

Metallathiirenes. 5.¹ Bis- and Tris(methimazolyl)borato Thiocarbamoyl Complexes of Molybdenum(II)

Mark R. St.-J. Foreman,[†] Anthony F. Hill,^{*,†,‡} Never Tshabang,[‡]
Andrew J. P. White,[†] and David J. Williams[†]

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ,
U.K., and Research School of Chemistry, Institute of Advanced Studies,
Australian National University, Canberra, Australian Capital Territory, Australia

Received August 25, 2003

Summary: Thiocarbamoyl complexes $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{H}_n\text{B}(\text{mt})_{4-n}\}]$ ($n = 1, 2$) are obtained from the reactions of $[\text{Mo}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})_2(\text{tmeda})]$ and $\text{Na}[\text{H}_n\text{B}(\text{mt})_{4-n}]$ or via reactions of the salts $\text{Na}[\text{Mo}(\text{CO})_{2+n}\{\text{H}_n\text{B}(\text{mt})_{4-n}\}]$ with Me_2NCSCl . For $n = 2$, the complex displays agostic B–H–Mo coordination in both solution and the solid state.

Chart 1. Thiocarbamoyl (Thiocarboxamide) Coordination

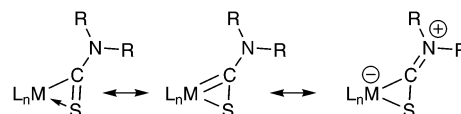
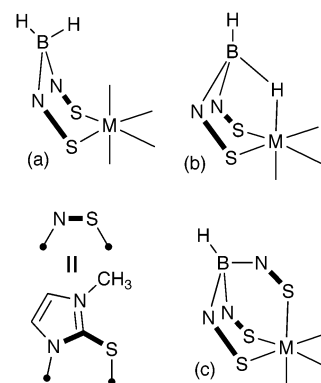


Chart 2. Methimazolyl-Derived Ligands^a



^a Legend: (a) $\kappa^2\text{-S,S}'\text{-H}_2\text{B}(\text{mt})_2$; (b) $\kappa^3\text{-H,S,S}'\text{-H}_2\text{B}(\text{mt})_2$; (c) $\kappa^3\text{-S,S',S}'\text{-HB}(\text{mt})_3$

Introduction

We have reported previously the synthesis of a range of thioaroyl¹ and thiocarbamoyl (thiocarboxamide)² (Chart 1) complexes of molybdenum(II) and tungsten(II), though at the time structural data were not available for these compounds. In unrelated work, our studies on the chemistry of poly(methimazolyl)borates $\text{H}_n\text{B}(\text{mt})_{4-n}$ ($n = 1, 2$; mt = methimazolyl; Chart 2) led to the observation of an unprecedented B–H activation process which resulted in the formation of the first metallaboratrane.³ For such a process to occur, an agostic B–H–Ru interaction was proposed, and we have since begun to explore the organotransition-metal chemistry of these ligands in search of similar B–H activation processes. Herein, we report the synthesis of the molybdenum thiocarbamoyl complexes $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ (**1**) and $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{H}_2\text{B}(\text{mt})_2\}]$ (**2**) and the structural characterization of the latter, which reveals an agostic B–H–Mo interaction.

Results and Discussion

The complex $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ (**1**) could be obtained in high yields by either of the two complementary routes indicated in Scheme 1. Thus, treating $\text{Na}[\text{HB}(\text{mt})_3]$ with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ provides the salt $\text{Na}[\text{Mo}(\text{CO})_3\{\text{HB}(\text{mt})_3\}]$ (**Na-3**). The formation of this air-sensitive salt has been inferred previously in the synthesis of $[\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$;⁴ however, it was not isolated and no data were provided. We find that in the solid state the infrared spectrum (Nujol) contains four strong absorptions (1918, 1871, 1836, and

1786 cm^{-1}) in addition to two weak absorptions at 2063 and 1994 cm^{-1} . From this it may be inferred that the symmetry at molybdenum is substantially less than the ideal C_3 , presumably due to solid-state effects and/or close ion pairing with the counteranion. However, this does not appear to involve the borohydride group, since a sharp, weak absorption is observed at 2338 cm^{-1} . In dichloromethane solution, the spectrum simplifies such that only three CO absorptions are observed at 1930, 1879, and 1800 cm^{-1} in addition to $\nu(\text{BH})$ at 2338 cm^{-1} . Similar data are obtained from thf solutions (2337, 1926, 1876, and 1813 cm^{-1}). These values may be compared with those for $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (in thf: 1901, 1796, 1746 cm^{-1}).⁵ On the basis of infrared data for a large range of complexes of the form $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\text{-}(\text{L})]$ we have suggested that the $\text{HB}(\text{mt})_3$ ligand is particularly electron releasing, relative to other more familiar facial (pseudo)tridentate ligands,⁶ following similar observations by Reglinski for the complexes $[\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\text{L}]$ ($\text{L} = \eta\text{-C}_5\text{H}_5, \text{HB}(\text{pz})_3, \text{HB}(\text{mt})_3$).⁴ It therefore seems likely that this arises in part from a

* To whom correspondence should be addressed at the Australian National University.

[†] Imperial College London.

[‡] Australian National University.

(1) Part 4: Cook, D. J.; Hill, A. F. *Organometallics* **2003**, *22*, 3502.
(2) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **2001**, *20*, 2468.

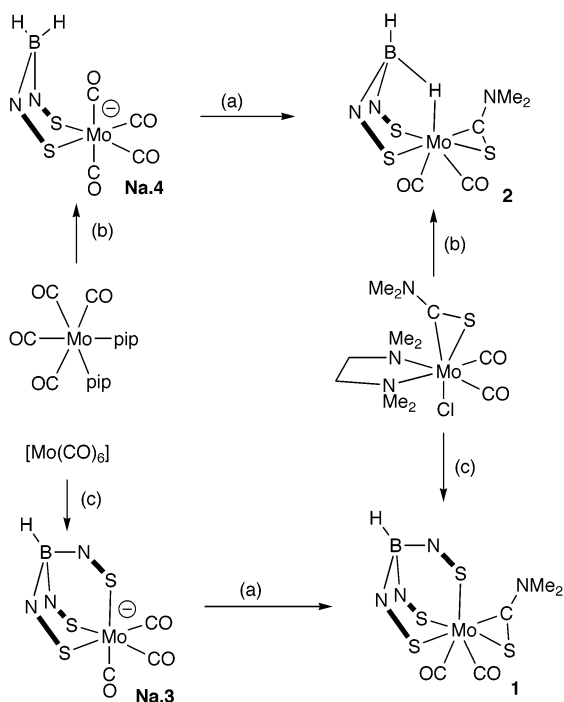
(3) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.

(4) Garner, M.; Lehmann, M.-A.; Reglinski, J.; Spicer, M. D. *Organometallics* **2001**, *20*, 5233.

(5) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Click, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920.

(6) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3831.

Scheme 1. Synthesis of
[Mo(η^2 -SCNMe₂)(CO)₂(H_nB(mt)_{4-n})] (n = 1, 2)



^a Legend: (a) Me₂NCSCl; (b) Na[H₂B(mt)₂]; (c) Na[HB(mt)₃]; pip = piperidine.

π -dative component to the S–M bonding which is less pronounced in the case of the anionic d⁶-octahedral complex **3**[−]. However, it should also be noted that the appearance of three carbonyl absorptions for both salts indicates C_s symmetry consistent with ion-pairing, thus requiring caution in interpretation.

Treating a thf solution of **Na-3** with *N,N*-dimethylthiocarbamoyl chloride results in the immediate formation of the complex **1**. Alternatively, with the preformed thiocarbamoyl complex [Mo(η^2 -SCNMe₂)Cl(CO)₂(tmeda)] as starting material,² treatment with Na[HB(mt)₃] provides **1** in 87% yield. The formulation rests convincingly on spectroscopic and elemental microanalytical data, which conform to precedent for molybdenum thiocarbamoyl complexes.^{2,8} Thus, the dicarbonylmolybdenum unit is confirmed by the appearance of two ν (CO) infrared absorptions (Nujol: 1924 and 1818 cm^{−1}), while the low-field region of the ¹³C{¹H} NMR spectrum contains three resonances (CDCl₃: 240.0, 238.4, 233.1 ppm) attributable to the carbonyl and thiocarbamoyl carbon nuclei. Since resonances for molybdenum thiocarbamoyls span the range 243–251 ppm,^{2,8} we cannot unambiguously differentiate between the CO and CS resonances. However, it seems most likely that the resonance to lowest field is due to the metallathiirene carbon. The MoSCNMe₂ unit appears static on the NMR time scale, giving rise to two resonances for the NMe₂

group in both the ¹³C{¹H} (44.0, 50.1 ppm) and ¹H (δ 3.65, 3.59) NMR spectra. The HB(mt)₃ ligand, however, appears to be undergoing a fluxional process that equilibrates the chemical environments of the three “mt” groups. Thus, a single broad ¹H resonance is observed at 3.72 ppm, which correlates with the ¹³C resonance at 35.0 ppm. Similarly, broad signals due to the mt heterocycle carbon nuclei appear at 160.8, 122.8, and 119.8 ppm. We have discussed previously the inversion of the chirality of the locally C₃-symmetric HB(mt)₃W unit in a range of alkylidyne complexes and surmised that the mechanism involves dissociation of one mt arm.⁶

The dihydrobis(methimazolyl)borate ligand H₂B(mt)₂ has been less studied⁹ than the corresponding tridentate ligand HB(mt)₃. Nevertheless, it is already becoming apparent that it shows an enhanced propensity for the formation of agostic B–H–M interactions, relative to Trofimenko’s pyrazolyl-derived scorpionates.¹⁰ This may be traced in part to the increased chelate size of the H₂B(mt)₂ vs H₂B(pz)₂ (pz = pyrazolyl) ligand, which favors a more concave boat geometry, bringing the bridgehead BH₂ group into closer proximity with the metal. The reaction of [Mo(η^2 -SCNMe₂)Cl(CO)₂(tmeda)] with Na[H₂B(mt)₂] was therefore investigated and found to provide the complex **2** in 80% yield. Although the dicarbonyl formulation is a prerequisite of employing a precursor with only two carbonyl ligands, it was also possible to prepare **2** directly by treating [Mo(pip)₂(CO)₄] (pip = piperidine) sequentially with Na[H₂B(mt)₂] and Me₂NCSCl, involving loss of two CO ligands. No attempt has been made at this point to isolate the metal carbonylate intermediate; however, since the reaction was performed at room temperature, we assume that it is the tetracarbonyl species Na[Mo(CO)₄{ κ^2 S,S’-H₂B(mt)₂}] (**Na-4**) on the basis of the similarity of the infrared spectrum (thf: ν (BH₂) 2336; ν (CO) 1928 vs, 1879 s, ca. 1860 sh, 1817 m cm^{−1}) with that of the precursor piperidine complex (1932 vs, 1892 sh, 1879 s, 1830 m cm^{−1}). Thus, decarbonylation would appear to occur after oxidation to molybdenum(II).

The infrared spectrum of **2** in solution shows only two ν (CO) absorptions (1944, 1849 cm^{−1}) in addition to two BH-associated absorptions at 2306 and 2406 cm^{−1}, which we ascribe to the agostic B–H–Mo and terminal B–H groups, respectively. In the solid state these are also apparent at 2261 and 2407 cm^{−1}, respectively; however, the carbonyl absorptions are subject to solid-state splitting effects. The agostic coordination of one B–H group was also evident from ¹H NMR data, which include a broad resonance at δ −5.04. Resonances attributable to the terminal B–H of H_nB(mt)_{4-n} ligands are characteristically very broad and to low field of

(7) Note that, in the case of Na[Mo(CO)₃(η -C₅H₅)], infrared data in more strongly solvating dmf indicate ion separation (ν (CO) 1895, 1775 cm^{−1}).⁵

(8) (a) Desmond, T.; Lalor, F. J.; O’Sullivan, B.; Ferguson, G. J. *Organomet. Chem.* **1990**, *381*, C33. (b) Ogric, C.; Lehotkay, Th.; Wurst, K.; Jaitner, P.; Kreissl, F. R. *J. Organomet. Chem.* **1997**, *541*, 71. (c) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Butcher, R. J. *Organometallics* **1995**, *14*, 3370. (d) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599. (e) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182.

(9) (a) Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680. (b) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *Dalton* **2000**, 891. (c) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I.; Ortner, K.; Alberto, R. *J. Am. Chem. Soc.* **2000**, *122*, 11240. (d) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **2001**, *632*, 41. (e) Maria, L.; Domingos, A.; Santos, I. *Inorg. Chem.* **2001**, *40*, 6863. (f) Garcia, R.; Domingos, A.; Paulo, A.; Santos, I.; Alberto, R. *Inorg. Chem.* **2002**, *41*, 2422. (g) Alvarez, H. M.; Tran, T. B.; Richter, M. A.; Alyounes, D. M.; Rabinovich, D.; Tanski, J. M.; Krawiec, M. *Inorg. Chem.* **2003**, *42*, 2149. (h) Alvarez, H. M.; Krawiec, M.; Donovan-Merkert, B. T.; Fouzi, M.; Rabinovich, D. *Inorg. Chem.* **2001**, *40*, 5736.

(10) (a) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

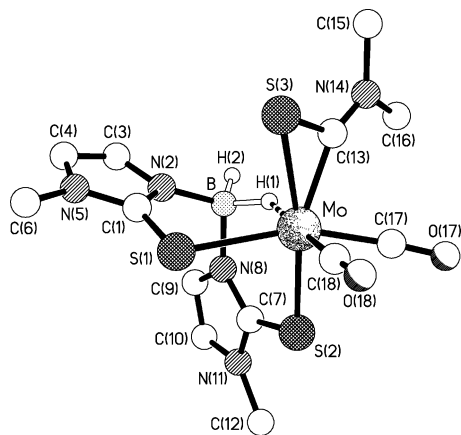


Figure 1. Molecular structure of **2**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**

Mo–S(1)	2.5859(9)	Mo–S(2)	2.4864(10)
Mo–S(3)	2.5730(11)	Mo–C(13)	2.076(3)
Mo–C(17)	1.964(4)	Mo–C(18)	1.937(4)
Mo–H(1)	1.92(4)	S(1)–C(1)	1.707(3)
S(2)–C(7)	1.716(4)	S(3)–C(13)	1.673(4)
C(13)–N(14)	1.302(5)		
H(1)–Mo–C(18)	178.6(12)	H(1)–Mo–C(17)	101.7(12)
C(18)–Mo–C(17)	77.34(18)	H(1)–Mo–C(13)	77.8(11)
C(18)–Mo–C(13)	101.04(16)	C(17)–Mo–C(13)	79.74(16)
H(1)–Mo–S(2)	81.5(12)	C(18)–Mo–S(2)	99.19(12)
C(17)–Mo–S(2)	78.01(13)	C(13)–Mo–S(2)	145.68(12)
H(1)–Mo–S(3)	96.1(12)	C(18)–Mo–S(3)	83.38(13)
C(17)–Mo–S(3)	110.94(13)	C(13)–Mo–S(3)	40.42(11)
S(2)–Mo–S(3)	171.05(4)	H(1)–Mo–S(1)	87.8(12)
C(18)–Mo–S(1)	93.46(12)	C(17)–Mo–S(1)	160.64(13)
C(13)–Mo–S(1)	119.06(11)	S(2)–Mo–S(1)	86.86(4)
S(3)–Mo–S(1)	84.41(4)	N(2)–B–N(8)	110.5(3)

SiMe₄, and in the case of **2** this was not unequivocally observed. The ¹³C{¹H} NMR spectrum of **2** suggests either that the molecule has a plane of symmetry or that a fluxional process operates to equilibrate both the carbonyl and the mt environments. The static structure found in the solid state (vide infra) has no element of symmetry, and accordingly, it seems most likely that fluxional behavior is being encountered, although the appearance of two sharp resonances (¹H and ¹³C) for the NMe₂ group indicates that this does not involve C–NMe₂ bond rotation. ¹¹B NMR spectra prove at present somewhat uninformative, in that both **1** and **2** give a single absorption at –2.43 and –8.00 ppm, respectively. ¹¹B data were not reported for the complex [Mo(η-C₃H₅)(CO)₂{HB(mt)₃}];⁴ however, we have observed a single resonance for this complex at –2.13 ppm. This resonance and that for **1** lie within the narrow range (–2.07 to –2.67 ppm) found for the complexes [W(≡CR)(CO)₂{HB(mt)₃}] (R = NⁱPr₂, C₆H₄Me-4, C₄H₃S-2, C≡CCMe₃, C₆H₃Me₂-2,6),⁶ suggesting that this parameter is not likely to be particularly informative, the boron being too remote from the metal center in the κ³S,S,S' coordination mode to respond to chemical differences.

The molecular structure of **2** (Figure 1, Table 1) was confirmed by an X-ray crystallographic study. If the thiocarbamoyl is considered as a single group, the coordination around molybdenum can be considered as approximating to pseudo-octahedral. The bonding between molybdenum and the thione donors is remarkable in that there is a large difference (100σ) between the two Mo–S bond lengths, presumably reflecting the

difference between the trans influences of carbonyl and thiocarbamoyl ligands. Differences of ca. 0.1 Å for Mo–S bond lengths have been observed previously: for example, for sulfur trans to carbonyl vs sulfur trans to allyl.⁴ A very similar effect occurs for the Mo–N bonds in the related complex [Mo(η²-SCNMe₂)(CO)₂{B(pz)₄}].^{8a} In light of these observations, one might cautiously suspect that the fluxionality apparent in solution involves dissociation of the mt group trans to the carbonyl ligand (S1). This weakening of the Mo–S(1) bond also appears to allow more flexibility in the geometry of this mt heterocycle, in that its mean plane lies at an angle of ca. 27° to that defined by Mo, S(1), and B. In contrast, for the more strongly bound mt group based on S(2), the corresponding angle is only ca. 4°. The Mo–B–S(1) and Mo–B–S(2) planes subtend an angle of ca. 91°, as expected for octahedral coordination at molybdenum.

The B–H hydrogen atoms, including that involved in agostic bonding to molybdenum, were located and refined freely to provide B–H(1) and Mo–H(1) separations of 1.22(4) and 1.92(4) Å, respectively, the former being marginally elongated relative to the terminal B–H(2) bond (1.05(5) Å). Agostic B–H–Mo interactions have been initially crystallographically confirmed in the dihydrobis(pyrazolyl)borato complexes [Mo(η-C₃H₅)(CO)₂{H₂B(pzMe₂)₂}]¹¹ and more recently in the complexes [Mo(η³-C₈H₁₁)(CO)₂{κ³-H₂B(pzMe₂)₂}],¹² [Mo(η³-C₄H₇)(CO)₂{κ³-H₂B(pzBr₃)₂}], and Mo(η³-C₄H₇)(CO)₂{κ³-H₂B(pzMe₂)₂}].¹³ The thiocarbamoyl shows a comparatively long Mo–S(3) separation of 2.5730(11) Å, while the Mo–C(13) separation of 2.076(3) Å suggests at best modest multiple-bond character. The C(13)–S(3) bond length of 1.673(4) Å, however, indicates considerable multiple-bond character and is significantly shorter (8σ and 11σ) than for the mt thione groups (1.707(3) and 1.716(4) Å). The C(13)–N(14) bond length of 1.302(5) Å is consistent with the trigonal nitrogen adopting a π-dative role toward the thiocarbamoyl carbon, being noticeably shorter than N–C bond lengths within the mt heterocycles.¹⁴ No significant intermolecular interactions are apparent.

Experimental Section

Conventional Schlenk and vacuum-line techniques were employed with the exclusion of air. The salt Na[HB(mt)₃] has been obtained by heating solid Na[BH₄] and Hmt as a melt.¹⁵ Samples prepared in this way are prone to contamination with Hmt and Na[H₂B(mt)₂] (each of which react with the molybdenum precursors) and often brown due to charring which results from inhomogeneous heating. For this study, our alternative procedure³ was employed, which makes use of refluxing xylenes as a means of moderating the reaction, controlling temperature, and maintaining homogeneity. This method provides colorless samples of high purity and a means

(11) Kosky, C. A.; Ganis, P.; Avitabile, G. *Acta Crystallogr.* **1971**, B27, 1859.

(12) Chowdhury, S. K.; Samanta, U.; Puranik, V. G.; Sarkar, A. *Organometallics* **1997**, 16, 2618.

(13) Rheingold, A. L.; Liable-Sands, L. M.; Incarvito, C. L.; Trofimenko, S. *Dalton* **2002**, 2297.

(14) A survey of structurally characterized thiocarbamoyl complexes of molybdenum is tabulated in the Supporting Information to provide a context for geometric parameters derived for **2** which fall within precedented ranges.

(15) (a) Soares, L. F.; Silva, R. M.; Smees, J.; Darensbourg, M. *Inorg. Synth.* **2002**, 33, 199. (b) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.

of easily recovering unreacted Hmt for future use. The thiocarbamoyl complex $[\text{Mo}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})_2(\text{tmeda})]_2$ has been described previously, and its reactions may be conveniently monitored (solution IR) by disappearance of the peaks at 1921 and 1811 cm^{-1} (thf). Other reagents were used as received from commercial sources, with the exception of solvents, which were distilled from appropriate drying agents under nitrogen. Elemental microanalytical data were obtained commercially from the University of North London Analytical Service.

Synthesis of $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$. A mixture of 2-mercapto-1-methylimidazole (5.20 g, 45.6 mmol), sodium borohydride (0.72 g, 19.0 mmol), and anhydrous tetrahydrofuran (240 mL) was heated under reflux under a N_2 atmosphere for 7 h until all the NaBH_4 had dissolved. The mixture was cooled and then evaporated to dryness using a rotary evaporator. Toluene (120 mL) was added to the residue, and the resulting suspension was then heated with stirring to the point of reflux and the hot solvent removed by decantation. The residue was once again suspended in toluene (120 mL) and brought to reflux before the solid was isolated by filtration and dried in air. Yield: 4.52 g (89%). NMR (CDCl_3 , 25 °C): ^1H , δ 3.40 (s, 6 H, CH_3), 6.70, 6.96 ((AB) $_2$, 4 H, $^3J_{\text{AB}} = 1.8$ Hz, NCHCHN). FAB-MS (negative ion): m/z (%) 239 (70) $[\text{M} - \text{Na}]^-$, 114.8 (100) $[\text{Hmt}]^-$.

Synthesis of $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ (1). (a) A suspension of $[\text{Mo}(\text{CO})_6]$ (2.75 g, 10.4 mmol) in acetonitrile (60 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure, and then thf (50 mL) was added, followed by $\text{Na}[\text{HB}(\text{mt})_3]$ (4.08 g, 10.4 mmol). The mixture was stirred for 50 min, cooled in an ice bath, and then treated with *N,N*-dimethylthiocarbamoyl chloride (1.29 g, 10.4 mmol). The ice bath was removed and the mixture stirred for 2 h and then freed of volatiles under reduced pressure. The residue was extracted with dichloromethane (2×100 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was concentrated in vacuo to ca. 50 mL and then diluted with light petroleum to precipitate a brown-red solid. The crude product was recrystallized from a mixture of dichloromethane and light petroleum at -20 °C. Yield: 5.37 g (9.08 mmol, 87%).

(b) A mixture of $[\text{Mo}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})_2(\text{tmeda})]_2$ (0.993 g, 2.54 mmol) and $\text{Na}[\text{HB}(\text{mt})_3]$ (1.05 g, 2.80 mmol) in thf (100 mL) was heated under reflux for 5 min and then freed of volatiles under reduced pressure. The residue was extracted with dichloromethane (2×30 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was diluted with light petroleum (30 mL) and the total solvent volume reduced in vacuo to ca. 30 mL and cooled to -20 °C overnight. The resulting crystals were isolated by decantation and dried in vacuo. Yield: 1.31 g (2.21 mmol, 87%). The complex is mildly air sensitive in the solid state. IR (cm^{-1}): in THF, 2396 w ($\nu(\text{BH})$), 1927 s, 1833 vs ($\nu(\text{CO})$); in CH_2Cl_2 , 2407 w ($\nu(\text{BH})$), 1932 s, 1837 vs ($\nu(\text{CO})$); in Nujol, 2421 sh, 2385 m ($\nu(\text{BH})$), 2311,¹⁶ 2210,¹⁶ 1924 vs, 1820 vs ($\nu(\text{CO})$), 1560 s, 1321 w, 1299 w, 1205 vs, 1155 s, 1121 w, 1088 w, 1043 w, 1012 w, 919 m, 825 m, 775 s. FAB-MS (nba matrix): m/z (%) 593 (18) $[\text{M}]^+$, 563 (17) $[\text{M} - \text{CO}]^+$, 537 (72) $[\text{M} - 2\text{CO}]^+$. NMR (CDCl_3 , 25 °C): ^1H , δ 3.59, 3.65 (s \times 2, 3 H \times 2, $\text{N}(\text{CH}_3)_2$), 3.72 (s br, 9 H, (mt)NCH $_3$), 6.83–8.84 (m, 6 H, NCH=CH);

^{11}B , δ -2.37 ; $^{13}\text{C}\{^1\text{H}\}$, δ 240.0, 238.4, 233.1 (MoCO and MoCS), 160.8 (br, N_2CS), 122.8 (br, NCH=CH), 119.8 (NCH=CH), 50.1 (SCNCH $_3$ correlates with δ_{H} 3.65), 44.0 (SCNCH $_3$ correlates with δ_{H} 3.59), 35.0 (mt-NCH $_3$ correlates with δ_{H} 3.72) (assignments confirmed by $^1\text{H}/^{13}\text{C}$ correlation and DEPT measurements). Anal. Found: C, 30.71; H, 2.73; N, 13.86. Calcd for $\text{C}_{17}\text{H}_{22}\text{BN}_7\text{O}_2\text{S}_4\text{Mo} \cdot 1.5\text{CH}_2\text{Cl}_2$: C, 30.91; H, 3.51; N, 13.64. Dichloromethane of solvation was confirmed by ^1H NMR integration.

Synthesis of $[\text{Mo}(\eta^2\text{-SCNMe}_2)(\text{CO})_2\{\text{H}_2\text{B}(\text{mt})_2\}]$ (2). (a) A suspension of $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ (0.807 g, 2.13 mmol) and $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$ (0.650 g, 2.48 mmol) in thf (40 mL) was stirred for 20 min, during which time the color faded slightly. The resulting solution was then treated with *N,N*-dimethylthiocarbamoyl chloride (0.264 g, 2.14 mmol), resulting in the immediate formation of a red solution. Stirring was continued for 1 h and then the solvent removed in vacuo. The residue was extracted (2×40 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was concentrated to ca. 20 mL and then diluted with light petroleum (30 mL) and cooled (-20 °C) to complete crystallization of the red product. Yield: 0.844 g (1.76 mmol, 82%).

(b) A mixture of $[\text{Mo}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})_2(\text{tmeda})]_2$ (1.00 g, 2.36 mmol) and $\text{Na}[\text{HB}(\text{mt})_2]$ (0.77 g, 2.94 mmol) in thf (100 mL) was heated under reflux for 2 min, resulting in a pale precipitate (NaCl). The mixture was cooled and then freed of volatiles under reduced pressure. The residue was treated as in (b) above to provide 2. Yield: 0.906 g (1.89 mmol, 80%). The complex is mildly air sensitive in the solid state. IR (cm^{-1}):

in THF, 1946, 1853 ($\nu(\text{CO})$); in CH_2Cl_2 , 2406 w ($\nu(\text{BH})$), 2306 m ($\nu(\text{BHM})$), 1944 vs, 1849 vs ($\nu(\text{CO})$); in Nujol, 2407 m ($\nu(\text{BH})$), 2261 m ($\nu(\text{BHM})$), 1958 w, 1924 vs, 1839 w, 1819 vs ($\nu(\text{CO})$), 1555 s, 1301 w, 1225 w, 1194 s, 1170 m, 1105 m, 1037 w, 931 m, 826 m. FAB-MS (nba matrix): m/z (%) 478 (42) $[\text{M}]^+$, 453 (75) $[\text{M} - \text{CO}]^+$, 423 (46) $[\text{M} - 2\text{CO}]^+$. NMR (CDCl_3 , 25 °C): ^1H , δ -5.04 (q br, hhw = 0.85 ppm = 230 Hz, $J(\text{BH}) \approx 90$ Hz), 3.59 (s, 6 H, (mt)NCH $_3$), 3.69, 3.72 (s \times 2, 3 H \times 2, SCNCH $_3$), 6.63 (d, 4 H, NCH=CH, $^3J(\text{HH}) = 1.8$ Hz); ^{11}B , δ -8.00 ; $^{13}\text{C}\{^1\text{H}\}$, δ 246.1 (MoCS), 233.4 (MoCO), 162.8 (br, $\text{N}_2\text{C}=\text{S}$), 122.4, 120.8 (NCH=CH), 50.5, 45.5 ($\text{N}(\text{CH}_3)_2$), 35.0 (mt-NCH $_3$). Anal. Found: C, 32.70; H, 3.78; N, 14.41. Calcd for $\text{C}_{13}\text{H}_{18}\text{BN}_5\text{O}_2\text{S}_3\text{Mo}$: C, 32.58; H, 3.79; N, 14.61. Crystal data for 2: $\text{C}_{13}\text{H}_{18}\text{BMoN}_5\text{O}_2\text{S}_3$, $M_r = 479.25$, monoclinic, $P2_1/n$ (No. 14), $a = 7.3714(8)$ Å, $b = 15.5380(13)$ Å, $c = 17.230(3)$ Å, $\beta = 90.847(11)^\circ$, $V = 1973.3(4)$ Å 3 , $Z = 4$, $D_c = 1.613$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 0.999$ mm^{-1} , $T = 293$ K, orange/red blocks; 3476 independent measured reflections, F^2 refinement, $R1 = 0.033$, $wR2 = 0.066$, 2735 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$), $2\theta_{\text{max}} = 50^\circ$, 238 parameters, CCDC 224389.

Acknowledgment. We are grateful to Professor J. L. Templeton for helpful insights. We gratefully acknowledge the financial support of the EPSRC (U.K.) and the Australian Research Council.

Supporting Information Available: Full details of the crystal structure determination of 2, including positional and thermal parameters and thermal ellipsoid plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM030584O

(16) Similar weak bands have been observed but not assigned in the solid-state spectra of $[\text{W}(\equiv\text{CR})(\text{CO})_2\{\text{HB}(\text{mt})_3\}]_2$.