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Contribution from the Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122,
Tulane University, New Orleans, Louisiana 70118, and Southern University, New Orleans, Louisiana 70126

Molecular Structure and Spectral Properties of Phosphatriazaadamantanemolybdenum Pentacarbonyl Complex

J. R. DeLERNO, L. M. TREFONAS,* M. Y. DARENSBOURG, and R. J. MAJESTE

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The crystal and molecular structure of $Mo(CO)_5[P(CH_2)_6N_3]$ has been determined by single-crystal x-ray diffraction techniques using a GE 490 automated diffractometer system. The compound crystallizes in the space group *Pbca* with eight formula weights in a unit cell of dimensions $a = 14.357$ (2) Å, $b = 26.509$ (2) Å, and $c = 8.1528$ (6) Å. The structure was solved by means of a three-dimensional Patterson function and refined by block-diagonal least squares to a value of $R = 0.069$ for 1194 statistically significant reflections. The ligand has been shown to bind to the molybdenum through the phosphorus with a Mo–P bond of 2.48 Å. The rigidity of the phosphorus cage which exists both in the solid and in solution allows for a crystallographic estimate of Tolman's widely used steric factor, the "ligand cone angle". Infrared spectral properties are compared to metal carbonyl derivatives of other phosphorus cage compounds.

Introduction

A novel phosphatriazaadamantane, PTA (Figure 1), and its analogues have recently been reported[1] in the literature. This tetrabasic nonchelating cage compound readily forms complexes with low-valent metal carbonyls in which the ligand is apparently phosphorus bound.[2] Multicomplexation of the ligand has been observed in the preparation of $[W(CO)_5PTA]_2Hg_2Cl_4$.[3] Since the detailed geometry of this cage system is unknown, and in light of the recent interest in phosphorus-containing cage molecules,[4-8] the molecular structure of a PTA derivative, $Mo(CO)_5PTA$, was determined and is the subject of this report.

Experimental Section

$Mo(CO)_5PTA$ was prepared[2] and recrystallized from boiling hexane. Tetraphosphorus trisulfide was recrystallized from benzene and over a period of days at room temperature displaced piperidine from $Mo(CO)_5(NHC_6H_{11})$ in hexane solution yielding $Mo(CO)_5P_4S_3$ as identified by its principal ν_{CO} bands in the infrared spectrum.[4] Infrared spectra were taken on a Perkin-Elmer 521 spectrophotometer.

X-Ray Data. A platelike crystal of the molybdenum complex approximately 0.25 mm long on the face side and with a thickness of 0.10 mm was mounted on a General Electric XRD-5 diffractometer with the (001) axis as the spindle axis. Extinctions for the reflections with $h = 2n + 1$ in the ($hk0$) data, those with $l = 2n + 1$ in the ($h0l$) data, and those with $k = 2n + 1$ in the ($0kl$) data combined with *mmm* symmetry in reciprocal space uniquely characterize the orthorhombic space group *Pbca*. Lattice constants were determined by a least-squares fit of 15 carefully measured 2θ values (1° TOA and 0.05° slit) at $2\theta > 70°$ where the Cu $K\alpha_1$, $K\alpha_2$ doublet is easily resolved.

The resultant lattice constants and their estimated standard deviations are $a = 14.357 \pm 0.002$ Å, $b = 26.509 \pm 0.002$ Å, and $c = 8.1528 \pm 0.0006$ Å.

The calculated density of 1.68 g/cm^3 for eight molecules per unit cell agrees with an experimentally measured (using flotation techniques) density of 1.71 (2) g/cm^3.

A set of three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-counter, stationary-crystal method. Balanced nickel–cobalt filters with copper $K\alpha$ radiation were used to measure all reflections out to a 2θ maximum of 100°. A total of 1887 independent reflections were measured with 1194 considered as statistically significant based on the criterion

$$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 100$$

where the σ's were based solely on counting statistics for the 10-s count. The intensities were corrected for α_1–α_2 splitting as a function of 2θ and for absorption as a function of ϕ (linear $\mu = 84.5$ cm^{-1} with a ratio of 1.18:1 in the absorption correction). Lorentz–polarization corrections were made and the intensities reduced to structure amplitudes in the usual manner.

Structure Determination. The three-dimensional Patterson function clearly indicated the Mo–Mo, Mo–P interactions although there was an ambiguity with respect to the P–P interactions. A Fourier map based only on the Mo position ($R = 0.42$)[5] and another based on the Mo, P positions ($R = 0.34$) gave similar results. The adamantane-like structure was easily deciphered although the anisotropy of the Mo partially masked the locations of the carbonyl groups. A series of least-squares cycles was run using the Mo, P and adamantane ring (11 atoms). This refinement lowered the value of the residual index to $R = 0.26$ and a Fourier map was calculated at this point. Four of the five carbonyl groups were readily evident, with the carbon of the fifth group still partially obscured by the Mo peak. Another cycle involving least-squares and Fourier refinement led to the location of the fifth carbonyl group. The Mo was assigned anisotropic temperature factors, the remaining atoms retaining isotropic temperature factors, and ten cycles of least-squares refinement resulted in a value of $R = 0.145$. All of the 21 atoms were then converted to anisotropic temperature factors and ten additional cycles of block-diagonal

* To whom correspondence should be addressed at the University of New Orleans.

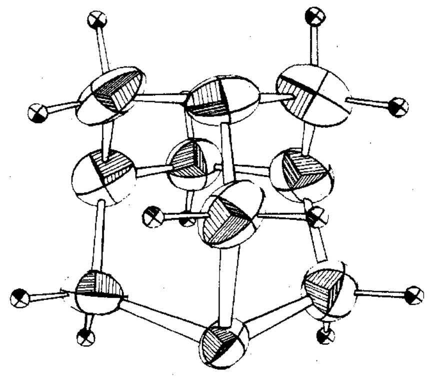

Figure 1.

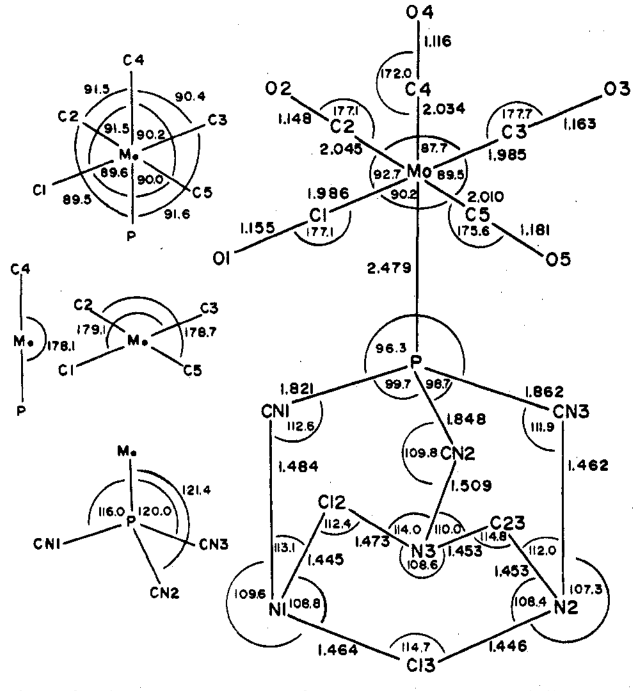

Figure 2. Schematic drawing of the molecule with bond distances and bond angles indicated.

refinement led to an $R = 0.074$. Methylene hydrogen positions were calculated, based upon the usual geometric considerations, namely, tetrahedral angles and C–H = 1.0 Å. Inclusion of these hydrogens in a final structure factor calculation reduced the residual slightly, to its value of 0.069. A difference map at this stage showed no regions higher in density than 0.2 e/Å^3 except very near the molybdenum.

Results and Discussion

The least-squares coordinates and anisotropic temperature factors for the nonhydrogen atoms together with the estimated standard deviation (esd) for each parameter are summarized in Table I. The calculated hydrogen coordinates are listed in Table II. Figure 2 gives a schematic drawing of the molecule with the various bond distances and bond angles indicated on the figure. To summarize, the *maximum* esd values for these various distances and angles are given in Table III.

The structure of Mo(CO)$_5$PTA (Figure 2) is that of a slightly distorted octahedron with the PTA ligand phosphorus bound as previously suggested from ^{1}H and ^{31}P NMR data as well as ν_{CO} infrared analysis.[2] The usual[9] C–O distances of 1.15 Å are observed for all CO groups in the molecule. The Mo–C average distance (2.01 ± 0.02 Å) is within the range (1.93–2.01 Å) usually cited for phosphine-substituted molybdenum carbonyls[10] but is shorter than the approximately 2.06 Å found in Mo(CO)$_6$,[11] Mo(CO)$_5$PF$_3$,[12] and Mo(CO)$_5$P$_4$S$_3$.[4] On the other hand the Mo–P bond distance of 2.48 Å observed here is identical with the Mo–P distance in Mo(CO)$_5$P$_4$S$_3$, in which the unique apical phosphorus of the P$_4$S$_3$ cage is molybdenum bound.[4] A much shorter Mo–P distance of 2.37 Å is observed for Mo(CO)$_5$PF$_3$.[12] In view of the discrepancy in Mo–C and Mo–P bond lengths for the phosphorus cage derivatives, the ν_{CO} spectral properties and Cotton–Kraihanzel force constants[13] were investigated.

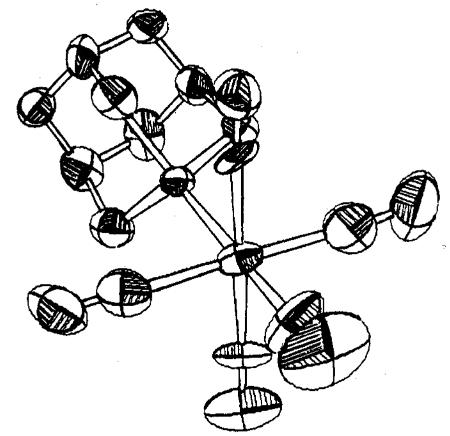

Figure 3. View of the molecule.

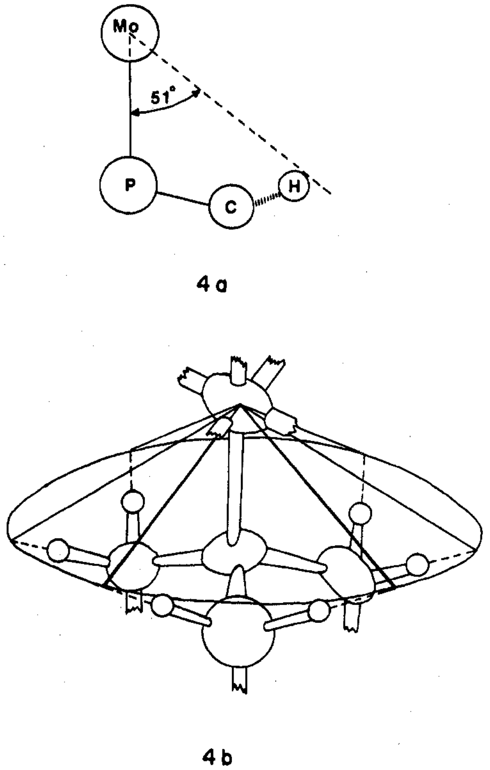

Figure 4. The half cone angle (a) as defined by the angle between the Mo–P bond axis and the line from Mo to a point tangent to the van der Waals radius of H. This point is obtained by extending the C–H bond axis from 1.0 Å to a distance of 2.1 Å, assuming the van der Waals radius of H to be 1.1 Å. Twice this angle, 102°, is Tolman's steric factor, the ligand cone angle, as represented in part b.

The hexane solution spectrum of Mo(CO)$_5$PTA shows ν_{CO} of 2070.0 (w, $A_1^{(2)}$), 1958.0 (mw, $A_1^{(2)}$), and 1948.0 (s, E) cm^{-1} corresponding to C–K force constants $k_{trans} = 15.71$ and $k_{cis} = 15.91$ mdyn/Å. The Mo(CO)$_5$P$_4$S$_3$ complex has ν_{CO} at considerably higher frequencies, 2085 (w, $A_1^{(2)}$), 1984 (sh, $A_1^{(1)}$), and 1978 (s, E) cm^{-1} [14] with correspondingly higher force constants, $k_{trans} = 16.09$ and $k_{cis} = 16.33$ mdyn/Å. A comparison of these force constants with a series of LMo(CO)$_5$ complexes[15] would place PTA with those ligands considered

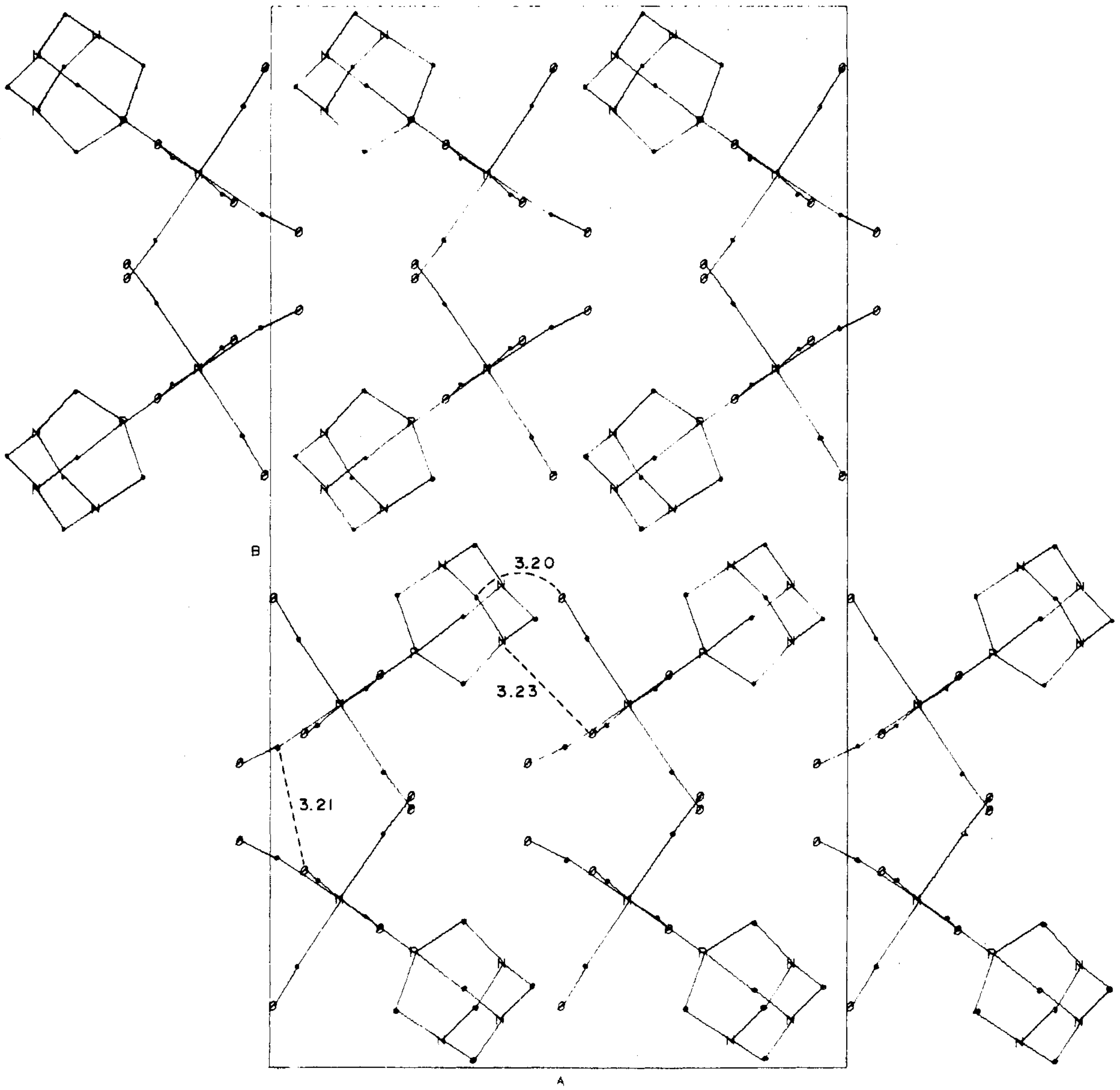

Figure 5. Contents of the unit cell projected down the *c* axis. Intermolecular contacts less than 3.5 Å are indicated.

to be rather good σ-donating ligands such as PPh_3. The Mo–P distance of 2.52 Å of $(CO)_4MO(PPh_2CH_2PPh_2)$[16] and $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(CN)_2CH_3$[17] is consistent with the spectral results. A similar comparison of the force constants of $Mo(CO)_5P_4S_3$ would place P_4S_3 with those ligands considered to be good π-accepting ligands, such as PCl_3 and PF_3. This conclusion is supported by the longer Mo–C bond lengths in $Mo(CO)_5P_4S_3$ and $Mo(CO)_5PF_3$. This comparison of spectral and bond length data thus suggests the Mo–P distance of $Mo(CO)_5P_4S_3$ to be abnormally long.

The angle defined according to Figure 4a (P--Mo--H, where Mo--H is the line from the center of Mo to the van der Waals radius (1.1 Å) of a methylene hydrogen) may be taken as an approximation of the steric requirement of the coordinated ligand. Twice this angle can be related to the volume swept out by the ligand (Figure 4b) and is a rather exact measurement of the "ligand cone angle" (LCA) as defined by Tolman.[18] Due to the rigid nature of the PTA molecule the cone angle calculated in this particular case would be the same whether for the crystal or for the PTA molecule in solution. It thus affords a suitable basis for comparison to Tolman's molecular model measurements as well as to modifications of individual LCA's as based on solution studies of formation constants[19] and on NMR measurements.[20] The resulting LCA of 102 ± 0.5° is most readily compared to the value of 99 ± 2° predicted for molybdenum-bound $P(OCH_2)_3CCH_3$ according to the molecular model measurements of Tolman.[18]

Sterically trimethylphosphine differs from PTA in that the CH_3 groups of the former are not rigid, thus sweeping a cone angle that is ca. 12° larger than that of PTA. Both ligands are small, however, compared to the more common PPh_3, PPh_2Me, $P(n\text{-}Bu)_3$, etc. The electronic properties of PTA and PMe_3 as inferred from ν_{CO} and force constant calculations are fairly similar.[21] The admixture of electronic and steric properties appears to be important in ^{31}P NMR correlations[22] and the change in ^{31}P chemical shift on ligand coordination again indicates the two ligands to be similar ($\Delta\delta(^{31}P) = \delta_{\text{free L}} - \delta_{Mo(CO)_5L}$; $\Delta\delta_{L=PTA} = -42$ ppm (DMSO solution); $\Delta\delta_{L=PMe_3} = -44$ ppm (benzene solution).[19] Hence the PTA ligand which is an easily handled solid is a suitable alternative to PMe_3 in studies requiring a range of ligands of varying steric and electronic properties.

A calculation of all contact distances between molecules shows that there are no appreciable close contacts which might lead to distortions due to crystal packing. Figure 5, a projection of the contents of the unit cell down the *c* axis, lists all contacts between molecules that are less than 3.5 Å. Thus the crystal structure as well as solution studies[2] (^1H NMR)

Table I. Fractional Coordinates and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M0	1.1230 (1)	0.3416 (1)	0.6006 (2)	46 (1)	9 (0)	180 (3)	−3 (0)	0 (2)	7 (1)
P	1.2525 (4)	0.3913 (2)	0.4808 (6)	39 (3)	7 (1)	113 (9)	0 (1)	−6 (5)	0 (2)
N1	1.3003 (11)	0.4738 (6)	0.2932 (18)	59 (10)	15 (3)	103 (30)	−3 (5)	12 (15)	3 (8)
N2	1.4033 (10)	0.4546 (5)	0.5244 (19)	52 (10)	13 (3)	130 (30)	−10 (4)	−9 (14)	−5 (7)
N3	1.4044 (10)	0.4019 (6)	0.2778 (21)	44 (10)	18 (3)	184 (37)	−1 (4)	33 (16)	−6 (9)
CN1	1.2189 (12)	0.4459 (7)	0.3589 (25)	37 (11)	15 (4)	183 (47)	−9 (5)	7 (18)	−6 (10)
CN2	1.3379 (14)	0.3622 (7)	0.3401 (26)	56 (12)	13 (3)	185 (46)	1 (5)	−13 (20)	−3 (10)
CN3	1.3351 (14)	0.4254 (7)	0.6176 (25)	68 (13)	10 (3)	128 (37)	−1 (5)	−14 (20)	−3 (9)
C12	1.3588 (13)	0.4434 (7)	0.1883 (24)	54 (13)	13 (3)	134 (36)	−1 (5)	−2 (20)	9 (9)
C13	1.3566 (14)	0.4930 (6)	0.4292 (25)	77 (14)	9 (3)	161 (44)	−9 (6)	42 (21)	1 (9)
C23	1.4570 (13)	0.4231 (8)	0.4134 (27)	44 (11)	24 (4)	156 (42)	−3 (6)	0 (20)	−2 (12)
C1	1.0483 (12)	0.4046 (6)	0.6005 (24)	44 (11)	7 (3)	151 (36)	−13 (4)	−13 (18)	22 (9)
C2	1.0825 (14)	0.3233 (8)	0.3677 (29)	50 (12)	17 (4)	245 (55)	−6 (6)	−10 (22)	−3 (12)
C3	1.1995 (14)	0.2792 (6)	0.6005 (30)	77 (14)	5 (3)	296 (53)	−15 (5)	9 (25)	32 (11)
C4	1.0140 (18)	0.3030 (10)	0.6984 (34)	86 (18)	28 (6)	285 (63)	−16 (9)	−3 (30)	51 (16)
C5	1.1697 (16)	0.3576 (8)	0.8270 (31)	73 (16)	22 (5)	252 (57)	−12 (7)	28 (25)	0 (13)
O1	1.0082 (9)	0.4424 (5)	0.6030 (18)	68 (9)	19 (3)	185 (28)	3 (4)	−13 (15)	−4 (8)
O2	1.0612 (12)	0.3149 (6)	0.2348 (22)	110 (13)	19 (3)	296 (41)	5 (5)	−54 (19)	−24 (9)
O3	1.2467 (11)	0.2436 (6)	0.5978 (26)	90 (10)	15 (3)	532 (56)	1 (5)	−12 (25)	10 (11)
O4	0.9486 (13)	0.2868 (8)	0.7502 (34)	92 (14)	43 (5)	671 (80)	−16 (7)	133 (28)	42 (18)
O5	1.1932 (14)	0.3697 (8)	0.9601 (22)	140 (16)	40 (5)	203 (38)	−19 (7)	−29 (21)	27 (11)

[a] Anistropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Thermal parameters are $\times 10^4$; esd's in parentheses refer to the last decimal place.

Table II. Hydrogen Fractional Coordinates (Isotropic Thermal Parameter Fixed at 4.0 Å^2)

Atom[a]	x	y	z
H6	1.1814 (0)	0.4706 (0)	0.4240 (0)
H6	1.1790 (0)	0.4350 (0)	0.2606 (0)
H7	1.3057 (0)	0.3453 (0)	0.2399 (0)
H7	1.3755 (0)	0.3339 (0)	0.3936 (0)
H8	1.3680 (0)	0.4011 (0)	0.6941 (0)
H8	1.2988 (0)	0.4500 (0)	0.6918 (0)
H9	1.4044 (0)	0.4656 (0)	0.1344 (0)
H9	1.3162 (0)	0.4282 (0)	0.1002 (0)
H10	1.3101 (0)	0.5121 (0)	0.5031 (0)
H10	1.4009 (0)	0.5185 (0)	0.3843 (0)
H11	1.4844 (0)	0.3935 (0)	0.4796 (0)
H11	1.5120 (0)	0.4430 (0)	0.3707 (0)

[a] Numbers following H refer to bonding atom.

Table III. Maximum Estimated Standard Deviations in the Molecular Parameters

Distances	Esd, Å	Angles	Esd, Å
Mo-P	0.005	MoPC	0.7
Mo-C	0.015	MoCO	1.4
P-N	0.020	CMoP	1.0
P-C	0.020	CPC	0.9
N-C	0.025	NCN	1.4
C-C	0.026	CNC	1.4

shows the environment of the nitrogen sites to be little affected by coordination. The preparation of PTA-bridged metal centers is currently under investigation.

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Registry No. $Mo(CO)_5[P(CH_2)_6N_3]$, 54340-47-5; $Mo(CO)_5P_4S_3$, 28667-92-7.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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