

Synthesis and structure of metallophosphenium complexes derived from related cyclic and acyclic aminohalophosphines

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Abstract

The reactions of $[(\text{CH}_3)_2\text{N}]_2\text{PCl}$, $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{N}]_2\text{PCl}$, $(\text{C}_6\text{H}_5)\overline{\text{NCH}_2\text{CH}_2\text{N}(\text{C}_6\text{H}_5)}\text{PCl}$ and $(\text{C}_6\text{H}_5\text{CH}_2)\overline{\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}\text{PCl}$ with $\text{NaMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ in THF result in the formation of the respective metallophosphenium complexes, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MoP}(\text{NR}_2)_2$. The compounds have been characterized by infrared and NMR spectroscopy and the single crystal X-ray diffraction structure determination of one complex, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}[\overline{\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}]$, has been completed.

Aminophosphines have been found to be ideal precursors for the generation of metallophosphenium complexes, L_nMPX_2 ($\text{X} = \text{amide}$), in which the MPX_2 fragment has a planar geometry [1,2*]. Two generally useful synthetic methods have been employed. One method [1] utilizes a reaction of a transition metal carbonyl hydride and an aminophosphine while the second method [2*] employs reactions of transition metal carbonylates with aminohalophosphines. These schemes suggest that either sterically congested or unencumbered phosphines may be employed; however, systematic studies of steric influences have not been reported. We report here reactions of $\text{Na}(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$ with four aminohalophosphines possessing differing substituents on the nitrogen atoms which provide a small range of steric effects. The results give guidance for additional studies of more sterically demanding examples.

Experimental

Standard inert atmosphere techniques were used for the manipulations of all reagents. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrome-

* This and other references marked with asterisks indicate notes occurring in the list of references.

ter. The samples were prepared as Nujol mulls and the spectra were calibrated with polystyrene film absorptions. The NMR spectra were obtained on a Varian FT-80A spectrometer. Spectral standards were ^{31}P (85% H_3PO_4), and ^{13}C , ^1H ($(\text{CH}_3)_4\text{Si}$). The aminochlorophosphines were prepared by standard methods [3,4]. $[\text{MoCp}(\text{CO})_3]_2$ was purchased from Strem Chemicals and the sodium salt was prepared by sodium amalgam reduction of the dimer in THF [5].

Preparation of the complexes

In a typical synthesis, 10.0 mmol of aminochlorophosphine was added by syringe or from an evacuated Schlenk vessel to 10.1 mmol of $\text{NaCpMo}(\text{CO})_3$ in 100 ml dry THF cooled to -78°C . The solution was stirred and slowly warmed to 25°C . Carbon monoxide was evolved and the light yellow carbonylate solution became dark red. The mixture was stirred for 12 h at 25°C and then filtered under dry nitrogen. The filtrate was evaporated, extracted into benzene to remove traces of NaCl, filtered and the filtrate evaporated to dryness. The remaining oils were washed with cold hexane: $\text{CpMo}(\text{CO})_2\text{P}(\text{NMe}_2)_2$ (I), red oil, yield 82%, $\text{CpMo}(\text{CO})_2\text{P}(\text{NBenz}_2)_2$ (II), red-yellow solid, 87% yield, $\text{CpMo}(\text{CO})_2\text{P}(\text{c-N}_2\text{Benz}_2)$ (III), yellow solid, 88% yield and $\text{CpMo}(\text{CO})_2\text{P}(\text{c-N}_2\text{Ph}_2)$ (IV), orange solid, 72% yield [6*]. Anal.: I: Found: C, 38.7; H, 4.8; N, 7.9. $\text{MoPO}_2\text{N}_2\text{C}_{11}\text{H}_{17}$ calcd.: C, 39.3; H, 5.1; N, 8.3%. II: Found: C, 64.1; H, 5.2; N, 4.0; Mo, 15.1; P 5.1. $\text{MoPO}_2\text{N}_2\text{C}_{35}\text{H}_{33}$ calcd.: C, 65.6; H, 5.2; N, 4.4; Mo, 15.0; P, 4.8%. III: Found: C, 55.7; H, 4.3; N, 5.0. $\text{MoPO}_2\text{N}_2\text{C}_{23}\text{H}_{23}$ calcd.: C, 56.8; H, 4.8; N, 5.8%. IV: Found: C, 52.9, H, 4.5; N, 6.0. $\text{MoPO}_2\text{N}_2\text{C}_{31}\text{H}_{25}$ calcd.: C, 55.0; H, 4.2; N, 6.1%. Spectroscopic characterization data are summarized in Table 1.

X-Ray crystallographic structure determination

A yellow crystal $0.40 \times 0.25 \times 0.18$ mm, of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2[\overline{\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)\text{-CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}]$ (III) was obtained from a THF/pentane solution held at 0°C and the crystal was lodged in a glass capillary under dry nitrogen. The crystal was centered on the Syntex P3/F automated diffractometer and determinations of the crystal class, the orientation matrix and accurate unit cell parameters were performed in a standard manner [7]. Details of the data collection are summarized in Table 2. Inspection of the collected data revealed systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ and the monoclinic space group $P2_1/c$ was indicated. An empirical absorption correction based on ψ scans was applied; the agreement factor was 10.7% before the correction and 4.0% after the correction. The estimated maximum and minimum transmission factors were 0.476 and 0.124. The redundant and equivalent data were averaged and converted to unscanned $|F_o|$ values following corrections for Lorentz and polarization effects.

All calculations were performed on the Syntex P3 structure solution system by using SHELXTL programs [8*]. Neutral atom scattering factors were employed and corrections were made for both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion. The function minimized during least squares refinements was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma(|F|)^2 + |g|F_o^2]$; $g = 0.00679$.

The solution and refinement of the structure were based on 3129 independent reflections with $I \geq 2.5\sigma(I)$. Analysis of a Patterson map revealed the coordinates

Table 2

Summary of crystal and data collection parameters for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}[\overline{\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{-CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}]$

(A) Crystal parameters at 25 °C

Crystal system: Monoclinic

Space group: $P2_1/c$ a 13.087(4) Å V 2159(1) Å³ b 8.564(3) Å $Z = 4$ c 19.345(6) Å $F(000) = 992$ β 95.21(3)° ρ (calcd) 1.50 g cm⁻³ $M_r = 486.36$ μ (Mo- $K\alpha$) 6.9 cm⁻¹*(B) Data collection parameters*Radiation: Mo- $K\alpha$ (λ 0.71069 Å)

Monochromator: highly oriented graphite crystal

Scan speed: 5–30 deg. min⁻¹ (in 2θ)Scan range: from $[2\theta(K_{\alpha_1}) - 1.25]^\circ$ to $[2\theta(K_{\alpha_2}) + 1.3]^\circ$ 2θ limits: $1^\circ \leq \pm h, +k, +l \leq 55^\circ$

Background counting time/total scan time: 0.25

Standards monitored: 2/96 reflections; $[\bar{2}14,222]$; no significant changes in intensity observed.

Reflections collected: 5602

Unique reflections: 4934

Unique data used: 3129 with $I > 2.5 \sigma(I)$

Number of variables refined: 328

GOF = $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2} = 1.004$ $w = [\sigma(F)^2 + |g|F_o^2]^{-1}$; $g = 0.00679$ $R_F = [\sum ||F_o| - |F_c||] / \sum |F_o| = 0.0761$ $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.0794$

of the molybdenum atom. A difference Fourier synthesis yielded the positions of all of the remaining non-hydrogen atoms. Refinement of the positional and individual isotropic thermal parameters of the non-hydrogen atoms gave convergence at R_F 13.8%. Individual anisotropic thermal parameters were applied to the non-hydrogen atoms and refinement gave R_F 8.9%. The hydrogen atoms were included in idealized positions and given an isotropic thermal parameter equal to 1.3 times the U_{equiv} of the parent carbon atom. The final least-squares refinement gave R_F 7.6%, R_{wF} 7.9% and GOF = 1.004. A final difference Fourier synthesis revealed the two highest peaks, 2.07 and 1.76 e/Å³ to be less than 0.91 Å from the molybdenum atom and the remaining peaks were less than 0.80 e/Å³. Non-hydrogen atom positional parameters are presented in Table 3.

Description of the structure

The crystals contain ordered monomeric units of III with no significant intermolecular interactions; the shortest non-hydrogen intermolecular distance is 3.80 Å between a cyclopentadienyl carbon atom and a phosphorus atom. A view of the molecular unit is shown in Fig. 1. Summaries of bond distances and angles are given in Tables 4 and 5.

The molecular unit displays C_s - m symmetry and the molybdenum atom has a pseudooctahedral piano-stool geometry provided by a pentahapto Cp ring, two

(Continued on p. 235)

Table 3

Positional parameters for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}[\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.4067(1)	0.1686(1)	0.1344(1)	4.78(3)	6.15(3)	3.90(3)	0.04(3)	0.86(2)	0.16(3)
P	0.2849(2)	0.2513(2)	0.1977(1)	5.69(11)	6.69(11)	4.17(10)	-0.04(9)	1.51(8)	0.55(9)
O(1)	0.2579(5)	0.1439(8)	0.0013(3)	7.8(4)	12.4(6)	5.6(4)	1.0(4)	-1.3(3)	-1.7(4)
O(2)	0.4375(5)	0.5175(7)	0.0953(4)	8.6(4)	7.3(4)	7.5(4)	-1.0(3)	0.0(3)	0.6(3)
N(1)	0.1850(6)	0.3708(9)	0.1826(4)	7.9(5)	8.6(5)	5.0(4)	2.4(4)	2.3(3)	6.3(3)
N(2)	0.2605(6)	0.2221(9)	0.2786(3)	7.6(4)	8.6(5)	5.0(4)	1.3(4)	2.8(3)	1.6(4)
C(1)	0.3097(6)	0.1590(10)	0.0521(5)	5.3(4)	8.0(5)	5.9(5)	0.8(4)	1.1(4)	-0.9(4)
C(2)	0.4262(6)	0.3876(10)	0.1077(4)	5.9(4)	7.1(4)	4.5(4)	-0.8(4)	0.6(3)	0.7(4)
C(3)	0.3255(7)	0.1380(12)	0.3298(5)	6.6(5)	10.3(7)	5.6(5)	-0.8(5)	0.9(4)	1.6(5)
C(4)	0.2727(5)	0.0049(10)	0.3618(4)	5.0(4)	7.8(5)	4.8(4)	0.7(4)	1.8(3)	0.1(4)
C(5)	0.3018(7)	-0.0349(11)	0.4307(4)	8.5(6)	9.4(6)	4.4(4)	0.6(5)	2.2(4)	0.2(4)
C(6)	0.2576(10)	-0.1645(13)	0.4597(6)	12.1(9)	10.3(8)	7.6(7)	0.8(6)	4.9(6)	2.5(6)
C(7)	0.1873(8)	-0.2517(15)	0.4542(7)	9.1(7)	10.8(8)	11.6(9)	2.4(6)	5.9(7)	2.3(7)
C(8)	0.1571(7)	-0.2142(12)	0.3551(6)	6.9(6)	8.1(6)	11.4(9)	-0.1(5)	2.2(6)	-0.2(6)
C(9)	0.2001(7)	-0.0889(12)	0.3257(5)	7.7(6)	8.5(6)	6.0(5)	0.0(5)	0.6(4)	0.4(5)
C(10)	0.1800(9)	0.3192(13)	0.3034(5)	10.6(8)	11.0(8)	6.3(6)	3.3(6)	4.2(5)	1.2(5)
C(11)	0.1167(8)	0.3721(15)	0.2390(6)	7.7(6)	13.5(9)	7.3(6)	2.4(6)	3.7(5)	1.2(6)
C(12)	0.1405(7)	0.4169(12)	0.1143(5)	7.0(5)	9.0(6)	6.1(5)	0.8(5)	1.2(4)	0.3(5)
C(13)	0.1124(6)	0.5866(11)	0.1093(4)	6.5(4)	8.2(5)	3.7(4)	0.2(4)	1.6(3)	-0.4(4)
C(14)	0.1173(7)	0.7018(12)	0.1349(5)	6.7(5)	10.1(7)	5.0(5)	-1.0(5)	0.0(4)	-0.1(4)
C(15)	0.1542(10)	0.8577(12)	0.1260(6)	11.4(9)	7.4(6)	7.0(6)	-1.6(6)	1.7(6)	0.2(5)
C(16)	0.0620(9)	0.8978(12)	0.0925(5)	11.9(8)	7.6(5)	6.3(6)	1.6(6)	3.2(6)	1.6(5)
C(17)	-0.0044(7)	0.7873(12)	0.0679(5)	7.2(5)	10.3(7)	5.3(5)	2.7(5)	1.6(4)	1.3(5)
C(18)	0.0181(6)	0.6297(12)	0.0765(4)	5.1(4)	9.3(6)	4.9(4)	0.0(4)	1.2(4)	-0.1(4)
C(19)	0.4665(7)	-0.0649(11)	0.1896(6)	6.8(5)	7.6(5)	9.4(7)	0.5(5)	1.5(5)	1.6(5)
C(20)	0.5350(7)	0.0526(12)	0.2133(5)	7.4(6)	9.2(6)	6.0(5)	1.0(5)	-0.4(4)	0.3(5)
C(21)	0.5824(6)	0.1091(12)	0.1575(5)	5.7(4)	8.6(5)	6.6(5)	0.1(4)	1.1(4)	0.3(5)
C(22)	0.5440(8)	0.0300(13)	0.0980(5)	8.4(6)	9.6(7)	5.6(5)	2.6(6)	1.5(5)	-0.2(5)
C(23)	0.4734(8)	-0.0798(11)	0.1175(6)	8.0(6)	6.7(5)	12.0(9)	1.5(5)	-2.4(6)	-1.2(6)

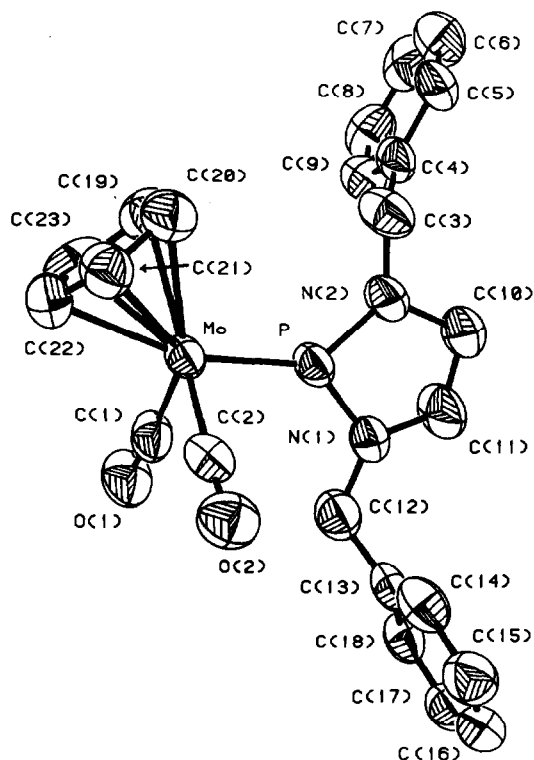


Fig. 1. Molecular geometry and atom labeling scheme for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}\{\overline{\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}\}$.

Table 4

Selected bond distances for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}\{\overline{\text{PN}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)}\}$

Mo–P	2.212(2)	P–N(1)	1.666(8)
Mo–C(1)	1.946(8)	P–N(2)	1.643(7)
Mo–C(2)	1.968(9)	C(1)–O(1)	1.150(10)
Mo–C(19)	2.366(10)	C(2)–O(2)	1.151(11)
Mo–C(20)	2.381(9)	C(19)–C(20)	1.397(14)
Mo–C(21)	2.358(8)	C(20)–C(21)	1.380(14)
Mo–C(22)	2.317(11)	C(21)–C(22)	1.390(14)
Mo–C(23)	2.334(10)	C(22)–C(23)	1.395(15)
C(10)–C(11)	1.503(15)	C(23)–C(19)	1.411(16)
N(2)–C(10)	1.458(14)	N(1)–C(11)	1.471(13)
N(2)–C(3)	1.439(11)	N(1)–C(12)	1.449(11)
C(3)–C(4)	1.496(13)	C(12)–C(13)	1.500(14)
C(4)–C(5)	1.394(11)	C(13)–C(14)	1.366(13)
C(5)–C(6)	1.393(15)	C(14)–C(15)	1.377(15)
C(6)–C(7)	1.327(16)	C(15)–C(16)	1.361(16)
C(7)–C(8)	1.397(17)	C(16)–C(17)	1.343(14)
C(8)–C(9)	1.359(15)	C(17)–C(18)	1.388(14)
C(9)–C(4)	1.384(12)	C(18)–C(13)	1.385(11)

Table 5

Selected bond angles for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}[\overline{\text{P}}\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\overline{\text{N}}(\text{CH}_2\text{C}_6\text{H}_5)]$

Mo–C(1)–O(1)	174.1(7)	Mo–P–N(1)	133.9(3)
Mo–C(2)–O(2)	176.8(7)	Mo–P–N(2)	133.6(3)
C(1)–Mo–C(2)	85.2(3)	N(1)–P–N(2)	92.5(4)
C(1)–Mo–P	91.0(3)	C(2)–Mo–P	87.6(2)
P–N(2)–C(3)	125.3(6)	P–N(1)–C(12)	124.8(6)
P–N(2)–C(10)	115.8(6)	P–N(1)–C(11)	113.2(6)
C(3)–N(2)–C(10)	117.3(7)	C(12)–N(1)–C(11)	117.0(7)
N(2)–C(3)–C(4)	113.6(7)	N(1)–C(12)–C(13)	113.5(7)
N(2)–C(10)–C(11)	105.0(8)	N(1)–C(11)–C(10)	106.6(8)
C(3)–C(4)–C(5)	119.0(7)	C(12)–C(13)–C(14)	122.3(8)
C(3)–C(4)–C(9)	123.7(7)	C(12)–C(13)–C(18)	119.4(8)
C(4)–C(5)–C(6)	119.5(8)	C(13)–C(14)–C(15)	122.2(9)
C(5)–C(6)–C(7)	122.2(1.0)	C(14)–C(15)–C(16)	118.6(1.0)
C(6)–C(7)–C(8)	119.2(1.1)	C(15)–C(16)–C(17)	120.6(1.0)
C(7)–C(8)–C(9)	119.3(1.0)	C(16)–C(17)–C(18)	121.3(9)
C(8)–C(9)–C(4)	122.6(9)	C(17)–C(18)–C(13)	119.0(8)
C(9)–C(4)–C(5)	117.1(8)	C(18)–C(13)–C(14)	118.2(9)
C(19)–C(20)–C(21)	108.4(9)	C(22)–C(23)–C(19)	108.1(9)
C(20)–C(21)–C(22)	108.9(9)	C(23)–C(19)–C(20)	107.0(9)
C(21)–C(22)–C(23)	107.6(9)		

terminal carbonyl groups and the phosphorus atom of the phosphonium fragment. The Mo, P and two N atoms lie in a plane which approximates the C_s - m symmetry plane and that plane is nearly perpendicular to both the $\text{Mo}(\text{CO})_2$ plane (interplanar angle 85.6°) and the Cp ring plane (interplanar angle 95.3°). The geometries about the phosphorus and nitrogen atoms are trigonal planar indicating approximate sp^2 hybridization for these atoms.

Discussion

The reactions of $\text{NaCpMo}(\text{CO})_3$ with the amino chlorophosphines $[(\text{CH}_3)_2\text{N}]_2\text{-P-Cl}$, $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{N}]_2\text{-P-Cl}$, $(\text{C}_6\text{H}_5\text{CH}_2)\overline{\text{N}}\text{CH}_2\text{CH}_2\overline{\text{N}}(\text{CH}_2\text{C}_6\text{H}_5)\text{-P-Cl}$ and $(\text{C}_6\text{H}_5)\overline{\text{N}}\text{-CH}_2\text{CH}_2\overline{\text{N}}(\text{C}_6\text{H}_5)\text{-P-Cl}$ result in the formation of metallophosphonium complexes $\text{CpMo}(\text{CO})_2\{\text{P}[\overline{\text{N}}(\text{CH}_3)_2]_2\}$ (I), $\text{CpMo}(\text{CO})_2\{\text{P}[\overline{\text{N}}(\text{CH}_2\text{C}_6\text{H}_5)_2]_2\}$ (II), $\text{CpMo}(\text{CO})_2\overline{\text{P}}\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\overline{\text{N}}(\text{CH}_2\text{C}_6\text{H}_5)$ (III) and $\text{CpMo}(\text{CO})_2[\overline{\text{P}}\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\text{-CH}_2\overline{\text{N}}(\text{C}_6\text{H}_5)]$ (IV) in high yields. The compounds are very air sensitive and the spectroscopic properties are similar to those for $\text{CpMo}(\text{CO})_2[\overline{\text{P}}\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\overline{\text{N}}(\text{CH}_3)]$ (V) [2*]. Each compound shows two strong carbonyl stretching frequencies in the region, $1954\text{--}1815\text{ cm}^{-1}$, which is consistent with the presence of two terminal CO ligands on each Mo atom [1,2*]. It is important to note that the two carbonyl bands in the acyclic ligand complexes I and II appear at higher frequencies than the corresponding bands in the cyclic complexes III and V. This suggests that the acyclic phosphonium ligand fragments may be slightly better π acceptors than the cyclic analogues. The ^{31}P NMR spectra show single low field resonances typical of other $\text{CpMo}(\text{CO})_2\text{PX}_2$ compounds [1,2*]. It is noteworthy that comparison of the shifts for the related acyclic and cyclic pairs of complexes, I and V and II and III reveals that the lower field shift occurs with the acyclic ligand. The $^{13}\text{C}\{^1\text{H}\}$ and

^1H NMR spectra for each complex have been fully assigned and those assignments are summarized in Table 1.

Even after several years of attention, there are relatively few reports of single crystal X-ray structure determinations for metallophosphenium complexes. The structure of the cyclic metallophosphenium complex III, with its potentially large steric contributions, is reported here and compared with the structures of the closely related cyclic compounds V and $\text{CpMo}(\text{CO})_2\overline{\text{POCH}_2\text{CH}_2\text{N}[\text{C}(\text{CH}_3)_3]}$ (VI) [7]. Each compound has a classical piano-stool geometry with the Mo, P and N or O substituent atoms lying in a plane which bisects the $\text{Mo}(\text{CO})_2$ plane. The average Mo–CO and MoC \equiv O distances, 1.957(9) and 1.150(11) Å, and the OC(1)–Mo–C(2)O angle $85.2(3)^\circ$ are very similar to the corresponding parameters in V, 1.945(1), 1.152(3) Å, $85.3(3)^\circ$ and in VI, 1.948(4), 1.158(5) Å, $86.1(2)^\circ$. The average Mo–C(ring) distance, 2.351(10) Å, also is similar to the average distances in V, 2.351 Å, and VI, 2.333 Å and to a range of Mo–Cp ring distances, 2.30–2.38 Å, established from a series of complexes [9–13].

The Mo–P distance, 2.212(2) Å, is essentially identical to the distances in V, 2.213(1) Å and VI, 2.207(1) Å. As we have noted previously [2*,7], distances in this range are much shorter than the typical range associated with Mo \leftarrow P dative bond distances, 2.40–2.57 Å [14], for molybdenum compounds containing phosphine ligands. The short Mo–P distances and planar Mo–PX₂ geometry in these metallophosphenium complexes have consequently been suggested to indicate a degree of Mo=P multiple bonding [1,2*,7]. The average P–N distance, 1.654(8) Å, is intermediate between the P–N distances in V, 1.645(5) Å and VI, 1.660(3) Å, and all are shorter than the nominal P–N single bond distance 1.78(3) Å [15]. This P–N bond shortening has been previously attributed to multiple bonding in the planar PN₂ or PNO unit [2*,7].

Strong steric effects might be expected to reveal themselves in an unexpectedly long Mo=P distance, an angular distortion in the $\text{CpMo}(\text{CO})_2$ fragment, or perhaps in the formation of a stable pyramidal $\text{CpMo}(\text{CO})_3\text{PX}_2$ metallophosphane complex. Pyramidal metallophosphanes have been observed by Malisch and coworkers [16–18] with PX₂ units where X = alkyl, aryl, halogen or alkoxide; however, the appearance of these compounds is not likely a result of steric constraints. The geometry has not been isolated when X = amide. In the metallophosphenium complexes described here, maximum steric congestion most certainly has not yet been achieved; however, space filling models suggest that the potential steric congestion provided by III compared to V is significant. Nonetheless, no major structural or stoichiometry modification is detected. The benzyl groups simply rotate away from the $\text{CpMo}(\text{CO})_2$ fragment, and a stable configuration with normal bonding parameters is achieved. These compounds provide useful information for the design of new metallophosphenium complexes with more serious steric constraints. Additional studies of compounds with greater steric demands, e.g., with substituted Cp rings (Me_5C_5 and $(\text{Me}_3\text{Si})_3\text{C}_6\text{H}_2$) and more bulky amide groups, are in progress.

Additional material. Tables of observed and calculated structure factors and hydrogen atom positional parameters can be obtained from RTP.

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