Transition-Metal-Mediated Reactions of Cyclenphosphorane: Synthesis and Reactivity of HcyclenPMo(CO)$_5$, a Species with a Transannular P- - -N Interaction

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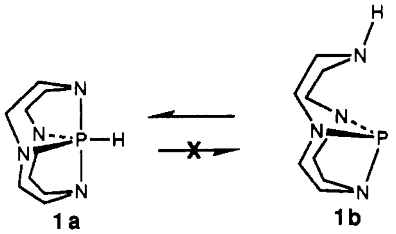
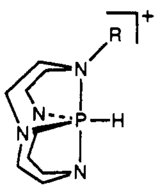
The reaction of cyclenphosphorane (cyclenPH) with Mo(CO)$_6$ in refluxing toluene yields HcyclenPMo(CO)$_5$ (**4**), in which the phosphorus is bonded to the molybdenum. The geometry around phosphorus is best described as a trigonal bipyramid with two nitrogens and the molybdenum at the equatorial positions and two nitrogens at the axial positions. The N–H axial nitrogen interacts with the phosphorus through its lone pair of electrons in a transannular arrangement with a P- - -N distance of 2.356 (23) Å. Reactions of **4** with electrophiles occur for the most part at the secondary amine of the HcyclenP ligand, even though its lone pair is involved in the transannular interaction. Protonation with HBF$_4$ yields [H$_2$cyclenPMo(CO)$_5$]BF$_4$ (**5**), in which the phosphorous is pentacoordinate and both axial nitrogens are protonated, while treatment with THF·BH$_3$ gives H(BH$_3$)cyclenPMo(CO)$_5$ (**6**), the borane adduct of a secondary amine. Reaction of **4** with CF$_3$SO$_3$CH$_3$ in a 2:1 molar ratio yields two products, CH$_3$cyclenPMo(CO)$_5$ (**7**) and [H$_2$cyclenPMo(CO)$_5$]CF$_3$SO$_3$ (**8**). The former is the methyl analogue of the starting material **4**, while the latter contains the same cation as **5**. Treatment of **4** with DMAD results in addition of the N–H across the triple bond to give the enamine (*cis*-CH$_3$O$_2$CCH=CCO$_2$CH$_3$)cyclenPMo(CO)$_5$ (**9**). X-ray data for **9**: C$_{17}$H$_{23}$N$_4$O$_9$PMo, monoclinic, space group $c2/c$, a = 27.10 (3) Å, b = 12.063 (14) Å, c = 14.688 (10) Å, β = 94.12 (7)°, Z = 8, R = 0.029, R_w = 0.028.

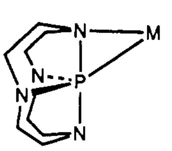
Previous work by Richman and Atkins[1] has shown that cyclenphosphorane (cyclenPH) exists only as the "closed" tautomer **1a**. They have suggested that stabilization of this trigonal-bipyramidal (tbp) form is due to the constraint of the twelve-membered ring, since incorporation of larger tetraaza rings around phosphorus shows the presence of both open and closed tautomers. Thus far, reactions of cyclenPH have yielded a variety of pentacoordinate phosphorus derivatives, as illustrated in structures A–F (M = metal substituent).[2-4] In only two instances has the open form been observed (by bidentate coordination to rhodium and platinum) in η^2-HcyclenPRhClPPh$_3$ (**2**)[5] and (η^2-RcyclenPPtClPPH$_3$)X (**3a**, R = H, X = BF$_4$; **3b**, R = CH$_3$, X = CF$_3$SO$_3$).[2e,f] Even in these cases, subsequent reactions have converted the phosphorus back to the pentacoordinate geometry. In an effort to stabilize the open tautomer of cyclenPH without bidentate coordination and force it to subsequently react in this form, we have selectively complexed the phosphorus to a metal, which results in partial displacement of one of the nitrogens away from the phosphorus. We herein report the synthesis and structure of HcyclenPMo(CO)$_5$ (**4**) as well as its reactivity, which demonstrate the unique ability of the metal substituent to alter reaction pathways at the cyclenP unit. Preliminary accounts of this chemistry have been communicated.[6]



1a **1b** (1)



A
(R = H, CH$_3$)



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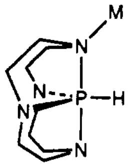

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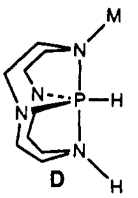
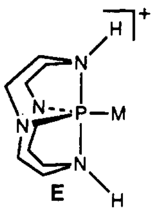
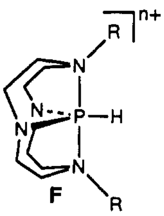


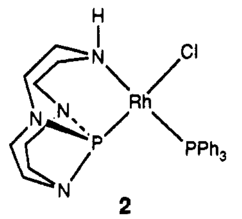
D



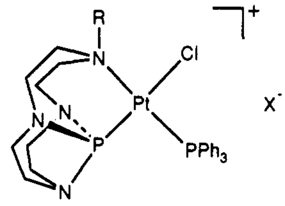
E



F
(R = H, n = 2
R = BH$_3$, n = 0)



2



3a (R = H, X = BF$_4$)
3b (R= CH$_3$, X = CF$_3$SO$_3$)

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[1] (a) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149. (b) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333.

(2) (a) Bouvier, F.; Dupart, J.-M.; Riess, J. G. *Inorg. Chem.* **1988**, *27*, 427. (b) Lattman, M.; Chopra, S. K.; Burns, E. G. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 185. (c) Lattman, M.; Burns, E. G.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Inorg. Chem.* **1987**, *26*, 1926. (d) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M.; *Organometallics* **1986**, *5*, 677. (e) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 681. (f) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 2594. (g) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49/50*, 459.

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Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents $Mo(CO)_6$, 85% $HBF_4 \cdot O(C_2H_5)_2$, 1.0 M $THF \cdot BH_3$, $CF_3SO_3CH_3$, and $CH_3O_2CC{\equiv}CCO_2CH_3$ (DMAD) were obtained commercially and used without further purification, except for $Mo(CO)_6$, which was sublimed prior to use. CyclenPH was prepared by a literature method.[2d] All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.132 (^1H), 81.026 (^{31}P), and 50.327 (^{13}C) MHz. ^{31}P and ^{13}C spectra are proton-decoupled unless otherwise indicated. ^1H resonances were measured relative to residual proton solvent peaks, while ^{13}C resonances were measured relative to solvent peaks (both referenced to Me_4Si). ^{31}P resonances were measured relative to external 85% H_3PO_4. ^{11}B NMR resonances were measured relative to external $BF_3 \cdot O(C_2H_5)_2$. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained either on a Carlo Erba Strumentazione Model 1106 Elemental Analyzer or from Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of HcyclenPMo(CO)$_5$ (4). A solution of cyclenPH (0.20 g, 1.0 mmol) and $Mo(CO)_6$ (0.30 g, 1.13 mmol) was refluxed in toluene (5 mL) for 4 h. The volatiles were then pumped off and the residue recrystallized from hot hexanes (10 mL), yielding **4** as an off-white, air-stable, crystalline solid (0.41 g, 95%). Mp: 110–112 °C. Anal. Calcd for $C_{13}H_{17}MoN_4O_5P$: C, 35.80; H, 3.93; N, 12.84. Found: C, 35.92; H, 3.93; N, 12.95. ^1H NMR ($CDCl_3$): δ 1.47 (br, 1 H), 2.3–3.3 (comp m, 16 H). ^{13}C NMR (THF-d_8): δ 49.3 (CH_2, s), 50.6 (CH_2, s), 50.9 (CH_2, s), 52.5 (CH_2, d, $^2J_{PC}$ = 22 Hz), 207.4 (CO, d, $^2J_{PC}$ = 13 Hz), 212.0 (CO, d, $^2J_{PC}$ = 32 Hz). IR (hexanes, cm^{-1}): ν_{CO} 1945 (vs), 2060 (w); ν_{NH} (KBr) 3400 (vw).

Synthesis of [H$_2$cyclenPMo(CO)$_5$]BF$_4$ (5). A stirred solution of **4** (135 mg, 0.30 mmol) in hexanes (3 mL) was treated dropwise with 85% $HBF_4 \cdot O(C_2H_5)_2$ (48 μL, 0.28 mmol). After stirring for 8 h, the resulting precipitate was filtered, washed with hexanes and ether, and pumped dry to yield **5a** as a white, air-stable, solid (144 mg, 98%). Mp: 185–187 °C dec. Anal. Calcd for $C_{13}H_{18}BF_4MoN_4O_5P$: C, 29.80; H, 3.46; N, 10.69. Found: C, 29.21; H, 3.57; N, 10.74. NMR (CD_3CN): ^1H δ 2.8–3.4 (comp m, 16 H), 4.8 (br, 2 H); ^{13}C δ 45.3 (CH_2, d, $^2J_{PC}$ = 2 Hz), 45.4 (CH_2, d, $^2J_{PC}$ = 2 Hz), 206.1 (CO, d, $^2J_{PC}$ = 13 Hz), 211.0 (CO, d, $^2J_{PC}$ = 41 Hz). IR (CH_3CN, cm^{-1}): ν_{CO} 1937 (vs), 2065 (w).

Synthesis of H(BH$_3$)cyclenPMo(CO)$_5$ (6). A stirred solution of **4** (250 mg, 0.573 mmol) in hexanes at 0 °C was treated dropwise with 1.0 M $THF \cdot BH_3$ (0.57 mL, 0.57 mmol). The reaction mixture was allowed to warm to ambient temperature, and the mixture was stirred for 8 h. The resulting precipitate was filtered, washed with hexanes, and pumped dry to yield **6** as a white, air-stable solid (201 mg, 79%). Mp: 180–182 °C dec. Anal. Calcd for $C_{13}H_{20}BMoN_4O_5P$: C, 34.69; H, 4.48; N, 12.45. Found: C, 33.86; H, 4.63; N, 12.81. NMR ($CDCl_3$): ^1H δ 4.17 (NH, br, 1 H), 2.6–3.6 (CH, comp m, 16 H), 0.8–2.2 (BH, v br); ^{13}C δ 41.5 (CH_2, d, $^2J_{PC}$ = 10 Hz), 47.7 (CH_2, d, $^2J_{PC}$ = 6 Hz), 50.7 (CH_2, s), 52.1 (CH_2, d, $^2J_{PC}$ = 5 Hz), 204.7 (CO, d, $^2J_{PC}$ = 12 Hz), 208.7 (CO, d, $^2J_{PC}$ = 32 Hz); $^{11}B\{^1H\}$ δ −15.3. IR ($CHCl_3$, cm^{-1}): ν_{CO} 1935 (vs), 2060 (w). This product slowly decomposes in solution.

Reaction of 4 with CF$_3$SO$_3$CH$_3$. A stirred solution of **4** (90 mg, 0.21 mmol) in hexanes (10 mL) was treated dropwise with $CF_3SO_3CH_3$ (11.5 μL, 0.10 mmol). Stirring was continued for 18 h, during which time a white precipitate formed. The white precipitate was filtered from the supernatant. The supernatant was evaporated to dryness, yielding CH_3cyclenPMo(CO)$_5$ (**7**) as a white, air-stable solid (42 mg, 93%). Mp: 110–112 °C. Anal. Calcd for $C_{14}H_{19}MoN_4O_5P$: C, 37.35; H, 4.25; N, 12.44. Found: C, 37.48; H, 4.31; N, 12.15. NMR (C_6D_6): ^1H δ 1.8–2.6, 3.1–3.3 (CH_2, comp m), 2.27 (CH_3, s); ^{13}C δ 43.0 (CH_3, s), 48.3 (CH_2, d, $^2J_{PC}$ = 4 Hz), 51.5 (CH_2, s), 53.5 (CH_2, d, $^2J_{PC}$ = 6 Hz), 57.6 (CH_2, s), 206.7 (CO, d, $^2J_{PC}$ = 12 Hz), 210.9 (CO, d, $^2J_{PC}$ = 33 Hz). IR (hexanes, cm^{-1}): ν_{CO} 1939 (vs), 2060 (w).

Table I. Crystal Data and Data Collection Parameters for 9

chem formula	λ(Mo Kα) = 0.710 73 Å
$C_{17}H_{23}N_4O_9PMo$	μ = 6.49 mm^{-1}
fw 554.3	no. of measd reflns 4655
cryst syst monoclinic	no. of unique reflns 4247
space group $C2/c$	no. of obsd reflns 2934
a = 27.10 (3) Å	no. of params refined 310
b = 12.063 (14) Å	data/param ratio 9.5:1
c = 14.688 (10) Å	transm coeff (max, min) 0.571, 0.560
β = 94.12 (7)°	R^a = 0.029
V = 4789 (8) Å^3	R_w = 0.028
Z = 8	k^a = 0.0002
T = 299 K	$F(000)$ = 2256
ρ_{calcd} = 1.537 g cm^{-3}	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$, and $w = 1/[\sigma^2(F_o) + k(F_o)^2]$.

The white precipitate was washed with hexanes and pumped dry to yield [H$_2$cyclenPMo(CO)$_5$]CF$_3$SO$_3$ (**8**) as a white, air-stable solid (65 mg, 100%). Mp: 202–204 °C dec. Anal. Calcd for $C_{14}H_{18}F_3MoN_4O_8PS$: C, 28.68; H, 3.09; N. 9.56. Found: C, 28.52; H, 3.51; N, 9.06. Spectra are similar to **5a**.

Synthesis of (*cis*-CH$_3$O$_2$CCH=CCO$_2$CH$_3$)cyclenPMo(CO)$_5$ (9). A stirred solution of **4** (100 mg, 0.23 mmol) in hexanes (10 mL) was kept at −40 °C in the drybox freezer overnight. After removal from the freezer, DMAD (28 μL, 0.23 mmol) was immediately added dropwise to the stirred solution. The mixture was stirred for 48 h, during which time a precipitate slowly formed. The precipitate was filtered, washed with hexanes, and pumped dry to yield **9** as a brown, air-stable solid (75 mg, 56%). Mp: 158–160 °C dec. Anal. Calcd for $C_{19}H_{23}MoN_4O_9P$: C, 39.46; H, 4.01; N, 9.69. Found: C, 39.92; H, 4.15; N, 9.17. NMR ($CDCl_3$): ^1H δ 2.6–3.9 (CH_2, comp m), 3.61 (CH_3, s), 3.91 (CH_3, s), 4.63 (CH, s); ^{13}C δ 45.6 (CH_2, br), 50.87 (CH_3, s), 51.6 (CH_2, s), 52.2 (CH_2, s), 52.9 (CH_3, s), 54.3 (CH_2, d, $^2J_{PC}$ = 6 Hz), 87.2 (alkene CH, s), 153.7 (alkene CN, s), 165.9 (CO_2, s), 167.4 (CO_2, s), 204.9 (CO, d, $^2J_{PC}$ = 12 Hz), 209.3 (CO, d, $^2J_{PC}$ = 32 Hz). IR (THF, cm^{-1}): ν_{CO} 1938 (vs), 2062 (w).

X-ray Structural Determination and Refinement. Colorless crystals of **9** were grown from a solution of hexanes and THF. Crystals were mounted on an automatic Nicolet R3m/V diffractometer for data collection. The pertinent crystallographic data are summarized in Table I. The unit cell parameters were determined by a least-squares fit of 25 reflections in the range $15 \le 2\theta \le 25°$. The space group assignment was consistent with systematic absences. Three standard reflections were remeasured during the data collection after every 100 reflections; no significant decay was observed. All data were corrected for decay and Lorentz–polarization effects. Data were corrected for absorption based on ψ-scans. The structure was solved by direct methods using SHELXTL-PLUS[7] and subsequent difference Fourier methods. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[8] Full matrix least-squares refinements were carried out by using only the observed reflections $F \ge 6.0\sigma(F)$, the function minimized being $\sum w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were refined anisotropically. All hydrogens were included in the refinement with fixed isotropic thermal parameters. In addition, the hydrogens attached to the CH_2 groups were included in calculated positions by using a riding model. Details of the X-ray data for **4** and **6** can be found elsewhere.[6]

Results

We previously reported[6a] that the reaction of cyclenPH with $Mo(CO)_6$ in refluxing toluene gave the monosubstituted product HcyclenPMo(CO)$_5$ (**4**). The ^{31}P chemical

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(6) (a) Khasnis, D. V.; Lattman, M.; Siriwardane, U.; Chopra, S. K. *J. Am. Soc.* **1989**, *111*, 3103. (b) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *J. Chem. Soc., Chem. Commun.* **1989**, 1538.

(7) Sheldrick, G. M. *SHELXTL-PLUS88, Structure Determination Software Programs*; Nicolet Instrument Corp.: 5225-5 Verona Road, Madison, WI 53711, 1988.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. ^{31}P NMR Data (ppm)

compd	solvent	δ
$HcyclenPMo(CO)_5$ (4)	$CDCl_3$	116
$[H_2cyclenPMo(CO)_5]BF_4$ (5a)	CD_3CN	40
$H(BH_3)cyclenPMo(CO)_5$ (6)	$CDCl_3$	154
$CH_3cyclenPMo(CO)_5$ (7)	C_6D_6	122
$[H_2cyclenPMo(CO)_5]CF_3SO_3$ (8)	CD_3CN	40
(*cis*-RCH=CR)cyclenPMo(CO)$_5$ (9)[a]	$CDCl_3$	134

[a] R = CO_2CH_3.

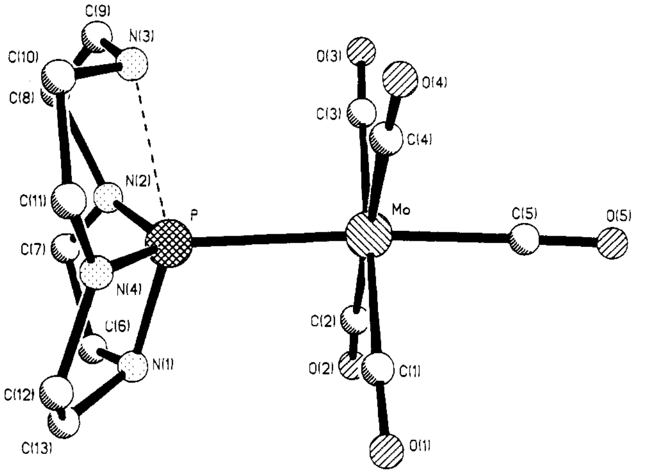
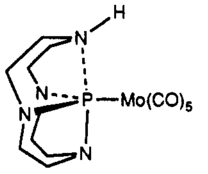


Figure 1. Computer-generated drawing of 4. Hydrogen atoms omitted for clarity.

shift of 4 at +116 ppm (Table II) is about 100–150 ppm further downfield than either cyclenPH (δ −55), or the pentacoordinate cyclenP–metal derivatives (structures A–F), and suggests a lower coordination number for phosphorus. A direct P–Mo bond is supported by the observation of PC coupling to the carbonyl carbons in the ^{13}C NMR spectrum (see Experimental Section). These data support a structure for 4 in which one of the P–N bonds is cleaved and the proton is transfered from phosphorus to nitrogen resulting in an ordinary phosphine–metal derivative. However, the X-ray crystal structure of 4 (Figure 1 and Table III) revealed a unique geometry for the coordinated phosphorus. Instead of the phosphorus being close to tetrahedral, as would be expected for coordinated phosphines, it is a distorted tbp. The Mo, N(2), and N(4) atoms are at the equatorial positions of the phosphorus, while N(1) occupies one axial position. The other axial site is occupied by N(3), which is involved in a transannular interaction with P through its lone pair of electrons. Although the P–N(3) distance of 2.356 (23) Å is about 0.4 Å longer than other P–N axial bonds in related cyclenP–metal derivatives, it is well within the sum of the van der Waals radii. Thus, the cyclen ring has the correct bite to stabilize the tbp geometry around phosphorus and does so in this case via a transannular interaction.



4

The products obtained from the reaction of 4 with Lewis acids turn out to be remarkably acid dependent. For example, treatment of 4 with HBF_4 led to $[(H_2cyclenP)Mo(CO)_5]BF_4$ (5), in which the phosphorus is fully pentacoordinate with both axial nitrogens protonated, whereas with $THF\cdot BH_3$, 4 behaved as a simple secondary amine to give the borane adduct $H(BH_3)cyclenPMo(CO)_5$ (6).[6]

Table III. Selected Bond Lengths (Å) and Angles (deg) for 4, 6, and 9

	4	6	9
Mo–P	2.533 (5)	2.483 (1)	2.503 (3)
P–N(1)	1.809 (20)	1.711 (2)	1.716 (4)
P–N(2)	1.749 (20)	1.707 (2)	1.667 (4)
P–N(3)	2.356 (23)		
P–N(4)	1.666 (20)	1.690 (2)	1.685 (4)
N(3)–B		1.633 (5)	
N(3)–C(14)			1.357 (5)
C(14)–C(15)			1.343 (6)
Mo–P–N(1)	107.7 (7)	117.8 (1)	117.6 (1)
Mo–P–N(2)	117.6 (9)	120.2 (1)	118.7 (1)
Mo–P–N(3)	98.6 (9)		
Mo–P–N(4)	120.4 (8)	117.2 (1)	115.1 (1)
N(1)–P–N(2)	82.8 (11)	93.1 (1)	93.2 (2)
N(1)–P–N(3)	153.5 (13)		
N(1)–P–N(4)	90.7 (9)	94.9 (1)	93.4 (2)
N(2)–P–N(3)	82.0 (12)		
N(2)–P–N(4)	120.8 (12)	108.7 (1)	114.1 (2)
N(3)–P–N(4)	78.8 (13)		
P–N(1)–C(6)	110.6 (18)	110.0 (2)	109.9 (3)
P–N(1)–C(13)	107.1 (17)	107.6 (2)	107.5 (3)
C(6)–N(1)–C(13)	112.1 (25)	114.4 (2)	115.2 (3)
P–N(2)–C(7)	126.6 (22)	109.6 (2)	112.1 (3)
P–N(2)–C(8)	118.7 (16)	121.1 (2)	125.3 (3)
C(7)–N(2)–C(8)	107.5 (20)	120.0 (2)	119.3 (3)
P–N(4)–C(11)	125.6 (20)	122.9 (2)	123.2 (2)
P–N(4)–C(12)	114.0 (16)	111.6 (2)	113.5 (3)
C(11)–N(4)–C(12)	120.4 (23)	121.6 (2)	118.2 (3)
C(9)–N(3)–C(10)	121.4 (25)	114.6 (2)	119.0 (3)
B–N(3)–C(9)		112.3 (2)	
B–N(3)–C(9)		111.8 (2)	
C(9)–N(3)–C(14)			122.0 (3)
C(10)–N(3)–C(14)			118.4 (3)

The isolation of the closed from upon protonation and the open form upon treatment with borane led us to examine other electrophiles to see which form of the cyclenP unit would predominate under different conditions. To our surprise, treatment of 4 with methyl triflate in a 1:1 molar ratio led to two products, 7 and 8, with ^{31}P chemical shifts of 40 and 122 ppm, respectively. These could be separated by their differing solubilities (7 is soluble in hexanes while 8 is soluble in acetonitrile and THF). The spectral properties of 8 were virtually identical with these of 5, suggesting it to be $[H_2cyclenPMo(CO)_5]CF_3SO_3$. The ^1H NMR spectrum of 7 shows a sharp singlet at δ 2.27, supporting the presence of a methyl group. In fact, the identical products were isolated when the reaction was carried out in a 2:1 (4:methyl triflate) ratio, suggesting that 7 is $CH_3cyclenPMo(CO)_5$, the methyl analogue of 4. Elemental analyses also supported this formulation. Methylation appears to induce proton transfer from an intermediate to unreacted 4.

Finally, we attempted a reaction that only a secondary, and not a tertiary, amine would undergo. Addition of the N–H of a secondary amine across the triple bond of an activated alkyne is a well-known route to enamines.[9] The reaction of 4 with DMAD yields a single product, (*cis*-$CH_3O_2CCH{=}CCO_2CH_3$)cyclenPMo(CO)$_5$ (9). Support for this structure comes from the ^1H NMR spectrum: the vinyl proton appears as a singlet at δ 4.63. In addition, the ^{31}P NMR chemical shift is in the open form region while IR and ^{13}C NMR spectra indicate the presence of an intact $Mo(CO)_5$ unit. The structure of 9 was confirmed by X-ray crystallography (see below).

The above reactions are summarized in Scheme I.

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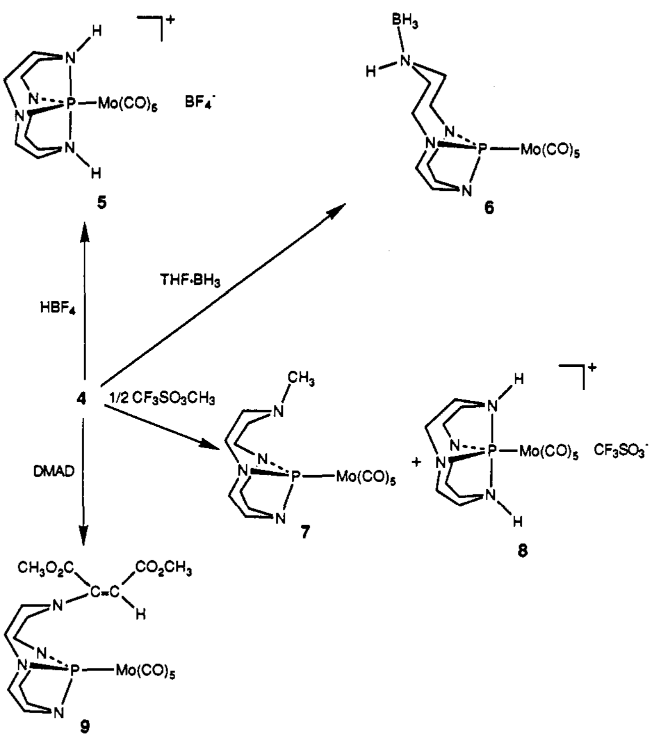
(9) Haynes, L. W. In *Enamines*; Cook, A. G., Ed.; Marcell Dekker: New York, 1969; p 95.

Scheme I

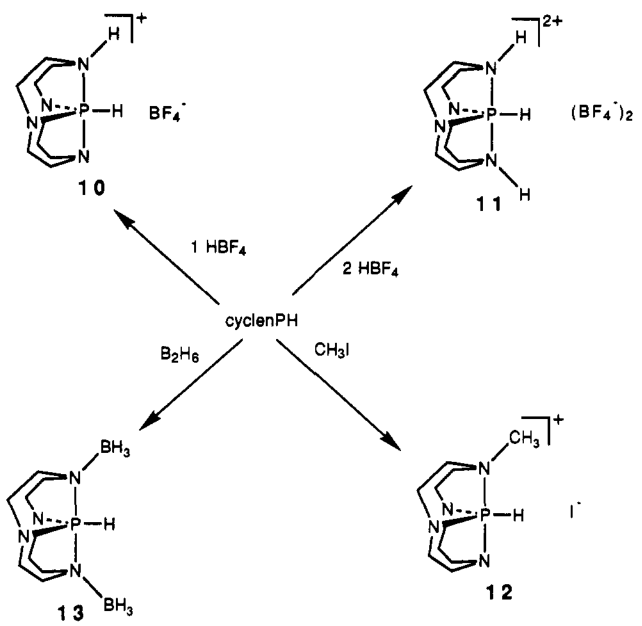


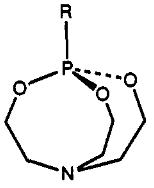
Discussion

The coordination of cyclenPH to Mo(CO)$_5$ transfers the proton from the phosphorus to the nitrogen; subsequent reactivity appears to be dominated by the secondary amine, even though its lone pair participates in the transannular interaction. The reaction of 4 with DMAD looks to be a simple N–H addition across the triple bond of an activated alkyne. Only the cis product is found, which parallels other results that show cis addition to occur in aprotic solvents.[10]

The products obtained from the reactions of 4 with HBF$_4$, methyl triflate, and THF·BH$_3$ can be compared and contrasted with the products **10–13** obtained from cyclenPH and HBF$_4$ (1:1 and 1:2 molar ratios),[2a] methyl iodide,[2a] and diborane,[4] illustrated in Scheme II. Only in the case of addition of 2 mol of HBF$_4$ to cyclenPH and 1 mol to 4 are similar products obtained. Significantly, the ^{31}P NMR chemical shifts of all of the products in Scheme II are in the −20 to −50 ppm range, implying that all contain pentacoordinate phosphorus. Thus, the N(H)- - -P and N(C)- - -P interactions in **10** and **12** are strong enough to form a full bond, while in **4** and **7** they are not, a feature that may be the key to the reactivity of **4**. Why these interactions are different may be related to the ability of other species to form transannular bonds in some cases and not in others. For example, the phosphatranes **14–17** have been reported.[11] In most cases, when R yields an overall neutral compound, no transannular P–N bond is formed (**14**, **16**); where R gives a cationic species, the P–N bond is formed (**15**, **17**). While there are exceptions, it appears that the polarizing ability of the full positive charge is the primary controlling factor in formation of the transannular bond in **14–17**, and may be in **4**, **7**, **10**, and **12**, as well.

Scheme II





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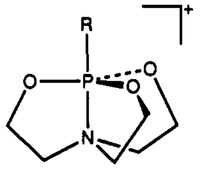

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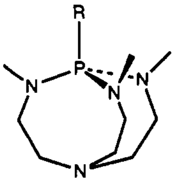

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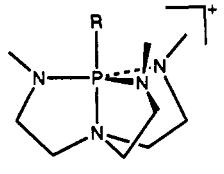

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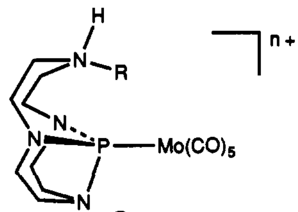
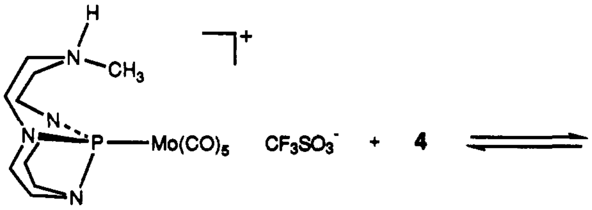


G (n = 0 for BH$_3$, 1 for H, CH$_3$)

Several mechanisms can account for the products observed in the reactions of 4 with HBF$_4$, methyl triflate, and THF·BH$_3$. One is that the initial reaction does occur at the secondary amine lone pair, which is followed by proton transfer. Thus, species G may be formed first. (Note that the stereochemistry of R in structure G is known only for R = BH$_3$; the same stereochemistry is indicated for R = CH$_3$, although there is no firm evidence for this.) With



7 + **8** (2)

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(10) Dolfini, J. E. *J. Org. Chem.* **1965**, *30*, 1298.

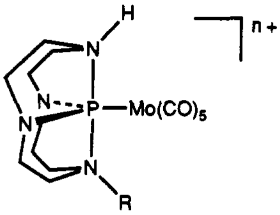
(11) (a) Lensink, C.; Xi, S. K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478. (b) Gudat, D.; Lensink, C.; Schmidt, H.; Xi, S. K.; Verkade, J. G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 21. (c) Carpenter, L. E., II; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084. (d) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607.

$R = H$ or CH_3, proton transfer then occurs to give either **5**, or **7** and **8**. For $R = H$, the transfer could occur either to unreacted **4** or to the other nitrogen in G, while with $R = CH_3$, G would most likely lose a proton to unreacted **4** to give the observed products (reaction 2). This is directly analogous to the addition of an alkyl halide to a secondary amine, in which proton transfer is rapid, to produce equilibrium 4.[12] In the present case (2) is shifted

$$RX + R_2NH \rightarrow R_3NH^+X^- \qquad (3)$$

$$R_3NH^+X^- + R_2NH \rightleftharpoons R_3N + R_2NH_2^+X^- \qquad (4)$$

to the right by the stability of the bis-protonated species (see E and **11**). With $R = BH_3$, proton transfer may not be a favorable process and structure G can be isolated. Another mechanism may involve initial attack at the axial nitrogen "trans" to the N–H to give H. This would give **5** directly. Species H could then either transfer a proton from one axial nitrogen to the other with concomitant cleavage of the P–N(B) bond to form **6** or yield **7** and **8** in a reaction analogous to (2). Alternatively, initial reaction sites may be different in the reactions.



H (n = 0 for BH_3, 1 for H, CH_3)

The metal carbonyl fragment does not appear to take part in these reactions. Moreover, spectral data indicate that the electronics of $Mo(CO)_5$ do not change significantly, even in the cationic derivatives; the C≡O absorption bands in the IR spectra shift by no more than 10 cm^{-1} while the ^{13}C C≡O NMR chemical shifts fall within about a 3 ppm range. Thus, both the geometric and electronic changes are centered at the cyclenP ligand.

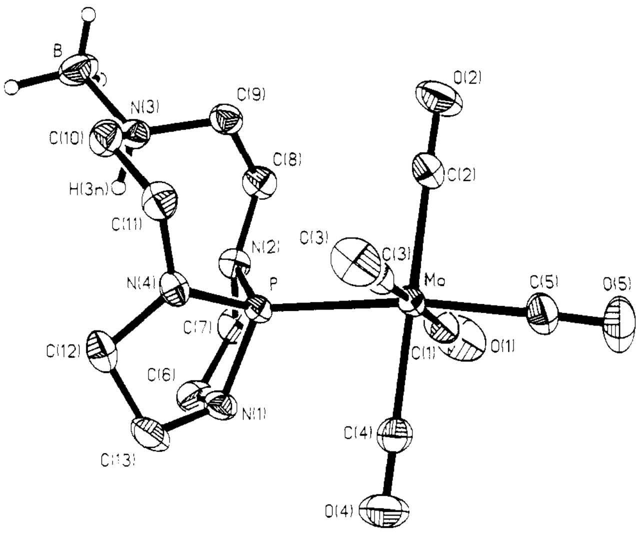


Figure 2. Computer-generated drawing of **6**. Hydrogen atoms omitted for clarity.

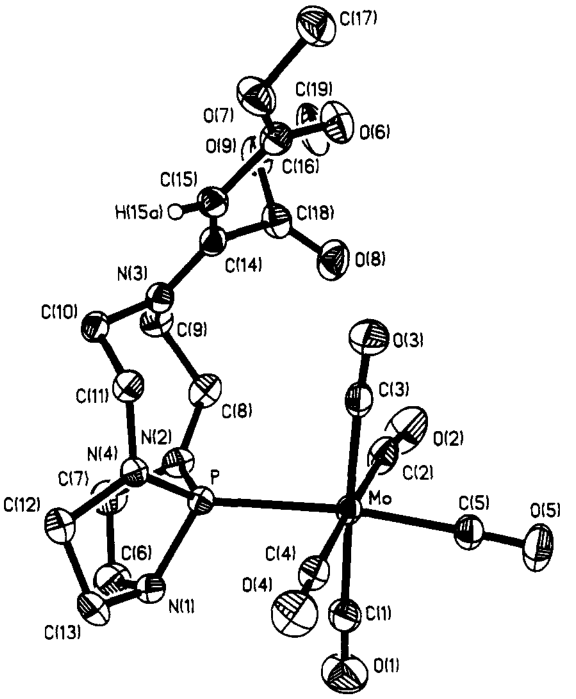


Figure 3. Computer-generated drawing of **9**. Hydrogen atoms omitted for clarity.

The X-ray crystal structures of **6** and **9** are illustrated in Figures 2 and 3, and selected bond angles and lengths are listed in Table III. The most significant differences among the structures of **4**, **6**, and **9** occur in the eight-membered ring containing P and N(3). The transannular interaction in **4** is no longer present in **6** and **9**. In all three derivatives the conformation of the eight-membered ring is different and is best described as a boat–boat form in **4**, a boat–chain form in **6**, and a crown form in **9**. The conversion of the boat–boat to the boat–chair occurs via rotation about the four (C–C and C–N) bonds connected to C(9) and C(10) and most likely results from steric repulsion between the borane and carbonyls in **6**. The elimination of the transannular interaction produces a tilting "up" of the PN_3 unit, which is evident by the sum of the Mo–P–N(2), Mo–P–N(4), and N(2)–P–N(4) angles, which has decreased to 346.1 (2) and 347.9 (2)° in **6** and **9**, respectively. Also, the Mo–P–N(1) angle has increased by about 10° compared to **4**, and the N(2)–P–N(4) angle has decreased to be closer to the tetrahedral geometry. The P–N(1) bond has lost its "hypervalency" in **6** and **9** and has decreased by about 0.1 Å to be more in line with the other P–N bond lengths. The geometry of the two five-membered rings around phosphorus does not vary greatly, and the sums of the bond angles around the nitrogens show that N(1) is close to pyramidal (sum = 330–333°), while N(2) and N(4) are close to planar (sum = 351–360°).[13]

In summary, the complexation of cyclenPH to $Mo(CO)_5$ has demonstrated (1) the ability of the cyclen ring to stabilize the tbp geometry around phosphorus via a transannular interaction in **4**, (2) that this interaction is significantly weaker than in corresponding cationic species where the phosphorus is bound to hydrogen, as in **10** and **12**, and (3) that subsequent reactivity of the complex occurs at the secondary amine, even though its lone pair is involved in the transannular interaction. Although intermediates involving the metal carbonyl fragment cannot be ruled out, it appears that the primary function of the $Mo(CO)_5$ unit is to facilitate transfer of the proton from phosphorus to nitrogen in cyclenPH.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Robert A. Welch Foundation, and SMU (Seed Grant) for generous financial support. We also

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[12] March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New york, 1977; p 378.

[13] The sum of the bond angles around N(3) in **9** shows the enamine nitrogen to be essentially planar. Previous structural studies on enamines have shown nitrogen geometries that vary from planar to pyramidal. See: Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108.

thank Mr. Jonathan M. Burton for assistance in preparing cyclen.

Supplementary Material Available: Tables of full crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, bond distances, bond angles, torsion angles, and hydrogen atom coordinates for **9** (7 pages); tables of observed and calculated structure factors for **9** (16 pages). Ordering information is given on any current masthead page.

Multiple Bonds between Main-Group Elements and Transition Metals. 85.[1] Tetramethyloxoosmium(VI): Synthesis, Gas-Phase Molecular Structure, Photoelectron Spectroscopy, and Electrochemistry

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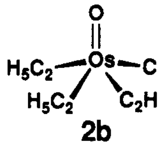
Tetramethyloxoosmium(VI) (**2a**), the first example of methylosmium oxides $(CH_3)_xOs_yO_z$, has been synthesized from osmium tetraoxide (**1a**) and dimethylzinc (19% yield) or methyltris(isopropoxy)titanium (50% yield). A more directed synthesis (60% yield) is methylation of the glycolate osmium(VI) complex $O{=}\overline{Os(OCH_2CH_2O})_2$ (**1b**), which precursor compound is in turn accessible from **1a** in quantitative yield. The thermally labile *ethyl* derivative tetraethyloxoosmium(VI) (**2b**), the first well-characterized example of its class $(C_2H_5)_xOs_yO_z$, is also reported. The title compound **2a** is an orange, air-stable, volatile, crystalline compound that melts at 74 °C without decomposition. The gas-phase average molecular structure of **2a**, as determined by electron diffraction techniques, is consistent with a theoretical model having C_4 symmetry, with the most important parameters being $r_a(Os–C) = 209.6\ (3)$ pm, $r_a\ (Os{=}O) = 168.1\ (4)$ pm, and $\angle(OOsC) = 112.2\ (5)°$. According to PE spectroscopic data, the d ionization of **2a** occurs at 8.55 eV. The title compound **2a** undergoes irreversible oxidation at +2.2 V, reversible reduction at −1.58 V (cyclic voltammetry).

Introduction

Simple organorhenium oxides such as methyltrioxorhenium(VII), CH_3ReO_3, have proven effective catalysts in olefin oxidation, olefin metathesis, and olefination of aldehydes.[2,3] In spite of this rather well-established high-oxidation-state rhenium chemistry, little is known about similar and analogous compounds of any other transition metal.[2,4] Osmium tetraoxide, OsO_4, like dirhenium heptaoxide, Re_2O_7, is soluble in organic solvents. As a consequence of this similarity, one should expect alkyl and aryl derivatives of the type $R_xOs_yO_z$ to be accessible as well. Wilkinson et al.[5] have reported the preparation of the oxoosmium(VI) complexes $[(CH_3)_3SiCH_2]_4OsO$ (12% yield), $[2,4,6\text{-}(CH_3)_3C_6H_2]_2OsO_2$ (29%), and $[2,6\text{-}(CH_3)_2C_6H_3]_2OsO_2$ (44%). Recently, the synthesis of $[(CH_3)_3SiCH_2]_4OsO$ was improved by Shapley et al. (54% yield), who used $[P(C_6H_5)_4]_2[OsO_2Cl_4]$ (two-step preparation OsO_4 (ex), 87% yield) as the starting material.[6] However, no single example of a *methyl*osmium oxide has become known in the literature. In the present paper we describe the first successful, directed synthesis of a most simple organoosmium oxide, $(CH_3)_4OsO$ (**2a**). The ethyl derivative $(C_2H_5)_4OsO$ (**2b**) has been prepared for the sake of comparison with regard to thermal stability. The gas-phase molecular structure of the novel parent compound tetramethyloxoosmium(VI) (**2a**), determined by electron



2b

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[‖] Universität Frankfurt am Main.

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