

Syntheses, Reactivity, and Crystal Structures of Molybdenum Complexes with Pyridine-2-thionate (pyS)-Containing Ligands: Crystal Structures of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]_2(\mu\text{-}\eta^1, \eta^2\text{-pyS})_2$, *exo*- $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\eta^2\text{-pyS})(\eta^2\text{-dppe})]$, $[\text{Mo}(\text{CO})_3(\eta^1\text{-SC}_5\text{H}_4\text{NH})(\eta^2\text{-dppm})]$, and $[\text{Mo}(\text{CO})(\eta^2\text{-pyS})_2(\eta^2\text{-dppm})]$

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The doubly bridged pyridine-2-thionate (pyS) dimolybdenum complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]_2(\mu\text{-}\eta^1, \eta^2\text{-pyS})_2$ (**1**) is accessible by the reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}]$ with pySK in methanol at room temperature. Complex **1** reacts with piperidine in acetonitrile to give the complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-pyS})(\text{C}_5\text{H}_{10}\text{NH})]$ (**2**). Treatment of **1** with 1,10-phenanthroline (phen) results in the formation of complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^1\text{-pyS})(\text{phen})]$ (**3**), in which the pyS ligand is coordinated to Mo through the sulfur atom. Four conformational isomers, *endo,exo*-complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\eta^2\text{-pyS})(\eta^2\text{-diphos})]$ (diphos = dppm, **4a–4d**; dppe, **5a–5d**), are accessible by the reactions of **1** with dppm and dppe in refluxing acetonitrile. Homonuclear shift-correlated 2-D $^{31}\text{P}\{^1\text{H}\}\text{--}^{31}\text{P}\{^1\text{H}\}$ NMR experiments of the mixtures **4a–4d** have been employed to elucidate the four stereoisomers. The reaction of **4** and pySK or $[\text{Mo}(\text{CO})_3(\eta^1\text{-SC}_5\text{H}_4\text{NH})(\eta^2\text{-dppm})]$ (**6**) and O₂ affords allyl-displaced seven-coordinate bis(pyridine-2-thionate) complex $[\text{Mo}(\text{CO})(\eta^2\text{-pyS})_2(\eta^2\text{-dppm})]$ (**7**). All of the complexes are identified by spectroscopic methods, and complexes **1**, **5d**, **6**, and **7** are determined by single-crystal X-ray diffraction. Complexes **1** and **5d** crystallize in the orthorhombic space groups *Pbcn* and *Pbca* with *Z* = 4 and 8, respectively, whereas **6** belongs to the monoclinic space group *C2/c* with *Z* = 8 and **7** belongs to the triclinic space group *P $\bar{1}$* with *Z* = 2. The cell dimensions are as follows: for **1**, *a* = 8.3128(1) Å, *b* = 16.1704(2) Å, *c* = 16.6140(2) Å; for **5d**, *a* = 17.8309(10) Å, *b* = 17.3324(10) Å, *c* = 20.3716(11) Å; for **6**, *a* = 18.618(4) Å, *b* = 16.062(2) Å, *c* = 27.456(6) Å, β = 96.31(3)°; for **7**, *a* = 9.1660(2) Å, *b* = 12.0854(3) Å, *c* = 15.9478(4) Å, α = 78.4811(10)°, β = 80.3894(10)°, γ = 68.7089(11)°.

Introduction

A variety of allyl complexes of molybdenum(II) containing bidentate anionic sulfur donor ligands such as dithiocarbamates have been described.¹ For example, an early report²

concerns the dithiocarbamate molybdenum complex $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{py})(\eta^2\text{-S}_2\text{CNR})]$ (R = Me₂, Et₂), prepared by treating $[\text{Mo}(\eta^2\text{-BPY})(\eta^3\text{-allyl})(\text{CO})_2\text{Br}]$ with NaS₂CNR in the presence of py. More recently Shiu et al.³ used $[\text{Mo}(\text{CH}_3\text{-CN})_2(\eta^3\text{-allyl})(\text{CO})_2\text{Br}]$ to react with NaS₂CNR (R = C₄H₈, Et₂), forming a 16-electron complex, $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\eta^2\text{-S}_2\text{CNR})]$. Recently we prepared the 18-electron allyl dithiocarbonate $[\text{Mo}(\text{CH}_3\text{CN})(\eta^3\text{-allyl})(\text{CO})_2(\eta^2\text{-S}_2\text{COEt})]$ complex.⁴ The 18-electron allyl dialkyldithiophosphate complexes

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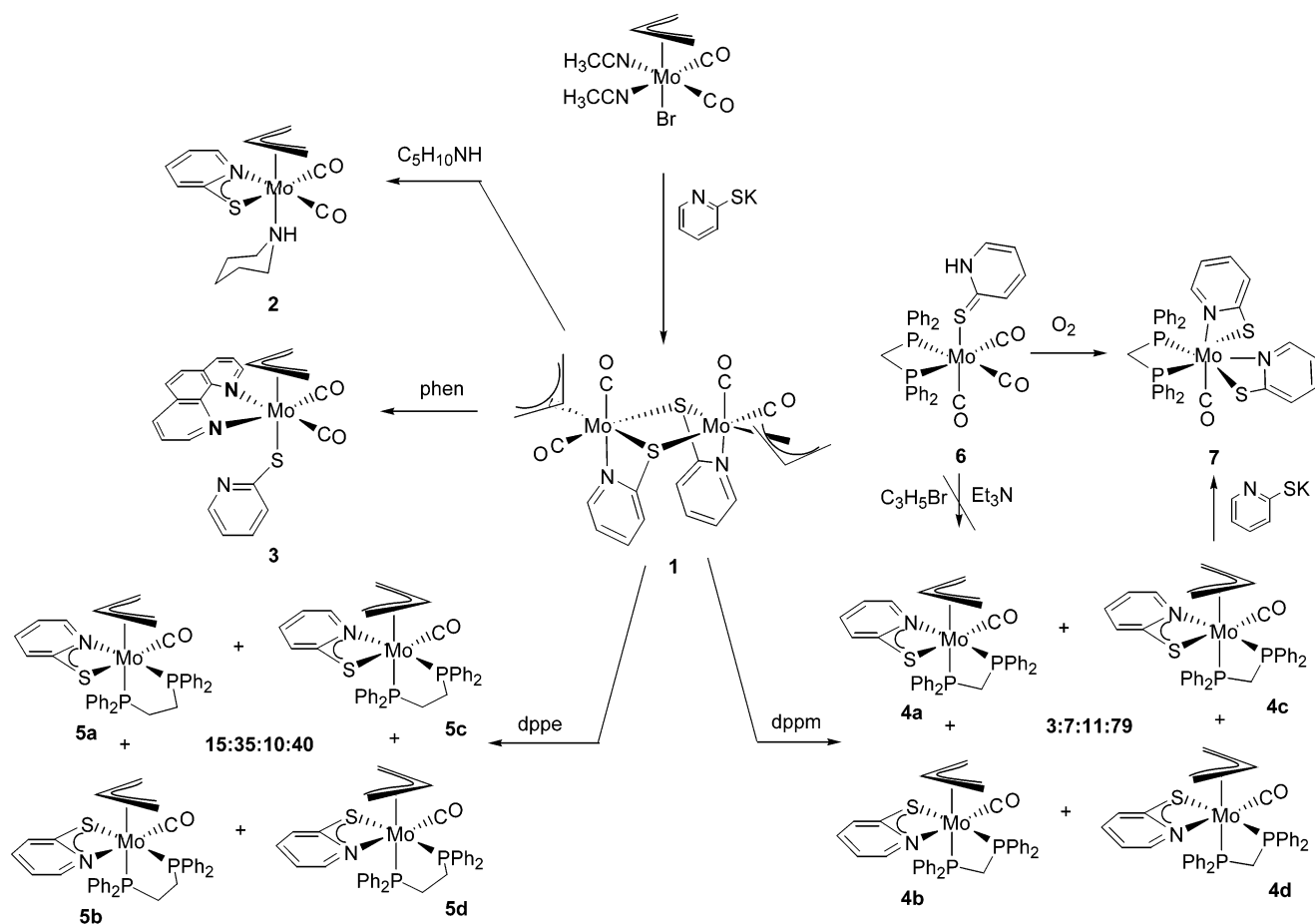
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Scheme 1



$[\text{Mo}(\text{CH}_3\text{CN})(\eta^3\text{-allyl})(\text{CO})_2\{\eta^2\text{-S}_2\text{P}(\text{OR}_2)\}]^5$ ($\text{R} = \text{Et}, \text{Ph}$) and $[\text{Mo}_2(\eta^3\text{-allyl})_2(\text{CO})_4\{\eta^2\text{-S}_2\text{P}(\text{OR}_2)\}_2(\mu\text{-NH}_2\text{NH}_2)]$ have also been described.⁵ The 16-electron allyl dithio complexes such as $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\eta^2\text{-S}_2\text{CNR})]^6$ ($\text{R} = \text{Et}, \text{C}_4\text{H}_8, \text{C}_5\text{H}_{10}$) and $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\eta^2\text{-Pz}^*\text{BR}_2)]^7$ ($\text{R} = \text{H}, \text{Et}, \text{Ph}$) containing sulfur or nitrogen bidentate ligands have also been studied. However, no detailed information has been presented on a mixed bidentate (N, S) ligand such as pySH.

Carlton⁸ and Baker⁹ described the preparation and characterization of the alkyne pyridine-2-thionate (pyS) complexes $[\text{W}(\text{CO})(\text{pyS})(\eta^2\text{-MeC}_2\text{Me})]$ and $[\text{W}(\text{CO})(\text{NCMe})(\text{pyS})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$. However, no allyl complexes of molybdenum(II) containing pyS have been described. In a previous paper¹⁰ we described the preparation and characterization of the first doubly bridged pyS allyl dimolybdenum(II) complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{CO})_2]_2(\mu\text{-}\eta^1, \eta^2\text{-pyS})_2$ (**1**). Herein, we report the reactions of **1** with nitrogen and phosphine ligands as well as the characterization of four

conformational isomers of $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})(\eta^2\text{-diphos})(\eta^2\text{-pyS})]$ by 2-D $^{31}\text{P}\{^1\text{H}\}-^{31}\text{P}\{^1\text{H}\}$ NMR experiments.

Results and Discussion

Syntheses. The reactions of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{Br})]$ with NaS_2CNR ($\text{R} = \text{Me}_2, \text{Et}_2, \text{C}_4\text{H}_8, \text{C}_5\text{H}_{10}$) or KS_2COEt produced the 16-electron allyl dithiocarbamate complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-S}_2\text{CNR})]^3$ or the 18-electron allyl dithiocarbonate complex $[\text{Mo}(\text{CH}_3\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-S}_2\text{COEt})]^4$. We expected that the reaction of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{Br})]$ with pyS would produce a 16-electron pyridine-2-thionate complex, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-pyS})]$, or an 18-electron acetonitrile solvate complex, $[\text{Mo}(\text{CH}_3\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-pyS})]$. Instead, we obtained a dimer, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]_2(\mu\text{-}\eta^1, \eta^2\text{-pyS})_2$ (**1**) (Scheme 1). Complex **1** and $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{CO})_2\text{Br}]$ and pySK react in methanol at room temperature, producing the novel doubly bridged pyridine-2-thionate complex **1** in good yield. The air-stable yellow complex **1** is soluble in DMSO and slightly soluble in CH_2Cl_2 , CH_3CN , and THF.

Although the dinuclear compound **1** is held by sulfur bridges and is thermally stable, these bridges are easily cleaved. Thus, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^2\text{-pyS})(\text{C}_5\text{H}_{10}\text{NH})]$ (**2**) and $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\eta^1\text{-pyS})(\text{phen})]$ (**3**) complexes were produced by the reactions of **1** and piperidine, $\text{C}_5\text{H}_{10}\text{NH}$, or 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$, in dichloromethane at ambient temperature. The yellow compound **2** is slightly air-sensitive,

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soluble in polar solvent, and slightly soluble in *n*-hexane. The air-stable red compound **3** is soluble in dichloromethane, and insoluble in diethyl ether and *n*-hexane.

The respective reactions of **1** and dpmp or dppe in refluxing acetonitrile result in the isolation of the mixtures of four *endo,exo* conformational isomers, $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\eta^2\text{-pyS})(\eta^2\text{-diphos})]$ (diphos = dpmp, **4a–4d**; dppe, **5a–5d**), in good yields with *endo*-PN:*endo*-PS:*exo*-PN:*exo*-PS ratios of 3:7:11:79 and 15:35:10:40. The orientations of *endo* and *exo* are defined to the open face of the allyl group and carbonyl group in the same direction in the former and opposite directions in the latter.¹¹ The PS or PN means one phosphorus atom of the diphos ligand and the sulfur or nitrogen atom of the pyS ligand in the *trans* position of the pseudooctahedral geometry of complexes **4** and **5**. In an attempt to synthesize **4a–4d**, we treated $[\text{Mo}(\text{CO})_3(\eta^1\text{-pySH})(\eta^2\text{-dpmp})]$ (**6**) with allyl bromide in the presence of Et₃N in acetonitrile at room temperature. However, at higher temperatures only decomposition was observed.

A number of pyridine-2-thionate complexes of group VIII B have been prepared,¹² and the pyridine-2-thionate ligand can be monodentate, with a metal–sulfur bond, it can chelate to one metal, or it can bridge two or three metal centers. Thus, the reaction of **4** with excess pySK in refluxing acetonitrile produces a bis(pyridine-2-thionate) complex, $[\text{Mo}(\text{CO})(\eta^2\text{-pyS})_2(\eta^2\text{-dpmp})]$ (**7**), in good yield. Complex **7** can also be obtained from the dichloromethane solution of complex **6** with continuous stirring in the air for 24 h. Complex **6** can be produced by the reaction of $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})(\eta^2\text{-dpmp})]$ and pySH in MeOH at room temperature for 1 h. The air-stable red complexes **6** and **7** are soluble in chlorinated solvents, and insoluble in diethyl ether and *n*-hexane. Attempts to obtain a bisalkyne complex such as $[\text{Mo}\{\eta^2\text{-S}_2\text{P}(\text{OEt}_2)_2\}_2(\text{PhC}\equiv\text{CPh})_2]$ ¹⁵ from the reaction of **1** with PhC≡CPh were unsuccessful. No reaction occurred under the same reaction conditions. The isolated compounds **1–7** were already of good purity, but analytically pure samples could be obtained by slow *n*-hexane diffusion into a dichloromethane solution at 4 °C.

IR and MS Spectroscopy. The IR spectrum of **1** shows four terminal carbonyl stretching bands, which is similar to those of other 16-electron complexes, $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\eta^2\text{-L})]$ (L = Et₂NCS₂, C₄H₈NCS₂, C₅H₁₀NCS₂, Et₂BPz₂, Ph₂BPz₂), that were crystallographically characterized^{7a} in the case of L = Et₂BPz₂. The solution-phase IR spectra of **2** and **3** show the two carbonyls with equal intensity, indicating that the two carbonyls are mutually *cis*. In KBr and solution-phase IR spectra, only one terminal carbonyl stretching band is found in **4** and **5**, although four isomers are known to be present in different ratios. The IR spectrum of **6** shows two terminal carbonyl stretchings at 1915 and 1806 cm⁻¹ (A₁ + E) that reveal a typical pattern for a *fac*-L₃M(CO)₃ unit with

an octahedral geometry. Only one terminal carbonyl stretching band is found at 1807 cm⁻¹ in **7**.

We could not obtain the parent peak [M⁺] molecular mass with the typical Mo isotope distribution of **1** from the FAB mass spectrum. The FAB mass spectra of **2–5** and **6** and **7** show parent peaks with the typical Mo isotope distribution corresponding to [M⁺] and [M⁺ – CO] molecular masses, respectively.

NMR Spectroscopy. The room temperature ¹H NMR spectrum of **1** shows five allyl proton resonances at δ 1.00, 1.33, 3.06, 3.43, and 3.83 with equal intensity. The ¹³C{¹H} NMR spectrum of **1** reveals two singlets at lowest field, which are assigned to the carbon atoms of the four terminal carbonyl groups (Supporting Information, spectrum A). Similar spectroscopic observations of the carbonyl group and allyl moiety in ¹³C{¹H} and ¹H NMR spectra lead us to believe that complex **2** contains the same solution intramolecular trigonal twist behavior as the 18-electron dithio complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^2\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{CH}_3\text{CN})(\text{CO})_2]$,⁵ $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^2\text{-S}_2\text{P}(\text{OEt}_2)\}(\text{C}_5\text{H}_{10}\text{NH})(\text{CO})_2]$,⁵ and $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^2\text{-S}_2\text{COEt}_2)(\text{CH}_3\text{CN})(\text{CO})_2]$.⁴ From the AM₂X₂ pattern of the allyl group in the ¹H NMR spectra and the equivalent resonance of the terminal carbon of the allyl group as well as the resonance of the carbonyl group in the ¹³C{¹H} NMR spectra of **3**, it looks as if the geometry of **3** has a mirror plane through the center carbon of the allyl group, Mo, and coordinating S atom of the pyS ligand. The most likely structure is shown with the allyl group and the η¹-pyS ligand occupying the axial sites and the 1,10-phenanthroline ligand and the two carbonyl ligands in the equatorial plane. This structure is different from those of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\eta^1\text{-O}_2\text{CCF}_3)(\text{Phen})(\text{CO})_2]$ ¹³ and $[\text{Mo}(\text{CH}_3\text{CN})(\eta^3\text{-C}_5\text{H}_7)(\text{Phen})(\text{CO})_2]$ [BF₄]¹⁴ but similar to the X-ray crystallographically determined geometry of the complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\eta^1\text{-S}_2\text{P}(\text{OEt}_2)_2\}(\text{Phen})(\text{CO})_2]$.¹⁵ Variable-temperature (VT) (213–298 K) ¹H NMR experiments were used to confirm that there does not exist any intramolecular trigonal twist behavior in complex **3** under low-temperature conditions due to the steric hindrance of 1,10-phenanthroline and pyS ligands.

Unambiguous assignment of the ¹H and ¹³C{¹H} NMR spectra of **4** and **5** are difficult because of the multiple coupling between the diphos ligand and five protons of the allyl group and the mixtures of the four isomers. However, the ³¹P{¹H} NMR spectra of **4** and **5** clearly show eight sets of doublet resonance. Homonuclear shift-correlated 2-D ³¹P{¹H}–³¹P{¹H} NMR experiments of the mixtures **4a–4d** have been employed to elucidate the four isomers (Figure 1). From our early report,¹¹ *exo*-complexes show larger *J*_{P–P} coupling constants than *endo*-complexes in the dithiodiphos molybdenum complexes (dithio = Et₂NCS₂, C₄H₈NCS₂, (EtO)₂PS₂, EtOCS₂; diphos = dpmp, dppe, dppea). The conformation of the CO ligand and nitrogen atom of the pyS

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Table 1. Crystal Data and Refinement Details for Complexes **1**, **5d**, **6**, and **7**

	1	5d	6	7
empirical formula	C ₂₀ H ₁₈ N ₂ O ₄ S ₂ Mo	C ₃₅ H ₃₃ NOP ₂ S ₂ Mo	C ₃₃ H ₂₇ NO ₃ P ₂ S ₂ Mo	C ₃₆ H ₃₀ N ₂ OP ₂ S ₂ Mo
fw	606.36	673.56	675.50	728.62
cryst syst	orthorhombic	orthorhombic	monoclinic	triclinic
space group	Pbcn	Pbca	C2/c	P1
<i>a</i> , Å	8.3128(1)	17.8309(10)	18.618(4)	9.1660(2)
<i>b</i> , Å	16.1704(2)	17.3324(10)	16.062(2)	12.0854(3)
<i>c</i> , Å	16.6140(2)	20.3716(11)	27.456(6)	15.9478(4)
α, deg	90	90	90	78.4811(10)
β, deg	90	90	96.31(3)	80.3894(10)
γ, deg	90	90	90	68.7089(11)
<i>V</i> , Å ³	2233.28(5)	6295.9(6)	6149.3(21)	1604.23(7)
<i>Z</i>	4	8	8	2
ρ _{calcd} , g cm ⁻³	1.803	1.421	1.459	1.508
μ(Mo Kα), mm ⁻¹	1.339	0.613	0.633	0.672
λ, Å	0.71073	0.71073	0.71073	0.71073
<i>T</i> , K	295	295	293	150
θ range, deg	2.45–27.50	1.92–27.50	1.49–24.97	1.83–27.50
no. of independent rflns	2558	7233	5402	7357
no. of variables	137	370	371	398
R ^a	0.051	0.036	0.034	0.043
R _w ^b	0.106	0.090	0.078	0.098
S ^c	1.159	1.030	1.041	1.087

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}$; $w = 1/s^2(|F_o|)$. ^c Goodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{params}})]^{1/2}$.

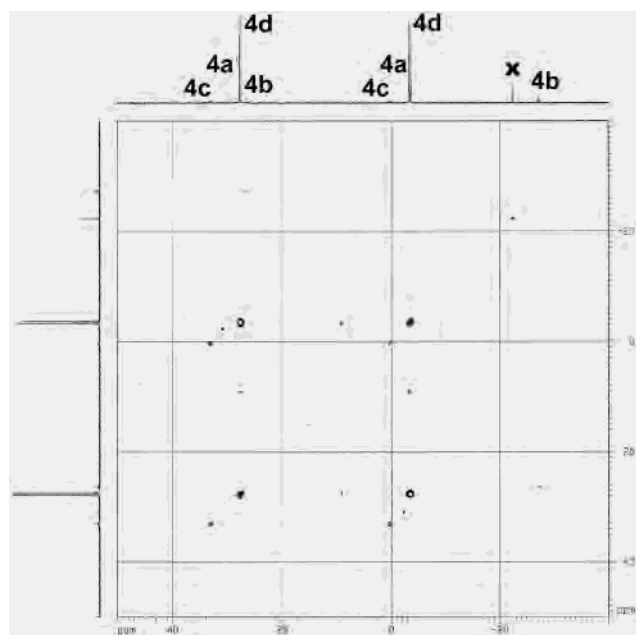


Figure 1. Homonuclear shift-correlated 2-D NMR spectrum for ³¹P nuclei with ¹H decoupling for the mixture **4a–4d** in acetone-*d*₆. “x” is the impurity.

ligand in the *trans* position is more stable than other isomers because of the good π -bonding CO ligand competition for the d orbital of the molybdenum atom. The ratio of the four isomers *endo*-PN, *endo*-PS, *exo*-PN, and *exo*-PS is 3:7:11:79 by integrating from the ³¹P{¹H} NMR spectra of **4**. One can conclude that the dpmm ligand improves the formation of *exo*-products. To simplify the variable-temperature ¹H and ³¹P{¹H} NMR experiments, the mixtures of **4a–4d** are recrystallized to obtain the mixtures of **4a** and **4c** to investigate the fluxional behavior. In the range of 213–273 K, the ratio was retained and no ¹H and ³¹P{¹H} NMR spectra were changed. In the range of 273–323 K, the ¹H NMR resonances of **4c** became broad at 288 K and the resonances appeared decomposed at 313 K (Supporting Information, spectrum B). We have recently shown that it

is possible to convert *endo*-[Mo(η^3 -C₃H₅)(CO)(η^2 -S₂CNC₄H₈)-(η^2 -dpmm)] to the *exo*-form by allyl rotation.^{11b} Since no other information could be obtained, we are not in a position to define the formative mechanism further.

The ¹H NMR spectra of **6** and **7** exhibit resonances at δ 4.40 and δ 4.17 attributed to the methylene protons of the dpmm ligand, and the corresponding resonances in the ¹³C-{¹H} NMR spectra appear at δ 48.9 and δ 40.1, respectively. The ³¹P{¹H} NMR spectra of **6** and **7** show the two dpmm resonances at δ 0.4 and δ 14.6 and 15.4, respectively. The AB pattern results from two inequivalent phosphorus atoms in **7**, and the downfield resonance relative to that of **6** shows the lower electron density of the two phosphorus atoms due to the high oxidation state of Mo(II).

X-ray Single-Crystal Structures of 1, *exo*-5d, 6, and 7. To confirm the novel doubly bridging, chelating, and monodentate pyS ligands, complexes **1**, *exo*-**5d**, **6**, and **7** were confirmed by single-crystal X-ray diffraction studies. The ORTEP diagrams with atom labels of complexes **1**, *exo*-**5d**, **6** and **7** are shown in Figures 2–5. Bond distances, bond angles, atomic coordinates, and equivalent isotropic displacement coefficients for important atoms are listed in Tables 2 and 3. Complex **1** (Figure 2) is a dimer with each pyS unit chelating through sulfur and nitrogen to one metal center and bridging both the metals through sulfur. In the structure, the coordination geometry around the molybdenum atom is a distorted octahedron with an N atom and an S atom from the pyS ligand, one sulfur atom from another pyS ligand, and two carbonyl groups and the allyl group occupying the six coordination sites. The Mo–S distances are not equal, and the Mo₂S₂ ring is nonplanar with a dihedral angle of 31.15(4)° between the Mo(1)S(1)Mo(1A) and Mo(1)S(1A)–Mo(1A) planes. The distortions from octahedral geometry appear to be associated with the small interligand angles 64.43(12)° (SMoN angles in chelate rings) and 95.70(5)° (SMoS angles). The structure confirms the nonequivalent allyl groups. The sulfur atom of the pyS ligand is *trans* to the

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**, **5d**, **6**, and **7**

bond lengths		bond angles	
Compound 1			
Mo(1)–C(1)	1.970(7)	N(1)–Mo(1)–S(1)	64.43(12)
Mo(1)–C(2)	1.948(7)	C(4)–Mo(1)–S(1)	152.60(18)
Mo(1)–C(3)	2.349(6)	N(1)–Mo(1)–C(1)	166.5(2)
Mo(1)–C(4)	2.209(6)	S(1A)–Mo(1)–C(2)	159.95(18)
Mo(1)–C(5)	2.305(6)	S(1A)–Mo(1)–N(1)	86.74(11)
Mo(1)–N(1)	2.253(5)	C(1)–Mo(1)–C(2)	77.9(2)
Mo(1)–S(1)	2.5669(14)	C(1)–Mo(1)–S(1)	102.09(18)
Mo(1)–S(1A)	2.6184(14)	C(3)–C(4)–C(5)	116.1(7)
C(3)–C(4)	1.393(8)	S(1A)–Mo(1)–S(1)	80.54(5)
C(4)–C(5)	1.402(9)	Mo(1A)–S(1)–Mo(1)	95.70(5)
Compound 5d			
Mo(1)–C(1)	1.908(3)	N(1)–Mo(1)–S(1)	63.34(5)
Mo(1)–C(2)	2.295(3)	P(1)–Mo(1)–P(2)	77.50(2)
Mo(1)–C(3)	2.303(3)	N(1)–Mo(1)–C(1)	161.44(9)
Mo(1)–C(4)	2.328(3)	S(1)–Mo(1)–P(2)	152.16(2)
Mo(1)–N(1)	2.311(2)	C(3)–Mo(1)–P(1)	169.66(11)
Mo(1)–S(1)	2.5588(7)	C(2)–C(3)–C(4)	120.8(4)
Mo(1)–P(1)	2.5166(6)	N(1)–C(5)–S(1)	112.40(17)
Mo(1)–P(2)	2.4400(6)	Mo(1)–C(1)–O(1)	175.5(2)
C(2)–C(3)	1.353(5)	C(3)–Mo(1)–C(1)	83.27(13)
C(3)–C(4)	1.320(5)	Mo(1)–C(1)–O(1)	175.5(2)
Compound 6			
Mo(1)–C(1)	1.974(4)	C(1)–Mo(1)–C(2)	96.84(15)
Mo(1)–C(2)	1.965(4)	C(1)–Mo(1)–C(3)	87.4(2)
Mo(1)–C(3)	1.944(4)	C(2)–Mo(1)–C(3)	84.17(15)
Mo(1)–S(1)	2.5806(11)	C(1)–Mo(1)–S(1)	94.50(11)
Mo(1)–P(1)	2.5350(10)	C(1)–Mo(1)–P(1)	164.68(11)
Mo(1)–P(2)	2.5115(10)	C(1)–Mo(1)–P(2)	97.62(11)
C(1)–O(1)	1.153(4)	S(1)–Mo(1)–C(3)	176.88(11)
C(2)–O(2)	1.160(4)	C(2)–Mo(1)–P(2)	163.15(11)
C(3)–O(3)	1.157(4)	P(1)–Mo(1)–P(2)	67.64(3)
Compound 7			
Mo(1)–C(1)	1.910(4)	N(1)–Mo(1)–S(1)	63.29(8)
Mo(1)–P(1)	2.4554(8)	N(2)–Mo(1)–S(2)	64.37(7)
Mo(1)–P(2)	2.4577(8)	P(1)–Mo(1)–P(2)	66.20(3)
Mo(1)–N(1)	2.247(3)	N(1)–Mo(1)–N(2)	86.36(9)
Mo(1)–N(2)	2.307(3)	S(1)–Mo(1)–S(2)	140.27(3)
Mo(1)–S(1)	2.5692(9)	N(1)–Mo(1)–S(2)	85.22(7)
Mo(1)–S(2)	2.5125(8)	N(2)–Mo(1)–S(1)	88.73(7)
C(1)–O(1)	1.184(4)	P(1)–Mo(1)–N(1)	160.06(8)
P(1)–C(12)	1.842(3)	P(1)–Mo(1)–S(1)	136.34(3)
P(2)–C(12)	1.836(3)	P(2)–Mo(1)–S(2)	141.79(3)
S(1)–C(2)	1.732(3)	P(2)–Mo(1)–N(2)	112.95(7)
S(2)–C(7)	1.740(4)	C(1)–Mo(1)–N(2)	161.94(12)

allyl, S(1)–Mo(1)–C(4) = 152.60(18)°, while the nitrogen atom of the pyS ligand is *trans* to one carbonyl, N(1)–Mo(1)–C(1) = 166.5(2)°. The remaining carbonyl is *trans* to the sulfur atom of another pyS ligand, S(1A)–Mo(1)–C(2) = 159.95(18)°. The molybdenum–sulfur bond (*trans* to allyl), 2.5669(14) Å, is significantly shorter than the molybdenum–sulfur bond (*trans* to carbonyl), 2.6184(14) Å, because of the greater *trans* effect induced by the CO group than the allyl group. The S(1)–Mo(1)–N(1) angle of 64.43–(12)° in **1** is similar to 63.6(1)° in Mo₂(CO)₉(pyS)¹⁶ within experimental error. The Mo–Mo distance of **1** is 3.8446(9) Å, indicating no significant metal–metal interaction. To our knowledge, group VIB complexes containing M–S and M–N bonds involving a pyS moiety as a doubly bridged bidentate ligand have not been reported in the literature, although groups VB¹⁷ and VIIB¹² metal complexes with pyS ligands are known.

The ORTEP plot of complex *exo-5d* is shown in Figure 3. The molybdenum atom is a pseudooctahedron with one

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Important Atoms of **1**, **5d**, **6**, and **7**^a

atom	x	y	z	B _{eq}
Compound 1				
Mo(1)	–449(1)	3473(1)	1365(1)	46(1)
S(1)	1969(2)	3185(1)	2284(1)	48(1)
O(1)	–817(6)	5386(3)	1511(3)	78(2)
O(2)	2117(6)	4202(3)	215(3)	83(1)
N(1)	368(5)	2145(3)	1416(3)	47(1)
C(1)	–721(8)	4677(4)	1485(3)	60(2)
C(2)	1155(8)	3902(4)	619(4)	59(2)
C(3)	–3066(8)	3809(4)	945(4)	69(2)
C(4)	–2495(8)	3076(4)	610(4)	68(2)
C(5)	–1212(9)	3153(5)	68(4)	73(2)
C(6)	1569(6)	2168(3)	1955(3)	47(1)
C(7)	2385(8)	1454(3)	2189(4)	60(2)
C(8)	1926(8)	714(4)	1847(4)	68(2)
C(9)	714(8)	696(4)	1299(4)	65(2)
C(10)	–51(8)	1418(3)	1087(4)	58(2)
Compound 5d				
Mo	2495(1)	7439(1)	4908(1)	31(1)
S(1)	2773(1)	6529(1)	3956(1)	42(1)
P(1)	2038(1)	8134(1)	3900(1)	35(1)
P(2)	2112(1)	8688(1)	5347(1)	33(1)
O(1)	4038(1)	8225(1)	4973(1)	69(1)
N(1)	1578(1)	6544(1)	4657(1)	38(1)
C(1)	3438(1)	7956(2)	4946(1)	42(1)
C(2)	3073(3)	6470(2)	5486(2)	80(1)
C(3)	2841(2)	6998(2)	5931(2)	73(1)
C(4)	2125(2)	7181(2)	5982(1)	57(1)
C(5)	1890(1)	6175(1)	4140(1)	38(1)
C(6)	1519(2)	5583(2)	3812(2)	52(1)
C(7)	815(2)	5375(2)	4016(2)	63(1)
C(8)	490(2)	5757(2)	4538(2)	57(1)
C(9)	3710(5)	2314(4)	10478(2)	52(1)
C(10)	3704(6)	1539(5)	9960(2)	61(1)
C(11)	4636(5)	1477(4)	9181(2)	47(1)
Compound 6				
Mo	2209(1)	3729(1)	1117(1)	38(1)
S(1)	877(1)	3122(1)	1041(1)	53(1)
P(1)	2122(1)	4310(1)	1996(1)	42(1)
P(2)	1817(1)	5710(1)	1183(1)	44(1)
N(1)	1337(2)	1322(3)	611(1)	50(1)
C(1)	2272(2)	3709(3)	404(1)	48(1)
C(2)	2648(2)	2269(3)	1261(1)	45(1)
C(3)	3198(2)	4255(3)	1196(1)	50(1)
C(4)	784(2)	1828(3)	805(1)	48(1)
C(5)	155(2)	1178(4)	808(1)	62(1)
C(6)	142(2)	100(4)	655(2)	72(1)
C(7)	738(3)	–377(4)	483(2)	73(1)
C(8)	1326(2)	246(4)	457(2)	65(1)
C(9)	1955(3)	5786(3)	1857(1)	66(1)
Compound 7				
Mo	7155(1)	2631(1)	7727(1)	25(1)
S(1)	7875(1)	499(1)	7378(1)	37(1)
S(2)	6835(1)	3695(1)	8983(1)	33(1)
P(1)	5115(1)	4591(1)	7370(1)	25(1)
P(2)	6099(1)	2881(1)	6356(1)	25(1)
O(1)	9549(3)	3707(2)	6600(2)	40(1)
N(1)	9149(3)	1191(3)	8376(2)	31(1)
N(2)	5534(3)	2161(3)	8907(2)	31(1)
C(1)	8646(4)	3259(3)	7004(2)	31(1)
C(2)	9297(4)	202(3)	8063(2)	33(1)
C(3)	10470(4)	–902(3)	8280(2)	42(1)
C(4)	11518(5)	–950(4)	8821(3)	53(1)
C(5)	11384(5)	56(4)	9136(3)	54(1)
C(6)	10193(4)	1126(4)	8904(2)	40(1)
C(7)	5562(4)	2909(3)	9425(2)	30(1)
C(8)	4640(4)	3016(4)	10220(2)	39(1)
C(9)	3710(5)	2314(4)	10478(2)	52(1)
C(10)	3704(6)	1539(5)	9960(2)	61(1)
C(11)	4636(5)	1477(4)	9181(2)	47(1)

^a ESDs refer to the last digit printed.

sulfur and one nitrogen atom of the pyS ligand, two phosphorus atoms of the dppe ligand, and the carbonyl and allyl groups occupying the six coordination sites. Clearly, the open face of the allyl group is oriented away from the

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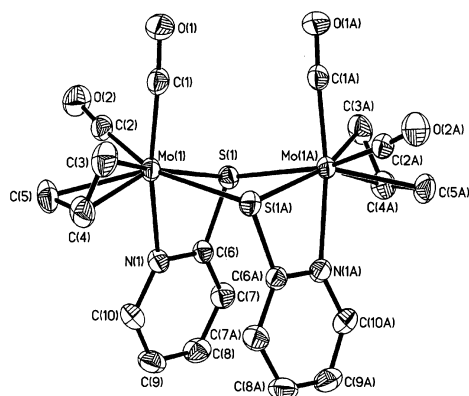


Figure 2. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for complex **1**.

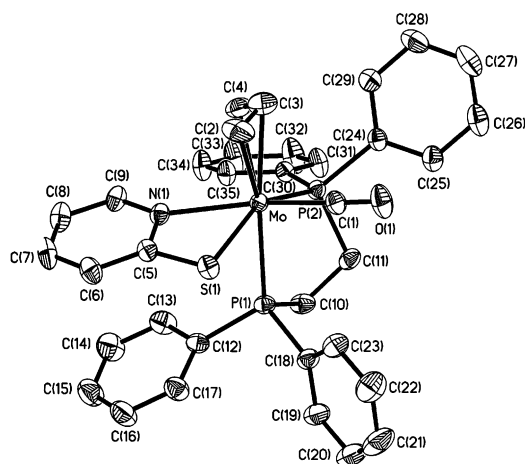


Figure 3. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for complex **5d**.

carbonyl group, and the structure confirms the unequivalent allyl group in *exo-5d*. The sulfur atom of the pyS ligand is *trans* to the diphos, $S(1)-Mo-P(2) = 152.16(2)^\circ$, while the nitrogen atom of the pyS ligand is *trans* to the carbonyl, $N(1)-Mo-C(1) = 161.44(9)^\circ$, in *exo-5d*. The Mo–S and Mo–allyl bond distances in **1** and *exo-5d* are consistent with the values reported for Mo^{II}–S and numerous Mo–allyl systems.¹⁸ The bond distances and intercarbon angles of the allyl groups in **1** (1.393(8) and 1.394(7) Å and 116.1(7)°) and *exo-5d* (1.353(5) and 1.320(5) Å and 120.8(4)°) are insignificantly different and in the region of those of related Mo^{II}–allylic compounds (1.31–1.42 Å, 115–125°).¹⁸

The coordination geometry around the molybdenum atom of **6** (Figure 4) is approximately an octahedron with the two phosphorus atoms, three carbonyls, and pySH group occupying the six coordination sites. The structure confirms

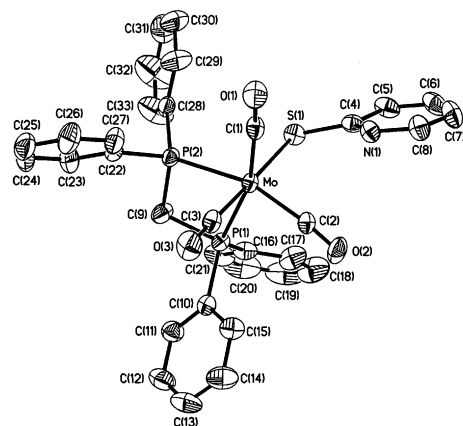


Figure 4. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for complex **6**.

an equivalent dppm ligand. Two phosphorus atoms of the dppm ligand and one sulfur atom of the thione ligand, SC_5H_4NH , are *trans* to three carbonyl groups: $P(1)-Mo-C(1) = 164.68(11)^\circ$, $P(2)-Mo-C(2) = 163.15(11)^\circ$, and $S(1)-Mo-C(3) = 176.88(11)^\circ$, respectively. The structure is compatible with the $^{31}P\{^1H\}$ NMR spectra of **6** and complex $[Mo(CO)_3(CH_3CN)(\eta^2-dppm)]$,¹⁹ which was crystallographically characterized. The Mo(1)–S(1) bond distance, 2.5806(11) Å, is longer than those of **1**, **5d**, and **7** (2.5588(7)–2.5692(9) Å) because of the thione ligand of SC_5H_4NH and Mo(0) of **6**.

The seven-coordinate bis(pyridine-2-thionate) tungsten(II) complex $[W(\eta^2-pyS)_2(CO)_3]$ has been described by Hoff²⁰ and co-workers. A possible consequence of the pyS ligand's relatively small size and bite angle is that it may favor higher coordination numbers. The crystal structure of the seven-coordinate bis(pyridine-2-thionate) molybdenum(II) complex **7** is shown in Figure 5. The structure of **7** is approximately a pentagonal bipyramid as is that of $[W(\eta^2-pyS)_3(NO)]$.²⁰ The CO ligand is roughly *trans* to one of the coordinating nitrogen atoms of the pyS ligand ($C1-Mo-N2 = 161.4(7)^\circ$), and the remaining five donor atoms are approximately planar. A planarity calculation of the five atoms S1, N1, S2, P1, and P2 reveals an average deviation of 0.25 Å. The molybdenum–nitrogen bond of 2.247(3) Å (*trans* to the phosphorus atom of the dppm ligand) is significantly shorter than the molybdenum–nitrogen bond of 2.307(3) Å (*trans* to the carbonyl) because of the greater *trans* effect induced by the CO group than the dppm group.

The Mo–P bond lengths of **5d**, **6**, and **7** are in the region of 2.4400(6)–2.5350(10) Å, and appear to be normal. The Mo–C–O angles of **1**, **5d**, **6**, and **7** are essentially linear in the region of 173.6(3)–178.3(3)° and similar to those found for other terminal carbonyls contained in Mo systems. The Mo–CO (1.908(3)–1.974(4) Å) and C–O distances are both

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(19) Crystal data for $[Mo(CO)_3(CH_3CN)(\eta^2-dppm)]$: $C_{30}H_{25}NO_3P_2Mo$ ($M_r = 605.39$), monoclinic, space group $P2_1/c$, $a = 10.930(4)$ Å, $b = 18.516(8)$ Å, $c = 15.173(4)$ Å, $V = 2902.1(10)$ Å³, $Z = 4$, $\rho_{calcd} = 1.386$ g cm⁻³, $\mu = 0.592$ mm⁻¹, observed reflections 3772, $\theta_{range} = 1.80$ – 22.50° . Data were collected with Mo K α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer at 295(2) K. The total number of parameters was 335. $R1 = 0.047$, $wR2 = 0.077$, $GOF = 1.001$, and $\Delta F = 0.473$ and -0.367 e Å⁻³.

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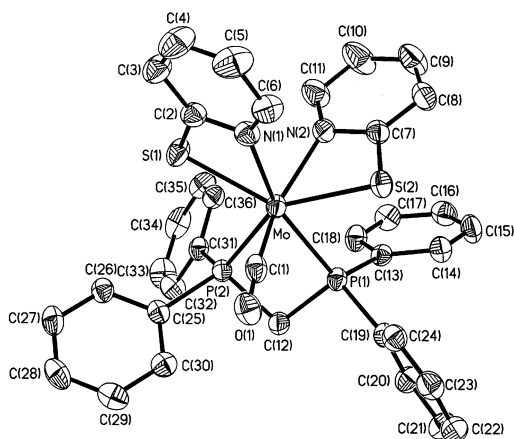


Figure 5. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for complex **7**.

within the range of values reported for other molybdenum carbonyl complexes. The N–Mo–S angles (63.29(8)–64.43(12)°) in complexes **1**, **5d**, and **7** are similar to those of complexes $[\text{Mo}_2(\text{pyS})(\text{CO})_9]^{16}$ (63.6(1)°), $[\text{W}(\text{pyS})(\text{CO})(\text{CH}_3\text{-CN})(\text{MeC}_2\text{Me})_2]^{19}$ (63.6(5)°), $[\text{W}(\text{pyS})_2(\text{CO})_3]$ (64.83(9)°), $[\text{W}(\text{pyS})_2(\text{NO})_2]$ (65.88(8)°), and $[\text{W}(\text{pyS})_3(\text{NO})]^{20}$ (65.85(7)°).

Conclusion

In this paper we report the syntheses and X-ray crystal structures of pyridine-2-thionate molybdenum complexes. In complex **1**, each pyS ligand chelates to one Mo atom through the nitrogen and sulfur atoms, and σ -bond to the other Mo atom through the sulfur atom, resulting in a four-membered ring, in which the two pyS ligands act as doubly bridged five-electron ligands. In complexes **2**, **4**, **5**, and **7**, the pyS ligand acts as a chelating three-electron ligand. In complex **3**, the pyS ligand acts as a one-electron ligand through sulfur coordination and the thione ligand, $\text{SC}_5\text{H}_4\text{NH}$, acts as a two-electron ligand through sulfur coordination in **6**. The bis-(pyridine-2-thionate) complex **7** is a stable saturated seven-coordinate compound, in contrast to $[\text{Mo}(\eta^2\text{-S}_2\text{CNet})_2(\text{CO})_3]$ and $[\text{W}(\text{SPh})_2(\text{phen})(\text{CO})_3]$, both of which readily lose CO to form stable six-coordinate dicarbonyl complexes.

Experimental Section

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-500 WB FT-NMR spectrometer and are reported in units of δ (ppm) with residual protons in the solvent as an internal standard (CDCl_3 , δ 7.24; CD_3CN , δ 1.93; C_6D_6 , δ 7.15; $\text{C}_2\text{D}_6\text{CO}$, δ 2.04). IR spectra were measured on a Nicolet Avator-320 instrument and were referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF, and benzene were distilled from sodium–benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol was distilled from magnesium. All other solvents and reagents were of reagent grade and were used as received. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation located at the National Taiwan University. Mo-

(CO)₆, dpmm, and dppe were purchased from Strem Chemical; pySH, Et₃N, 1,10-phenanthroline, C₅H₁₁N, and C₃H₅Br were purchased from Merck.

[Mo($\eta^3\text{-C}_3\text{H}_5$)(CO)₂]($\mu\text{-}\eta^1,\eta^2\text{-pyS}$)₂ (1**).** pySK (0.258 g, 2.0 mmol) was dissolved in MeOH (10 mL), and the solution was added to a flask (100 mL) containing $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}]$ (0.714 g, 2.0 mmol) in CH₂Cl₂ (10 mL) at room temperature. After 2 min yellow solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL), and subsequently dried under vacuum, yielding 0.594 g (98%) of **1**. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1937(vs), 1922(vs), 1875(vs), 1858(vs). ¹H NMR (500 MHz, DMSO-*d*₆, 298 K): δ 1.00, 1.33 (d, $J_{\text{H-H}} = 9.6$ Hz, 2H, H_{anti} of allyl), 3.06, 3.43 (br, 2H, H_{syn} of allyl), 3.83 (m, 1H, CH of allyl), 6.77 (d, $J_{\text{H-H}} = 8.1$ Hz, 1H, SCCH), 6.83 (t, $J_{\text{H-H}} = 6.3$ Hz, 1H, NCHCH), 7.39 (t, $J_{\text{H-H}} = 7.7$ Hz, 1H, SCCHCH), 7.88 (d, $J_{\text{H-H}} = 4.6$ Hz, 1H, NCH). ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆, 298 K): δ 51.9, 62.9 (s, C=CH₂), 74.6 (s, C=CH₂), 117.3 (s, 5-C of pyS), 126.2 (s, 3-C of pyS), 136.9 (s, 4-C of pyS), 146.2 (s, 6-C of pyS), 176.7 (s, 2-C of pyS), 228.9, 231.2 (s, CO). Anal. Calcd for C₂₀H₁₈N₂O₄S₂Mo₂: C, 39.61; H, 2.99; N, 4.62. Found: C, 39.80; H, 2.60; N, 4.50.

[Mo($\eta^3\text{-C}_3\text{H}_5$)(CO)₂($\eta^2\text{-pyS}$)(C₅H₁₀NH)] (2**).** A solution of **1** (0.606 g, 1.0 mmol) in CH₂Cl₂ (20 mL) was treated with C₅H₁₀NH (0.1 mL, 1.2 mmol) at ambient temperature. Instantly, the reaction mixture turned to bright yellow. After 10 min of stirring, the solution was dried in vacuo. Subsequently, *n*-hexane (40 mL) was added to the solution, and a yellow precipitate was formed. The precipitate was collected by filtration (G4) and dried in vacuo to yield 0.356 g (92%) of **2**. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1924(vs), 1838(vs). ¹H NMR (500 MHz, CDCl₃, 298 K): δ 1.16, 1.26 (d, $J_{\text{H-H}} = 8.9$ Hz, 2H, H_{anti} of allyl), 1.64 (m, 6H, NCH₂CH₂CH₂), 2.88 (m, 4H, NCH₂), 3.20, 3.51 (br, 2H, H_{syn} of allyl), 3.60 (m, 1H, CH of allyl), 3.89 (br, 1H, NH), 6.71 (t, $J_{\text{H-H}} = 6.1$ Hz, 1H, NCHCH), 6.87 (d, $J_{\text{H-H}} = 8.2$ Hz, 1H, SCCH), 7.25 (t, $J_{\text{H-H}} = 7.1$ Hz, 1H, SCCHCH), 7.67 (br, 1H, NCH). ¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K): δ 23.8 (s, NCH₂CH₂CH₂), 25.1 (s, NCH₂CH₂), 46.1 (s, NCH₂), 54.2, 62.6 (s, C=CH₂), 70.7 (s, C=CH₂), 117.3 (s, 5-C of pyS), 125.0 (s, 3-C of pyS), 136.0 (s, 4-C of pyS), 147.0 (s, 6-C of pyS), 170.3 (s, 2-C of pyS), 226.6 (s, CO). MS (FAB, NBA, *m/z*): 389 [M⁺], 321 [M⁺ – CO], 293 [M⁺ – 2CO]. Anal. Calcd for C₁₅H₁₉N₂O₂SMo: C, 46.51; H, 4.95; N, 7.23. Found: C, 46.85; H, 5.01; N, 7.12.

[Mo($\eta^3\text{-C}_3\text{H}_5$)(CO)₂($\eta^2\text{-pyS}$)(phen)] (3**).** To **1** (0.606 g, 1.0 mmol) dissolved in CH₂Cl₂ (20 mL) with continuous stirring under a stream of dry nitrogen was added 1,10-phenanthroline (0.18 g, 1.0 mmol). The color of the solution changed from yellow to red immediately, and a red precipitate formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and then dried in vacuo to yield 0.44 g (92%) of **3**. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1932(vs), 1923(vs), 1845(vs), 1834(vs). ¹H NMR (500 MHz, CDCl₃, 298 K): δ 1.58 (d, $J_{\text{H-H}} = 9.8$ Hz, 2H, H_{anti} of allyl), 3.11 (d, $J_{\text{H-H}} = 6.3$ Hz, 2H, H_{syn} of allyl), 3.66 (m, 1H, CH of allyl), 6.00 (d, $J_{\text{H-H}} = 8.2$ Hz, 1H, SCCH), 6.45 (t, $J_{\text{H-H}} = 4.9$ Hz, 1H, NCHCH), 6.89 (t, $J_{\text{H-H}} = 7.1$ Hz, 1H, SCCHCH), 6.99 (d, $J_{\text{H-H}} = 3.1$ Hz, 1H, NCH), 7.75, 7.76 (d, $J_{\text{H-H}} = 5.1$ Hz, 2H, 3-H of phen), 7.78 (s, 2H, 5-H of phen), 8.32 (d, $J_{\text{H-H}} = 8.1$ Hz, 2H, 4-H of phen), 9.16 (d, $J_{\text{H-H}} = 5.1$ Hz, 2H, 2-H of phen). ¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K): δ 53.4 (s, CCH₂), 72.7 (s, CCH₂), 117.5 (s, 5-C of pyS), 122.2 (s, 3-C of pyS), 135.9 (s, 4-C of pyS), 149.5 (s, 6-C of pyS), 176.7 (s, 2-C of pyS), 124.8 (s, 5,6-C of phen), 127.2 (s, 3,8-C of phen), 137.4 (s, 4,7-C of phen), 149.5 (s, 2,9-C of phen), 228.9 (s, CO). MS (FAB, NBA, *m/z*): 486 [M⁺], 458 [M⁺ – CO], 430 [M⁺ – 2CO], 389 [M⁺ – 2CO –

C₃H₅]. Anal. Calcd for C₂₂H₁₇N₃O₂SMo: C, 54.66; H, 3.55; N, 8.70. Found: C, 54.89; H, 3.42; N, 8.75.

[Mo(η^3 -C₃H₅)(CO)(η^2 -pyS)(η^2 -dppm)] (4a–4d). MeCN (40 mL) was added to a flask (100 mL) containing **1** (0.606 g, 1.0 mmol) and bis(diphenylphosphino)methane (dppm) (0.768 g, 2.0 mmol). The solution was refluxed for 1 h, and an IR spectrum indicated completion of the reaction. After the solution was cooled and removal of the solvent in vacuo, the residue was redissolved in CH₂Cl₂ (10 mL), *n*-Hexane (20 mL) and diethyl ether (20 mL) were added to the solution, and an orange precipitate was formed. The precipitate was collected by filtration (G4), washed with diethyl ether (2 × 10 mL) and *n*-hexane (2 × 10 mL), and then dried in vacuo, yielding 1.16 g (88%) of **4a–4d**. Further purification was accomplished by recrystallization from 1/10 CH₂Cl₂/*n*-hexane. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1794(vs). MS (FAB, NBA, *m/z*): 661 [M⁺], 633 [M⁺ – CO], 591 [M⁺ – CO – C₃H₅]. Anal. Calcd for C₃₄H₃₁NOP₂SMo: C, 61.91; H, 4.74; N, 2.12. Found: C, 62.00; H, 4.42; N, 2.02. ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K): (**4a**) δ –2.3, 30.8 (d, ²J_{P–P} = 37.5 Hz), (**4b**) δ –27.1, 26.3 (d, ²J_{P–P} = 51.2 Hz), (**4c**) δ 0.3, 33.1 (d, ²J_{P–P} = 58.3 Hz), (**4d**) δ –3.5, 27.6 (d, ²J_{P–P} = 65.0 Hz). ¹H NMR (500 MHz, CDCl₃, 298 K, **4d**): δ 1.72, 1.84 (d, ²J_{H–H} = 11.2 Hz, 2H, H_{anti} of allyl), 2.85, 4.36 (m, 2H, H_{syn} of allyl), 3.85 (dt, 2H, PCH₂CH₂, J_{H–H} = 15.1 J_{P–H} = 10.1 Hz), 4.24 (m, 2H, PCH₂CH₂), 5.26 (m, 1H, CH of allyl), 6.38–7.79 (m, 28H, Ph and pyS). ¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K): δ 39.9 (t, ²J_{P–C} = 19.6 Hz, PCH₂), 54.8, 74.2 (d, ²J_{P–C} = 9.4, 13.8 Hz, C=CH₂), 98.3 (s, C=CH₂), 115.0 (s, 5-C of pyS), 121.5–136.3 (m, 3-C of pyS, 4-C of pyS, Ph), 147.4 (s, 6-C of pyS), 177.6 (s, 2-C of pyS), 231.8 (t, ²J_{P–C} = 12.2 Hz, CO).

[Mo(η^3 -C₃H₅)(CO)(η^2 -pyS)(η^2 -dippe)] (5a–5d). The synthesis and workup were similar to those used in the preparation of complex **4**. Complex **5** was isolated in 92% yield as a red-orange microcrystalline solid. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1793(vs). MS (FAB, NBA, *m/z*): 675 [M⁺], 647 [M⁺ – CO], 605 [M⁺ – CO – C₃H₅]. Anal. Calcd for C₃₅H₃₃NOP₂SMo: C, 62.41; H, 4.94; N, 2.08. Found: C, 62.80; H, 4.45; N, 1.75. ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K): (**5a**) δ 59.4, 85.8 (d, ²J_{P–P} = 22.8 Hz), (**5b**) δ 52.5, 79.6 (br), (**5c**) δ 85.0, 88.5 (d, ²J_{P–P} = 67.3 Hz), (**5d**) δ 64.6, 88.8 (d, ²J_{P–P} = 42.7 Hz).

[Mo(CO)₃(η^1 -SC₅H₄NH)(η^2 -dppm)] (6). MeOH (20 mL) was added to a flask (100 mL) containing [Mo(CH₃CN)(η^2 -dppm)(CO)₃] (0.605 g, 1.0 mmol) and pySH (0.111 g, 1.0 mmol) at room temperature. After 1 h red solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL), and subsequently dried under vacuum, yielding 0.66 g (98%) of **6**. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1915(vs), 1806(vs). ³¹P{¹H} NMR (202 MHz, CD₃CN, 298 K): δ 0.4. ¹H NMR (500 MHz, CD₃CN, 298 K): δ 4.40 (m, 2H, PCH₂), 6.63–7.62 (m, 24H, Ph and pyS), 12.7 (br, 1H, NH). ¹³C{¹H} NMR (125 MHz, CD₃CN, 298 K): δ 48.9 (t, ²J_{P–C} = 18.9 Hz, PCH₂), 116.3 (s, 5-C of pyS), 121.5–136.3 (m, 3-C of pyS, 4-C of pyS, Ph), 148.9 (s, 6-C of pyS), 179.8 (s, 2-C of pyS), 210.4 (t, ²J_{P–C} = 8.68 Hz, *trans*-CO), 218.9 (t, ²J_{P–C} = 15.22 Hz, *cis*-CO). MS (FAB, NBA, *m/z*): 649 [M⁺ – CO], 621 [M⁺ – 2CO], 592 [M⁺ – 3CO]. Anal. Calcd for C₃₃H₂₆NO₃P₂SMo: C, 58.76; H, 3.89; N, 2.08. Found: C, 58.90; H, 3.76; N, 1.94.

[Mo(CO)(η^2 -pyS)₂(η^2 -dppm)] (7). Method A. CH₂Cl₂ (40 mL) was added to a flask (100 mL) containing **6** (0.675 g, 1.0 mmol), and the solution was stirred in air at room temperature. After 24 h red solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL), and subsequently dried under vacuum, yielding 0.28 g (38%) of **7**.

Method B. Complex **4** (0.659 g, 1.0 mmol) and pySK (0.202 g, 2.0 mmol) was reacted in refluxing CH₃CN for 2 h. After the

solution was cooled and removal of the solvent in vacuo, MeOH (10 mL) was added to the residue, and a red precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and then dried in vacuo, yielding 0.49 g (71%) of **7**. IR (KBr, cm⁻¹): $\nu(\text{CO})$ 1807(vs). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K): δ 15.4, 14.6 (d, ²J_{P–P} = 123.5 Hz). ¹H NMR (500 MHz, CDCl₃, 298 K): δ 4.17 (t, 4H, CH₂), 6.63–7.62 (m, 32H, Ph and SNC₃H₄). ¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K): δ 40.1 (t, ²J_{P–C} = 22.2 Hz, PCH₂), 116.5, 116.8 (s, 5-C of pyS), 121.5–135.7 (m, 3-C of pyS, 4-C of pyS, Ph), 147.8, 148.0 (s, 6-C of pyS), 172.9, 176.7 (s, 2-C of pyS), 231.6 (s, CO). MS (FAB, NBA, *m/z*): 702 [M⁺ – CO]. Anal. Calcd for C₃₆H₃₀N₂O₁P₂S₂Mo: C, 59.34; H, 4.15; N, 3.85. Found: C, 59.50; H, 3.96; N, 3.72.

Single-Crystal X-ray Diffraction Analyses of **1**, **5d**, **6**, and **7**.

Single crystals of **1**, **5d**, **6**, and **7** suitable for X-ray diffraction analyses were grown by recrystallization from 20/1 *n*-hexane/CH₂Cl₂. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their ESDs after corrections for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.²¹

A suitable single crystal of **1** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with θ values in the range from 2.45° to 27.50°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the $\theta/2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2.06 to 8.24° min⁻¹. The θ scan angle was determined for each reflection according to the equation $0.70 \pm 0.35 \tan \theta$. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 14552 unique measured data, 2558 reflections of which with $I > 2\sigma(I)$ were considered observed. The first step of the structure solution used the heavy-atom method (Patterson synthesis), which revealed the positions of the metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.²² The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1–2 Å² larger than the equivalent B_{iso} value of the atom to which they were bonded. The final residuals of this refinement were $R = 0.051$ and $R_w = 0.106$.

The procedures for **5d**, **6**, and **7** were similar to those for **1**. The final residuals of this refinement were $R = 0.036$ and $R_w = 0.09$ for **5d**, $R = 0.034$ and $R_w = 0.078$ for **6**, and $R = 0.043$ and $R_w = 0.098$ for **7**. Selected bond distances and angles and selected final atomic coordinates are listed in Tables 2 and 3.

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Supporting Information Available: $^{13}\text{C}\{^1\text{H}\}$, $^1\text{H}-^1\text{H}$ COSY, and $^1\text{H}-^{13}\text{C}$ HMQC NMR spectra of **1** in DMSO, $^{31}\text{P}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ VT, and ^1H VT spectra of **4a-4d**, and X-ray crystallographic

files, in CIF format, for the structures of complexes **1**, **5d**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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