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Template Synthesis and Reactions of Tricarbonylmolybdenum Phosphadithiamacrocycle Complexes

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Treatment of $[Me_4N]_2[PhP(CH_2CH_2S)_2]$ with $[Mo(CO)_3(NCMe)_3]$ affords the reactive intermediate $[Me_4N]_2[Mo(CO)_3\{PhP(CH_2CH_2S)_2\}]$ (**1**), which undergoes oxidation to afford $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**2**). Reaction of **1** with a variety of dichloroalkanes produces $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2X\}]$ ($X = CH_2CH_2$, $CH_2CH_2CH_2$, CH_2CHMe or $CH_2CH(OH)CH_2$). The structure of $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$ (**3**) has been established by X-ray crystallography and consists of a $Mo(CO)_3$ fragment facially coordinated by the tridentate $c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2$ ligand. Reaction of **3** with bromine affords seven-coordinate $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**7**), the X-ray crystal structure of which reveals a carbonyl-capped octahedral geometry. Treatment of **3** with sulfur results in loss of the $Mo(CO)_3$ fragment and isolation of $c\text{-}PhPS(CH_2CH_2S)_2CH_2CH_2$ (**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 $c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2$. Crystal data: **2**, $C_{20}H_{26}MoP_2S_4$, triclinic $P\bar{1}$, $a = 8.105(3)$ Å, $b = 8.263(3)$ Å, $c = 17.663(4)$ Å, $\alpha = 100.29(2)°$, $\beta = 99.78(2)°$, $\gamma = 98.81(2)°$, $Z = 2$; **3**, $C_{15}H_{17}MoO_3PS_2$, monoclinic $P2_1/n$, $a = 9.600(3)$ Å, $b = 15.594(5)$ Å, $c = 11.335(3)$ Å, $\beta = 93.01(2)°$, $Z = 4$; **7**, $C_{14}H_{17}Br_2MoO_2PS_2$, monoclinic $P2_1/c$, $a = 17.039(3)$ Å, $b = 8.686(2)$ Å, $c = 12.466(3)$ Å, $\beta = 100.52(2)°$, $Z = 4$; **8**, $C_{12}H_{17}PS_3$, monoclinic $P2_1$, $a = 6.651(4)$ Å, $b = 7.313(2)$ Å, $c = 14.687(9)$ Å, $\beta = 101.62(3)°$, $Z = 2$.

Introduction

Our study of mixed phosphathiamacrocycles attempts to combine the areas of phosphine coordination chemistry and the more recent developments in thiamacrocycle 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 $M(CO)_3$ ($M = Cr$, 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 $c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2$ (**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 $PhP(CH_2CH_2SH)_2$ 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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Table 1. Analytical[a] and Physical Data

compd	appearance	yield (%)	$\nu_{max}(CO)^b$ (cm^{-1})	analysis (%) C	analysis (%) H	M^c
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	$C_{20}H_{26}MoP_2S_4$	$C_{15}H_{17}MoO_3PS_2$	$C_{14}H_{17}Br_2MoO_2PS_2$	$C_{12}H_{17}PS_3$
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	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1$
temp (K)	173	173	173	291
cell constants				
a (Å)	8.105(3)	9.600(3)	17.039(3)	6.651(4)
b (Å)	8.263(3)	15.594(5)	8.686(2)	7.313(2)
c (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)			
V (Å^3)	1126.4(6)	1694.4(9)	1814.1(7)	699.7(6)
Z	2	4	4	2
D_c (g cm^{-3})	1.63	1.71	2.08	1.37
μ (mm$^{-1)}$	1.10	1.122	5.45	0.595
wR_2 (F^2, all reflcns)	0.0516	0.0552	0.150	
d	0.0205	0.0202	0.0917	
e	1.0660	1.3702	0.0	
R_1 (F, $F_o > 4\sigma(F_o)$)	0.0201	0.0225	0.0577	
R (F, $F_o > 3\sigma(F_o)$)				0.070
R' (F, $F_o > 3\sigma(F_o)$)				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 $[Me_4N]_2[Mo(CO)_3\{PhP(CH_2CH_2S)_2\}]$. A solution of $PhP(CH_2CH_2SH)_2$ (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 $[Me_4N]_2[PhP(CH_2CH_2S)_2]$, 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 $[Me_4N]_2[Mo(CO)_3\{PhP(CH_2CH_2S)_2\}]$ (**1**) (1.83 g, 67%) after removal of the solvent *via* a cannular tube and drying *in vacuo*.

Preparation of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$. 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 $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**2**) (0.14 g, 20%)

Preparation of $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$. 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 $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$ (**3**) (1.35 g, 70%). The complexes $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH(Me)\}]$ (**4**), $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2CH_2)\}]$ (**5**), and $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CHOHCH_2)\}]$ (**6**) were prepared by analogous procedures.

Preparation of $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$. Bromine (0.018 g, 0.11 mmol) was added dropwise to a solution of **3** (0.050 g, 0.11 mmol) in CH_2Cl_2 (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 $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**7**) (0.046 g, 67%).

Preparation of $PhPS(SCH_2CH_2S)_2(CH_2CH_2)$. 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 CH_2Cl_2. Removal of the solvent from a band with an R_f value of 0.36 afforded $PhPS(SCH_2CH_2S)_2(CH_2CH_2)$ (**8**) (0.076 g, 18%). NMR (CD_2Cl_2): ^1H δ 7.98−7.50 (m, Ph, 5 H), 3.32−2.65 (m, CH_2, 12 H); $^{13}C\{^1H\}$ δ 131.9−129.0 (m, Ph), 36.2 [d, PCH_2, J(PC) 52 Hz], 35.3 (s, SCH_2CH_2S), 28.3 [d, PCH_2CH_2S, J(PC) 5 Hz]; $^{31}P\{^1H\}$ δ 47.5.

Reduction of $PhPS(SCH_2CH_2S)_2(CH_2CH_2)$. 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 $PhP(SCH_2CH_2S)_2(CH_2CH_2)$ 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 $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**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 $K\alpha$ 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, giving an overall time for data collection of *ca.* 7 h. The data frames were integrated using SAINT.[10]

The structure was solved by conventional direct methods procedures and was refined by full-matrix least-squares calculations on all F^2 data using Siemens SHELXTL 5.03.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters *ca.* 1.2 times the equivalent isotopic thermal parameters of their parent carbon atoms (C−H distances were allowed to refine). All calculations were carried out on a Silicon Graphics Indy or Indigo computer.

Crystals of $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$ (**3**) were obtained by slow evaporation of a CH_2Cl_2 solution, and small, poorly diffracting crystals of $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**7**) were obtained from CH_2Cl_2/hexane. Crystals were mounted, the data collected, and the structures solved and refined in a manner similar to **2**.

Crystal Structure Determination of 8. Crystals of $PhPS\{SCH_2CH_2S\}_2(CH_2CH_2)$ (**8**) were obtained from CH_2Cl_2. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo *K*α X-radiation ($\lambda = 0.710\ 73$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centered reflections in the range $22° < \theta < 25°$. The data were collected in the $\omega-2\theta$ scan mode, and three standard reflections were measured after every hour of exposure. A 1.2% loss of intensity was observed, which was linearly corrected during processing. The data were corrected for Lorentz and polarization factors, and an absorption correction was applied using ψ scans of nine reflections.[11] The structure was solved by direct methods,[12] locating all the non-hydrogen atoms. Hydrogen atoms were added in calculated positions with $B(\text{eq}) = 1.3B(\text{eq})$ of the attached atom. A weighting scheme of the form $w = 1/[\sigma^2(F_o) + (0.02F_o)^2]$ gave a satisfactory analysis of variance.[13] Neutral-atom scattering factors were taken from ref 14.

Results and Discussion

We found previously that the template synthesis of 9S3 can be adapted to prepare a range of carbon-functionalized derivatives.[15] The substituents were introduced *via* substituted 1,2-dibromopropanes, by cyclization with 3-thiapentane-1,5-dithiolate in the form of its molybdenum complex $[Mo(CO)_3\{S(CH_2CH_2S)_2\}]^{2-}$. This approach was adapted for the synthesis of nine- and ten-membered phosphadithiamacrocycles. Reaction of $[Me_4N]_2[PhP(CH_2CH_2S)_2]$ with $[Mo(CO)_3(NCMe)_3]$ affords $[Me_4N]_2[Mo(CO)_3\{PhP(CH_2CH_2S)_2\}]$ (**1**). The *o*-phenylene analogue of **1**, $[Me_4N]_2[Mo(CO)_3\{PhP(C_6H_4S)_2\}]$, was structurally characterized by Dilworth *et al.*,[16] but **1** was found to be too air-sensitive to characterize and was used immediately in cyclization reactions analogously to the 9S3 synthesis.[17] Exposure of a solution of **1** to air results in formation of red crystals of the molybdenum(IV) complex $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**2**). Compound **2** was characterized by elemental analysis and FAB-MS (Table 1) and also by a single-crystal X-ray diffraction study. The molecular structure, which is a distorted octahedron, is shown in Figure 1, and selected bond lengths and angles are given in Table 3. The structure was reported previously but with a considerably higher *R* value (9.8%);[9] however, the structural parameters are the same within error and will not be discussed further.

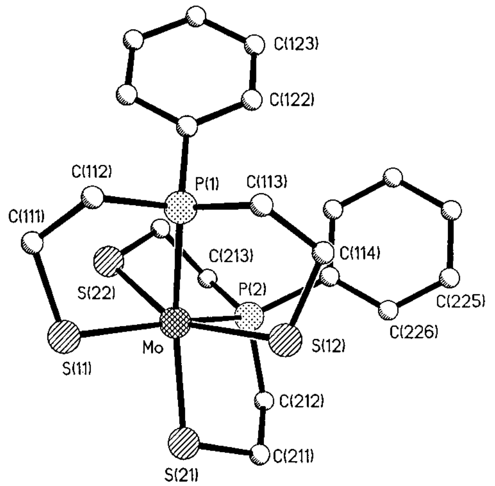

Figure 1. Molecular structure of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**2**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (**2**)

Mo−S(11)	2.3386(7)	Mo−S(21)	2.3404(10)
Mo−S(22)	2.3544(9)	Mo−S(12)	2.3648(8)
Mo−P(2)	2.4666(8)	Mo−P(1)	2.4772(10)
P(1)−C(113)	1.833(2)	P(1)−C(112)	1.845(2)
P(2)−C(213)	1.838(2)	P(2)−C(212)	1.849(2)
S(11)−C(111)	1.840(2)	S(12)−C(114)	1.821(2)
S(21)−C(221)	1.842(2)	S(22)−C(214)	1.828(2)
C(111)−C(112)	1.520(3)	C(113)−C(114)	1.526(3)
C(221)−C(212)	1.527(3)	C(213)−C(214)	1.524(3)
S(11)−Mo−S(21)	91.62(3)	S(11)−Mo−S(22)	83.64(3)
S(21)−Mo−S(22)	117.48(3)	S(11)−Mo−S(12)	117.93(3)
S(21)−Mo−S(12)	82.94(3)	S(22)−Mo−S(12)	151.07(2)
S(11)−Mo−P(2)	157.23(2)	S(21)−Mo−P(2)	83.38(3)
S(22)−Mo−P(2)	79.10(3)	S(12)−Mo−P(2)	83.60(3)
S(11)−Mo−P(1)	82.35(3)	S(21)−Mo−P(1)	155.58(2)
S(22)−Mo−P(1)	85.49(3)	S(12)−Mo−P(1)	79.15(3)
P(2)−Mo−P(1)	110.73(3)		

Reaction of **1** with a range of dichloroalkanes affords air-stable molybdenum tricarbonyl complexes with cyclic phosphadithiamacrocycles (Scheme 1). Both nine-membered (**3** and **4**) and ten-membered (**5** and **6**) rings are formed in reasonable yields. Compound **4** contains a pendant methyl group, while **6** has a pendant hydroxyl functionality. The hydroxyl group on the carbon backbone in **6** is not expected to compete in coordination to soft metal centers and could be easily transformed into amines or other substituents with potential for linking to proteins for nuclear medical purposes.[18] The new compounds were characterized by infrared spectroscopy, elemental analyses, and, in the case of **3** and **4**, FAB-MS, in which molecular ions were observed (Table 1). The low solubility of **3**−**6** prevented the acquisition of high-quality NMR spectra. The structure of **3** was established by a single-crystal X-ray diffraction study. The molecular structure is shown in Figure 2, and selected bond lengths and angles are given in Table 4. The structure is similar to that of $Mo(9S3)(CO)_3$ with **L** facially coordinated to the tricarbonylmolybdenum fragment.[19] The angles between the carbonyls are close to 90°, indicating a pseudooctahedral geometry; however, the chelate bite angles of **L** are all less than 90° (average 81.4°) but only slightly less than the situation in $[Mo(9S3)(CO)_3]$ (average 82.8°). The

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Scheme 1

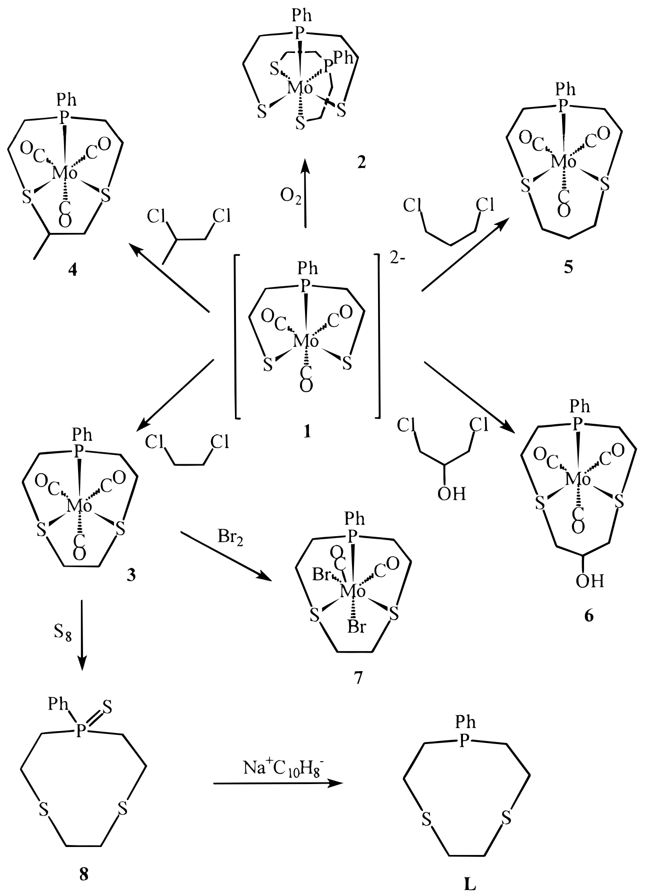

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$ (**3**)

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)		

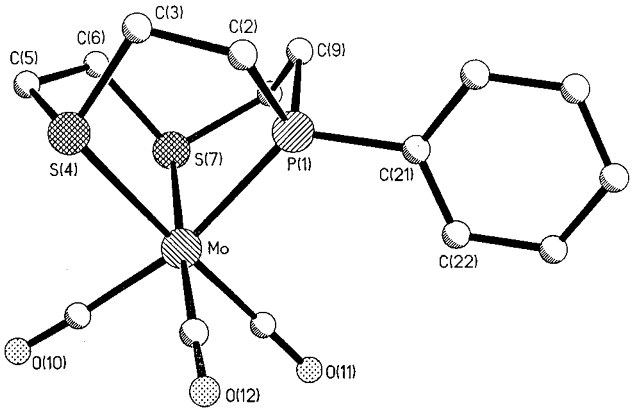

Figure 2. Molecular structure of $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}]$ (**3**).

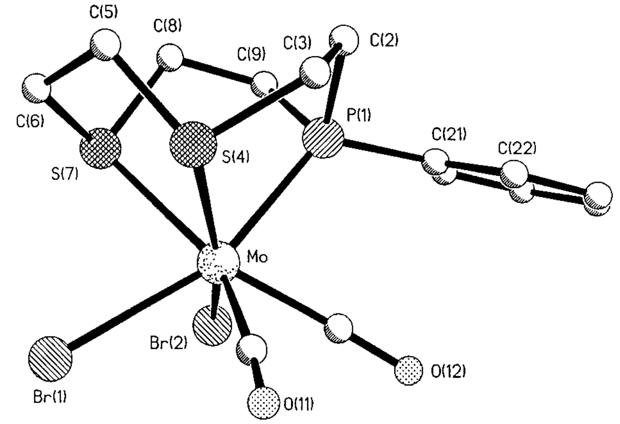

Figure 3. Molecular structure of $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**7**).

average Mo−C bond distance (1.969 Å) is longer than that observed in $[Mo(9S3)(CO)_3]$ (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 $[Mo(9S3)(CO)_3]$ (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 $[Mo\{c\text{-}(HPC_3H_6)_3\}(CO)_3]$ [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 η^3-**L** in $[Cu(\eta^3\text{-}\mathbf{L})(\eta^1\text{-}\mathbf{L})][PF_6]$ is similar to that in **3**, but in **3** the phenyl ring lies perpendicular to the plane of the nine-member ring while in $[Cu(\eta^3\text{-}\mathbf{L})(\eta^1\text{-}\mathbf{L})][PF_6]$ it lies in the same plane to minimize steric interactions with η^1-**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 $[Mo(9S3)(CO)_3]$ (1827 cm^{-1})[21] and $[Mo\{c\text{-}(HPC_3H_6)_3\}(CO)_3]$ (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 $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**7**). Similar results have been observed with tridentate triphosphine macrocycles of molybdenum and tungsten.[23] No evidence was obtained for the presumed intermediate $[Mo(CO)_3\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br]Br$. 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

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Mo(CO)_2\{c\text{-}PhP(CH_2CH_2S)_2CH_2CH_2\}Br_2]$ (**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 $[Mo(CO)_3\{c\text{-}(Pr^iPC_3H_6)_3\}Br]^+$ [23] and $[W(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\}I_2]$.[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 $[Cu(\eta^3\text{-}\mathbf{L})(\eta^1\text{-}\mathbf{L})][PF_6]$, 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.

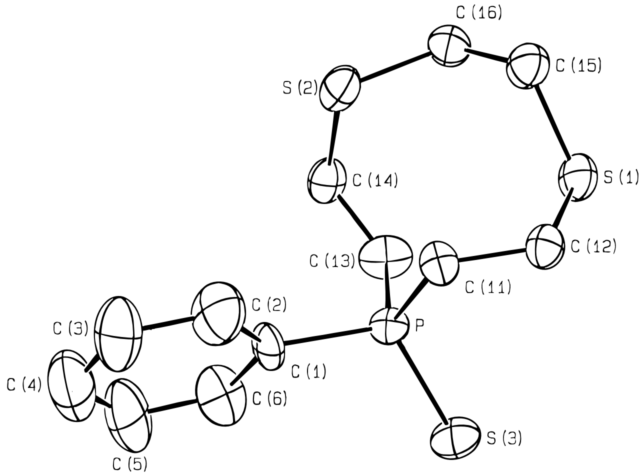

Figure 4. Molecular structure of $c\text{-}PhPS(SCH_2CH_2S)_2(CH_2)_2$ (**8**).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $c\text{-}PhSP(CH_2CH_2S)_2CH_2CH_2$ (**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)		

It is difficult to displace **L** from **3**, and we previously reported that treatment of **3** with $[PhP(CH_2CH_2S)_2]^{2-}$ 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 $[S(CH_2CH_2S)_2]^{2-}$. 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 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 η^1-**L** in $[Cu(\eta^3\text{-}\mathbf{L})(\eta^1\text{-}\mathbf{L})][PF_6]$.[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.

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