mode and hence contribute four electrons to the clusters. Although in principle alkynes can behave as two- or four-electron donors, the latter property is dominant in cluster chemistry, as seen in the thermal or photochemical reactions of $M_3(CO)_{12}$ with $RC{\equiv}CR$.[14,16] It is significant that while four-electron donor character is exhibited by both $PhC{\equiv}CPh$ and $PhC{\equiv}CC{\equiv}CPh$ in their respective reactions with III and V, there is no carbonyl displacement from III and only a single CO group is substituted in V. Clearly Ru–Ru bond cleavage is a favored reaction pathway under these mild conditions.

The stereochemical changes from III to IV also provide a nice illustration of the application of the skeletal electron counting rules to cluster reactions.[17] Addition of $PhC{\equiv}CPh$ to the nido cluster III based on a tetrahedron with one vertex missing (five skeletal electron pairs) generates an arachno cluster IV with a geometry derived from that of a pentagonal bipyramid with two missing vertices (eight skeletal pairs, five vertices). In this case the two PhC fragments are part of the cluster framework and the skeleton can be readily related to the seven-vertex polyhedron. The closo cluster V (seven skeletal pairs, six vertices; C(13) is a skeletal atom) might be expected, from the counting rules to undergo skeletal expansion to a closo polyhedron with two more skeletal atoms on addition of an acetylene with loss of one CO group. Alternatively, if V is considered as a nido octahedron with one missing vertex (C(13) not considered a skeletal atom), addition of an acetylene and CO loss should afford a nido eight-vertex polyhedron. The skeletal geometry of VI counting C(15) and C(16) as skeletal atoms is difficult to relate to a regular polyhedron. The structure is best viewed in terms of the edge opening of a square-pyramidal 74-electron species on two-electron addition.

Registry No. I, 87984-98-3; II, 80800-57-3; III, 82055-65-0; IV, 87985-00-0; V, 78179-75-6; VI, 87985-01-1.

Supplementary Material Available: Tables of thermal parameters, remaining bond lengths and angles, and structure factors for IV and VI (44 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Metallophosphenium Ion Complexes Derived from Aminohalophosphites. Crystal and Molecular Structure of $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$

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The reactions of $R\overline{NCH_2CH_2OP}X$ (R = CH_3, C_2H_5, $C(CH_3)_3$, C_6H_5; X = F, Cl) with $NaMo(\eta^5\text{-}C_5H_5)(CO)_3$ in THF at 25 °C result in the formation of a series of metallophosphenium ion complexes $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}R]$. The complexes have been characterized by infrared and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and a single-crystal X-ray diffraction analysis of $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$ has been completed. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 12.072 (2) Å, b = 9.957 (2) Å, c = 13.349 (3) Å, β = 108.09 (1)°, Z = 4, V = 1525.2 (5) Å^3, and ρ = 1.58 g cm^{-3}. Least-squares refinement gave R_f = 3.5% and R_{wF} = 3.0% on 2310 unique reflections with $I > 2.5\sigma(I)$. The molecular structure displays a pseudooctahedral molybdenum atom bonded to a $(\eta^5\text{-}C_5H_5)$ ring, two terminal carbonyls, and the phosphorus atom of the phosphenium ion $[\overline{POCH_2CH_2N}C(CH_3)_3{}^+]$. The phosphenium ion is planar and the Mo–P bond distance, 2.207 (1) Å, is short.

Introduction

The reactions of metal carbonyl anions with diaminohalophosphines in a strongly polar solvent (THF)[1] produce a series of molecular metallophosphenium ion complexes that can be considered to contain a dicoordinate diaminophosphenium ion, $(R_2N)_2P^+$, covalently bonded to an anionic organometallic fragment.[2-4] The structures and properties of these complexes are found to be very dependent upon the orbital templates and electronic properties of the constituent species. For example, toward six d-electron (16 valence electron) metal fragments of the type $MCp(CO)_2^-$ (M = Cr, Mo, W) a diaminophosphenium ion acts as a terminal ligand, and a planar MPN_2 structural unit is formed in the complexes.[2] The cation σ donates an in-plane phosphorus lone pair to an empty d_{z^2} orbital on the metal fragment while the metal back-donates electron density to the out-of-plane PN_2 π^* orbital on the cation. The resulting metal–phosphorus bond distances are unusually short, and the P–N bond distances are longer than is found in $\{[(i\text{-}Pr)_2N]_2P^+\}[AlCl_4^-]$.[5] On the other hand, the eight d-electron (18 valence electron) fragment $MCp(CO)_2^-$ (M = Fe) is unable to accept a phosphorus lone pair. Consequently, the phosphorus atom rehybridizes to

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(1) Abbreviations used in the text include: THF = tetrahydrofuran; Cp = $\eta^5\text{-}C_5H_5$; Cp* = $(CH_3)_5C_5$.

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a pyramidal geometry and the cation acts only as an electron acceptor in the formation of $FeCp(CO)_2[(R_2N)_2P]$.[4] With a ten d-electron fragment $Co(CO)_4^-$, aminohalophosphines form a unique bimetallic complex in which two phosphenium ions act as semibridging ligands.[3] These examples demonstrate that the coordination abilities of diaminophosphenium ions are rich and varied, and there is increasing evidence that the ions have chemical parallels with several small molecule ligands including NO^+, SO_2, and CR_2.

A question has arisen as to whether two amide substituents are required to stabilize phosphenium ions and their complexes. Addressing this question Cowley and co-workers have reported the formation of a series of monoaminophosphenium ions,[6] $(R_2N)(R')P^+$, and a coordination complex, $\{Fe(CO)_4[(t\text{-}Bu)(Me_2N)P]^+\}$,[7] as well as syntheses for two phosphenium ions without an amide group, $(t\text{-}Bu)Cp^*P^+$ and $(Cp_2Fe)_2P^+$.[8] Malisch and co-workers[9] have examined reactions of $NaMCp(CO)_3$ (M = Cr, Mo, W) with PF_3, PCl_3, and halophosphites in a nonpolar solvent. Eighteen electron complexes of the type $MCp(CO)_3PX_2$ are obtained, and the chemistry of these complexes is consistent with the presence of a lone pair and pyramidal geometry at the phosphorus atom. In the case of a cyclic phosphite, photolysis of the complexes $MCp(CO)_3\overline{POC(CH_3)_2C(CH_3)_2O}$ results in the formation of dimeric compounds $[MCp(CO)_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$. This chemistry shows that amide groups are not a necessary condition for the formation of phosphenium ions or metallophosphenium ion complexes; however, substituents that assist in the delocalization of charge through conjugation or back-donation to phosphorus appear to stabilize these species. In an effort to better understand factors that control the formation of metallophosphenium ion complexes, we have examined a wide range of metal anion–halophosphine reactions. We report here on the reactions of $NaMoCp(CO)_3$ with several cyclic aminohalophosphites and the determination of the molecular structure of one complex, $MoCp(CO)_2\overline{POCH_2CH_2N}C(CH_3)_3$.

Experimental Section

General Information. Standard inert atmosphere techniques were used for the manipulations of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer. The samples were prepared as Nujol mulls, and the spectra were calibrated with polystyrene film absorptions. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian FT-80A NMR spectrometer. Spectral standards were $(CH_3)_4Si$ (^{13}C, ^1H) and 85% H_3PO_4 (^{31}P).

Materials. The aminohalophosphites $R\overline{NCH_2CH_2OP}Cl$ (R = CH_3 (1), CH_3CH_2 (2), $C(CH_3)_3$ (3), C_6H_5 (4) were prepared by a procedure described in the literature.[10] $[MoCp(CO)_3]_2$ was purchased from Strem Chemicals, and the sodium salt was prepared by sodium amalgam reduction of the dimer in dry THF.[11] All solvents were rigorously dried with an appropriate drying agent and degassed. All solvent transfers were accomplished by vacuum distillation.

Preparation of the Complexes. Typically, a combination of 3.7 mmol of a ligand, $R\overline{NCH_2CH_2OP}Cl$, and 3.3 mmol of $NaMoCp(CO)_3$ in 50 mL of THF was stirred in a Schlenk vessel for 24 h at 25 °C. Reaction was indicated by a color change from pale yellow to red and by evolution of CO. In each case, approximately 90–95% of the CO expected from a 1:1 reaction of ligand and metal anion was recovered with a Toepler pump. The resulting reaction mixture was filtered under an inert atmosphere, and the THF was removed from the filtrate by vacuum evaporation. The crude products were extracted into benzene and filtered, and the benzene was evaporated leaving red viscous oils which are soluble in THF and benzene and slightly soluble in hydrocarbons. The yields of isolated products are 70–80%. Great difficulty was encountered in obtaining completely satisfactory elemental analyses for these extremely air- and heat-sensitive complexes; therefore, characterization is based upon spectroscopic data and the X-ray crystal structure analysis of one complex.

Characterization Data. Infrared data in the carbonyl region are listed for the four complexes: $MoCp(CO)_2[\overline{POCH_2CH_2N}CH_3]$ (**5**), $MoCp(CO)_2[\overline{POCH_2CH_2N}CH_2CH_3]$ (**6**), $MoCp(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$ (**7**), and $MoCp(CO)_2[\overline{POCH_2CH_2N}C_6H_5]$ (**8**). Infrared spectrum (cm^{-1}; mull): **5**, 1934, 1862; **6**, 1970, 1895; **7**, 1920, 1845; **8**, 1948, 1870. Phosphorus-31 NMR (**1**–**4**, $CDCl_3$: **5**–**8**, C_6D_6): **1**, δ 172; **2**, 171; **3**, 169; **4**, 161; **5**, 266; **6** 266; **7**, 258; **8**,[12] 250. Carbon-13 NMR (**1**–**4**, $CDCl_3$; **5**–**8**, C_6D_6): **1**, δ 70.19 ($^2J_{COP}$ = 9.6 Hz), 48.16 ($^2J_{CNP}$ = 7.3 Hz), 30.18 ($^2J_{CNP}$ = 14.1 Hz); **2**, 69.69 ($^2J_{COP}$ = 9.5 Hz), 45.48 ($^2J_{CNP}$ = 7.4 Hz), 39.09 ($^2J_{CNP}$ = 13.3 Hz), 13.38 ($^3J_{CCNP}$ = 10.3 Hz); **3**, 69.63 ($^2J_{COP}$ = 8.1 Hz), 52.63 ($^2J_{CNP}$ = 6.9 Hz), 41.19 ($^2J_{CNP}$ = 7.9 Hz), 28.36 ($^3J_{CCNP}$ = 11.8 Hz); **4**, 70.10 ($^2J_{COP}$ = 9.6 Hz), 44.19 ($^2J_{CNP}$ = 6.2 Hz), 140.7 ($^2J_{CP}$ = 11.4 Hz), 129.1, 121.8 (J_{CP} = 2.2 Hz), 116.7 (J_{CP} = 13.8 Hz); **5**, 88.59, 68.49 ($^2J_{COP}$ = 9.7 Hz), 50.05 ($^2J_{CNP}$ = 2.3 Hz), 31.87 ($^2J_{CNP}$ = 13.9 Hz); **6**, 87.69, 67.41 ($^2J_{COP}$ = 10.1 Hz), 46.11 ($^2J_{CNP}$ = 2.3 Hz), 38.94 ($^2J_{CNP}$ = 15.8 Hz), 14.16 ($^3J_{CCNP}$ = 1.1 Hz); **7**, 89.16 ($^2J_{CMoP}$ = 1.5 Hz), 66.69 ($^2J_{COP}$ = 9.5 Hz), 55.02 ($^2J_{CNP}$ = 6.8 Hz), 46.64, 30.35 ($^3J_{CCNP}$ = 4.1 Hz); **8**,[12] 89.73 ($^2J_{CMoP}$ = 1.4 Hz), 69.35 ($^2J_{COP}$ = 11.0 Hz), 52.40 ($^2J_{CNP}$ = 2.5 Hz), 141.0 ($^3J_{CCNP}$ = 11.0 Hz), 129.8, 129.1–125.3 (4 peaks). Proton NMR (**1**–**4**, $CDCl_3$; **5**–**8**, C_6D_6) **1**, δ 4.36 ($^3J_{HCOP}$ = 4.0, $^3J_{HCCH}$ = 7.4 Hz), 3.08 ($^3J_{HCNP}$ = 9.7, $^3J_{HCCH}$ = 7.4 Hz), 2.66 ($^3J_{HCNP}$ = 15.5 Hz); **2**, 4.34 ($^3J_{HCOP}$ = 4.1, $^3J_{HCCH}$ = 6.8 Hz), 3.1, 1.19 ($^3J_{HCCH}$ = 6.9 Hz); **3**, 4.33 ($^3J_{HCOP}$ = 4.4, $^3J_{HCCH}$ = 7.6 Hz), 3.13 ($^3J_{HCNP}$ = 7.8, $^3J_{HCCH}$ = 7.8 Hz), 1.28 ($^4J_{HCCNP}$ = 2.0 Hz); **4**, 4.69 ($^3J_{HCOP}$ = 5.4, $^3J_{HCCH}$ = 7.1 Hz), 3.55 ($^3J_{HCNP}$ = 5.6, $^3J_{HCCH}$ = 7.1 Hz), 7.2; **5**, 5.25, 3.68 ($^3J_{HCOP}$ = 7.9, $^3J_{HCCH}$ = 6.7 Hz), 2.62 ($^3J_{HCNP}$ = 10.4 Hz), 2.43 ($^3J_{HCNP}$ = 8.5, $^3J_{HCCH}$ = 6.7 Hz); **6**, 5.20, 4.1–2.2 (complex overlap of resonances), 0.96 ($^3J_{HCCH}$ = 7.0 Hz); **7**, 5.23, 3.62 ($^3J_{HCOP}$ = 7.1, $^3J_{HCCH}$ = 7.1 Hz), 2.71 ($^3J_{HCNP}$ = 7.1, $^3J_{HCCH}$ = 7.1 Hz), 1.36; **8**, 7.1, 5.03, 3.65 (m), 2.91 (m).

Crystal Structure Determination. Single crystals of **7** were grown from a saturated THF solution at 0 °C. A suitable crystal, 0.09 mm × 0.21 mm × 0.46 mm, was lodged in a glass capillary and sealed under dry nitrogen. The crystal was centered on a P3/F automated diffractometer, and determinations of the crystal class, the orientation matrix, and accurate unit cell parameters were performed in a standard manner.[13] The data were collected at 19 °C by the θ–2θ technique using Mo Kα radiation, a scintillation counter, and a pulse height analyzer. Details of the data collection are summarized in Table I. Inspection of the data revealed systematic absences $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, and the monoclinic space group $P2_1/n$ was indicated. An empirical absorption correction based on ψ scans was applied to the data; the agreement factor on the ψ scans was 2.4% before the absorption correction and 1.6% after the absorption correction. The estimated maximum and minimum transmission factors were 0.658 and 0.591. The redundant and equivalent data were av-

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(12) This spectrum was recorded from a sample dissolved in THF.

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Table I. Summary of Crystal and Data Collection Parameters for $\mathrm{Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]}$

(A) Crystal Parameters at 19 °C

crystal system: monoclinic
space group: $P2_1/n$
$a = 12.072\ (2)$ Å $V = 1525.2\ (5)$ Å^3
$b = 9.957\ (2)$ Å $Z = 4$
$c = 13.349\ (3)$ Å $F(000) = 736$
$\beta = 108.09\ (1)^\circ$ $\rho(\text{calcd}) = 1.58$ g cm^{-3}
$M_r = 363.21$ $\mu(\text{Mo K}\alpha) = 9.45$ cm^{-1}

(B) Data Collection Parameters

radiatn: Mo Kα ($\bar{\lambda} = 0.710\,69$ Å)
monochromator: highly oriented graphite crystal
scan speed: 6–30 deg min^{-1} (in 2θ)
scan range: from $[2\theta(\text{K}\alpha_1) - 1.1]^\circ$ to $[2\theta(\text{K}\alpha_2) + 1.2]^\circ$
2θ limits: $1^\circ \leqslant +h, +k, \pm l \leqslant 55^\circ$
background counting time/total scan time: 0.5
standards monotired: 3/93 reflections; [400, $0\bar{6}0$, 006]; no significant changes in intensity observed
reflctns collected: 3893
unique reflctns: 3525
unique data used: 2310 with $I > 2.5\sigma(I)$
number of variables refined: 172
GOF = 1.367
$R_F = 3.5\%$
$R_{wF} = 3.0\%$
$w = [\sigma(F)^2 + |g|F_o{}^2]^{-1}$; $g = 0.00005$

Table II. Non-Hydrogen Atom Positional Parameters and Their Esd's for $\mathrm{Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]}$

atom	x	y	z
Mo	0.30340 (3)	0.65882 (3)	0.50141 (3)
P	0.15659 (8)	0.70026 (9)	0.56237 (7)
O(1)	0.2640 (3)	0.3510 (3)	0.4683 (2)
O(2)	0.4696 (3)	0.5889 (3)	0.7234 (2)
O(3)	0.0794 (2)	0.8346 (2)	0.5264 (2)
N	0.0869 (2)	0.6524 (3)	0.6458 (2)
C(1)	0.2765 (3)	0.4654 (4)	0.4826 (3)
C(2)	0.4055 (3)	0.6147 (4)	0.6410 (3)
C(3)	0.4266 (4)	0.6947 (6)	0.4011 (4)
C(4)	0.4350 (5)	0.8045 (6)	0.4627 (4)
C(5)	0.3300 (7)	0.8693 (5)	0.4338 (5)
C(6)	0.2547 (4)	0.7963 (6)	0.3510 (4)
C(7)	0.3163 (6)	0.6888 (6)	0.3321 (4)
C(8)	0.0139 (3)	0.7617 (4)	0.6664 (3)
C(9)	−0.0143 (3)	0.8487 (4)	0.5706 (3)
C(10)	0.1158 (3)	0.5379 (4)	0.7221 (3)
C(11)	0.0067 (3)	0.4934 (4)	0.7478 (3)
C(12)	0.2097 (4)	0.5810 (4)	0.8233 (3)
C(13)	0.1586 (4)	0.4183 (4)	0.6735 (3)

eraged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure. All calculations were performed on a SHELXTL structure determination system.[14] Neutral atom scattering factors and anomalous dispersion factors were used for all non-hydrogen atoms during the subsequent refinement. Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included for all non-hydrogen atoms. The function[15] minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$.

The solution and refinement of the structure were based on 2310 independent reflections with $I \geq 2.5\sigma(I)$. Analysis of a Patterson map revealed the coordinates of the molybdenum atom. Two difference Fourier syntheses gave the positions of all remaining non-hydrogen atoms in the structure. Refinement of the positional and individual isotropic thermal parameters on the non-hydrogen atoms gave convergence at $R_F = 8.0\%$. Individual anisotropic thermal parameters were applied, and refinement gave $R_F = 4.7\%$. The hydrogen atoms' coordinates were set in idealized positions, and the atoms were given isotropic thermal parameters equal to 1.2 times the U_{equiv} of the parent carbon atom. A final least-squares refinement gave $R_F = 3.5\%$, $R_{wF} = 3.0\%$, and GOF = 1.367. A final difference Fourier synthesis showed no unusual features with no peak greater than 0.34 e Å^{-3}. Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom positional parameters are available.[16] Non-hydrogen atom positional parameters are summarized in Table II.

Results and Discussion

In a manner similar to that observed with cyclic and acyclic diaminohalophosphines,[2] the aminohalophosphites $\mathrm{R\overline{NCH_2CH_2OP}Cl}$ (**1–4**; R = Me, Et, *t*-Bu, and Ph) undergo heterolytic cleavage of the phosphorus–chlorine bond in the presence of $\mathrm{NaMoCp(CO)_3}$ in THF. The course of the reaction is summarized by the following equation. The resulting metallophosphenium ion complexes, $\mathrm{MoCp(CO)_2[\overline{POCH_2CH_2N}R]}$ R = Me (**5**), Et (**6**), *t*-Bu (**7**), and Ph (**8**), are obtained in good yield as extremely air- and heat-sensitive oils. On standing in THF at 0 °C one of these complexes, **7**, crystallizes as a red solid. As might be expected from the choice of solvent no evidence for complexes of the general type $\mathrm{MoCp(CO)_3[\overline{POCH_2CH_2N}R]}$ was obtained. The low thermal stability of the complexes **5–8** contrasts with the high thermal stability of the previously examined diaminophosphenium ion complexes.[2-4]

$$\underset{\textbf{1–4}}{\mathrm{R\overline{NCH_2CH_2OP}Cl}} + \mathrm{NaMoCp(CO)_3} \xrightarrow{\mathrm{THF}} \underset{\textbf{5–8}}{\mathrm{MoCp(CO)_2[\overline{POCH_2CH_2N}R]}} + \mathrm{CO} + \mathrm{NaCl}$$

The infrared spectra of **5–8** show two strong bands in the terminal carbonyl region, 1970–1920 cm^{-1} and 1895–1845 cm^{-1}. The band pattern is exactly that expected for complexes containing a $\mathrm{MoCp(CO)_2}$ fragment, and the frequencies are similar to those reported for several $\mathrm{MoCp(CO)_2[(R_2N)_2P]}$ complexes.[2,17] The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **5–8** show a singlet centered at 266, 266, 258, and 250 ppm, respectively. These resonances appear downfield of the resonances for the respective neutral aminochlorophosphites **1–4**, 172, 171, 169, and 161 ppm. The large downfield shifts in **5–8** are typical of the shifts found upon formation of most metallophosphenium ion complexes.[18]

The ^{13}C and ^{1}H NMR spectra for the aminochlorophosphites and their respective metallophosphenium ion complexes confirm that the cyclic ligand backbone remains intact in **5–8**. The C(8) resonances[19] (50.05, 46.11, 46.64, and 52.40 ppm) are shifted slightly downfield from the

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(14) The SHELXTL package of programs for calculations and plots is described in: "SHELXTL Users Manual, Revision 3", G. M. Sheldrick, July 1981, Nicolet XRD Corp. SHELXTL uses scattering factors and anomalous dispersion terms taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. IV.

(15) Discrepancy indices are defined as follows: $R_F = [\sum||F_o| - |F_c||]/\sum|F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, and the goodness of fit GOF = $[w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables.

(16) Supplementary material.

(17) Infrared data (cm^{-1}) for related compounds include the following: $\mathrm{MoCp(CO)_2L}$ (L = $\mathrm{P(NMe_2)_2}$) 1954, 1876; $\mathrm{P[N(benzyl)_2]_2}$ 1920, 1839; $\mathrm{\overline{PN(benzyl)CH_2CH_2N}(benzyl)}$ 1905, 1833; $\mathrm{\overline{PN(CH_3)CH_2CH_2N}CH_3}$ 1894, 1815.

(18) The ^{31}P shifts (ppm) for the complexes listed in ref 17 are 301, 297, 269, and 257, respectively. Further evidence for heterolytic P–halogen bond scission in **5–8** is provided by the formation of **5** from $\mathrm{F\overline{POCH_2CH_2N}CH_3}$. The neutral ligand shows a doublet in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectrum, δ 140 ($J_{\mathrm{PF}} = 1140$ Hz), and the P–F coupling is absent in the subsequent product **5**.

(19) The atom number scheme is that adopted for the crystal structure description of **7**, and it is shown in Figure 1.

Table III. Selected Bond Distances (Å) and Their Esd's for $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$

Mo-C(1)	1.956 (4)	C(1)-O(1)	1.157 (5)
Mo-C(2)	1.939 (4)	C(2)-O(2)	1.159 (5)
Mo-C(3)	2.317 (6)	Mo-P	2.207 (1)
Mo-C(4)	2.324 (6)	P-N	1.660 (3)
Mo-C(5)	2.343 (6)	N-C(8)	1.479 (5)
Mo-C(6)	2.349 (6)	N-C(10)	1.497 (4)
Mo-C(7)	2.332 (5)	P-O(3)	1.616 (3)
C(3)-C(4)	1.353 (8)	O(3)-C(9)	1.435 (5)
C(4)-C(5)	1.367 (9)	C(8)-C(9)	1.495 (5)
C(5)-C(6)	1.396 (8)	C(10)-C(11)	1.526 (6)
C(6)-C(7)	1.372 (9)	C(10)-C(12)	1.530 (5)
C(7)-C(3)	1.364 (7)	C(10)-C(13)	1.522 (6)

Table IV. Selected Bond Angles (deg) and Their Esd's for $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$

C(1)-Mo-P	96.4 (1)	Mo-P-N	145.7 (1)
C(2)-Mo-P	91.8 (1)	Mo-P-O(3)	120.0 (1)
C(1)-Mo-C(2)	86.1 (2)	N-P-O(3)	94.1 (1)
Mo-C(1)-O(1)	176.7 (4)	P-O(3)-C(9)	114.5 (2)
Mo-C(2)-O(2)	177.8 (4)	P-N-C(8)	111.7 (2)
C(3)-C(4)-C(5)	108.8 (4)	P-N-C(10)	128.0 (2)
C(4)-C(5)-C(6)	107.2 (5)	C(8)-N-C(10)	117.4 (3)
C(5)-C(6)-C(7)	107.2 (5)	O(3)-C(9)-C(8)	107.2 (3)
C(6)-C(7)-C(3)	108.3 (5)	N-C(8)-C(9)	104.9 (3)
C(7)-C(3)-C(4)	108.6 (5)	N-C(10)-C(11)	109.8 (3)
C(11)-C(10)-C(12)	109.8 (3)	N-C(10)-C(12)	109.9 (3)
C(11)-C(10)-C(13)	107.5 (3)	N-C(10)-C(13)	110.1 (3)
C(12)-C(10)-C(13)	109.8 (3)		

corresponding resonances in the neutral tricoordinate ligands, and the $^2J_{CNP}$ values are reduced. The C(9) resonances (68.49, 67.41, 66.69, and 69.35 ppm), on the other hand, are shifted slightly upfield from the corresponding resonance in the neutral ligand, and the coupling constants $^2J_{COP}$ are slightly larger than in **1**–**4**. The resonances for the α-carbon atom on the nitrogen atom, C(10) (31.87, 38.94, 55.02, and 141.0 ppm), reflect the nature of the organic substituent group. The Cp carbon atom resonances appear as a singlet or doublet in **5**–**8**: 88.59, 87.69, 89.16 (^2J = 1.5 Hz), 89.73 ppm (^2J = 1.4 Hz). The ^1H NMR spectra for **5**–**8** show resonances in the ranges 5.3–5.0, 3.7–3.6, and 2.9–2.4 ppm which can be assigned to protons on the Cp ring, CH_2O, and CH_2N, respectively.

The chemical and spectroscopic properties of **5**–**8** are consistent with the assignment of a molecular structure similar to that found for the cyclic diaminophosphenium ion analogue $MoCp(CO)_2[\overline{PN(CH_3)CH_2CH_2N}CH_3]$ (**9**). Based upon the spectroscopic data above, however, it is not possible to rule out the formation of complexes containing an η^2 side-on bonded or "slipped" phosphenium ion $\overline{POCH_2CH_2N}R^+$ (**10**). A number of side-on bonded metal-SO_2 complexes have been observed[20] including a d^6 Mo complex $Mo(CO)_3(o\text{-phen})(SO_2)$,[21] and the orbital templates for **10** and $MoCp(CO)_2^-$ appear to allow for this bonding mode. Consequently, an x-ray diffraction crystal structure analysis of **7** was undertaken in order to determine the coordination mode of **10**.

The structure determination for **7** confirms the composition $MoCp(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$ and an η^1 bonding mode for **10**. A view of the molecule is shown in Figure 1. Interatomic distances and angles are summarized in Tables III and IV, and least-squares planes are available.[16]

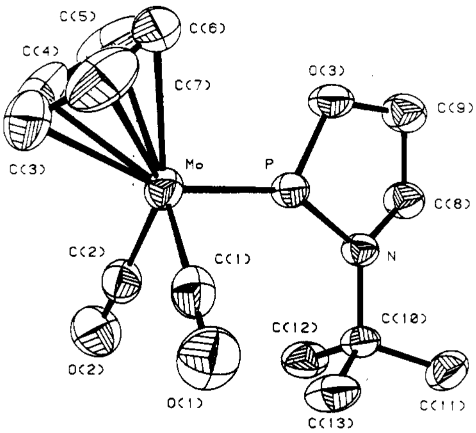

Figure 1. Molecular geometry and atom labeling scheme for $Mo(\eta^5\text{-}C_5H_5)(CO)_2[\overline{POCH_2CH_2N}C(CH_3)_3]$.

The structure of **7** is closely related to that reported for **9**.[2] The Mo atom geometry is pseudooctahedral and comprised of an η^5-C_5H_5 ring, two terminal carbonyls, and the phosphorus atom of **10**. The average[22] Mo—CO and MoC≡O distances, 1.948 (9) and 1.158 (1) Å, and the C(1)–Mo–C(2) angle, 86.1 (2)°, compare favorably with the corresponding average parameters in **9**, 1.945 (1), 1.152 (3) Å, and 85.3 (3)°, respectively. The average Mo–C ring distance, 2.333 (6) Å, is slightly shorter than the corresponding average distance in **9**, 2.351 (3) Å; however, the distance in **7** falls within a range of Mo–Cp ring distances, 2.30–2.38 Å, established from a wide variety of complexes.[23–27] The Cp ring is planar (maximum atomic deviation 0.001 Å), and the Mo–Cp ring centroid distance is 2.021 Å. The average inter-ring C–C distance is 1.370 (7) Å.

The Mo, P, N, and O atoms form a plane[28] which is nearly perpendicular to the $Mo(CO)_2$ plane (interplanar angle 85.5°) and to the Cp plane (interplanar angle 89.3°). The sums of the angles about the phosphorus atom (359.8°) and nitrogen atom (357.1°) also indicate a trigonal-planar geometry about each of these atoms. The Mo–P distance, 2.207 (1) Å, is slightly shorter than the Mo–P distance in **9**, 2.213 (1) Å, and both of these distances are much shorter than the unusual range of Mo←P dative bond distances involving phosphine ligands, 2.40–2.57 Å.[29] Such bond shortening has been interpreted to indicate a degree of Mo⇁P multiple bonding in **9**, and the same reasoning suggests significant multiple bonding in **7**. The P–N bond distance in **7**, 1.660 (3) Å, is slightly longer than

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[20] Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47.

[21] Kubas, G. J.; Ryan, R. R.; McCarty, V. *Inorg. Chem.* **1980**, *19*, 3003.

[22] The standard deviations on the averaged bond distances are defined as follows: $\sigma_l = [\sum_m (l_m - \bar{l})^2/m(m-1)]^{1/2}$ where $\bar{l}$ = average distance, l_m = individual distance, and m = number of related distances.

[23] A summary of Mo—C and MoC≡O bond distances is presented in: Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920.

[24] Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3020.

[25] Malito, J. T.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1253.

[26] Adams, R. D.; Collins, D. E.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

[27] Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197.

[28] A plane containing Mo, P, N and O(3) was calculated and the atomic deviations from the plane in order are 0.011, –0.033, 0.013, and 0.009 Å. The atoms C(8), C(9), and C(10) also show small deviations from this plane: 0.382, –0.044, and 0.147 Å, respectively.

[29] Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974; Brown, I. D.; Brown, M. C.; Hawthorne, F. C. "Bond Index to the Determinations of Inorganic Crystal Structures"; Institute for Materials Research, McMaster University: Canada, 1969–1977.

the average P–N bond distance in **9**, 1.645 (5) Å, and it can be cautiously compared with P–N bond distances in the cyclic aminochlorophosphites $\mathrm{ClPOCH_2CH_2NCH_3}$,[30] 1.692 (13) Å, and $\mathrm{ClPOCH_2CH_2NPh}$,[31] 1.653 (5) Å, which were determined by electron diffraction methods. The P–O(3) bond distance, 1.616 (3) Å, is shorter than the typical P–O single bond, 1.71 Å, yet longer than a typical P=O double bond, 1.40 Å.[29,32] The P–O(3) distance also can be compared to P–O distances in $\mathrm{ClPOCH_2CH_2NCH_3}$,[30] 1.622 (13) Å, $\mathrm{ClPOCH_2CH_2NPh}$,[31] 1.620 (5) Å, $\mathrm{ClPOCH_2CH_2O}$,[33] 1.631 (7) Å, and $\mathrm{OCH_2CH_2OP(O)OMe}$,[34] 1.59 (1) Å.

The N–P–O angle in **7**, 94.1 (1)°, is slightly smaller than the O–P–O angle in $\mathrm{OCH_2CH_2OPCl}$, 95.7°. It is slightly larger than the N–P–N angle in **9**, 92.1 (3)°,[2] and the N–P–O angles in $\mathrm{ClPOCH_2CH_2NCH_3}$,[29] 93.9°, and $\mathrm{ClPOCH_2CH_2NPh}$,[30] 92.7°. With relation to the question of phosphenium ion side-on coordination or "slippage", the Mo–P–N angle, 145.7 (1)°, is much larger than the Mo–P–O angle, 120.0 (1)°, which would appear to be consistent with displacement of the organometallic fragment toward the P–O unit; however, the Mo–O(3) interatomic distance, 3.32 Å, suggests that there is no significant direct bonding interaction between the Mo and O(3) atoms. The slight displacement probably results from steric interactions between the *t*-Bu group on the nitrogen atom and the carbonyl groups.

Several studies of σ-donating and π-accepting abilities of neutral, tricoordinate aminophosphines and phosphites have appeared.[35] Based on that work, it has been concluded that phosphites are generally better π-accepting ligands than aminophosphines; however, no clear agreement on relative σ-donating strengths has been found. With a formal positive charge on the phosphorus atom in phosphenium ions, it is expected that the π-accepting ability of these ligands will be greater than in their corresponding neutral phosphine precursors. The σ-donor ability of the cationic ligands, on the other hand, should be less than in the neutral phosphines. In the η^1 complexes **7** and **9**, it, therefore, might be anticipated that the phosphenium ion **10** would be a better π-accepting ligand than $\mathrm{[PN(CH_3)CH_2CH_2NCH_3^+]}$. The slightly higher carbonyl stretching frequencies and slightly shorter Mo–P bond distance in **7** are consistent with this reasoning. Extrapolating this trend to the phosphite phosphenium ion $\mathrm{[POC(CH_3)_2C(CH_3)_2O^+]}$ examined by Malisch,[9] it would be expected that this ligand would be a particularly strong π-acceptor,[36] and the complex $\mathrm{MoCp(CO)_2[POC(CH_3)_2C(CH_3)_2O]}$ should have the shortest Mo–P bond distance in the series. This complex, however, was not obtained.[9] Instead an η^1 pyramidal phosphenium ion complex, $\mathrm{MoCp(CO)_3[POC(CH_3)_2C(CH_3)_2O]}$, was isolated. This complex appears to have the phosphenium ion acting solely as a π-acceptor in a fashion similar to $\mathrm{FeCp(CO)_2[PN(CH_3)CH_2CH_2NCH_3]}$,[4] and it may be assumed that the σ-donor strength of this phosphenium ion is too small to cause displacement of carbon monoxide without photochemical promotion. This suggestion is completely consistent with the bonding model outlined here, and the structure of **7** is consistent with the mixed aminophosphite phosphenium ion **10** having intermediate electronic properties between the diaminophosphenium ion and the phosphite phosphenium ion. Further studies of these ligands and their phosphenium ion chemistry in other solvents and with different metal fragments are in progress.

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Supplementary Material Available: A listing of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom positional parameters, and least-squares planes (10 pages). Ordering information is given on any current masthead page.

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[36] Infrared spectra (cyclohexane) for $\mathrm{MoCp(CO)_3[POC(CH_3)_2C(CH_3)_2O]}$ show three bands at 1998, 1932, and 1922 cm^{-1} consistent with the molecular structure and a ^{31}P chemical shift δ 299.1.[9]