

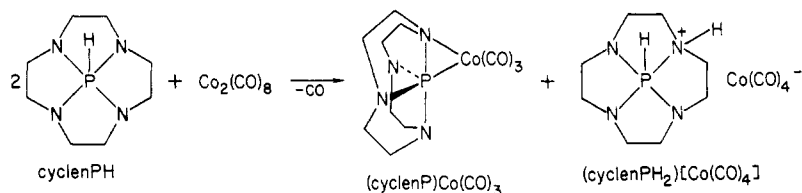
# Reactions of "Cyclenphosphorane" with Transition-Metal Carbonyl Dimers and Hydrides: Synthesis of Phosphoranide Adducts and Metal Carbonyl Anions and the X-ray Crystal Structure of (cyclenP)MoCp(CO)<sub>2</sub>

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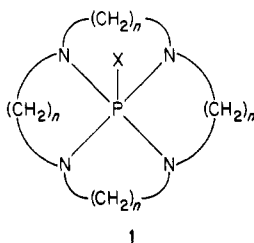
Cyclenphosphorane (cyclenPH) reacts with transition-metal carbonyl dimers to yield mononuclear derivatives, e.g.



Similarly, cyclenPH reacts with [MoCp(CO)<sub>3</sub>]<sub>2</sub> (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) to yield (cyclenP)MoCp(CO)<sub>2</sub> and (cyclenPH<sub>2</sub>)[MoCp(CO)<sub>3</sub>]. The only isolable product from the reaction of cyclenPH with Mn<sub>2</sub>(CO)<sub>10</sub> is (cyclenPH<sub>2</sub>)[Mn(CO)<sub>5</sub>]. No reaction is observed between cyclenPH and [FeCp(CO)<sub>2</sub>]<sub>2</sub>. All of the metal carbonyl salts are stable in THF solution except for (cyclenPH<sub>2</sub>)[Co(CO)<sub>4</sub>] which loses H<sub>2</sub> and CO upon heating to yield (cyclenP)Co(CO)<sub>3</sub>. cyclenPH also reacts with HWcP(CO)<sub>3</sub> to give (cyclenPH<sub>2</sub>)[WcP(CO)<sub>3</sub>]. Addition of CH<sub>3</sub>I to (cyclenPH<sub>2</sub>)[WcP(CO)<sub>3</sub>] affords (cyclenPH<sub>2</sub>)I and CH<sub>3</sub>WcP(CO)<sub>3</sub>. The X-ray crystal structure of (cyclenP)MoCp(CO)<sub>2</sub> was obtained. The crystal is monoclinic with a space group of P2<sub>1</sub>/c. The unit cell parameters are a = 8.605 (2) Å, b = 8.584 (2) Å, c = 22.157 (3) Å, β = 93.84 (2)°, and Z = 4.

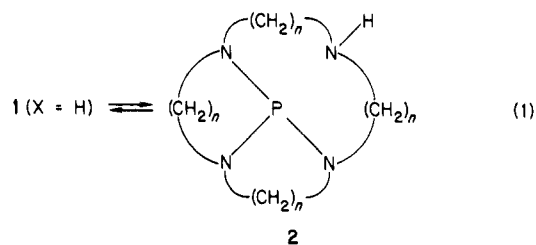
## Introduction

The synthesis of molecules containing pentacoordinate phosphorus bonded to cyclic tetraamino moieties, viz., 1



(X = F, n = 2;<sup>1a</sup> X = H, n = 2 and/or 3<sup>1b,c</sup>) was first reported by Richman and Atkins. More recently, species with X = OCH<sub>3</sub> or SCH<sub>3</sub>, n = 2, have been synthesized.<sup>2</sup>

These molecules should exhibit novel reactivity patterns for the following reasons: (1) the presence of a labile P-X bond (and potentially labile P-N bonds), (2) the presence of lone pairs of electrons on the nitrogen atoms, and (3) the fact that an equilibrium can exist in solution, when X = H, between the phosphorane 1 and the phosphine 2. When all n = 2 or three n = 2 and one n = 3, only the phosphorane is observed; with the two possible arrangements of two n = 2 and two n = 3, both tautomers are observed; with all n = 3 only the phosphine is observed. This behavior was attributed to bonding configuration changes due to ring size.<sup>1b,c</sup>



All three types of reactivity listed above have been observed. Under X-ray irradiation, cyclenPH<sup>3</sup> yields the tetracoordinate phosphoranide radical, cyclenP<sup>•</sup>.<sup>4</sup> When treated with butyllithium and cyclenPF, cyclenPH yields the diphosphorane cyclenP-Pcyclen.<sup>5</sup> cyclenPH forms a bis(borane) adduct where two nitrogen atoms are coordinated to BH<sub>3</sub> groups; here, only the phosphorane tautomer is observed.<sup>6</sup> This contrasts with the bis(borane) adducts formed by cyclamPH<sup>3</sup> where both tautomers 1 and 2 are

(1) (a) Richman, J. E. *Tetrahedron Lett.* 1977, 559. (b) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* 1978, 4333. (c) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* 1978, 5149.

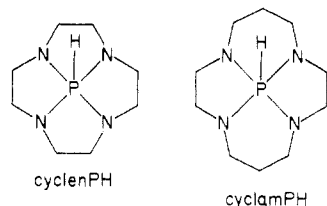
(2) Richman, J. E.; Kubale, J. J. *Am. Chem. Soc.* 1983, 105, 749.

(3) The cyclic molecules 1,4,7,10-tetraazacyclododecane and 1,4,8,11-tetraazacyclotetradecane have been termed "cyclen" and "cyclam", respectively (Collman, J. P.; Schneider, P. W. *Inorg. Chem.* 1966, 5, 1380). The words "cyclenphosphorane" (1, all n = 2) and "cyclamphosphorane" (1, alternating n = 2 and m = 3 bridges) have been used to describe the corresponding pentacoordinate phosphorus molecules (see ref 1 and 7). We use the abbreviations cyclenPX and cyclamPX to represent 1 (all n = 2) and 1 (alternating n = 2 and m = 3), respectively.

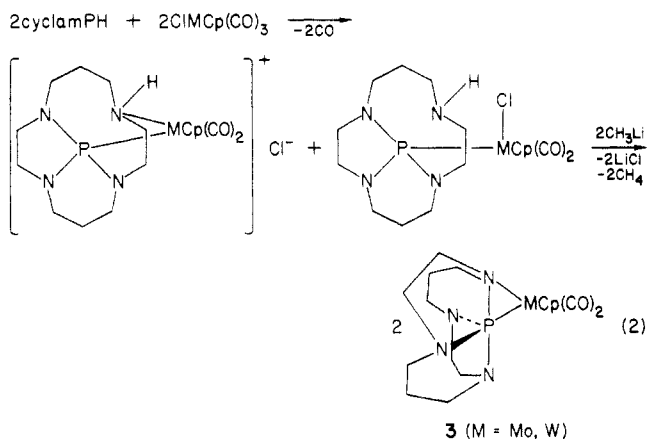
(4) Hamerlinck, J. H. H.; Hermkens, P. H. H.; Schipper, P.; Buck, H. M. *J. Chem. Soc., Chem. Commun.* 1981, 358.

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observed, the latter of which has phosphine-BH<sub>3</sub> and amine-BH<sub>3</sub> linkages.<sup>6,7</sup> cyclamPH also reacts with transition-metal carbonyl halides to give adducts of the open form **2** as initial products. Subsequent reaction with methyl lithium, however, leads to the bridging pentacoordinate phosphorus species (cyclamP)MCP(CO)<sub>2</sub> (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>; M = Mo (**3a**), W (**3b**) (reaction 2).<sup>8</sup> When



hydride is removed from **1** and/or **2** (X = H), phosphonium salts where all four nitrogens are bound to phosphorus (e.g., cyclenP<sup>+</sup>, cyclamP<sup>+</sup>) are formed exclusively, regardless of whether *n* = 2 and/or 3.<sup>9</sup>

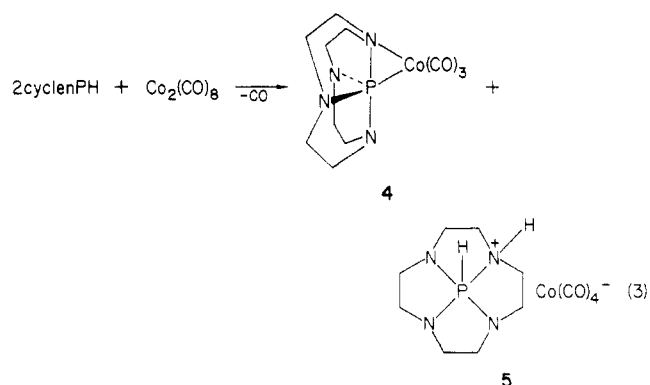
From these observations, it appears that the initial equilibria observed by Atkins and Richman play an important role in determining the reactivity patterns of cyclic tetraaminophosphoranes. However, subsequent reaction conditions can overcome the equilibria determined by ring size.

Our interests in the synthesis, structure, and reactivity of metallophosphoranes led us to explore the reactions of cyclenPH with transition-metal species. The reactions of cyclenPH with Co<sub>2</sub>(CO)<sub>8</sub>, [MoCp(CO)<sub>3</sub>]<sub>2</sub>, Mn<sub>2</sub>(CO)<sub>10</sub>, [FeCp(CO)<sub>2</sub>]<sub>2</sub>, and HCp(CO)<sub>3</sub> are reported here, as well as the X-ray crystal structure of (cyclenP)MoCp(CO)<sub>2</sub>.

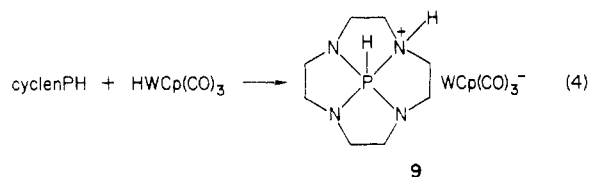
## Results

Our expectation that the phosphorane form of cyclenPH would be observed exclusively in its reactions with transition metals was fully borne out by our observations. In general, cyclenPH reacts with Co<sub>2</sub>(CO)<sub>8</sub>, [MoCp(CO)<sub>3</sub>]<sub>2</sub>, and Mn<sub>2</sub>(CO)<sub>10</sub> to give mononuclear derivatives. Although the reactions appear to parallel one another, the stabilities

of the final products are quite varied. For example, when cyclenPH is allowed to react with Co<sub>2</sub>(CO)<sub>8</sub> in a 2:1 molar ratio, a covalent and an ionic product are produced according to reaction 3.



The reaction is complete at low temperature and (cyclenP)Co(CO)<sub>3</sub> (**4**) is obtained as an air-stable solid. The salt (cyclenPH<sub>2</sub>)[Co(CO)<sub>4</sub>] (**5**) is stable in THF solution at ambient temperature in an inert atmosphere. However, at elevated temperatures spontaneous loss of H<sub>2</sub> and CO occurs, resulting in the covalent species **4**. The corresponding reaction of cyclenPH with [MoCp(CO)<sub>3</sub>]<sub>2</sub> yields the analogous products (cyclenP)MoCp(CO)<sub>2</sub> (**6**) and (cyclenPH<sub>2</sub>)[MoCp(CO)<sub>3</sub>] (**7**), although elevated temperatures (refluxing THF) are required. Also, prolonged refluxing of the mixture of **6** and **7** does not convert the salt to the covalent species. The only isolable product in the reaction of cyclenPH with Mn<sub>2</sub>(CO)<sub>10</sub> (refluxing THF) is the salt (cyclenPH<sub>2</sub>)[Mn(CO)<sub>5</sub>] (**8**). No reaction is observed between cyclenPH and [FeCp(CO)<sub>2</sub>]<sub>2</sub> in either refluxing THF or refluxing dioxane. In a related experiment, cyclenPH abstracts the proton from HCp(CO)<sub>3</sub> to give (cyclenPH<sub>2</sub>)[WCp(CO)<sub>3</sub>] (**9**) at low temperature (reaction 4).



[The geometries of the pentacoordinate phosphorus atoms in **3** and **4** are drawn as trigonal bipyramids (tbp's). Structural evidence supports this (see later). However, the exact geometries of cyclenPH and cyclenPH<sub>2</sub><sup>+</sup> are not known.]

Spectral data for the various products (and cyclenPH) are collected in Table I. The <sup>31</sup>P chemical shifts of the covalent transition-metal phosphorane adducts<sup>8</sup> (or metallophosphoranes)<sup>10</sup> **4** and **6** appear downfield from cyclenPH. Downfield shifts are commonly observed in metallo-substituted pentacoordinate phosphorus molecules compared to non-metalated species.<sup>8,10,11</sup> Because of the bridging nature of the cyclenP moiety, the methylene groups give rise to multiple <sup>13</sup>C signals. The ν<sub>CO</sub> region of the IR shows bands of approximately equal intensity, three for (cyclenP)Co(CO)<sub>3</sub> and two for (cyclenP)MoCp(CO)<sub>2</sub>.

(5) (a) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955. (b) Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3378.

(6) Dupart, J. M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051.

(7) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776.

(8) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.

(9) (a) Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1292. (b) Richman, J. E.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 5265.

(10) (a) Lattman, M.; Anand, B. N.; Garrett, D. R.; Whitener, M. A. *Inorg. Chem. Acta* **1983**, *76*, L139. (b) Lattman, M.; Morse, S. A.; Cowley, A. H.; Lasch, J. G.; Norman, N. C. *Inorg. Chem.* **1985**, *24*, 1364.

(11) (a) Jeanneaux, F.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 4272. (b) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 284. (c) Lattman, M.; Chopra, S. K.; Morse, S. A.; Chu, S. S. C.; de Meester, P. J. *Organomet. Chem.* **1985**, *294*, 347.

Table I. Spectral Data for Compounds<sup>a</sup>

compd	<sup>31</sup> P, ppm	<sup>13</sup> C, ppm		IR, cm <sup>-1</sup>	
		cyclen	other	$\nu_{\text{PH}}$	$\nu_{\text{CO}}$
cyclenPH <sup>b</sup>	-55 ( <sup>1</sup> J <sub>PH</sub> = 630 Hz)	44.6 ( <sup>2</sup> J <sub>PC</sub> = 8 Hz)		2285 m	
(cyclenP)Co(CO) <sub>3</sub> (4)	1	55.9, 48.9, 48.8, 45.1, 44.8, 43.8, 43.6	c		2026 vs, 1853 vs, 1832 vs
(cyclenP)MoCp(CO) <sub>2</sub> (6)	-1	59.6, 48.7, 45.3, 44.9, 44.4, 44.2	248.5, 248.1, 91.8		1924 vs, 1834 vs
(cyclenPH <sub>2</sub> )[Co(CO) <sub>4</sub> ] (5)	-40 ( <sup>1</sup> J <sub>PH</sub> = 729 Hz)	43.7	c	2370 w	1885 vs
(cyclenPH <sub>2</sub> )[MoCp(CO) <sub>3</sub> ] (7)	-47 ( <sup>1</sup> J <sub>PH</sub> = 696 Hz)	44.5 ( <sup>2</sup> J <sub>PC</sub> = 9 Hz)	236.4, 86.8		1890 s, 1770 vs <sup>d</sup>
(cyclenPH <sub>2</sub> )[Mn(CO) <sub>5</sub> ] (8)	-50 ( <sup>1</sup> J <sub>PH</sub> = 653 Hz)	45.0 ( <sup>2</sup> J <sub>PC</sub> = 7 Hz)	239.8	e	1915 sh, 1895 vs, 1860 vs, 1822 sh
(cyclenPH <sub>2</sub> )[WCp(CO) <sub>3</sub> ] (9)	-44 ( <sup>1</sup> J <sub>PH</sub> = 717 Hz)	44.2 ( <sup>2</sup> J <sub>PC</sub> = 8 Hz)	226.6, 85.1	2390 w <sup>f</sup>	1888 s, <sup>g</sup> 1770 vs <sup>d</sup>
(cyclenPH <sub>2</sub> )I (10)	-45 ( <sup>1</sup> J <sub>PH</sub> = 738 Hz)	42.8 (br) <sup>h</sup>			

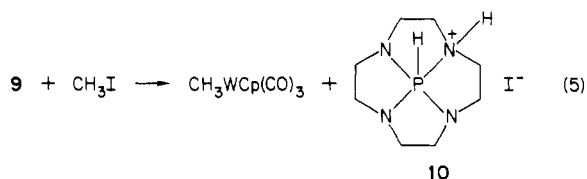
<sup>a</sup>Data obtained in THF solution except for cyclenPH and (cyclenPH<sub>2</sub>)I which were obtained in CDCl<sub>3</sub>. <sup>b</sup>Reported data:<sup>1b</sup> <sup>31</sup>P,  $\delta$  -54.5 (<sup>1</sup>J<sub>PH</sub> = 621 Hz); <sup>13</sup>C,  $\delta$  45.0 (<sup>2</sup>J<sub>PC</sub> = 8.8 Hz); <sup>1</sup>H,  $\delta$  6.88 (d, 1 H, <sup>1</sup>J<sub>PH</sub> = 628 Hz), 3.03, 2.83 (m, 16 H). <sup>c</sup>No <sup>13</sup>C signals due to CO were observed. <sup>d</sup>These bands exhibit a barely discernable splitting with maxima at ca. 1775 and 1765 cm<sup>-1</sup>. <sup>e</sup>Obscured by other signals. <sup>f</sup>In CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>g</sup>Small intensity absorptions at 1920 and 2020 cm<sup>-1</sup> also observed. <sup>h</sup>In more concentrated solutions, the <sup>13</sup>C signal sharpens,  $\delta$  42.8 (<sup>2</sup>J<sub>PC</sub> = 8 Hz). <sup>1</sup>H NMR:  $\delta$  7.53 (d, 1 H, <sup>1</sup>J<sub>PH</sub> = 737 Hz), 7.4 (br, 1 H), 3.20, 2.99 (br, 16 H).

Both 4 and 6 give mass spectra which show a small molecular ion as well as sequential loss of CO. The base peak for 4 is at *m/e* 199 and corresponds to cyclenP<sup>+</sup> while the base peak for 6 is at *m/e* 360 and corresponds to (cyclenP)MoCp<sup>+</sup>.

The IR spectra of the four metal carbonyl containing salts exhibit CO stretching frequencies in good agreement with those reported earlier for identical anions.<sup>12</sup> The presence of a P-H bond in these species is verified by the observation of a doublet (<sup>1</sup>J<sub>PH</sub> = 650–730 Hz) in the proton-coupled <sup>31</sup>P NMR spectrum which collapses to a singlet in the decoupled spectrum. The <sup>31</sup>P chemical shifts,  $\delta$  -40 to -50, are consistent with pentacoordinate phosphorus (e.g., cyclenPH has a <sup>31</sup>P resonance at -55 ppm).

Though spectral data indicated the reactions to be clean (except for Mn), isolation of large quantities of analytically pure metal carbonyl salts proved difficult. However, analytically pure samples of most of the salts could be obtained in moderate to low yields (see Experimental Section).

A further reaction was attempted with 9; (cyclenPH<sub>2</sub>)[WCp(CO)<sub>3</sub>] was found to react with an equivalent amount of CH<sub>3</sub>I according to reaction 5. (cyclenPH<sub>2</sub>)I (10) is an isolable, moisture-sensitive solid, soluble in chlorinated solvents. The <sup>31</sup>P and <sup>13</sup>C spectra of 10 are similar to those of the metal carbonyl salts (Table I).

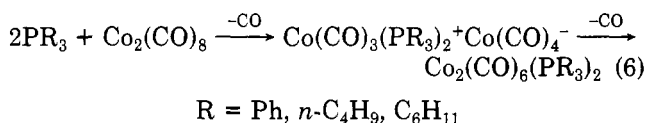


## Discussion

**1. Reactions.** The new covalent compounds isolated in these reactions, 4 and 6, are similar to the bidentate systems obtained by Riess and co-workers<sup>8,11</sup> through other routes. In fact, the molybdenum derivative 6 obtained here differs from 3a<sup>8</sup> by only two methylene groups. However, in addition to the different reactivity patterns exhibited by cyclamPH and cyclenPH, there are some structural differences between the metalated derivatives (see section 2).

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Turning now to the metal carbonyl salts, the fact that (cyclenPH<sub>2</sub>)[Co(CO)<sub>4</sub>] undergoes spontaneous loss of CO and H<sub>2</sub> at elevated temperatures is not very surprising since other Co(CO)<sub>4</sub><sup>-</sup> salts are known to lose CO under similar conditions (reaction 6).<sup>13</sup>

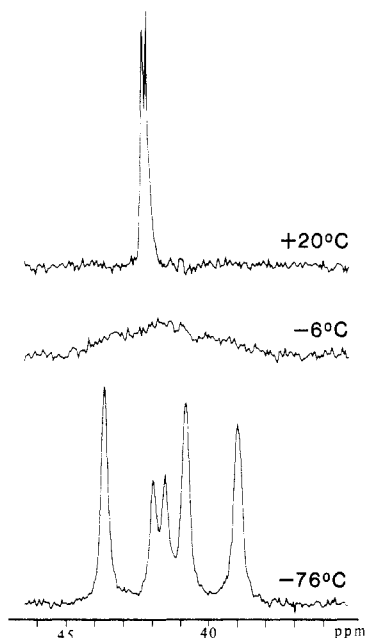


The fact that the reactions between cyclenPH and Co<sub>2</sub>(CO)<sub>8</sub>, [MoCp(CO)<sub>3</sub>]<sub>2</sub>, and Mn<sub>2</sub>(CO)<sub>10</sub> afford the salts 5, 7, and 8, respectively, suggests that similar mechanisms are involved and, most likely, either (cyclenP)Mn(CO)<sub>4</sub>, or a precursor leading to its formation, is unstable under the reaction conditions and decomposes. A number of mechanisms for these reactions can account for the observed products, but speculation at this time is premature and further work is needed to propose a reliable mechanism. The formation of (cyclenPH<sub>2</sub>)[WCp(CO)<sub>3</sub>] from cyclenPH and HCp(CO)<sub>3</sub> appears to be a simple proton abstraction; however, an electron-transfer mechanism cannot be ruled out.<sup>4,5,14</sup> In a recent kinetic study,<sup>14</sup> strong nitrogen bases were found to react with metal carbonyl hydrides to yield metal carbonyl salts. For example, treatment of HCp(CO)<sub>3</sub> with (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N yielded (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH[WCp(CO)<sub>3</sub>]. Weak bases such as pyridine did not react, and no evidence of CO substitution was observed. This behavior contrasts with that of phosphines and phosphites which typically react with metal carbonyl hydrides via CO substitution.<sup>15</sup>

An interesting trend is found in the <sup>31</sup>P NMR spectra of the cyclenPH<sub>2</sub><sup>+</sup> metal carbonyl salts: a more upfield chemical shift is accompanied by a decrease in the P-H coupling constant. In fact, a linear regression yields the equation  $\delta(^{31}\text{P}) = 0.121(^{1}J_{\text{PH}}) - 129$  (correlation coefficient (*r*) = 0.0943). The spread of chemical shifts and coupling constants is large considering only the anion is being changed. However, many transition-metal carbonyl salts are known to exist as contact and/or solvent-separated ion pairs<sup>12</sup> in solution and such interactions could account for the observed range. The only case where the IR spectrum definitely suggests a contact ion pair is in (cyclenPH<sub>2</sub>)-[Mn(CO)<sub>5</sub>] where shoulders were detected in the  $\nu_{\text{CO}}$  region

(13) (a) McCleverty, J. A.; Davison, A.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3890. (b) Szabo, P.; Fekete, L.; Bor, G.; Nagy-Magos, Z.; Marko, L. *J. Organomet. Chem.* **1968**, *12*, 245.

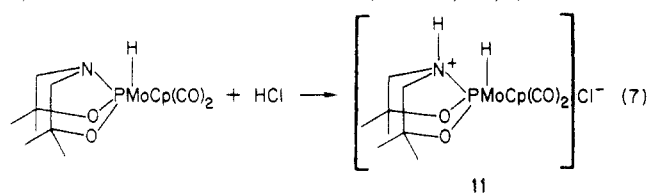
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(15) See, for example: (a) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715. (b) Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445.



**Figure 1.** Variable-temperature  $^{13}\text{C}$  NMR spectrum of (cyclenPH<sub>2</sub>)I (10).

(1822 and 1915  $\text{cm}^{-1}$ ). Similar spectral observations for  $\text{Na}[\text{Mn}(\text{CO})_5]$  in THF have been attributed to a contact ion pair.<sup>12d,e</sup>

The cyclenPH<sub>2</sub><sup>+</sup> salts are novel in a number of respects. First of all, only recently has a species been isolated that has a phosphorus bound to a protonated nitrogen (reaction 7).<sup>16</sup> The usual reaction of HX (X = Cl, Br, I) with a PN



linkage is to cleave the bond thereby yielding P-X and N-H containing species.<sup>17</sup> Thus, the isolation of 10 and 11 is quite unusual. The stability exhibited by cyclenPH<sub>2</sub><sup>+</sup> may stem, in part, from the original equilibrium of cyclenPH which exists only in the phosphorane form 1 (see above).

Secondly, there is at least one exchange process occurring in the cyclenPH<sub>2</sub><sup>+</sup> cations as is clear from the behavior of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra which vary with both concentration and temperature. The broad resonance assigned to the N-H proton in the  $^1\text{H}$  NMR spectrum of (cyclenPH<sub>2</sub>)I sharpens as the concentration of the sample is increased. The  $^{13}\text{C}$  signal also sharpens with concentration (see Table I). In addition, spectral changes in the  $^{13}\text{C}$  spectrum are observed as the temperature is lowered (see Figure 1). At -6 °C, only a barely discernible broad resonance is seen. At -76 °C, five distinct peaks appear.

Two different exchange processes could account for the observed spectra. One is pseudorotation<sup>18</sup> accompanied by proton transfer among the nitrogens. Another could be P-N bond cleavage (of the P-N<sup>+</sup>-H linkage), accom-

(16) Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 7985.

(17) (a) Kraihanzel, C. S. *J. Organomet. Chem.* **1974**, *73*, 137. (b) Fluck, E.; Haubold, W. "Organic Phosphorus Compounds"; Maier, L., Kosolapoff, G. M., Eds.; Wiley: New York, 1975; Vol. 6, p 579.

(18) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. As an alternative to interchanging equivalent trigonal-bipyramid (tbp) structures by pseudorotation, cyclenPH<sub>2</sub><sup>+</sup> or cyclenPH could have a square-pyramid (sp) structure with all four nitrogen atoms at the base of a sp.

**Table II.** Selected Bond Distances (Å)<sup>a</sup> for (cyclenP)MoCp(CO)<sub>2</sub> (6) and (cyclamp)MoCp(CO)<sub>2</sub> (3a)<sup>b</sup>

atom 1	atom 2	dist	
		6	3a
Mo	P	2.431 (1)	2.444 (2)
Mo	N1	2.257 (2)	2.223 (5)
Mo	C9	2.363 (4)	
Mo	C10	2.414 (3)	
Mo	C11	2.379 (3)	
Mo	C12	2.302 (4)	
Mo	C13	2.294 (4)	
Mo	C20	1.920 (4)	
Mo	C21	1.952 (3)	
P	N1	1.852 (2)	1.854 (5)
P	N2	1.699 (3)	1.697 (6)
P	N3	1.733 (2)	1.696 (7)
P	N4	1.698 (2)	1.670 (7)
O1	C21	1.159 (4)	
O2	C20	1.161 (4)	

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup>Data from ref 8. Atom numbering for 3a is similar to that in Figure 1.

**Table III.** Selected Bond Angles (deg)<sup>a</sup> for (cyclenP)MoCp(CO)<sub>2</sub> (6) and (cyclamp)MoCp(CO)<sub>2</sub> (3a)<sup>b</sup>

atom 1	atom 2	atom 3	angle	
			6	3a
P	Mo	N1	46.35 (6)	46.4 <sup>c</sup>
P	Mo	C9	143.8 (1)	
P	Mo	C10	110.28 (9)	
P	Mo	C11	94.8 (1)	
P	Mo	C12	112.8 (1)	
P	Mo	C13	148.5 (1)	
P	Mo	C20	78.3 (1)	
P	Mo	C21	113.18 (9)	
C20	Mo	C21	77.9 (1)	
Mo	P	N1	61.88 (7)	60.5 (2)
Mo	P	N2	113.60 (9)	116.4 (2)
Mo	P	N3	119.6 (1)	116.2 (2)
Mo	P	N4	116.23 (9)	118.0 (2)
N1	P	N2	88.2 (1)	87.8 (3)
N1	P	N3	178.5 (1)	176.6 (3)
N1	P	N4	88.4 (1)	93.8 (3)
N2	P	N3	90.9 (1)	93.5 (3)
N2	P	N4	120.7 (1)	117.6 (3)
N3	P	N4	90.9 (1)	88.4 (4)
Mo	N1	P	71.76 (8)	73.1 <sup>c</sup>
Mo	N1	C1	120.0 (2)	
Mo	N1	C3	119.3 (2)	
P	N1	C1	110.7 (2)	
P	N1	C3	112.3 (2)	
C1	N1	C3	114.3 (3)	
P	N2	C4	117.0 (2)	
P	N2	C5	113.6 (2)	
C4	N2	C5	116.9 (3)	
P	N3	C6	110.2 (3)	
P	N3	C7	113.3 (2)	
C6	N3	C7	117.9 (6)	
P	N4	C2	113.8 (2)	
P	N4	C8	112.2 (2)	
C2	N4	C8	117.1 (3)	
Mo	C20	O2	176.0 (3)	
Mo	C21	O1	175.2 (3)	

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup>Data from ref 8. Atom numbering for 3a is similar to that in Figure 1. <sup>c</sup>Calculated value.

panied by proton transfer and P-N bond reforming.<sup>19</sup> The present data cannot differentiate between these mechanisms. It has been suggested previously<sup>1b</sup> that cyclenPH undergoes pseudorotation, and it appears to do so at both ambient and low temperatures since no spectral changes

(19) We thank a reviewer for suggesting this mechanism.

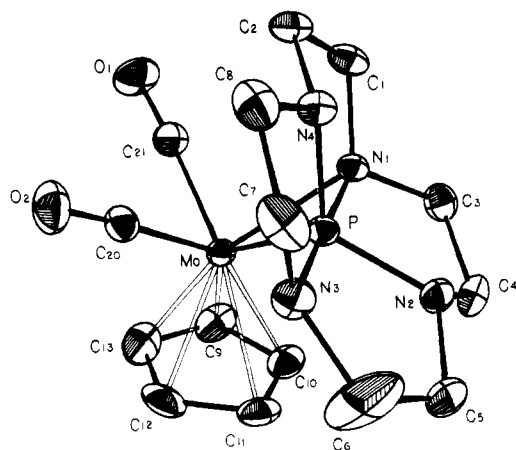


Figure 2. ORTEP plot of (cyclenP)MoCp(CO)<sub>2</sub> (6).

are observed down to  $-76\text{ }^{\circ}\text{C}$ .<sup>18</sup>

**2. Structure of (cyclenP)MoCp(CO)<sub>2</sub> (6).** The structure of 6, determined by X-ray diffraction, is illustrated in Figure 2. Bond lengths and bond angles are listed in Tables II and III, respectively. Also included in the tables are pertinent data for the cyclam derivative 3a<sup>8</sup> for comparison purposes.

The Mo-P and Mo-N bond lengths are within normal ranges.<sup>20</sup> The phosphorus atom adopts a distorted tbp geometry with N<sub>1</sub> and N<sub>3</sub> as the axial substituents and Mo, N<sub>2</sub>, and N<sub>4</sub> as the equatorial ones. While the N<sub>1</sub>-P-N<sub>3</sub> angle is almost linear (178.5°), the three equatorial atoms do not lie in the plane of the phosphorus atom [sum of equatorial angles about P is 350.5 (3)°]. This is due, most likely, to the severe constraint of the cyclic P-Mo-N<sub>1</sub> bonds. The N<sub>2</sub>-P-N<sub>4</sub> angle of 120.7 (1)° is normal for a tbp while the other two equatorial angles of 113.60 (9)° (Mo-P-N<sub>2</sub>) and 116.23 (9)° (Mo-P-N<sub>4</sub>) are contracted significantly from the ideal angle of 120°. It is interesting to note that all of the N-P-N angles are very close to those expected for an ideal tbp.

The P-Mo-N<sub>1</sub> triangle causes severe distortion in the bond lengths of the cyclenP moiety. Thus, the expected<sup>21</sup> two equal axial and two equal equatorial bond lengths (the latter being shorter) are not found. What is observed is one extremely long P-N<sub>1</sub> axial bond of 1.852 (2) Å and three P-N bonds of about 1.70 Å (though the other axial bond, P-N<sub>3</sub>, is slightly longer than the two P-N equatorial bonds).

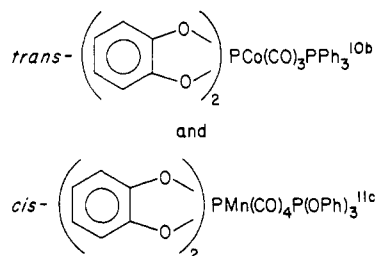
These data are similar to those found for 3a (Tables II and III). Small differences are found in the Mo-N<sub>1</sub>, P-N<sub>3</sub>, and P-N<sub>4</sub> bond distances which are slightly longer in the cyclen derivative. Also, the N<sub>4</sub>P skeletal angles more closely approximate the ideal tbp in 6.

Larger differences between the structures are observed when examining the angles about the three tricoordinate nitrogen atoms. The sum of the angles about N<sub>2</sub>, N<sub>3</sub>, and N<sub>4</sub> are 347.5 (7)°, 341.4 (1.1)°, and 343.1 (7)°, respectively, in 6 and 350 (1.5)°, 357 (2.1)°, and 360 (2.1)°, respectively, in 3a. While N<sub>2</sub> is pyramidal in both cases, N<sub>3</sub> and N<sub>4</sub> are pyramidal in the cyclen derivative and virtually planar in the cyclam molecule. These differences are reflected in the longer (by 0.02–0.04 Å) P-N<sub>3</sub> and P-N<sub>4</sub> bonds in 6 and

are in accord with the observed trend that P-N bond lengths decrease as the N hybridization changes from sp<sup>3</sup> to sp<sup>2</sup>.<sup>22</sup>

The structures of two other cyclenPX derivatives are known, cyclenPF<sup>1a</sup> and cyclenP-Pcyclen.<sup>5</sup> The details of the cyclenPF structure are somewhat sketchy; however, the geometry about phosphorus is midway between a tbp and square pyramid (sp) and the sum of the angles about the nitrogen atoms are 352° (N<sub>eq</sub>) and 347° (N<sub>ax</sub>). Both P atoms in cyclenP-Pcyclen are identical and are 32.9% distorted<sup>23</sup> along the Berry coordinate<sup>18</sup> from tbp to sp. Comparative structural data are as follows: bond lengths, P-N<sub>ax</sub> = 1.782 (2) Å, P-N<sub>eq</sub> = 1.694 (2) Å; bond angles, N<sub>ax</sub>-P-N<sub>ax</sub> = 169.6 (1)°, N<sub>eq</sub>-P-N<sub>eq</sub> = 131.1 (1)°, N<sub>eq</sub>-P-N<sub>ax</sub> = 87.9° (average value). The sum of the angles about the nitrogen atoms are 351.1° (N<sub>eq</sub>) and 343.2° (N<sub>ax</sub>).

Finally, it is noted that the structures of two nonbridging metallophosphoranes have been reported.



Both of these molecules have pentacoordinate phosphorus atoms with distorted tbp geometries.

### Experimental Section

All reactions and manipulations were carried out in an atmosphere of prepurified dinitrogen or under vacuum unless otherwise indicated. Solvents were rigorously dried over appropriate drying agents and distilled and deoxygenated prior to use. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer and NMR spectra on an IBM WP200SY multinuclear NMR spectrometer resonating at 200.132 (<sup>1</sup>H), 50.327 (<sup>13</sup>C), and 81.026 (<sup>31</sup>P) MHz. All <sup>13</sup>C and <sup>31</sup>P spectra are proton-decoupled unless otherwise indicated. <sup>1</sup>H spectra were run in 10-mm NMR tubes in CDCl<sub>3</sub>, and peak positions were measured relative to the residual CHCl<sub>3</sub> signal, referenced to Me<sub>4</sub>Si. In CDCl<sub>3</sub> solution, <sup>13</sup>C and <sup>31</sup>P spectra were run in 10-mm NMR tubes. With other solvents, the sample solution was put into an 8-mm NMR tube and inserted into a 10-mm NMR tube containing D<sub>2</sub>O as a lock solvent. <sup>13</sup>C signals were measured relative to solvent peaks, referenced to Me<sub>4</sub>Si. <sup>31</sup>P signals were referenced to external H<sub>3</sub>PO<sub>4</sub>. Mass spectra were recorded on a Hewlett-Packard 5988A GC/MS system. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada, and Galbraith Laboratories, Inc., Knoxville, TN.

The metal carbonyl dimers were obtained commercially and used without further purification except for Mn<sub>2</sub>(CO)<sub>10</sub> and Co<sub>2</sub>(CO)<sub>8</sub>, which were sublimed in vacuo prior to use. The hydride HWCp(CO)<sub>3</sub> was prepared as described in the literature.<sup>24</sup>

**Synthesis of cyclenPH.** The cyclen precursors TsN-(CH<sub>2</sub>CH<sub>2</sub>NHTs)<sub>2</sub>,<sup>25</sup> Na<sub>2</sub>TsN(CH<sub>2</sub>CH<sub>2</sub>NTs)<sub>2</sub>,<sup>26</sup> TsN-(CH<sub>2</sub>CH<sub>2</sub>OTs)<sub>2</sub>,<sup>27</sup> and tetratosylcyclen<sup>28</sup> (Ts = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>-)

(22) (a) Romming, C.; Songstad, J. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 689. (b) Romming, C.; Songstad, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 187 and references therein.

(23) This value is obtained by using unit bond lengths in the dihedral angle method. (Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.*, **1977**, *99*, 3318.) The value falls to 25.3% with use of actual bond lengths. See ref 5.

(24) Poyet, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(25) Koyama, H.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 481.

(26) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1982**, *58*, 86.

(27) Pettit, G. R.; Chamberland, M. R.; Green, B. *Can. J. Chem.* **1967**, *45*, 1555.

(28) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.

(20) Normal ranges for comparable Mo-P and Mo-N bonds are about 2.3–2.6 and 2.1–2.4 Å, respectively. See: Brown, I. D.; Brown, M. C.; Hawthorne, F. C. *BIDICS* 1969–1981, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.

(21) (a) Holmes, R. R. *Acc. Chem. Res.*, **1979**, *12*, 257. (b) Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, D.C., 1980; Vol. 1.

**Table IV. Pertinent Crystallographic and Intensity Data Collection Parameters for (cyclenP)MoCp(CO)<sub>2</sub> (6)**

formula	C <sub>15</sub> H <sub>21</sub> MoN <sub>4</sub> O <sub>2</sub> P
fw	416.27
cryst system	monoclinic
space group	P2 <sub>1</sub> /c
a/Å	8.605 (2)
b/Å	8.584 (2)
c/Å	22.157 (3)
β/deg	93.84 (2)
Z	4
ρ(calcd)/g cm <sup>-3</sup>	1.697
μ(Mo Kα)/cm <sup>-1</sup>	8.96
λ(Mo Kα)/Å	0.710 69 (graphite-monochromated)
cryst size/mm	0.25 × 0.20 × 0.15
reflectns measd	±h, ±k, ±l for 2θ = 2.0–50.0°
reflectns collected	3161 total yielding 3080 unique
no. of obsd data [I > 3σ(I)]	2448
R	0.0228
R <sub>w</sub>	0.0254
temp/K	298
agreement factor for av reflectns	0.029
decay of standard	<4%

were prepared by literature methods. cyclen was prepared by a modified literature procedure for a related compound:<sup>29</sup> tetraatosylcyclen (250 g, 0.317 mol) was stirred with 500 mL of concentrated sulfuric acid at 100 °C for 48 h. The mixture was then cooled in an ice bath and ca. 2L of anhydrous ether slowly added. The resulting precipitate was filtered, washed with anhydrous ether, and pumped dry. The solid was opened to air and dissolved in ca. 300 mL of water and the solution immersed in an ice bath. About 200 g of NaOH was then slowly added. The resulting precipitate was filtered, dried, and washed with CHCl<sub>3</sub>. The water was pumped off from the aqueous solution and the residue also washed with CHCl<sub>3</sub>. Both CHCl<sub>3</sub> layers were combined and the solvent removed to yield crude cyclen (46.0 g). Sublimation (95–120 °C, 0.2 torr) yielded pure cyclen (33.6 g, 62% overall).

cyclenPH was prepared by a modified literature procedure:<sup>1b</sup> cyclen (9.60 g, 57.0 mmol) and P(NMe<sub>2</sub>)<sub>3</sub> (15.0 mL, 82.5 mmol) were heated together in a flask equipped with a reflux condenser at 80–85 °C for 11 h. Excess P(NMe<sub>2</sub>)<sub>3</sub> was pumped off and the product sublimed (60–90 °C, 0.2 torr), yielding pure cyclenPH (9.35 g, 83%).

**Reaction of cyclenPH and Co<sub>2</sub>(CO)<sub>8</sub>.** cyclenPH (0.323 g, 1.61 mmol) and Co<sub>2</sub>(CO)<sub>8</sub> (0.317 g, 0.927 mmol) were added to a flask, the flask was immersed in a –78 °C bath, and 10 mL of cold hexane was added. The mixture was stirred, allowed to warm to ambient temperature over 1 h, and stirred for another 4 h, yielding a yellow solution and precipitate. The volatiles were pumped off, and the residue was washed by adding a small amount of hexane and syringing out the yellow solution along with some white insoluble solid. The mixture was filtered through a frit. This was repeated until the washings were almost colorless. A green solid remained which adhered to the sides of the flask. Removal of the hexane yielded pure (cyclenP)Co(CO)<sub>3</sub> as an air-stable, yellow solid (0.201 g, 73%); mp 141–143 °C. Anal. Calcd for C<sub>11</sub>H<sub>16</sub>CoN<sub>4</sub>O<sub>3</sub>P: C, 38.60; H, 4.72; N, 16.38; P, 9.05. Found: C, 38.63; H, 5.07; N, 15.75; P, 8.79.

The solid remaining on the frit was pumped dry, yielding pure (cyclenPH<sub>2</sub>)[Co(CO)<sub>4</sub>] as a slightly gray solid (0.122 g, 41%). Anal. Calcd for C<sub>12</sub>H<sub>18</sub>CoN<sub>4</sub>O<sub>4</sub>P: C, 38.72; H, 4.88; N, 15.05; P, 8.32. Found: C, 38.48; H, 4.96; N, 15.04; P, 8.53.

**Formation of (cyclenP)Co(CO)<sub>3</sub> (4) from (cyclenPH<sub>2</sub>)[Co(CO)<sub>4</sub>] (5).** A sample of 5, in THF, was stirred at ambient temperature for 42 h. No spectral changes were observed. Another sample was heated at 55 °C for 40 h. Spectral data indicated almost total conversion to the covalent species 4. A few low intensity impurity peaks were detected in the final solution. No further purification was attempted.

**Reaction of cyclenPH and [MoCp(CO)<sub>3</sub>]<sub>2</sub>.** cyclenPH (0.381 g, 1.90 mmol) and [MoCp(CO)<sub>3</sub>]<sub>2</sub> (0.466 g, 0.951 mmol) were

**Table V. Positional Parameters and Their Estimated Standard Deviations<sup>a</sup>**

atom <sup>b</sup>	x	y	z	B, Å <sup>2</sup>
Mo	0.31654 (3)	0.14859 (3)	0.16999 (1)	2.308 (4)
P	0.20914 (8)	0.28129 (9)	0.07937 (3)	2.20 (1)
O1	0.6730 (3)	0.0867 (4)	0.1724 (1)	5.41 (7)
O2	0.3417 (4)	–0.1120 (3)	0.0756 (1)	5.16 (7)
N1	0.3591 (3)	0.3839 (3)	0.1287 (1)	2.29 (5)
N2	0.0828 (3)	0.4267 (3)	0.0937 (1)	2.82 (5)
N3	0.0681 (3)	0.1898 (3)	0.0321 (1)	3.42 (6)
N4	0.3284 (3)	0.2969 (3)	0.0217 (1)	2.61 (5)
C1	0.5005 (3)	0.4106 (4)	0.0964 (1)	3.14 (6)
C2	0.4930 (4)	0.3061 (4)	0.0416 (1)	3.16 (7)
C3	0.2974 (4)	0.5242 (4)	0.1565 (2)	3.32 (7)
C4	0.1195 (4)	0.5193 (4)	0.1469 (2)	3.52 (7)
C5	–0.0803 (4)	0.3846 (5)	0.0807 (2)	4.27 (8)
C6	–0.0860 (5)	0.2487 (7)	0.0434 (3)	9.7 (1)
C7	0.1085 (5)	0.1799 (5)	–0.0298 (2)	4.39 (8)
C8	0.2848 (5)	0.1904 (4)	–0.0275 (2)	3.94 (8)
C9	0.3075 (5)	0.1352 (6)	0.2764 (2)	4.74 (9)
C21	0.5414 (4)	0.1167 (4)	0.1710 (2)	3.44 (7)
C10	0.1874 (4)	0.2351 (5)	0.2573 (2)	3.98 (8)
C11	0.0800 (4)	0.1538 (5)	0.2195 (2)	4.20 (8)
C12	0.1344 (5)	0.0001 (5)	0.2151 (2)	5.25 (9)
C13	0.2763 (5)	–0.0096 (5)	0.2510 (2)	5.66 (9)
C20	0.3323 (4)	–0.0098 (4)	0.1095 (2)	3.22 (7)
H1	0.501 (4)	0.519 (4)	0.084 (1)	3.0 (7)*
H2	0.591 (4)	0.397 (4)	0.123 (1)	3.7 (8)*
H3	0.537 (3)	0.200 (3)	0.051 (1)	2.1 (6)*
H4	0.549 (4)	0.351 (4)	0.010 (2)	3.9 (8)*
H5	0.335 (3)	0.618 (4)	0.135 (1)	2.3 (7)*
H6	0.328 (4)	0.534 (5)	0.199 (2)	5 (1)*
H7	0.072 (4)	0.476 (4)	0.185 (2)	3.4 (8)*
H8	0.084 (4)	0.626 (4)	0.141 (2)	4.4 (9)*
H9	–0.130 (4)	0.468 (5)	0.066 (2)	6 (1)*
H10	–0.122 (5)	0.355 (6)	0.119 (2)	9 (1)*
H11	–0.171 (4)	0.189 (5)	0.030 (2)	6 (1)*
H12	–0.101 (4)	0.265 (4)	0.017 (2)	3.2 (8)*
H13	–0.071 (4)	0.743 (4)	0.053 (2)	4.2 (9)*
H14	0.027 (3)	0.083 (5)	–0.042 (2)	4 (1)*
H15	0.317 (4)	0.231 (4)	–0.065 (2)	4.4 (9)*
H16	0.333 (4)	0.087 (4)	–0.020 (2)	4.1 (8)*
H17	0.614 (4)	0.670 (5)	0.196 (2)	5 (1)*
H18	0.184 (4)	0.339 (4)	0.268 (2)	3.6 (8)*
H19	–0.011 (4)	0.191 (4)	0.203 (2)	4.4 (9)*
H20	–0.085 (5)	0.424 (5)	0.307 (2)	5 (1)*
H21	0.322 (5)	–0.094 (5)	0.257 (2)	6 (1)*

<sup>a</sup> Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(\frac{1}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

<sup>b</sup> Labeling system: H1, H2 on C1; H3, H4 on C2; H5, H6 on C3; H7, H8 on C4; H9, H10 on C5; H11, H12 on C6; H13, H14 on C7; H15, H16 on C8; H17 on C9; H18 on C10; H19 on C11; H20 on C12; H21 on C13.

dissolved in 15 mL of THF and refluxed for 5 days. The reaction mixture was filtered to remove a small amount of solid precipitate. The volatiles were pumped off, the residue was washed with hexane, and the washings were discarded. The residue was further washed with cyclohexane until the washings were almost colorless. Evaporation of the cyclohexane led to pure (cyclenP)MoCp(CO)<sub>2</sub> as an air-stable, yellow solid (0.293 g, 74%); mp 176–178 °C. Anal. Calcd for C<sub>15</sub>H<sub>21</sub>MoN<sub>4</sub>O<sub>2</sub>P: C, 43.27; H, 5.09; N, 13.46; P, 7.44. Found: C, 43.18; H, 5.04; N, 13.24; P, 6.46.

The remaining dark, oily residue was washed repeatedly with toluene. This dissolved the last traces of 6, but also dissolved some of the salt 7. The washings were continued until no 6 was observed in the IR spectrum. The remaining solid was pumped dry to yield (cyclenPH<sub>2</sub>)[MoCp(CO)<sub>3</sub>] as a gray solid (0.080 g, 19%). Anal. Calcd for C<sub>16</sub>H<sub>23</sub>MoN<sub>4</sub>O<sub>3</sub>P: C, 43.05; H, 5.20; N, 12.56; P, 6.94. Found: C, 43.52; H, 5.29; N, 12.12; P, 6.00.

**Reaction of cyclenPH and Mn<sub>2</sub>(CO)<sub>10</sub>.** cyclenPH (0.200 g, 1.00 mmol) and Mn<sub>2</sub>(CO)<sub>10</sub> (0.195 g, 0.500 mmol) were dissolved in 10 mL of THF, and the mixture was refluxed for 5 days, yielding a yellow solution and a small amount of precipitate. Spectral data indicated the formation of (cyclenPH<sub>2</sub>)[Mn(CO)<sub>5</sub>] in solution.

However, small amounts of  $\text{Mn}_2(\text{CO})_{10}$  and some phosphorus-containing species were present. After filtration, the volatiles were removed and the residue was washed with hexane and dried to yield impure  $(\text{cyclenPH}_2)[\text{Mn}(\text{CO})_5]$  as a yellow solid (0.18 g).

**Reaction of cyclenPH and  $\text{HWCp}(\text{CO})_3$ .** cyclenPH (0.112 g, 0.559 mmol) and  $\text{HWCp}(\text{CO})_3$  (0.214 g, 0.641 mmol) were added to a flask, the flask was immersed in a  $-78^\circ\text{C}$  bath, and 5 mL of cold THF was added. The mixture was stirred and allowed to warm to ambient temperature over 1 h, yielding a pink solution and white precipitate. The mixture was filtered and the solid washed thoroughly with hexane. The solid was further washed twice with 1-mL portions of THF (a minimum of THF should be used since the product is reasonably soluble in THF). The solid was pumped dry yielding pure  $(\text{cyclenPH}_2)[\text{WCp}(\text{CO})_3]$  as an off-white powder (0.210 g, 70%). Anal. Calcd for  $\text{C}_{16}\text{H}_{23}\text{N}_4\text{O}_3\text{PW}$ : C, 35.97; H, 4.35; N, 10.49; P, 5.80. Found: C, 36.05; H, 4.39; N, 10.35; P, 6.17.

**Reaction of  $\text{CH}_3\text{I}$  and  $(\text{cyclenPH}_2)[\text{WCp}(\text{CO})_3]$  (9).** A reaction mixture (in THF) prepared as above using cyclenPH (0.15 g, 0.75 mmol) and  $\text{HWCp}(\text{CO})_3$  (0.25 g, 0.75 mmol) was treated with  $\text{CH}_3\text{I}$  (0.047 mL, 0.75 mmol) and stirred for 1 h at ambient temperature. The solid which precipitated was filtered, washed with THF, and dried to yield pure  $(\text{cyclenPH}_2)\text{I}$  as an off-white solid (0.18 g, 73%); mp  $174\text{--}175^\circ\text{C}$ . Anal. Calcd for  $\text{C}_8\text{H}_{18}\text{IN}_4\text{P}$ : C, 29.28; H, 5.54; N, 17.08; P, 9.44. Found: C, 29.06; H, 5.65; N, 16.61; P, 9.16. Removal of the volatiles from the original THF supernatant left spectroscopically pure  $\text{CH}_3\text{WCp}(\text{CO})_3$  (0.22 g, 84%).

**X-ray Structure Determination.** 6 was recrystallized from THF yielding transparent yellow crystals. A suitable single crystal was mounted on an Enraf-Nonius CAD-4F diffractometer. A total of 3080 independent reflections were collected in the  $\theta/2\theta$  scan mode. Of these, 2448 were considered observed with  $I > 3\sigma(I)$  and used in the solution and refinement of the structure.

(30) For IR,  $^{13}\text{C}$ , and  $^1\text{H}$  spectra of  $\text{CH}_3\text{WCp}(\text{CO})_3$  see: (a) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* 1978, 154, 151. (b) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* 1966, 5, 1401.

Data were corrected for Lorentz and polarization effects. (An empirical absorption correction was also applied.) The structure was solved by standard Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and included in the subsequent refinement. Unit weights were used in the weighting scheme. Final refinement yielded  $R = 0.0228$  and  $R_w = 0.0254$  with no chemically significant peaks present in the final difference Fourier map. Complex neutral atom scattering factors were used throughout.<sup>31</sup> All calculations were performed on a DEC PDP 11/44 computer using Enraf-Nonius SDP Plus structure solution programs.<sup>32</sup>

Pertinent crystallographic data are summarized in Table IV and atomic positional parameters listed in Table V.

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**Registry No.** 4, 100349-94-8; 5, 100334-12-1; 6, 100349-95-9; 7, 100334-14-3; 8, 100334-16-5; 9, 100334-18-7; 10, 100349-96-0; cyclenPH, 64317-97-1; tetratosylcyclen, 52667-88-6; cyclen, 294-90-6;  $\text{P}(\text{NMe}_2)_3$ , 1608-26-0;  $\text{Co}_2(\text{CO})_8$ , 15226-74-1;  $[\text{MoCp}(\text{CO})_3]_2$ , 12091-64-4;  $\text{Mn}_2(\text{CO})_{10}$ , 10170-69-1;  $\text{HWCp}(\text{CO})_3$ , 12128-26-6;  $\text{CH}_3\text{WCp}(\text{CO})_3$ , 12082-27-8.

**Supplementary Material Available:** Tables of complete bond distances and angles, thermal parameters, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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## Preparation of Oligomeric and Polymeric $\alpha,\omega$ -Bis(trimethylsiloxy)polymethylchlorosiloxanes and Their Reactions with Alkylolithium Reagents

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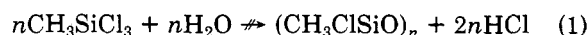
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A series of  $\alpha,\omega$ -bis(trimethylsiloxy)polymethylchlorosiloxanes ( $\text{MD}^{\text{Cl}}_n\text{M}$ ) ( $n = 1\text{--}5$  and  $\sim 35$ ) as well as  $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$  have been prepared by the palladium on carbon-catalyzed exchange reaction of  $\text{MD}^{\text{H}}_n\text{M}$  with allyl or benzyl chloride. The reaction of these with alkylolithium reagents in ether at  $-78^\circ\text{C}$  has been studied. Alkylation without cleavage of the siloxane backbone is observed with the oligomers  $\text{MD}^{\text{Cl}}_n\text{M}$ . On the other hand,  $\text{MD}^{\text{H}}\text{M}$  and  $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$  undergo facile siloxane cleavage. Some cleavage is also observed with the polymer  $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ . The spectral properties, in particular  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR, of both  $\text{MD}^{\text{H}}_n\text{M}$  and  $\text{MD}^{\text{Cl}}_n\text{M}$  are reported. The interpretation of the  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of siloxane oligomers which are chiral at both Si and C is discussed.

We have been interested in the development of methods to modify siloxane oligomers and polymers without breaking Si-O bonds.<sup>1-3</sup> The following abbreviations will be used:  $\text{M} = (\text{CH}_3)_3\text{SiO}_{0.5}$ ,  $\text{D} = (\text{CH}_3)_2\text{Si}(\text{O}_{0.5})_2$ ,  $\text{D}^{\text{H}} =$

$\text{CH}_3\text{Si}(\text{O}_{0.5})_2\text{H}$ , and  $\text{D}^{\text{Cl}} = \text{CH}_3\text{Si}(\text{O}_{0.5})_2\text{Cl}$ . While it is possible to prepare  $\alpha,\omega$ -dichloropermethylosiloxane oligomers and polymers ( $\text{Cl-D}_n\text{-Cl}$ ) by reaction of dimethyldichlorosilane with a limited amount of water (eq 1),<sup>4</sup> it is



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