266 *Organometallics* **2005,** *24,* 266−271

Investigations of Pyridine-2-thiol as a Ligand: Synthesis and X-ray Structures of the Mixed Mo−Mn Dinuclear Complex $CpMoMn(CO)_3(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}pyS)(\mu\text{-}\eta^1\text{-}pyS)$, the Electron-Deficient Trimolybdenum Cluster $Cp_3Mo_3(\mu\text{-}CO)_2(\mu\text{-}S)(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}NC_5H_4)$, and the Mononuclear $CpMo(CO)_2(\mu\text{-}\eta^2\text{-}pyS)$

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The reaction of $Mn_2(CO)_6(pyS)_2$ (**1**) with $(CpMo(CO)_3)_2$ (**2**) at 110 °C gives the heterodinuclear complex $CpMoMn(CO)_3(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}pyS))(\mu\text{-}\eta^1\text{-}pyS)$ (**3**), the mononuclear molybdenum complex $CpMo(CO)_2(\mu\text{-}\eta^2\text{-}pyS)$ (**4**), and the 46-electron trimolybdenum cluster $Cp_3Mo_3(\mu\text{-}CO)_2(\mu\text{-}S)(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}NC_5H_4)$ (**5**). Compound **4** could also be prepared in high yield from the reaction of **2** with pyridine-2-thiol at 110 °C. Compound **3** represents a rare example of a Mo−Mn heterodinuclear complex containing a μ-η^2-pyridine-2-thiolato, a μ-η^1-pyridine-2-thiolato, and a cyclopentadienyl ligand. The 46-electron compound **5** represents a unique example of a trimolybdenum compound containing three cyclopentadienyl ligands, an ortho-metalated pyridyl ligand, a capping sulfido, a bridging sulfido, and two semibridging CO ligands. Curiously, although this complex is formally electron deficient, it is unreactive toward two-electron donors. The structures of all the compounds have been unambiguously established by single-crystal X-ray crystallography.

Introduction

The chemistry of mixed-metal clusters has been of enduring interest because of the unique chemistry resulting from having two metals with different chemical properties in close proximity and also because of their potential catalytic applications.[1−11] Deeming et al.[12,13] reported a series of Re−Ru mixed-metal complexes from the reaction of $Re_2(CO)_6(pyS)_2$ with $Ru_3(CO)_{12}$. One aspect of the ongoing research interest in our laboratory is the preparation of mixed-metal complexes from the reactions of $M_2(CO)_6(pyS)_2$ (M = Mn, Re) with $M_3(CO)_{10}L_2$ (M = Os, Ru, Fe; L = CO, MeCN).[14] Interest in metal pyridine-2-thiolato complexes stems from their structural diversity, important biological roles, and potential application as precursors for metal−sulfide materials.[15−18]

A large number of group 7 and 8 heterobimetallic complexes have been reported.[19] However, little attention has been paid to the chemistry of heteronuclear

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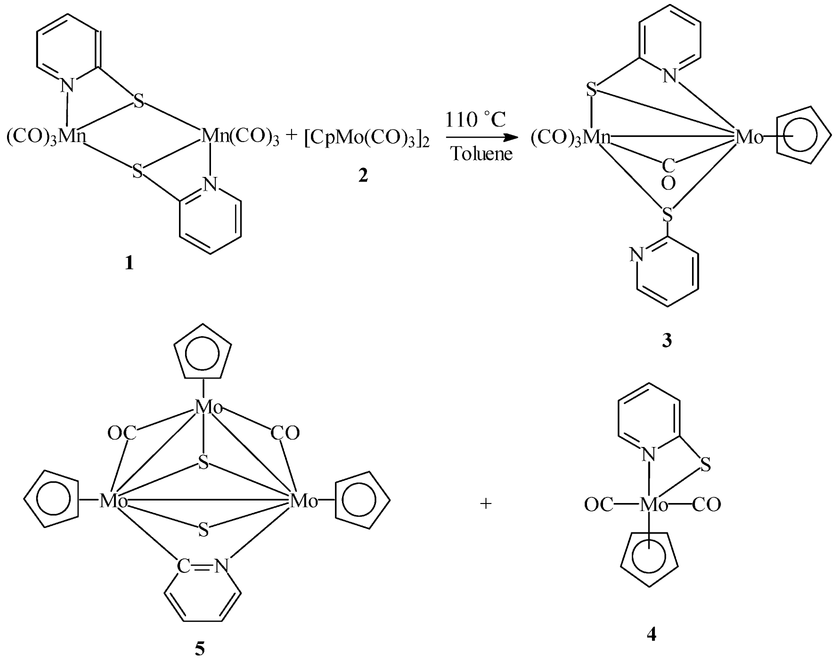
Scheme 1



complexes containing group 6 and 7 metal atoms. Mays et al.[20] reported the heterodinuclear complex CpMoMn(CO)$_6$(μ-PPh$_2$)(μ-H) and the homodinuclear complex Cp$_2$Mo$_2$(CO)$_4$(μ-PPh$_2$)(μ-H) from the photolytic reaction of CpMoMn(CO)$_8$ with Ph$_2$PH. The heterodinuclear complex MoMn(CO)$_4$(μ-C$_5$H$_4$(PR$_2$)) was reported from the reaction of (BrMn(CO)$_4$)$_2$ with the anionic species (C$_5$H$_4$(PR$_2$)Mo(CO)$_3$)$^-$.[21] Mays and co-workers[22] reported the trinuclear MoMn$_2$ cluster (Cp(CO)$_2$Mo)$_2$Mn(CO)$_4$P, containing a naked phosphorus atom, from the reaction of Cp$_2$(CO)$_4$Mo$_2$(μ-PH$_2$)$_2$(μ-H) with Mn$_2$(CO)$_{10}$. Adams et al.[23] have recently reported the heterodinuclear compounds CpMoMn(CO)$_5$(μ-E$_2$) (E = S, Se) from the reactions of CpMoMn(CO)$_8$ with elemental sulfur and selenium in the presence of trimethylamine *N*-oxide. To date, there are few known examples of neutral trinuclear carbonyl clusters of molybdenum[24] in comparison with those known for ruthenium and osmium.[25] This is mainly due to the lack of a convenient molybdenum-containing starting material. As part of our continuing studies into the versatility of pyridine-2-thiolato compounds in the synthesis of mixed-metal complexes, we have now studied the reaction of Mn$_2$(CO)$_6$(pyS)$_2$ (**1**) with (CpMo(CO)$_3$)$_2$ (**2**), where a trimolybdenum compound is realized and where the versatility of the pyridine-2-thiol further illustrated.

Results and Discussion

Treatment of **1** with 2 equiv of **2** in refluxing toluene results in the formation of the dinuclear mixed-metal compound CpMoMn(CO)$_3$(μ-CO)(μ-η^2-pyS)(μ-η^1-pyS) (**3**), the mononuclear molybdenum compound CpMo(CO)$_2$(μ-η^2-pyS) (**4**), and the trimolybdenum cluster Cp$_3$Mo$_3$(μ-CO)$_2$(μ-S)(μ_3-S)(μ-η^2-NC$_5$H$_4$) (**5**) in 22, 15, and 10% yields, respectively (Scheme 1).

The solid-state structure of **3** is shown in Figure 1, crystal data are listed in Table 1, and selected bond distances and angles are collected in Table 2. The molecule consists of a heterodinuclear framework containing a manganese and a molybdenum atom with four

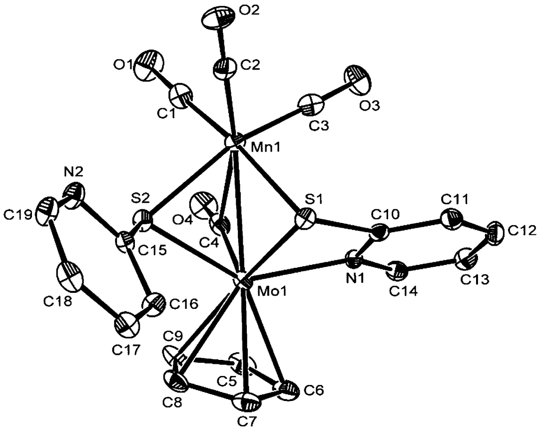


Figure 1. Solid-state structure of CpMoMn(CO)$_3$(μ-CO)(μ-η^2-pyS))(μ-η^1-pyS) (**3**). Thermal ellipsoids are at the 50% probability level.

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Table 1. Crystal Data and Structure Refinement Details for 3−5

	3	**4**	**5**
empirical formula	$C_{19}H_{13}O_4MnMoN_2S_2$	$C_{12}H_9O_2MoNS$	$C_{22}H_{19}O_2Mo_3NS_2$
formula wt	548.34	327.22	681.36
temp (K)	150(2)	150(2)	120(2)
wavelength	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
unit cell dimens			
a (Å)	10.680(2)	6.3568(12	13.2230(5)
b (Å)	12.092(2)	12.563(2)	16.7951(5)
c (Å)	15.335(2)	14.658(2)	9.5772(3)
α (deg)	90	90	90
β (deg)	90	94(14)	95.2087(11)
γ (deg)	90	90	90
V (Å^3)	1980.5(6)	1166.6(3)	2118.14(12)
Z	4	4	4
calcd density (Mg m^{-3})	1.839	1.863	2.137
abs coeff (mm^{-1})	1.511	1.289	1.967
F(000)	1088	648	1328
cryst size (mm)	0.40 × 0.10 × 0.10	0.40 × 0.10 × 0.05	0.20 × 0.10 × 0.02
θ range for data collecn (deg)	2.14−25.34	2.14−25.30	3.00−27.50
limiting indices	$-12 \leq h \leq 12$	$0 \leq h \leq 7$	$-16 \leq h \leq 17$
	$0 \leq k \leq 14$	$-15 \leq k \leq 0$	$-21 \leq k \leq 19$
	$0 \leq l \leq 18$	$-17 \leq l \leq 17$	$-12 \leq l \leq 11$
no. of rflns collected	3558	2298	16 841
no. of indep reflns	3558 (R_{int} = 0.0000)	2065 (R_{int} = 0.0132)	4819 (R_{int} = 0.0792)
max and min transmissn	0.9297 and 0.8272		0.9617 and 0.6945
refinement method	full-matrix least squares on F^2		
no. of data/restraints/params	3558/0/262	2065/0/155	4819/0/271
goodness of fit on F^2	1.045	1.041	0.950
final R indices ($I > 2\sigma(I)$)	R1 = 0.0255, wR2 = 0.0615	R1 = 0.0261, wR2 = 0.0708	R1 = 0.0366, wR2 = 0.0663
R indices (all data)	R1 = 0.0318, wR2 = 0.0632	R1 = 0.0349, wR2 = 0.0737	R1 = 0.0676, wR2 = 0.0745
largest diff peak and hole (e Å^{-3})	0.316 and −0.489	0.555 and −0.900	0.883 and −0.993

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Mo(1)−C(4)	1.937(4)	Mn(1)−S(2)	2.3380(10)
Mo(1)−N(1)	2.190(3)	Mn(1)−S(1)	2.3859(11)
Mo(1)−S(2)	2.4328(9)	S(1)−C(10)	1.768(4)
Mo(1)−S(1)	2.5228(9)	S(2)−C(15)	1.807(4)
Mo(1)−Mn(1)	2.7316(7)		
N(1)−Mo(1)−S(2)	135.65(8)	S(1)− Mn(1)−C(4)	98.23(9)
N(1)−Mo(1)−S(1)	78.25(3)	S(2)− Mn(1)−Mo(1)	56.72(3)
S(2)−Mo(1)−Mn(1)	53.46(2)	Mn(1)−S(1)−Mo(1)	67.56(3)
S(1)−Mo(1)−Mn(1)	53.83(3)	Mn(1)−S(2)−Mo(1)	69.83(13)
S(2)−Mn(1)−S(1)	82.92(4)	Mo(1)−C(4)−Mn(1)	71.69(12)

carbonyl groups, a cyclopentadienyl ligand, and two pyridinethiolato ligands. One carbonyl group spans the Mn−Mo bond as a weak semibridge: Mn−C(4) = 2.648(4) Å, Mo−C(4) = 1.937(4) Å, and Mo−C(4)−O(4) = 165.2(3)°. Mn is ligated by three terminal CO ligands, while the cyclopentadienyl ligand is attached to the Mo atom in an η^5 fashion. The Mo−Mn bond distance of 2.7316(7) Å is significantly shorter than the corresponding distance found in $CpMoMn(CO)_4(\mu\text{-}PPh_2)(\mu\text{-dppm})(\mu\text{-}H)$ (3.09(1) Å)[20a] but slightly shorter than the Mo−Mn bond length in $CpMoMn(CO)_5(\mu\text{-}S_2)$ (2.8421(10) Å),[23] clearly indicative of a Mo−Mn single bond. The average Mo−Cp distance (2.334 Å) is comparable to the Mo−Cp distance of 2.34(2) Å in $CpMoMn(CO)_3)(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^3\text{-}CH_2C(Me)CHMe)$.[20a] The Mo−N bond distance of 2.190 (3) Å is shorter than the Mo−N bond distance of 2.261(5) Å in $Mo_2(CO)_4(\mu\text{-pyS})_2(PPh_3)_2$.[26] The molybdenum−sulfur bond distances (Mo(1)−S(1) = 2.5228(9) Å, Mo(1)−S(2) = 2.4328(9) Å) are comparable to the corresponding distances in $Mo_2(CO)_4(\mu\text{-pyS})_2(PPh_3)_2$ (Mo−S = 2.460(1), 2.497(2) Å),[26] and the Mn−S distances (Mn(1)−S(1) = 2.385(11) Å, Mn(1)−S(2) = 2.3380(10) Å) are shorter than the average Mn−S distance observed in **1** (2.431(1) Å).[27] The $\mu\text{-}\eta^1$-pyS and $\mu_3\text{-}\eta^2$-pyS ligands donate three and five electrons, respectively, to make **3**, a 34-valence-electron saturated bimetallic compound with each metal atom achieving the expected 18-electron configuration. The spectroscopic data for **3** in solution are consistent with the structure found in the solid state. Its IR spectrum in solution contains four ν_{CO} absorptions at 2006, 1997, 1869, and 1801 cm^{-1}, the first three bands having the typical pattern of compounds having $Mn(CO)_3$ fragments and the latter indicating the presence of a semibridging carbonyl ligand. In addition to the well-separated resonances for the two nonequivalent heterocyclic ligands, the ^{1}H NMR spectrum shows a singlet at δ 5.72 due to the cyclopentadienyl protons.

The solid-state structure of **4** is shown in Figure 2, crystal data are listed in Table 1, and selected bond distances and angles are collected in Table 3. The molecule crystallizes in the endo conformation, in which the mouth of the pyS group faces the "Cp ring".[28] The pyridine-2-thiolato ligand coordinates to Mo via the S and N atoms, thus serving as a chelating ligand. The Mo−N bond distance of 2.183(2) Å is identical with that found in **3** and comparable to the corresponding distance observed in the mononuclear complexes $CpMo(CO)_2(\eta^3\text{-}CH_2CRNH)$ (R = Ph; 2.228(2) Å)[29] and a $CpMo(CO)_2(\eta^3\text{-}CH_2CRNCHMe_2)$ (R = Me; 2.215(4) Å).[30] The Mo−S

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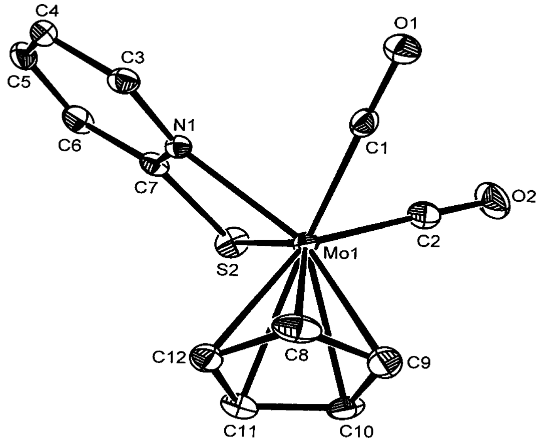

Figure 2. Solid-state structure of CpMo(CO)$_2$(μ-η^2-pyS) (**4**). Thermal ellipsoids are at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4

Mo(1)−N(1)	2.183(2)	Mo(1)−S(2)	2.5227(9)
Mo(1)−C(9)	2.276(3)	Mo(1)−C(8)	2.319(3)
Mo(1)−C(10)	2.299(3)	Mo(1)−C(12)	2.396(3)
Mo(1)−C(11)	2.385(3)		
C(2) −Mo(1)−C(1)	75.21(11)	C(1) −Mo(1)−N(1)	81.98(9)
C(2) −Mo(1)−N(1)	118.19(10)	N(1)−Mo(1)-S(2)	64.43(6)

distance of 2.5227(9) Å in **4** is identical with the Mo(1)−S(1) distance in **3** (2.5228(9) Å). The S atom lies above the Mo−N(1)−C(7) plane, and this is related to the preference of the four-membered chelating ligand (pyS) for a small bite angle (S−Mo−N) at the molybdenum of 64.43(6)°. This angle at the Mo center is considerably distorted from the idealized tetrahedral limits, due to the presence of a Cp ligand trans to pyS. The overall structure of **4** is very similar to that of CpMo(CO)$_2$(η^3-CH$_2$CRNH), with the exception that the pyS group coordinates to the Mo atom instead of the η^3-CH$_2$CRNH group.[30] The spectroscopic data for **4** are consistent with the solid-state structure.

The solid-state structure of **5** is depicted in Figure 3, crystal data are listed in Table 1, and selected bond distances and angles are given in Table 4. The structure consists of an isosceles Mo$_3$ triangle, with two elongated but almost equal metal−metal bonds (Mo(1)−Mo(2) = 2.9763(5) Å and Mo(1)−Mo(3) = 3.0104(5) Å) and one significantly shorter metal−metal bond (Mo(2)−Mo(3) = 2.7508(5) Å). It is a structurally unique compound with three cyclopentadienyl ligands, one triply bridging sulfido, one doubly bridging sulfido, two weakly semibridging carbonyls, and an ortho-metalated pyridyl ligand. Each metal atom is attached to a Cp ligand in a η^5 fashion. There is no crystallographic 3-fold axis present within **5**, but there is a mirror plane passing through S(1), S(2), Mo(1), and C(7). The three cyclopentadienyl−molybdenum moieties are positioned at vertexes of the Mo$_3$ triangle. Both of the carbonyl ligands exhibit weak semibridging coordination modes: one between Mo(1) and Mo(3) (Mo(1)−C(1) = 1.953(5) Å, Mo(3)···C(1) = 2.616(4) Å, Mo(1)−C(1)−O(1) = 162.8(4)°) and the other between Mo(1) and Mo(2) (Mo(1)−C(2) = 1.947(4) Å, Mo(2)···C(2) = 2.616(4) Å, Mo(1)−C(2)−O(2) = 161.4(4)°). There is a bridging ortho-metalated pyridyl ligand and a symmetrically bridging sulfido ligand (Mo(2)−S(1) = 2.2988(11) Å, Mo(3)−S(1) = 2.3039(10) Å) across the Mo(1)−Mo(2) edge. The metal−sulfur distances involving the bridging sulfido ligand are comparable to the corresponding average distance (2.285 Å) found in (μ_3-As)(μ-O)$_2$(μ-S)-Mo$_3$Cp$_3$.[31] The triply bridging sulfido ligand caps the molybdenum triangle in a symmetrical manner (Mo(1)−S(2) = 2.3824(11) Å, Mo(2)−S(2) = 2.3805(10) Å, Mo(3)−S(2) = 2.3845(11) Å). The Mo(2)−N(1) bond distance of 2.149(4) Å and the Mo(3)−C(18) bond distance of 2.150(4) Å are typical for Mo−N and Mo−C single bonds, respectively.[32] Compound **5** can be compared to Cp$_3$Mo$_3$(μ-S)$_3$(μ_3-S)[33] with regard to the capping sulfur atom as well as the three Mo-bound Cp ligands. The Mo(2)−N(1) distance of 2.149(4) Å in **5** is slightly shorter than that of the corresponding distance of 2.183(2) Å found in **4**. The C(1)−Mo(1)−C(2) angle, being 91.17(17)°, is a clear indication that the two semibridging CO groups are primarily bonded to Mo(1). The acute angle Mo(2)−Mo(1)−Mo(3) of 54.705(11)° is significantly smaller than that of either Mo(2)−Mo(3)−Mo(1) (62.017(12)°) or Mo(3)−Mo(2)−Mo(1) (63.278(12)°). Presumably, the appreciable double-bond character of Mo(2)−Mo(3) bond causes the Mo(2)−Mo(1)−Mo(3) angle to shrink to a value of 54.705(11)°

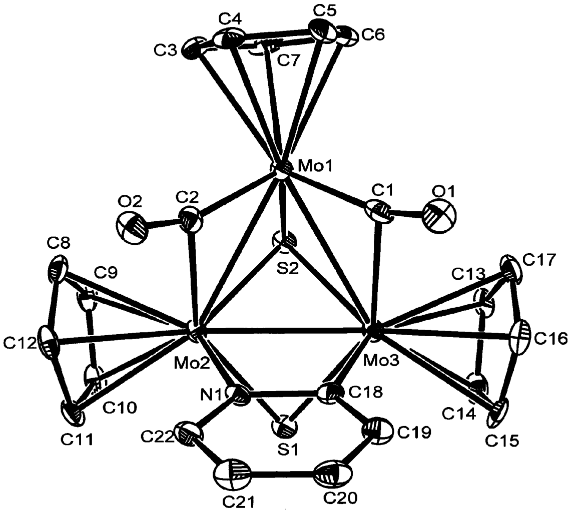

Figure 3. Solid-state structure of Cp$_3$Mo$_3$(μ-CO)$_2$(μ-S)(μ_3-S)(μ-η^2-NC$_5$H$_4$) (**5**). Thermal ellipsoids are at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5

Mo(1)−C(2)	1.947(4)	Mo(1)−Mo(3)	3.0104(5)
Mo(1)−C(1)	1.953(5)	Mo(2)−S(1)	2.2988(11)
Mo(1)-M(2)	2.9763(5)	Mo(2)−S(2)	2.3805(10)
Mo(2)−N(1)	2.149(4)	Mo(2)−Mo(3)	2.7508(5)
Mo(2)···C(2)	2.616(4)	Mo(3)−S(1)	2.3039(10)
Mo(1)−S(2)	2.3824(11)	Mo(3)−S(2)	2.38545(11)
C(2)−Mo(1)−C(1)	91.17(17)	S(2)−Mo(2)−Mo(1)	62.017
S(2)−Mo(1)−Mo(2)	51.30(3)	Mo(2)−S(2)−Mo(1)	77.35(3)
S(2)−Mo(1)−Mo(3)	50.87(3)	Mo(1)−S(2)−Mo(3)	78.32(3)
Mo(2)−Mo(1)−Mo(3)	54.705(11)	Mo(1)−C(2)−Mo(2)	79.96(15)
S(1)−Mo(2)−S(2)	80.70(4)	Mo(3)−Mo(2)−Mo(1)	63.278(12)
S(1)−Mo(2)−C(2)	140.14(9)	Mo(2)−S(1)−Mo(3)	73.40(3)
N(1)−Mo(2)−C(2)	69.43(13)	Mo(2)−S(2)−Mo(3)	70.52(3)

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relative to the other two acute angles. The bite angle Mo(2)−S(1)−Mo(3) of 73.40(3)° is sufficiently higher than that of the corresponding angle observed in the doubly bridged S-bound compound $(\mu_3\text{-As})(\mu\text{-O})_2(\mu\text{-S})\text{Mo}_3\text{Cp}_3$ (52.0°).[31] Electron counting shows that compound **5** contains a total of 46 valence electrons, making it an electron-deficient cluster. The local electron count for each Mo atom in **5** will depend on which metal is assigned as the two-electron acceptor from the capping sulfur atom. The most logical choice is Mo(1), which is not involved in bonding to the μ-pyridyl ligand. This gives an 18e count to Mo(3) and a 17e count to Mo(1) and Mo(2). The spectroscopic data of **5** are in agreement with the solid-state structure. The infrared spectrum shows two strong bands at 1821 and 1775 cm^{-1}, indicating that both carbonyl groups are semibridging. In addition to three resonances at δ 6.31, 6.23, and 5.13 for the cyclopentadienyl protons, the ^{1}H NMR spectrum of **5** in the aromatic region contains two doublets at δ 8.43 and 8.41 and two triplets at δ 6.87 and 6.50, characteristic of an ortho-metalated NC_5H_4 ligand. The mechanism of formation of **5** remains obscure**,** as attempts to obtain **5** by the reaction of **2** with elemental sulfur and pyridine at 110 °C, by photolysis of **2** in the presence of these reagents or by the reaction of **3** with **4** in the presence of **2**, have failed. It seems reasonable to propose that some unknown intermediate on the way to **3** reacts with excess **2** to give **5**.

Conclusions

In summary, the reaction between **1** and **2** provides a straightforward synthesis of the MoMn heterodinuclear complex **3**, the simple mononuclear molybdenum compound **4**, and the 46-electron trimolybdenum cluster **5**, containing three cyclopentadienyl ligands and an ortho-metalated pyridyl ligand supported by triply and doubly bridging sulfido ligands. The facile cleavage of the sulfur−carbon bonds illustrated by the formation of **5** is reminiscent of the many literature examples where transition-metal centers cleave the sulfur−aromatic carbon bond under relatively mild conditions.[33]

Interestingly, compound **3** contains one semibridging and three terminal CO ligands, while in **5**, both the carbonyl ligands are semibridging. The cyclopentadienyl ligand remains intact in three complexes during the course of reactions, thus acting as "spectator ligands". We must note, however, that even though compound **5** is formally unsaturated, it does not react with simple Lewis bases such as CO and PPh_3 under ordinary conditions. This thermodynamic preference for unsaturated (46e) rather than saturated (48e) structures was also observed for $\text{Cp}_2\text{FeMo}_2(\text{CO})_6(\mu_3\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2)_2$[34] and $\text{Cp}_2\text{FeMo}_2(\text{CO})_5(\mu\text{-OP(OEt)}_2)(\mu\text{-P(OEt)}_2)$[35] and might be both steric and electronic in origin. Both of these compounds as well as **5** contain relatively bulky cyclopentadienyl ligands as well as face-capping and/or multiple-edge-bridging ligands. It is well-known from molecular orbital calculations that the site and rate of nucleophilic attack on electron-deficient clusters depends primarily on the accessibility of the LUMO.[36] It may be that the presence of the bulky cyclopentadienyl ligand and the multiple bridges in **5** make such an orbital kinetically inaccessible. At elevated temperatures **5** does react slowly with CO to give **4**, perhaps by cleavage of one of the bridging ligand bonds.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Reagent-grade solvents were freshly distilled from appropriate drying agents. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Varian Unity Plus 400 or Bruker DPX 400 instruments. Elemental analyses were performed at the microanalytical laboratories of the Department of Chemistry, University College London. The compound $\text{Mn}_2(\text{CO})_6(\text{pyS})_2$ was prepared according to the published procedure.[27] The compound $(\text{CpMo(CO)}_3)_2$ was purchased from Aldrich and used as received.

Reaction of $\text{Mn}_2(\text{CO})_6(\text{pyS})_2$ (1) with $(\text{CpMo(CO)}_3)_2$ (2). A toluene solution (35 mL) of **1** (0.105 g, 0.211 mmol) and **2** (0.150 g, 0.306 mmol) was heated to reflux under nitrogen for 16 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave five bands, which afforded the following compounds in order of elution: **2** (0.025 g), **1** (0.005 g), $\text{CpMoMn(CO)}_3(\mu\text{-CO})(\mu\text{-}\eta^2\text{-pyS})(\mu\text{-}\eta^1\text{-pyS})$ (**3**) as red crystals (0.026 g, 22%), $\text{CpMo(CO)}_2(\mu\text{-}\eta^2\text{-pyS})$ (**4**) (0.030 g, 15%) as red crystals, and $\text{Cp}_3\text{Mo}_3(\mu\text{-CO})_2(\mu\text{-S})(\mu_3\text{-S})(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4)$ (**5**) as green crystals (0.014 g, 10%) from hexane/CH_2Cl_2 at 4 °C.

Analytical and spectroscopic data are as follows for **3**. Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{MnMoN}_2\text{O}_4\text{S}_2$: C, 41.61; H, 2.3; N, 5.11. Found: C, 41.78; H, 2.52; N, 5.18. IR (ν_{CO}, CH_2Cl_2): 2006 (s), 1917 (s), 1869 (m) cm^{-1}, IR (ν_{CO}, KBr): 2001 (vs), 19174 (s), 1864 (s), 1801 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 8.33 (m, 1H), 7.81 (m, 1H), 7.40 (m, 3H), 7.00 (m, 1H), 6.93 (m, 1H), 6.76 (m, 1H), 5.72 (s, 5H). MS: *m/z* 550.

Analytical and spectroscopic data are as follows for **4**. Anal. Calcd for $\text{C}_{12}\text{H}_9\text{MoNO}_2\text{S}$: C, 44.04; H, 2.78; N, 4.28. Found: C, 44.22; H, 2.95; N, 4.35. IR (ν_{CO}, CH_2Cl_2): 1960 (s), 1869 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.96 (d, 1H, $J = 6.4$ Hz), 7.29 (t, 1H, $J = 6.4$ Hz), 6.70 (t, 1H, $J = 6.4$ Hz), 6.59 (d, 1H, $J = 6.4$ Hz), 5.56 (s, 5H). MS: *m/z* 329 (M^+).

Analytical and spectroscopic data are as follows for **5**. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{Mo}_3\text{NO}_2\text{S}_2$: C, 38.78; H, 2.82; N, 2.06. Found: C, 38.92; H, 2.95; N, 2.12. IR (ν_{CO}, CH_2Cl_2): 1821 (vs), 1765 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 8.43 (d, 1H, $J = 5.6$ Hz), 8.41 (d, 1H, $J = 5.6$ Hz), 6.87 (t, 1H, $J = 5.6$ Hz), 6.50 (t, 1H, $J = 5.6$ Hz), 6.31 (s, 5H), 6.23 (s, 5H). 5.13 (s, 5H). MS: *m/z* 681.

Reaction of 2 with Pyridine-2-thiol. A toluene solution (25 mL) of **2** (0.100 g, 0.024 mmol) and pyridine-2-thiol (0.045 g, 0.024 mmol) was heated to reflux for 3 h. The solvent was removed under reduced pressure, and the residue was separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) gave two bands. The first band gave unconsumed **1** (0.005 g), while the second band gave **4** (0.094 g, 70%).

Reaction of 5 with CO. Carbon monoxide gas (1 atm) was bubbled through a refluxing toluene solution (15 mL) of **5** (0.025 g, 0.037 mmol) for 5 h. The solvent was removed under reduced pressure, and the residue was chromatographed as above to give **4** (0.006 g, 50%) as the only product.

Crystal Structure Determination of 3−5. Suitable crystals of **3**−**5** were grown by slow evaporation of a dichloromethane/hexane solvent mixture at 4 °C, and crystallographic measurements for all the complexes were made on a Bruker Nonius Kappa CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 150 ± 2

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K for **3** and **4** and at 120 ± 2 K for **5**. The structures were solved by direct methods (SHELXS-96)[37] and refined on F^2 by full-matrix least squares (SHELXL-97)[38] using all unique data. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in the calculated positions. The absolute structure of compound **3**, which crystallized in a noncentrosymmetric space group, was determined by evaluation of the Flack parameter, which was −0.02(2) or close enough to zero to ensure the absolute structure was correct.[39]

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Supporting Information Available: Text and tables giving details of the X-ray crystallographic structure determination for **3**−**5**.[40] This material is available free of charge via the Internet at http://pubs.acs.org.

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