7.3 (2)	6.18 (9)	0.9 (1)	4.58 (6)	−0.7 (1)
N(1)	0.1725 (2)	0.8287 (6)	0.4911 (2)	7.4 (2)	6.5 (2)	5.4 (1)	−2.4 (2)	2.8 (1)	−2.5 (1)
N(2)	−0.0827 (2)	−0.2152 (7)	0.4378 (2)	5.9 (1)	6.6 (2)	6.4 (2)	−1.4 (2)	3.7 (1)	0.9 (2)
N(3)	−0.2378 (2)	−0.0598 (6)	0.1887 (2)	5.9 (1)	6.8 (2)	7.7 (2)	−2.8 (1)	2.7 (1)	−0.0 (2)
C(1)	−0.0060 (2)	−0.0307 (5)	0.1416 (2)	3.7 (1)	3.0 (1)	3.4 (1)	0.0 (1)	1.82 (8)	0.1 (1)
C(2)	0.1471 (2)	0.1024 (6)	0.2752 (2)	2.9 (1)	3.9 (2)	4.1 (1)	0.5 (1)	1.98 (8)	0.6 (1)
C(3)	0.1187 (2)	0.4713 (5)	0.1976 (2)	3.1 (1)	3.7 (2)	3.8 (1)	−0.1 (1)	2.12 (7)	−0.2 (1)
C(4)	−0.0314 (2)	0.3331 (5)	0.0660 (2)	3.7 (1)	3.7 (2)	3.6 (1)	−0.7 (1)	1.96 (8)	0.3 (1)
C(5)	0.1232 (2)	0.1311 (6)	0.1150 (2)	4.2 (1)	3.7 (2)	3.8 (1)	0.1 (1)	2.21 (9)	−0.1 (1)
C(6)	0.0220 (2)	0.5341 (5)	0.3218 (2)	3.9 (1)	2.8 (1)	3.1 (1)	0.3 (1)	1.63 (8)	−0.1 (1)
C(7)	0.1162 (2)	0.5024 (6)	0.3972 (2)	4.7 (2)	4.4 (2)	3.4 (1)	−0.3 (1)	1.2 (1)	−0.3 (1)
C(8)	0.1483 (2)	0.6853 (6)	0.4509 (2)	4.5 (1)	5.3 (2)	3.0 (1)	−1.0 (1)	1.33 (9)	−0.6 (1)
C(9)	−0.0259 (2)	0.1094 (5)	0.3169 (2)	3.0 (1)	2.7 (1)	3.2 (1)	0.3 (1)	1.62 (7)	0.6 (1)
C(10)	−0.0756 (2)	0.1471 (6)	0.3700 (2)	4.0 (1)	4.4 (2)	4.1 (1)	1.6 (1)	2.74 (8)	1.9 (1)
C(11)	−0.0839 (2)	−0.0536 (8)	0.4059 (2)	3.3 (1)	7.1 (3)	3.8 (1)	−0.3 (2)	2.0 (1)	−0.1 (2)
C(12)	−0.1380 (2)	0.3976 (5)	0.1824 (2)	2.7 (1)	3.5 (2)	3.5 (1)	0.6 (1)	1.33 (8)	0.7 (1)
C(13)	−0.2006 (2)	0.2421 (6)	0.1161 (2)	2.6 (1)	5.2 (2)	4.8 (1)	0.2 (1)	1.32 (9)	1.2 (1)
C(14)	−0.2226 (2)	0.0710 (6)	0.1556 (2)	3.0 (1)	5.4 (2)	5.4 (2)	−1.3 (1)	1.3 (1)	−0.0 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(2)′	0.0454 (9)	0.343 (2)	0.5218 (8)	1.9 (3)	H(6)	−0.050 (2)	−0.009 (5)	0.280 (2)	3.5 (7)
C(11)′	−0.0061 (7)	0.258 (2)	0.4594 (7)	4.5 (3)	H(7)	−0.127 (2)	0.196 (5)	0.339 (2)	4.2 (8)
H(1)	0.020 (2)	0.650 (5)	0.283 (2)	3.9 (7)	H(8)	−0.136 (2)	0.520 (4)	0.148 (2)	3.0 (6)
H(2)	−0.021 (2)	0.561 (5)	0.343 (2)	3.8 (7)	H(9)	−0.158 (2)	0.435 (5)	0.218 (2)	4.8 (8)
H(3)	0.114 (2)	0.391 (6)	0.430 (2)	6.4 (9)	H(10)	−0.244 (2)	0.311 (5)	0.090 (2)	4.6 (8)
H(4)	0.154 (2)	0.487 (5)	0.375 (2)	4.3 (8)	H(11)	−0.172 (2)	0.193 (6)	0.079 (2)	6.8 (10)
H(5)	0.035 (2)	0.079 (4)	0.357 (1)	2.5 (6)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for $Mo(CO)_5P(CH_2CH_2CN)_3$ (2)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.05846 (2)	0.20884 (5)	0.17123 (2)	2.897 (9)	2.89 (1)	2.672 (9)	0.06 (1)	1.608 (7)	0.12 (1)
P(1)	−0.02574 (5)	0.3093 (1)	0.24942 (5)	2.80 (3)	2.84 (4)	2.68 (3)	0.22 (3)	1.49 (2)	0.26 (3)
O(1)	−0.0464 (2)	−0.2043 (5)	0.1205 (2)	6.6 (1)	3.7 (1)	6.4 (1)	−1.5 (1)	2.7 (1)	−0.4 (1)
O(2)	0.2073 (2)	0.0200 (6)	0.3455 (2)	4.7 (1)	9.2 (2)	5.1 (1)	2.1 (1)	2.01 (8)	2.8 (1)
O(3)	0.1590 (2)	0.6298 (5)	0.2177 (2)	4.8 (1)	4.1 (1)	7.3 (1)	−1.2 (1)	2.81 (8)	−1.2 (1)
O(4)	−0.0880 (2)	0.3948 (5)	−0.0052 (2)	5.1 (1)	7.3 (2)	4.0 (1)	−0.3 (1)	0.97 (9)	2.0 (1)
O(5)	0.1701 (2)	0.0633 (6)	0.0813 (2)	6.4 (1)	8.4 (2)	6.2 (1)	0.2 (1)	4.65 (6)	−1.2 (1)
N(1)	0.1651 (3)	0.8223 (7)	0.4875 (2)	8.0 (2)	6.9 (2)	5.4 (1)	−2.5 (2)	3.4 (1)	−2.3 (2)
N(2)	−0.0836 (2)	−0.2130 (7)	0.4384 (2)	5.4 (1)	6.0 (2)	5.5 (1)	−0.6 (2)	3.1 (1)	1.3 (2)
N(3)	−0.2378 (3)	−0.0689 (7)	0.1850 (3)	7.5 (2)	7.9 (3)	8.1 (2)	−3.6 (2)	3.1 (1)	−0.3 (2)
C(1)	−0.0085 (2)	−0.0568 (6)	0.1386 (2)	3.9 (1)	4.1 (2)	3.3 (1)	0.1 (1)	1.89 (9)	0.1 (1)
C(2)	0.1536 (2)	0.0870 (6)	0.2836 (2)	3.6 (1)	4.1 (2)	4.4 (1)	0.4 (1)	2.64 (8)	0.7 (1)
C(3)	0.1235 (2)	0.4793 (6)	0.2011 (2)	3.3 (1)	3.8 (2)	3.7 (1)	0.2 (1)	2.00 (9)	−0.3 (1)
C(4)	−0.0356 (2)	0.3309 (6)	0.0581 (2)	3.9 (1)	3.7 (2)	3.5 (1)	−0.9 (1)	1.95 (9)	0.3 (1)
C(5)	0.1294 (2)	0.1201 (7)	0.1132 (2)	3.7 (1)	4.6 (2)	3.8 (1)	−0.4 (2)	2.12 (9)	−0.6 (1)
C(6)	0.0156 (2)	0.5248 (6)	0.3239 (2)	4.6 (1)	3.0 (2)	3.3 (1)	0.2 (1)	1.97 (9)	0.3 (1)
C(7)	0.1091 (3)	0.4968 (7)	0.3977 (2)	4.9 (2)	4.5 (2)	3.3 (1)	−0.2 (2)	1.5 (1)	−0.3 (2)
C(8)	0.1413 (2)	0.6795 (7)	0.4488 (2)	5.2 (2)	5.6 (2)	3.0 (1)	−0.9 (2)	2.0 (1)	−0.6 (1)
C(9)	−0.0294 (2)	0.1046 (6)	0.3179 (2)	3.1 (1)	3.4 (2)	3.6 (1)	0.7 (1)	1.96 (8)	0.9 (1)
C(10)	−0.0800 (2)	0.1391 (7)	0.3694 (2)	3.8 (1)	5.0 (2)	4.1 (1)	1.6 (1)	2.65 (9)	2.1 (1)
C(11)	−0.0850 (2)	−0.0573 (8)	0.4078 (2)	3.3 (1)	5.8 (3)	3.7 (1)	−0.0 (2)	2.0 (1)	0.1 (2)
C(12)	−0.1415 (2)	0.3866 (6)	0.1832 (2)	3.6 (1)	4.3 (2)	3.8 (1)	0.9 (1)	2.20 (9)	0.9 (1)
C(13)	−0.2015 (2)	0.2373 (7)	0.1161 (2)	2.7 (1)	6.8 (3)	4.0 (1)	−0.1 (2)	1.3 (1)	0.5 (2)
C(14)	−0.2231 (3)	0.0652 (8)	0.1538 (3)	3.8 (2)	6.9 (3)	5.5 (2)	−1.7 (2)	1.9 (1)	−0.4 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(2)′	0.044 (2)	0.330 (4)	0.523 (2)	3.2 (6)	H(6)	−0.053 (2)	−0.012 (5)	0.281 (2)	4.1 (8)
C(11)′	−0.013 (1)	0.253 (4)	0.454 (1)	5.9 (6)	H(7)	−0.124 (2)	0.180 (5)	0.341 (2)	4.1 (9)
H(1)	0.011 (2)	0.626 (5)	0.292 (2)	3.6 (8)	H(8)	−0.139 (2)	0.501 (5)	0.157 (2)	3.2 (7)
H(2)	−0.033 (2)	0.546 (6)	0.343 (2)	5.4 (10)	H(9)	−0.164 (2)	0.419 (4)	0.216 (2)	1.9 (6)
H(3)	0.106 (2)	0.388 (7)	0.430 (2)	6.0 (10)	H(10)	−0.252 (2)	0.286 (6)	0.083 (2)	4.8 (9)
H(4)	0.149 (2)	0.459 (6)	0.375 (2)	4.5 (9)	H(11)	−0.176 (2)	0.191 (5)	0.082 (2)	4.3 (9)
H(5)	0.028 (2)	0.074 (5)	0.354 (2)	3.4 (8)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for $Mo(CO)_5P(C_6H_5)_3$ (3)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.27897 (2)	0.44813 (2)	0.26963 (2)	3.608 (7)	2.989 (7)	3.733 (8)	−1.233 (6)	0.660 (7)	−0.554 (7)
P(1)	0.35911 (6)	0.25613 (5)	0.15244 (6)	3.20 (2)	3.01 (2)	3.44 (2)	−1.06 (2)	0.56 (2)	−0.44 (2)
O(1)	0.0952 (3)	0.5846 (2)	−0.0012 (3)	7.3 (1)	5.8 (1)	6.1 (1)	−1.52 (9)	−0.7 (1)	1.59 (9)
O(2)	−0.0110 (2)	0.4107 (2)	0.3637 (3)	5.24 (8)	6.1 (1)	8.4 (1)	−2.18 (7)	2.72 (8)	−0.78 (9)
O(3)	0.4464 (3)	0.3345 (2)	0.5563 (2)	6.4 (1)	7.3 (1)	5.1 (1)	−1.44 (9)	−0.43 (9)	0.28 (9)
O(4)	0.5574 (2)	0.5060 (2)	0.1725 (3)	7.52 (9)	7.8 (1)	10.7 (1)	−4.75 (7)	4.01 (9)	−1.5 (1)
O(5)	0.2145 (2)	0.6774 (2)	0.4310 (3)	6.7 (1)	4.43 (8)	8.2 (1)	−1.82 (7)	1.2 (1)	−2.62 (8)
C(1)	0.1619 (3)	0.5330 (2)	0.0921 (3)	4.9 (1)	3.8 (1)	5.1 (1)	−1.59 (8)	0.8 (1)	−0.2 (1)
C(2)	0.0936 (3)	0.4207 (2)	0.3286 (3)	4.4 (1)	3.7 (1)	4.8 (1)	−1.27 (8)	1.04 (9)	−0.55 (9)
C(3)	0.3879 (3)	0.3740 (2)	0.4519 (3)	4.3 (1)	4.4 (1)	4.2 (1)	−1.12 (9)	0.47 (9)	−0.65 (9)
C(4)	0.4604 (3)	0.4835 (2)	0.2080 (2)	5.5 (1)	4.4 (1)	5.7 (1)	−2.42 (8)	1.5 (1)	−0.9 (1)
C(5)	0.2357 (3)	0.5944 (2)	0.3714 (3)	4.4 (1)	3.9 (1)	5.4 (1)	−1.58 (8)	0.8 (1)	−0.8 (1)
C(6)	0.2685 (2)	0.2334 (2)	−0.0204 (3)	3.15 (8)	3.50 (9)	3.5 (1)	−0.72 (7)	0.62 (8)	−0.45 (8)
C(7)	0.2246 (3)	0.1362 (2)	−0.0518 (3)	4.5 (1)	4.0 (1)	4.3 (1)	−1.23 (9)	0.0 (1)	−0.56 (9)
C(8)	0.1546 (3)	0.1244 (3)	−0.1828 (3)	5.7 (1)	5.5 (1)	5.8 (1)	−1.7 (1)	−0.5 (1)	−2.0 (1)
C(9)	0.1289 (4)	0.2071 (3)	−0.2835 (3)	5.8 (2)	6.9 (2)	4.3 (1)	0.2 (1)	−0.5 (1)	−1.4 (1)
C(10)	0.1729 (4)	0.3028 (3)	−0.2552 (3)	6.4 (2)	5.8 (2)	3.7 (1)	0.5 (1)	0.6 (1)	0.1 (1)
C(11)	0.2412 (3)	0.3164 (2)	−0.1243 (3)	5.3 (1)	4.2 (1)	4.1 (1)	−1.0 (1)	0.8 (1)	−0.0 (1)
C(12)	0.5504 (2)	0.2222 (2)	0.1208 (3)	3.29 (8)	3.11 (8)	4.5 (1)	−1.17 (7)	0.75 (8)	−0.52 (8)
C(13)	0.5989 (3)	0.1962 (3)	−0.0108 (3)	4.3 (1)	5.4 (1)	4.7 (1)	−1.38 (9)	1.25 (9)	−1.1 (1)
C(14)	0.7439 (3)	0.1757 (3)	−0.0276 (3)	5.0 (1)	7.1 (2)	6.1 (1)	−1.9 (1)	2.5 (1)	−1.6 (1)
C(15)	0.8417 (3)	0.1809 (3)	0.0841 (4)	3.6 (1)	5.8 (1)	8.0 (2)	−1.65 (9)	1.7 (1)	−0.9 (1)
C(16)	0.7959 (3)	0.2056 (3)	0.2155 (4)	3.5 (1)	5.9 (1)	6.7 (2)	−1.49 (9)	0.1 (1)	−1.0 (1)
C(17)	0.6514 (3)	0.2271 (2)	0.2341 (3)	3.8 (1)	5.0 (1)	4.5 (1)	−1.19 (9)	0.68 (9)	−0.5 (1)
C(18)	0.3491 (3)	0.1336 (2)	0.2538 (2)	4.2 (1)	3.06 (8)	3.12 (9)	−1.12 (7)	0.31 (8)	−0.12 (8)
C(19)	0.2218 (3)	0.1353 (2)	0.3103 (3)	5.4 (1)	3.7 (1)	6.0 (1)	−1.32 (9)	2.0 (1)	−0.3 (1)
C(20)	0.2055 (3)	0.0416 (3)	0.3779 (3)	7.7 (1)	5.2 (1)	6.4 (1)	−3.0 (1)	3.2 (1)	−0.6 (1)
C(21)	0.3182 (4)	−0.0540 (2)	0.3936 (3)	9.5 (2)	4.1 (1)	4.3 (1)	−3.0 (1)	−0.1 (1)	0.8 (1)
C(22)	0.4460 (4)	−0.0566 (2)	0.3408 (3)	6.7 (1)	3.8 (1)	5.1 (1)	−1.2 (1)	−0.8 (1)	0.5 (1)
C(23)	0.4596 (3)	0.0362 (2)	0.2709 (3)	4.6 (1)	4.2 (1)	4.5 (1)	−1.22 (9)	0.0 (1)	0.3 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)	0.244 (3)	0.079 (2)	0.014 (3)	3.8 (5)	H(9)	0.858 (3)	0.211 (3)	0.284 (3)	6.3 (8)
H(2)	0.131 (3)	0.060 (3)	−0.199 (3)	7.0 (8)	H(10)	0.618 (3)	0.246 (2)	0.327 (3)	5.0 (7)
H(3)	0.084 (4)	0.203 (3)	−0.375 (4)	7.8 (9)	H(11)	0.144 (3)	0.198 (2)	0.295 (3)	5.2 (7)
H(4)	0.161 (3)	0.358 (3)	−0.314 (3)	6.8 (8)	H(12)	0.126 (3)	0.047 (3)	0.412 (3)	6.6 (8)
H(5)	0.270 (3)	0.382 (2)	−0.107 (3)	4.6 (6)	H(13)	0.319 (3)	−0.113 (2)	0.438 (3)	5.5 (7)
H(6)	0.540 (2)	0.191 (2)	−0.089 (3)	3.7 (5)	H(14)	0.525 (3)	−0.117 (3)	0.346 (3)	6.6 (8)
H(7)	0.777 (3)	0.162 (3)	−0.112 (3)	6.2 (7)	H(15)	0.537 (2)	0.035 (2)	0.243 (2)	3.3 (5)
H(8)	0.940 (3)	0.170 (3)	0.065 (3)	5.9 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

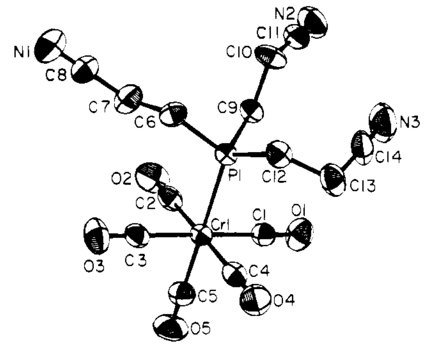

Figure 1. ORTEP view of the molecule of $Cr(CO)_5[P(CH_2CH_2CN)_3]$ (**1**). The atom numbering scheme applies also to the molybdenum analogue, **2**. Atoms are represented by thermal ellipsoids scaled to enclose 30% of the electron density.

$(CH_2CH_2CN)_3$, and 0.21 g (1.2 mmol) of $AgNO_3$ was stirred under nitrogen at ambient temperature for 2 h. The solvent was removed under reduced pressure and the product extracted into hot methanol, filtered through Celite, and stored at −10 °C to afford off-white crystals. Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution. The chromium derivative was prepared in a completely analogous manner.

$Mo(CO)_5P(C_6H_5)_3$ was synthesized as previously described.[6]

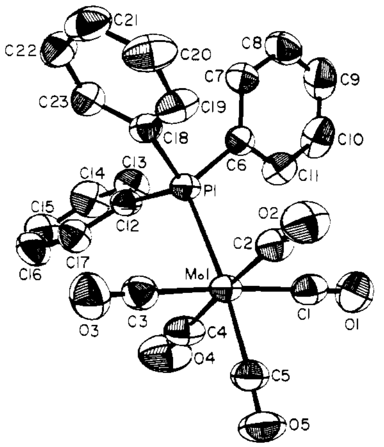

Figure 2. ORTEP view of the molecule of $Mo(CO)_5(PPh_3)$, showing the atom numbering scheme.

Crystals were obtained from a $CHCl_3/CH_3OH$ solution at −10 °C.

Infrared Spectra. The infrared spectra were recorded in matched 1.0-mm NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

X-ray Crystallography. Crystals suitable for X-ray analysis were attached to the end of a thin glass fiber with epoxy cement and mounted on either a Syntex P$\bar{1}$ or Enraf-Nonius CAD-4F automatic diffractometer. The procedures used for data collection as well as methods used in the solution and refinement of the structure were

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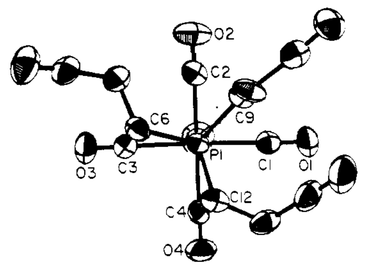

Figure 3. View of **1** and **2** looking down the P-M-CO_{ax} axis.

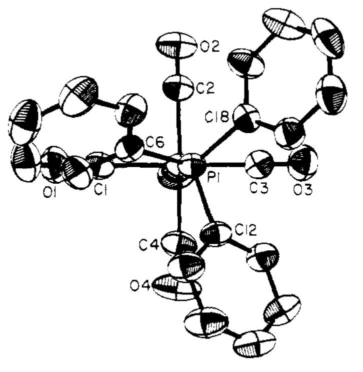

Figure 4. View of **3** looking almost directly down the P-Mo-CO_{ax} axis.

Table V. Bond Distances for the Compounds $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo)

atoms	dist, Å M = Cr	 M = Mo
M-P(1)	2.364 (1)	2.506 (1)
M-C(1)	1.884 (4)	2.034 (5)
M-C(2)	1.893 (4)	2.044 (5)
M-C(3)	1.891 (4)	2.048 (5)
M-C(4)	1.896 (4)	2.048 (5)
M-C(5)	1.876 (4)	2.008 (4)
P(1)-C(6)	1.837 (4)	1.841 (4)
P(1)-C(9)	1.837 (4)	1.836 (4)
P(1)-C(12)	1.840 (4)	1.839 (4)
O(1)-C(1)	1.138 (4)	1.135 (5)
O(2)-C(2)	1.139 (4)	1.134 (5)
O(3)-C(3)	1.138 (4)	1.134 (5)
O(4)-C(4)	1.137 (4)	1.133 (5)
O(5)-C(5)	1.136 (4)	1.145 (5)
N(1)-C(8)	1.125 (5)	1.126 (6)
N(2)-C(11)	1.189 (7)	1.161 (6)
N(2)'-C(11)'	1.17 (2)	1.25 (4)
N(3)-C(14)	1.126 (5)	1.135 (6)
C(6)-C(7)	1.531 (6)	1.525 (6)
C(7)-C(8)	1.457 (6)	1.454 (7)
C(9)-C(10)	1.533 (5)	1.535 (6)
C(10)-C(11)	1.488 (7)	1.489 (7)
C(10)-C(11)'	1.62 (2)	1.58 (3)
C(12)-C(13)	1.530 (6)	1.513 (7)
C(13)-C(14)	1.450 (7)	1.453 (8)
C(6)-H(1)	1.01 (4)	0.85 (4)
C(6)-H(2)	0.97 (4)	1.05 (5)
C(7)-H(3)	0.93 (5)	0.93 (5)
C(7)-H(4)	0.90 (4)	0.97 (4)
C(9)-H(5)	0.95 (3)	0.91 (4)
C(9)-H(6)	0.97 (4)	0.97 (4)
C(10)-H(7)	0.85 (4)	0.74 (4)
C(12)-H(9)	1.01 (4)	0.90 (4)
C(12)-H(10)	0.87 (4)	0.86 (4)
C(13)-H(11)	0.80 (4)	0.84 (4)
C(13)-H(12)	1.02 (5)	0.95 (4)

standard and have been described previously for both Syntex[7] and CAD-4[8] data. Pertinent crystallographic parameters for the three compounds are summarized in Table I.

Results

Structures. Atomic positional and thermal parameters for $Cr(CO)_5P(CH_2CH_2CN)_3$ (**1**), $Mo(CO)_5P(CH_2CH_2CN)_3$ (**2**), and $Mo(CO)_5P(C_6H_5)_3$ (**3**) are listed in Tables II, III, and IV, respectively. Figures 1 and 2 show the molecular structures and labeling schemes for $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo) and $Mo(CO)_5P(C_6H_5)_3$, respectively. Figures 3 and 4 present views looking down the P-M bond for the two types of compounds. Bond distances and angles for **1** and **2** are presented in Tables V and VI while those for **3** are given in Tables VII and VIII, respectively.

Compounds **1** and **2** are isomorphous and have crystal symmetry conforming to the monoclinic space group $P2_1/n$. Each molecule occupies a general position within the unit cell. The metal atoms, M = Cr and Mo, are octahedrally coordinated with C-M-C angles of 89.9 (2) (average) and 89.9 (2)° (average) and P-M-C angles of 90.2 (1) (average) and 90.2 (1)° (average) for the Cr and Mo compounds, respectively (see Table IX). The M-P distances are 2.364 (1) and 2.506 (1) Å, respectively. As expected, the compounds show two distinctly different M-CO distances (Table IX). The carbonyl that is trans to the $P(CH_2CH_2CN)_3$ ligand has a significantly shorter M-CO distance than do the carbonyl groups occupying the equatorial plane. For **1** (M = Cr) the M-CO_{ax} and M-CO_{eq} distances are 1.876 (4) and 1.891 (4) Å (average), and for **2** (M = Mo) the corresponding distances are 2.008 (4) and 2.044 (5) Å (average), respectively. As shown in Figure 3, the $P(CH_2CH_2CN)_3$ ligand is oriented so that the P-C(9) bond bisects the equatorial C(1)-M(1)-C(2) angle. This may be quantitatively expressed by the C(1)-M(1)-P(1)-C(6) torsional angles of 45.8 and 46.2° for the Cr and Mo compounds, respectively. Minimization of steric interactions between the $P(CH_2CH_2CN)_3$ ligand and the equatorial carbonyl ligands is accomplished as follows. First, there is a tilting of the phosphine toward the center of the C(1)-M(1)-C(2) group by approximately 3°. Second, the C(7)-C(8)-N group is rotated up and away from the equatorial plane so that the P(1)-C(9)-C(10) plane is essentially perpendicular to the equatorial plane as evidenced by M(1)-P(1)-C(9)-C(10) torsional angles of 179.2 and 178.9° for **1** and **2**, respectively. This also results in a slight increase in the M(1)-P(1)-C(9) angle from the expected 109.5 to 112.6 (1)° in **1** and **2**. Finally, there is a compression of the C(6)-P(1)-C(12) angle to 99.3 (2) and 99.9 (2)° in **1** and **2**, respectively, as a result of interactions between the C(6) and C(12) carbon atoms with the C(3)-O(3) and C(4)-O(4) carbonyl ligands. The C(7)-C(8)-N(1) and C(13)-C(14)-N(3) groups point away from the equatorial plane and give M(1)-P(1)-C-C torsional angles of 60.0 (average) and 57.9° (average) for **1** and **2**, respectively. Both compounds show a slight disordering of the C(11)-N(2) group. The extent of the disordering is approximately 15% in **1** and 10% in **2**.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$. As in **1** and **2**, each molecule occupies a general position within the unit cell. The geometry about the Mo atom is that of a slightly distorted octahedron. The C-Mo-C angles have an average value of 89.2 (1)° whereas the P-Mo-C angles for cis CO groups range from 87.39 (9) to 96.45 (9)°. The Mo-P distance is 2.560 (1) Å. Again, there are two distinctly different Mo-CO distances (see Table IX). The Mo-CO_{ax} distance is 1.995 (3) Å while the Mo-CO_{eq} distances average

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Table VI. Bond Angles for the Compounds $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo)

atoms	angles, deg		atoms	angles, deg	
	M = Cr	M = Mo		M = Cr	M = Mo
P(1)-M(1)-C(1)	89.2 (1)	89.5 (1)	C(9)-C(10)-C(11)	107.3 (3)	107.8 (4)
P(1)-M(1)-C(2)	88.7 (1)	88.8 (1)	C(9)-C(10)-C(11)′	107.1 (6)	105 (1)
P(1)-M(1)-C(3)	90.8 (1)	90.6 (1)	C(11)-C(10)-C(11)′	99.2 (6)	100 (1)
P(1)-M(1)-C(4)	92.0 (1)	91.9 (1)	N(2)-C(11)-C(10)	174.3 (5)	175.6 (5)
P(1)-M(1)-C(5)	177.0 (1)	177.4 (1)	N(2)′-C(11)′-C(10)	177 (1)	175 (3)
C(1)-M(1)-C(2)	90.8 (2)	91.0 (2)	P(1)-C(12)-C(13)	115.7 (3)	116.5 (4)
C(1)-M(1)-C(3)	178.4 (2)	178.5 (2)	C(12)-C(13)-C(14)	113.3 (4)	112.7 (4)
C(1)-M(1)-C(4)	89.2 (2)	89.3 (6)	N(3)-C(14)-C(13)	177.9 (5)	178.2 (5)
C(1)-M(1)-C(5)	89.8 (2)	89.9 (2)	C(7)-C(6)-H(1)	112 (2)	113 (3)
C(2)-M(1)-C(3)	90.9 (2)	90.5 (2)	C(1)-C(6)-H(2)	112 (2)	115 (2)
C(2)-M(1)-C(4)	179.3 (2)	179.2 (1)	H(1)-C(6)-H(2)	109 (3)	105 (3)
C(2)-M(1)-C(5)	88.5 (2)	88.6 (2)	C(6)-C(7)-H(3)	108 (3)	106 (3)
C(3)-M(1)-C(4)	89.2 (2)	89.2 (2)	C(6)-C(7)-H(4)	108 (3)	110 (2)
C(3)-M(1)-C(5)	90.2 (2)	90.0 (2)	C(8)-C(7)-H(3)	111 (3)	112 (3)
C(4)-M(1)-C(5)	90.9 (2)	90.6 (2)	C(8)-C(7)-H(4)	104 (3)	110 (2)
M(1)-P(1)-C(6)	117.6 (2)	117.9 (2)	H(3)-C(7)-H(4)	114 (4)	107 (4)
M(1)-P(1)-C(9)	112.6 (1)	111.6 (1)	C(10)-C(9)-H(5)	108 (2)	110 (2)
M(1)-P(1)-C(12)	117.3 (2)	117.1 (2)	C(10)-C(9)-H(6)	110 (2)	109 (2)
C(6)-P(1)-C(9)	103.4 (2)	103.3 (2)	H(5)-C(9)-H(6)	107 (3)	106 (3)
C(6)-P(1)-C(12)	99.3 (2)	99.9 (2)	C(9)-C(10)-H(7)	112 (3)	110 (4)
C(9)-P(1)-C(12)	104.6 (2)	105.2 (2)	C(11)-C(10)-H(7)	109 (3)	112 (4)
M(1)-C(1)-O(1)	179.2 (3)	179.5 (4)	C(11)′-C(10)-H(7)	121 (3)	121 (4)
M(1)-C(2)-O(2)	179.2 (4)	179.1 (3)	C(13)-C(12)-H(9)	106 (2)	109 (2)
M(1)-C(3)-O(3)	179.4 (3)	179.5 (4)	C(13)-C(12)-H(10)	111 (3)	110 (2)
M(1)-C(4)-O(4)	179.1 (4)	178.6 (4)	H(9)-C(12)-H(10)	109 (3)	106 (3)
M(1)-C(5)-O(5)	178.4 (4)	177.7 (4)	C(12)-C(13)-H(11)	100 (3)	112 (3)
P(1)-C(6)-C(7)	114.2 (3)	114.1 (3)	C(12)-C(13)-H(12)	108 (3)	111 (2)
C(6)-C(7)-C(8)	111.4 (4)	111.4 (4)	C(14)-C(13)-H(11)	110 (3)	103 (3)
N(1)-C(8)-C(7)	178.8 (5)	179.0 (6)	C(14)-C(13)-H(12)	111 (3)	109 (3)
P(1)-C(9)-C(10)	119.0 (3)	118.6 (3)	H(11)-C(13)-H(12)	114 (4)	108 (4)

Table VII. Bond Distances (Å) for $Mo(CO)_5P(C_6H_5)_3$

Mo(1)-P(1)	2.560 (1)	C(15)-C(16)	1.370 (6)
Mo(1)-C(1)	2.067 (4)	C(16)-C(17)	1.379 (5)
Mo(1)-C(2)	2.037 (3)	C(18)-C(19)	1.384 (4)
Mo(1)-C(3)	2.030 (4)	C(18)-C(23)	1.380 (4)
Mo(1)-C(4)	2.051 (4)	C(19)-C(20)	1.380 (5)
Mo(1)-C(5)	1.995 (3)	C(20)-C(21)	1.375 (6)
P(1)-C(6)	1.835 (3)	C(21)-C(22)	1.370 (6)
P(1)-C(12)	1.838 (3)	C(22)-C(23)	1.372 (5)
P(1)-C(18)	1.830 (3)	C(7)-H(1)	0.92 (3)
O(1)-C(1)	1.137 (4)	C(8)-H(2)	0.89 (4)
O(2)-C(2)	1.130 (4)	C(9)-H(3)	0.94 (5)
O(3)-C(3)	1.140 (4)	C(10)-H(4)	0.86 (4)
O(4)-C(4)	1.127 (4)	C(11)-H(5)	0.92 (4)
O(5)-C(5)	1.142 (4)	C(13)-H(6)	0.90 (3)
C(6)-C(7)	1.389 (4)	C(14)-H(7)	0.89 (4)
C(6)-C(11)	1.387 (4)	C(15)-H(8)	0.96 (4)
C(7)-C(8)	1.380 (5)	C(16)-H(9)	0.85 (4)
C(8)-C(9)	1.366 (6)	C(17)-H(10)	0.98 (4)
C(9)-C(10)	1.365 (7)	C(19)-H(11)	0.93 (4)
C(10)-C(11)	1.377 (5)	C(20)-H(12)	0.85 (4)
C(12)-C(13)	1.382 (4)	C(21)-H(13)	0.84 (4)
C(12)-C(17)	1.390 (4)	C(22)-H(14)	0.91 (4)
C(13)-C(14)	1.381 (5)	C(23)-H(15)	0.81 (3)
C(14)-C(15)	1.361 (6)		

Table VIII. Bond Angles (Deg) for $Mo(CO)_5P(C_6H_5)_3$

P(1)-Mo(1)-C(1)	96.45 (9)	P(1)-C(6)-C(7)	122.6 (2)
P(1)-Mo(1)-C(2)	94.48 (9)	P(1)-C(6)-C(11)	119.3 (2)
P(1)-Mo(1)-C(3)	87.39 (9)	C(7)-C(6)-C(11)	118.1 (3)
P(1)-Mo(1)-C(4)	87.6 (1)	C(6)-C(7)-C(8)	120.1 (4)
P(1)-Mo(1)-C(5)	174.4 (1)	C(7)-C(8)-C(9)	120.7 (4)
C(1)-Mo(1)-C(2)	88.9 (1)	C(8)-C(9)-C(10)	120.0 (4)
C(1)-Mo(1)-C(3)	176.1 (1)	C(9)-C(10)-C(11)	119.9 (4)
C(1)-Mo(1)-C(4)	89.2 (1)	C(6)-C(11)-C(10)	121.1 (4)
C(1)-Mo(1)-C(5)	88.0 (1)	P(1)-C(12)-C(13)	123.5 (2)
C(2)-Mo(1)-C(3)	90.0 (1)	P(1)-C(12)-C(17)	118.3 (2)
C(2)-Mo(1)-C(4)	177.3 (1)	C(13)-C(12)-C(17)	118.1 (3)
C(2)-Mo(1)-C(5)	89.0 (1)	C(12)-C(13)-C(14)	120.3 (4)
C(3)-Mo(1)-C(4)	91.7 (2)	C(13)-C(14)-C(15)	121.0 (4)
C(3)-Mo(1)-C(5)	88.2 (1)	C(14)-C(15)-C(16)	119.5 (4)
C(4)-Mo(1)-C(5)	89.0 (1)	C(15)-C(16)-C(17)	120.3 (4)
Mo(1)-P(1)-C(6)	118.74 (9)	C(12)-C(17)-C(16)	120.8 (3)
Mo(1)-P(1)-C(12)	111.67 (9)	P(1)-C(18)-C(19)	118.9 (2)
Mo(1)-P(1)-C(18)	116.50 (9)	P(1)-C(18)-C(23)	123.4 (2)
C(6)-P(1)-C(12)	103.4 (1)	C(19)-C(18)-C(23)	117.6 (3)
C(6)-P(1)-C(18)	101.9 (1)	C(18)-C(19)-C(20)	120.9 (4)
C(12)-P(1)-C(18)	102.6 (1)	C(19)-C(20)-C(21)	119.9 (4)
Mo(1)-C(1)-O(1)	176.3 (3)	C(20)-C(21)-C(22)	120.1 (4)
Mo(1)-C(2)-O(2)	176.7 (3)	C(21)-C(22)-C(23)	119.3 (4)
Mo(1)-C(3)-O(3)	178.1 (3)	C(18)-C(23)-C(22)	122.1 (4)
Mo(1)-C(4)-O(4)	177.8 (4)		
Mo(1)-C(5)-O(5)	178.3 (3)		

2.046 (4) Å. The $P(C_6H_5)_3$ ligand is bonded in a manner analogous to that observed in compounds **1** and **2**. As shown in Figure 4, one of the phenyl groups is oriented so that the P(1)–C(18) bond lies approximately over the bisector of the equatorial C(2)–Mo(1)–C(3) angle, as evidenced by a C(2)–Mo(1)–P(1)–C(18) torsional angle of 47.2°. The phenyl groups adopt a propeller-like configuration with Mo(1)–P(1)–C–C torsional angles ranging from 124 to 135.5°. There is also a tilting of the $P(C_6H_5)_3$ ligand by ca. 6° relative to the Mo(1)–C(5) bond. Unlike the situation in **1** and **2**, however, the ligand is not tilted toward the C(2)–Mo(1)–C(3) plane in order to minimize steric repulsions. In **3**, these repulsions are reduced by a compression of the C–P–C angles from the expected 109.5 to 102.6 (1)° (average) and by tilting of the ligand toward the P–C(12) bond. The tilting results in a compression of the Mo(1)–P(1)–C(12) angle to 111.67 (9)°, as compared to 118.74 (9) and 116.50 (9)° for the remaining Mo–P(1)–C angles, and a further 6° rotation of the C(12)–phenyl ring. This gives a Mo(1)–P(1)–C(12)–C(13) torsional angle of 124° as compared to 133 and 135.5° for the remaining phenyl rings.

Infrared Spectra. Unfortunately the $M(CO)_5P(CH_2CH_2CN)_3$ derivatives are extremely insoluble in noninteracting solvents such as saturated hydrocarbons where ν(CO) bandwidths are narrow. It was necessary to carry out solution infrared investigations in CH_2Cl_2, since these species are only slightly soluble in the less polar $CHCl_3$ solvent. Under these

Table IX. Comparison of Structural Parameters for the Compounds $M(CO)_5PR_3$ (M = Cr, Mo, W)

compd	M–P, Å	M–CO_{ax}, Å	M–CO_{eq}, Å	C–O_{ax}, Å	C–O_{eq}, Å	ref
$Cr(CO)_5P(C_6H_5)_3$	2.422 (1)	1.844 (4)	1.880 (4) av	1.154 (5)	1.147 (6) av	4
$Cr(CO)_5P(CH_2CH_2CN)_3$	2.364 (1)	1.876 (4)	1.891 (4) av	1.136 (4)	1.138 (4) av	this work
$Cr(CO)_5P(CH_3)_2SH$	2.344 (2)	1.829 (2)	1.87 (2) av	1.194 (1)	1.15 (1) av	9
$Cr(CO)_5P(OC_6H_5)_3$	2.309 (1)	1.861 (4)	1.896 (4) av	1.136 (6)	1.131 (6) av	4
$Mo(CO)_5P(C_6H_5)_3$	2.560 (1)	1.995 (3)	2.046 (4) av	1.142 (4)	1.134 (4) av	this work
$Mo(CO)_5P(CH_2CH_2CN)_3$	2.506 (1)	2.008 (4)	2.044 (5) av	1.145 (5)	1.134 (5) av	this work
$Mo(CO)_5[P(CH_2)_6N_3]$	2.479 (5)	2.034 (5)	2.01 (2) av	1.12 (2)	1.16 (2) av	10
$Mo(CO)_5PF_3$[a]	2.37 (1)	2.063 (6)	2.063 (6)	1.154 (5)	1.154 (5)	11
$W(CO)_5P[C(CH_3)_3]_3$	2.686 (4)	1.98 (2)	2.01 (2) av	1.13 (3)	1.15 (3) av	12

[a] Molecular structure determined in the gas phase by electron diffraction.

Table X. Infrared Spectral Data in the ν(CO) Region for $M(CO)_5L$ Derivatives

		ν(CO), cm^{-1}		
M	L	$A_1^{(2)}$	$A_1^{(1)}$	E
Cr	$P(OC_6H_5)_3$[a]	2078	1969	1960
Cr	$P(OCH_3)_3$[a]	2075	1965	1950
Cr	$P(CH_2CH_2CN)_3$	2068	1966	1944
Cr	PPh_3[a]	2066	1945	1945
Mo	$P(OCH_3)_3$	2080	1967[b]	1953
Mo	$P(CH_2CH_2CN)_3$	2077	1965[b]	1952
Mo	$P(C_6H_5)_3$	2073	1945[b]	1949

[a] Taken from ref 16. [b] These peaks, which show up as shoulders on the strong E mode vibration, are believed accurate to ±5 cm^{-1}.

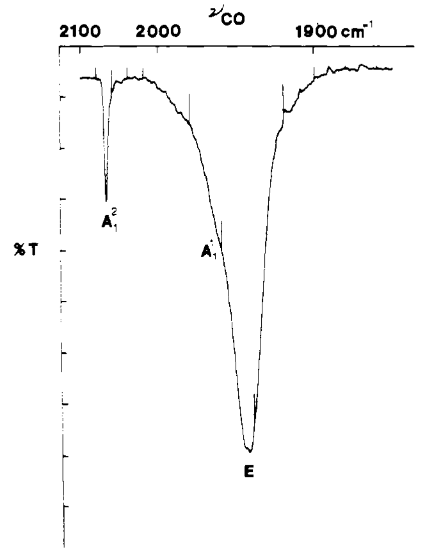

Figure 5. ν(CO) infrared spectrum of $Cr(CO)_5P(CH_2CH_2CN)_3$ in CH_2Cl_2. $A_1^{(1)}$ vibrational mode appears as a shoulder on the high-energy side of the very strong E vibrational mode.

conditions the ν(CO) peak widths are broad, making it difficult to delineate the $A_1^{(1)}$ and E vibrational modes (See Figure 5). Nevertheless it is possible to assess from comparative spectra measured under identical circumstances that the $P(CH_2CH_2CN)_3$ ligand is more akin to the good π-acceptor ligand $P(OCH_3)_3$ than to $P(C_6H_5)_3$ in its bonding properties to zerovalent metals (Table X). Similar conclusions have been reached on the basis of ν(CO) infrared and ^{13}C NMR results in $Ni(CO)_3L$ complexes.[2,13,14]

Discussion

We have employed the compounds $M(CO)_5[P(CH_2CH_2CN)_3]$ (M = Cr, Mo) to evaluate the bonding capabilities of the unusual phosphine $P(CH_2CH_2CN)_3$ toward low-valent transition metals. Both the M–P and M–CO bond lengths and the infrared spectrum in the CO stretching region have been measured. We have considered it advisable to study both the Cr and Mo compounds to ensure that there is nothing unique about the observations for any one metal. In the case of chromium, structural data for a triarylphosphine compound, $Cr(CO)_5PPh_3$, were already in the literature; we have also provided data for the molybdenum analogue, $Mo(CO)_5PPh_3$. The parallel behavior of corresponding sets of Cr and Mo compounds is well illustrated by the differences in the M–P$(CH_2CH_2CN)_3$ and M–PPh_3 bond lengths, which are 2.364 (1) – 2.422 (1) = –0.058 (2) Å for M = Cr and 2.506 (1) – 2.560 (1) = –0.054 (2) Å for M = Mo.

All available metal–phosphorus bond length data (Table IX) clearly indicate that the tris(2-cyanoethyl)phosphine ligand is a good π acceptor, compatible with the nature of the metal–phosphorus bond as inferred from spectroscopic measurements. It is apparent from these data and the respective ΔHNP values that the donor/acceptor ratio increases in the order $P(OC_6H_5)_3 < P(CH_2CH_2CN)_3 < P(C_6H_5)_3$. An important point to be made concerning metal–phosphorus bond strengths in low-valent metal complexes is that although good π-accepting ligands afford the strongest metal–phosphorus bonds (e.g., see Mo–PF_3 distance in Table IX), good σ-donor ligands can also lead to strong metal–phosphorus bonding. Indeed several kinetic studies strongly suggest that alkylphosphines, which are effecient σ donors with only minimal π-accepting ability, may be very tightly bound to zerovalent metal derivatives.[15,16]

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Registry No. **1**, 75673-06-2; **2**, 75673-07-3; **3**, 14971-42-7; $[(C_2H_5)_4N][Mo(CO)_5Br]$, 15003-38-0; $[(C_2H_5)_4N][Cr(CO)_5Br]$, 14780-93-9; $Mo(CO)_5P(OCH_3)_3$, 15631-20-6.

Supplementary Material Available: Tables of observed and calculated structure factors for all three compounds (29 pages). Ordering information is given on any current masthead page.

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