Metallathiirenes. 4.[1] Thioaroyl Complexes of Molybdenum(II) and Tungsten(II)

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Received April 9, 2003

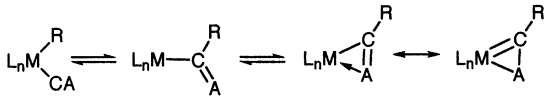
Synthetic routes to a range of thioaroyl complexes of tungsten and molybdenum are reported. Successive treatment of $[M(CO)_6]$ (M = Mo, W) with LiC_6H_4OMe-4·LiBr, $(CF_3CO)_2O$, and 2,2-bipyridyl (bipy) provides $[M(\equiv CC_6H_4OMe\text{-}4)Br(CO)_2(bipy)]$, which react with methylthiirane to provide the thioaroyl complexes $[M(\eta^2\text{-}SCC_6H_4OMe\text{-}4)Br(CO)_2(bipy)]$ and the dithiocarboxylate complexes $[M(\eta^2\text{-}S_2CC_6H_4OMe\text{-}4)Br(CO)_2(bipy)]$. $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl), $[Mo(\equiv CC_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$ (obtained from $[Mo(\equiv CC_6H_4OMe\text{-}4)Br(CO)_2(\gamma\text{-picoline})_2]$ and $K[HB(pz)_3]$), and $[Mo(\equiv C_4H_3S\text{-}2)(CO)_2\{HB(pz)_3\}]$ (obtained directly from $[Mo(CO)_6]$, 2-thienyllithium, $(CF_3CO)_2O$, and $K[HB(pz)_3]$) react with methylthiirane to provide primarily $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ in addition to small amounts of the corresponding dithiocarboxylates $[Mo(\eta^2\text{-}S_2CR)(CO)_2\{HB(pz)_3\}]$, which also arise from treatment of $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ with methylthiirane or elemental sulfur. $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{HB(pz)_3\}]$ failed to react with methyllirane, while $[Mo(\equiv CC_6H_4OMe\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ provided exclusively the dithiocarboxylate derivative. The mixed selenothiocarboxylates $[Mo(\eta^2\text{-}SSeCR)(CO)_2\{HB(pz)_3\}]$ (R = C_6H_4OMe-4, C_4H_3S-2) are obtained by treating $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ with Li_2Se_2, while $[Mo(\eta^2\text{-}SOCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ results from hydrolysis of the product of the reaction of $[Mo(\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ with $[Me_2SSMe]BF_4$. Alkylation of $[Mo(\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ with $[Et_3O]BF_4$ provides the thiolatocarbene salt $[Mo(\eta^2\text{-}EtSCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$, while the analogues $[Mo(\eta^2\text{-}MeSCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]BF_4$ and $[Mo(\eta^2\text{-}MeSCC_4H_3S\text{-}2)(CO)_2\{HB(pz)_3\}]BF_4$ result from the reactions of $[Mo(\equiv CR)(CO)_2\{HB(pz)_3\}]$ with $[Me_2SSMe]BF_4$. The reactions of these salts with the nucleophiles $Li[Et_3BH]$ and Me_3CSH provide the thioalkyl complexes $[Mo(\eta^2\text{-}MeSCHC_4H_3S\text{-}2)(CO)_2\{HB(pz)_3\}]$, $[Mo(\eta^2\text{-}MeSCHC_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$, and $[Mo(\eta^2\text{-}MeSC(SCMe_3)C_6H_4OMe\text{-}4)(CO)_2\{HB(pz)_3\}]$. The heterobimetallic thioaroyl complex $[MoFe(\mu\text{-}SCC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ is obtained from the reaction of $[Mo(\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ with $[Fe_2(CO)_9]$.

Introduction

The acyl ligand is ubiquitous in organotransition-metal chemistry, while iminoacyls provide a commonly encountered tangent to the σ-organometallic chemistry of isonitriles. However, acyl analogues based on replacement of oxygen by the heavier chalcogens (Scheme 1) remain rare. We have recently reported general routes to thiocarbamoyl complexes of molybdenum and tungsten and suggested that the thiocarbamoyl amino substituent is intimately involved in the bonding in such "metallathiirenes".[1] We now wish to report the synthesis of thioaroyl complexes of these metals, wherein hyperconjugation into the metallathiirene system is precluded, reducing the stability but significantly enhancing the reactivity and synthetic utility.

In contrast to acyl and iminoacyl chemistry, where CO and isonitriles are readily introduced as ligands for subsequent coupling with σ-organyls, the molecules CA (A = S, Se, Te) are not independently stable in condensed phases, although a variety of routes exist for their construction within a coordination complex.[2] Indeed, the first examples of thioaroyl ligands arose from the migratory insertion reactions of σ-aryl−thiocarbonyl complexes.[3] It was shown, furthermore, that even hydride ligands may undergo such processes to provide isolable thioformyl complexes.[4] Such a process is not generally observed for hydrido−carbonyl complexes, although it is often inferred. Since these initial studies by Roper and co-workers, further examples have arisen in related systems within group 8,[5,6] including the

Scheme 1. Acyl and Heteroacyl Ligands[a]



[a] A = O, S, Se, Te, NR.

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(1) Part 3: Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **2001**, *20*, 2468.

(2) For a review of thiocarbonyl ligands see: Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

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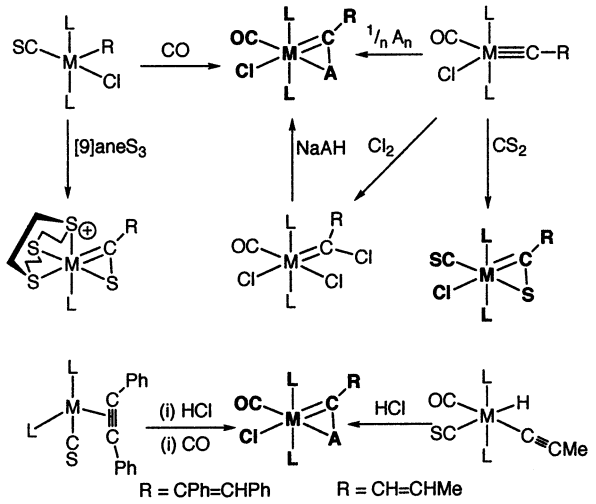
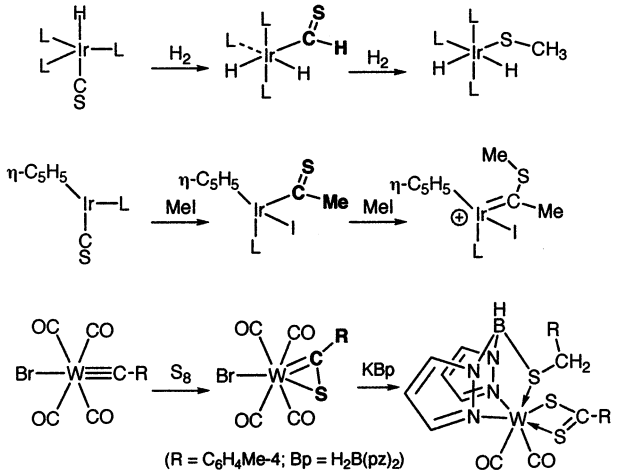
10.1021/om030261s CCC: $25.00
Publication on Web 07/24/2003

Scheme 2. Chalcoacyl and Aroyl Complexes[a]



[a] M = Ru, Os; L = PPh_3; R = aryl, vinyl, silyl (not all combinations).

Scheme 3. Proposed Intermediacy of Thioacyl Complexes[a]



[a] L = PPh_3.

coupling of silyl and thiocarbonyl ligands;[7] once again, this is a reaction rarely observed for silyl−carbonyl complexes.[8] These transformations are summarized in Scheme 2. The key to the stability and ready formation of these thioacyl complexes appears to lie in the combination of (i) the HSAB compatibility of sulfur and divalent ruthenium or osmium and (ii) the adopted pseudo-octahedral geometry, placing a π-acid (CO) trans to the π-donor sulfur and a π-donor halide trans to the π-acidic acyl carbon. Indeed, this arrangement is also observed in related acyl and aroyl complexes, where the HSAB argument alone is less convincing.[9] Thus, the unusual stability of these thioacyl examples appears peculiar to group 8.

For earlier transition-metal triads, the migratory insertion approach, while applicable in principle, is in practice not suitable because no σ-organyl−thiocarbonyl complexes exist yet for these metals. Accordingly, with the exception of bimetallic thioacyl complexes,[10,11] there have been very few reports[12] of simple mononuclear thioacyl ligands outside group 8: the complexes [Zr(η^2-SCCHR$_2$)Cl(η-C$_5$H$_5$)$_2$] (CR$_2$ = C(CMe$_3$)$_2$, cyclo-CCMe$_2$(CH$_2$)$_3$CMe$_2$)[12a] arise from the sequential treatment of [Zr(Bu)$_2$(η-C$_5$H$_5$)$_2$] with thioketenes S=C=CR$_2$ and HCl, and a similar thioketene protonation sequence provides [Co(η^2-SCCHR$_2$)(PMe$_3$)(η-C$_5$H$_5$)]$^+$ from [Co(η^2-SCCR$_2$)(PMe$_3$)(η-C$_5$H$_5$)] (CR$_2$ = cyclo-CCMe$_2$(CH$_2$)$_3$CMe$_2$).[12b] A thioformyl complex has been proposed as an intermediate in the hydrogenation of [IrH(CS)(PPh$_3$)$_3$] to provide [IrH$_2$(SCH$_3$)(PPh$_3$)$_3$], and in support of this, the isolable thioformyl complex [IrCl$_2$\{C(H)=S\}(CO)(PPh$_3$)$_2$] was obtained by nucleophilic (hydride) attack on the thiocarbonyl ligand of [IrCl$_2$(CS)(CO)(PPh$_3$)$_2$]$^+$.[12c] Thioacyl intermediates have also been proposed in the reactions of [M(C$_6$F$_5$)(CS)(PPh$_3$)$_2$] (M = Rh, Ir) and [Rh(CS)(PPh$_3$)(η-C$_5$H$_5$)] with iodomethane to provide (methylthio)ethylidene complexes.[12d,e] We have also had reason to invoke thioaroyl intermediates in the formation of the unusual scorpionate complex [W(η^2-S$_2$CR′)(CO)$_2$\{κ^3-HB(SCH$_2$R)(pz)$_2$\}] (Scheme 3; hereafter R^1 = C$_6$H$_4$Me-4, R^2 = C$_6$H$_4$OMe-4, R^3 = C$_4$H$_3$S-2, pz = pyrazolyl).[13]

Roper's alternative synthetic approach to thioacyls involved the addition of elemental chalcogens to the alkylidyne complex [Os(≡CR)Cl(CO)(PPh$_3$)$_2$] to provide what remains, after two decades, the only complete series of chalcoacyl complexes [Os(η^2-ACR)Cl(CO)(PPh$_3$)$_2$] (Scheme 2; A = S, Se, Te).[14] This approach would appear attractive for groups 5−7, wherein alkylidyne complexes are readily available in a range of oxidation states, geometries, and coordination environments via a variety of synthetic protocols.[15] This has, however, not proven to be the case: Stone showed that elemental sulfur or selenium adds to the alkylidyne

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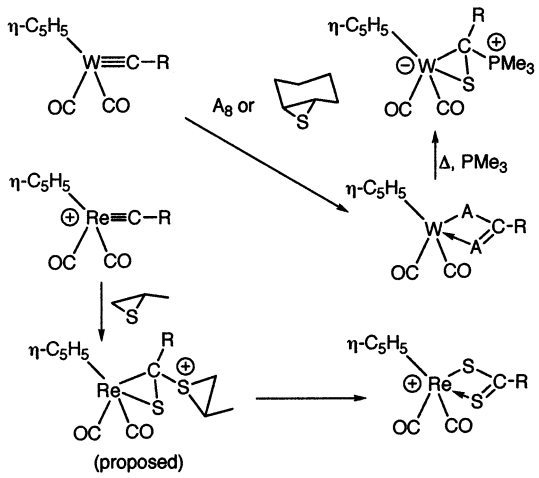
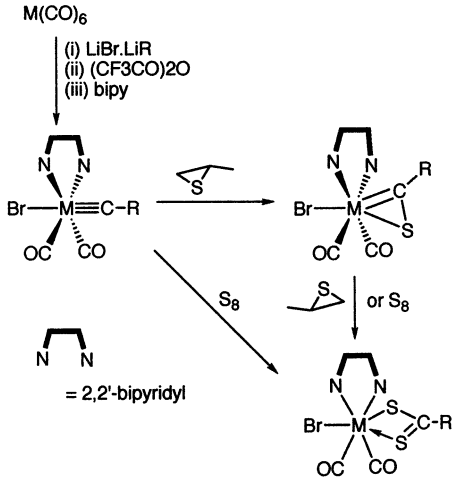
Scheme 4. Dichalcocarboxylate Complex Formation[a]



[a] R = C_6H_4Me-4, A = S, Se.

Scheme 5. Bipyridyl Thioaroyl Complexes[a]



[a] M = Mo, W; R = C_6H_4OMe-4.

complexes [W(≡CR)$(CO)_2(\eta$-$C_5H_5)$] and [Mo(≡CCH_2-CMe_3){$P(OMe)_3$}$_2(\eta$-$C_5H_5)$] to provide dithio- or diselenocarboxylato complexes. Thioacyl intermediates could be neither isolated nor observed, even when steric encumbrance was exaggerated about the metal, e.g., in the complexes [M(≡CR)$(CO)_2(\eta$-$C_5Me_5)$] (R = $C_6H_3Me_2$-2,6),[17] or when the milder sulfur transfer agent cyclohexene episulfide was employed.[18] Notably, in the case of [W(η^2-S_2CR)$(CO)_2(\eta$-$C_5H_5)$] (R = C_6H_5, R^1), one sulfur can be removed by heating with excess PMe_3, although this reagent ultimately traps the resulting thioacyl complex as the phosphosphium ylide [W{η^2-SC(PMe_3)R}-$(CO)_2(\eta$-$C_5H_5)$].[19] Similarly, the cationic rhenium complex [Re(≡CR)$(CO)_2(\eta$-$C_5H_5)]^+$ reacted with methylthiirane to provide a dithiocarboxylate, for which the intermediacies of a sulfonium carbene and a thioether-stabilized thioaroyl were invoked (Scheme 4).[20]

We wish to report herein that methylthiirane can indeed be used as an effective sulfur transfer reagent for the synthesis of group 6 thioaroyl complexes and that, in contrast to related thiocarbamoyl complexes, the metallathiirene unit is synthetically versatile. Aspects of this work have provided the basis of a preliminary report.[21]

Results and Discussion

A range of alkylidyne complexes of low-valent tungsten and molybdenum have been investigated. Initially, the reactions of the alkylidyne complexes [M(≡CR^2)Br-$(CO)_2$(bipy)] (M = Cr, Mo, W) with methylthiirane were studied. These complexes are obtained in "one pot" via a modified Mayr synthesis: the reaction of the appropriate metal hexacarbonyl with a diethyl ether solution of LiR^2 (obtained from Li and BrR^2) provides the acylate [M{=C(OLi)R^2}$(CO)_5$]. This was not isolated but treated with trifluoroacetic anyhdride at low temperature (dry ice/propanone) followed by 2,2′-bipyridyl. This approach conveniently provides the alkylidyne complexes in high to moderate yields (M = W (86%), Mo (70%), Cr (52%)) and usually in sufficient purity for further synthetic work.

Both the molybdenum and tungsten alkylidyne complexes react with methylthiirane in dichloromethane to provide a blue precipitate and a purple supernatant. In both cases, the precipitate is by far the major product and is formulated as the thioaroyl complex [M(η^2-SCR^2)-$Br(CO)_2$(bipy)]. The supernatant contained approximately 5% of a complex formulated as the dithiocarboxylate [M(η^2-S_2CR^2)$Br(CO)_2$(bipy)], which is also the sole product of the reaction of these alkylidyne complexes with elemental sulfur (Scheme 5). The feature of the thiocarbamoyl complexes which allowed their isolation, i.e., very low solubility, also compromised full spectroscopic characterization. The complexes are essentially insoluble in all common solvents, although a ^{1}H NMR spectrum can be obtained in d_6-DMSO. This confirms the presence of the bipyridyl and anisyl groups but is otherwise uninformative. The appearance of four signals for the bipyridyl ligand suggests that the complex contains a plane of symmetry that includes the thioaroyl ligand. This is the geometry that was observed for the recently reported and corresponding thiocarbamoyl complex [Mo(η^2-$SCNMe_2$)$Cl(CO)_2$(bipy)].[1] The complexes are, however, not sufficiently stable in DMSO for the acquisition of useful ^{13}C{^{1}H} NMR data; complete decomposition occurrs over a period of 30 min. The FAB mass spectrum, however, provides confirmation of the gross formulation with isotopic clusters observed for the molecular ion, in addition to identifiable fragments arising from sequential loss of the bromide and/or carbonyl ligands. The infrared spectrum features two carbonyl associated absorptions at 1973 s and 1870 vs cm^{-1} for the molybdenum complex and 1952 s and 1856 vs cm^{-1} for the tungsten complex. Interestingly, the

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ratio of intensities is reversed for the corresponding dithiocarboxylates, such that the higher frequency absorption is more intense, providing a profile similar to that observed for the complex $[W(\eta^2\text{-}S_2CR^1)(CO)_2(\eta\text{-}C_5H_5)]$.[16]

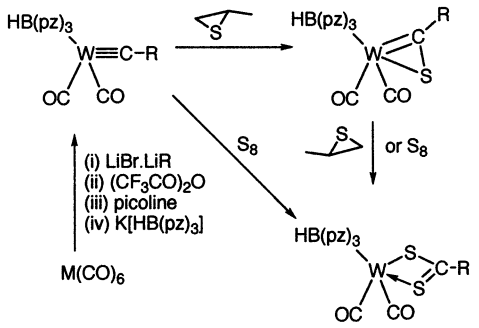
In the case of the analogous chromium alkylidyne complex, no reaction was observed (IR) after 3 days at room temperature. Although curtailing our efforts in chromium chemistry, this observation did, however, afford some economy. Commercially available $Mo(CO)_6$ containing 5% $Cr(CO)_6$ could be used for the preparation of the molybdenum thioaroyl complex, with the unreacted chromium alkylidyne remaining in solution.

The insolubility of the bipyridyl complexes not only compromised their characterization but also limited their synthetic utility, and these were not pursued further. The complex $[Mo(\equiv CR^2)Br(CO)_2(\gamma\text{-picoline})_2]$ was also investigated; however, intractable brown oils were obtained, which were also not pursued. Suspecting that picoline lability might have been a factor contributing to this problem, the substitution-inert complex $[Mo(\equiv CR^2)(CO)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) was prepared from the reaction of $[Mo(\equiv CR^2)Br(CO)_2(\gamma\text{-picoline})_2]$ with $K[HB(pz)_3]$. The characterization of $[Mo(\equiv CR^2)(CO)_2\{HB(pz)_3\}]$ does not call for comment, related complexes having been previously reported by Stone.[23]

A slow reaction ensues between $[Mo(\equiv CR^2)(CO)_2\{HB(pz)_3\}]$ and methylthiirane in dichloromethane to provide a dark solution which, as in the case of the bipyridyl complexes above, contains a blue major compound in addition to a minor purple compound. These are formulated as the thioaroyl and dithiocarboxylate complexes, respectively, on the basis of spectroscopic data (vide infra). Various attempts were made to eliminate the dithiocarboxylate side product, with only limited success. Addition of $[Bu_4N]Br$ to activate the thiirane leads to an increase in reaction rate, which is accompanied by a loss of selectivity and increase in the proportion of dithiocarboxylate. Heating the reaction mixture under reflux results in intractable brown oils. Reducing the proportion of methylthiirane to 0.8 equiv leads to a mixture of starting material and the two products. The one intriguing observation was, however, that by carrying out the reaction in the dark, the dithiocarboxylate formation could be minimized. Thus, it appears that the first sulfur addition is faster than the second, which is also photoassisted. Pure samples of each complex were obtained by careful cryostatic chromatography (−40 °C) on silica gel.

The complex $[Mo(\eta^2\text{-}SCR^2)(CO)_2\{HB(pz)_3\}]$ is sufficiently soluble to obtain satisfactory spectroscopic data: the ^1H NMR spectrum includes characteristic resonances due to the 4-anisyl group, in addition to three unresolved broad singlets due to the H^3, H^4, and H^5 protons of the pyrazolyl groups. In principle, the three pyrazolyl groups should be chemically distinct or have environments in the ratio of 2:1, depending on the ground-state orientation of the thioaroyl ligand. The observation that these are chemically equivalent suggests that the complex is fluxional on the ^1H (and ^{13}C) NMR time scale(s). A similar fluxionality is observed in the case of the related thiocarbamoyl complex $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{RB(pz)_3\}]$ (R = H,[1] pz[24a]) and the acyls $[Mo(\eta^2\text{-}OCR)(CO)_2\{HB(pz)_3\}]$ (R = Me, Ph).[24b] It is not yet clear whether this arises from a Bailar twist process or whether interconversion is via intermediates of reduced coordination number arising from dissociation of a pyrazolyl chelate or monodentate coordination of the thioaroyl/thiocarbamoyl ligand. The $^{13}C\{^1H\}$ NMR spectrum is unremarkable, other than further indicating the chemical equivalence of the three pyrazolyl groups and the resonance due to the thioaroyl carbon. This appears at δ 278.0 and is downfield from that of the corresponding dithiocarboxylate (δ 250.4). We have recently collated data for a range of heteroacyl analogues of the form $[M(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ (M = Mo, W; R = NR_2, SR, OR, R) (see Scheme 6) and the related thioaroyl complexes[1] and find that the thioaroyl carbons resonate to lower field of analogous thiocarbamoyl resonances but to higher field of monothioalkoxycarbonyls. The infrared spectrum of $[M(\eta^2\text{-}SCR^2)(CO)_2\{HB(pz)_3\}]$ includes two carbonyl-associated absorptions at 1976 and 1891 cm^{-1}, to lower frequency of the alkylidyne precursor but to substantially higher frequency of those for the related thiocarbamoyl complex $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{HB(pz)_3\}]$ (CH_2Cl_2: 1942, 1848 cm^{-1}),[1] suggesting a strong net acceptor role for the thioaroyl ligand.

Scheme 6. $HB(pz)_3$ Thioaroyl Complexes[a]



[a] R = C_6H_4Me-4, C_6H_4OMe-4, C_4H_3S-2.

In a manner similar to the synthesis of $[Mo(\eta^2\text{-}SCR^2)(CO)_2\{HB(pz)_3\}]$, the analogous complexes $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ (R = R^1, R^3) were prepared from the alkylidyne precursors $[Mo(\equiv CR)(CO)_2\{HB(pz)_3\}]$ and methylthiirane in high yields. Again, dithiocarboxylate derivatives were obtained as minor side products, which could be removed only by low-temperature chromatography. The spectroscopic data for these thioaroyls were essentially comparable to those for the thioanisyl complex and require no further discussion. It should, however, be pointed out that the 2-thienyl derivative reacted more rapidly than the tolyl and anisyl derivatives, possibly due to a modest decrease in the steric bulk of the five-membered heterocycle ring. In support of this, we note that there is no reaction between methylthiirane and the sterically congested complex $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{HB(pz)_3\}]$, while the reaction of $[Mo(\equiv CR^2)(CO)_2(\eta\text{-}C_5H_5)]$ with methylthiirane provided only the dithiocarboxylate derivative $[Mo(S_2$-

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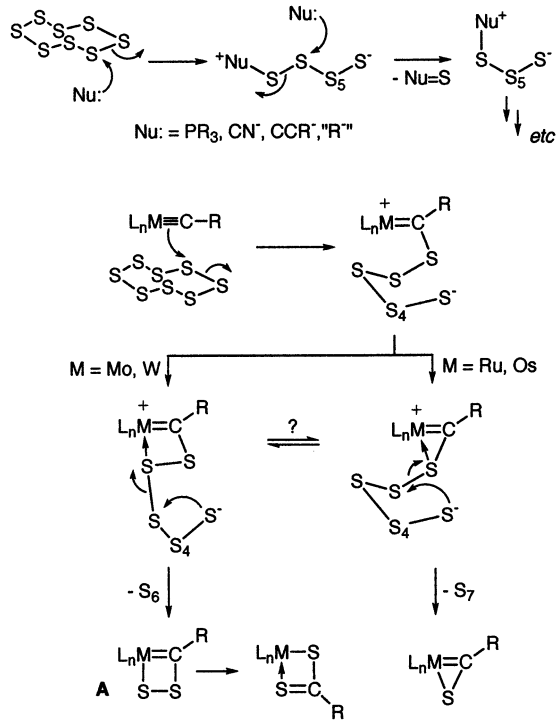
(24) (a) Desmond, T.; Lalor, F. J.; O'Sullivan, B.; Ferguson, G. *J. Organomet. Chem.* **1990**, *381*, C33. (b) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

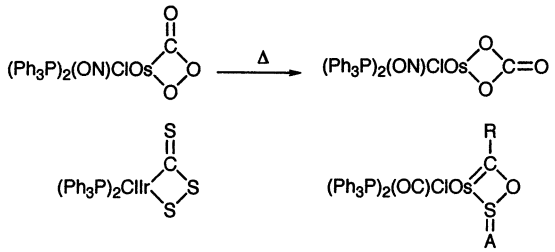
$CR^2)(CO)_2(\eta\text{-}C_5H_5)]$, which was obtained directly from $[Mo(\equiv CR^2)(CO)_2(\eta\text{-}C_5H_5)]$ and elemental sulfur. Presumably the second sulfur addition to this complex is considerably more rapid than for the tris(pyrazolyl)borate complexes, possibly due to less steric crowding around the molybdenum center.

The observed success of methylthiirane in the synthesis of thioaroyl complexes can only be descibed as fortuitous, given the failure of cyclohexene episulfide to allow the isolation of these intermediates en route to dithiocarboxylates[18] and the failure of methylthiirane to provide thioacyls of rhenium. The actual mechanism for sulfur atom transfer remains unclear. The complexes $[Mo(\equiv CR)(CO)_2L]$ ($L = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, $HB(pz)_3$, $HB(pzMe_2)_3$) are generally inert to associative ligand substitution at the 18-electron molybdenum centers under these mild conditions, although substitution may be effected photochemically via the intermediacy of ketenyl complexes.[25] The present reactions, however, proceed in the dark, and so direct attack at the metal center seems unlikely. Indeed, the isolable and substitution-labile ketenyl complex $[Mo\{\eta^2\text{-}C(=O)CR^2\}(NCMe)(CO)\{HB(pzMe_3)_3\}]$ failed to react with methylthiirane to generate either thioaroyl or dithiocarboxylate complexes. Attack at the carbyne carbon by the sulfur seems most likely, as proposed by Geoffroy[20] for the isoelectronic, though far more electrophilic, rhenium complex $[Re(\equiv CR^1)(CO)_2(\eta\text{-}C_5H_5)]^+$. The resulting sulfonio carbene was then proposed to eliminate propene, to generate a putative thiaroyl complex analogous to those described above. However, in the rhenium case this cationic metallathiirene is presumably more prone to nucleophilic attack by a second thiirane to generate the final dithiocarboxylate. In the (neutral) molybdenum chemistry, the electrophilicity appears sufficiently reduced to slow this second reaction and allow the interception of the thioaroyl complex. When isolated thiaroyl complexes were exposed to methylthiirane (or elemental sulfur), complete conversion to the dithiocarboxylate was observed, although this required between 5 (C_3H_6S) and 7 days (S_8) to proceed to completion. This mechanism would seem plausible for sulfur atom transfer from episulfides. However, one more observation needs to be explained, and that is the slow reaction of the thioacyl complexes with thiiranes or elemental sulfur, when the direct synthesis of dithiocarboxylate complexes from alkylidynes and elemental sulfur is substantially faster, complete in hours rather than days. It seems likely that while thiiranes may only transfer one atom of sulfur, cyclo-S_8 cannot undergo a concerted extrusion of a single sulfur atom. cyclo-S_8 may serve as a nucleophile, illustrated by the isolation of transition-metal complexes, e.g., $[Ag(S_8)_2]AsF_6$.[26] Alternatively, it may act as an electrophile in reactions with lithium organyls, phosphines, and cyanide. In these reactions, the solvent dependence of kinetic data has been taken to support rate-limiting ring opening of the S_8 ring by the nucleophile (Nu) to generate dipolar linear $^+Nu{-}S_7{-}S^-$ species (Scheme 7).[27] It seems plausible that the

Scheme 7. Electrophilic Behavior of cyclo-S_8



Scheme 8. Perchalcometallacycles[a]



[a] A = O, NR.

alkylidyne acts as a nucleophile in reactions with elemental sulfur and that the intermediate cleaves by delivering two atoms of sulfur in the case of group 6 metals and one atom in the case of group 8 metals (Scheme 7). This interpretation is consistent with the nucleophilic role of such alkylidyne complexes in their reactions with unsaturated metal complexes[23] and boranes.[28] While d^6 alkylidynes of the form $[W(\equiv CR)(CO)_2L]$ ($L = \eta\text{-}C_5R'_5$, $HB(pz)_3$, $\eta^5\text{-}C_2B_9H_9R'_2$; $R' = H$, Me)) show ambiphilic behavior, Roper's d^8 alkylidynes $[M(\equiv CR)Cl(CO)(PPh_3)_2]$ (M = Ru, Os) are generally unreactive toward nucleophiles, suggesting an electrophilic role for the attacking chalcogen. The suggested intermediacy of a perthioacyl ligand (A, Scheme 7) is novel; however, support comes from related chalcometallacycles (Scheme 8), which include Roper's peroxycarbonyl,[30] Kubota's perthiothiocarbonyl,[31] and the metal-

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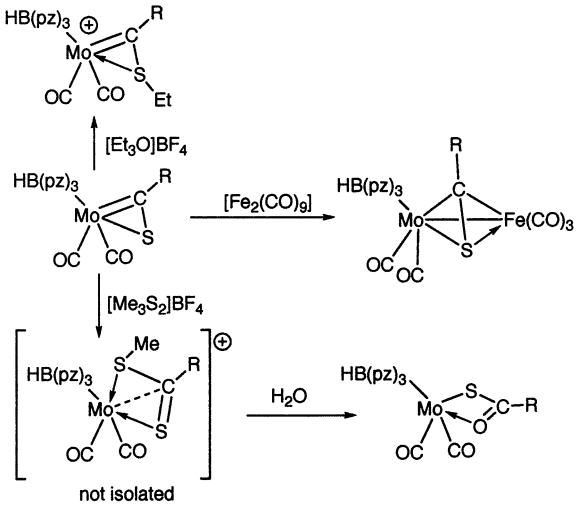
lacycles arising from the cycloaddition of iminooxosulfuranes or sulfur dioxide to group 8 alkylidynes.[32] Notably, the thermal peroxycarbonyl/carbonate interconversion is akin to the perthioacyl/dithiocarboxylate rearrangement proposed in Scheme 7.

No reaction was observed between the complex [Mo(η^2-SCR^2)(CO)$_2${HB(pz)$_3$}] and elemental selenium or tellurium, even when ultrasonic irradiation was employed for a prolonged period. This observation supports the argument that monochalcoacyl complexes are not intermediates in the synthesis of dichalcocarboxylates from elemental chalcogens. It was, however, possible to add selenium to the thioacyl complex by delivering it in a more nucleophilic form. For this purpose a solution of dilithiodiselenide proved effective, providing instantaneously the mixed selenothiocarboxylate complex [Mo(κ^2-SSeCR^2)(CO)$_2${HB(pz)$_3$}]. The solution of Li_2Se_2 could be prepared in a separate vessel (from selenium and Li[Et$_3$BH]), or alternatively, addition of Li[Et$_3$BH] directly to a mixture of the thioacyl complex and elemental selenium achieved similar yields. We are unaware of any other examples of mixed thio-/selenocarboxylate complexes; however, spectroscopic data confirm the formulation, including the appearance of a molecular ion in the FAB mass spectrum and the low-field ^{13}C-{^{1}H} resonance (249.7 ppm) showing coupling to selenium ($^1J(^{77}Se^{13}C)$ = 23 Hz). Unfortunately, a similar reaction was not observed using Li_2Te_2, and accordingly, tellurocarboxylate ligands remain unknown.[33] We have previously noted the facile extrusion of tellurium from L$_n$MTeC(=S) rings.[37] This contrasts with the addition of tellurium to the metal−carbon multiple bonds of [Os(≡CR^1)Cl(CO)(PPh$_3$)$_2$][14] and [Os(=CH$_2$)Cl(NO)(PPh$_3$)$_2$][38] to provide the telluroacyl and telluroformaldehyde complexes [Os(η^2-TeCR^1)Cl(CO)(PPh$_3$)$_2$] and [Os(η^2-TeCH$_2$)Cl(NO)(PPh$_3$)$_2$], respectively. Within group 6, this has provided an important access to the chemistry of telluroaldehyde and telluroketone complexes.[39] The failure of either [Mo(η^2-SCR^2)(CO)$_2${HB(pz)$_3$}] to react with selenium or tellurium or [Mo(≡CR^2)(CO)$_2${HB(pz)$_3$}] to react with tellurium would therefore appear to be a kinetic phenomenon rather than a reflection of thermodynamic instability of the anticipated dichalcocarboxylates, given that [Mo(η^2-SSeCR^2)(CO)$_2${HB(pz)$_3$}] was obtained via an alternative route (vide supra).

With these thioacyl complexes in hand, we have briefly investigated their reactivity. Roper's group 8 examples can be alkylated on sulfur, but only by potent alkylating agents (e.g., MeOSO$_2$CF$_3$),[3] presumably since

Scheme 9. Reactions of Thioacyl Complexes with Electrophiles[a]



[a] R = C$_6$H$_4$Me-4, C$_6$H$_4$OMe-4 (not all combinations).

coordination of the sulfur to the metal center reduces its nucleophilicity. Furthermore, this bidentate coordination, once adopted, appears to be very strongly adhered to: e.g., the reaction of [Os(η^2-SCR^1)Cl(CO)(PPh$_3$)$_2$] with dithiocarbamate results in halide replacement and phosphine loss rather than opening of the osmathiirene ring.[3] The alkylation of [Mo(η^2-SCR^1)(CO)$_2${HB(pz)$_3$}] with Meerwein's reagent [Et$_3$O]BF$_4$ occurs readily at sulfur to provide the bidentate thiolatocarbene carbene complex [Mo(η^2-EtSCR^1)(CO)$_2${HB(pz)}]BF$_4$ in 53% yield (Scheme 9). No reaction, however, occurs with the milder alkylating agent iodomethane. The first example of a mononuclear bidentate thiolato carbene[3] arose from alkylation of [Os(η^2-SCR^1)Cl(CA)(PPh$_3$)$_2$] (A = O, NR^1), although in this case the thioether coordination was hemilabile and could be opened by reaction with halides. More closely related to the present example are the complexes [W(η^2-MeSCH)(CO)$_2${HB(pz)$_3$}]$^+$ and [M(η^2-MeSCR^1)(CO)(L)(η-C$_5$H$_5$)]$^+$ (M = W, Mo; L = CO, PMe$_3$). The former[40] arises from the protonation of the thiolatocarbyne complex [W(≡CSMe)(CO)$_2${HB(pz)$_3$}], while the latter[41] is obtained via the electrophilic attack by [MeSSMe$_2$]BF$_4$ (synthetically equivalent to "MeS$^+$") on the M≡C bonds of [M(≡CR^1)(CO)L(η-C$_5$H$_5$)]. Accordingly, there exist sufficient published spectroscopic data to make characterization of [Mo(η^2-EtSCR^1)(CO)$_2${HB(pz)}]BF$_4$ both straightforward and unambiguous. In addition to routine characterizational data, the ^{13}C NMR resonance attributable to the carbene carbon appears at 248.1 ppm. This is moved to higher field of the precursor complex and may be

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(33) N.B.: monotellurocarboxylate complexes have recently been isolated for platinum and palladium, involving monodentate coordination through tellurium.[34] Ditellurocarbamates and xanthates have been mentioned in the patent literature as precursors to zinc telluride,[35] and hypothetical tetratellurooxalate complexes have been the subject of theoretical studies.[36]
(34) Kato, S.; Niyomura, O.; Kawahara, Y.; Kanda, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1677.
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compared to that observed for [Mo(η^2-MeSCPh)(CO)$_2$(η-C_5H_5)]BF_4 (249.5 ppm).[41i] The salts [Mo(η^2-MeSCR)(CO)$_2${HB(pz)$_3$}]BF_4 (R = R^2, R^3) were also obtained from the reactions of the carbyne complexes [Mo(≡CR)(CO)$_2${HB(pz)$_3$}] with [$MeSSMe_2$]BF_4. Notably, although the thiocarbamoyl complex [Mo(η^2-SCNMe$_2$)(CO)$_2$(η-C_5H_5)] may be alkylated on sulfur with [Me_3O]BF_4 to provide [Mo(η^2-MeSCNMe$_2$)(CO)$_2$(η-C_5H_5)]BF_4,[42] the corresponding reaction of [Mo(η^2-SCNMe$_2$)(CO)$_2${HB(pz)$_3$} with [Et_3O]BF_4 fails.[1]

Kreissl showed that methylthiolato carbene complexes obtained from the reactions of alkylidynes with [$MeSSMe_2$]BF_4 react with a further 1 equiv of this methylsulfonium transfer reagent to provide [W{η^3-(MeS)$_2$$CR^1$}(CO)$_2$($\eta$-$C_5H_5$)]$(BF_4)_2$. The reaction of [Mo($\eta^2$-SC$R^1$)(CO)$_2${HB(pz)$_3$}] with [$MeSSMe_2$]$BF_4$ was therefore investigated and found to yield, after chromatography, the neutral thiocarboxylate complex [Mo(η^2-OSCR^1)(CO)$_2${HB(pz)$_3$}]. This result is consistent with the successful transfer of 'MeS^+' to the Mo=C bond to generate a cationic complex of a methyldithiotoluate, which hydrolyzed during chromatography, presumably due to activation at the dithioester through coordination to the electrophilic "Mo(CO)$_2${HB(pz)$_3$}$^+$" center. This complex extends the series [Mo(η^2-SACR)(CO)$_2${HB(pz)$_3$}] (A = O, S, Se) and is an isomer of the aryloxythiocarbonyl complex [Mo(η^2-SCOR^1)(CO)$_2${HB(pz)$_3$}], which we have recently reported.[1] The difference in ν(CO) frequencies for these two isomers reflects the π-acidity of the aryloxythiocarbonyl ligand (CH_2Cl_2: 1994, 1878 cm^{-1}) and the π-basicity of the thiocarboxylate ligand (CH_2Cl_2 1959, 1855 cm^{-1}).

Heterobimetallic thioacyl complexes [MFe(μ-SCR^1)(CO)$_5$L] (M = Mo, W; L = η-C_5H_5, η-C_5Me_5) result from the addition of elemental sulfur to the bridging carbyne ligands of the complexes [MFe(μ-CR^1)(CO)$_5$L].[10,17,23] The analogous bridging thiocarbamoyl complex [MoFe(μ-SCN^{i}Pr$_2$)(CO)$_5${HB(pz)$_3$}] may be prepared similarly via the sequential treatment of [Mo(≡CN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}] with [$Fe_2(CO)_9$] and sulfur. However, the reverse sequence, i.e., initial addition of sulfur to generate [Mo(η^2-SCN^{i}Pr$_2$)(CO)$_2${HB(pz)$_3$}], fails, as does the reaction of [Mo(η^2-SCNMe$_2$)(CO)$_2${HB(pz)$_3$}] with [$Fe_2(CO)_9$].[1] In contrast, treating a dichloromethane solution of [Mo(η^2-SCR^1)(CO)$_2${HB(pz)$_3$}] with [$Fe_2(CO)_9$] leads to a slow reaction, which may be accelerated ultrasonically, to provide an orange complex. Spectroscopic data (IR, ^{1}H and ^{13}C{^{1}H} NMR) confirm the identity of the product as [MoFe(μ-SCR^1)(CO)$_5${HB(pz)$_3$}] by comparison with those previously published for the alternative route.[23] Furthermore, a molecular ion is observed in the FAB mass spectrum, in addition to fragments arising from loss of three, four, and five carbonyl ligands. These two reactions, alkylation and Fe(CO)$_3$ addition to the thioaroyl ligand, succeed where they fail for thiocarbamoyl complexes, a result which is perhaps counterintuitive, given that the π-dative amino group of thiocarbamoyl ligands might be expected to increase the nucleophilicity of sulfur, relative to thioaroyl ligands. A curious reaction occurs between [Mo(η^2-SCR^3)(CO)$_2$-{HB(pz)$_3$}] and $CuCl_2$ in dichloromethane; the only isolable product is the precursor alkylidyne complex [Mo(≡CR^3)(CO)$_2${HB(pz)$_3$}], albeit in low yield (15%) after chromatographic purification. The re-formation of the metal−carbon triple bond via sulfur abstraction is of interest, given that the majority of thiocarbonyl ligand syntheses rely on the extrusion of sulfur from η^2-coordinated carbon disulfide.[2]

The reactivities of the bidentate methylthiolato carbene complexes [Mo(η^2-MeSCR)(CO)$_2${HB(pz)$_3$}]BF_4 were briefly investigated. Although Roper had shown that chloride would open the osmacycle of [Os(η^2-MeSCR^1)Cl(CNR^1)(PPh_3)$_2$]O_3CF_3 to provide the neutral monodentate carbene complex [$OsCl_2${=C(SMe)R^1}(CNR^1)(PPh_3)$_2$],[3] the majority of reactions of the *monodentate* thiolatocarbenes L_nM=CH(SMe)$^+$ (L_nM = OsCl(CO)$_2$(PPh_3)$_2$,[4] OsCl(CO)(CNR^1)(PPh_3)$_2$,[4] Fe(CO)$_2$(η-C_5H_5)[43]) involve direct nucleophilic attack at the carbene carbon. The majority of reactions of the tungsten complex [W(η^2-MeSCH)(CO)$_2${HB(pz)$_3$}]$^+$ with nucleophiles resulted in complexes which (ultimately) retain the WCS metallacyclic motif and also arise from nucleophilic attack at the carbene carbon. Thus, e.g., the reactions with thiols (RSH) under basic conditions provide [W(η^2-MeSCHSR)(CO)$_2${HB(pz)$_3$}], with the exceptions of hydrosulfide and benzyl mercaptide, which instead each provide a mixture of [W(≡CSMe)(CO)$_2${HB(pz)$_3$}] and [W(η^2-MeSCHSMe)(CO)$_2${HB(pz)$_3$}].[40a] A similar mixture is obtained from the reaction of [W(η^2-MeSCH)(CO)$_2${HB(pz)$_3$}]$^+$ with hydride donors (NaH, $NaBH_4$) rather than formation of the thiolatomethyl complex [W(η^2-CH_2SMe)(CO)$_2$-{HB(pz)$_3$}], although related complexes are known to be stable, resulting from, e.g., the reaction of metal carbonylates with $ClCH_2SMe$.[44]

The reaction of [Mo(η^2-MeSCR^2)(CO)$_2${HB(pz)$_3$}]BF_4 with *tert*-butyl mercaptan in the presence of a nonnucleophilic base (DBU) results in the formation of the neutral orange bis(thioalkyl)alkyl complex [Mo{η^2-MeSC(SCMe$_3$)R^2}(CO)$_2${HB(pz)$_3$}] in high yield after chromatography on alumina. In principle, two isomers are possible, depending on which of the SMe and $SCMe_3$ groups coordinate to the molybdenum center. Only one isomer is apparent from the IR spectrum of the product both in solution and in the solid state, on the basis of the observation of two ν(CO) bands (CH_2Cl_2: 1950, 1820 cm^{-1}). In contrast, Angelici obtained two isomers in a temperature- and solvent-dependent ratio from the reactions of the tungsten complex [W(η^2-MeSCH)(CO)$_2$-{HB(pz)$_3$}]$^+$ with mercaptides (RS^-: R = Me, Et, ^{i}Pr). The isomerism arose from the relative positions of the SCH_3 and thiolate substituents straddling the WCS metallacycle.[40] This appears to occur in the present example, presumably because the added steric bulk of the anisyl (vs H) substituent exaggerates steric factors, which are also augmented by the use of the bulky $SCMe_3$ group. It seems most likely that the thiolate nucelophile attacks the WCS face opposite the sterically cumbersome HB(pz)$_3$ ligand, such that the $SCMe_3$ and Me groups are anti with respect to the WCS metallacycle. The FAB mass spectrum of the complex [Mo{η^2-MeSC(SCMe$_3$)R^2}(CO)$_2${HB(pz)$_3$}] includes substantial isotope clusters attributable to the molecular ion, in addition to loss of two carbonyl ligands and, most

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Table 1. Comparative Spectroscopic Data for Thioaroyl and Dichalcocarboxylate Complexes

	$\delta(^{13}C)$ (ppm)	ν(CO) (cm^{-1})[a]
[**Mo**]CR^{1} [b]	293.1	1998, 1921
[**Mo**]CR^{2}	294.2	1991, 1906
[**Mo**]CR^{3}	276.8	1996, 1913
[**Mo**]SCR^{1}	280.4	1979, 1893
[**Mo**]SCR^{2}	278.0	1976, 1891
[**Mo**]SCR^{3}	261.6	1980, 1897
[**Mo**]$OSCR^{1}$	251.6	1959, 1855
[**Mo**]$SSCR^{1}$	249.1	1953, 1871
[**Mo**]$SSCR^{2}$	250.9	1965, 1890
[**Mo**]$SeSCR^{2}$	249.7	1943, 1861
[**Mo**]$SeSCR^{3}$	249.6	1945, 1857
[**Mo**]$CSOR^{1}$	284.6	1993, 1879

[a] In CH_2Cl_2. [b] Taken from ref 23. Legend: [**Mo**] = $Mo(CO)_2\{HB(pz)_3\}$; $R^1 = C_6H_4Me$-4; $R^2 = C_6H_4OMe$-4; $R^3 = C_4H_3S$-2.

abundantly, one $SCMe_3$ group. No peaks were assignable to fragmentations involving loss of the SMe group, which is therefore presumed to be bound to the metal. This suggests that scrambling of SMe and $SCMe_3$ groups between coordinated and pendant positions does not occur. The ^{13}C NMR features a peak at δ 65.88 attributable to the tungsten-bound carbon of the alkyl ligand, which may be compared with the values of δ 61.79 and 71.69 reported for the two isomers of [W{η^2-MeSC(SMe)H}$(CO)_2\{HB(pz)_3\}$].[40a]

In contrast to the reaction of [W(η^2-MeSCH)$(CO)_2$-$\{HB(pz)_3\}$] with $NaBH_4$, which provides [W(≡CSMe)-$(CO)_2\{HB(pz)_3\}$] and [W{η^2-CH$(SMe)_2$}$(CO)_2\{HB(pz)_3\}$] (vide supra),[40a] a clean reaction occurs between [Mo(η^2-MeSCR$)(CO)_2\{HB(pz)_3\}]BF_4$ and Li[Et_3BH] to provide the thiolatoalkyl complexes [Mo(η^2-MeSCHR$)(CO)_2\{HB$-$(pz)_3\}$] (R = R^2, R^3) in high yield. Once again, attack by the nucleophile ("H^-") would seem most likely to occur opposite the bulky $HB(pz)_3$ ligand, although this could not be confirmed unequivocally from the spectroscopic data. Nevertheless, these data do confirm that, in both cases, two isomers are present in solution. In the case of R = 2-thienyl, the ratio of isomers is close to comparable (ca 5:4), while for the slightly bulkier R = C_6H_4OMe-2 the ratio is approximately 15:1 (in CH_2Cl_2). Angelici has discussed this type of isomerism and concluded that interconversion most probably proceeds via simple inversion at the coordinated sulfur, rather than dissociation of the thiolate group from tungsten.[40a]

The isolation of moderately stable thioaroyl complexes of tungsten and molybdenum establishes that there is nothing inherently unstable about them, merely that they are reactive and that this requires careful control of conditions during their synthesis. The reactivity is primarily associated with the nucleophilicity of the sulfur atom, although some reactions, such as the addition of further methylthiirane to provide dithiocarboxylates, points toward electrophilic character for the thioacyl carbon. This is further supported by the synthesis of a mixed selenothiocarboxylate complex by employing the nucleophilic reagent Li_2Se_2 as a selenium delivery agent. Data for this range of dichalcocarboxylate complexes are collected in Table 1. The thioaroyl ligand, once constructed, serves as a precursor for heterobimetallic thioaroyl complexes (bridge-assisted metal−metal bond formation) and for thiolatocarbenes upon electrophilic alkylation, complementing existing routes to such complexes.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk and vacuum-line techniques. Solvents were purified by distillation from an appropriate drying agent (ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH_2). Light petroleum refers to that fraction with bp 40−60 °C.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker WH-400 NMR and JEOL JNM EX270 NMR spectrometers and calibrated against internal Me_4Si (^1H) or $CDCl_3$ ($^{13}C\{^1H\}$). Unless otherwise indicated, NMR data were acquired from saturated solutions in $CDCl_3$ at room temperature. Infrared spectra were recorded using Perkin-Elmer 1720-X FT-IR and 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. Unless indicated, reagents were commercially available and used as received from commercial sources (Aldrich). The salt $K[HB(pz)_3]$[45] was prepared according to a published procedure. Alkylidyne precusors were generally prepared via minor modifications of the Mayr protocol.[22]

Preparation of *trans,cis,cis*-[W(≡CR^2)$Br(CO)_2$(bipy)]. Tungsten hexacarbonyl (5.30 g, 15.1 mmol) was suspended in diethyl ether (40 mL), and 4-anisolyllithium (from Li and BrR^2, 15.1 mL, 1.0 mol dm^{-3}, 15.1 mmol) was added dropwise over a 15 min period. The resulting dark orange solution was cooled (dry ice/propanone) and trifluoroacetic anhydride (2.1 mL, 15 mmol) added in small portions, with stirring, until the initial deep purple color dissipated after each addition. The resulting deep red solution was warmed gradually to room temperature and 2,2′-bipyridyl (2.40 g, 15.1 mmol) added, resulting in the precipitation of crude product. The supernatant was decanted, the solid extracted with a mixture of dichloromethane and light petroleum (2:1), and the extract filtered through a plug of alumina (ca. 10 × 4 cm). Concentration of the red solution and storage at −20 °C yielded crystals of *trans,cis,cis*-[W(≡CR^2)-$Br(CO)_2$(bipy)]. Yield: 7.71 g (86%). IR (CH_2Cl_2): ν(CO) 1985 s, 1899 vs cm^{-1}. IR (Nujol): ν(CO) 1974 s, 1875 vs cm^{-1}. ^1H NMR: δ 3.75 [s, 3 H, CH_3], 6.69, 7.20 [$(AB)_2$, 4 H, $^3J(AB) = 8.0$ Hz, C_6H_4], 7.56, 8.08, 8.23, 9.22 [8 H, bipy]. FAB-MS: *m*/*z* 596 $[M]^+$, 568 $[M - CO + H]^+$, 538 $[M - 2CO]^+$, 515 $[M - Br]^+$, 369 $[M - CO - Br - R^2]^+$. Anal. Found: C, 39.4; H, 2.5; N, 4.7. Calcd for $C_{20}H_{15}BrNO_3W$: C, 40.37; H, 2.54; N, 4.71.

Preparation of [Mo(≡CR^2)$(CO)_2\{HB(pz)_3\}$]. A solution of [Mo(≡CR^2)$Br(CO)_2$(γ-picoline)$_2$] (3.00 g, 5.6 mmol) in dichloromethane (60 mL) was treated with potassium hydrotris-(pyrazol-1-yl)borate (1.44 g, 5.70 mmol). The orange suspension was stirred for 12 h and allowed to settle. The orange supernatant was decanted from the solid residue and chromatographed on alumina (ca 15 × 4 cm) using diethyl ether as the eluant. The bright orange fraction was diluted with light petroleum (60 mL) and concentrated under reduced pressure to the point of crystallization. Subsequent storage of the solution at −20 °C produced orange microcrystals of [Mo(≡CR^2)$(CO)_2\{HB(pz)_3\}$]. Yield: 2.40 g (87%). IR (CH_2Cl_2): ν(CO) 1991 s, 1906 vs cm^{-1}. IR (Nujol): ν(CO) 1978 s, 1913 s cm^{-1}. ^1H NMR: δ 3.83 [s, 3 H, CH_3], 6.17, 6.22 [t × 2, 3 H, H^4(pz)], 6.81, 7.51 [$(AB)_2$, 4 H, $^3J(AB) = 8.0$ Hz, C_6H_4]; 7.64, 7.67, 7.91 [s, d × 2, 6 H, $H^{3,5}$(pz)]. $^{13}C\{^1H\}$ NMR: δ 294.2 [Mo≡C], 226.0 [CO], 159.9 [$C^1(C_6H_4)$], 149.4, 140.1 [$C^{2,3,5,6}(C_6H_4)$], 143.0, 135.4, 131.2, 113.5, 105.2 [C(pz)], 124.7 [$C^4(C_6H_4)$], 55.4 [CH_3] ppm. FAB-MS: *m*/*z* 484 $[M]^+$, 456 $[M - CO]^+$, 428 $[M - 2CO]^+$. Anal. Found: C, 47.5; H, 3.2; N, 17.7. Calcd for $C_{19}H_{17}BMoN_6O_3$: C, 47.14; H, 3.54; N, 17.36.

(45) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288. (b) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

Preparation of [Mo(≡CR³)(CO)₂{HB(pz)₃}]. Molybdenum hexacarbonyl (3.00 g, 11.4 mmol) was suspended in diethyl ether (50 mL), and 2-thienyllithium (11.4 mL, 1.0 mol dm^{-3}, 11.4 mmol, Aldrich) was added dropwise over a 15 min period, resulting in an orange solution. The mixture was cooled (dry ice/propanone) and then treated with trifluoroacetic anhydride (1.2 mL, 11.4 mmol), resulting in the immediate formation of a deep purple solution. The cooling bath was removed and the mixture warmed slowly. At the point where the last vestige of purple coloration dissipated, potassium hydrotris(pyrazolyl)borate (3.05 g, 12.1 mmol) was added in one portion and the mixture warmed gradually with stirring to room temperature, resulting in the vigorous evolution of carbon monoxide and the formation of a deep orange-red suspension. After it was stirred for 30 min at room temperature, the solution was transferred via cannula filtration to a second Schlenk vessel and concentrated under reduced pressure to ca. 20 mL. The solution was then transferred to a chromatography column (ca. 30 × 3 cm, silica) and eluted with a mixture of diethyl ether and hexane (1:1) to provide an orange eluate, which was diluted with light petroleum (50 mL) and reduced in vacuo, yielding bright orange microcrystals. Yield: 5.02 g (96%). IR (CH_2Cl_2): ν(CO) 1996 s, 1913 s cm^{-1}. IR (Nujol): ν(CO) 1992 s, 1899 s cm^{-1}. ^{1}H NMR: δ 6.21, 6.26 [s × 2, 3 H, H⁴(pz)], 6.94, 7.21, 7.36 [3 H, C_4H_3S], 7.70 [H^{3,5}-(pz)]. ^{13}C{^{1}H} NMR: 276.8 [Mo≡C], 225.9 [CO], 144.3, 135.5, 105.5 [C(pz)], 143.1, 130.6, 127.7, 126.6 [C(C_4H_3S)]. FAB-MS: *m/z* 462 $[M]^+$, 434 $[M - CO]^+$, 406 $[M - 2CO]^+$. Anal. Found: C, 41.6; H, 2.6; N, 18.3. Calcd for $C_{16}H_{13}BMoN_6O_2S$: C, 41.77; H, 2.85; N, 18.26.

Preparation of *trans,cis,cis*-[W(η²-SCR²)Br(CO)₂(bipy)]. [W(≡CR²)Br(CO)₂(bipy)] (0.48 g, 0.80 mmol) was dissolved in dichloromethane (40 mL), methylthiirane (0.06 mL, 0.80 mmol) was added, and the mixture was stirred for 10 min. The red solution was then left to stand without stirring for 24 h, resulting in the precipitation of dark blue microcrystals from the resulting purple solution. The product was isolated by decantation, washed with diethyl ether (3 × 30 mL), and dried in vacuo. Yield: 0.35 g (69%). IR (CH_2Cl_2): ν(CO) 1952 s, 1856 s cm^{-1}. IR (Nujol): ν(CO) 1954 s, 1871 s cm^{-1}. ^{1}H NMR: δ 3.87 [s, 3 H, CH_3], 6.94, 7.88 [$(AB)_2$, 4 H, ^3J(AB) = 8.0 Hz, C_6H_4], 7.22, 7.89, 8.31, 8.95 [8 H, bipy]. Useful ^{13}C{^{1}H} NMR data were not obtained, due to insolubility and solution instability (vide supra). FAB-MS: *m/z* 628 $[M]^+$, 600 $[M - CO]^+$, 572 $[M - 2CO]^+$, 538 $[M - 2CO - S]^+$. Anal. Found: C, 38.3; H, 2.3; N, 4.4. Calcd for $C_{20}H_{15}BrN_2O_3SW$: C, 38.30; H, 2.41; N, 4.47.

Preparation of *trans,cis,cis*-[Mo(η²-SCR²)Br(CO)₂(bipy)]. [Mo(≡CR²)Br(CO)₂(bipy)] (2.00 g, 4.00 mmol) was dissolved in dichloromethane (100 mL) and methylthiirane (0.29 mL, 4.0 mmol) added. The orange solution was stirred for 10 min and then left to stand without stirring for 20 h, whereupon a purple solution formed and blue crystals separated. The mother liquor was removed using a cannula, and the crystals were washed with diethyl ether (3 × 30 mL) and dried in vacuo. Yield: 1.70 g (79%). IR (CH_2Cl_2): ν(CO) 1962 s, 1870 vs cm^{-1}. IR (Nujol): ν(CO) 1962 s, 1872 vs cm^{-1}. ^{1}H NMR (ppm, 25 °C, d_6-DMSO): δ 4.14 [s, 3 H, CH_3], 8.38, 7.49 [$(AB)_2$, 4 H, ^3J(AB) = 8.0 Hz, C_6H_4], 9.13, 8.87, 8.55, 8.03 [8 H, bipy]. Useful ^{13}C{^{1}H} NMR data were not obtained, due to insolubility and solution instability (vide supra). FAB-MS: *m/z* 540 $[M]^+$, 511 $[M - CO]^+$, 484 $[M - 2CO]^+$, 453 $[M - CO - Br]^+$, 407 $[M - 2CO - Br]^+$, 329 $[M - 2CO - bipy]^+$. Anal. Found: C; 43.8, H; 2.2, N; 5.2. Calcd for $C_{20}H_{15}BrMoN_2O_3S$: C, 44.55; H, 2.80; N, 5.19.

Preparation of [Mo(η²-SCR²)(CO)₂{HB(pz)₃}]. [Mo(≡CR²)(CO)₂{HB(pz)₃}] (1.00 g, 1.90 mmol) was dissolved in dichloromethane (20 mL) and methylthiirane (0.14 mL, 1.9 mmol) added. The orange solution was stirred in the dark for 12 h. The resulting intense purple solution was chromatographed on a water-cooled column (50 × 4 cm) loaded with alumina. Elution with diethyl ether allowed the separation of a dark blue-purple fraction. Dilution with hexane, concentration, and storage of the solution at −20 °C resulted in the deposition of pure, crystalline [Mo(η²-SCR²)(CO)₂{HB(pz)₃}]. Yield: 0.99 g (93%). IR (CH_2Cl_2): ν(CO) 1976 s, 1891 vs cm^{-1}. IR (Nujol): ν(CO) 1974 s, 1895 vs cm^{-1}. ^{1}H NMR: δ 3.94 [s, 3 H, OCH_3], 6.24, 7.39, 7.74 [s(br) × 3, 9 H, pz], 7.09, 8.04 [$(AB)_2$, 4 H, ^3J(AB) = 8.0 Hz, C_6H_4]. ^{13}C{^{1}H} NMR: δ 278.0 [CS], 233.6 [CO], 162.5 [C^l(C_6H_4)], 136.8, 113.8, 106.0 [C(pz)], 137.0, 136.9 [C^{2,3,5,6}(C_6H_4)], 124.8 [C^4(C_6H_4)], 55.6 [CH_3] ppm. FAB-MS: *m/z* 518 $[M]^+$, 592 $[M - CO]^+$, 562 $[M - 2CO]^+$. Anal. Found: C, 43.3; H, 3.2; N, 16.7. Calcd for $C_{19}H_{17}BMoN_6O_3S$: C, 44.21; H, 3.32; N, 16.28. Under these experimental conditions, the second purple fraction was obtained only in sufficient quantities (1−3%) to identify it, by comparison of infrared and ^{1}H NMR data, as the dithiocarboxylate complex [Mo(κ²-S_2CR^2)-$(CO)_2${HB(pz)₃}], described below.

Preparation of [Mo(η²-SCR³)(CO)₂{HB(pz)₃}]. [Mo(≡CR³)(CO)₂{HB(pz)₃}] (2.00 g, 4.30 mmol) was dissolved in dichloromethane (20 mL) and methylthiirane (0.31 mL, 4.30 mmol) added. The initially orange solution was stirred for 4 h. resulting in the formation of an intense blue-purple solution. Concentration of this solution followed by chromatographic purification on silica gel (30 × 3 cm) using diethyl ether as the eluant yielded a dark blue band. This was diluted with hexane (30 mL), concentrated under reduced pressure to ca. 10 mL, and stored at −20 °C for 24 h. The resulting dark blue crystals were filtered off and dried in vacuo. Yield: 1.92 g (90%). IR (CH_2Cl_2): ν(CO) 1980 s, 1897 vs cm^{-1}. IR (Nujol): ν(CO) 1988 s, 1878 vs cm^{-1}. ^{1}H NMR: δ 6.24 [t, 3 H, H⁴(pz)], 7.27−8.05 [9 H, H^{3,5}(pz) and C_4H_3S]. ^{13}C{^{1}H} NMR: δ 261.6 [CS], 233.7 [CO], 149.5, 145.2, 143.6, 142.2 [C$^{2-4}$(C_4H_3S)], 135.6, 129.1, 105.9 [C(pz)] ppm. FAB-MS: *m/z* 494 $[M]^+$, 466 $[M - CO]^+$, 438 $[M - 2CO]^+$. Anal. Found: C, 39.1; H, 3.0; N, 17.0. Calcd for $C_{16}H_{13}BMoN_6O_2S_2$: C, 39.05; H, 2.66; N, 17.07.

Preparation of [MoFe(μ-SCR¹)(CO)₅[HB(pz)₃}]. [Mo(η²-SCR¹)(CO)₂{HB(pz)₃}] (0.50 g, 1.00 mmol) was dissolved in dichloromethane (30 mL) and diiron nonacarbonyl (0.40 g, 1.10 mmol) added. The suspension was stirred for 12 h and then placed in an ultrasonic bath for a further 6 h. The supernatant was decanted from solid biproducts and unreacted [$Fe_2(CO)_9$], concentrated under reduced pressure, and chromatographed (alumina, diethyl ether eluant). The major orange fraction was collected, diluted with hexane, and then concentrated under reduced pressure to ca. 15 mL. Storage at −20 °C provided orange microcrystals. Yield: 0.28 g (44%). IR (CH_2Cl_2): ν(CO) 2051 s, 1982 vs, 1843 br cm^{-1} (lit.[23] IR (CH_2Cl_2): 2058 s, 1985 s, 1859 s cm^{-1}).[23] IR (Nujol): ν(BH) 2489, ν(CO) 2047 s, 1969 vs, 1958 vs, 1839 s cm^{-1}. ^{1}H NMR: δ 2.41 [s, 3 H, CH_3], 6.10, 6.25, 6.33 [t × 3, 3 H, H⁴(pz)], 7.19−7.86 [10 H, H^{3,5}(pz)]. ^{13}C-{^{1}H} NMR: δ 231.8, 226.8, 209.9, 209.7, 208.0 [CO], 144.7, 129.4, 106.0 [C(pz)], 142.9 [C^1(C_6H_4)], 136.6, 135.7 [C^{2,3,5,6}-(C_6H_4)], 105.7 [FeWSC], 21.3 [CH_3] ppm (N.B.: literature values[23] in CD_2Cl_2/CH_2Cl_2). FAB-MS: *m/z* 640 $[M]^+$, 558 $[M - 3CO]^+$, 530 $[M - 4CO]^+$, 502 $[M - Fe(CO)_3]^+$.

Preparation of [Mo(κ²-S₂CR²)(CO)₂{HB(pz)₃}]. [Mo{η²-SCR²)(CO)₂{HB(pz)₃}] (0.20 g, 0.38 mmol) was dissolved in diethyl ether (30 mL) and (i) elemental sulfur (0.20 g, 0.76 mmol) or (ii) methylthiirane (0.03 mL, 0.38 mmol) added. The solutions were stirred for (i) 7 days and (ii) 5 days, respectively. The resulting purple solutions were chromatographed on a water-cooled column loaded with alumina, with diethyl ether as eluant, to obtain purple fractions. Addition of ethanol and concentration of the solutions to minimum volume yielded [Mo-(κ²-S_2CR^2)$(CO)_2${HB(pz)₃}] Yield: (i) 0.15 g (74%); (ii) 0.17 g (80%). IR (CH_2Cl_2): ν(CO) 1951 vs, 1867 s cm^{-1}. IR (Nujol): ν(CO) 1940 vs, 1868 s cm^{-1}. ^{1}H NMR: δ 3.88 [s, 3 H, CH_3], 6.25 [t, 3 H, H⁴(pz)], 6.91, 8.00 [$(AB)_2$, 4 H, C_6H_4], 7.68, 8.16 [d × 2, 6 H, H^{3,5}(pz)]. ^{13}C{^{1}H} NMR: δ 250.4 [S_2C], 222.3 [CO], 163.6 [C^1(C_6H_4)], 145.2, 135.9 [C^{2,3,5,6}(C_6H_4)], 124.8 [C^4(C_6H_4)], 136.8, 113.7, 105.9 [C(pz)], 55.6 [CH_3] ppm. FAB-MS: *m/z* 494

$[M - 2CO]^+$. Anal. Found: C, 39.6; H, 2.7; N, 16.2. Calcd for $C_{19}H_{17}BMoN_6O_3S_2$: C, 41.62; H, 3.13; N, 15.33.

Preparation of [Mo(κ^2-S_2CR^1)(CO)$_2${HB(pz)$_3$}]. [Mo(η^2-SCR^1)(CO)$_2${HB(pz)$_3$}] (0.50 g, 1.00 mmol) was dissolved in diethyl ether (30 mL) and methylthiirane (0.08 mL, 1.0 mmol) added. The solution was stirred for 5 days. Purification of the resulting deep purple solution was achieved by column chromatography (alumina, diethyl ether eluant). The product was recrystallized from ethanol solution at −20 °C. Yield: 0.45 g (85%). IR (CH_2Cl_2): ν(CO) 1953 vs, 1871 s cm^{-1}. IR (Nujol): ν(CO) 1932 vs, 1857 s cm^{-1}. ^{1}H NMR: δ 2.40 [s, 3 H, CH_3], 6.27, 6.63 [t × 2, 3 H, H^4(pz)], 7.23, 7.98 [$(AB)_2$, 4 H, ^3J(AB) = 8.1 Hz, C_6H_4], 7.73, 8.25 [d × 2, 6 H, $H^{3,5}$(pz)]. $^{13}C\{^1H\}$ NMR: δ 249.1 [S_2C], 222.4 [CO], 146.4, 135.9 [$C^{2,3,5,6}(C_6H_4)$], 143.3 [$C^1(C_6H_4)$], 140.5 [$C^4(C_6H_4)$], 129.1, 122.8, 106.3 [C(pz)], 21.7 [CH_3] ppm. FAB-MS: *m/z* 478 $[M - 2CO]^+$. Anal. Found: C, 43.2; H, 3.1; N, 16.4. Calcd for $C_{19}H_{17}BMoN_6O_2S_2$: C, 42.88; H, 3.22; N, 15.79. The tungsten analogue [W(η^2-S_2CR^1)(CO)$_2$-{HB(pz)$_3$}] has been described.[13] N.B.: the reaction of [Mo(≡CR^1)(CO)$_2${HB(pz)$_3$}] with sulfur in refluxing tetrahydrofuran provides [Mo(η^3-S_2CR^1)(═O){HB(pz)$_3$}].[46]

Preparation of [Mo(κ^2-$OSCR^1$)(CO)$_2${HB(pz)$_3$}]. [Mo(η^2-SCR^1)(CO)$_2${HB(pz)$_3$}] (0.50 g, 1.00 mmol) was dissolved in dichloromethane (20 mL) and excess dimethyl(methylthio)-sulfonium tetrafluoroborate (0.39 g, 2.0 mmol) added until no more starting material was observable in the IR spectrum and a red solution had formed. The solution was chromatographed on a column loaded with silica (ca. 20 × 6 cm) using a mixture of dichloromethane and hexane (1:1) as the eluant. The initial red-orange fraction was collected and concentrated under reduced pressure, yielding red crystals of the dichloromethane hemisolvate (^{1}H NMR). Yield: 0.34 g (65%). IR (CH_2Cl_2): ν(CO) 1959 vs, 1855 s cm^{-1}. IR (Nujol): ν(CO) 1946 vs, 1860 s; ν(C−O) 1603 w cm^{-1}. ^{1}H NMR: δ 2.38 [s, 3 H, CH_3], 6.24 [t, 3 H, H^4(pz)], 7.18, 7.83 [$(AB)_2$, 4 H, ^3J(AB) = 8.0 Hz, C_6H_4], 7.73, 8.10 [$H^{3,5}$(pz)]. $^{13}C\{^1H\}$ NMR: δ 251.6 [SOC], 209.7 [CO], 144.9, 136.0, 105.7 [C(pz)], 128.9, 125.4 [$C^{2,3,5,6}(C_6H_4)$], 21.8 [CH_3] ppm. FAB-MS: *m/z* 462 $[M - 2CO]^+$. Anal. Found: C, 42.4; H, 3.4; N, 14.7. Calcd for $C_{19}H_{17}BMoN_6O_3S{\cdot}0.5CH_2Cl_2$: C, 41.92; H, 3.25; N, 15.04.

Preparation of [Mo(κ^2-$SSeCR^2$)(CO)$_2${HB(pz)$_3$}]. [Mo(η^2-SCR^2)(CO)$_2${HB(pz)$_3$}] (0.20 g, 0.40 mmol) was dissolved in tetrahydrofuran (10 mL) and gray selenium (0.04 g, 0.50 mmol) added. Dropwise addition of a solution of lithium triethylborohydride (0.40 mL, 1.0 mol dm^{-3}, 0.40 mmol, Aldrich) resulted in an instantaneous reaction, producing a bright purple solution. After the mixture was stirred for 30 min, the solvent was removed in vacuo and the residue redissolved in diethyl ether (10 mL). Purification via column chromatography (alumina, 15 × 3 cm, diethyl ether eluant) provided an initial bright purple fraction, which was diluted with hexane (20 mL) and concentrated under reduced pressure. Storage at −20 °C resulted in the deposition of dark purple crystals. Yield: 0.20 g (87%). An analytical sample of the dichloromethane monosolvate (^{1}H NMR) was crystallized from a mixture of dichloromethane and hexane. Alternatively, a solution of Li_2Se_2 could be prepared in a separate Schlenk flask from Li[Et_3BH] and selenium and added to give the product in comparable yield. IR (CH_2Cl_2): ν(CO) 1943 vs, 1861 s cm^{-1}. IR (Nujol): ν(CO) 1934 vs, 1861 s cm^{-1}. ^{1}H NMR: δ 3.87 [s, 3 H, CH_3], 6.25 [t, 3 H, H^4(pz)], 6.89, 7.99 [$(AB)_2$, 4 H, C_6H_4, ^3J(AB) = 8.2 Hz], 7.69, 8.20 [d × 2, 6 H, $H^{3,5}$(pz)]. $^{13}C\{^1H\}$ NMR: δ 249.7 [SeSC, ^1J(SeC) = 23 Hz], 223.5 [CO], 163.7 [$C^1(C_6H_4)$], 145.5, 135.9, 105.9 [C(pz)], 138.8 [$C^4(C_6H_4)$], 124.6, 113.9 [$C^{2,3,5,6}(C_6H_4)$], 55.5 [CH_3] ppm. FAB-MS: *m/z* 597 $[M + H]^+$, 568 $[M - CO]^+$, 540 $[M - 2CO]^+$. Anal. Found: C, 35.6; H, 2.0; N, 12.0. Calcd for $C_{19}H_{17}BMoN_6O_3SSe{\cdot}CH_2Cl_2$: C, 35.32; H, 2.82; N, 12.36.

(46) Hughes, A. K.; Malget, J. M.; Goeta, A. E. *J. Chem. Soc., Dalton Trans.* **2001**, 1927.

Preparation of [Mo(κ^2-S_2CR^2)(CO)$_2$(η-C_5H_5)]. [Mo(≡CR^2)-(CO)$_2$(η-C_5H_5)] (0.60 g, 1.80 mmol) was dissolved in dichloromethane (20 mL) and methylthiirane (0.13 mL, 1.8 mmol) added. The initially bright orange solution became deep red over 15 min. A further 0.26 mL (3.6 mmol) of methylthiirane was added and the solution stirred for 4 h. Concentration of the solution and addition of an equal volume of hexane gave a red solution, which was purified by chromatographic separation on silica (15 × 3 cm). Eluting with a mixture of dichloromethane and hexane (1:1) provided a red eluate, the volume of which was reduced to ca. 10 mL in vacuo. Storage at −20 °C yielded purple microcrystals. Yield: 0.61 g (85%). IR (CH_2Cl_2): ν(CO) 1965 vs, 1890 s cm^{-1}. IR (Nujol): ν(CO) 1945 vs, 1859 s cm^{-1}. ^{1}H NMR: δ 3.84 [s, 3 H, CH_3], 5.51 [s, 5 H, C_5H_5], 6.84, 7.88 [$(AB)_2$, 4 H, C_6H_4]. $^{13}C\{^1H\}$ NMR: δ 250.9 [S_2C], 231.9 [CO], 163.4 [$C^1(C_6H_4)$], 137.7 [$C^4(C_6H_4)$], 123.8, 113.5 [$C^{2,3,5,6}(C_6H_4)$], 92.9 [C_5H_5], 55.6 [CH_3] ppm. FAB-MS: *m/z* 406 $[M]^+$, 346 $[M - 2CO]^+$. Anal. Found: C, 44.6; H, 2.8. Calcd for $C_{15}H_{12}MoO_3S_2$: C, 45.01; H, 3.02.

Preparation of [Mo(κ^2-$SSeCR^3$)(CO)$_2${HB(pz)$_3$}] [Mo(η^2-SCR^3)(CO)$_2${HB(pz)$_3$}] (0.20 g, 0.41 mmol) was dissolved in tetrahydrofuran (10 mL) and gray selenium (0.04 g, 0.51 mmol) added. Dropwise addition of a solution of lithium triethylborohydride (0.41 mL, 1.0 mol dm^{-3}, 0.41 mmol, Aldrich) resulted in an instantaneous reaction, producing a bright blue solution. After the mixture was stirred for 1 h, the solvent was removed under reduced pressure. The residue was then redissolved in diethyl ether (10 mL). Purification by column chromatography (alumina, 15 × 3 cm) with diethyl ether as eluant produced a blue initial fraction, which was collected, diluted with hexane (20 mL), and concentrated under reduced pressure. Storage at −20 °C resulted in the deposition of dark blue crystals Yield: 0.21 g (90%). IR (CH_2Cl_2): ν(CO) 1945 vs, 1864 s cm^{-1}. IR (Nujol): ν(CO) 1928 vs, 1857 s cm^{-1}. ^{1}H NMR: δ 6.26 [t, 3 H, H^4(pz)], 7.09 [t, 1 H, $H^4(C_4H_3S)$], 7.56 [d, 1 H, $H^3(C_4H_3S)$], 7.70, 8.18 [d × 2, 6 H, $H^{3,5}$(pz)]. $^{13}C\{^1H\}$ NMR: δ 249.6 [SeSC], 211.3 [CO], 145.5, 135.9, 106.0 [C(pz)], 131.3, 128.8, 124.2 [$C(C_4H_3S)$] ppm. FAB-MS: *m/z* 572 $[M + H]^+$, 516 $[M - 2CO]^+$. Anal. Found: C, 33.4; H, 2.2; N, 14.4. Calcd for $C_{16}H_{13}$-$BMoN_6O_2S_2Se$: C, 33.65; H, 2.29; N, 14.71.

Preparation of [Mo(η^2-$EtSCR^1$)(CO)$_2${HB(pz)$_3$}]BF_4. [Mo(η^2-SCR^1)(CO)$_2${HB(pz)$_3$}] (0.20 g, 0.40 mmol) was dissolved in a mixture of dichloromethane and diethyl ether (1:1, 10 mL) and then treated with a solution of triethyloxonium tetrafluoroborate in dichloromethane (0.40 mL, 1.0 mol dm^{-3}, 0.40 mmol, Aldrich). A slow color change from blue-purple to yellow occurred over a 5 h period, as a yellow product precipitated. The reaction liquor was decanted off and the product washed with diethyl ether (2 × 10 mL) and dried in vacuo. The product could be recrystallized from a mixture of dichloromethane and hexane at −20 °C. Yield: 0.13 g (53%). IR (CH_2Cl_2): ν(CO) 2056 s, 1992 vs cm^{-1}. IR (Nujol): ν(CO) 2050 s, 1973 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.40 [t, 3 H, CH_2CH_3, ^3J(HH) = 7.6], 2.57 [s, 3 H, $C_6H_4CH_3$], 2.83 [q, 2 H, ^3J(HH) = 7.6, SCH_2], 6.45, 6.49, 6.52 [t × 3, 1 H × 3, H^4(pz), ^3J(HH) = 2.3]. 7.33, 7.57, 7.97, 7.99, 7.80, 8.14 [d × 6, 1 H × 6, $H^{3,5}$(pz), ^3J(HH) = 2.3], 7.61, 8.04 [$(AB)_2$, 4 H, C_6H_4, ^3J(AB) = 8.3 Hz]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 248.1 [CS], 219.1 [CO], 148.8 [$C^1(C_6H_4)$], 147.9 [C^4-(C_6H_4)], 145.6, 140.3, 109.6 [s(br) × 3, pz], 136.7, 133.2 [$C^{2,3,5,6}$-(C_6H_4)], 40.4 [SCH_2], 23.9 [$C_6H_4CH_3$], 15.9 [CH_2CH_3] ppm. FAB-MS: *m/z* 531 $[M]^+$, 500 $[M - S]^+$, 475 $[M - 2CO]^+$, 343 $[SMoHB(pz)_3]^+$. Anal. Found: C, 40.8; H, 3.4; N, 14.3. Calcd for $C_{21}H_{22}B_2F_4MoN_6O_2S$: C, 40.94; H, 3.60; N, 13.64.

Preparation of [Mo(η^2-$MeSCR^2$)(CO)$_2${HB(pz)$_3$}]BF_4. [Mo(≡CR^2)(CO)$_2${HB(pz)$_3$}] (0.30 g, 0.60 mmol) was dissolved in dichloromethane (15 mL), forming a bright orange solution. Slow addition of dimethyl(methylthio)sulfonium tetrafluoroborate (0.12 g, 0.60 mmol) resulted in a change in solution color to light brown. While the solution was stirred for 30 min, a yellow solid precipitated. Recrystallization of the crude precipitate from a mixture of propanone and hexane at −20 °C

provided bright yellow microcrystals. Yield: 0.36 g (94%). IR (CH_2Cl_2): ν(CO) 2053 s, 1986 vs cm^{-1}. IR (Nujol): ν(CO) 2055 s, 1988 vs cm^{-1}. FAB-MS: *m*/*z* 533 $[M]^+$, 503 $[M - CO]^+$, 477 $[M - 2CO]^+$, 343 $[M - 2CO - Me - CR^2]^+$. These data may be compared with those for the SEt derivative described above. NMR data were not obtained due to low solubility.

Preparation of [Mo(η^2-MeSCHR^2)(CO)$_2${HB(pz)$_3$}]. [Mo(η^2-CH_3SCR^2)(CO)$_2${HB(pz)$_3$}]BF_4 (0.36 g, 0.60 mmol) was suspended in dichloromethane (15 mL), and a solution of lithium triethylborohydride (0.60 mL, 1.0 mol dm^{-3}, 0.60 mmol, Aldrich) was added dropwise. When the mixture was stirred for 1 h, a dark orange solution formed. The solution was concentrated and chromatographed on alumina (15 × 3 cm) at room temperature using diethyl ether as the eluant. Addition of light petroleum (20 mL) to the initial orange band and concentration under reduced pressure afforded orange microcrystals. An analytical sample of a dichloromethane hemisolvate (^{1}H NMR) was obtained from a mixture of dichloromethane and hexane at −20 °C. Yield: 0.25 g (76%). IR (CH_2Cl_2): ν(CO) 1949 s, 1812 vs cm^{-1}. IR (Nujol): ν(CO) 1941 s, 1806 s cm^{-1}. ^{1}H NMR: δ 2.10 [s, 3 H, SCH_3], 3.86 [s, 3 H, OCH_3], 5.79 [s, 1 H, MoCH], 6.10 [s(br), 3 H, H^4(pz)], 6.98, 7.47 [$(AB)_2$, 4 H, C_6H_4], 7.59−8.10 [m, 6 H, H^{3,5}(pz)]. ^{13}C{^{1}H} NMR: δ 234.8, 229.7 [CO], 158.8 [C^1(C_6H_4)], 146.3, 144.3, 139.7, 135.6 [C^{2,3,5,6}(C_6H_4)], 131.9 [C^4(C_6H_4)], 133.3, 113.6, 105.7 [C(pz)], 72.4 [MoCH], 55.3 [OCH_3], 19.9 [SCH_3] ppm. FAB-MS: *m*/*z* 534 $[M]^+$, 506 $[M - CO]^+$, 478 $[M - 2CO]^+$, 458 $[M - CO - SCH_3]^+$, 428 $[M - C_6H_4OCH_3]^+$. Anal. Found: C, 42.3; H, 3.3; N, 14.6. Calcd for $C_{20}H_{21}BMoN_6O_3S\cdot 0.5CH_2Cl_2$: C, 42.8; H, 3.9; N, 14.6.

Preparation of [Mo{η^2-MeSC(SCMe$_3$)R^2}(CO)$_2${HB(pz)$_3$}]. [Mo(η^2-CH_3SCR^2)(CO)$_2${HB(pz)$_3$}]BF_4 (0.10 g, 0.20 mmol) was suspended in dichloromethane (10 mL) and then treated with 2-methyl-2-propanethiol (0.02 mL, 0.20 mmol) and DBU (0.20 mL, excess). An immediate reaction was observed with the formation of a deep orange solution. After it was stirred for 15 min, the mixture was transferred to a chromatography column loaded with alumina. Elution with diethyl ether provided an orange fraction, from which the solvent was removed under reduced pressure. The residue was recrystallized from a mixture of dichloromethane and light petroleum at −20 °C. Yield: 0.08 g (80%). IR (CH_2Cl_2): ν(CO) 1950 s, 1820 vs cm^{-1}. IR (Nujol): ν(CO) 1950 s, 1831 s cm^{-1}. ^{1}H NMR: δ 1.11 [s, 9 H, CCH_3], 2.68 [s, 3 H, SCH_3], 3.70 [s, 3 H, OCH_3], 6.03−7.95 [m, 13 H, H(pz) and C_6H_4]. ^{13}C{^{1}H} NMR: δ 237.9, 233.6 [CO], 157.9 [C^1(C_6H_4)], 145.4−104.9 [C(pz) and C_6H_4], 55.2 [OCH_3], 51.1 [S*C*Me$_3$], 31.2 [C*C*H$_3$], 23.7 [SCH_3] ppm. FAB-MS: *m*/*z* 622 $[M]^+$, 594 $[M - CO]^+$, 566 $[M - 2CO]^+$, 533 $[M - SCMe_3]^+$, 477 $[M - 2CO - CMe_3]^+$. Anal. Found: C, 46.5; H, 4.2; N, 13.0. Calcd for $C_{24}H_{29}BMoN_6O_3S_2$: C, 46.46; H, 4.71; N, 13.55.

Preparation of [Mo(η^2-MeSCHR^3)(CO)$_2${HB(pz)$_3$}]. [Mo(≡CR^3)(CO)$_2${HB(pz)$_3$}] (0.30 g, 0.70 mmol) was dissolved in dichloromethane (15 mL) and dimethyl(methylthio)sulfonium tetrafluoroborate (0.13 g, 0.70 mmol) added in small quantities, providing in situ a yellow solution of [Mo(η^2-CH_3SCR^3)(CO)$_2$-{HB(pz)$_3$}]BF_4, identified by IR spectroscopy. The solvent was removed and the oily residue suspended in diethyl ether (10 mL). Treatment of this suspension with a solution of lithium triethylborohydride (0.70 mL, 1.0 mol dm^{-3}, 0.70 mmol, Aldrich) resulted in the immediate darkening of the solution color to an intense orange. The supernatant was transferred to a chromatography column (alumina) by cannula filtration. Elution with diethyl ether provided an intense orange eluate, which was subsequently diluted with hexane. Slow concentration of the solution resulted in the precipitation of bright orange crystals. Yield: 0.27 g (82%). IR (CH_2Cl_2): ν(CO) 1957 s, 1818 vs cm^{-1}. IR (Nujol): 1944 s, 1804 s cm^{-1}. ^{1}H NMR: δ 2.10 [s, 3 H, SCH_3], 5.59, 5.75 [s × 2, 1 H, MoCHS], 6.14 [s(br), 3 H, H^4(pz)], 6.82−7.22 [m, 3 H, C_4H_3S], 7.57−7.97 [m, 6 H, H^{3,5}(pz)]. ^{13}C{^{1}H} NMR: δ 235.3, 233.8, 228.8, 226.1 [CO], 146.6−105.7 [C(pz) and C_4H_3S], 21.4, 20.6 [SCH_3] ppm. FAB-MS: *m*/*z* 510 $[M]^+$, 482 $[M - CO]^+$, 454 $[M - 2CO]^+$, 435 $[M - CO, SCH_3]^+$, 406 $[M - 2CO, SCH_3]^+$. Anal. Found: C, 40.7; H, 2.7; N, 15.5. Calcd for $C_{17}H_{17}BMoN_6O_2S_2$: C, 40.18; H, 3.37; N, 16.54.

OM030261S