

Template Synthesis and Reactions of Tricarbonylmolybdenum Phosphadithiamacrocyclic Complexes

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Treatment of $[\text{Me}_4\text{N}]_2[\text{PhP}(\text{CH}_2\text{CH}_2\text{S})_2]$ with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ affords the reactive intermediate $[\text{Me}_4\text{N}]_2[\text{Mo}(\text{CO})_3\{\text{PhP}(\text{CH}_2\text{CH}_2\text{S})_2\}]$ (**1**), which undergoes oxidation to afford $[\text{Mo}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{S})_2\}_2]$ (**2**). Reaction of **1** with a variety of dichloroalkanes produces $[\text{Mo}(\text{CO})_3\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{X}\}]$ ($\text{X} = \text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2$, CH_2CHMe or $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$). The structure of $[\text{Mo}(\text{CO})_3\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}]$ (**3**) has been established by X-ray crystallography and consists of a $\text{Mo}(\text{CO})_3$ fragment facially coordinated by the tridentate $\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2$ ligand. Reaction of **3** with bromine affords seven-coordinate $[\text{Mo}(\text{CO})_2\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}\text{Br}_2]$ (**7**), the X-ray crystal structure of which reveals a carbonyl-capped octahedral geometry. Treatment of **3** with sulfur results in loss of the $\text{Mo}(\text{CO})_3$ fragment and isolation of $\text{c-PhPS}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2$ (**8**), the X-ray structure of which shows a nine-membered ring with the phosphorus center bearing phenyl and sulfide substituents. Reduction of **8** with sodium naphthalenide affords the parent ligand $\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2$. Crystal data: **2**, $\text{C}_{20}\text{H}_{26}\text{MoP}_2\text{S}_4$, triclinic $P\bar{1}$, $a = 8.105(3)$ Å, $b = 8.263(3)$ Å, $c = 17.663(4)$ Å, $\alpha = 100.29(2)^\circ$, $\beta = 99.78(2)^\circ$, $\gamma = 98.81(2)^\circ$, $Z = 2$; **3**, $\text{C}_{15}\text{H}_{17}\text{MoO}_3\text{PS}_2$, monoclinic $P2_1/n$, $a = 9.600(3)$ Å, $b = 15.594(5)$ Å, $c = 11.335(3)$ Å, $\beta = 93.01(2)^\circ$, $Z = 4$; **7**, $\text{C}_{14}\text{H}_{17}\text{Br}_2\text{MoO}_2\text{PS}_2$, monoclinic $P2_1/c$, $a = 17.039(3)$ Å, $b = 8.686(2)$ Å, $c = 12.466(3)$ Å, $\beta = 100.52(2)^\circ$, $Z = 4$; **8**, $\text{C}_{12}\text{H}_{17}\text{PS}_3$, monoclinic $P2_1$, $a = 6.651(4)$ Å, $b = 7.313(2)$ Å, $c = 14.687(9)$ Å, $\beta = 101.62(3)^\circ$, $Z = 2$.

Introduction

Our study of mixed phosphathiamacrocycles attempts to combine the areas of phosphine coordination chemistry and the more recent developments in thiamacrocyclic coordination chemistry.¹ The chemistry of complexes containing phosphine ligands has been studied intensively, and a vast number of mono- and didentate phosphine complexes are known, some of which have important catalytic properties. In comparison, thioethers are relatively weakly bound ligands.² However, thioether macrocycles and in particular 1,4,7-trithiacyclononane (9S3) are capable of producing metal complexes of high thermodynamic and kinetic stability.^{3,4} The unique properties of 9S3 are a result of the combination of the macrocyclic effect with a conformation which is ideal for facial tridentate coordination, and many 9S3 complexes exhibit interesting electronic and electrochemical properties. These observations lead to the speculation as to whether the combination of the nine-membered-ring conformational properties with phosphine donor centers might offer complexes with even greater stability and novelty. Recent reports suggest that syntheses of triphosphacyclononane complexes using a group 6 metal tricarbonyl template are difficult.⁵

Previous reports have addressed the preparation of mixed phosphathiamacrocycles, although they all concern ring sizes of 11 or greater.^{6–8} Eleven-membered phosphathiatriheteromacrocycles of the type 2,6,10-triheterobenzo[11]crown-3 have been prepared by the high-dilution reactions of a bis(nucleophile) with a bis(electrophile), and coordination to $\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$, Mo , W) fragments has been demonstrated.^{7,8}

Our studies have concentrated on the synthesis of mixed phosphathiacyclononanes, and we have previously reported the synthesis of $\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2$ (**L**) by a high-dilution method.¹ This paper reports the template synthesis and reactivity of phosphadithiacyclononanes and related cyclodecanes.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk tube and vacuum line techniques, and all solvents were freshly distilled under a nitrogen atmosphere and over appropriate drying agents. Petroleum ether (bp 40–60 °C) and dichloromethane were distilled over calcium hydride, and tetrahydrofuran was distilled over potassium. The compound $\text{PhP}(\text{CH}_2\text{CH}_2\text{SH})_2$ was prepared by a literature method.⁹ Fast atom bombardment and chemical ionization spectra were recorded by the EPSRC Mass Spectrometry Service at the University of Swansea with a VG ZAB-E instrument. FAB spectra were recorded from a matrix sample with NOBA. Infrared spectra

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- (1) Smith, R. J.; Powell, A. K.; Barnard, N.; Dilworth, J. R.; Blower, P. *J. J. Chem. Soc., Chem. Commun.* **1993**, 54.
- (2) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, 81, 365.
- (3) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, 35, 1.
- (4) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, 72, 1.
- (5) Edwards, P. G.; Fleming, J. S.; Liyanage, S. S.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 1801.

- (6) Champness, N. R.; Frampton, C. S.; Reid, G.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1994**, 3031.

- (7) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davies, R. E. *J. Am. Chem. Soc.* **1980**, 102, 139.

- (8) Fox, M. A.; Campbell, K. A.; Kyba, E. P. *Inorg. Chem.* **1981**, 20, 4163.

- (9) Blower, P. J.; Dilworth, J. R.; Leigh, G. J.; Neaves, B. D.; Normanton, F. B.; Hutchinson, J.; Zubietta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2647.

Table 1. Analytical^a and Physical Data

compd	appearance	yield (%)	$\nu_{\max}(\text{CO})^b$ (cm ⁻¹)	analysis (%)		M^c
				C	H	
2	red solid	20		43.8 (43.5)	5.0 (4.7)	554
3	yellow solid	70	1920 s, 1822 s, 1796 s	40.4 (41.3)	3.7 (3.9)	438
4	yellow solid	61	1922 s, 1822 s, 1790 s	42.1 (42.7)	4.0 (4.3)	452
5	yellow solid	37	1922 s, 1794 s	42.7 (42.7)	4.8 (4.3)	
6	yellow solid	32	1924 s, 1804 s	41.1 (41.2)	4.9 (4.1)	
7	orange solid	67	1948 s, 1888 m	29.8 (29.6)	3.1 (3.0)	
8	white solid	18		48.0 (50.0)	5.8 (5.9)	

^a Calculated values are given in parentheses. ^b Recorded as Nujol mulls. ^c Fast atom bombardment (FAB) mass spectroscopy.

Table 2. Details of the X-ray Structure Analyses for Compounds **2**, **3**, **7**, and **8**^a

	2	3	7	8
formula	C ₂₀ H ₂₆ MoP ₂ S ₄	C ₁₅ H ₁₇ MoO ₃ PS ₂	C ₁₄ H ₁₇ Br ₂ MoO ₂ PS ₂	C ₁₂ H ₁₇ PS ₃
fw	552.53	436.32	568.13	288.4
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁
temp (K)	173	173	173	291
cell constants				
<i>a</i> (Å)	8.105(3)	9.600(3)	17.039(3)	6.651(4)
<i>b</i> (Å)	8.263(3)	15.594(5)	8.686(2)	7.313(2)
<i>c</i> (Å)	17.663(4)	11.335(3)	12.466(3)	14.687(9)
α (deg)	100.29(2)			
β (deg)	99.78(2)	93.01(2)	100.52(2)	101.62(3)
γ (deg)	98.81(2)			
<i>V</i> (Å ³)	1126.4(6)	1694.4(9)	1814.1(7)	699.7(6)
<i>Z</i>	2	4	4	2
<i>D</i> _c (g cm ⁻³)	1.63	1.71	2.08	1.37
μ (mm ⁻¹)	1.10	1.122	5.45	0.595
<i>wR</i> ₂ (<i>F</i> ² , all reflns)	0.0516	0.0552	0.150	
<i>d</i>	0.0205	0.0202	0.0917	
<i>e</i>	1.0660	1.3702	0.0	
<i>R</i> ₁ (<i>F</i> , <i>F</i> _o > 4σ(<i>F</i> _o))	0.0201	0.0225	0.0577	
<i>R</i> (<i>F</i> , <i>F</i> _o > 3σ(<i>F</i> _o))				0.070
<i>R'</i> (<i>F</i> , <i>F</i> _o > 3σ(<i>F</i> _o))				0.096

^a $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (dP)^2 + eP$; $P = [\max(F_o, 0) + 2F_c^2]/3$.

were recorded with a Perkin-Elmer 983G spectrophotometer, and NMR spectra were recorded with a JEOL GX 270 instrument. Elemental analyses were performed by Mr. A. J. Fassam at the University of Kent. Analytical and physical data for the new compounds are given in Table 1.

Preparation of [Me₄N]₂[Mo(CO)₃{PhP(CH₂CH₂S)₂}]. A solution of PhP(CH₂CH₂SH)₂ (1.00 g, 4.34 mmol) in 25% methanolic tetramethylammonium hydroxide (3.66 mL, 8.80 mmol) was stirred for 3 min. Removal of the solvent *in vacuo* afforded a quantitative yield of [Me₄N]₂[PhP(CH₂CH₂S)₂], which was then stirred for 20 h with a solution of [Mo(CO)₃(NCMe)₃], prepared by refluxing [Mo(CO)₆] (1.15 g, 4.36 mmol) for 3 h in MeCN (15 mL). The resulting solution was then cooled to -20 °C to afford bright yellow crystals of [Me₄N]₂[Mo(CO)₃{PhP(CH₂CH₂S)₂}] (**1**) (1.83 g, 67%) after removal of the solvent *via* a cannular tube and drying *in vacuo*.

Preparation of [Mo{PhP(CH₂CH₂S)₂}₂]. A solution of **1** (0.50 g, 1.23 mmol) in acetonitrile (25 mL) and methanol (10 mL) was exposed to the air for 4 weeks. The dark red crystals that formed were washed with methanol (20 mL) to afford [Mo{PhP(CH₂CH₂S)₂}₂] (**2**) (0.14 g, 20%).

Preparation of [Mo(CO)₃{c-PhP(CH₂CH₂S)₂CH₂CH₂}]. To a suspension of **1** (1.73 g, 3.1 mmol) in MeCN (20 mL) was added 1,2-dichloroethane (0.31 g, 3.1 mmol) dropwise. After 30 min, the solvent was removed *via* a cannular tube, and the green-yellow product was dried *in vacuo*, washed with methanol (30 mL), and dried *in vacuo* to afford [Mo(CO)₃{c-PhP(CH₂CH₂S)₂CH₂CH₂}] (**3**) (1.35 g, 70%). The complexes [Mo(CO)₃{c-PhP(CH₂CH₂S)₂CH₂CH(Me)}] (**4**), [Mo(CO)₃{c-PhP(CH₂CH₂S)₂CH₂CH₂CH₂}] (**5**), and [Mo(CO)₃{c-PhP(CH₂CH₂S)₂CH₂CHOHCH₂}] (**6**) were prepared by analogous procedures.

Preparation of [Mo(CO)₂{c-PhP(CH₂CH₂S)₂CH₂CH₂}Br₂]. Bromine (0.018 g, 0.11 mmol) was added dropwise to a solution of **3** (0.050 g, 0.11 mmol) in CH₂Cl₂ (15 mL) over a 10 min period. The mixture was then stirred for 30 min, during which an orange-yellow precipitate

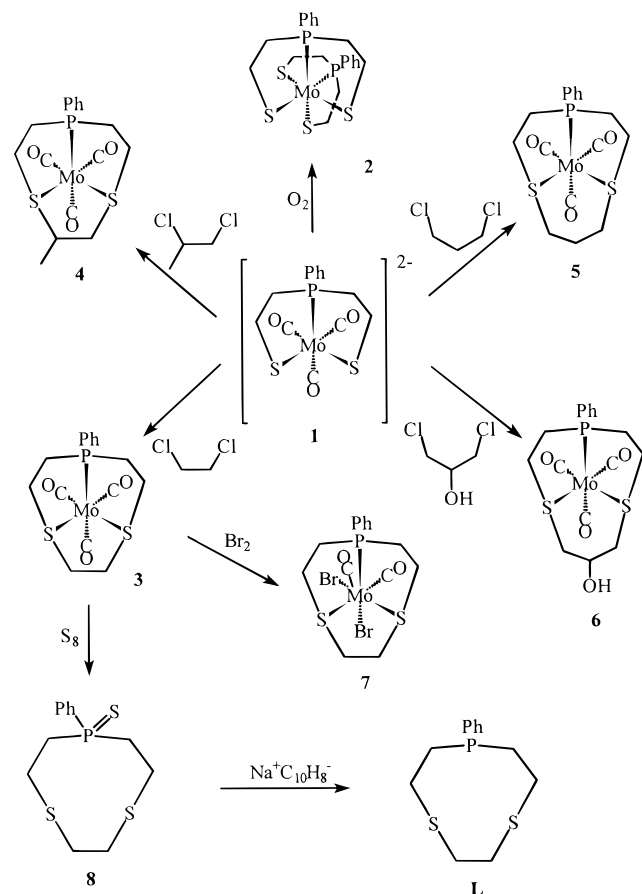
formed. The solvent was removed *via* a cannular tube, and the solid was washed with diethyl ether and then dried *in vacuo* to afford [Mo(CO)₂{c-PhP(CH₂CH₂S)₂CH₂CH₂}Br₂] (**7**) (0.046 g, 67%).

Preparation of PhPS(SCH₂CH₂S)₂(CH₂CH₂). Sulfur (0.407 g, 15.9 mmol) and **3** (0.5 g, 1.47 mmol) were refluxed in toluene (100 mL) for 12 h. The black solution was filtered and the solvent removed *in vacuo*. The green solid was chromatographed on silica gel 62, 60–200 mesh, by eluting with CH₂Cl₂. Removal of the solvent from a band with an *R_f* value of 0.36 afforded PhPS(SCH₂CH₂S)₂(CH₂CH₂) (**8**) (0.076 g, 18%). NMR (CD₂Cl₂): ¹H δ 7.98–7.50 (m, Ph, 5 H), 3.32–2.65 (m, CH₂, 12 H); ¹³C{¹H} δ 131.9–129.0 (m, Ph), 36.2 [d, PCH₂, *J*(PC) 52 Hz], 35.3 (s, SCH₂CH₂S), 28.3 [d, PCH₂CH₂S, *J*(PC) 5 Hz]; ³¹P{¹H} δ 47.5.

Reduction of PhPS(SCH₂CH₂S)₂(CH₂CH₂). A sample of **8** (0.12 g, 0.44 mmol) was treated with a freshly prepared THF solution of sodium naphthalenide (0.9 mmol), and the mixture was stirred for 24 h. The reaction mixture was then hydrolyzed and the solvent removed *in vacuo*. GC-MS analysis of the product mixture revealed a molecular ion for PhP(SCH₂CH₂S)₂(CH₂CH₂) at *m/z* 257.

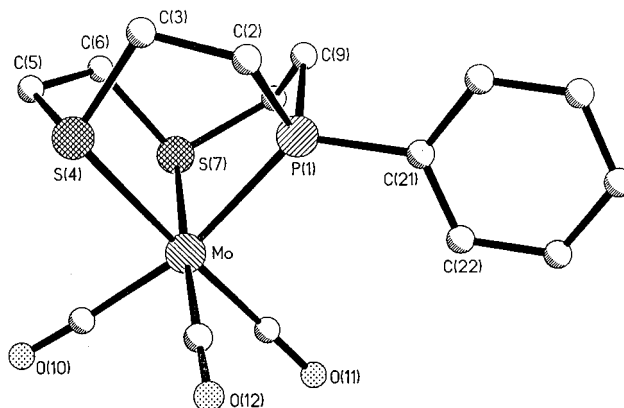
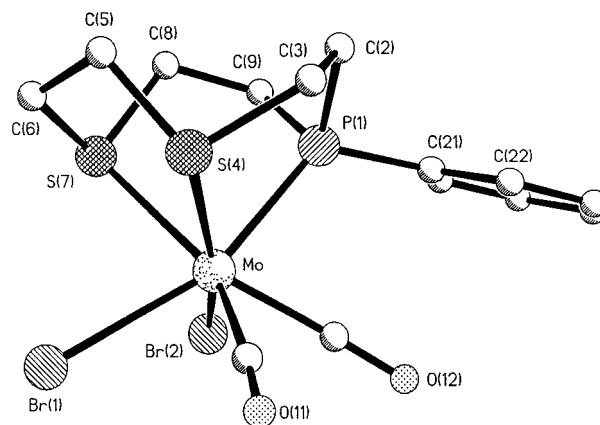
Crystal Structure Determinations of **2, **3**, and **7**.** Details of the X-ray structure analyses are summarized in Table 2. Crystals of [Mo{PhP(CH₂CH₂S)₂}₂] (**2**) were obtained from MeCN/MeOH solution. A crystal was mounted on a glass fiber, and low-temperature data were collected on a Siemens SMART area-detector three-circle diffractometer (Mo Kα X-radiation, graphite monochromator, $\lambda = 0.710 73$ Å). For three settings of ϕ , narrow data “frames” were collected for 0.3° increments in ω . A total of 1271 frames of data were collected, affording rather more than a hemisphere of data for the complex. At the end of data collection, the first 50 frames of data were recollected to establish that crystal decay had not taken place during the course of data collection. The substantial redundancy in data allowed empirical absorption corrections to be applied using multiple measurements of equivalent reflections. Data frames were collected for 10 s per frame,

Scheme 1

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for $[\text{Mo}(\text{CO})_3\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}]$ (**3**)

Mo—C(11)	1.951(2)	Mo—C(12)	1.973(2)
Mo—C(10)	1.983(2)	Mo—P(1)	2.4704(10)
Mo—S(4)	2.5186(8)	Mo—S(7)	2.5281(9)
P(1)—C(2)	1.843(2)	P(1)—C(9)	1.859(2)
C(2)—C(3)	1.521(3)	C(3)—S(4)	1.845(2)
S(4)—C(5)	1.823(2)	C(5)—C(6)	1.525(3)
C(6)—S(7)	1.836(2)	S(7)—C(8)	1.832(2)
C(8)—C(9)	1.524(3)	C(10)—O(10)	1.157(3)
C(11)—O(11)	1.169(3)	C(12)—O(12)	1.159(3)
C(11)—Mo—C(12)	86.58(10)	C(11)—Mo—C(10)	92.44(9)
C(12)—Mo—C(10)	91.08(9)	C(11)—Mo—P(1)	98.33(7)
C(12)—Mo—P(1)	95.90(6)	C(10)—Mo—P(1)	167.48(7)
C(11)—Mo—S(4)	176.93(7)	C(12)—Mo—S(4)	96.02(6)
C(10)—Mo—S(4)	89.15(7)	P(1)—Mo—S(4)	79.81(2)
C(11)—Mo—S(7)	94.35(7)	C(12)—Mo—S(7)	177.12(6)
C(10)—Mo—S(7)	91.60(7)	P(1)—Mo—S(7)	81.28(2)
S(4)—Mo—S(7)	82.98(2)		

average Mo—C bond distance (1.969 Å) is longer than that observed in $[\text{Mo}(\text{9S3})(\text{CO})_3]$ (1.947 Å), and the longest Mo—C bond is *trans* to the phosphorus center, reflecting the greater π -acceptor ability of phosphines compared with thioether ligands. The Mo—S bonds are similar in **3** (2.523 Å) and $[\text{Mo}(\text{9S3})(\text{CO})_3]$ (2.520 Å) but longer than the Mo—thiolate bonds in **2** (average 2.350 Å). The Mo—P bond in **3** [2.4704(10) Å] is similar to those in **2** [average 2.4719(10) Å] and $[\text{Mo}\{\text{c-}(\text{HPC}_3\text{H}_6)_3\}(\text{CO})_3]$ [average 2.476(1) Å].²⁰ In general, the substitution of a phenylphosphine fragment for a thioether results in minimal geometric change. The conformation of $\eta^3\text{-L}$ in

**Figure 2.** Molecular structure of $[\text{Mo}(\text{CO})_3\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}]$ (**3**).**Figure 3.** Molecular structure of $[\text{Mo}(\text{CO})_2\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}\text{Br}_2]$ (**7**).

$[\text{Cu}(\eta^3\text{-L})(\eta^1\text{-L})][\text{PF}_6]$ is similar to that in **3**, but in **3** the phenyl ring lies perpendicular to the plane of the nine-member ring while in $[\text{Cu}(\eta^3\text{-L})(\eta^1\text{-L})][\text{PF}_6]$ it lies in the same plane to minimize steric interactions with $\eta^1\text{-L}$.¹

With approximate C_s symmetry, three carbonyl bands would be expected in the infrared spectra of **3–6** corresponding to vibrations of $(A')_2$ and A'' symmetries. This is observed for **3** and **4**, but for **5** and **6** only two bands are resolved and the spectrum has the appearance of a facial tricarbonyl complex possessing C_{3v} symmetry.²¹ A simple comparison of the relative degree of metal electron density can be made using a calculated weighted average of the carbonyl stretching frequencies. The calculated values for compounds **3–6** range from 1846 to 1837 cm^{-1} , and comparison with the values for $[\text{Mo}(\text{9S3})(\text{CO})_3]$ (1827 cm^{-1})²¹ and $[\text{Mo}\{\text{c-}(\text{HPC}_3\text{H}_6)_3\}(\text{CO})_3]$ (1881 cm^{-1})^{20,22} confirms the greater π -acidity of the phosphine functionality.

Oxidative addition of bromine to **3** results in carbonyl substitution and formation of neutral seven-coordinate $[\text{Mo}(\text{CO})_2\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}\text{Br}_2]$ (**7**). Similar results have been observed with tridentate triphosphine macrocycles of molybdenum and tungsten.²³ No evidence was obtained for the presumed intermediate $[\text{Mo}(\text{CO})_3\{\text{c-PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2\}\text{Br}]\text{Br}$. The structure of **7** was established by a single-crystal X-ray diffraction study. The molecular structure is shown in Figure 3, and selected bond lengths and angles are given in Table 5. The coordination geometry around molybdenum

(20) (a) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700. (b) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Hackney, M. L. J.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 2811.

(21) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1989**, *28*, 4128.

(22) Coles, S. J.; Edwards, P. G.; Fleming, J. S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 1139.

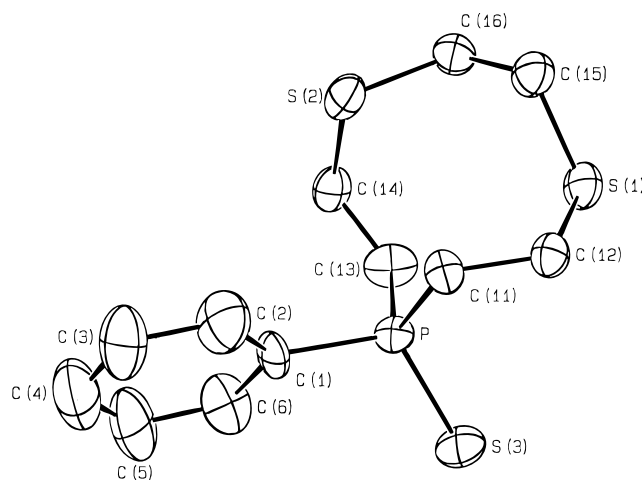
(23) Coles, S. J.; Edwards, P. G.; Fleming, J. S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 4091.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Mo(CO)₂{c-PhP(CH₂CH₂S)₂CH₂CH₂}Br₂] (**7**)

Mo—C(11)	1.949(9)	Mo—C(12)	1.941(10)
Mo—P(1)	2.439(2)	Mo—S(4)	2.516(2)
Mo—S(7)	2.616(2)	Mo—Br(2)	2.6411(13)
Mo—Br(1)	2.6585(13)	P(1)—C(21)	1.813(9)
P(1)—C(2)	1.836(8)	P(1)—C(9)	1.830(8)
C(2)—C(3)	1.540(12)	C(3)—S(4)	1.817(9)
S(4)—C(5)	1.826(8)	C(5)—C(6)	1.516(11)
C(6)—S(7)	1.831(8)	S(7)—C(8)	1.835(8)
C(8)—C(9)	1.494(11)	C(11)—O(11)	1.142(10)
C(12)—O(12)	1.183(11)		
C(11)—Mo—C(12)	67.3(5)	C(11)—Mo—P(1)	118.3(3)
C(12)—Mo—P(1)	77.4(3)	C(11)—Mo—S(4)	75.7(3)
C(12)—Mo—S(4)	118.2(3)	P(1)—Mo—S(4)	79.14(8)
C(11)—Mo—S(7)	145.7(4)	C(12)—Mo—S(7)	147.0(3)
P(1)—Mo—S(7)	80.57(7)	S(4)—Mo—S(7)	80.82(7)
C(12)—Mo—Br(2)	76.7(3)	C(11)—Mo—Br(2)	112.6(3)
P(1)—Mo—Br(2)	94.03(6)	S(4)—Mo—Br(2)	116.14(6)
S(7)—Mo—Br(2)	80.72(6)	C(12)—Mo—Br(1)	123.0(3)
C(11)—Mo—Br(1)	79.9(3)	P(1)—Mo—Br(1)	158.20(6)
S(4)—Mo—Br(1)	95.32(6)	S(7)—Mo—Br(1)	77.73(6)
Br(2)—Mo—Br(1)	84.51(4)		

appears as a capped octahedron. The octahedron is defined by the sulfur, phosphorus, and bromine atoms and one carbonyl carbon [C(12)], the cap being the other carbonyl carbon atom [C(11)] on the triangular face defined by S(4), Br(1), and C(12). Carbonyl ligands have been found to cap in the related structures of [Mo(CO)₃{c-(PrⁱPC₃H₆)₃}Br]⁺²³ and [W(CO)₂{MeS(CH₂)₂S-(CH₂)₂SMe]₂.²⁴ **L** still occupies facial coordination sites and the average bite angle (80.1°) is similar to that of **3**, but the phenyl ring has rotated in a manner similar to that observed for [Cu(η³-**L**)(η¹-**L**)](PF₆), revealing greater steric congestion at the metal center.¹ The Mo—P bond distance [2.439(2) Å] has decreased relative to that in **3** [2.4704(10) Å] despite the increase in coordination number, possibly reflecting the high formal oxidation state of molybdenum in **7**. The distance for Mo—S(4) [2.516(2) Å] where the sulfur is *trans* to a bromide ligand is similar to the Mo—S distances found in **3**, but the distance for Mo—S(7) [2.616(2) Å] where the sulfur is *trans* to a carbonyl ligand is significantly longer.

It is difficult to displace **L** from **3**, and we previously reported that treatment of **3** with [PhP(CH₂CH₂S)₂]²⁻ or ethanedithiolate results merely in recovery of unreacted **3**.¹ This contrasts with [Mo(CO)₃(9S3)], from which 9S3 is readily displaced with the parent dithiolate [S(CH₂CH₂S)₂]²⁻. Thus the incorporation of the phosphine donor increases the kinetic inertness of **3** relative to [Mo(CO)₃(9S3)]. However, reaction of **3** with sulfur in refluxing toluene results in removal of the Mo(CO)₃ fragment and isolation of compound **8**. The structure of **8** was established by a single-crystal X-ray diffraction study. The molecular structure is shown in Figure 4, and selected bond lengths and angles are given in Table 6. The molecule contains a nine-membered ring with three dimethylene groups alternating among

**Figure 4.** Molecular structure of c-PhPS(SCH₂CH₂S)₂(CH₂)₂ (**8**).**Table 6.** Selected Bond Lengths (Å) and Angles (deg) for c-PhSP(CH₂CH₂S)₂CH₂CH₂ (**8**)

S(1)—C(12)	1.815(9)	S(1)—C(15)	1.801(9)
S(2)—C(14)	1.805(9)	S(2)—C(16)	1.792(9)
S(3)—P	1.963(3)	P—C(1)	1.827(7)
P—C(11)	1.831(7)	P—C(13)	1.828(9)
C(11)—C(12)	1.51(1)	C(13)—C(14)	1.53(1)
C(15)—C(16)	1.53(1)		
C(12)—S(1)—C(15)	104.9(4)	C(14)—S(2)—C(16)	105.7(4)
S(3)—P—C(1)	113.3(3)	S(3)—P—C(11)	111.6(3)
S(3)—P—C(13)	110.4(3)	C(1)—P—C(11)	105.3(4)
C(1)—P—C(13)	104.8(5)	C(11)—P—C(13)	111.1(4)
P—C(1)—C(2)	122.5(7)	P—C(1)—C(6)	118.3(6)
C(2)—C(1)—C(6)	119.2(9)	P—C(11)—C(12)	115.0(5)
S(1)—C(12)—C(11)	117.2(6)	P—C(13)—C(14)	117.1(6)
S(2)—C(14)—C(13)	119.4(6)	S(1)—C(15)—C(16)	116.8(6)
S(2)—C(16)—C(15)	119.0(7)		

S(1), S(2), and P. The P—S(3) distance [1.963(3) Å] indicates double-bond order, while all other bond lengths and angles are normal for single bonds. The ring adopts a conformation with approximate 2-fold symmetry about a line from P to the midpoint of C(15)—C(16). The geometry is similar to that observed for η¹-**L** in [Cu(η³-**L**)(η¹-**L**)](PF₆).¹

In conclusion, the structural results presented in this paper confirm the ability of **L** to coordinate facially in a manner similar to the coordination of 9S3. The reactivity studies show that the phosphine-containing complexes are more resistant to dissociation than their 9S3 analogs. These properties suggest applications in the design of kinetically inert complexes containing soft metal centers.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2**, **3**, **7**, and **8** are available on the Internet only. Access information is given on any current masthead page.

(24) Baker, P. K.; Harris, S. D.; Durrant, M. C.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1994**, 1401.