Metallathiirenes. 3.[1] Thiocarbamoyl and Alkoxythiocarbonyl Complexes of Molybdenum(II) and Tungsten(II)

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Synthetic routes to thiocarbamoyl (thiocarboxamide) complexes of divalent molybdenum and tungsten are reported: The reaction of *fac*-[Mo(CO)$_3$(NCMe)$_3$] with *N*,*N*-dimethyl thiocarbamoyl chloride (Me$_2$NC(=S)Cl) at low temperature provides a thermally labile intermediate (**1**) presumed on the basis of subsequent transformations to be [Mo(η^2-SCNMe$_2$)Cl(CO)$_3$(NCMe)]. Reactions of **1** with K[HB(pz)$_3$] (pz = pyrazol-1-yl), NaC$_5$H$_5$, bipy, or tmeda provide the complexes [Mo(η^2-SCNMe$_2$)(CO)$_2${HB(pz)$_3$}] (**2**), [Mo(η^2-SCNMe$_2$)(CO)$_2$(η-C$_5$H$_5$)] (**3**), [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(bipy)] (**4**), and [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(tmeda)] (**5**), respectively. The complex *cis*,*cis*,*trans*-[Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(PPh$_3$)$_2$] (**6**) results from the oxidative addition of Me$_2$NC(=S)Cl to [Mo(NCMe)$_2$(CO)$_2$(PPh$_3$)$_2$] and is one of two isomers obtained from the reaction of **1** with PPh$_3$. The complex **2** may also be obtained from reaction of (i) K[Mo(CO)$_3${HB(pz)$_3$}] with Me$_2$NC(=S)Cl; (ii) [Mo(CO)$_3$(η^6-C$_7$H$_8$)] with Me$_2$NC(=S)Cl and K[HB(pz)$_3$]; and (iii) K[HB(pz)$_3$] with either **5** or **6**. Sequential treatment of either [Mo(CO)$_3$(NCMe)$_3$] or [Mo(CO)$_3$(η^6-C$_7$H$_8$)] with ClC(=S)OR (R = C$_6$H$_4$Me-4, C$_6$H$_5$) and K[HB(pz)$_3$] provides the complexes [Mo(η^2-SCOR)(CO)$_2${HB(pz)$_3$}] [R = C$_6$H$_4$Me-4 (**7a**), C$_6$H$_5$ (**7b**)]. Attempts to prepare a mononuclear thiocarbamoyl complex by addition of elemental sulfur or propene episulfide to the aminomethylidyne complex [Mo(≡CN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}] (**8**) were unsuccessful; however addition of [Fe$_2$(CO)$_9$] to **8** provided the thermally unstable complex [MoFe(μ-CN^{i}Pr$_2$)(CO)$_5${HB(pz)$_3$}] (**9**), which reacts with sulfur to provide the heterobimetallic bridging thiocarbamoyl complex [MoFe(μ-SCN^{i}Pr$_2$)(CO)$_5${HB(pz)$_3$}] (**10**). Treating *fac*-[W(CO)$_3$(NCMe)$_3$] sequentially with Me$_2$NC(=S)Cl and K[HB(pz)$_3$] provided [W(η^2-SCNMe$_2$)(CO)$_2${HB(pz)$_3$}] (**11**); however replacing Me$_2$NC(=S)Cl with ClC(=S)OC$_6$H$_4$-Me-4 led to [WCl(CO)$_3${HB(pz)$_3$}] (**12**).

Introduction

We have recently shown that thioaroyl complexes of group 6 and 8 metals are accessible via the addition of propene episufide to benzylidyne complexes.[1] In contrast to thioacyl complexes of group 8 metals,[1−3] the group 6 examples are thermally labile. Furthermore, they are particularly reactive species and are prone to the addition of excess sulfur or propene episulfide to provide dithiocarboxylate ligands[1,4] or, in one case, intramolecular hydroboration by a dihydrobis(pyrazolyl)borate co-ligand.[5] To further investigate the reasons for this dichotomy in stability and reactivity, we have turned our attention to the synthesis of heteroatom-substituted thioacyl complexes of tungsten and molybdenum, i.e., those featuring thiocarbamoyl and alkoxythiocarbonyl ligands (Chart 1).

Thiocarbamoyl ligands show a strong tendency to adopt bidentate coordination, more so than alkoxythiocarbonyl or thioacyl ligands. This is presumably due to the ability of the amino "lone pair" to contribute via conjugation to the metal−ligand bonding. Further to the valence bond representations for thiocarbamoyl ligands indicated in Chart 1, a consideration of the valence orbitals of the [SCNMe$_2$]$^+$ cation (Figure 1) is useful. This suggests that in addition to σ-donation and π-acceptance, which fall within the conventional Dewar−Chatt−Duncanson model for side-on coordination of a multiple bond, there also exists the possibility of π-donation from sulfur to the metal, perpendicular to the MCS plane. The topology of this $\perp\pi$-donation depicted in Figure 1 reveals the contribution from the nitrogen

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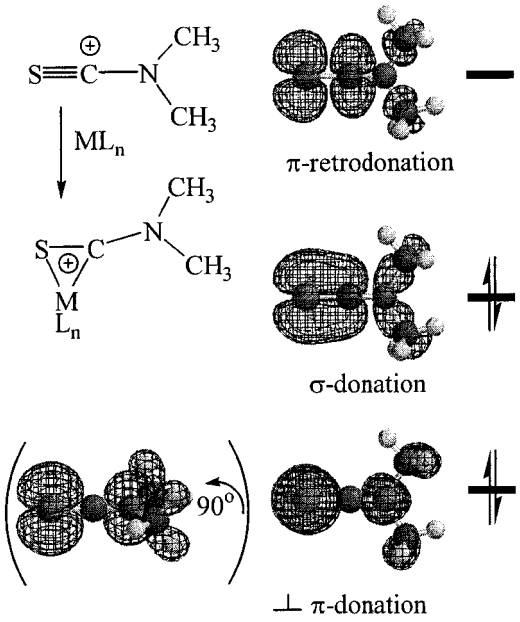
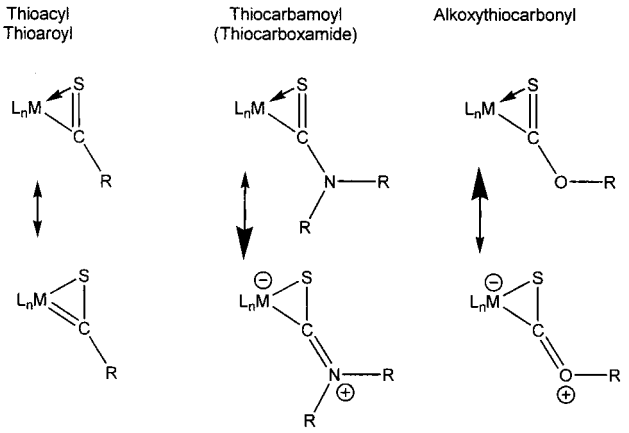


Figure 1. $[Me_2NCS]^+$ frontier orbitals.

Chart 1



p orbital, which is orthogonal to the MCS plane and absent in simple thioacyl and thioaryl ligands.

Thiocarbamoyl (thiocarboxamide) complexes have previously been prepared by a variety of synthetic routes.[6] Most generally, metal carbonylates have been shown to react with *N*,*N*-dimethylthiocarbamoyl chloride, $Me_2NC(=S)Cl$, via nucleophilic displacement of the chloride[7] or by oxidative addition such that both chloride and thiocarbamoyl ligands result.[8] These two approaches are most relevant to the work to be described herein; however alternative approaches have included (i) nucleophilic attack by an amine on an electrophilic thiocarbonyl complex;[9] (ii) reaction of hydrosulfide with haloaminocarbene[10] or isonitrile[11] ligands; (iii) electrophilic attack at a coordinated isothiocyanate;[12] (iv) cleavage of a dithiocarbamate ligand;[13] and (v) C−H activation of thioformamides.[14]

Results and Discussion

Baker has reported and extensively exploited the versatile complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W),[15] which are conveniently obtained by halogenation of $[M(CO)_3(NCMe)_3]$.[16] We hoped that a similar oxidative addition of $Me_2NC(=S)Cl$ to $[Mo(CO)_3(NCMe)_3]$ would lead to a complex of the form $[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_x(NCMe)_y]$ ($x + y = 4$). This indeed appears to be the case; however the complex formed is quite thermally labile: Addition of $Me_2NC(=S)Cl$ to a cold (−30 °C) solution of $[Mo(CO)_3(NCMe)_3]$ in acetonitrile led to a gradual color change from pale yellow to orange. Attempts to isolate the resulting complex met with comprehensive failure. Removal of solvent or prolonged stirring at room temperature led to the formation of a completely insoluble blue compound, which is presumably polymeric in nature. Thiocarbamoyl ligands have already been shown to have a strong propensity for bridging two metals,[6,17] and in this case the oligomerization appears to be irreversible, at least in acetonitrile under ambient conditions. Nevertheless, subsequent ligand exchange reactions carried out on the intermediate are consistent with it being $[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_3(NCMe)]$ (**1**). Treating a solution of **1** generated in situ with $K[HB(pz)_3]$ (pz = pyrazol-1-yl) results in the formation of the thermally stable complex $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{HB(pz)_3\}]$ (**2**) in modest yield (45% based on $[Mo(CO)_6]$) (Scheme 1). This complex has been prepared previously by Lalor via an alternative route.[18] The complex **2** may also be prepared via the reaction of $[Mo(CO)_3(NCMe)_3]$ with $K[HB(pz)_3]$ (to provide $K[Mo(CO)_3\{HB(pz)_3\}]$ in situ) followed by $Me_2NC(=S)Cl$; however this sequence only proceeds in an overall yield of 15%. The approach follows that described previously for the cyclopentadienyl analogue $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2(\eta\text{-}C_5H_5)]$ (**3**),[7a] which results from the reaction of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ with $Me_2NC(=S)Cl$. More conveniently, the reaction of $[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_2(tmeda)]$ (**5**) (vide infra) with NaC_5H_5 provides **3** in 84% yield. Better yields (46%) of **2** are also obtained from the reaction of $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ with $Me_2NC(=S)Cl$ in dichloromethane followed by treatment with $K[HB(pz)_3]$. In this case the reaction takes 48 h to proceed to completion in contrast to the

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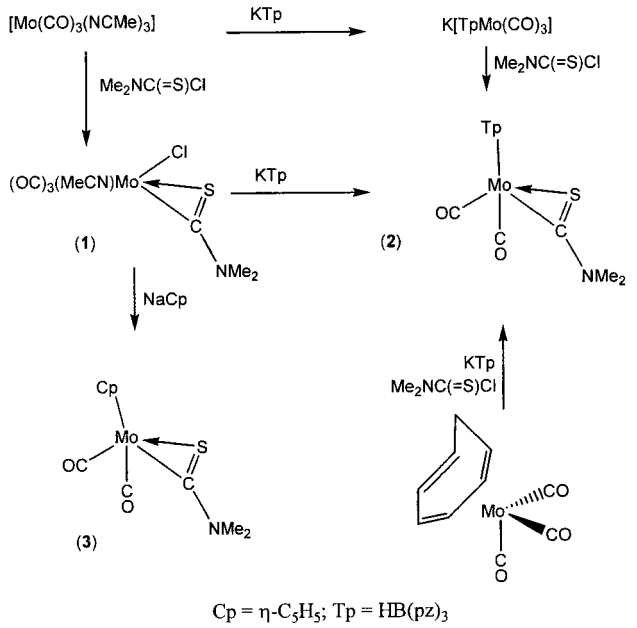
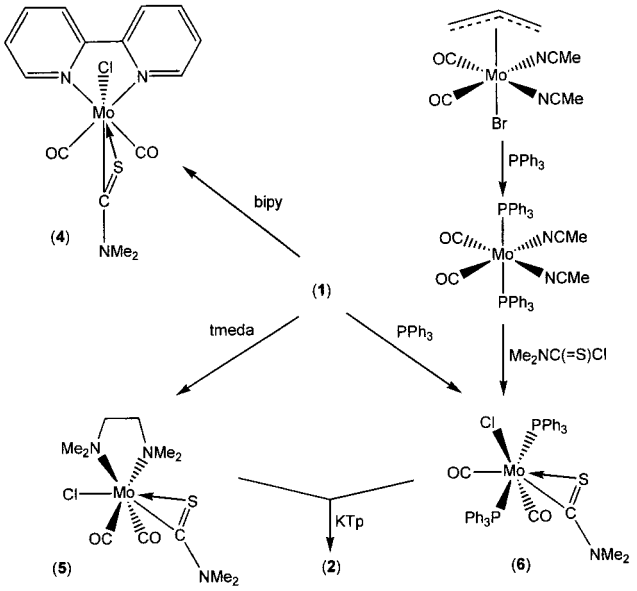
Scheme 1



Scheme 2



reaction of **1** with K[HB(pz)$_3$], which is virtually instantaneous. Presumably the reaction rate is controlled by the partial dissociation of the cycloheptatriene ring prior to oxidative addition of the thiocarbamoyl chloride.

The complex **1** also serves as a precursor to new thiocarbamoyl complexes (Scheme 2). Treating an acetonitrile solution of **1** (generated in situ) with 2,2′-bipyridyl leads to the precipitation of a brown crude product. From this can be extracted (thf) a deep orange complex formulated as [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(bipy)] (**4**) in 58% yield (based on [Mo(CO)$_6$]). The infrared spectrum includes two carbonyl absorptions at 1910 and 1828 cm^{-1} (CH_2Cl_2 solution), suggesting that while the molybdenum center is formally divalent, it is comparatively π-basic. Two methyl resonances are observed in the ^{1}H NMR spectrum, consistent with hindered rotation about the (partially multiple) C−N bond of the thiocarbamoyl ligand, while the appearance of only four resonances for the bipy protons suggests this ligand lies perpendicular to a molecular plane of symmetry. The low-field section of the ^{13}C{^{1}H} NMR spectrum consists of two peaks attributable on intensity grounds to the thiocarbamoyl (223.0) and carbonyl (204.7 ppm) carbon nuclei, respectively. This would appear to suggest that either (i) assuming a static structure, the plane of the thiocarbamoyl ligand lies between the two chemically equivalent *cis* carbonyl ligands or (ii) rotation of the carbamoyl ligand is rapid on the ^{13}C NMR time scale. FAB-mass spectroscopy reveals, in addition to a well-resolved molecular ion, isotope clusters attributable to loss of carbonyl and chloride ligands. No peaks could however be identified that correspond to loss of or fragmentation of the thiocarbamoyl ligand.

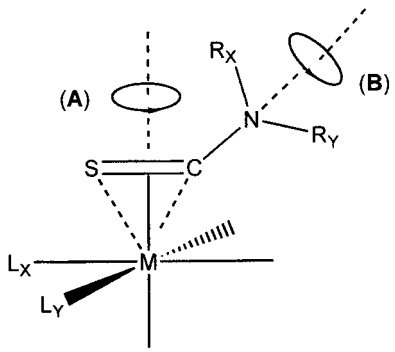


Figure 2. Fluxionality of η^2-thiocarbamoyl ligands. Process A equilibrates sites L_X and L_Y. Process B equilibrates sites R_X and R_Y.

A similar reaction ensues between **1** and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) at low temperature to provide a deep orange complex [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(tmeda)] (**5**) in high yield (79%). The complex **5** is thermally stable, and in general spectroscopic data for **5** are comparable to those for **4** with the exception that broadening of the ^{1}H NMR resonances due to the tmeda (δ 2.88, 3.11) and thiocarbamoyl (δ 3.61, 3.73) ligands is apparent at room temperature, suggesting the onset of a fluxional process. The fluxionality apparent in this and subsequently described complexes appears to involve rotation of the entire thiocarbamoyl ligand about an axis approximately normal to the C−S bond since the effect is to chemically equilibrate the environments of similar co-ligands, but leaves the methyl groups of the thiocarbamoyl ligand chemically distinct (Figure 2). Thus at no time have we observed a process consistent with rotation about the C−N multiple bond. Similar fluxionality has been discussed previously for thiocarbamoyl complexes.[18] Once again the thiocarbonyl ^{13}C{^{1}H} NMR resonance (245.2 ppm) appears to low field of the single carbonyl resonance (230.9 ppm). In parallel studies[19] we have recently prepared the complex [Mo{σ-C(=O)N^{i}Pr$_2$}I(CO)$_3$(tmeda)] from the reaction of [Mo(η^2-OCN^{i}Pr$_2$)I(CO)$_4$] with tmeda, and it is of interest to note the failure of a carbonyl ligand in this complex to dissociate and thereby allow bidentate carbamoyl coordination. The complex **5** serves as a thermally stable but reactive precursor for ligand exchange reactions. Thus, for example, reactions of **5** with K[HB(pz)$_3$] or NaC_5H_5 provide the complexes **2** and **3** in spectroscopically quantitative yields.

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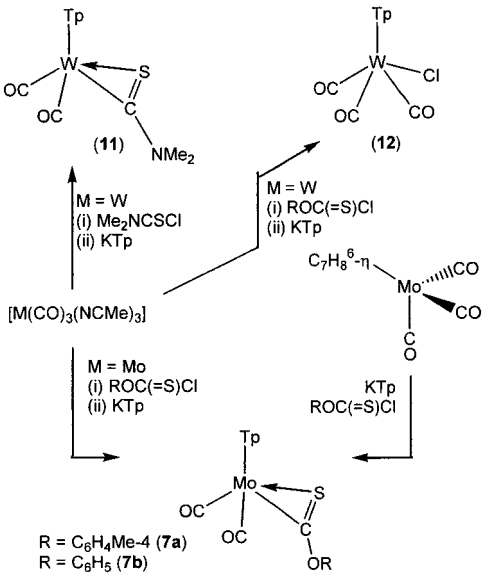
The unstable complex $[Mo(\eta^2\text{-}OCN^iPr_2)I(CO)_4]$ reacts with triphenylphosphine to provide a stable monosubstitution product, *mer*-$[Mo(\eta^2\text{-}OCN^iPr_2)I(CO)_3(PPh_3)]$,[19] and it seemed that an analogous complex, $[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_3(PPh_3)]$, would be readily accessible. Attempts to introduce triphenylphosphine into the coordination sphere of **1** were however complicated by the apparent formation of an inseparable mixture of two isomers of $[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_2(PPh_3)_2]$, which vary in the *cis* or *trans* disposition of the two phosphine ligands. An alternative approach however allowed the isolation of the *cis, cis, trans* isomer specifically. The complex $[Mo(NCMe)_2(CO)_2(PPh_3)_2]$ results from the reaction of $[Mo(\eta^3\text{-}CH_2CHCH_2)Br(NCMe)_2(CO)_2]$ with excess triphenylphoshine.[20] Treating this complex with $Me_2NC(=S)Cl$ leads to a smooth oxidative addition and formation of *cis,cis,trans*-$[Mo(\eta^2\text{-}SCNMe_2)Cl(CO)_2(PPh_3)_2]$ (**6**) in moderate yield (52%) (Scheme 2). Characterization of this complex remains incomplete due to its low solubility in all common solvents and its slow decomposition in those in which it is soluble. As with the previous complexes, however, **6** reacts with $K[HB(pz)_3]$ to provide **2** in 88% yield, a conversion that supports its formulation.

While thiocarbamoyl ligands are comparatively resistant to amine protonolysis, alkoxythiocarbonyls may often be converted to thiocarbonyls by treatment with Brønstead or Lewis acids. For example, we have recently described a convenient preparation of $[IrCl(CS)(PPh_3)_2]$ based on the protonolysis of the aryloxythiocarbonyl complex $[IrHCl\{C(=S)OC_6H_4Me\text{-}4)(CO)(PPh_3)_2]$.[21] The thiocarbonyl chemistry of tungsten has been extensively studied by Angelici,[22,23] revealing an impressive synthetic utility for the preparation of a wide range of organosulfur ligands. Unfortunately, the key starting material for this work is $[W(CS)(CO)_5]$,[23] which is only obtained in 12% yield. The yield for the corresponding molybdenum complex is only 2−4%, a fact that somewhat curtails the study of molybdenum thiocarbonyl chemistry. We therefore hoped that the strategies employed above, if applied to the synthesis of alkoxythiocarbonyl complexes, might provide an alternative entry point for molybdenum thiocarbonyl chemistry.[24]

Treating an acetonitrile solution of $[Mo(CO)_3(NCMe)_3]$ with 4-tolyl chlorothionoformate $(ClC(=S)OC_6H_4Me\text{-}4)$ results in the formation of a deep red solution. No attempt was made to isolate the intermediate; however subsequent treatment with $K[HB(pz)_3]$ resulted in the formation of the deep red complex, $[Mo(\eta^2\text{-}SCOC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (**7a**), in reasonable yield (69% based on $[Mo(CO)_6]$). A similar process employing $ClC(=S)OC_6H_5$ provides $[Mo(\eta^2\text{-}SCOC_6H_5)(CO)_2\{HB(pz)_3\}]$ (**7b**) in lower yield (49%). Lower yields (52%) of **7a** are also obtained when $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ is treated with $ClC(=S)OC_6H_4Me\text{-}4$ and $K[HB(pz)_3]$ in dichloromethane (Scheme 3). The formulation of **7a** follows from spectroscopic data, these being generally similar to those for **2**. Thus two carbonyl infrared absorptions are observed at 1993 and 1876 cm^{-1}, to somewhat higher frequency of those observed for **2**, suggesting an enhanced π-acidity for alkoxythiocarbonyl ligands relative to thiocarbamoyls (vide infra). The ^1H NMR spectrum of **7a** clearly reveals the operation of a fluxional process at room temperature: The pyrazolyl protons give rise to only two peaks [δ 7.73 (6 H), 6.24 (3 H)] and the AA′BB′ system of the tolyl group appears as only a broad single resonance [δ 7.25]. While the $^{13}C\{^1H\}$ resonance for the carbonyl ligands (233.3) is shifted to high field of that for **2**, the thiocarbonyl resonance (284.6 ppm) is moved dramatically to lower field. FAB-MS data confirm the gross formulation of **7a** and also include fragmentations due to loss of carbonyl ligands and the entire aryloxythiocarbonyl ligand. Perhaps surprisingly, there are no fragmentations attributable to loss of the aryloxide group. We have observed the prevalence of fragmentations due to aryloxide elimination among the FAB-MS data for aryloxythiocarbonyl complexes of iridium and noted that such processes are also reflected in the solution chemistry.[21] Unfortunately for our present purposes, the absence of such fragmentations for **7a** is also mirrored in its reactivity: The complex fails to react with either HCl or HBF_4 to provide thiocarbonyl complexes. In a similar manner, the thiocarbamoyl complex **2** failed to react with HCl, HBF_4, or $[Et_3O]BF_4$ under ambient conditions. Heating **2** with elemental sulfur or propene episulfide in refluxing thf also failed to provide the dithiocarbamate complex $[Mo(S_2CNMe_2)(CO)_2\{HB(pz)_3\}]$, while the reactions of sulfur with either $[Mo(\eta^2\text{-}SCC_6H_4OMe)(CO)_2\{HB(pz)_3\}]$ or $[Mo(\equiv CC_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$ readily provide the dithiocarboxylate complex $[Mo(S_2CC_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$.[1] The anticipated ultimate products of electrophilic attack at the sulfur of bidentate thiocarbamoyl ligands would be bidentate thiolatocarbene complexes. These would appear entirely reasonable and have copious precedent, via alternative synthetic strategies.[1,7,25,26] The bidentate thiocarbamoyl and thioalkoxycarbonyl binding mode *in these complexes* however appears particular unreactive. This reinforces observa-

Scheme 3



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(24) For chromium an alternative entry is already available employing the desulfurization of coordinated CS_2: (a) Fenster, A. E.; Butler, I. S. *J. Organomet. Chem.* **1974**, *13*, 915. (b) Caillet, P.; Jaouen, G. *J. Organomet. Chem.* **1975**, *91*, C53.

tions by Roper[27] that in the case of dithioalkoxycarbonyls the mode of coordination, i.e., *monohapto* or *dihapto*, effects the acid lability of the thiolate substituent, the latter being generally deactivated toward electrophilic attack. In the case of **6a** the mode of coordination of the thioalkoxycarbonyl ligand is *dihapto* and accordingly deactivated toward acids.

As noted above, thioaroyl complexes, e.g., [Mo(η^2-SCC_6H_4OMe-4)$(CO)_2${$HB(pz)_3$}] related to **2** and **7**, are readily obtained by addition of propene episulfide to appropriate alkylidyne complexes.[1] Given the stability of thiocarbamoyl complexes discussed above, it seemed reasonable that a similar addition of sulfur to an aminomethylidyne complex would also provide access to thiocarbamoyls. The reaction of [Mo(=CN^iPr_2)$(CO)_2$-{$HB(pz)_3$}] (**8**) with elemental sulfur was therefore investigated and found not to occur. In a similar manner, propene episulfide fails to react with **8**. This may be for one of two possible reasons: First the N^iPr_2 group is sterically cumbersome and might be expected to offer some kinetic protection to the Mo≡C multiple bond. This seems however unlikely since the sterically encumbered complex [Mo(≡$CC_6H_3Me_2$-2,6)$(CO)_2$(η-C_5Me_5)] reacts readily with sulfur to provide [Mo($S_2CC_6H_3Me_2$-2,6)$(CO)_2$(η-C_5Me_5)].[28] It seems more likely that the initial step involves nucleophilic attack by the sulfur of S_8 or SC_3H_6, and this is disfavored by the less electrophilic amino-substituted alkylidyne. Furthermore, arguing against steric factors, the complex **8** does react with $[Fe_2(CO)_9]$ to provide the thermally labile heterobimetallic alkylidyne complex [MoFe(μ-CN^iPr_2)$(CO)_5$] (**9**) (Scheme 4). Although this appears to be the first example of the use of a terminal mononuclear aminomethylidyne complex in bridge-assisted metal−metal bond formation, the process follows the copious precedent provided by Stone for hydrocarbon-based alkylidyne ligands.[29] Thus the formulation of **9** rests on a comparison of spectroscopic data with those for the general class of compounds [MFe(μ-CR)$(CO)_5$(L)] (M = Cr, Mo, W; R = Me, Ph, $C_6H_4NMe_2$, C_6H_4Me-4, $C_6H_3Me_2$-2,6; L = η-C_5H_5, η-C_5Me_5, $HB(pz)_3$). The complex **9** gives rise to five carbonyl absorptions in an intensity ratio [CH_2Cl_2: 2036s, 1969m, 1945m, 1891w, 1827w(br)] similar to those observed for the complex [MoFe(μ-$CC_6H_3Me_2$-2,6)$(CO)_5$(η-C_5R_5)] [R = H: 2053s, 1995s, 1977s, 1933w, 1896w(br);[30] R = Me: 2038vs, 1975s, 1965s, 1859w(br)[28]] although shifted to slightly lower frequency, consistent with the increased electron-donating ability of the amino substituent. While the precursor **8** gives rise to one doublet and one heptet ^{1}H NMR resonance, the spectrum for the complex **9** includes two heptets and two doublets for the N^iPr_2 group. Thus the two isopropyl groups are chemically distinct but straddle a molecular mirror plane. This is consistent with the

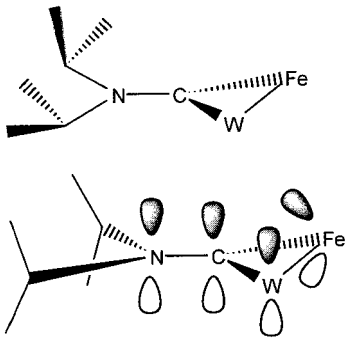
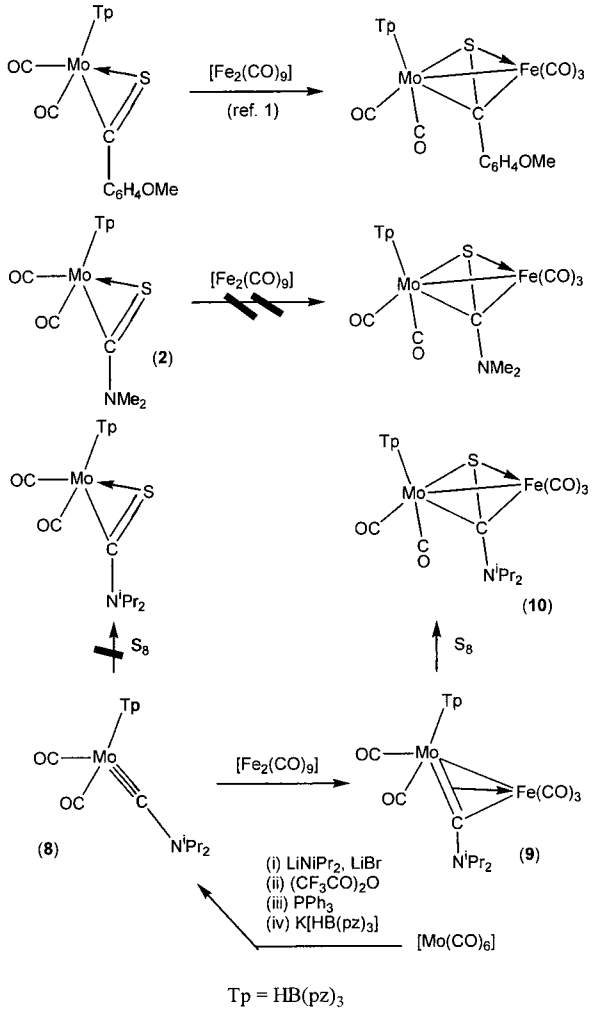


Figure 3. Orientational possibilities for the bridging aminomethylidyne ligand in **8**.

Scheme 4



C−N−C and Fe−C−Mo units being coplanar (Figure 3), even though this might be expected to be disfavored on steric grounds. The role of the Mo≡C group as "four-electron" donor[31] to the "$Fe(CO)_3$" fragment would clearly be enhanced were the nitrogen to also conjugate into the unsaturated MoCFe system, and this is possible with such an arrangement. Attempts to obtain $^{13}C\{^1H\}$ NMR data for **9** were unsuccessful due to decomposition during the acquisition, the major product being regener-

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(31) For theoretical treatments of alkylidyne complexes acting as "four-electron donors" see ref 30 and: Dossett, S. J.; Hill, A. F.; Howard, J. A. K.; Nasir, B. A.; Spaniol, T. P.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1871.

ated **8**. This loss of the "$Fe(CO)_3$" group is unexpected; however we note that **8** also fails to react with $[Co_2(CO)_8]$, despite this being one of the most general reactions for alkylidynes of the form $[M(\equiv CR)(CO)_2(L)]$.[29]

Despite the instability of **9**, it is possible to convert it to a heterodinuclear thiocarbamoyl complex. Thus a purple solution of **9** reacts rapidly with elemental sulfur to provide the yellow and thermally stable thiocarbamoyl complex $[MoFe(\mu\text{-}SCN^iPr_2)(CO)_5\{HB(pz)_3\}]$ (**10**). Similar reactions have been described for related bimetallic hydrocarbon-based alkylidyne complexes.[28,32,33] In the present case, the addition of sulfur to one of the prochiral FeCMo faces provides a tetrahedral FeMoCS core, and the resulting chirality is manifest in the appearance of two methine heptets and four methyl doublets (δ 0.87, 1.42, 1.50, 1.59) in the ^{1}H NMR spectrum of **10**. The infrared spectrum of **10** includes four carbonyl absorptions (1948, 1932, 1850, and 1832 cm^{-1}), and while the intensity profile is similar to that for $[MoFe(\mu\text{-}SCC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$,[33a] the absorptions are moved to significantly lower frequency. Although thiocarbamoyl ligands have been previously observed in bi-[34] and trinuclear[35] complexes, we believe this is the first heterobimetallic example with a transverse arrangement of C−S and metal−metal vectors. The thioaroyl complex $[Mo(\eta^2\text{-}SCC_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$ reacts with $[Fe_2(CO)_9]$ to provide the thioaroyl-bridged bimetallic complex $[MoFe(\mu\text{-}SCC_6H_4OMe\text{-}4)(CO)_5\{HB(pz)_3\}]$.[1] It is therefore somewhat surprising that the thiocarbamoyl complex **2** fails to react with $[Fe_2(CO)_9]$ to provide $[MoFe(\mu\text{-}SCNMe_2)(CO)_5\{HB(pz)_3\}]$ given the isolation of **10**. These results taken together tend to encourage caution in drawing too strong an analogy between thioacyl and thiocarbamoyl ligands. Thus each of the structural motifs detailed in Scheme 4 can be constructed; however some of the apparent kinetic barriers preventing their interconversion are surprising.

Tungsten Complexes. Preliminary attempts to extend the above methods to tungsten met with varied success. The synthesis of a thiocarbamoyl complex was readily achieved; however the approach has failed so far for the introduction of aryloxythiocarbonyl ligands. Treating a solution of $[W(CO)_3(NCMe)_3]$ with $Me_2NC(=S)Cl$ resulted in an oxidative addition similar to that described for the formation of **1**; however while the formation of **1** requires approximately 5 min at (−30 °C), the formation of the tungsten analogue requires 30 min at this temperature to go to completion. Subsequent addition of $K[HB(pz)_3]$ resulted in the formation of $[W(\eta^2\text{-}SCNMe_2)(CO)_2\{HB(pz)_3\}]$ (**11**) in reasonable yield (60%) (Scheme 3). Spectroscopic data for **11** are essentially comparable to those for **2**: Two carbonyl absorptions are observed in the infrared spectrum at 1923 and 1818 cm^{-1} (CH_2Cl_2). As with **2**, the operation of a fluxional process is evident from the appearance of the pyrazolyl-derived ^{1}H NMR resonances as a triplet (δ 6.20) and two doublets (δ 7.74, 7.64). Only at temperatures below −40 °C do the pyrazolyl environments become resolved. This fluxionality does not however chemically equilibrate the methyl groups, which remain distinct (δ 3.78, 3.73). On intensity grounds, the two closely positioned low-field $^{13}C\{^1H\}$ resonances at 249.7 and 241.5 ppm are assigned to the thiocarbamoyl and carbonyl nuclei, respectively. Treating an acetonitrile solution of $[W(CO)_3(NCMe)_3]$ with $ClC(=S)OC_6H_4Me\text{-}4$ (−30 °C) followed by addition of $K[HB(pz)_3]$ fails to result in the isolation of an aryloxythiocarbonyl complex. Rather, spectroscopic data for the yellow product reveal it to be $[WCl(CO)_3\{HB(pz)_3\}]$ (**12**), which has been described previously by Angelici.[36]

Table 1. Selected Infrared and Carbon-13 NMR Data for the Complexes $[M(\eta^2\text{-}X{=}C{-}Y)(CO)_2\{HB(pz)_3\}]$

			IR (CH_2Cl_2)			NMR ($CDCl_3$)	
			ν(CO)		k_{CK}[a]	δ^{13}C(XCY)	δ^{13}C(CO)
M	X	Y	(cm^{-1})		(Nm^{-1})	(ppm)	(ppm)
Mo	S	$OC_6H_4Me\text{-}4$	1993	1879	15.15	284.6	233.3
Mo	S	OC_6H_5	1994	1878	15.15	284.0	233.1
Mo	S	$C_6H_4Me\text{-}4$	1979	1893	15.14	280.4	233.2
Mo	S	$C_6H_4OMe\text{-}4$	1976	1891	15.10	278.0	233.6
Mo	O	Me[b]	1980	1850	14.82	268	236
Mo	O	Ph[b]	1965	1852	14.72	254	239
Mo	S	NMe_2	1942	1848	14.51	251.3	242.7
Mo	O	N^iPr_2	1937	1820	14.26	204.8	245.1
W	S	NMe_2	1923	1818	14.14	249.7	241.5
W	O	N^iPr_2	1924	1803	14.04	205.7	245.3

[a] Cotton Kraihanzel force constant. [b] Taken from ref 37.

Concluding Remarks. The isolation of the complexes **2**, **6**, **11**, our recent report on the complexes $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ (R = $C_6H_4OMe\text{-}4$, $C_6H_4Me\text{-}4$, $C_4H_3S\text{-}2$),[1] and related carbamoyl complexes $[M(\eta^2\text{-}OCN^iPr_2)(CO)_2\{HB(pz)_3\}]$ (M = Mo, W)[19] allow for a comparison of spectroscopic data for a range of "metallathiirene" and "metallaoxirene" $L_nM(\eta^2\text{-}X{=}C{-}Y)$ (X = O, S; Y = amino, alkoxy, aryl) compounds. Thus Table 1 collates infrared and $^{13}C\{^1H\}$ NMR data for the various analogues, including the complexes $[Mo(\eta^2\text{-}OCR)(CO)_2\{HB(pz)_3\}]$ (R = Me, Ph) described by Curtis.[37] The infrared data provide a rough indication of the variation in metal basicity which is reflected in the force constants[38] of the carbonyl co-ligands. From this the following points may be noted *within this series*: (i) As expected the $\nu_{(CO)}$ and $k_{(CK)}$ values for tungsten analogues are lower than those for the related molybdenum examples, this being a generally observed phenomenon for isostructural pairs of carbonyl complexes of 4d and 5d metals.[39] (ii) The aryloxythiocarbonyl ligand appears the most strongly π-acidic, although

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this is essentially comparable to that of thioaroyl ligands and greater than for aroyl and acyl ligands. (iii) Thiocarbamoyls are comparatively π-basic ligands, while carbamoyls themselves are the most electron releasing. From the $^{13}C\{^1H\}$ NMR data it can be seen that for the thioacyl, thioaroyl, and aryloxythiocarbonyl complexes the resonances attributed to these ligands appear to low field of that for the carbonyl ligand and the trend in their chemical shift parallels that for the infrared data. In the case of carbamoyl ligands this resonance is dramatically shifted to high field of the carbonyl ligand. The carbonyl resonance appears somewhat insensitive to the nature of the metallathiirene/oxirene substituents, but correlates loosely with the infrared data.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent [ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons and acetonitrile from CaH_2]. With the exception of the intermediate **1**, which was not isolated, all other new compounds described were indefinitely stable as solids under air in ambient conditions, although these were routinely stored in a freezer. Solutions of compound **6** and **9** gradually decomposed; however all other products showed no apparent air sensitivity. Schlenk-line techniques were nevertheless routinely employed. The use of low-temperature column chromatography does not reflect thermal instability of the compounds, but rather a tendency to elute poorly at room temperature, in addition to the general improvement in resolution offered by thermostatically controlled low temperatures. Reactions were monitored by thin-layer chromatography (and FT-IR spectroscopy) under ambient conditions. In most cases chromatography could be replaced by repeated fractional crystallizations; however this resulted in substantially lower yields and occasional reductions in product purity.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WH-400 NMR or JEOL JNM EX270 NMR spectrometers and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using Perkin-Elmer 1720-X FT-IR or Mattson Research Series 1 spectrometers. FAB mass spectrometry was carried out with an Autospec Q mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental microanalytical data were obtained from the ICSTM microanalytical service. All reagents were commercially available and used as received from commercial sources (Aldrich). The compounds [Mo(η^6-C_7H_8)$(CO)_3$],[40] [$Mo(CO)_3(NCMe)_3$],[41] [$W(CO)_3(NCMe)_3$],[41] and K[$HB(pz)_3$][42] were prepared according to published procedures.

Preparation of [Mo(η^2-SCNMe$_2$)$(CO)_2${HB(pz)$_3$}] (2). (i) Molybdenum hexacarbonyl (3.00 g, 11.4 mmol) was suspended in acetonitrile (40 mL) and heated under reflux for 24 h, to generate *fac*-[$Mo(NCMe)_3(CO)_3$]. The yellow solution was cooled to −30 °C and *N*,*N*-dimethylthiocarbamoyl chloride (1.39 g, 11.4 mmol) added in one portion. A darkening of the yellow solution was observed immediately. After stirring for 5 min, a dark orange solution had resulted. Subsequent addition of K[$HB(pz)_3$] (3.05 g, 12.1 mmol) at this point and slow warming to room temperature resulted in the formation of a deep red/orange suspension. The solid byproducts were allowed to settle, and the reaction liquor was transferred to a second Schlenk tube via a cannula. Removal of the solvent in vacuo afforded a dark oil, which was extracted with dichloromethane (2 × 10 mL). The combined extracts were chromatographed on alumina (ca. 50 × 6 cm) at −30 °C eluting with a mixture of diethyl ether and hexane (2:1). The initial intense orange band was collected, reduced in volume to ca. 20 mL, and diluted with hexane (20 mL). Slow removal of solvent led to the solution becoming cloudy. Storage of the concentrated solution at −20 °C (24 h) yielded orange microcrystals of [Mo(η^2-SCNMe$_2$)$(CO)_2${HB(pz)$_3$}] (**2**). Yield: 2.30 g (45%).

(ii) Molybdenum hexacarbonyl (3.00 g, 11.4 mmol) and K[$HB(pz)_3$] (3.05 g, 12.1 mmol) were suspended in acetonitrile and heated under reflux for 24 h. The resulting orange solution was slowly cooled to 0 °C in an ice bath and *N*,*N*-dimethylthiocarbamoyl chloride (1.39 g, 11.4 mmol) added in one portion. The suspension gradually became dark red-brown in color. Removal of the solvent and dissolution with dichloromethane followed by chromatography (alumina, diethyl ether eluant, −20 °C) resulted in the elution of an orange fraction, from which [Mo(η^2-SCNMe$_2$)$(CO)_2${HB(pz)$_3$}] (**2**) was isolated as described in (i) above. Yield: 0.35 g (14%).

(iii) [Mo(η^2-SCNMe$_2$)Cl$(CO)_2$(tmeda)] (**4**) (vide infra, 0.20 g, 0.50 mmol) was dissolved in dichloromethane (20 mL) and K[$HB(pz)_3$] (0.13 g, 0.50 mmol) added. An instantaneous reaction occurred with the visible darkening of the solution to deep orange. Chromatographic separation (alumina, diethyl ether eluant, 25 °C) yielded a bright orange fraction, from which [Mo(η^2-SCNMe$_2$)$(CO)_2${HB(pz)$_3$}] (**2**) was isolated as in (i) above. Yield: 0.22 g (95%).

(iv) A suspension of *trans*-[Mo(η^2-SCNMe$_2$)(Cl)$(CO)_2(PPh_3)_2$] (**5**) (vide infra, 0.20 g, 0.30 mmol) in tetrahydrofuran (20 mL) was treated with K[$HB(pz)_3$] (0.06 g, 0.30 mmol) and stirred for 1 h. The resulting orange suspension was freed of solvent under reduced pressure and the residue extracted with a mixture of dichloromethane and light petroleum (1:1, 10 mL) and purified by chromatography (alumina, −20 °C) eluting with the same solvent mixture. The bright orange zone was collected and reduced to a small volume, resulting in the crystallization of bright orange [Mo(η^2-SCNMe$_2$)$(CO)_2${HB(pz)$_3$}] (**2**). Yield: 0.10 g (88%).

(v) A solution of [Mo(η^6-C_7H_8)$(CO)_3$] (1.00 g, 3.7 mmol) in dichloromethane (20 mL) was treated with *N*,*N*-dimethylthiocarbamoyl chloride (0.45 g, 3.7 mmol) and K[$HB(pz)_3$] (0.93 g, 3.7 mmol), and the mixture stirred for 48 h. Purification was achieved by chromatography on silica gel (ca. 50 × 4 cm) using diethyl ether as the eluant. The major orange band was collected and the product isolated as for (i) above. Yield: 0.77 g (46%). IR CH_2Cl_2: ν(CO) 1942vs, 1848s [ν(CO)] cm^{-1}; Nujol: 1912s, 1812s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 3.75, 3.83 [s × 2, 3 H × 2, CH_3], 6.20 [t, 3 H, H^4(pz)], 7.64, 7.74 [d × 2, 3 H × 2, H^3, H^5(pz)] ppm. $^{13}C\{^1H\}$: 251.3 [CS], 242.7 [CO], 145.5, 144.4, 136.2, 135.3, 107.1, 105.9 [pz], 50.7, 45.5 [CH_3] ppm. FAB-MS *m*/*z* 455 $[M]^+$, 425 $[M - CO]^+$, 399 $[M - 2CO]^+$. Anal. Found: C, 37.0; H, 3.4; N, 21.2. Calcd for $C_{14}H_{16}BMoN_7O_2S$: C, 37.1; H, 3.6; N, 21.6.

Preparation of [Mo(η^2-SCNMe$_2$)$(CO)_2$(η^2-C_5H_5)] (3). A suspension of [Mo(η^2-SCNMe$_2$)Cl$(CO)_2$(tmeda)] (0.20 g, 0.50 mmol) in tetrahydrofuran (20 mL) was treated with a solution of NaC_5H_5 also in tetrahydrofuran (0.50 mL, 1.0 mol dm^{-3}, 0.50 mmol). An immediate darkening of the solution to red was observed. After stirring for 1 h, the reaction liquor was passed through a short plug of alumina (ca. 15 × 2 cm) and [Mo(η^2-SCNMe$_2$)$(CO)_2$(η^2-C_5H_5)] crystallized from the eluate by addition of hexane and cooling to −30 °C. Yield: 0.13 g (84%). IR CH_2Cl_2: 1943vs, 1847s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 3.61, 3.73 [s × 2, 3 H × 2, CH_3], 5.42 [s, 5 H, C_5H_5]. $^{13}C\{^1H\}$: 243.5 [CS], 222.6 [CO], 93.6 [C_5H_5], 49.7, 46.6

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[CH_3] ppm. IR and ^{1}H NMR data may be compared with those reported previously.[7]

Preparation of [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(bipy)] (4). Molybdenum hexacarbonyl (3.00 g, 11.4 mmol) was suspended in acetonitrile (40 mL) and heated under reflux for 24 h, to generate *fac*-[Mo(NCMe)$_3$(CO)$_3$]. The yellow solution was cooled to −30 °C and *N*,*N*-dimethylthiocarbamoyl chloride (1.39 g, 11.4 mmol) added. A darkening of the yellow solution was observed immediately, and, after stirring for 5 min, 2,2-bipyridyl (1.80 g, 11.4 mmol) was added. This resulted in a further darkening of the solution. A dark brown precipitate had formed after stirring for 1 h. The crude solid was filtered off and washed with acetonitrile (3 × 40 mL). Purification was achieved by extraction of this solid with tetrahydrofuran (3 × 20 mL) and elution of the combined extracts through alumina (ca. 15 × 6 cm). The orange fraction was collected, diluted with hexane, and then concentrated under reduced pressure to provide [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(bipy)] (**3**). Yield: 2.60 g (58%). IR CH_2Cl_2: 1937 s, 1840s [ν(CO)] cm^{-1}. Nujol: 1931s, 1846s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 3.41, 3.74 [s × 2, 3 H × 2, CH_3], 7.40, 7.94, 8.13, 9.15 [bipy]. ^{13}C{^{1}H}: 223.0 [CS], 204.7 [CO], 153.1, 137.2, 125.2, 123.2, 121.9 [C(bipy)], 29.7, 29.6 [CH_3] ppm. FAB-MS *m*/*z* 433 [M]$^+$, 407 [M − CO]$^+$, 398 [M − Cl]$^+$, 377 [M − 2CO]$^+$, 342 [M − 2CO, Cl]$^+$. Anal. Found: C, 41.8; H, 3.0; N, 10.7. Calcd for $C_{15}H_{14}ClMoN_3O_2S$: C, 42.0; H, 3.3; N, 9.8.

Preparation of [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(tmeda)] (5). Molybdenum hexacarbonyl (1.50 g, 5.7 mmol) was suspended in acetonitrile (30 mL) in a flame-dried Schlenk tube and heated under reflux for 24 h. The resulting yellow solution was cooled to −40 °C and *N*,*N*-dimethylthiocarbamoyl chloride (0.68 g, 5.70 mmol) added. The solution was stirred for 10 min, becoming deep orange. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (tmeda, 0.83 mL, 5.7 mmol) was then added and the mixture stirred while warming to room temperature. The solution was concentrated in volume under reduced pressure to ca. 15 mL, yielding a bright orange precipitate of pure [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(tmeda)] (**4**). Yield: 3.20 g (79%). IR CH_2Cl_2: 1923s, 1810s [ν(CO)] cm^{-1}. Nujol: 1911s, 1797s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 2.88, 3.11 [s(br) × 2, 16 H, tmeda]; 3.61, 3.73 [s × 2, 3 H × 2, $SCNCH_3$]. ^{13}C{^{1}H}: 245.2 [CS], 230.9 [CO], 59.8, 57.1, 55.7, 52.4 [tmeda], 51.1, 45.0 [$SCNCH_3$] ppm. FAB-MS *m*/*z* 393 [M]$^+$, 365 [M − CO]$^+$, 358 [M − Cl]$^+$, 337 [M − 2CO]$^+$, 302 [M − 2CO, Cl]$^+$, 269 [M − 2CO, Cl, S]$^+$. Anal. Found: C, 33.5; H, 5.4; N, 10.9. Calcd for $C_{11}H_{22}ClMoN_3O_2S$: C, 33.7; H, 5.7; N, 10.7.

Preparation of [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(PPh$_3$)$_2$] (6). Molybdenum hexacarbonyl (5.28 g, 20.0 mmol) and 3-bromoprop-1-ene (2.6 mL, 20.0 mmol) were suspended in acetonitrile (40 mL) and benzene (40 mL) and heated under reflux for 24 h. Upon cooling, an orange precipitate of [Mo(η-C_3H_5)(Br)(CH$_3$CN)$_2$(CO)$_2$] was isolated by filtration. This precipitate and triphenylphosphine (15.8 g, 60.3 mmol) were suspended in acetonitrile (60 mL) and heated under reflux for 15 min, resulting in the deposition of a bright yellow precipitate of [Mo(CH$_3$CN)$_2$(CO)$_2$(PPh$_3$)$_2$].

[Mo(CH$_3$CN)$_2$(CO)$_2$(PPh$_3$)$_2$] (1.00 g, 1.30 mmol) was suspended in dichloromethane (15 mL) and *N*,*N*-dimethylthiocarbamoyl chloride (0.16 g, 1.3 mmol) added. An immediate darkening of the reaction liquor was observed, followed by the deposition of an orange precipitate, which was complete after 20 min. The product was isolated by filtration and washed successively with acetonitrile (10 mL), dichloromethane (2 × 10 mL), and diethyl ether (2 × 10 mL) to provide [Mo(η^2-SCNMe$_2$)Cl(CO)$_2$(PPh$_3$)$_2$]. Yield: 0.55 g (52%). IR CH_2Cl_2: 1952s, 1848vs [ν(CO)] cm^{-1}. Nujol: 1952s, 1849s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{31}P: 40.1 ppm. FAB-MS *m*/*z* 766 [M − Cl]$^+$, 678 [M − Cl, CSNMe$_2$]$^+$, 538 [M − PPh$_3$]$^+$, 505 [M − PPh$_3$, Cl]$^+$. The compound was not completely characterized due to its low solubility and solution stability, which precluded satisfactory recrystallization. Further support for its formulation however comes from the reaction of **6** with K[HB(pz)$_3$] to provide **2**.

Preparation [Mo(η^2-SCOC$_6$H$_4$Me-4)(CO)$_2${HB(pz)$_3$}] (7a). (i) Molybdenum hexacarbonyl (1.50 g, 5.70 mmol) in acetonitrile (30 mL) was heated under reflux for 24 h. The resulting yellow solution was cooled to −30 °C and *p*-tolyl chlorothionoformate (0.9 mL, 5.7 mmol) added. Stirring at this temperature for 15 min resulted in the formation of an intense orange solution. Addition of K[HB(pz)$_3$] (1.45 g, 5.8 mmol) resulted in vigorous evolution of carbon monoxide and the formation of a red suspension, which was allowed to return to ambient temperature. The reaction liquor was freed of solvent and extracted with diethyl ether (3 × 10 mL), and the combined extracts were purified by chromatography (alumina, ca. 30 × 6 cm, diethyl ether eluant). The orange zone, which eluted with diethyl ether, was diluted with ethanol, concentrated, and cooled (−30 °C) to provide deep red crystals of [Mo(η^2-SCOC$_6$H$_4$Me-4)(CO)$_2${HB(pz)$_3$}] (**7a**). Yield: 2.02 g (69%).

(ii) A solution of [Mo(η^6-C_7H_8)(CO)$_3$] (1.00 g, 3.7 mmol) in dichloromethane (20 mL) was treated with K[HB(pz)$_3$] (0.93 g, 3.7 mmol) followed by *p*-tolyl chlorothionoformate (0.5 mL, 3.7 mmol). The orange suspension was stirred for 24 h and the resulting mixture chromatographed on silica gel (ca. 50 × 6 cm). Slow elution with a mixture of light petroleum and dichloromethane (2:1) facilitated the separation of the major orange product from several minor side-product bands. Reducing the eluate volume resulted in the deposition of red [Mo(η^2-SCOC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (**7a**) (0.99 g, 52%). IR CH_2Cl_2: 1993s, 1879vs [ν(CO)] cm^{-1}. Nujol: 1985s, 1855s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 2.41 [s, 3 H, CH_3], 6.24, 7.73 [s(br) × 2, 9 H, H(pz)], 7.25 [s(br), 4 H, C_6H_4]. ^{13}C{^{1}H}: 284.6 [CS], 233.3 [CO], 159.2 [C^1(C_6H_4)], 144.4 [C^4(C_6H_4)], 136.7, 135.6 [C^{2,3,5,6}(C_6H_4)], 130.0, 119.3, 105.8 [pz], 21.0 [CH_3] ppm. FAB-MS *m*/*z* 518 [M]$^+$, 490 [M − CO]$^+$, 460 [M − 2CO]$^+$, 366 [M − CSOC$_6$H$_4$Me]$^+$ Anal. Found: C, 39.3; H, 2.9; N, 14.5. Calcd for $C_{19}H_{17}BMoN_6O_3S.CH_2Cl_2$ C, 40.0; H, 3.2; N, 14.0. Unsatisfactory analytical data presumably reflect variable solvation.

Preparation of [Mo(η^2-SCOPh)(CO)$_2${HB(pz)$_3$}] (7b). A suspension of molybdenum hexacarbonyl (1.50 g, 5.70 mmol) in acetonitrile (30 mL) was heated under reflux for 24 h. The resulting yellow solution was cooled to −30 °C and phenyl chlorothionoformate (0.6 mL, 5.7 mmol) added. Stirring at this temperature for 15 min resulted in the formation of an intense orange solution. Addition of K[HB(pz)$_3$] (1.45 g, 5.8 mmol) resulted in vigorous evolution of carbon monoxide and the formation of a red suspension. The mixture was then allowed to return to ambient temperature. The reaction liquor was freed of solvent, the residue was extracted with diethyl ether (3 × 10 mL), and the combined extracts were purified by chromatography on alumina (ca. 30 × 6 cm, −20 °C). The orange zone was eluted and the product isolated as for **6a** above to provide red crystals of [Mo(η^2-SCOPh)(CO)$_2${HB(pz)$_3$}] (**7b**). Yield: 1.41 g (49%). IR CH_2Cl_2: 1994vs, 1878s [ν(CO)] cm^{-1}. Nujol: 1989s, 1857s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 6.25, 7.73 [s(br) × 2, 9 H, pz], 7.34−7.46 [m, 5 H, C_6H_5]. ^{13}C{^{1}H}: 284.0 [CS], 233.1 [CO], 160.9 [C^1(C_6H_5)], 144.6 [C^4(C_6H_5)], 135.6, 126.9 [C^{2,3,5,6}(C_6H_5)], 129.5, 119.6, 105.8 [pz] ppm. FAB-MS *m*/*z* 504 [M]$^+$, 476 [M − CO]$^+$, 448 [M − 2CO]$^+$. Anal. Found: C, 42.5; H, 3.0; N, 16.4. Calcd for $C_{18}H_{15}BMoN_6O_3S$: C, 43.0; H, 3.0; N, 16.7.

Preparation of [Mo(≡CN^{i}Pr$_2$)Br(CO)$_3$(PPh$_3$)]. This intermediate in the preparation of **8** was prepared by Mayr's acyl-oxide abstraction approach[43] applied to the synthesis of aminomethylideyne complexes:[44] Diisopropylamine (3.00 g, 30

(43) For a general review of the chemistry of alkylidyne complexes including a discussion of oxide-absrtaction strategies see: Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227.

(44) (a) Anderson, S.; Hill, A. F. *J. Organomet. Chem.* **1990**, *394*, C24. (b) Anderson, S.; Cook, D. J.; Hill, A. F. *J. Organomet. Chem.* **1993**, *463*, C3.

mmol) was added to diethyl ether (40 mL) and cooled in an ice bath. A solution of methyllithium (19.5 mL, 1.54 mol dm^{-3}, 30 mmol) prepared from bromomethane and lithium was then added dropwise and the resulting solution of "$LiN^iPr_2 \cdot LiBr$" allowed to warm to room temperature. In a separate flask, molybdenum hexacarbonyl (5.28 g, 20 mmol) was suspended in diethyl ether (20 mL). The solution of the lithium reagent was added dropwise until the metal carbonyl had been consumed (monitored by IR spectroscopy). The resulting yellow solution was cooled (dry ice/propanone) and then treated with a solution of trifluoroacetic anhydride (3.10 mL, 22 mmol) in diethyl ether (20 mL). After stirring at low temperature for 15 min, the mixture was allowed to warm slowly to 0 °C. At this point triphenylphosphine (7.86 g, 30 mmol) was added and the mixture left to warm to ambient temperature. The mixture was stirred for 10 h to provide a yellow precipitate. The supernatant was discarded by decantation and the residue extracted with a mixture of dichloromethane and light petroleum (2:1, 5 × 20 mL). The combined extracts were filtered through diatomaceous earth, concentrated, and chromatographed (silica gel, −30 °C, dichloromethane eluant) to provide [Mo(≡CN^iPr_2)Br$(CO)_3(PPh_3)$]. Yield: 6.89 g (54%). IR Nujol: 2043, 1973, 1932 [ν(CO)], 1564 [ν(CN)] cm^{-1}. CH_2Cl_2: 2054, 1983, 1948 [ν(CO)], 1534 [ν(CN)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.12 [d, 12 H, CH_3, J(HH) = 6.9 Hz], 2.97 [h, 2 H, NCH], 7.33−7.72 [m, 15 H, P(C_6H_5)$_3$]. ^{13}C{^{1}H}: 249.1 [d, Mo≡C, J(PC) = 12.5], 212.1 [d, MoCO (*trans* to P), J(PC) = 41.1], 205.5 [d, MoCO (*cis* to P), J(PC) = 9.0 Hz], 135.1−127.9 [C_6H_5], 50.6 [NCH], 22.1 [CH_3] ppm. ^{31}P{^{1}H}: 27.2 ppm. FAB-MS: *m/z* 635 $[HM]^+$, 579 $[M - 2CO]^+$, 556 $[M - Br]^+$, 528 $[M - CO,Br]^+$, 507 $[MoBrPPh_3CN^iPr]^+$, 439 $[MoPPh_3Br]^+$, 358 $[MoPPh_3]^+$, 102 $[NH_2{}^iPr_2]^+$. Anal. Found: C, 52.9; H, 4.6; N, 2.2. Calcd for $C_{28}H_{29}BrMoNO_3P$: C, 53.0; H, 4.6; N, 2.2.

Preparation of [Mo(≡CN^iPr_2)$(CO)_2${HB(pz)$_3$}] (8). [Mo(≡CN^iPr_2)$(CO)_3(PPh_3)$Br] (0.63 g, 1.00 mmol) was placed in a Schlenk tube with K[HB(pz)$_3$] (0.27 g, 1.10 mmol) and the vessel evacuated for several minutes, then back-filled with nitrogen. Tetrahydrofuran (25 mL) was added, and the mixture stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue chromatographed (silica gel, −30 °C), eluting with a mixture of dichloromethane and hexane (2:3). The product was then isolated by concentration and cooling (−30 °C) of the major orange fraction. Yield: 0.38 g (80%). IR Nujol: 2469 [ν(BH)], 1937, 1835 [ν(CO)], 1516 [νCN)] cm^{-1}. CH_2Cl_2: 2480 [ν(BH)], 1951, 1852 [ν(CO)], 1527 [ν(CN)] cm^{-1}. NMR ($CDCl_3$, 25 °C). ^{1}H δ 1.44 [d, 12 H, CH_3, J(HH) = 7.0 Hz], 3.55 [h, 2H, NCH], 6.15. 6.16 [t × 2, 3 H, H^4(pz)], 7.35 [m, 3 H, H^5(pz)], 7.64, 7.74 [d × 2, 3 H, H^3(pz)]. ^{13}C{^{1}H}: 260.5 [Mo≡C], 230.2 [MoCO], 143.8 [C^3(pz)], 134.8 [C^5(pz)], 104.8 [C^4(pz)], 52.7 [NCH], 23.3 [CH_3] ppm. FAB-MS: *m/z* 479 $[M]^+$, 451 $[M - CO]^+$, 423 $[M - 2CO]^+$, 380 [Mo{HB(pz)$_3$}$CN^iPr]^+$, 309 [Mo{HB(pz)$_3$}]$^+$. Anal. Found: C, 45.1; H, 5.5; N, 20.3. Calcd for $C_{18}H_{24}BMoN_7O_2$: C, 45.3; H, 5.1; N, 20.6.

Preparation of [MoFe(μ-CN^iPr_2)$(CO)_5${HB(pz)$_3$}] (9). [Mo(≡CN^iPr_2)$(CO)_2${HB(pz)$_3$}] (**8**, 0.10 g, 0.20 mmol) was dissolved in diethyl ether (20 mL), and [$Fe_2(CO)_9$] (0.20 g, 0.50 mmol) added. On stirring at room temperature overnight, a purple solution resulted. The ether was then removed under vacuum, and the residue chromatographed at low temperature (−30 °C, alumina, diethyl ether eluant). The product [MoFe{μ-CN^iPr_2}$(CO)_5${HB(pz)$_3$}] was then isolated from the initial purple band. Yield: 0.09 g (70%). IR Nujol: 2471 [ν(BH)], 2041, 1966, 1943, 1877, 1817 [ν(CO)] cm^{-1}. CH_2Cl_2: 2487 [ν(BH)], 2036, 1969, 1945, 1891, 1827 [ν(CO)] cm^{-1}. NMR ^{1}H: δ 0.91 [d, 6 H, CH_3, J(HH) = 6.9 Hz], 1.73 [d, 6 H, CH_3, J(HH) = 6.9 Hz], 3.75, 4.38 [h × 2, 2 H, NCH], 6.10, 6.67 [2 × t, 3H, H^4-(pz)], 7.35 [m, 3H, H^5(pz)], 7.70, 8.62 [m, s, 2H, H^3(pz)]. The complex was insufficiently stable for the acquisition of satisfactory ^{13}C{^{1}H} NMR and elemental microanalytical data.

Preparation of [MoFe(μ-SCN^iPr_2)$(CO)_5${HB(pz)$_3$}] (10). [MoFe{μ-CN^iPr_2}$(CO)_5${HB(pz)$_3$}] (**9**, 0.035 g, 0.06 mmol) was dissolved in tetrahydrofuran (20 mL) and sulfur (14 mg, 0.06 mmol) added. After stirring at room temperature overnight, the reaction mixture changed from purple to yellow. The solvent was then removed under vacuum, and the residue chromatographed at low temperature (−30 °C, alumina, diethyl ether eluant). The product was then isolated from the first yellow band. Yield: 0.03 g (80%). IR Nujol: 2481 [ν(BH)], 1938, 1926, 1845, 1827 [ν(CO)] cm^{-1}. CH_2Cl_2: 2485 [ν(BH)], 1948, 1932, 1850, 1832 [ν(CO)] cm^{-1}. NMR ^{1}H: δ 0.87, 1.42, 1.50, 1.59 [d × 4, 3 H × 4, CH_3, J(HH) = 6.9 Hz], 3.49, 4.11 [h × 2, 2 H, NCH], 6.15, 6.19 [t × 2, 3 H, H^4(pz)], 7.31 [m, 3 H, H^5(pz)], 7.71 [m, 3H, H^3(pz)]. Anal. Found: C, 40.2; H, 4.0; N, 12.8. Calcd for $C_{21}H_{24}BFeMoN_6O_5S$: C, 39.7; H, 3.8; N, 13.3.

Preparation of [W(η^2-$SCNMe_2$)$(CO)_2${HB(pz)$_3$}] (11). Tungsten hexacarbonyl (1.00 g, 2.8 mmol) was suspended in acetonitrile (20 mL) and heated under reflux for 72 h. The solution was cooled to −30 °C and treated with *N,N*-dimethylthiocarbamoyl chloride (0.35 g, 2.8 mmol), resulting in a slow darkening of the solution to orange over a 30 min period. Addition of K[HB(pz)$_3$] (0.72 g, 2.9 mmol) resulted in a further darkening of color. The mixture was allowed to return to ambient temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the orange residue redissolved in dichloromethane (15 mL). Purification by chromatography (alumina, dichloromethane eluant, −20 °C) yielded a bright orange eluate, which was diluted with hexane (50 mL) and reduced in volume to effect crystallization of [W(η^2-$SCNMe_2$)$(CO)_2${HB(pz)$_3$}] (**9**). Yield: 0.92 g (60%). IR CH_2Cl_2: 1923vs, 1818s [ν(CO)] cm^{-1}. Nujol: 1904s, 1795s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 3.73, 3.78 [s × 2, 3 H × 2, CH_3], 6.20 [t, 3 H, H^4(pz)], 7.65, 7.84 [d × 2, 3 H × 2, H^3, H^5(pz)]. ^{13}C{^{1}H}: 249.7 [CS], 241.5 [CO], 145.5, 135.4, 106.2 [C(pz)], 50.3, 45.2 [CH_3] ppm. FAB-MS *m/z* 541 $[M]^+$, 485 $[M - 2CO]^+$. Anal. Found: C, 31.0; H, 3.0; N, 17.9. Calcd for $C_{14}H_{16}BN_7O_2$SW C, 31.0; H, 3.0; N, 18.1.

Preparation of [WCl$(CO)_3${HB(pz)$_3$}] (12). A suspension of tungsten hexacarbonyl (2.00 g, 5.7 mmol) in acetonitrile (30 mL) was heated under reflux for 72 h. Upon cooling to −30 °C the yellow solution was treated with *p*-tolyl chlorothionoformate (0.87 mL, 5.7 mmol), followed by K[HB(pz)$_3$] (1.45 g, 5.8 mmol). After stirring for 1 h, the reaction liquor was passed through a short plug of alumina (ca. 20 × 4 cm) and reduced in volume, resulting in the precipitation of a golden yellow product. The crude product was recrystallized from a mixture of dichloromethane and hexane (−20 °C). Yield: 1.62 g (55%). IR CH_2Cl_2: 2035s, 1947vs, 1902br [ν(CO)] cm^{-1}. Nujol: 2036m, 1940vs, 1894s [ν(CO)] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 6.31 [t, 3 H, H^4(pz)], 7.70 [d, 3 H, H^5(pz)], 8.24 [d, 3 H, H^3(pz)]. ^{13}C{^{1}H}: 238.5 [CO], 146.2 [C^3(pz)], 136.6 [C^5(pz)], 107.1 [C^4-(pz)] ppm. FAB-MS *m/z* 488 $[M - CO]^+$, 462 $[M - 2CO]^+$, 432 $[M - 3CO]^+$, 397 $[M - 3CO, Cl]^+$. Anal. Found: C, 28.2; H, 2.0; N, 16.0. Calcd for $C_{12}H_{10}BClN_6O_3W$: C, 27.9; H, 2.0; N, 16.3. These data may be compared with those previously reported.[36]

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