mated standard deviations are listed in Table II; bond lengths and bond angles are listed in Table III.

Registry No. **1**, 57680-64-5; **2**, 57671-89-3; **8a**, 104489-87-4; **8b**, 104489-84-1; **8d**, 104489-95-4; **9c**, 104489-88-5; **10a**, 104489-89-6; **10b**, 104489-85-2; **10c**, 104489-92-1; **10d**, 104505-66-0; **11a**, 77681-64-2; **11b**, 104489-86-3; **11c**, 104505-65-9; **11d**, 104489-94-3; **12c**, 104489-90-9; **13d**, 104531-45-5; **15b**, 77659-95-1; **15d**, 104489-91-0; η^5-CpFeCO$_2$Br, 12078-20-5; η^5-CpFeCO$_2$Cl, 12107-04-9; η^5-CpRuCO$_2$Cl, 32611-12-4.

Supplementary Material Available: Table V, least-squares planes, and Table VI, atomic coordinates for hydrogen atoms (2 pages); listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Syntheses of Secondary-Amine-Substituted Bis(phosphino) Molybdenum Tetracarbonyl Complexes

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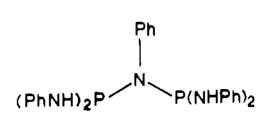
Received April 3, 1986

Reaction of PhN(PCl$_2$)$_2$, PhN[P(NHPh)$_2$]$_2$, or the 1,3,2,4-diazadiphosphetidines [(PhNH)PNPh]$_3$ and [(PhNH)P$_2$(NPh)$_2$]$_2$NPh with norbornadiene–Mo(CO)$_4$ yields the cis complexes PhN(PCl$_2$)$_2$Mo(CO)$_4$ (**5**), PhN[P(NHPh)$_2$]$_2$Mo(CO)$_4$ (**6**), [(PhNH)PNPh]$_3$Mo(CO)$_4$ (**7**), and [(PhNH)P$_2$(NPh)$_2$]$_2$NPhMo(CO)$_4$ (**8**) in high yields. Reactions of nor·Mo(CO)$_4$ with PhN[P(NHPh)$_2$]$_2$ or a PhN[P(NHPh)$_2$]$_2$–(PhNH)$_3$P mixture or (PCl$_3$)$_2$Mo(CO)$_4$ with PhNH$_2$/Et$_3$N yields **6** quantitatively, in reactions that involve metal-templated P–N bond condensation reactions. **5** reacts with PhNH$_2$/Et$_3$N or *i*-PrNH$_2$/Et$_3$N to form **6** or *i*-PrN[(*i*-PrNH)$_3$(PhNH)P$_2$]Mo(CO)$_4$ (**9**), respectively. **6** has been characterized structurally by single-crystal X-ray crystallography. Crystals of **6**·$^1/_2$C$_6$H$_6$ are hexagonal, space group $P6_122$, with a = 15.604 (4) Å, b = 15.604 (4) Å, c = 28.712 (4) Å, and Z = 6. The structure, solved by direct methods, refined to R = 0.074 and R_w = 0.085 for 539 observed reflections. The complex is a bis(phosphino)amino complex in which phosphorus atoms are coordinated to cis positions of the Mo(CO)$_4$ moiety. Comparison of physical and spectral properties of **5**, **7**, **8**, and **9** with those of **6** allows the former compounds to be characterized as bis(phosphino)amine complexes. In every case bis(phosphino) phosphorus coordination to the Mo(CO)$_4$ moiety occurs; no evidence for 1,3,2,4-diazadiphosphetidine terminal phosphorus or ring coordination is seen. Reaction of *cis*-(PhNPCl)$_2$ or *cis*-[(PhNH)PNPh]$_2$ with nor·Mo(CO)$_4$ yields intractable products.

Introduction

Recently, we reported the preparation and structural characterization of the secondary-amino- and 1,3,2,4-diazadiphosphetidinyl-substituted bis(phosphino)amines **1**–**3**.[2-6] Because they are phosphorus(III) compounds that contain N–H bonds and a P$_2$N$_2$ ring functionality, they are potentially valuable intermediates for the synthesis of novel bis(phosphino)amine–metal complexes, heteroatom-substituted phosphorus–nitrogen ring compounds, and new phosphorus–nitrogen polymers. The chemistry of **1**–**3** is so far largely unexplored; however, it is known that they are relatively labile; e.g., **1** undergoes aniline elimination and ring closure to [(PhNH)PNPh]$_2$ (**4**) (eq 1)[6,7] and **2** undergoes oligomer interconversion to a mixture of **4** and **2**.[3,6] Consequently, there may be advantages to stabilizing compounds such as **1**–**3** by their coordination to metal centers.



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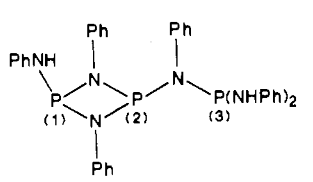

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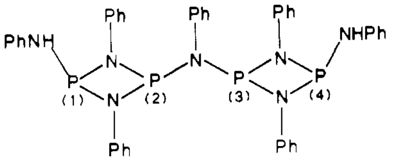

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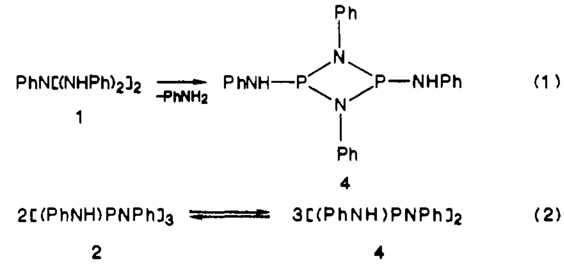

In order to more fully develop the chemistry of amine-substituted phosphines such as **1**–**4**, we have undertaken a study of their coordination properties and syntheses on metal moiety centers. We have sought to stabilize the aminophosphines and subsequently develop routes to otherwise inaccessible systems. in addition, since metal coordination of 1,3,2,4-diazadiphosphetidine ring systems has been studied only slightly,[8-11] their coordination characteristics toward metals continue to be of interest. A preliminary report of the synthesis of PhN[P(NHPh)$_2$]$_2$Mo(CO)$_4$ has been published.[12]

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0020-1669/86/1325-4152$01.50/0

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags or in evacuated systems.[13] Infrared, ^1H NMR (90.0 MHz), and mass spectra were obtained on Perkin-Elmer 337G, Varian EM 390, and Varian MAT CH-5 spectrometers, respectively. Phosphorus-31 NMR spectra were obtained on a JEOL PFT 100 spectrometer. ^1H and ^{31}P NMR chemical shifts were measured relative to internal $(CH_3)_4Si$ and external H_3PO_4, respectively; $+\delta$ values are downfield from the standard.

Nor·$Mo(CO)_4$ (nor = norbornadiene),[14] $(PCl_3)_2Mo(CO)_4$,[15] PhN-$(PCl2)_2$,[16] $[(PhNH)_2P]_2NPh$,[5] $(PhNH)_3P$,[5] $[(PhNH)PNPh]_3$,[3] and $[(PhNH)P_2(NPh)_2]_2NPh$[4] were prepared and purified as described previously. Aniline, diethyl ether, benzene, and toluene were distilled from CaH_2. Chloroform and CH_2Cl_2 were distilled from P_4O_{10}.

***cis*-PhN$(PCl_2)_2$Mo$(CO)_4$ (5).** A toluene solution of nor·$Mo(CO)_4$ (5.0 mmol) was added to $PhN(PCl_2)_2$ (5.0 mmol) in toluene at 25 °C. After 15 h, the solution was filtered, passed through a 2-cm alumina column, reduced in vacuo to one-fifth volume, and finally cooled to −78 °C. Crystallization occurs yielding **5** (mp 77.5–79.0 °C; 85% yield). Anal. Calcd for $C_{10}H_5NP_2Cl_4MoO_4$: C, 23.89; H, 1.00; N, 2.79; P, 12.32. Found: C, 23.85; H, 1.08; N, 2.64; P, 12.35. ^1H NMR (CD_2Cl_2): δ 7.40–7.65 (m, C_6H_5). ^{31}P NMR (C_6D_6): δ 122.4 (s). MS, parent and five most intense envelopes: *m/e* (relative intensity) 511 (0.2; $C_{10}H_5O_4P_2N^{35}Cl^{37}Cl_3{}^{100}Mo^+$); 391 (12), 188 (9), 157 (50), 122 (100), 76 (80). IR (Nujol), characteristic absorptions: 2060 (s), 1988 (m), 1970 (s), 1940 (w), 1235 (m), 964 (m), 940 (m), 869 (m), 557 (s) cm^{-1}. **5** is very soluble in benzene, toluene, $CHCl_3$, and CH_2Cl_2.

***cis*-PhN$[P(NHPh)_2]_2$Mo$(CO)_4$ (6). (A) $[(PhNH)_2P]_2NPh$ + nor·Mo$(CO)_4$.** A benzene solution of $PhN[P(NHPh)_2]_2$ (5.0 mmol) was added slowly to nor·$Mo(CO)_4$ (5.0 mmol) in benzene (50 mL) at 25 °C. After 15 h, volatile reaction materials were removed in vacuo. Recrystallization of the resulting solid from toluene yielded $PhN[P(NHPh)_2]_2 \cdot Mo(CO)_4 \cdot {}^1/_2C_7H_8$ (**6**·$^1/_2C_7H_8$; mp 188 °C dec; yield 80%). Anal. Calcd for $C_{34}H_{29}P_2N_5O_4Mo \cdot {}^1/_2C_7H_8$: C, 58.06; H, 4.29; N, 9.03; P, 7.99. Found: C, 57.98; H, 4.28; N, 8.91; P, 7.89. ^1H NMR (C_6D_6): δ 6.70–7.33 (m, area 25, C_6H_5), 4.56 (d, area 4, $^2J_{HNP}$ = 3.60 Hz, NH). ^{31}P NMR (C_6D_6): δ 95.6. MS, parent and six most intense envelopes: *m/e* (relative intensity) 731 (41; $C_{34}H_{29}P_2N_5O_4{}^{98}Mo^+$), 647 (69), 434 (80), 371 (56), 307 (100), 122 (67), 77 (68). IR (Nujol), characteristic absorptions: 3380 (w), 3328 (m), 2024 (s), 1924 (s), 1912 (s), 1888 (s), 1878 (s), 1226 (s), 1178 (w), 945 (m), 918 (m), 880 (m), 572 (m) cm^{-1}. **6** is soluble in $CHCl_3$, moderately soluble in benzene, toluene, and CH_2Cl_2, and slightly soluble in hexane.

(B) $(PhNH)_3P$–$PhN[P(NHPh)_2]_2$ + nor·Mo$(CO)_4$. $(PhNH)_3P$ (2.0 mmol) was dissolved in benzene (15 mL). Within minutes equilibration to an approximately equimolar $(PhNH)_3P$–$PhN[P(NHPh)_2]_2$ mixture occurred.[17] This solution was added slowly to a stirred nor·$Mo(CO)_4$ (1.1 mmol)–benzene solution. After 15 h, the solution turned orange and exhibited ^{31}P NMR spectral resonances at δ 108.7 and 95.8 (relative area 1:3). Upon removal of volatile reaction materials in vacuo at 25–40 °C and redissolution of the resulting solid in benzene, only the δ 95.8 ^{31}P NMR peak was present. Recrystallization from benzene yielded **6**·$^1/_2C_6H_6$ (70% yield).

(C) $(PCl_3)_2$Mo$(CO)_4$ + PhNH$_2$. $PhNH_2$ (8.0 mmol) in benzene was allowed to react with $(PCl_3)_2Mo(CO)_4$ (1.3 mmol) and $(Et)_3N$ (10.0 mmol) in benzene at 0 °C. The reaction solution showed ^{31}P NMR spectral resonances at δ 108.4 (d, J = 9.7 Hz) and δ 96.1 (s) (relative area 4:1). After filtration of Et_3NHCl, removal of volatile reaction materials in vacuo, and redissolution in benzene, only the δ 96.1 resonance remained. Recrystallization of reaction solids from toluene yielded **6**·$^1/_2C_7H_8$ (yield 85%).

***cis*-$[(PhNH)PNPh]_3$·Mo$(CO)_4$ (7). $[(PhNH)PNPh]_3$ + nor·Mo$(CO)_4$.** Nor·$Mo(CO)_4$ (0.43 mmol) in benzene was added slowly to a suspension of $[(PhNH)PNPh]_3$ (0.43 mmol) in benzene at 25 °C. After 10 h, a tan suspension formed. Filtration of this solid yielded **7**, $[(PhNH)PNPh]_3Mo(CO)_4$ (mp 160 °C; yield 60%). Anal. Calcd for $C_{40}H_{33}N_6P_3O_4N_6$ (mol wt 850.57): C, 56.48; H, 3.91; N, 9.88; P, 10.92. Found (mol wt (CH_2Cl_2, osmometry) 834): C, 56.98; H, 3.97; N, 9.83; P, 10.74. ^1H NMR $(CDCl_3)$: δ 3.62 (d, area 1, $^3J_{HNP}$ = 6.0 Hz, NH), 4.96 (d, area 2, $^3J_{HNP}$ = 5.0 Hz, NH), 6.50–7.70 (m, area 30, C_6H_5). ^{31}P NMR $(CD_2Cl_2/C_6D_6$, Figure 1 A): δ 102.7 (d, $^2J_{HNP}$ = 6.0 Hz, P(1)), 129.6 (d, $^2J_{P(2)P(3)}$ = 74.2 Hz, P(2)), 94.5 (broad s, P(3)). MS: sample decomposed at temperatures sufficient to volatilize it; highest mass envelope at *m/e* 486. IR (KBr), characteristic absorptions: 3311 (w), 2028 (s), 1942–1887 (vs, 3 absorptions, poorly resolved), 1261 (s), 961 (s), 944 (m), 929 (vs), 500 (s) cm^{-1}. **7** is soluble in benzene and toluene, moderately soluble in $CHCl_2$ and $CHCl_3$, and slightly soluble in Et_2O.

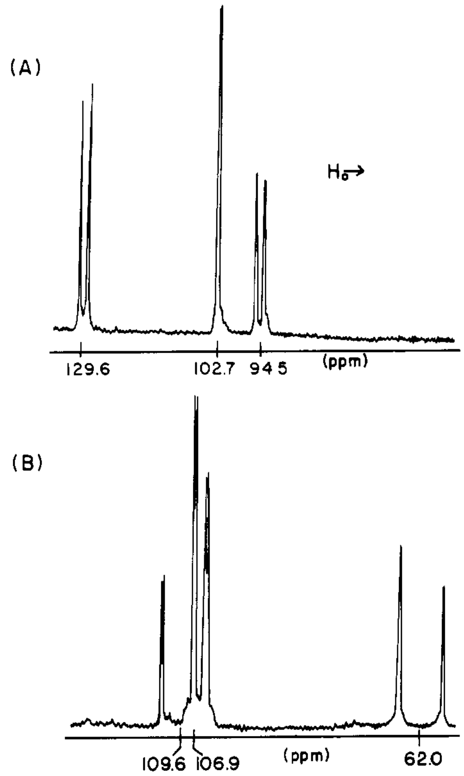

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (A) $PhN[P(NHPh)_2]_2Mo(CO)_4$ (**6**) and (B) $[(PhNH)PNPh]_3$ (**2**).

***cis*-$[(PhNH)P_2(NPh)_2]_2$NPhMo$(CO)_4$ (8).** Nor·$Mo(CO)_4$ (3.0 mol) and $[(PhNH)P_2(NPh)_2]_2NPh$ (3.0 mol) were allowed to react in toluene (80 mL) at 25 °C. After 5 h, a white solid formed. The reaction solution was filtered, evaporated to two-thirds volume, and cooled to 0 °C. **8** crystallized as a monotoluene solvate (mp 326–328 °C dec; yield 74%). Anal. Calcd for $C_{53}H_{45}P_4N_7O_4Mo$: C, 59.83; H, 4.23; N, 9.22; P, 11.66. Found: C, 58.38; H, 4.34; N, 9.07; P, 11.80. ^1H NMR $(CDCl_3)$: δ 6.60–7.72 (m, area 35, C_6H_5), 3.87 (d, area 2, $^2J_{HPN}$ = 6.60 Hz, NH). ^{31}P NMR (C_6D_6): δ 107.7 (broad s, P(1) and P(4); sharpens on ^1H decoupling), 132.2 (s, P(2), and P(3)). MS, highest mass and six most intense envelopes: *m/e* (relative intensity): 428 (3), 213 (7), 153 (21), 124 (11), 122 (29), 92 (100, 91 (24). IR (Nujol), characteristic absorptions: 3338 (w), 2036 (s), 1946 (s), 1937 (m), 1911 (s), 1238 (m), 950 (w), 940 (m), 896 (m), 880 (m), 864 (m), 510 (w) cm^{-1}. **8** is very soluble in $CHCl_3$, moderately soluble in CH_2Cl_2, and slightly soluble in benzene, toluene, and Et_2O.

8 with 3–5-fold molar excesses of Ph_3P or *n*-Bu_3P in $CHCl_3$ was heated under N_2 for 20 h. ^{31}P NMR analysis of the reaction mixture showed no reaction.

Reaction of nor·Mo$(CO)_4$ with *cis*-$[(PhN)PCl]_2$ or *cis*-$[(PhNH)PNPh]_2$ (4). Solutions of *cis*-$[(PhN)PCl]_2$ (5.0 mmol) or *cis*-$[(PhNH)PNPh]_2$ (5.0 mmol) in $CHCl_3$ were added slowly to nor·$Mo(CO)_4$ (5.0 mmol) in $CHCl_3$ at 25 °C. ^{31}P NMR spectra were obtained during reaction. Initially, the *cis*-$[(PhN)PCl]_2$–nor·$Mo(CO)_4$ reaction showed a complex resonance group at δ 185.5–193.4. the $[(PhNH)PNPh]_2$–nor·$Mo(CO)_4$ reaction yielded complex resonances in the δ 89–127 region. Spectra of both reactions became more complex with time. Attempts to separate the reaction mixtures by fractional crystallization or thin-layer chromatography were unsuccessful.

Reactions of PhN$(PCl_2)_2$Mo$(CO)_4$ (5). (A) With PhNH$_2$. $PhNH_2$ (20 mmol) in toluene was added slowly to **5** (5.0 mmol) and Et_3N (20 mmol) in toluene at 0 °C. After 10 h at 25 °C, Et_3NHCl was filtered, the filtrate was passed through a 2-cm alumina column, and the solution was evaporated to dryness. Recrystallization from benzene yielded **6**·$^1/_2C_6H_6$ (yield 85%).

(B) With *i*-PrNH$_2$. *i*-$PrNH_2$ (5.0 mmol) and **5** (5.0 mmol) were allowed to react for 10 h in toluene at 25 °C. The ^{31}P NMR spectrum of the reaction solution showed primarily a pair of equal-area doublets

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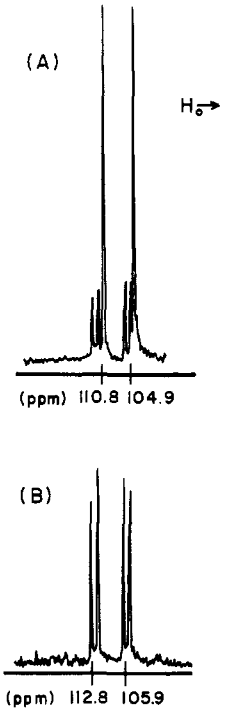

Figure 2. $^{31}P\{^1H\}$ NMR spectra of $PhN(PCl_2)_2Mo(CO)_4$–*i*-$PrNH_2$ reaction product(s) after (A) reagent combination and (B) reaction completion to form **9**

at δ 112.7 and 105.9 ($^2J_{PP}$ = 51.3 Hz) and a small (ca. 10% total area) singlet at δ 110.7. Passage of the reaction solution through a 2-cm aluminum column, evaporation of the solution to dryness in vacuo, and recrystallization from benzene yielded *cis*-*i*-$PrNH[(i\text{-}PrNH)_3(PhNH)P_2]\cdot Mo(CO)_4$ (**9**) (mp 155–175 °C; 69% yield). Anal. Calcd for $C_{22}H_{37}P_2N_5O_4Mo$: C, 44.52; H, 6.24; N, 11.80; P, 10.46. Found: C, 43.58; H, 6.37; N, 11.13; P, 10.16. ^1H NMR (CD_2Cl_2): δ 6.76–7.36 (m, area 5, C_6H_5), 3.20–3.90 (broad s, area 4, NH), 1.45 (d of d, area 4, $^3J_{HNCH}$ = 6.60 Hz, $^4J_{HH}$ = 2.30 Hz, CH), 1.15–1.35 (broad, complex, area 24, CH_3). ^{31}P NMR (C_6D_6): δ 112.8 (d, area 1, $^2J_{PP}$ = 51.3 Hz), 105.9 (d, area 1). MS, parent and most intense envelopes: *m/e* (relative intensity) 595 (25, $C_{22}H_{37}P_2N_5O_4{}^{98}Mo^+$), 511 (57), 424 (33), 390 (30), 365 (38), 147 (43), 92 (46), 58 (100). IR (Nujol), characteristic absorptions: 3375 (w), 2015 (s), 1922 (s), 1909 (s), 1889 (s), 1871 (s), 1280 (m), 1165 (w), 886 (m), 865 (m), 855 (m), cm^{-1}.

In another experiment, the ^{31}P NMR spectrum (Figure 2) was obtained immediately after reagent combination. The spectrum exhibited mainly two singlets at δ 110.8 and 105.9 (**10**) along with the small doublets at δ 112.8 and 105.9 attributable to **9**. When the solution was allowed to stand, the doublets increased in intensity. After removal of volatile reaction materials and redissolution of the solid, the singlets disappeared.

Thermolyses of $PhN[P(NHPh)_2]_2\cdot Mo(CO)_4$ (6). **6** in toluene was heated at 100 °C. After 3 h, the ^{31}P NMR spectrum showed that slight decomposition had occurred. Complex uninterpretable NMR spectral features developed. Further heating resulted in decomposition to intractable uncharacterized products. Heating solid **6** at 130–140 °C in vacuo for 8 h resulted in no decomposition. No sublimation of **6** or evolution of $PhNH_2$ or CO occurred.

Thermolysis of *cis*-$[(PhNH)PNPh]_3\cdot Mo(CO)_4$ (7). **7** in toluene was heated to 100 °C. ^{31}P NMR spectral resonances due to **7** decreased as complex resonances in the δ 90.6–149.4 region appeared. A singlet at δ 94.6 became the largest peak in the spectrum. CO evolution occurred. After 8 h at 100 °C, volatile reaction materials were removed in vacuo. Recrystallization of the solid from benzene or toluene yielded a material enriched in the δ 94.6 peak. Thin-layer chromatographic separation of components was unsuccessful. MS analysis exhibited a complex series of ion envelopes assignable to aminophosphine–molybdenum carbonyl species. The highest detectable ion envelope occurred at *m/e* 798.

Data Collection and Structure Analysis for $6\cdot{}^1/_2C_6H_6$. Data were collected at 295 ± 2 K on a Syntex P$\bar{1}$ automated diffractometer (Mo Kα radiation, graphite monochromator). Crystal data and refinement results are summarized in Table I. The cell parameters were determined on the diffractometer and refined by least-squares fit to 19 centered reflections in the range 21° ≤ 2θ ≤ 35°. Data were collected in shells of increasing 2θ. In the shell from 30 to 35°, less than 8% of the data measured was observed. No further shells were collected. The Mo atom was located by direct methods. Other atoms were located from three-dimensional difference maps. The halves of the molecule are related by a twofold rotation axis. Only the Mo and P atoms were treated anisotropically. All phenyl rings were treated as rigid groups.[18] One of the phenyl rings (Ph3) was found to be disordered and was included in two locations at half-occupancy. The benzene solvent, which was highly disordered, was present in a ratio of one-half molecule of solvent per molecule of **6**. The full ring was included at one -fourth occupancy across a symmetry plane. The hydrogens of **6** were located in three-dimensional difference maps and included in fixed, idealized positions.[19] No attempt

Table I. Summary of Crystal Data for $PhN[P(NHPh)_2]_2Mo(CO)_4\cdot{}^1/_2C_6H_6$ ($6\cdot{}^1/_2C_6H_6$)

formula	$MoP_2N_5O_4C_{37}H_{32}$
fw	768.574
color of cryst	colorless
cryst dimens, mm	0.16 × 0.10 × 0.30
space group	$P6_122$
$a = b$, Å	15.604 (4)
c, Å	28.712 (4)
Z, molecules/cell	6
vol, $Å^3$	6054 (2)
d_{calcd}, g/cm^3	1.26
d_{obsd},[a] g/cm^3	1.22
wavelength, Å	0.710 69
linear abs coeff, cm^{-1}	4.4
hkl range	$+h,\pm k,+l$
$F(000)$	2358
scan mode	θ–2θ
scan speed, deg/min	var, 2.0–24.0
scan width, deg	0.6 below 2θ for $K\alpha_1$ to 0.6 above 2θ for $K\alpha_2$
2θ range, deg	3.0–35.0
no. of total data	3783
no. of unique data	858
R_{eq}	0.10
no. of obsd data, $(F_o)^2 > 3.0\sigma(F_o)^2$	539
abs cor	none
R	0.074
R_w	0.085
goodness of fit for last cycle	2.43

[a] Determined by using flotation methods.

Table II. Positional Parameters for the Nongroup Atoms of $PhN[P(NHPh)_2]_2Mo(CO)_4$ (**6**)

atom	x/a	y/b	z/c	B, $Å^2$
Mo	0.0494 (3)	0.5247	0.0833	6.6[a]
P	0.2035 (7)	0.6407 (7)	0.0415 (3)	4.8[a]
N(1)	0.282 (2)	0.6409	0.0833	4.2 (8)
N(2)	0.245 (2)	0.607 (2)	−0.0035 (8)	5.8 (7)
N(3)	0.239 (2)	0.756 (2)	0.0264 (8)	6.2 (6)
O(1)	−0.101 (2)	0.529 (2)	0.015 (1)	11.8 (9)
O(2)	0.028 (2)	0.677 (2)	0.149 (1)	13 (1)
C(1)	−0.047 (3)	0.525 (3)	0.041 (2)	12 (1)
C(2)	0.034 (3)	0.619 (3)	0.125 (2)	10 (1)
H(1)N(2)	0.312	0.787	0.026	7.4
H(1)N(3)	0.282	0.711	0.166	7.0

[a] B_{eq} is defined by the trace of the $\mathbf{B}_{ij}$ matrix.

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(18) The group coordinates used were as defined by: Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773. The quantity minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum w[(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The standard deviation of an observation of unit weight is defined as $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV the number of variables. The weights, *w*, were calculated from counting statistics as $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$. $\sigma(F_o^2) = RLP\{TSC + BACK + [P(TSC - BACK)]^2\}^{1/2}$, where TSC is the total number of counts accumulated during the measurement scan, BACK is the total number of counts accumulated during the background measurement, and RLP is the reciprocal Lorentz–polarization correction; *P*, a damping factor, was given a value of 0.04: Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563. Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(19) The isotropic thermal parameters for the hydrogens were set to be 1 greater than those of the atom to which they were attached.

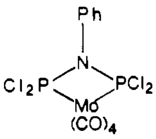
was made to locate solvent hydrogen atoms. All calculations were done by using only observed reflections, and scattering factors were those for neutral atoms.[20] Final positional parameters are given in Table II. Group positional and thermal parameters are given in the supplementary material. All programs were contained in or derived from Syntex (now Nicolet) data reduction routines, the MULTAN 78 package,[21] and the Northwestern University Crystallographic Computing Package of Dr. J. A. Ibers.

Results and Discussion

nor·$Mo(CO)_4$ reacts with the bis(phosphino)amines **1**–**3** and $PhN(PCl_2)_2$ to form *cis*-bis(phosphino)amine $Mo(CO)_4$ complexes **5**–**8** according to

$$cis\text{-nor}\cdot Mo(CO)_4 + NP_2 \xrightarrow[-C_7H_8]{} cis\text{-}NP_2Mo(CO)_4 \qquad (3)$$

NP_2 = bis(phosphino)amines $PhN(PCl_2)_2$, **1**, **2**, **3**



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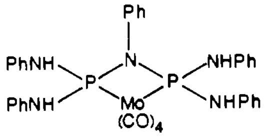

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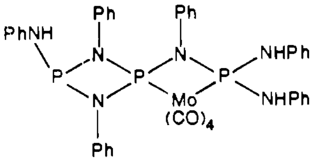

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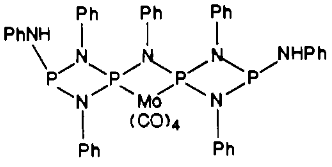

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As reported previously for nor·$Mo(CO)_4$ reactions with monodentate aminophosphines[22–28] or with the bidentate $RN(PF_2)_2$ (R = Me, Ph) ligands,[29,30] reactions proceed smoothly in benzene or toluene at 25 °C. Only slight CO evolution was observed in any system. Examination of the reaction mixtures by ^{31}P NMR spectral analysis indicates that in each case the product isolated is the major product. However, in each reaction small quantities of other products generally were evident. These were not isolated or characterized. They are assumed to be other than simple 1:1 complexes, e.g. bi-monoligated or $PhN[P(NHPh)_2]_2$ bridged dimetal complexes.[30]

Compound **6** has been structurally characterized in the solid by a single-crystal X-ray analysis of the $\mathbf{6}\cdot{}^1/_2C_6H_6$ solvate. Complexes **5**–**8** in solution have been characterized by physical and spectral data. The structure of **6** is shown in Figure 3. Selected structural parameters are listed in Table III. Least-squares planes, deviations of atoms from planes, and dihedral angles between planes are summarized in the supplementary material. **6** consists of a bis(phosphino)amine molecule bonded through the phosphorus atoms to cis positions of the $Mo(CO)_4$ moiety. The MoP_2N ring atoms are crystallographically coplanar. The dihedral angle between the bridging-imido phenyl ring Ph(1) and the MoP_2N plane is 103°. The ring atoms and CO groups have approximate C_{2v} molecular symmetry and are likely distorted from perfect symmetry by crystal-packing forces.

Table III. Structural Parameters for $PhN[P(NHPh)_2]_2Mo(CO)_4$ (**6**)

	Bond Lengths (Å)		
Mo–P	2.48 (1)	N(3)–C(31)A[a]	1.5 (1)
P–N(1)	1.71 (2)	N(3)–C(31)B	1.20 (8)
P–N(2)	1.65 (2)	Mo–C(1)	1.94 (5)
P–N(3)	1.66 (3)	Mo–C(2)	2.01 (5)
N1–C(11)	1.40 (3)	C(1)–O(1)	1.15 (4)
N2–C(21)	1.41 (3)	C(2)–O(2)	1.17 (4)
	Bond Angles (deg)		
Mo–P–N(1)	95.2 (7)	C(1)–Mo–C(1)′	95 (3)
P–Mo–P′[b]	65.8 (2)	C(1)–Mo–C(2)	89 (2)
P–N(1)–P′	104 (2)	C(1)–Mo–C(2)′	83 (2)
Mo–P–N(2)	123 (1)	C(1)′–Mo–C(2)	83 (2)
Mo–P–N(3)	126.0 (1)		
N(2)–P–N(3)	100.0 (1)	C(2)–Mo–C(2)′	168 (2)
N(1)–P–N(2)	99 (1)	C(1)–Mo–P	100 (1)
N(1)–P–N(3)	110 (1)	C(1)–Mo–P′	165 (1)
P–N(1)–C(11)	128 (1)	C(2)–Mo–P	100 (1)
P–N(2)–C(21)	126 (2)	C(2)–Mo–P′	90 (1)
P–N(3)–C(31)A	121 (3)	O(1)–C(1)–Mo	177 (4)
P–N(3)–C(31)B	135 (3)	O(2)–C(2)–Mo	178 (4)

[a] The A and B designations refer to different positions of the disordered phenyl group. [b] Primes designate atoms related by the symmetry operation x, $1.0 + x - y$, $^1/_6 - z$.

The bond distances and angles in **6**, where comparable, are consistent with those reported for other aminophosphine molybdenum(0) complexes. The P–Mo, P–N, Mo–C, and C–O distances are generally within the range observed previously;[31–38] however, because of disorder in the crystal, bond distances accurate enough to allow highly detailed comparisons were not obtained. Deviations from perfect octahedral bonding around Mo are seen and expected. Particularly significant is the small ∠P–Mo–P′ of 65.6° imposed by the limited distortability of the $PhN[P(NHPh)_2]_2$ ligand. Typically larger P–Mo–P angles are seen in bis(phosphino) complexes, e.g. 100.2° in *cis*-$(Et_3P)_2MonCO)_4$.[39] Distortion of CO ligands away from the bis(phosphino)amine unit, i.e. ∠C(1)–Mo–P (100°) and ∠C(2)–Mo–P (100°) and the decreased C–Mo–C angles among the CO units of the $Mo(CO)_4$ moiety are in the direction expected in view of the steric bulk of the $PhN[P(NHPh)_2]_2$ units.

Characterization of **5**–**8** in solution is based upon physical and spectral (^1H and ^{31}P NMR, IR, and MS) data. In addition, the assignment of structures to **5**, **7**, and **8** is aided by comparison of their spectral properties with those of **6** and with the ligands **1**–**4**. Molecular weight measurements by osmometry for **7** and **8** and from mass spectra for **5** confirm their assignment as 1:1 mononuclear complexes. The observation of CO region infrared spectral patterns characteristic of octahedrally based metal tetracarbonyls supports the assignment of **5**–**8** as cis metal complexes.[22,24–26,28,40,41] Assignment of the mode of $Mo(CO)_4$ coordination to **2** or **3** in **7** or **8** can be made from ^{31}P NMR spectral correlations. Of particular interest in **7** and **8** is that coordination of the ligands to the $Mo(CO)_4$ moiety appears to involve exclu-

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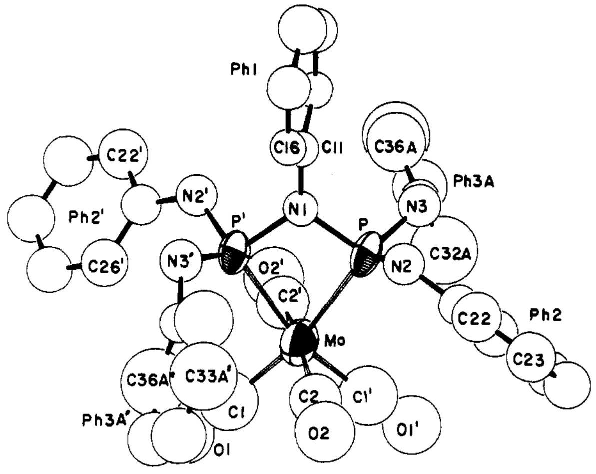
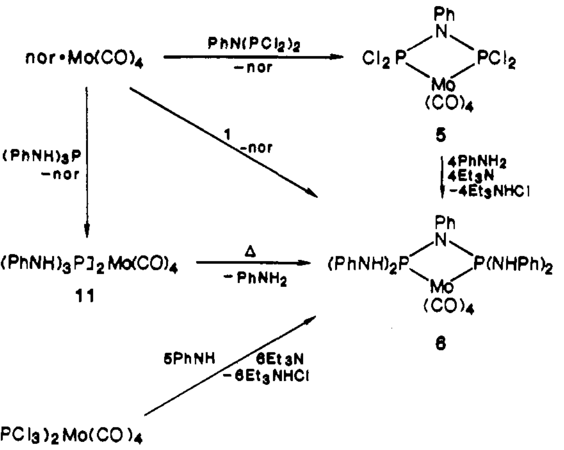


Figure 3. Structure of $PhN[P(NHPh)_2]_2Mo(CO)_4$ (**6**). Thermal ellipsoids are drawn at the 50% probability level. Isotropically refined atoms are shown as open circles. Ph(3B) is omitted for clarity.

sively the >P–N(Ph)–P< unit and does not involve the 1,3,2,4-diazadiphosphetidine rings or the terminal ring phosphorus atoms. The spectrum of **2** is an ABX pattern of resonances at δ 106.9, 109.6, and 62.0 (Figure 1B) assigned to atoms P(1), P(2), and P(3), respectively. Strong coupling in the bis(phosphino)amine unit [$J_{P(2)P(3)}$ = 363 ± 2 Hz] and weak coupling between ring phosphorus atoms ($J_{P(1)P(2)}$ = 12.3 Hz) is observed.[3] Upon coordination of **2** to form **7**, coordination shifts (Δδ) of +20 and +32.5 for the δ 109.6 (to δ 129.6 in **7**) and δ 62.0 (to δ 94.5 in **7**) resonances occur. The remaining resonance at δ 106.9 is shifted slightly to δ 102.7 in **7**. Assuming the phosphorus atoms of **2** coordinated to the $Mo(CO)_4$ unit undergo the large coordination chemical shifts analogous to what has been reported for *cis*-$[(Me_2N)_3P]_2Mo(CO)_4$[23] and the nearly unaffected resonance (Δδ = −4.2) is assigned to P(1), the resonances at δ 129.6 and 94.5 in **7** are assigned to P(2) and P(3), respectively. The $J_{P(2)P(3)}$, value remains large (74.2 Hz), but it is decreased considerably from J = 363 ± 2 Hz in **2**. In a similar way, ^{31}P NMR spectral data with the structure in **8** can be correlated. Ligand **3** exhibits resonances at δ 112.5 and 108.5 assigned to atom pairs P(1), P(4), and P(2), P(3), respectively. Because the δ 112.5 resonance sharpens upon ^1H decoupling, it is assigned to atoms P(1) and P(4), which contain the bonded PhNH groups.[2,4] Similarly in **8**, upon coordination, the δ 108.5 resonance is shifted downfield to δ 132.2. Since the δ 132.2 resonance is not affected by ^1H decoupling and has undergone the coordination shift, it is determined that the associated phosphorus atoms contain no terminal PhNH groups, are the internal P(2), P(3) atoms, and are coordinated to the $Mo(CO)_4$ moiety.

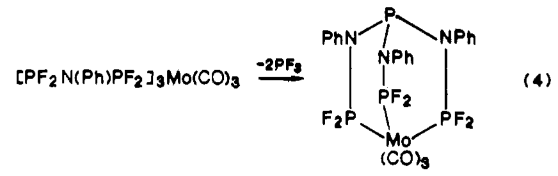
Reactions of $RN(PF_2)_2$ (R = Me, Ph) with metal carbonyls or carbonyl derivatives have been studied extensively recently by King and co-workers.[29–31,34,35] Norbornadiene Group VIB (6)[42] metal tetracarbonyls, nor·$M(CO)_4$ (M = Cr, Mo, W), react with $RN(PF_2)_2$ to form either chelate complexes $RN(PF_2)_2M(CO)_4$ or monoligate monometallic complexes $[RN(PF_2)_2]_2M(CO)_4$, depending on reaction conditions. Further reactions, under thermolysis or photolysis conditions, yielded interesting series of dinuclear species. e.g. $[MeN(PF_2)_2]_4M_2(CO)_3$ and $[MeN(PF_2)_2]_5M_2(CO)$ where M = Mo and W.[29,30] Because we have not yet studied the products of nor·$Mo(CO)_4$–bis(phosphino)amine reactions under a wide variety of reaction conditions, it is unclear whether or not the myriad of products observed in the $RN(PF_2)_2$–metal carbonyl systems will be accessible. Ligands **1**–**3** are likely structurally more bulky than the $RN(PF_2)_2$ ligands and as a result might be less inclined to form stable bis chelate complexes or dinuclear metal complexes.

Scheme I



Complex **6** also forms in high yield by reaction of **5** with $PhNH_2$, in the presence of Et_3N (Scheme I), by reaction of *cis*-$(PCl_3)_2Mo(CO)_4$ with $PhNH_2$ in presence of Et_3N, and by reactions of nor·$Mo(CO)_4$ with $(PhNH)_3P$. Examination of the $(PCl_3)_2Mo(CO)_4$–$PhNH_2$ reaction mixture immediately after reaction shows a major resonance at δ 108.4 tentatively assigned to **11** and a minor resonance at δ 96.1 (**6**). However, upon removal of volatile reaction materials in vacuo, conversion of **11** to **6** occurs. After solvent and $PhNH_2$ are removed, only **6** is present. Further support for the assignment of the δ 108.4 resonance to **11** is obtained when $(PhNH)_3P$ in a $(PhNH)_3P$–$[(PhNH)_2P]_2Ph$ mixture is allowed to react directly with nor·$Mo(CO)_4$. Immediately after reaction, resonances at δ 108.7 and 95.8 are seen. Again, removal of volatile reaction materials results in conversion of **11** to **6**. So far, all attempts to isolate the bis cis complex **11** have failed.

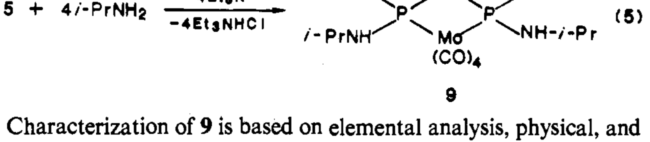
The $(PCl_3)_2Mo(CO)_4$–$PhNH_2$ and $(PhNH)_3P$–nor·$Mo(CO)_4$ reactions are especially interesting because they involve formation of P–N–P bond units at a metal template center. A similar "template" reaction of $[PF_2N(Ph)PF_2]_3Mo(CO)_3$ to form the novel cage complex **12** has been reported previously.[34] It seems likely that reactions of this



12 (4)

type may have considerable utility for the preparation of entire new classes of phosphorus–nitrogen compounds.

Reaction of the alkylamine *i*-$PrNH_2$ with **5** yields the unsymmetrically substituted bis(phosphino)amine complex **9** according to



9 (5)

Characterization of **9** is based on elemental analysis, physical, and spectral data. Crystals satisfactory for X-ray analysis were not obtained. The ^{31}P NMR spectrum exhibits two, coupled doublets at δ 112.8 and 105.9 (J = 51.3 Hz) in the region expected for the phosphorus atoms of a coordinated bis(phosphino)amine, on the basis of comparisons with spectral data for **6**–**8**. Although the ^1H NMR data are complex, they are interpretable in terms

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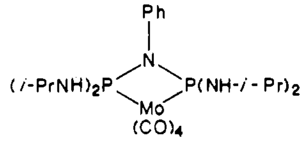
[42] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

of the assigned structure. The resonance at δ 6.76–7.36 (area 5) is due to a phenyl group. The resonance at δ 3.20–3.90 (area 4), δ 1.45 (area 4), and δ 1.15–1.35 (area 24) can be assigned to the NH, CH, and CH_3 protons, respectively.

From ^{31}P NMR spectral data obtained on the **5**–*i*-$PrNH_2$ reaction mixtures at early reaction times, evidence for an intermediate (**10**) in the formation of **9** and an indication of how reaction leads to **9** instead of **13** is obtained. Immediately after mixing of the reagents, the ^{31}P NMR spectrum shows two, equal-area singlets at δ 110.8 and 104.9 (Figure 2A, **10**). After the sample is allowed to stand, these decrease as the doublets increase. After removal of volatile materials and redissolution of product, only **9** (Figure 2B) is seen. The ^1H NMR spectrum of the solution in Figure 2A is complex, although the expected phenyl and *i*-Pr protons are identifiable. On the basis of the available data we suggest tentatively that intermediate **10** is a [triaminophosphine]$_2Mo(CO)_4$ complex formed as



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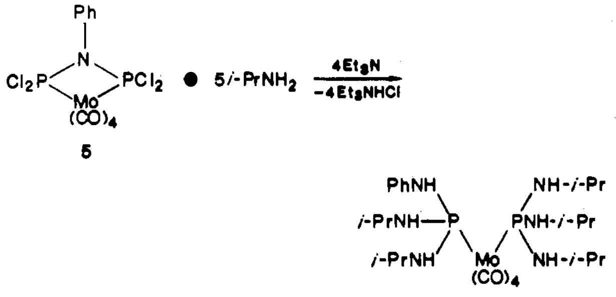

5

10

(6)

Subsequently, upon removal of volatile reaction materials, condensation of **10** to **9** with *i*-$PrNH_2$ elimination occurs. Whether opening of the P_2NMo ring occurs before or after amination of the P–Cl bonds cannot be determined from our data. Why amine elimination from **10** occurs to form the *i*-PrN-bridged product **9** to the exclusion of the PhN-bridged product **12** is unclear. Further studies to determine the generality of this reaction are in progress currently.

Reactions of *cis*-[(PhNH)PNPh]$_2$ (**4**) and *cis*-[(PhN)PCl]$_2$ with nor·$Mo(CO)_4$ are not clean. Reaction in both cases results in solutions with complex ^{31}P NMR spectra, the resonances of which could not be assigned. Whether $Mo(CO)_4$ coordination occurs exclusively at phosphorus, at the diazadiphosphetidine ring, or at both is unclear. The complexity of these reactions stands in contrast to those reported by others[8-11] where discrete diazadiphosphetidine–metal carbonyl complexes are claimed. Further study of diazadiphosphetidine–metal moiety complexation are currently in progress.

Acknowledgment. Support of this work by National Science Foundation Grants CHE-7909497 and CHE-8312856, a Chinese Ministry of Defense Fellowship for H.-J.C., and a grant of computer time from the University of Colorado Computing Center is gratefully acknowledged.

Registry No. **5**, 82991-08-0; **6**$\cdot{}^1/_2(C_6H_6)$, 104130-71-4; **7**, 104130-72-5; **8**, 104130-73-6; **9**, 104130-74-7; **10**, 104130-75-8; nor·$Mo(CO)_4$, 12146-37-1; $(PCl_3)_2Mo(CO)_4$, 16244-51-2; PCl_3, 7719-12-2; $PhNH_2$, 62-53-3; $PhN(PCl_2)_2$, 39652-40-9; *i*-$PrNH_2$, 75-31-0.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters, rigid group derived parameters, planes, equations, and deviations from planes for **6**$\cdot{}^1/_2C_6H_6$ (3 pages); table of structure factors for **6**$\cdot{}^1/_2C_6H_6$ (2 pages). Ordering information is given on any current masthead page.