DOI: 10.1002/ejic.200700471

Poly(methimazolyl)borate Alkyne Complexes of Molybdenum and Tungsten

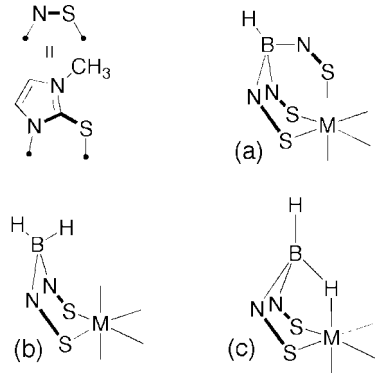
Anthony F. Hill,*[a] Never Tshabang,[a] and Anthony C. Willis[a]

Keywords: Alkyne / Molybdenum / Tungsten / Methimazolylborates / Scorpionates

Synthetic routes are reported to complexes of the form [MI(alkyne)(CO){$H_nB(mt)_{4-n}$}] (mt = methimazolyl; n = 1, 2; M = Mo, W) through the reactions of alkyne complexes $[WI_2(HC{\equiv}CSiMe_3)_2(CO)_2]$ or $[MI_2(RC{\equiv}CR)_2(NCMe)(CO)]$ (M = Mo, W; R = Me, Ph) with the salts $Na[H_nB(mt)_{4-n}]$. The derivative [MoI(PhC≡CPh)(CO){$HB(mt)_3$}] reacts with $Na[HB(mt)_3]$ to provide the complex [Mo(PhC≡CPh)(CO){$HB(mt)_3$}$_2$] in which the two $HB(mt)_3$ ligands adopt different non-interconverting coordination modes, κ^3-*S*,*S*′,*S*′′ and κ^1-*S*.

Introduction

Alkyne complexes of divalent molybdenum or tungsten[1] in which the metal centres are either ligated by dithiocarbamato[2] or tris(pyrazolyl)borato ligands,[3] display a rich chemistry that has been extensively developed by Templeton and co-workers. Tris- and bis(methimazolyl)borate ligands, discovered respectively by Reglinski[4] and Parkin[5] (Scheme 1), might be superficially considered as hybrids of these two classes of more familiar ligand, being anionic and presenting either three or two sulfur donors. Accordingly, a similarly rich chemistry might also be anticipated for alkyne complexes of Mo^{II} and W^{II} bearing these ligands. In passing one might also note that alkynes are recognised substrates for the molybdenum site of nitrogenase,[6] generating interest in the nature of alkyne binding to molydbenum complexes that feature a sulfur-rich coordination sphere. It is, however, increasingly found to be the case that methimazolylborato ligands may demonstrate quite unique coordination features distinct from those offered by dithiocarbamates or poly(pyrazolyl)borates. Whilst the $HB(mt)_3$ ligand displays geometrical flexibility associated with the intrinsically chiral but readily invertible C_3-[3.3.3]bicyclo $HB(mt)_3M$ cage,[7] the $H_2B(mt)_2$ chelate has an emerging propensity for 3-centre, 2-electron B–H–metal interactions (κ^3-*H*,*S*,*S*′ coordination),[8–11] behaviour that has on occasion also been demonstrated by the $HB(mt)_3$ ligand.[11b,12–15] Both of these features are manifest in the chemistry to be described, which concerns the synthesis of the first alkyne complexes ligated by poly(methimazolyl)borates.



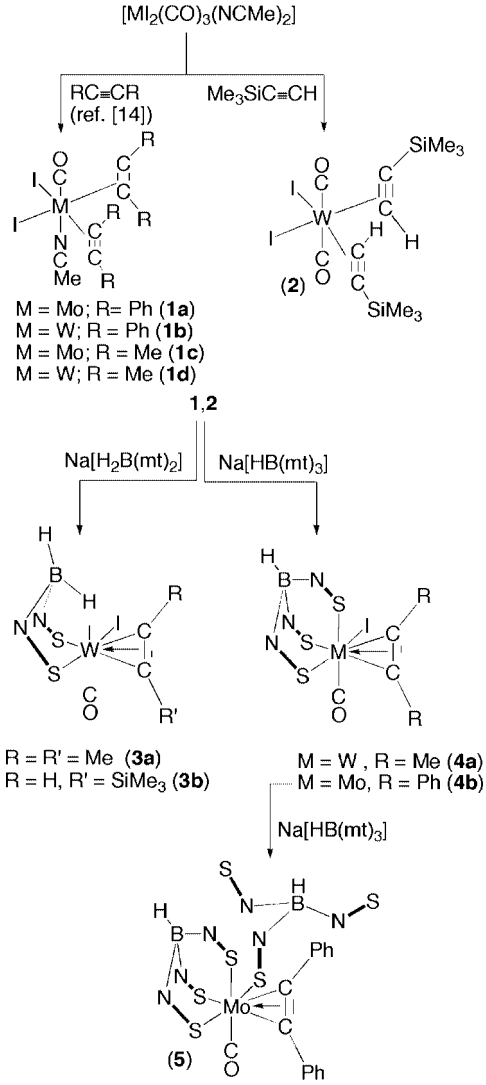
Scheme 1. Poly(methimazolyl)borato coordination. (a) κ^3-*S*,*S*′,*S*′′; (b) κ^2-*S*,*S*′; (c) κ^3-*H*,*S*′,*S*′′.

Results and Discussion

Baker's versatile complexes $[MI_2(PhC{\equiv}CPh)_2(NCMe)(CO)_2]$ [M = Mo (**1a**), W (**1b**)] which arise from the facile reactions of tolane with $[MI_2(NCMe)_2(CO)_3]$[1b,16] appeared to be suitable substrates for the introduction of poly(methimazolyl)borate ligands (Scheme 2). However, we find that in attempting to extend this protocol to the synthesis of a tungsten complex of ethynyltrimethylsilane, nitrile substitution occurs exclusively to provide the dicarbonyl complex $[WI_2(HC{\equiv}CSiMe_3)_2(CO)_2]$ (**2**). The formulation followed from spectroscopic data and was confirmed by a crystallographic study, the results of which are summarised in Figure 1. Considering each alkyne as a single ligand, the geometry at tungsten (which lies on a crystallographic twofold axis that bisects I1–W1–I1′; symmetry generated atoms in grey), may be described as pseudo-octahedral. The geometry adopted is optimal for satisfying the π-acidic character of the carbonyl ligands and both the π-acid and π-donor functions of the alkynes. The two carbonyl ligands are bent

[a] Research School of Chemistry, Institute of Advanced Studies, Australian National University,
Canberra, Australian Capital Territory, Australia
Fax: +61-2-61253-216
E-mail: a.hill@anu.edu.au

away from the alkyne ligands towards the π-basic iodide ligands [C1–W1–C1′ 162.5(3)°, C1–W1–I1 82.6(2), 84.3(2) °], however, if we loosely denote this as the *z*-axis ($d^4 = d^0_{xy}d^2_{xz}d^2_{yz}$) then each of the occupied d_{xz} and d_{yz} orbitals are able to retrodatively interact with both carbonyls and *one* π* orbital from each alkyne. This leaves the d_{xy} orbital vacant for donation from an occupied π-orbital of each alkyne.[1] Accordingly, the tungsten-alkyne bond lengths indicate a degree of W–C multiple bonding although these are significantly different (10σ), presumably due to the relative steric requirements of the silyl and hydrogen alkyne substituents.



Scheme 2. Synthesis of alkyne poly(methimazolyl)borate complexes.

The complexes **1d** and **2** react with the salt Na[H_2B-(mt)$_2$][8a] to provide the monoalkyne complexes [WI(RC≡CR′)(CO){H_2B(mt)$_2$}] [R = R′ = Me (**3a**); R = H, R′ = $SiMe_3$ (**3b**)]. Simple 18-electron rule arguments require that the H_2B(mt)$_2$ anion (charged formalism) provide a minimum of 6 valence electrons were the alkyne to provide the maximum 4 valence electrons on offer. Thus a 3-centre 2-electron B–H–W interaction must be invoked and its occurrence is substantiated both by ^{1}H NMR and IR spectroscopy: For **3b**, a high field resonance at δ_H = –5.10 ppm in the ^{1}H NMR spectrum and an infrared absorption at 2261 cm^{-1} (CH_2Cl_2) provide spectroscopic signatures for B–H–W interactions and may be compared with values of δ_H = –5.05 ppm and 2306 cm^{-1} for the structurally characterised complex [Mo(η^2-SCNMe$_2$)(CO)$_2${κ^3-*H*,*S*,*S*′-H_2B(mt)$_2$}].[8a] The complex [W(CO){H_2B(mt)$_2$}$_2$] which features both bidentate (κ^2-*S*,*S*′) and tridentate (κ^3-*H*,*S*,*S*′) coordinated H_2B(mt)$_2$ ligands[8b] has δ_H = –3.58 ppm and ν_{BHW} = 2246 cm^{-1} for the latter mode of coordination. For **3a** only one mt environment is observed on the ^{1}H and ^{13}C NMR timescales consistent with a stereochemically non-rigid molecule. For **3b**, however, whilst fluxionality is suggested by the ^{1}H NMR spectrum (300 MHz), distinct "mt" environments are resolved in the ^{13}C{^{1}H} NMR spectrum (75 MHz) at room temperature. Presumably, hemilability on the part of the B–H–W interaction allows access to a five coordinate stereochemically non-rigid intermediate.[7]

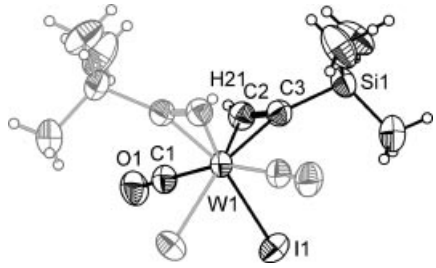


Figure 1. Geometry of **2** in a crystal of **2**·$(CH_3OH)_2$ (50% displacement ellipsoids; a rotation axis bisects I1–W–I1′; symmetry-generated atoms in grey). Selected bond lengths [Å] and angles (deg.): W1–I1 2.8547(4), W1–C1 2.081(5), W1–C2 2.099(6), W1–C3 2.148(5), Si1–C3 1.874(5), C2–C3 1.271(8), C3–W1–I1 88.43(14), C3–W1–C2 34.8(2), I1–W1–C2 89.74(15), C3–W1–C1 111.5(2), I1–W1–C1 84.33(15), C2–W1–C1 77.0(2).

In a similar manner to the syntheses of **3** a smooth reaction occurs between Na[HB(mt)$_3$] and **1d** to provide the complex [WI(CO)(MeC≡CMe){HB(mt)$_3$}] (**4a**) in moderate yields. The ^{1}H NMR spectroscopic data for **4a** suggest that there is only one species present in solution and since the complex has two stereogenic components, i.e., the chiral δ/λ C_3-HB(mt)$_3$Mo cage and *R*/*S*-MoI(CO)(PhCCPh) pyramid, it may be assumed that a racemate of enantiomers (δ*R*/λ*S* or δ*S*/λ*R*) arises through facile inversion of the HB(mt)$_3$W cage. Similarly facile inversion has been noted for the alkylidyne complexes [W(≡CR)(CO)$_2${HB(mt)$_3$}] (R = C_6H_4Me-4, N*i*Pr$_2$), and purported to proceed via a dissociative (mt) mechanism.[7] The alkyne ligand in **4a** gives rise to two ^{13}C resonances (δ_C 207.4, 206.9 ppm) (restricted rotation on the ^{13}C NMR timescale) in the region characteristic of 4-electron (σ+π) donor alkyne coordination.[1]

Although the corresponding molybdenum tolane complex [MoI(CO)(PhC≡CPh){HB(mt)$_3$}] (**4b**) could be similarly prepared by employing a 1:1 stoichiometry of **1a** and Na[HB(mt)$_3$], invariably a small amount of poorly soluble

material was formed as a side product. The yield of this could be maximised by the use of two equivalents of $Na[HB(mt)_3]$ or, alternatively, the reaction of $Na[HB(mt)_3]$ with isolated **4b**. The poor solubility of the side product compromised the acquisition of spectroscopic data other than from FAB-MS and IR spectra. Mass spectrometry indicated the gross composition $[Mo(CO)(\eta\text{-}PhC{\equiv}CPh)\{HB(mt)_3\}_2]$ (**5**) but gave no indication of the connectivity of this apparently 20–22 electron complex. The geometry was eventually established by crystallographic analysis, the results of which are summarised in Figure 2. The molecular geometry of the mononuclear complex is based on a pseudo-octahedral molybdenum centre that bears one $HB(mt)_3$ ligand coordinated in a conventional tridentate manner (κ^3-*S*,*S*′,*S*′′), whilst the second binds to molybdenum through a single sulfur donor (κ^3-*S*). Monodentate $HB(mt)_3$ coordination is unprecedented in transition metal chemistry, however we have previously identifed this mode of coordination in the tin derivative $Ph_3Sn\{HB(mt)_3\}$.[17] Copious structural data exist for molybdenum alkyne complexes,[18] however consideration of the parameters of **5** with those for the exemplary complexes $[Mo(PhC{\equiv}CPh)(\eta\text{-}C_5H_5)_2]$ (a 2-electron alkyne),[19] $[Mo(MeC{\equiv}CMe)_2(S_2Cpyr)_2]$ (a homoleptic sulfur donor set)[20] and $\{Mo(PhC{\equiv}CPh)(CO)_2[HB(pz')_3]\}^{n+}$ (n = 0, 1; pz′ = 3,5-dimethylpyrazol-1-yl, a redox pair),[21] reveals that the alkyne has particularly short Mo–C separations coupled with a long C–C bond. Such geometric features are typically associated with alkynes acting as "4-electron" σ+π donors to an octahedral d^4-metal centre. However, it is noteworthy that the ν_{CO} value for **5** (1790 cm^{-1}) is remarkably low and indicative of an exceptionally π-basic molybdenum centre. This contrasts dramatically with the value of 1960 cm^{-1} for the alkyne complex $[W(\eta\text{-}HC{\equiv}CH)(CO)(S_2CNEt_2)_2]$.[22] In a similar manner the neutral cyclopentadienone and vinyl ketene complexes $[W(CO)(S_2CNEt_2)_2(L)]$ (L = O=C-$(C_8H_{12})_2$,[23] $H_2C{=}CHCH{=}CO$[24]) have ν_{CO} = 1921 and 1960 cm^{-1}, whilst even the anionic complex $[W(CO)(SPh)(\kappa^2\text{-}S_2C_2Me_2)_2]^-$ has ν_{CO} = 1933 cm^{-1} although the oxidation state of the tungsten in this sulfur rich complex is open to debate.[25] Thus the very low ν_{CO} value for **5** is quite exceptional such that the geometric features of the alkyne may be as much to do with conventional retrodonation into the alkyne π* orbital as with depletion of the C≡C π-bonding orbitals.

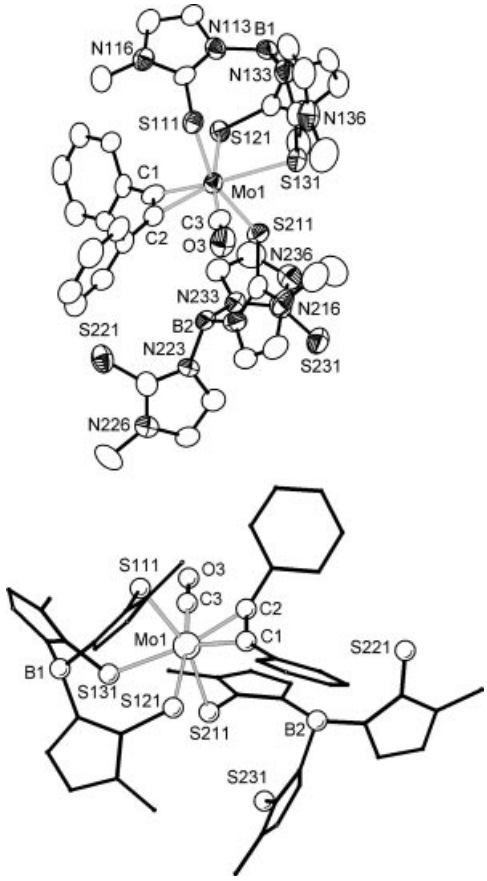


Figure 2. Top: Molecular geometry of **5**·$(CH_2Cl_2)_2$ (40% displacement ellipsoids, hydrogen atoms bound to carbon omitted). Bottom: Alternative simplified view. Selected bond lengths [Å] and angles (deg.) Mo1–S111 2.440(2), Mo1–S121 2.602(2), Mo1–S131 2.637(2), Mo1–S211 2.464(2), Mo1–C1 2.052(8), Mo1–C2 2.051(7), C1–C2 1.306(10), S111–Mo1–S121 93.74(6), S111–Mo1–S131 85.59(7), S121–Mo1–S131 85.39(6) S121–Mo1–S211 82.25(6), S131–Mo1–S211 75.97(7), C1–Mo1–C2 37.1(3), Mo1–S111–C112 107.0(2), Mo1–S121–C122 110.0(3), Mo1–S131–C132 107.7(2), Mo1–S211–C212 109.7(3), Mo1–C1–C11 148.7(6), Mo1–C2–C21 145.7(6).

Conclusions

Synthetic routes to lead compounds for the study of alkyne derivatives of molybdenum and tungsten ligated by methimazolylborate ligands $H_nB(mt)_{4-n}$ (n = 1,2) have been developed. In the case of dihydrobis(methimazolyl)borate derivatives, the propensity for 3c–2e B–H–metal interactions is manifest. In this respect, the behaviour of the $H_2B(mt)_2$ ligand is reminiscent of that first noted by Trofimenko, Kosky and Cotton[26] for the corresponding $H_2B(pzMe_2)_2$ ligand ($pzMe_2$ = 3,5-dimethylpyrazol-1-yl). However the inclusion of an extra atom in each of the arms of the $H_2B(mt)_2$ ligand (cf $pzMe_2$) results in an increased propensity for such 3c–2e B–H–metal interactions. In all cases, the alkyne coordination may be described as "4-electron," even for complex **5**, which has two alternative appended potential donors.

Experimental Section

All manipulations of air-sensitive compounds were carried out under dry and oxygen-free nitrogen using standard Schlenk and vacuum line techniques, with dried and degassed solvents. NMR spectra were obtained at 25 °C with a Varian Gemini spectrometer 300BB (^1H at 300.75 MHz, ^{13}C at 75.4 MHz, ^{11}B at 96.2 MHz). Mass Spectra were obtained with a ZAB-SEQ4F spectrometer (FAB, ACPI or ESI techniques) using matrices of either 3-nitrobenzyl alcohol (NBA) or acetonitrile and methanol (ESI). The elemental microanalysis was carried out by the microanalytical service of the Australian National University. The compounds $Na[H_2B$-

$(mt)_2]$,[8a] Na[HB(mt)$_3$],[27] $[MI_2(CO)_3(NCMe)_2]$[16a] and $[MoI_2(CO)(NCMe)(\eta^2\text{-PhC}{\equiv}\text{CPh})_2]$[16b] were prepared according to the indicated published procedures. Other reagents were used as received from commercial sources.

Synthesis of $[WI_2(CO)_2(\eta^2\text{-HC}{\equiv}\text{CSiMe}_3)_2]$ (2): Two equivalents of cold ethynyltrimethylsilane (0.70 g, 3.88 mmol) were added to a solution of $[WI_2(CO)_3(NCMe)_2]$ (1.50 g, 2.91 mmol) in CH_2Cl_2 (30 mL) at 0 °C in a foil-covered Schlenk tube. The reaction was warmed to room temperature, and left to stir for a further 12 h, after which time the colour had changed from brown to orange. The solvent was removed to dryness and diethyl ether (20 mL) was added and then the reaction flask was triturated for 20 min in an ultrasonic bath to provide an orange precipitate. The product was filtered and washed with diethyl ether (2 × 5 mL) and dried. The product was recrystallised from CH_2Cl_2 and petroleum ether (b.p. 40–60 °C). X-ray quality crystals of a methanol bis(solvate) were obtained by recrystallisation from a concentrated solution of methanol at –16 °C. Yield 1.34 g (78%). IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2089, 2070 cm^{-1}. (Nujol): $\tilde{\nu}_{CO}$ = 2099, 2075 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 0.38 (s, 18 H, CH_3), 11.1 (s, 2 H, C≡CH) ppm. ^{13}C{^{1}H}NMR (CD_2Cl_2, 25 °C): δ = 208.8 (CO), 195.3 (H*C*≡CSi), 173.5 (HC≡*C*Si), 0.33 ($SiCH_3$) ppm. $C_{12}H_{20}I_2O_2Si_2W$ (690.12): calcd. C 20.89, H 2.92, N 0.00; found C 21.07, H 3.05, N 0.00.

Crystal Data: $C_{12}H_{20}I_2O_2Si_2W{\cdot}(CH_3OH)_2$; M_W = 754.20, monoclinic, *C*2/*c*, *a* = 17.1441(4), *b* = 12.1896(3), *c* = 12.8038(5) Å, β = 97.6004(11)°, *V* = 2652.23(12) Å^3, *Z* = 4, D_c = 1.889 Mg m^{-3}, μ(Mo-K_α) = 6.785 mm^{-1}, *T* = 200(2) K, yellow plate 0.35 × 0.28 × 0.05 mm; 3054 independent measured reflections, *F* refinement, R_1 = 0.027, wR_2 = 0.030; 2144 independent observed absorption corrected reflections [$I > 3\sigma(I)$, $2\theta \leq 55°$], 106 parameters, CCDC-284294.

Synthesis of $[WI\{H_2B(mt)_2\}(CO)(\eta^2\text{-HC}{\equiv}\text{CSiMe}_3)]$ (3b): A mixture of $[WI_2(CO)_2(\eta^2\text{-HC}{\equiv}\text{CSiMe}_3)_2]$ (**2**: 0.50 g, 0.72 mmol) and Na[$H_2B(mt)_2$] (0.19 g, 0.72 mmol) was stirred in CH_2Cl_2 (20 mL) at room temperature under nitrogen for 3 h, after which time the color of the mixture had changed from orange to green. The suspension was filtered through diatomaceous earth to remove NaI. The green filtrate was reduced to a minimum and petroleum ether (b.p. 40–60 °C) (15 mL) added resulting in the formation of a green precipitate. The product was filtered and washed with diethyl ether (2 × 5 mL) and dried. The green product was recrystallised from CH_2Cl_2/Et_2O. Yield 0.28 g (54%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1923 (ν_{CO}), 2265 (ν_{BHW}), 2445 (ν_{BH}) cm^{-1}. IR (Nujol): $\tilde{\nu}$ = 1927 (ν_{CO}), 2263 (ν_{BHW}), 2420 (ν_{BH}) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = –0.43 (br., 1 H, BHW), 0.24 (s, 9 H, $SiCH_3$), 3.44 (s, 6 H, NCH_3), 6.98, 7.06 (d × 2, $^3J_{HH}$ = 1.8 Hz, 2 H, NHC=CHN), 13.1 (s, 1 H, HC≡C) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 229.5 (WCO), 203.2, 190.5 (C≡C), 161.4, (C=S), 123.6, 122.8 (NHC=CHN), 35.2 (NCH_3), 0.49 ($SiCH_3$) ppm. ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = –2.53 ppm. $C_{14}H_{22}BIN_4OS_2SiW$ (676.13): calcd. C 25.59, H 3.15, N 7.96; found C 25.56, H 3.54, N 7.99. MS (ESI): *m*/*z* (%) = 549.1 (65) [M – I]$^+$.

Synthesis of $[MoI\{HB(mt)_3\}(CO)(\eta^2\text{-PhC}{\equiv}\text{CPh})]$ (4b): A mixture of $[MoI_2(CO)(NCMe)(\eta^2\text{-PhC}{\equiv}\text{CPh})_2]$ (**1a**: 0.50 g, 0.65 mmol) and Na[HB(mt)$_3$] (0.24 g, 0.65 mmol) was stirred in CH_2Cl_2 (20 mL) at room temperature under N_2 for 3 h, after which time the color had changed from brown to a light green. Sodium iodide was removed by filtration through diatomaceous earth and the green filtrate was then concentrated to ca 2 mL. Dilution with petroleum spirit (b.p. 40–60 °C) (15 mL) precipitated the crude product, which was then recrystallised from CH_2Cl_2 and diethyl ether. Yield 0.28 g (56%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1933 (ν_{CO}), 2456 (ν_{BH}) cm^{-1}. IR (Nujol): $\tilde{\nu}$ = 1938 (ν_{CO}), 2404 (ν_{BH}) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 3.05, 3.87, 4.02 (3s, 3 × 3 H, NCH_3), 6.85, 6.92, 7.02 (3d, $^3J_{HH}$ = 1.8 Hz, 3 × 2 H, NHC=CHN), 7.36–7.72 (m, 10, C_6H_5) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 237.4 (MoCO), 207.4, 206.9 (C≡C), 162.6, 160.5, 159.8, (C=S), 126.5–129.0 (C_6H_5), 124.7, 123.0, 122.4, 121.2, 120.6, 120.1 (NHC=CHN), 36.4, 35.0, 34.5 (NCH_3) ppm. ^{11}B{^{1}H} NMR ([D_6]DMSO): δ = 0.71 ppm. ESI-MS: *m*/*z* (%) = 781.9 (5) [M – CH_3]$^+$, 655.1 (15) [M – I]$^+$. $C_{27}H_{26}BIMoN_6OS_3$ (780.38): calcd. C 41.56, H 3.36, N 10.77; found C 41.92, H 3.66, N 10.14.

Synthesis of $[Mo\{HB(mt)_3\}_2(CO)(\eta^2\text{-PhC}{\equiv}\text{CPh})]$ (5): One equivalent of Na[HB(mt)$_3$] (0.25 g, 0.33 mmol) was added to a solution of $[MoI\{HB(mt)_3\}(CO)(\eta^2\text{-PhC}_2\text{Ph})]$ (**4b**: 0.12 g, 0.33 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred at room temperature for 12 h resulting in the formation of an orange precipitate. The supernatant was then decanted and the orange product was washed with cold ethanol (20 mL) followed by cold diethyl ether (10 mL) and then dried in vacuo. N.B.: The product is poorly soluble in common organic solvents, compromising the acquisition of elemental and solution spectroscopic data. Yield 0.19 g (59%). IR (DMSO): $\tilde{\nu}$ = 1797 (ν_{CO}), 2449, 2407 (ν_{BH}) cm^{-1}. IR (Nujol): $\tilde{\nu}$ = 1790 (ν_{CO}), 2433, 2406 (ν_{BH}) cm^{-1}. APCI-MS: *m*/*z* (%) = 1029 (30) [M + Na]$^+$, 975 (25) [M – CO]$^+$. ^{11}B{^{1}H} NMR (96.2 MHz, [D_6]DMSO): δ = 2.00 ppm. Storage of a dilute solution of **5** in dichloromethane at –20 °C provided crystals of a dichloromethane bis-solvate. Satisfactory elemental microanalytical data not obtained due to partial desolvation.

Crystal Data: $C_{39}H_{42}B_2MoN_{12}OS_6{\cdot}(CH_2Cl_2)_2$, M_w = 1174.67, monoclinic, $P2_1/n$, *a* = 14.6842(3), *b* = 18.7132(6), *c* = 19.7601(6) Å, β = 107.6683(16)°, *V* = 5173.7(3) Å^3, *Z* = 4, D_c = 1.508 Mg m^{-3}, μ(Mo-K_α) = 0.749 mm^{-1}, *T* = 200(2) K, 9074 independent measured reflections, *F* refinement, R_1 = 0.064, wR_2 = 0.056; 4681 independent observed absorption corrected reflections [$I > 3\sigma(I)$, $2\theta \leq 50°$], 604 parameters.

CCDC-289494 and -289495 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the University of Botswana for a studentship (to N. T.) and the Australian Research Council (ARC) for financial support (DP034270).

[1] a) J. L. Templeton, *Adv. Organomet. Chem.* **1989**, *29*, 1; b) P. K. Baker, *Adv. Organomet. Chem.* **1996**, *40*, 45.
[2] G. Hogarth, *Prog. Inorg. Chem.* **2005**, *53*, 71.
[3] S. Tofimenko, *Scorpionates: The Coordination Chemistry of Poly(pyrazolyl)borate Ligands*, Imperial College Press, London, **1999**.
[4] M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975.
[5] C. Kimblin, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, *36*, 5680.
[6] A. J. L. Pombiero, R. L. Richards, *Coord. Chem. Rev.* **1990**, *104*, 13.
[7] M. R. St.-J. Foreman, A. F. Hill, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 3831.
[8] a) M. R. St.-J. Foreman, A. F. Hill, N. Tshabang, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 5593; b) R. J. Abernethy, A. F. Hill, H. Neumann, A. C. Willis, *Inorg. Chim. Acta* **2005**, *358*, 1605; c) A. F. Hill, M. K. Smith, *Dalton Trans.* **2006**, 28; d) I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2005**, *24*, 4889; e) M. R. St.-J. Foreman, A. F. Hill, M. K. Smith, N. Tshabang, *Organometallics* **2005**, *24*, 5224; f)

I. R. Crossley, A. F. Hill, E. R. Humphrey, M. K. Smith, *Organometallics* **2006**, *25*, 2242.
[9] a) R. Garcia, A. Domingos, A. Paulo, I. Santos, R. Alberto, *Inorg. Chem.* **2002**, *41*, 2422; b) R. Garcia, A. Paulo, A. Domingos, I. Santos, *J. Organomet. Chem.* **2001**, *632*, 41; c) R. Garcia, A. Paulo, A. Domingos, I. Santos, K. Ortner, R. Alberto, *J. Am. Chem. Soc.* **2000**, *122*, 11240.
[10] a) C. Kimblin, B. M. Bridgewater, T. Hascall, G. Parkin, *J. Chem. Soc. Dalton Trans.* **2000**, 891; b) C. Kimblin, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, *36*, 5680; c) C. Kimblin, B. M. Bridgewater, T. Hascall, G. Parkin, *J. Chem. Soc. Dalton Trans.* **2000**, 891.
[11] a) L. A. Philson, D. M. Alyounes, L. N. Zakharov, A. L. Rhenigold, D. Rabinovich, *Polyhedron* **2003**, *22*, 3461; b) H. M. Alvarez, J. M. Tanski, D. Rabinovich, *Polyhedron* **2004**, *23*, 395; c) L. A. Graham, A. R. Fout, K. R. Kuehne, J. L. White, B. Mookheri, F. M. Marks, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold, D. Rabinovich, *Dalton Trans.* **2005**, 171; d) H. M. Alvarez, M. Krawiec, B. T. Donovan-Merkert, M. Fouzi, D. Rabinovich, *Inorg. Chem.* **2001**, *40*, 5736.
[12] M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 4446.
[13] C. Kimblin, D. G. Chruchill, B. M. Bridgewater, J. N. Girard, D. A. Quarless, G. Parkin, *Polyhedron* **2001**, *20*, 1891.
[14] M. Careri, L. Elviri, M. Lafranchi, M. Marchio, C. Mora, M. A. Pellinghelli, *Inorg. Chem.* **2003**, *42*, 2109.
[15] S. L. Kuan, W. K. Leong, L. Y. Goh, R. D. Webster, *Organometallics* **2005**, *24*, 4639.
[16] a) P. K. Baker, S. G. Fraser, E. M. Keyes, *J. Organomet. Chem.* **1986**, *309*, 319; b) E. M. Armstrong, P. K. Baker, M. G. B. Drew, *Organometallics* **1988**, *7*, 319.
[17] A. F. Hill, M. K. Smith, *Chem. Commun.* **2005**, 1920.
[18] Cambridge Crystallographic Data Centre, *Conquest*®, Version 1.7, November **2006** release.
[19] A. De Cian, J. Colin, M. Schappacher, L. Ricard, R. Weiss, *J. Am. Chem. Soc.* **1981**, *103*, 1850 (Mo–C: 2.142, 2.145; C–C: 1.269 Å; Mo–C–CPh: 140.5, 140.1°).
[20] R. S. Herrick, S. J. N. Burgmayer, J. L. Templeton, *Inorg. Chem.* **1983**, *22*, 3275 (Mo–C: 2.019–2.082; C–C: 1.246, 1.236 Å; Mo–C–CMe: 138.2–143.5°).
[21] I. M. Barlett, N. G. Connelly, A. G. Orpen, M. J. Quayle, J. C. Rankin, *Chem. Commun.* **1996**, 2583 (n = 0: Mo–C: 2.137, 2.175; C–C: 1.282 Å; Mo–C–CPh: 144.8, 145.1°. n = 1: Mo–C: 2.041, 2.070; C–C: 1.335 Å; Mo–C–CPh: 147.1, 146.5°).
[22] L. Rickard, R. Weiss, W. E. Newton, G. J.-J. Chen, J. W. McDonald, *J. Am. Chem. Soc.* **1978**, *100*, 1318.
[23] M. A. Bennett, I. A. Boyd, G. B. Robertson, W. A. Wickramasinghe, *J. Organomet. Chem.* **1985**, *290*, 181.
[24] a) R. S. Herrick, S. J. N. Burgmayer, J. L. Templeton, *Inorg. Chem.* **1983**, *22*, 3275; b) J. L. Templeton, R. S. Herrick, C. A. Rusik, C. E. McKenna, J. W. McDonald, W. E. Newton, *Inorg. Chem.* **1985**, *24*, 1383.
[25] K.-M. Sung, R. H. Holm, *Inorg. Chem.* **2000**, *39*, 1275.
[26] a) S. Trofimenko, *Inorg. Chem.* **1970**, *9*, 2493; b) S. Trofimenko, *J. Am. Chem. Soc.* **1969**, *91*, 3183; c) C. A. Kosky, P. Ganis, G. Avitabile, *Acta Crystallogr., Sect. B* **1971**, *27*, 1859; d) F. A. Cotton, M. Jeremic, A. Shaver, *Inorg. Chim. Acta* **1972**, *6*, 543.
[27] A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **1999**, *38*, 2759.

Received: May 2, 2007
Published Online: July 23, 2007

