Trapping of a Phosphenium Ion and an Activated Alkyne into the Metal–Nitrogen Bond of Li[(η^2-cyclenP)Mo(CO)$_4$]. Insertion Reactions?

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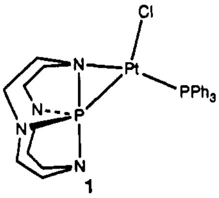
Deprotonation of HcyclenPMo(CO)$_5$ (**3**) with butyllithium leads to Li[(η^2-cyclenP)Mo(CO)$_4$] (**4**), which features a strained three-membered P—N—Mo ring. Isolation of butane indicates the reaction proceeds via deprotonation and loss of carbon monoxide rather than through an acyl complex intermediate. The N–Mo bond in **4** is readily cleaved by reaction with chlorodiphenylphosphine or dimethyl acetylenedicarboxylate (DMAD) leading to apparent insertion products of a phosphenium ion, (η^2-Ph$_2$PcyclenP)Mo(CO)$_4$ (**6**), and an alkyne, Li{[η^2-(MeO$_2$C)C═C(CO$_2$Me)cyclenP]Mo(CO)$_4$} (**7**). The X-ray crystal structure of **6** was obtained: $C_{24}H_{26}N_4O_4P_2Mo$, fw 592.4, monoclinic, $P2_1/n$, a = 13.108 (3) Å, b = 13.782 (3) Å, c = 15.168 (4) Å, β = 113.36 (2)°, V = 2515 (1) Å^3, Z = 4, R = 0.028, R_w = 0.041.

Our recent work with strained P–N–M three-membered ring systems[1] has demonstrated unusual reactivity for the nitrogen: although the nitrogen is four-coordinate, it behaves as if it has amide character. For example, treatment of (η^2-cyclenP)Pt(Cl)PPh$_3$ (**1**) with electrophiles can lead to P–N bond cleavage giving **2**.[1d] We sought to take advantage of the strained ring to demonstrate insertion into the N–M bond, since it has been suggested that reactions involving insertions of small molecules into amide–metal bonds are important in catalysis and organic synthesis.[2] However, due to the lability of the chloride and PPh$_3$ ligands, we were unable to substantiate insertion into the P–N–Pt ring of **1**.[3] In order to maximize chances of obtaining isolable insertion products, a system which exhibited enhanced ring reactivity while simultaneously incorporating other less labile ligands needed to be synthesized. We chose as our starting material HcyclenPMo(CO)$_5$ (**3**) (synthesized from cyclenPH and molybdenum hexacarbonyl) since previous reactivity demonstrated that the carbonyls, at least under electrophilic reaction conditions, were inert.[4]



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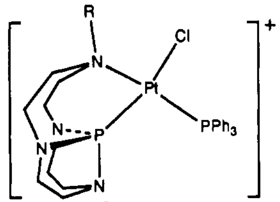
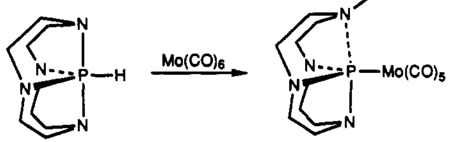


2 (R = H, Me)



cyclenPH **3** (1)

We herein report the synthesis of the first anionic η^2-cyclenPM (M = transition metal) derivative and its subsequent reactivity with chlorodiphenylphosphine and the activated alkyne dimethylacetylenedicarboxylate (DMAD) which lead to apparent insertion products.

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 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 starting material **3** was synthesized according to literature procedures. The reagents butyllithium (1.6 M in hexanes) chlorodiphenylphosphine (distilled prior to use), and DMAD were obtained commercially. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.132 (^{1}H), 50.327 (^{13}C), and 81.026 (^{31}P) MHz. ^{1}H resonances were measured relative to residual proton solvent peaks and referenced to Me$_4$Si. ^{13}C resonances were measured relative to solvent peaks and referenced to Me$_4$Si. ^{31}P resonances were measured relative to external 85% H$_3$PO$_4$. ^{13}C NMR spectra are proton-decoupled unless otherwise indicated. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

Li[(η^2-cyclenP)Mo(CO)$_4$] (4). A solution of **3** (150 mg, 0.330 mmol) in THF (2 mL) was treated dropwise with 1.6 M butyllithium in hexanes (255 μL, 0.38 mmol). After stirring for 18 h, 30 mL of hexanes was layered on top of the solution and allowed to slowly diffuse in. The resulting precipitate was filtered out, washed with hexanes, and allowed to dry, yielding **4** as a yellow powder (75 mg) which slowly decomposes in both the solid state and in solution. NMR (THF-d_8): ^{1}H δ 2.5–3.3 (comp m); ^{13}C (non-C≡O) δ 45.7 (CH$_2$, d, $^2J_{PC}$ = 14 Hz), 46.0 (CH$_2$, s), 50.5 (CH$_2$, s), 59.2 (CH$_2$, s). Isolation and identification of the butane product was accomplished by the following procedure. A 50-mL two-neck flask, equipped with a stir bar, vacuum stopcock, and septum, was charged with a solution of **3** (225 mg, 0.528 mmol) in THF (5 mL). The solution was frozen in liquid nitrogen and treated with 1.6 M butyllithium in hexanes (310 μL, 0.50 mmol). While frozen, the vessel was evacuated. The stopcock was then shut and the mixture allowed to warm to room temperature while stirring. After 3 h, the volatiles of the reaction were pumped onto

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[1] (a) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (b) de Meester, P.; Lattman, M.; Chu, S. S. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 162. (c) Lattman, M.; Burns, E. G.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Inorg. Chem.* **1987**, *26*, 1926. (d) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 681. (e) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 2594. (f) Siriwardane, U.; Khasnis, D. V.; Lattman, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *C45*, 1628. (g) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Phosphorus Sulfur Silicon* **1990**, *49/50*, 459. (h) Khasnis, D. V.; Lattman, M.; Siriwardane, U.; Zhang, H. *Organometallics*, in press.

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Table I. Crystal Data and Data Collection Parameters for 6

chem formula:	$C_{24}H_{26}N_4O_4P_2Mo$
fw =	592.4
cryst syst:	monoclinic
space group:	$P2_1/n$
a =	13.108 (3) Å
b =	13.782 (3) Å
c =	15.168 (4) Å
β =	113.36 (2)°
V =	2515 (1) Å^3
Z =	4
T =	293 K
ρ_{calcd} =	1.56 g cm^{-3}
λ(Mo Kα) =	0.71073 Å
cryst dimens:	0.20 × 0.35 × 0.15 mm
μ =	6.70 cm^{-1}
scan mode:	$\theta/2\theta$
2θ(min, max) =	3.0, 46.0°
h range:	$-14 \rightarrow +13$
k range:	$0 \rightarrow 15$
l range:	$0 \rightarrow 16$
no. of measd reflns:	3880
no. of unique reflns:	3516
no. of obsd reflns:	3039
no. of params refined:	316
GOF =	1.40
data/param ratio:	9.6/1
transmission coeff (max, min):	0.869, 0.698
R^a =	0.028
R_w =	0.041
$F(000)$ =	1208
residual elec dens (max, min):	0.53, −0.40 e Å^3

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$, and $w = 1/[\sigma^2(F_o) + 0.0006(F_o)^2]$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)^a
Mo	489 (1)	9275 (1)	7951 (1)	31 (1)
P(1)	729 (1)	7728 (1)	7253 (1)	40 (1)
P(2)	−1543 (1)	8936 (1)	6999 (1)	30 (1)
O(1)	471 (3)	10377 (3)	6112 (2)	88 (1)
O(2)	324 (3)	11293 (2)	8841 (2)	82 (1)
O(3)	636 (2)	8063 (2)	9772 (2)	74 (1)
O(4)	3088 (2)	9412 (2)	8930 (2)	67 (1)
C(1)	477 (3)	9971 (3)	6772 (3)	49 (1)
C(2)	349 (3)	10547 (3)	8522 (3)	47 (1)
C(3)	549 (3)	8515 (3)	9111 (2)	44 (1)
C(4)	2139 (3)	9370 (2)	8578 (2)	42 (1)
N(5)	2029 (2)	7227 (3)	7587 (2)	63 (1)
C(6)	1951 (3)	6171 (3)	7745 (3)	71 (2)
C(7)	773 (3)	5867 (3)	7390 (3)	65 (2)
N(8)	190 (2)	6720 (2)	7506 (2)	44 (1)
C(9)	−892 (3)	6672 (2)	7560 (2)	45 (1)
C(10)	−1863 (3)	6957 (2)	6638 (3)	45 (1)
N(11)	−1780 (2)	7929 (2)	6291 (2)	35 (1)
C(12)	−1591 (3)	8001 (3)	5392 (2)	50 (1)
C(13)	−600 (3)	7464 (3)	5355 (3)	61 (2)
N(14)	453 (3)	7755 (2)	6047 (2)	54 (1)
C(15)	1423 (4)	7350 (4)	5889 (3)	89 (3)
C(16)	2400 (3)	7472 (4)	6828 (3)	89 (2)
C(17)	−2477 (2)	8802 (2)	7627 (2)	33 (1)
C(18)	−2172 (3)	9219 (2)	8530 (2)	40 (1)
C(19)	−2910 (3)	9244 (2)	8978 (3)	50 (2)
C(20)	−3951 (3)	8839 (3)	8538 (3)	55 (2)
C(21)	−4256 (3)	8412 (3)	7651 (3)	53 (2)
C(22)	−3536 (3)	8390 (2)	7188 (2)	41 (1)
C(23)	−2353 (2)	9867 (2)	6144 (2)	34 (1)
C(24)	−2056 (3)	10844 (2)	6356 (2)	38 (1)
C(25)	−2708 (3)	11567 (2)	5779 (2)	46 (1)
C(26)	−3641 (3)	11355 (3)	4974 (2)	48 (1)
C(27)	−3936 (3)	10397 (3)	4750 (2)	48 (1)
C(28)	−3301 (3)	9653 (2)	5331 (2)	43 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the vacuum line and separated by trap-to-trap distillation through −78, −95, and −198 °C traps. IR analysis of the −198 °C trap revealed a mixture of THF and hydrocarbons. The contents of this trap were redistilled through a −131 °C trap. What passed through was identified as pure butane (0.25 mmol) by IR and vapor pressure measurements. While this represents a 50% yield based on stoichiometry, the reaction does not go to completion (see Results and Discussion).

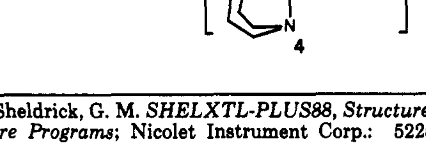
(η^2-Ph$_2$PcyclenP)Mo(CO)$_4$ (6). A solution of 3 (150 mg, 0.330 mmol) in THF (3 mL) was treated dropwise with 1.6 M butyllithium in hexanes (220 μL, 0.33 mmol). After stirring for 8 h, the reaction mixture was treated dropwise with ClPPh$_2$ (60 μL, 0.33 mmol). The resulting mixture was stirred for 6 h and filtered. The solid product was washed with THF and ether and pumped dry to yield 6 as an air-stable, white solid (80 mg, 40% based on 3). Dec pt: 210–212 °C. Anal. Calcd for $C_{24}H_{26}MoN_4O_4P_2$: C, 48.66; H, 4.42; N, 9.46. Found: C, 48.51; H, 4.34; N, 9.35. NMR (CD$_2$Cl$_2$/DMSO-d_6): ^{1}H δ 2.7–3.6 (CH$_2$, comp m, 16 H), 7.5 and 8.0 (CH, comp m, 10 H); ^{13}C (non-C≡O) δ 47.2 (CH$_2$, s), 50.8 (CH$_2$, s), 51.6 (CH$_2$, s), 52.2 (CH$_2$, d, $^2J_{PC}$ = 3 Hz), 128.5 (CH, d, J_{PC} = 10 Hz), 130.6 (CH, s), 132.2 (CH, d, J_{PC} = 16 Hz), 137.8 (CH, d, $^1J_{PC}$ = 25 Hz).

Li{[η^2-(CO$_2$Me)C═C(CO$_2$Me)cyclenP]Mo(CO)$_4$} (7). A solution of 4 (110 mg, 0.256 mmol), isolated according to the above procedure, in THF (1 mL) was treated dropwise with DMAD (32 μL, 0.26 mmol). After 1 h of stirring, the ^{31}P NMR spectrum indicated the reaction was complete. The reaction mixture was stirred for another 8 h, and then the volatiles were pumped off. The solid was washed with benzene and hexanes, and pumped dry to yield 7 as a THF-solvated, air-sensitive, brown solid. The ^{1}H NMR spectrum in CD$_3$OD indicated an approximate 7·2THF complex (115 mg, 64% based on unsolvated 4). Dec pt: 245–247 °C. Anal. Calcd for $C_{18}H_{22}LiMoN_4O_8P{\cdot}C_8H_{16}O_2$: C, 44.58; H, 5.47; N, 8.00. Found: C, 44.28; H, 5.26; N, 7.43. NMR (THF-d_8): ^{1}H δ 2.7–3.2 (CH$_2$, comp m, 16 H), 3.53 and 3.65 (CH$_3$, s, 6 H); ^{13}C (non-C≡O) δ 47.7 (CH$_2$, s), 49.6 (CH$_2$, s), 50.9 (CH$_3$, s), 51.5 (CH$_3$, s), 56.2 (CH$_2$, s), 133.3 (alkene CN, d, $^3J_{PC}$ = 7 Hz), 162.8 (CO$_2$, d, $^4J_{PC}$ = 4 Hz), 184.0 (CO$_2$, d, $^3J_{PC}$ = 4 Hz), 206.9 (alkene CMo, d, $^2J_{PC}$ = 11 Hz).

X-ray Structure Determination and Refinement. Crystals of 6 were grown from a solution of CH$_2$Cl$_2$/Et$_2$O. A suitable colorless, plate-shaped crystal was mounted on a Nicolet R$_{3m}$/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 $15 \leq 2\theta \leq 25°$. 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 Lorentz and polarization effects. Data were corrected for absorption on the basis of ψ-scans. The structure was solved by heavy-atom methods using SHELXTL-PLUS[5] and subsequent difference Fourier methods. Neutral-atom scattering factors and corrections of anomalous dispersion for heavy atoms were from common sources.[6] Full-matrix least-squares refinements were carried out using only the observed reflections [$I > 3.0\sigma(I)$], the function minimized being $\sum w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were refined anisotropically. All hydrogens were included in calculated positions with fixed isotropic thermal parameters. Atomic coordinates are listed in Table II.

Results and Discussion

Treatment of 3 with butyllithium leads to Li[(η^2-cyclenP)Mo(CO)$_4$] (4) (reaction 2). The ^{31}P chemical shift of



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(2)

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[6] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

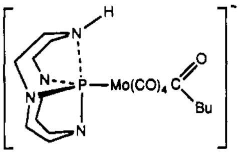
Table III. Selected NMR [ppm (Hz)] and IR (cm^{-1}) Data for Compounds[a]

cmpd	$\delta(^{31}P)$	$\delta(^{13}C_{C\equiv O})$ $(^2J_{PC})$	$\nu_{C\equiv O}$
3[b]	116	207.4 (13), 212.0 (32)	1945 (vs), 2060 (w)
4	20	218.0 (17), 224.0 (30), 228.6 (12)	1815 (vs), 1860 (vs), 1885 (sh), 1938 (m), 1990 (s)
6	99 (PC) 148 (PN) ($^2J_{PP}$ = 40)	210.8 (11, 11), 215.9 (11, 27), 217.3 (10, 35)	1900 (vs), 1920 (sh), 2015 (s)
7	128	213.6 (11), 221.4 (11), 223.0 (48)	1833 (vs), 1869 (sh), 1881 (vs), 1943 (m), 1992 (s)

[a] Solvents: IR spectra in THF; NMR spectra in THF-d_8 (**4** and **7**) and CD_2Cl_2/DMSO-d_6 (**6**). [a] Data from ref 4.

4 is at δ 20 which is 96 ppm further upfield than that of **3** (Table III), indicative of a full P—N bond rather than the transannular interaction found in **3** [P---N(H) distance 2.36 Å]. This chemical shift is in the same range as that for the neutral derivative (η^2-cyclenP)MoCp(CO)$_2$ (δ -1).[1a] In addition, both the IR and ^{13}C NMR spectra of **4** indicate a lower symmetry in the C≡O region, while the downfield shift in the ^{13}C resonances (each showing P—C coupling) and the lower values for $\nu_{C\equiv O}$ support its anionic nature. Although spectra indicate **4** to be the sole product, the reaction does not go to completion. For example, if **3** and butyllithium are mixed in a 1:1 ratio, the ^{31}P NMR spectrum indicates only about a 65% conversion. This percentage increases slightly with the addition of excess butyllithium but is still not complete even with a 2-fold excess of butyllithium.

The fact that **3** contains N-H as well as carbonyl functionalities brings up the question as to the mechanism by which **4** is formed. Metal carbonyls are known to react with alkyllithium reagents to yield acyl complexes.[7] If such a pathway is operable here, the acyl complex **5** should eliminate pentanal to give **4**. However, if **3** is directly deprotonated by butyllithium, followed by nitrogen attack at the metal, butane and carbon monoxide would be given off. Since butane can be isolated from the reaction mixture (see Experimental Section), the reaction proceeds via the latter pathway.



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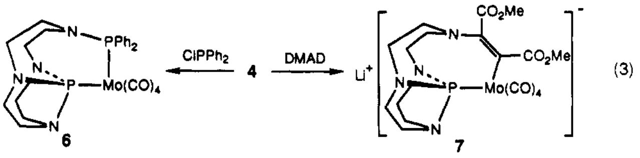
The negative charge on the anion of **4**, as well as the potential for salt elimination, should promote the reactivity of the P—N—M three-membered ring relative to previous neutral systems.[1] In fact, addition of chlorodiphenylphosphine to **4** leads to a species **6** having two different phosphorus atoms [$\delta(^{31}P)$ 99 (PC) and 148 (PN)] with a P—P coupling constant of 40 Hz. This coupling is reasonable for a cis arrangement of phosphorus atoms around molybdenum, and the downfield shift for the cyclenP phosphorus is indicative of P—N bond cleavage. Moreover, the $\nu_{C\equiv O}$ values have increased relative to **4**, while the ^{13}C C≡O resonances are further upfield and show couplings due to two inequivalent phosphorus atoms.

In essence, **6** is the product of the insertion of a phosphenium ion (R_2P:$^+$) into the Mo–N bond. This results in conversion of the bidentate four-electron (anionic) donor cyclenP:$^-$ ligand into a chelating diphosphine. The formulation of **6** was confirmed by an X-ray crystal structure which is shown in Figure 1; selected bond distances and angles are found in Table IV. The geometry around Mo



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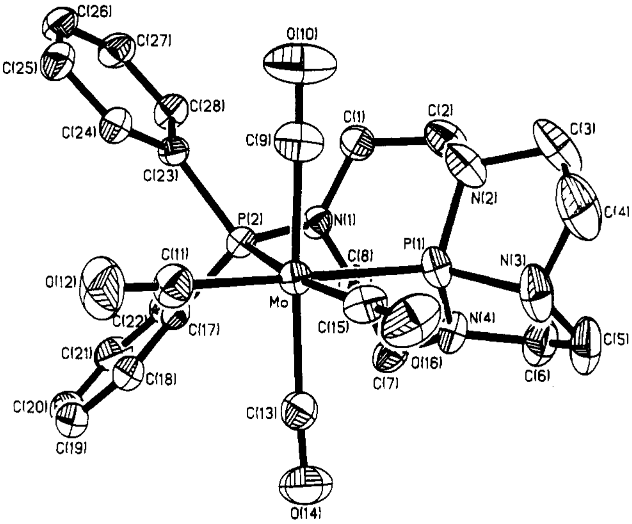

Figure 1. Computer-generated drawing of **6**. Hydrogen atoms omitted for clarity.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Mo–P(1)	2.456 (1)	Mo–P(2)	2.159 (1)
Mo–C(9)	2.024 (4)	Mo–C(11)	1.996 (4)
Mo–C(13)	2.021 (4)	Mo–C(15)	1.991 (4)
P(1)–N(2)	1.718 (3)	P(1)–N(3)	1.718 (3)
P(1)–N(4)	1.671 (3)	P(2)–N(1)	1.707 (3)
P(2)–C(17)	1.835 (4)	P(2)–C(23)	1.834 (3)
N(1)–C(1)	1.482 (5)	N(1)–C(8)	1.459 (4)
N(2)–C(2)	1.421 (4)	N(2)–C(3)	1.492 (7)
N(3)–C(4)	1.457 (7)	N(3)–C(5)	1.485 (6)
N(4)–C(6)	1.451 (5)	N(4)–C(7)	1.454 (5)
C(1)–C(2)	1.516 (6)	C(3)–C(4)	1.500 (6)
C(5)–C(6)	1.479 (6)	C(7)–C(8)	1.522 (4)
C(9)–O(10)	1.144 (5)	C(11)–O(12)	1.142 (5)
C(13)–O(14)	1.148 (5)	C(15)–O(16)	1.144 (4)
P(1)–Mo–P(2)	83.0 (1)	P(1)–Mo–C(9)	89.3 (1)
P(2)–Mo–C(9)	86.8 (1)	P(1)–Mo–C(11)	177.9 (1)
P(2)–Mo–C(11)	98.8 (1)	C(9)–Mo–C(11)	89.8 (2)
P(1)–Mo–C(13)	87.6 (1)	P(2)–Mo–C(13)	94.0 (1)
C(9)–Mo–C(13)	176.7 (2)	C(11)–Mo–C(13)	93.2 (2)
P(1)–Mo–C(15)	87.8 (1)	P(2)–Mo–C(15)	170.6 (1)
C(9)–Mo–C(15)	91.0 (1)	C(11)–Mo–C(15)	90.3 (1)
C(13)–Mo–C(15)	87.6 (1)	Mo–P(1)–N(2)	115.6 (1)
Mo–P(1)–N(3)	120.2 (1)	N(2)–P(1)–N(3)	95.1 (2)
Mo–P(1)–N(4)	119.0 (1)	N(2)–P(1)–N(4)	109.5 (1)
N(3)–P(1)–N(4)	93.3 (2)	Mo–P(2)–N(1)	113.5 (1)
Mo–P(2)–C(17)	119.5 (1)	N(1)–P(2)–C(17)	104.6 (1)
Mo–P(2)–C(23)	117.4 (1)	N(1)–P(2)–C(23)	102.4 (1)
C(17)–P(2)–C(23)	96.8 (1)	P(2)–N(1)–C(1)	118.0 (2)
P(2)–N(1)–C(8)	122.7 (2)	C(1)–N(1)–C(8)	117.2 (3)
P(1)–N(2)–C(2)	120.8 (3)	P(1)–N(2)–C(3)	109.3 (2)
C(2)–N(2)–C(3)	114.5 (3)	P(1)–N(3)–C(4)	106.0 (3)
P(1)–N(3)–C(5)	108.5 (3)	C(4)–N(3)–C(5)	114.9 (4)
P(1)–N(4)–C(6)	110.8 (3)	P(1)–N(4)–C(7)	124.1 (2)
C(6)–N(4)–C(7)	122.9 (3)	Mo–C(11)–O(12)	175.9 (4)
Mo–C(9)–O(10)	179.1 (3)	Mo–C(15)–O(16)	179.0 (3)
Mo–C(13)–O(14)	176.3 (3)		

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(7) Coleman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

is best described as distorted octahedral, while P(1) and P(2) are distorted tetrahedra. The geometry around N(1) is close to planar [sum of the bond angles = 357.9 (4)°] and is typical of aminophosphorus groups in which the nitrogen is relatively unconstrained (for example, not incorporated into small rings that may impose steric restrictions on geometry). The distance between P(1) and N(1) of 3.035 (3) Å indicates no significant interaction and far exceeds the corresponding distances in either the three-membered ring system such as **1** (ca. 1.9 Å)[1c] or transannulated **3** (2.36 Å). A significant trend is observed between the phosphorus chemical shift and the P–N distance: as the distance increases, the chemical shift moves further downfield, with the largest change occurring when going from a full P–N bond in **4** to a transannulated interaction in **3**.

The driving force for formation of **6** could be the elimination of lithium chloride; however, amide—metal bonds are known to insert a variety of organic molecules, particularly 1,2-dipoles.[2,8] Treatment of **4** with DMAD, an incipient 1,2-dipole, leads to a species **7** with a phosphorus chemical shift at δ 128, again indicative of P—N bond rupture. The IR and ^{13}C NMR spectra in the $C{=}O$ region are similar to **4**. Of the six additional resonances in the ^{13}C NMR spectrum, four show P—C coupling, which is readily explained by the insertion of DMAD into the Mo—N bond to give a metalated enamine. In fact, the additional carbon resonances for the alkene moiety are very close to those for another DMAD-inserted complex, $Cp_2Nb(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(CO_2Me)C{=}C(CO_2Me)H$.[9]

At this point, the mechanisms of the reactions involving the strained P–N–Mo ring are unknown. The traditional view of insertions into amide–metal bonds involves either the nitrogen initially forming a bond with the incoming electrophilic center in a stepwise reaction or a concerted path via a multicenter transition state.[8a] Either of these mechanisms may be operating in this system due to the unique geometry about the metalated nitrogen: previous structures on related systems have shown that the nitrogen is almost coplanar with the two methylene carbons and the metal to which it is bonded.[1] This should leave significant electron density above the plane, "trans" to the phosphorus, for amide-like behavior. However, alternative pathways are possible such as initial binding of the other axial nitrogen[10] to the incoming phosphine or alkyne, followed by rearrangement. (Our previous work[1,4,10] has shown that nitrogen reactivity occurs exclusively at the axial nitrogens of the cyclenP moiety.) If this latter pathway is operable, the observed products might be considered "formal" insertions.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates (4 pages). Ordering information is given on any current masthead page.

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(10) (a) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* 1990, *29*, 271. (b) Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M. *Organometallics* 1986, *5*, 2383.

Tetraaza Macrocyclic Derivatives of Arsenic: HcyclenAs, HcyclenAs·GaMe$_3$, and HcyclamAs

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Treatment of cyclen, a 12-atom tetraaza macrocycle, with tris(dimethylamino)arsine leads to HcyclenAs, the structure of which is best described as a distorted pseudo trigonal bipyramid (tbp) with two nitrogens and a lone pair of electrons at the equatorial positions and two nitrogens at the axial sites. One of the axial nitrogens is protonated and leads to a longer ("transannular") As⋯N distance [of 2.400 (7) Å]. A 1:1 complex, HcyclenAs·GaMe$_3$, is formed when HcyclenAs is treated with trimethylgallium where the site of complexation is the nonprotonated axial nitrogen. The geometry of the HcyclenAs moiety in the complex is essentially unchanged from the free ligand. Treatment of the larger 14-atom tetraaza macrocycle cyclam with tris(dimethylamino)arsine leads to the corresponding HcyclamAs species which has a structure similar to that of HcyclenAs except for a longer transannular interaction [2.722 (8) Å]. Thus, both macrocycles stabilize similar geometries about arsenic, and the three macrocyclic compounds can be envisioned as zwitterionic arsoranide (R_4As^-) species. Although cyclen also stabilizes a tbp geometry around phosphorus in cyclenPH, the latter contains a P–H rather than an N–H bond. The lack of an As–H bond is most likely due to the lower thermodynamic stability of this linkage. The X-ray data for HcyclenAs are as follows: $C_8H_{17}N_4As$, a = 21.532 (5) Å, b = 11.796 (2) Å, c = 17.396 (4) Å, β = 105.08 (2)°, monoclinic, $C2/c$, Z = 16. The X-ray data for HcyclenAs·GaMe$_3$ are as follows: $C_{11}H_{25}N_4GaAs$, a = 7.620 (2) Å, b = 13.073 (5) Å, c = 15.784 (5) Å, β = 90.0°, orthorhombic, $P2_12_12_1$, Z = 4. The X-ray data for HcyclamAs are as follows: $C_{10}H_{21}N_4As$, a = 15.866 (5) Å, b = 8.460 (3) Å, c = 9.333 (4) Å, β = 100.98 (3)°, monoclinic, $P2_1/c$, Z = 4.

The binding of macrocycles to transition metals has been extensively studied due to the novel properties of the resulting complexes such as high kinetic and thermodynamic stabilities, as well as the tendency of the macrocycle to

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