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Metal-Templated Synthesis of Macrocyclic (Triphosphine)molybdenum Complexes

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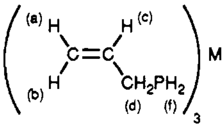
Reaction of $CH_2{=}CHCH_2PH_2$, $CH_2{=}CHCH_2CH_2PH_2$, and $CH{\equiv}CCH_2PH_2$ with (mesitylene)$Mo(CO)_3$ or (cycloheptatriene)$Mo(CO)_3$ yields the complexes $(CH_2{=}CHCH_2PH_2)_3Mo(CO)_3$ (**1**), $(CH_2{=}CHCH_2CH_2PH_2)_3Mo(CO)_3$ (**2**), and $(CH{\equiv}CCH_2PH_2)_3Mo(CO)_3$ (**3**), respectively. Reaction of $CH_2{=}CHCH_2PH_2$ and $CH{\equiv}CCH_2PH_2$ with *cis*-(piperidine)$_2Mo(CO)_4$ yields *cis*-$(CH_2{=}CHCH_2PH_2)_2Mo(CO)_4$ (**4**) and *cis*-$(CH{\equiv}CCH_2PH_2)_2Mo(CO)_4$ (**5**). Free-radical-initiated cyclooligomerization of **1** and **2** yields the triligated macrocyclic secondary-phosphine complexes *fac*-$[HP(CH_2)_3]_3Mo(CO)_3$ (**6**) and *fac*-$[HP(CH_2)_4]_3Mo(CO)_3$ (**7**). Under similar conditions, reaction of **4** yields an acyclic diphosphine complex characterized tentatively as *cis*-$[H_2P(CH_2)_3PH(CH_2CH{=}CH_2)]Mo(CO)_4$ (**8**). Compounds **1**–**7** and **10** have been characterized by spectral (^{31}P, ^{13}C, and ^1H NMR and IR and mass) data. **6** has been characterized in the solid state by single-crystal X-ray analysis. Crystalline **6** is monoclinic, space group $P2_1/c$, with $a = 12.606$ (3) Å, $b = 8.508$ (2) Å, $c = 15.420$ (2) Å, $\beta = 93.39$ (2)°, $d_o = 1.61$ g/mL, $d_c = 1.616$ g/mL, $Z = 4$, and $R = 0.026$, $R_w = 0.032$ for 2685 unique observed reflections. In the crystal, the P_3 macrocycle assumes a partial crown structure in which the complex has approximate C_s point symmetry. ^{31}P NMR spectral studies of the cyclooligomerization of **1** show the partially cyclized intermediates formed prior to **6**. The macrocyclic complexes **6** and **7** are kinetically stable, showing no sign of ligand displacement in reactions with Ph_3P, PF_3, KCN, or $P(OMe)_3$.

Introduction

Numerous studies during recent years have yielded new classes of polyphosphine macrocycles and macrocyclic metal complexes. Thus, phosphine macrocycles that contain two, three, or four phosphorus atoms as tertiary phosphine moieties (>P–R) in carbocyclic rings are well documented.[1-14] Although these are produced from often elegant syntheses, the methods usually cannot be applied to the synthesis of macrocycles that contain P–X bond functionality (X = H, OR, NR_2, halogen, etc.). Interestingly, only two examples of such phosphine macrocycles have appeared to date, a P–NEt_2 bond containing tetraphosphine[12] and a P–H bond containing triphosphine.[13]

Table I. NMR Spectra of *fac*-$(CH_2{=}CHCH_2PH_2)_3Mo(CO)_3$ (**1**) and *fac*-$(CH_2{=}CHCH_2CH_2PH_2)_3Mo(CO)_3$ (**2**)



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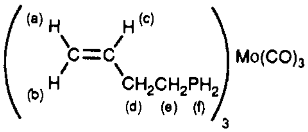

2

	1	2
	^{31}P NMR^{a-c}	
δ	−59.1 (t of d)	−67.2 (t)
$^1J(PH)$	295.0	285.5
$^2J(PH)$	21.5	
$^1J(^{95}Mo^{31}P)$	118.0	121.0
	^1H NMR^{d-f}	
$\delta H(a)$	5.10 (1)^f	51.1 (1)^g
$\delta H(b)$	5.00 (1)	4.9 (1)
$\delta H(c)$	5.90 (1)	5.5 (1)
$\delta H(d)$	2.36 (2)	2.1 (2)
$\delta H(e)$		1.6 (2)
$\delta H(f)$	3.92 (2)	3.8 (2)

^{a} 10% by volume in $CDCl_3$. ^{b} Abbreviations: t = triplet, d = doublet, s = singlet, q = quintet, m = multiplet, c = complex. ^{c} δ ±0.5 ppm; J ±1.0 Hz. ^{d} 10% by volume in C_6D_6. ^{e} Relative areas given in parentheses. ^{f} δ ±0.01 ppm. ^{g} δ ±0.1 ppm. ^{h} J data given in text.

Secondary phosphine macrocycles that contain multiple P–H bonds provide sites at which subsequent derivatization and/or molecular modification can occur. For example, poly(secondary phosphine) macrocycles or macrocyclic metal complexes could be incorporated into new classes of polyphosphine–metal polymers or metal cluster compounds, or they could be involved as side-chain units on inorganic or organic polymers. In order to obtain macrocyclic phosphines that can be so used, we have investigated the cyclooligomerization of molybdenum-coordinated alkenylphosphines. From these "templated" reactions we find that new classes of secondary macrocyclic phosphine metal complexes can be obtained in high yield. The results of our work are reported below. A preliminary report of this work has appeared.[14]

Experimental Section

Apparatus and Materials. All manipulations were carried out by using standard vacuum-line and inert-atmosphere techniques.[15] Infrared

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spectra (4000–400 cm^{-1}) were obtained on a Perkin-Elmer Model 467 spectrometer. ^{1}H NMR spectra were obtained at 90.0 MHz with a Varian EM 390 spectrometer. ^{31}P and ^{13}C NMR spectra were obtained by using JEOL PFT100 and Bruker WM-250 spectrometers equipped with standard ^{31}P and ^{13}C probe accessories. ^{1}H and ^{13}C (relative to internal Me_4Si) and ^{31}P (relative to external 85% H_3PO_4) NMR chemical shifts measured downfield from the standard are given positive (+δ) values.

Allylphosphine (2-phosphinopropene[16]), $CH{\equiv}CCH_2PH_2$,[16] $CH_2{=}CHCH_2CH_2PH_2$,[16] (mes)$Mo(CO)_3$[17] (mes = mesitylene), (cht)$Mo(CO)_3$[18] (cht = cycloheptatriene), and *cis*-(pip)$_2Mo(CO)_4$[19] (pip = piperidine) were prepared as described previously. AIBN [azobis(isobutyronitrile); Matheson Coleman and Bell], $P(OMe)_3$ (Strem Chemicals), PPh_3 (Strem Chemicals), and PMe_3 were used as obtained. PF_3 (PCR, Inc.) was passed through a −160 °C trap before use. Benzene and toluene were distilled from sodium–lead alloy. $CDCl_3$ (Stohler Isotopes) was distilled before use.

The organophosphines and organophosphine complexes described in this study are *highly malodorous* and likely *highly toxic*. Great care should be exercised in their handling.

Synthesis of *fac*-($CH_2{=}CHCH_2PH_2)_3Mo(CO)_3$ (1), *fac*-($CH_2{=}CHCH_2CH_2PH_2)_3Mo(CO)_3$ (2), and *fac*-($CH{\equiv}CCH_2PH_2)_3Mo(CO)_3$ (3). Typically, slightly more than 3 equiv of $CH_2{=}CHCH_2Ph_2$, $CH_2{=}CHCH_2CH_2PH_2$, or $CH{\equiv}CCH_2PH_2$ was allowed to react with a stirred suspension of (mes)$Mo(CO)_3$ (6.5 mmol) in benzene at 25 °C. After 48 h, benzene, unreacted phosphine, and mesitylene were removed in vacuo. Reaction products were redissolved in benzene, and the solution was passed through a 2-cm alumina column. Removal of benzene in vacuo, produced the pure complexes *fac*-($CH_2{=}CHCH_2PH_2)_3Mo(CO)_3$ (**1**), *fac*-($CH_2{=}CHCH_2CH_2PH_2)_3Mo(CO)_3$ (**2**), and *fac*-($CH{\equiv}CCH_2PH_2)_3Mo(CO)_3$ (**3**) (>90% yield). **1** and **2** were obtained as viscous oils and did not crystallize. **3** crystallized from toluene (mp = 130–131 °C).

The reaction of (cht)$Mo(CO)_3$ in benzene with slightly more than 3 equiv of $CH_2{=}CHCH_2PH_2$ at room temperature in 12 h followed by removal of solvent and cycloheptatriene in vacuo yields **1** (>95% yield).

Characterization of 1, 2, and 3. Anal. Calcd for **1** ($C_{12}H_{21}P_3MoO_3$): C, 35.84; H, 5.26; P, 23.10. Found: C, 35.74; H, 5.40; P, 23.44. Owing to sample oxidative instability, satisfactory elemental analytical data for **2** and **3** were not obtained. MS [compound, *m/e* (M^+ envelope)]: **1**, 404 ($^{98}Mo^{12}C_{12}{}^{16}O_3P_3H_{21}{}^+$); **2**, 446 ($^{98}Mo^{12}C_{15}{}^{16}O_3P_3H_{27}{}^+$); **3**, 398 ($^{98}Mo^{12}C_{12}{}^{16}O_2P_3H_{15}{}^+$). IR data are as follows (KBr, neat films, cm^{-1}. **1**: PH, 2299 (s); CO, 1954 (vs), 1864 (vs); C=C, 1633 (m). **2**: PH, 2304 (s); CO, 1963 (vs), 1878 (vs); C=C, 1642 (m). **3**: PH, 2311 (s); CO, 1981 (vs), 1892 (vs); C≡C, 2132 (s). ^{31}P NMR: **1** and **2**, data in Table I; **3** (C_6D_6), δ −57.5 (t, ^1J(PH) = 309 Hz, $^1J(^{95}Mo-^{31}P)$ = 126.5 Hz). ^{1}H NMR: **1** and **2**, data in Table I; coupling constants for **1** (measured by using ^{31}P hetero- and ^{1}H homonuclear decoupling) J = 1.9 (H_a–H_c), 9.9 (H_b–H_c), 17.2 (H_c–H_d), 7.1 Hz (H_a–H_b); coupling constants for **2** not measured in detail; **3** (C_6D_6), δ 3.8 (c, a2, PH_2), 1.9 (c, a2, CH_2), 1.6 (c, a1, CH). ^{13}C NMR (C_6D_6) for **1**: δ 26.4 (C_1), 135.4 (C_2), 117.0 (C_3), 217.7 (C≡O).

The ^{31}P NMR spectrum of **1** in toluene was examined over the temperature range of 25 to −90 °C. Except for a small downfield shift in resonances at −90 °C (ca. 5 ppm), the spectrum appeared independent of temperature.

Synthesis of *cis*-($CH_2{=}CHCH_2PH_2)_2Mo(CO)_4$ (4) and *cis*-($CH{\equiv}CCH_2PH_2)_2Mo(CO)_4$ (5). *cis*-(pip)$_2Mo(CO)_4$ in CH_2Cl_2 was allowed to react at 25 °C with slightly more than 2 equiv of $CH_2{=}CHCH_2PH_2$ or $CH{\equiv}CCH_2PH_2$. After 6 h, solvent, unreacted phosphine, and piperidine were removed in vacuo. The product oil was redissolved in benzene, and the solution was passed through a 2-cm alumina column. Upon removal of solvent, pure *cis*-($CH_2{=}CHCH_2PH_2)_2Mo(CO)_4$ (**4**) or *cis*-($CH{\equiv}CCH_2PH_2)_2Mo(CO)_4$ (**5**) was obtained (>90% yield). **4** and **5** were obtained as viscous oils, which upon repeated attempts did not crystallize from benzene, toluene, THF, hexane, or $CHCl_3$.

Characterization of 4 and 5. MS [compound, *m/e* (M^+)]: **4**, 358 ($^{98}Mo^{12}C_{10}{}^{16}O_4P_2H_{14}{}^+$); **5**, 354 ($^{98}Mo^{12}C_{10}{}^{16}O_4P_2H_{10}{}^+$). IR data are as follows (KBr, neat films, cm^{-1}). **4**: PH, 2321 (s); CO, 2032 (vs), 1942 (vs), 1928 (vs), 1899 (vs); C=C, 1634 (s). **5**: PH, 2340 (s); C≡C, 2127 (w); CO, 2040 (vs), 1950 (vs), 1925 (vs), 1896 (s). ^{31}P NMR (10% in C_6D_6): **4**, δ −67.2 (t, ^1J(PH) = 317 Hz); **5**, δ −64.2 (t, ^1J(PH) = 307 Hz). Owing to sample oxidative instability, elemental analyses were not obtained. ^{1}H NMR (C_6D_6): **4**, δ 3.80 (d of t, ^1J(PH) = 312 Hz, ^3J(HH) = 7.0 Hz, a4, PH_2), 2.15 (c, a4, CH_2), 4.95 (c, a4, $=CH_2$), 5.80 (c, a2, CH); **5**, δ 3.92 (d of t, ^1J(PH) = 310 Hz, ^3J(HH) = 6.2 Hz, a4, PH_2), 1.90 (c, a2, CH), 2.10 (c, a4, CH_2).

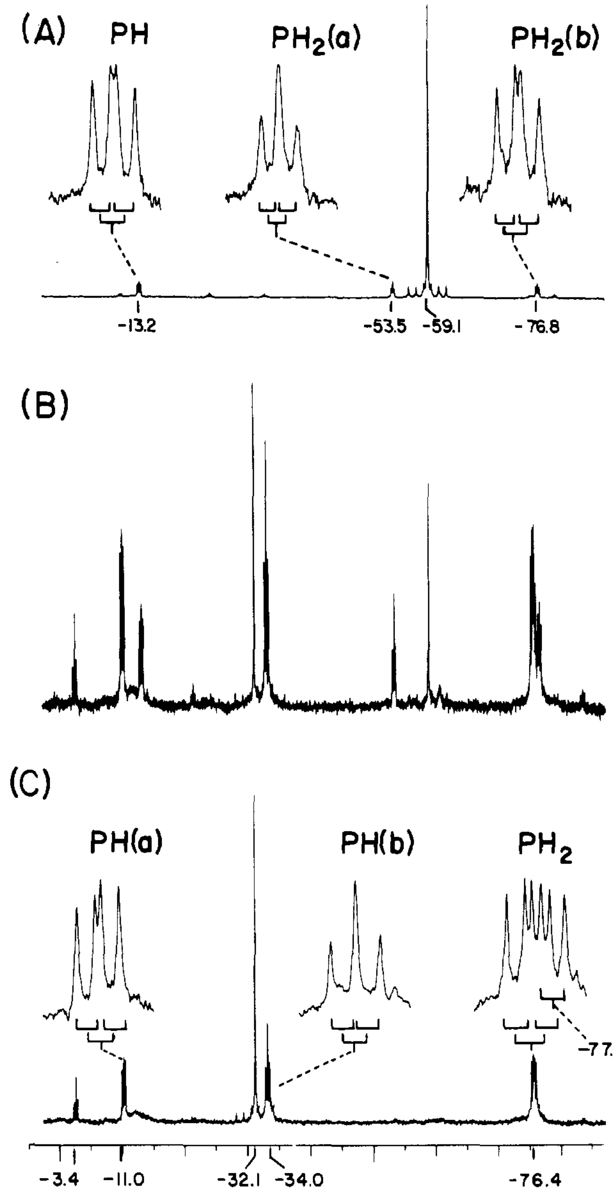

Figure 1. ^{31}P NMR spectra of AIBN-promoted cyclooligomerization of **1** at 80 °C: A, 5 min; B, 20 min; C, 40 min.

***fac*-[$HP(CH_2)_3]_3Mo(CO)_3$ (6) and *fac*-[$HP(CH_2)_4]_3Mo(CO)_3$ (7).** Typically, **1** or **2** (4–5 mM) and AIBN (ca. 1 mol %) in benzene were heated to reflux for 1.5 h. After cooling to ambient temperature, the solution was passed through a 2-cm alumina column. The column was washed with 100–150 mL of toluene. The washings, combined with the initial filtrate, were reduced in vacuo to 20–25 mL. When the solution was cooled to −25 °C, crystallization of **6** and **7** occurred (70–85% yield; mp 245 °C dec (**6**), 210 °C dec (**7**)). **6** and **7** are soluble in CH_2Cl_2, moderately soluble in benzene and toluene, and slightly soluble in hexane.

1, from $CH_2{=}CHCH_2PH_2$/(cht)$Mo(CO)_4$ reactions, functions cleanly in cyclization to **6** only if all traces of cycloheptatriene are removed in vacuo.

AIBN-promoted reactions of **1** as a function of reaction progress (time) were examined by ^{31}P NMR spectral analysis. Reactions were carried out in sealed NMR tubes. Reactions were generally complete in 90 min. ^{31}P NMR spectra of reaction solutions exhibited resonances due to intermediates **8** and **9** and finally **6** (Figure 1).

Irradiation of **1** in C_6D_6 (ca. 1 M) in either quartz of Pyrex reactors using a 275-W sunlamp results in slow conversion of **1** to **6**; however, the reaction was too slow to be viable as a synthetic method. Irradiation of **1** in an NMR tube yielded solutions whose ^{31}P NMR spectra were superimposable with those obtained in the AIBN-promoted series described above and shown in Figure 1. Around 30% conversion of **1** to **8** occurs

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Table II. Crystal Data for $[HP(CH_2)_3]_3Mo(CO)_3$ (**6**)

formula	$C_{12}H_{21}O_3P_3Mo$
fw	402.159
mp, °C	245 dec
space group	$P2_1/c$
cryst syst	monoclinic
a, b, c, Å	12.606 (3), 8.508 (2), 15.420 (2)
β, deg	93.39 (2)
Z	4
V, Å^3	1625.5 (6)
d_{calc}, g/cm^3	1.616
$F(000)$	816
μ, cm^{-1}	10.69
radiation (λ, Å)	Mo Kα (0.71069)
temp, K	294–297
scan technique; range, deg	θ–2θ; 3.0–55.0
reflcns measd	6223
unique reflcns	3594
R, R_w	0.0264, 0.0317

in 28 h; however, because yellow opaque solid forms on the NMR tube inner walls, reaction is slowed with time. After 246 h, **1** had reacted. **8** and **9** were major products, and ca. 10% of **6** had formed.

Heating of **6** with excess Ph_3P, PF_3, $P(OMe)_3$, PMe_3, or NaCN, or **7** with excess PMe_3 or Ph_3P in benzene for periods of 36–48 h at 80 °C, showed no evidence of displacement of the macrocyclic ligand.

Characterization of 6 and 7. Anal. Calcd for **6** ($C_{12}H_{21}MoO_3P_3$): C, 35.84; H, 5.26; P, 23.10. Found: C, 36.01; H, 5.41; P, 22.84. MS [compound, m/e (M^+)]: **6**, 404 ($^{98}Mo^{12}C_{12}H_{21}P_3{}^{16}O_3{}^+$); **7**, 446 ($^{98}Mo^{12}C_{15}H_{27}P_3{}^{16}O_3{}^+$). ^{31}P NMR (C_6D_6): **6**, δ −32.1 (d, $^1J(PH)$ = 318 Hz, $^1J(^{95}Mo-^{31}P)$ = 118.5 Hz); 7, δ −13.5 (d, $^1J(PH)$ = 312 Hz). ^1H NMR (C_6D_6): **6**, δ 4.70 (d, a1, PH), 1.8 (c, a6, CH_2); **7**, δ 4.80 (d, a1, PH), 1.60 (c, a8, CH_2). IR data are as follows (KBr, Nujol, cm^{-1}). **6**: CO, 1945 (vs), 1844 (vs). 7: CO, 1950 (vs), 1865 (vs).

AIBN-Promoted Reactions of 3–5. **4** (4 mmol) and AIBN (1–2 mol %) in benzene (50 mL) were heated to reflux for 30 min. The solution darkened and was cooled to room temperature and filtered. Volatile materials were removed in vacuo, leaving a dark orange oil, **10** (65% yield). Longer reaction times, e.g. 1.5 h, resulted in decomposition, as evidenced by formation of large quantities of dark insoluble products. IR (KBr, neat film, cm^{-1}): PH, 2316 (m), 2303 (m), 2291 (s); CO, 2034 (vs), 1942 (vs), 1921 (vs), 1917 (vs); C═C, 1637 (s). ^{31}P NMR: δ −25.4 (d, a1, $^1J(PH)$ = 324 Hz), −86.6 (t, a1, $^1J(PH)$ = 317 Hz). Both resonances collapse to doublets ($^2J(PMoP)$ = 33.0 Hz) upon ^1H decoupling. Owing to sample instability, elemental analyses were not obtained. MS: fragment ions observed; no M^+ ion seen.

3 or **5** with AIBN (1–2 mol %) when heated in toluene yielded only intractable products, which could not be isolated or characterized.

X-ray Analysis. **6** crystallizes from toluene in two habits, thin plates (form A) and needles (form B). Forms A and B gave identical mass and ^{31}P NMR spectra. Neither A nor B were suitable for X-ray analysis. Form A crystals were twinned; both fragments were indexed, yielding a = 13.14 (2) Å, b = 9.05 (1) Å, c = 13.79 (3) Å, and β = 92.4 (1)°. Form B crystals were of insufficient quantity to allow analysis. Recrystallization of **6** from CH_2Cl_2 produced colorless needles (similar in appearance to B above) suitable for X-ray analysis. Crystals of **7** suitable for X-ray analysis were not obtained.

Crystal data and essential data collection parameters are given in Table II. Complete details are given in the supplementary material. Data were collected on a Nicolet P$\bar{1}$ automated diffractometer.[20] The structure was solved by using Patterson techniques. In the final refinement, all non-hydrogen atoms were refined anisotropically by using scattering factors for neutral atoms.[21] The hydrogen atom positions were refined, with their isotropic thermal parameters held fixed at 1.2 times the thermal parameter of the atom to which they are attached. Final positional parameters are given in Table III. All calculations were carried out on a Cyber computer.[22]

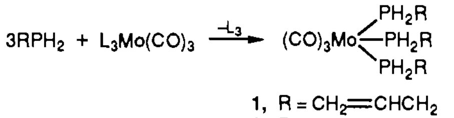
Results and Discussion

Table III. Positional and Thermal Parameters for the Non-Hydrogen Atoms of $[HP(CH_2)_3]_3Mo(CO)_3$ (**6**)[a]

atom	x	y	z	B_{eq},[b] Å
Mo	0.24243 (2)	0.15583 (3)	−0.00943 (1)	2.6
P1	0.11183 (6)	0.10502 (10)	0.10379 (5)	3.0
P2	0.38220 (6)	0.03489 (9)	0.08616 (5)	2.8
P3	0.28182 (7)	0.4110 (1)	0.06105 (6)	3.6
O1	0.2065 (3)	−0.1721 (4)	−0.0975 (2)	7.9
O2	0.4049 (2)	0.2438 (4)	−0.1492 (2)	5.4
O3	0.0583 (2)	0.3152 (4)	−0.1199 (2)	6.1
C1	0.2174 (3)	−0.0526 (4)	−0.0643 (2)	4.1
C2	0.3457 (3)	0.2094 (4)	−0.0973 (2)	3.5
C3	0.1265 (3)	0.2566 (4)	−0.0795 (2)	3.8
C4	0.1456 (3)	−0.0303 (5)	0.1934 (2)	4.2
C5	0.2586 (3)	−0.0238 (5)	0.2314 (2)	4.5
C6	0.3430 (3)	−0.0908 (5)	0.1758 (3)	4.5
C7	0.4866 (3)	0.1591 (4)	0.1375 (2)	3.7
C8	0.4947 (3)	0.3256 (4)	0.1032 (2)	3.9
C9	0.4040 (3)	0.4305 (5)	0.1299 (3)	4.6
C10	0.1818 (3)	0.5018 (4)	0.1283 (3)	4.8
C11	0.1353 (3)	0.3945 (5)	0.1944 (3)	4.9
C12	0.053 (3)	0.2765 (5)	0.1573 (3)	4.1
H1P1	0.023 (3)	0.048 (4)	0.078 (2)	4.1
H1P2	0.443 (3)	−0.064 (4)	0.047 (2)	3.8
H1P3	0.296 (3)	0.529 (4)	0.008 (2)	4.7

[a] Except for H atoms H1P1, H1P2, and H1P3. [b] B_{eq} is the equivalent isotropic thermal parameter calculated from the anisotropic thermal parameters as $B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$.

The phosphines CH_2═$CHCH_2PH_2$, CH_2═$CHCH_2CH_2PH_2$, and CH≡CCH_2PH_2 react with (mes)$Mo(CO)_3$ or (cht)$Mo(CO)_3$ in toluene at 25 °C to form tris(phosphine) complexes as

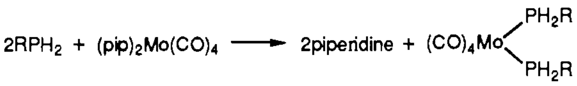


$$3RPH_2 + L_3Mo(CO)_3 \xrightarrow{-L_3} (CO)_3Mo(PH_2R)_3 \quad (1)$$

1, R = CH_2═$CHCH_2$
2, R = CH_2═CCH_2CH_2
3, R = CH≡CCH_2

L_3 = mesitylene, cycloheptatriene

Similarly, CH_2═$CHCH_2PH_2$ and CH≡CCH_2PH_2 react with *cis*-(pip)$_2Mo(CO)_4$ yielding the complex **4** or **5**. In each case,



$$2RPH_2 + (pip)_2Mo(CO)_4 \longrightarrow 2\text{piperidine} + (CO)_4Mo(PH_2R)_2 \quad (2)$$

4, R = CH_2═$CHCH_2$
5, R = CH≡CCH_2PH_2

reaction proceeds smoothly, in high yield (>95%). Reaction conditions are sufficiently mild that facial–meridional or cis–trans isomerization of the complexes, processes known to occur in other phosphine–molybdenum complexes,[23,24] is not evident. Resonances in the ^{31}P NMR spectrum that might suggest the presence of other isomers are not seen. Compounds **1**, **2**, **4**, and **5** are viscous liquids that we could not crystallize; however, **3** is a solid (mp = 130 °C). All are well-behaved monomeric compounds showing no evidence for intermolecular association in the solution phase or in the gas phase by ^{31}P or ^1H NMR or mass spectral analyses.

Spectral data unambiguously characterize the new (phosphine)molybdenum complexes **1–5** as tris- and bis(primary phosphine)molybdenum(0) complexes. Mass spectral ions corresponding to the parent molecular species (M^+) are seen in each case. The $^1J(PH)$ coupling constants observed in the ^{31}P NMR spectra are increased markedly (286–317 Hz) over the values (188–195 Hz) seen in the uncoordinated phosphines.[16] **1–3** are clearly monoisomeric and facial isomers, showing only single ^{31}P NMR resonances. The phosphine chemical shifts in **1**, **2**, and **3**,

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(20) For a more detailed description of the data collection procedures see: Coons, D. E.; Allured, V. S.; Noirot, M. D.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1982**, *21*, 1947.

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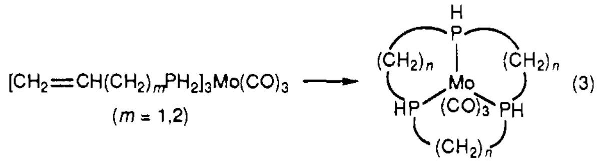
which are typical for (primary alkylphosphine)molybdenum(0) complexes[25,26] at δ −59.1, −67.2, and −57.5, are significantly shifted from their positions at δ −132.6, −140.5, and −130.4 in the uncoordinated species;[16] however, the magnitudes and downfield directions of the shifts are consistent with those reported earlier in (alkylphosphine)molybdenum complexes.[26] Similarly, the coordination shifts for **4** and **5** are as expected for phosphines in bis(phosphine)complexes.[26,27] ^{1}H NMR spectral resonances for each proton type in **1–5** are seen and can be assigned on the basis of comparison with data reported previously for the uncoordinated $CH_2{=}CHCH_2PH_2$, $CH_2{=}CHCH_2CH_2PH_2$, and $CH{\equiv}CCH_2PH_2$ ligands.[16]

Compounds **1–5** appear to involve exclusively phosphorus coordination; no evidence in either NMR or IR spectra for alkene or alkyne moiety coordination to the metal center is evident.[28,29] Examination of ^{31}P NMR spectra of **1** at temperatures down to −90 °C showed no significant spectral change, in either the form of chemical shifts, ^1J(PH) coupling constants, or the spectral pattern. Alkene and alkyne ^{1}H NMR spectral resonances are essentially unperturbed from their situation in the free phosphine.[16] Complexes **1–3** and **4** and **5** exhibit two and four strong CO absorptions, patterns characteristic of C_{3v} and C_{2v} isomers, respectively.[30] The stretching frequencies agree closely with those reported in numerous other molybdenum–phosphine complexes.[26,31] In **1**, **2**, and **4** the vinylic (C=C) absorptions[32] are shifted very little from their positions in the free phosphine, $CH_2{=}CHCH_2PH_2$.[16] Typically, π coordination of a C=C unit to a metal reduces the C=C frequency markedly. For example, the chelating phosphine $PhP(CH_2CH_2CH{=}CH_2)_2$ when coordinated to $Mo(CO)_4$ shows two distinct C=C stretching frequencies at 1637 and 1535 cm^{-1} due to uncoordinated and coordinated alkene groups.[29d]

The radical-promoted cyclooligomerizations of **1** and **2** yield the macrocyclic 1,5,9-triphosphacyclododecane and 1,6,11-triphosphacyclopentadecane[33] complexes **6** and **7** as



6 ($n = 3$), **7** ($n = 4$)

This reaction is best promoted by the chemical initiator AIBN, but it is also promoted under photolytic conditions. Similar behavior is well-documented in reactions of olefins with free phosphines[34,35] and metal-coordinated[36,37] phosphines, which produce acyclic organophosphine products. Reactions of **1** and **2** in toluene with 1–2 mol % AIBN typically reach completion after 1–2 h at 80 °C. Reaction mixtures, when examined by ^{31}P NMR spectral analysis, show mainly the macrocycle products (>80%) and only lesser amounts of reaction intermediate materials and/or otherwise uncharacterized species. Reaction of **3** with AIBN under similar circumstances yields only polymeric intractable products.

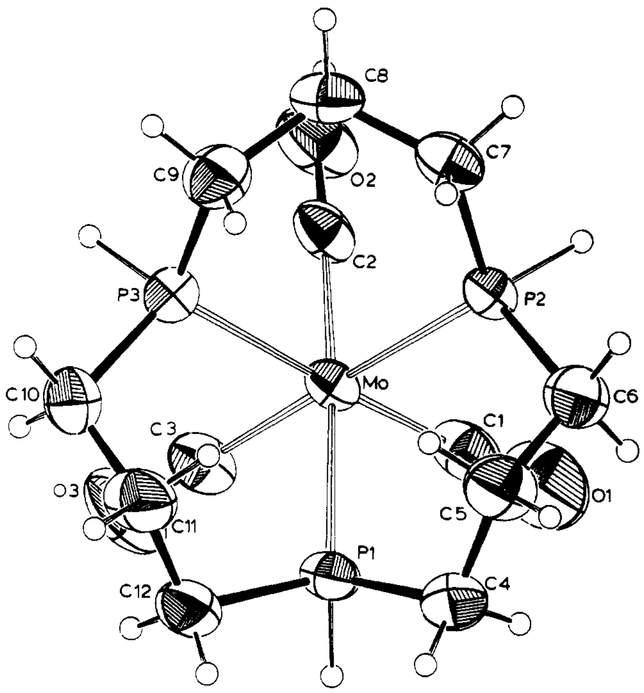


Figure 2. Structure and numbering scheme for $[HP(CH_2)_3]_3Mo(CO)_3$ (**6**). Thermal ellipsoids are shown at the 50% level.

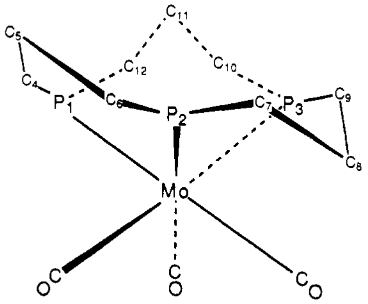


Figure 3. Side view of **6**, showing macrocycle ring conformation.

The structure of **6** is established unambiguously by a single-crystal X-ray study. The structure of **6**, shown in Figure 2, consists of a 12-membered $(HP(CH_2)_3)_3$ ring facially coordinated to the $Mo(CO)_3$ unit. The [12-ane]P$_3$ ring coordination results in the P–H bonds being oriented up and out from the plane of the three phosphorus atoms. The structural arrangement of coordinated groups around Mo is close to octahedral, indicating the [12-ane]P$_3$

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Table IV. Bond Lengths and Bond Angles in $[HP(CH_2)_3]_3Mo(CO)_3$ (**6**)

(a) Bond Lengths (Å)

Mo-P1	2.507 (1)	P2-C6	1.839 (4)
Mo-P2	2.455 (1)	P3-C9	1.826 (4)
Mo-P3	2.465 (1)	P3-C10	1.848 (5)
Mo-C1	1.983 (4)	C4-C5	1.510 (5)
Mo-C2	1.987 (3)	C5-C6	1.515 (6)
Mo-C3	1.962 (3)	C7-C8	1.518 (5)
C1-O1	1.142 (5)	C8-C9	1.525 (6)
C2-O2	1.162 (4)	C10-C11	1.512 (6)
C3-O3	1.146 (4)	C11-C12	1.512 (6)
P1-C4	1.829 (4)	P1-H1P1	1.26 (3)
P1-C12	1.841 (4)	P2-H2P2	1.32 (3)
P2-C7	1.831 (4)	P3-H3P3	1.31 (3)

(b) Bond Angles (deg)

P1-Mo-P2	89.27 (3)	C4-P1-C12	103.8 (2)
P2-Mo-P3	89.18 (3)	C9-P3-C10	102.5 (2)
P3-Mo-P1	88.18 (3)	C6-P2-C7	103.2 (2)
P1-Mo-C3	87.7 (1)	C4-P1-Mo	120.2 (1)
P1-Mo-C2	176.6 (1)	C12-P1-Mo	117.6 (1)
P1-Mo-C3	87.7 (1)	C6-P2-Mo	118.7 (1)
P2-Mo-C1	88.4 (2)	C7-P2-Mo	119.3 (1)
P2-Mo-C3	176.5 (2)	C9-P3-Mo	118.5 (1)
P2-Mo-C2	91.7 (2)	C10-P3-Mo	119.3 (1)
P3-Mo-C2	88.6 (1)	P1-C4-C5	116.2 (3)
P3-Mo-C1	177.4 (1)	C4-C5-C6	116.4 (3)
P1-Mo-C1	92.8 (1)	C5-C6-P2	115.8 (3)
P3-Mo-C3	89.0 (1)	P2-C7-C8	116.7 (2)
C1-Mo-C2	90.5 (1)	C7-C8-C9	146.3 (3)
C2-Mo-C3	91.2 (1)	C8-C9-P3	114.2 (3)
C3-Mo-C1	93.5 (1)	P3-C10-C11	115.5 (3)
Mo-C1-O1	177.4 (3)	C10-C11-C12	115.0 (4)
Mo-C2-O2	178.5 (3)	C11-C12-P1	115.4 (3)
Mo-C3-O3	179.5 (3)		

ring fits well without significant distortion of the bond angles at Mo. The [12-ane]P_3 ring adopts a partial "crown" form in which two of the 6-membered C/C/C/P/Mo/P rings (P1/Mo/P2/C6/C5/C4 and P1/Mo/P3/C10/C11/C12) are in chair conformations[38] and the other (P2/Mo/P3/C9/C8/C7) is in a boat conformation (Figure 3). This results in a complex in the crystal of approximate C_s symmetry. This conformation for coordinated 12-membered macrocycles in the solid does not appear to be unusual, since it is also assumed by [12-ane]S_3 and [12-ane]N_3 rings in their Ni^{2+} and $Mo_2O_4^{2+}$ complexes, respectively.[39,40] However, as with our [12-ane]P_3 system, the origin of this structural effect remains unclear. Carbon atoms C5 and C11 are above by as much as C8 is below the P_3 macrocycle plane. The C4/C5/C6-P1/P2/C4/C5, C10/C11/C12-P1/P3/C10/C12, and C7/C8/C9-P2/P3/C7/C9 interplane dihedral angles are 116.6, 115.1, and 64.6°, respectively. The Mo-P and Mo-C bond distances (Table IV) are entirely normal for a tris(phosphine) complex of molybdenum.[41,42] The Mo-P1 distance [2.507 (1) Å] is somewhat greater than the Mo-P2 and Mo-P3 distances (mean 2.460 Å), possibly the result of the conformational asymmetry that exists in the structure. It should be noted that, in solution, only one ^{31}P resonance is seen, indicating that boat-chair conformational interchange for the C/C/C/P/Mo/P rings may occur easily and that the asymmetric form seen in the crystal is the result of crystal packing forces.

The AIBN-promoted cyclooligomerizations of **4** and **5** in reactions that might be potential routes to coordinated 8- and 10-membered-ring diphosphines were unsuccessful. **4**, after being heated for 8 h in toluene in the presence of AIBN, reacted only to give what appears to be the partially cyclized product **10**. Mass

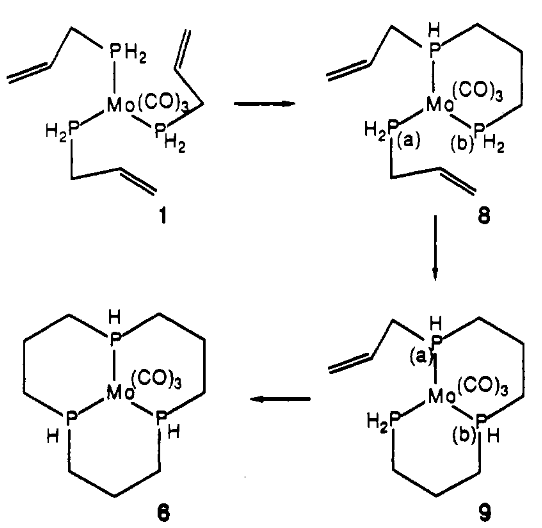
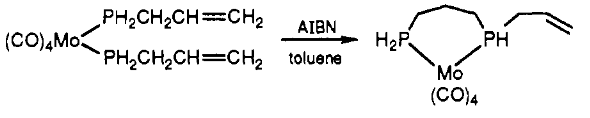


Figure 4. Structures of the cyclooligomerization intermediates **8** and **9**, showing phosphorus atom numbering scheme and proposed sequence of cyclooligomerization.



10 (4)

spectral data confirm the formula; ^{31}P NMR spectral data are consistent with other *cis*-bis(phosphine)molybdenum complexes,[26,27,37a] and IR data show the presence of an uncoordinated alkene moiety.[32] Further heating did not appear to yield a cyclized product; instead intractable products were obtained.

The metal-templated cyclooligomerization of **1** to form **6** was examined in greater detail by following the reaction by ^{31}P NMR spectroscopy as a function of time. $^{31}P\{^1H\}$ spectra from a typical reaction series collected after 5, 20, and 40 min in refluxing benzene are shown in Figure 1. Initially, the spectrum shows only a single resonance at δ -59.1 due to **1**. After 5 min, three equal-area multiplet resonances at δ -13.2, -53.5, and -76.8 appear and grow in intensity (Figure 1A). Subsequently, after 20 min (Figure 1B), another set of three equal-area resonances appear at δ -11.0, -34.0, and -76.4 along with the singlet at δ -32.1 due to **6** and minor resonances at δ -3.4 and -77.1. Further heating causes the three resonances at δ -11.0, -34.0, and -76.4 and the singlet from **6** to grow as the first set of three resonances decrease in intensity. Additional heating causes the disappearance of the intermediate peaks and the clear dominance of the singlet product (**6**).

Although spectra of the intermediate species are not perfectly clean, it is possible through analysis of the resonance multiplicities[43] and by correlating their chemical shifts with the resonances of known molybdenum-coordinated primary and secondary phosphines[25,27,37a] to make spectral assignments consistent with their being the partially cyclized intermediates **8** and **9** (Figure 4). The initially formed set of resonances at δ -13.2, -53.5, and -76.8, a doublet of doublets ($^2J(PP)$ = 32.4 Hz, $^2J(PP)$ = 24.6 Hz), a triplet ($^2J(PP)$ = 23.9 Hz), and doublet of doublets ($^2J(PP)$ = 32.4 Hz, $^2J(PP)$ = 24.6 Hz) are characteristic of coordinated secondary (PH) and primary (PH_2(a) and PH_2(b)) phosphine moieties, respectively. Such a pattern of two primary and one secondary coordinated phosphines can be assigned to species **8**. The second group of resonances at δ -11.0, -34.0, and -76.4, a doublet of doublets ($^2J(PP)$ = 32.0 Hz, $^2J(PP)$ = 24.1 Hz), a triplet ($^2J(PP)$ = 33.0 Hz), and doublet of doublets ($^2J(PP)$ = 33.5 Hz, $^2J(PP)$ = 24.2 Hz) are assigned to the coordinated

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secondary (PH(a) and PH(b) and primary PH_2) phosphine moieties of **9**, respectively. In both **8** and **9** the ^2J(PP) values of 24-33 Hz are typical of cis-molybdenum(0)-coordinated phosphines.[27] It is assumed that **8**-PH_2(b) and **9**-PH(b) appear as triplets only because of the close coincidence of the two ^2J coupling constants. That the resonances in **8** and **9** are in fact from secondary (PH) and primary (PH_2) phosphines is confirmed in the $^{31}P-^{1}H$ coupled spectra. Upon ^1H coupling, the **8**-PH, **9**-PH(a), and **9**-PH(b) resonances are broad doublets and the **8**-PH_2(a), **8**-PH_2(b), and **9**-PH_2 resonances are broad triplets of ^1J(PH) approximately equal to 300 and 330 Hz, respectively. Although broad, unresolved, and unassigned resonances in the base lines are seen, these are assumed to be due to traces of higher oligomeric or polymeric products and were not assigned. The possibility that the small well-defined resonance groups at δ −3.4 and −77.1 are due to minor amounts of dimolybdenum species or Markovnikov addition[38] products containing 5-membered C/C/P/Mo/P rings cannot be discounted.

On the basis of the spectral assignments above, the sequence of reactions shown in Figure 4 appears to be the major process that occurs during cyclooligomerization. Initial closure of one C_3P_2Mo ring results in **8**, a species containing a single 6-membered metallaphosphacycle ring. Subsequently, after the second step in cyclization occurs, a coordinated bicyclic system (**9**) begins to appear. Upon formation of the third ring, the final coordinated [12-ane]P_3 macrocycle (**6**) is formed. The reaction occurs in moderately well-defined steps, clearly the result of the metal's causing template cyclization and introducing order into the cyclooligomerization reaction. In the absence of metal coordination $CH_2{=}CHCH_2PH_2$ and $CH_2{=}CHCH_2CH_2PH_2$, under AIBN or photolytically promoted reaction conditions, yield different products in complex reaction mixtures.[44]

The [12-ane]P_3 and [15-ane]P_3 molybdenum complexes **6** and **7** showed (by ^{31}P NMR analysis) no decomposition during heating in toluene at 110 °C. Not surprisingly, both are stable to macrocyclic displacement. Exhaustive treatment of these complexes with Ph_3P, PF_3, KCN, or $P(OMe)_3$ resulted in no reaction. Further studies of ligand displacement in order to obtain the free [12-ane]P_3 and [15-ane]P_3 macrocycles are in progress and will be reported later.

Acknowledgment. Support of this work by grants from the National Science Foundation (CHE-7604290 and CHE-7909497), the Colorado Energy Research Institute, the Department of Energy/Solar Energy Institute (DE-FG02-80CS83112), and the University of Colorado Computing Center is gratefully acknowledged.

Supplementary Material Available: Listings of crystal data and refinement details, hydrogen atom coordinates, anisotropic thermal parameters, and least-squares planes (8 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis of Bis(trifluoromethyl)phenylthallium and Bis(trifluoromethyl)thallium Acetate. Oxidative Trifluoromethylation with Bis(trifluoromethyl)thallium(III) Compounds

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The reaction of $Cd(CF_3)_2$·glyme with $TlPhCl_2$ forms $TlPh(CF_3)_2$, which is isolated in 87% yield after 72 h. If $TlPh(OAc)_2$ is the thallium source, $TlPh(CF_3)_2$ is generated in 2 h; however, the isolated yield is lower because acetate reacts with $Cd(CF_3)_2$·glyme, resulting in CH_3COF. The interaction of $Cd(CF_3)_2$·glyme with $Tl(OAc)_3$ produces $Tl(CF_3)_2OAc$, 46%, within 45 min. The possibility of utilizing (trifluoromethyl)thallium(III) species in oxidative trifluoromethylation reactions was screened by employing several classic low-valent metallic species as substrates. The reaction of elemental mercury was the most informative, yielding $Hg(CF_3)_2$ in 77% yield in glyme but generating a mixture of $HgPh(CF_3)$ and $Hg(CF_3)_2$ when CH_2Cl_2 was the solvent. These results are interpreted by postulating mercury insertion into the Tl-Ph bond, resulting in $PhHgTl(CF_3)_2$, which decomposes to generate $HgPh(CF_3)$. The formation of $Hg(CF_3)_2$ is attributed to the reaction of $HgPh(CF_3)$ with $TlCF_3$.

Introduction

Due in part to the low activation energies commonly associated with their reactions, organometallic compounds of the group 3A (13) elements have long been extensively employed in diverse types of chemical transformations. Examples include hydrometalations, ligand-exchange procedures, and a variety of olefin telomerizations and polymerizations involving reactions of organoboron or organoaluminum compounds. Although less well studied, organothallium reagents are also occasionally utilized in more specialized applications: reactions like aromatic thallations, olefin oxythallations, or cyclopentadienations with TlCp.[1]

In contrast to the diverse and important niche that has been carved out for the perhydroalkyl reagents of the main group 3 (13) elements, surprisingly little is known about the preparation and the properties of the perfluoroalkyl derivatives. For example, only two trifluoromethyl-substituted boranes, CF_3BF_2 and $CF_3B(n\text{-}Bu)_2$, have ever been synthesized.[2,3] Other trifluoromethyl-boron-containing species that have been separated include the two anions $CF_3BF_3^-$ and $(CF_3)_2BF_2^-$.[4,5] Within this group of elements, the sole remaining trifluoromethyl derivatives that have been reported are $Tl(CF_3)_3$ and the trimethylphosphine adduct of that compound, $Tl(CF_3)_3PMe_3$, both derived from the reactions of thallium atoms with CF_3 radicals.[6] The utility of (trifluoromethyl)thallium compounds as reagents remains wholly unexplored.

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