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Poly(azolyl) chelate chemistry 14.[1] κ^2-*S*,*S*′ *vs* κ^3-H,*S*,*S*′- $H_2B(mt)_2$ (mt=methimazolyl)borate coordination in the complex $[W(CO)\{H_2B(mt)_2\}_2]$

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Dedicated to Professor F. Gordon A. Stone to record appreciation of his longstanding and continuing inspiration, leadership and innumerable contributions to science

Abstract

The reactions of $[M(\equiv CC_6H_2Me_3\text{-}2,4,6)X(CO)_2(L)_2]$ (M = Mo, W; X = Cl, Br; L = pyridine, 3,5-dimethylpyrazole) with $Na[H_2B(mt)_2]$ (mt = methimazolyl) are metal dependent, providing either the alkylidyne complex $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ or the bis(chelate) complex $[W(CO)\{\kappa^2\text{-}S,S'\text{-}H_2B(mt)_2\}\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$, the latter featuring both bi and tridentate coordination modes for the $H_2B(mt)_2$ ligand.

Keywords: Carbyne; Alkylidyne; Tungsten; Molybdenum; Borate; Agostic coordination

1. Introduction

In its short history, the dihydrobis(methimazolyl)borato ligand introduced by Parkin[2] has shown a propensity for entering into agostic coordination of one boron hydride to the metal center (Chart 1).[2–5] In an organometallic context this has been demonstrated for the complexes $[M(CO)_3\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$(M = Re, Tc) [3], and the thiocarbamoyl derivative $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ [5], although it is noteworthy that even the $HB(mt)_3$ chelate has been shown to adopt the κ^3-*H*,*S*,*S*′ coordination mode in the complex $[RuH(CO)(PPh_3)\{\kappa^3\text{-}H,S,S'\text{-}HB(mt)_3\}]$ [6], rather than the anticipated κ^3-*S*,*S*′,*S*″ mode. Agostic B–H–metal coordination of $H_nB(mt)_{4-n}$ ($n = 1,2$) ligands is of interest to us because such interactions are implicated in the formation of the metallaboratranes $[M(CO)(PPh_3)\{B(mt)_3\}](B \rightarrow M)$ (M = Ru [6,7], Os[1]) which feature dative bonds between the metal center and boron. A further intriguing feature of such interactions is their potential hemilability, as demonstrated for the complex $[Re(CO)_3\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ which readily coordinates ligands to provide the bidentate derivatives $[Re(CO)_3(L)\{\kappa^2\text{-}S,S'\text{-}H_2B(mt)_2\}]$ (L=CNCMe$_3$, PPh$_3$, imidazole, $NC_5H_4NMe_2$-4) [3]. We have previously attempted, without success, to obtain alkylidyne complexes κ^3-*H*,*N*,*N*′-co-ligated by the $H_2B(pz)_2$ (pz = pyrazol-1-yl) chelate, on the assumption that should hemilabile agostic B–H–M interactions occur, these would serve to mask a potentially vacant coordination site. However, in all cases the isolated complexes involved simple bidentate κ-*N*,*N*′ coordination of the chelate.[8,9] Nevertheless, the facile phospha-alkyne metathesis effected by the complex $[Mo(\equiv CC_6H_4\text{-}OMe\text{-}2)(CO)\{P(OMe)_3\}_2\{H_2B(pz)_2\}]$ [8] points towards

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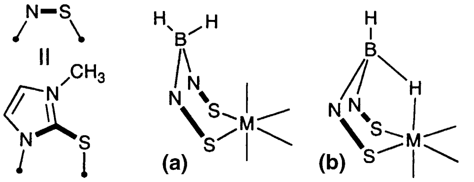

Chart 1. Coordination modes for $H_2B(mt)_2$ ligands. (a) κ^2-*S*,*S*′. (b) κ^3-*H*,*S*,*S*′.

intermediates of reduced coordination number that may well be transiently stabilized by B–H–Mo interactions. Herein we wish to report the synthesis of the alkylidyne complex $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{H_2B(mt)_2\}]$ which does indeed feature an agostic B–H–Mo interaction. However, we also report that extension of the procedure to the tungsten analogue provides instead the first example of a complex in which $H_2B(mt)_2$ ligands adopt both the κ^2-*S*,*S*′ and κ^3-*H*,*S*,*S*′ coordination mode within the same complex.

2. Results and discussion

The complexes $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)X(CO)_2(L)_2]$ (L = pic = γ-picoline, X = Br [9]; L = py = pyridine, X = Cl [10]) have been reported previously, however details of an expedient one pot procedure for the latter are included in the experimental section. Synthetic procedures for the preparation of the new compounds $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)Cl(CO)_2(py)_2]$ and $[M(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(Hpz^*)_2]$ (M = Mo, W; Hpz* = 3,5-dimethylpyrazole) are also included. These represent minor variations on the Mayr protocol for the synthesis of $[W(\equiv CPh)Cl(CO)_2(py)_2]$ [11], and the products give rise to characteristic, though otherwise unremarkable spectroscopic data and one example, $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(Hpz^*)_2]$ was the subject of a crystallographic study (see Experimental). All of these substrates include one labile halide ligand and two labile nitrogen heterocycles and are therefore synthetic equivalents of the "$[M(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2]^+$" fragment.

Treating a tetrahydrofuran solution of either $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)Cl(CO)_2(py)_2]$ or $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(Hpz^*)_2]$ with $Na[H_2B(mt)_2]$ results in the formation of a dark orange compound that may be isolated following column chromatography. This is formulated as the alkylidyne complex $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ (**1**) on the basis of spectroscopic data. The compound arises from either precursor and therefore does not retain the pyridine or dimethylpyrazole ligand, in contrast to the reaction of $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(pic)_2]$ (pic = γ-picoline) with $Na[H_2B(pz)_2]$ which provides the complex $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2(pic)\{H_2B(pz)_2\}]$ in which one picoline is retained [9]. Although we have not succeeded in obtaining crystallographic grade crystals, spectroscopic data for the new compound account for each of the alkylidyne, two carbonyl and $H_2B(mt)_2$ ligands, the latter in a symmetrical environment, at least on the ^{13}C and ^1H NMR timescales. In the $^{13}C\{^1H\}$ NMR spectrum (d_6-dmso), the alkylidyne ligand gives rise to a characteristic low field resonance at δ 298.8 which is noticeably broadened, as is that due to the carbonyl ligands at δ 222.7, possibly due to the onset of fluxionality. The ^1H NMR spectrum (CD_2Cl_2) for **1** is simple comprising four singlet resonances for the aryl and methimazolyl methyl groups and the mesityl methyne protons, in addition to an $(H_AH_B)_2$ system for the methimazolyl heterocycles. Thus the complex is either stereochemically non-rigid or has a static structure with a plane of symmetry. These data might suggest a coordinatively unsaturated molybdenum center, however the most noteworthy feature of the ^1H NMR spectrum is a very broad resonance centered at δ–3.42. Notably, this region is characteristic of an agostic B–H–Mo interaction (terminal B–H groups are generally manifest in resonances to low field of $SiMe_4$). The complexes $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{H_2B(mt)_2\}]$ [5], and $[Mo(\eta\text{-}C_3H_5)\text{-}(CO)_2\{H_2B(mt)_2\}]$ [12] give rise to resonances at δ −5.04 and −5.47, respectively, and each of these have crystallographically verified agostic B–H–Mo interactions. Assuming a static symmetric structure, the appearance of the B–H–Mo resonance to slightly lower field of those for the thiocarbamoyl and allyl complexes would be consistent with the superlative *trans* influence of alkylidyne ligands, weakening the supposed Mo–H interaction.

Attempts to extend this synthesis of **1** to the corresponding tungsten derivative have so far proven unsuccessful. Treating $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Cl(CO)_2(py)_2]$ or $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(Hpz^*)_2]$ with $Na[H_2B(mt)_2]$ in dichloromethane at room temperature or under reflux results in a very slow reaction. The infrared spectrum of the supernatant liquor reveals in addition to bands for the starting material [1986, 1903 cm^{-1}], two minor shoulders at 1971 and 1886 cm^{-1}. Even after prolonged periods (18 h under reflux) these signals never grow beyond ca. 20% of the intensity of bands for the starting material, however a broad band at 1785 cm^{-1} develops over this period. Given the observed data for $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\text{-}\{H_2B(mt)_2\}]$ (1981, 1905 cm^{-1}) and $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{HB(mt)_3\}]$ (1967, 1876 cm^{-1}) [13], we are inclined to suspect that the desired alkylidyne complex $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{H_2B(mt)_2\}]$ does indeed form, however it does not appear to persist under these conditions. We have so far failed to separate this intermediate by either fractional crystallization or column chromatography. Heating the same mixture of reagents in tetrahydrofuran under reflux reveals a similar process with an intermediate being observed with ν(CO) = 1969 and 1886 cm^{-1}. However, in this higher boiling solvent, the reaction may be driven to completion with resulting formation of a bright lime green precipitate. In a similar manner the reaction of $[W(\equiv CC_4H_3S\text{-}2)(O_2CCF_3)(CO)_2(tmeda)]$ [$\nu(CO) = 1986, 1898\ cm^{-1}$] with $Na[H_2B(mt)_2]$ in refluxing thf (3 days) provides a mixture of starting material and an intermediate [$\nu(CO) = 1968, 1881\ cm^{-1}$] presumed to be $[W(\equiv CC_4H_3S\text{-}2)(CO)_2\{H_2B(mt)_2\}]$ which is unstable under these conditions and also converts to the same green complex. This green product is only sparingly soluble in most organic solvents, such that ^1H NMR data could only be obtained from dilute solutions in d_6-dmso and useful $^{13}C\{^1H\}$ NMR data could not be obtained. The ^1H NMR spectrum is consistent with two methimazolyl environments [CH_3: δ 2.93, 3.47] and also reveals two broad resonances at δ 0.03 and −3.61. These data in combination with the appearance of a single CO associated IR absorption (dmso: $1771\ cm^{-1}$) are consistent with the compound being formulated as $[W(CO)\{H_2B(mt)_2\}_2]$ in which one $H_2B(mt)_2$ ligand adopts a tridentate κ^3-*H*,*S*,*S′* coordination whilst the second is simply bidentate κ^2-*S*,*S′*. [1] The APCI-mass spectrum supports this formulation with the appearance of peaks attributable to $[M + Na]^+$, $[M]^+$, $[M - CO]^+$ and $[M - Hmt]^+$ ions. This latter and highly abundant peak arising from loss of methimazole is significant (*vide infra*). The remarkably low value for ν(CO) is perhaps surprising for a neutral complex with a metal in a positive oxidation state. However it should be noted that the tungsten is ligated by four π-dative thione groups in addition to the *trans*-disposed B–H–Mo interaction, which is presumed to serve primarily as a σ-donor [2] [14]. Nevertheless, in the case of bis(dithiocarbamato) monocarbonyl complexes of tungsten(II), with which some analogy might be entertained, ν(CO) values are considerably higher. Illustrative complexes include $[W(CO)(S_2CNEt_2)_2(L)]$ which have ν(CO) values of 1960 (L = HC≡CH) [15], 1921 ($L = O{=}C(C_8H_{12})_2$) [16] and 1960 cm^{-1} ($L = H_2C{=}CHCH{=}CO$) [17]. The analogy between the electronic properties of bis(methimazolyl)borates and dithiocarbamates remains to be explored, however in these examples the ligand L serves as a 4-electron π-acid, i.e., electronically very distinct in nature from an agostic B–H–W interaction. Even the anionic complex $[W(CO)(SPh)(\kappa^2\text{-}S_2C_2Me_2)_2]^-$ has $\nu(CO) = 1933\ cm^{-1}$ although in this case the oxidation state of the tungsten might be described as intermediate between W^0 (bis-thione description) and W^{IV} (ene-dithiolate description) [18]. In any event, the very low ν(CO) value for **2** is quite exceptional.

The isolation of complex **2**, bearing the $H_2B(mt)_2$ ligand in two different coordination modes is noteworthy and immediately raises the question as to whether the two ligands interconvert. At room temperature as noted above two resonances are observed which may be assigned to terminal (δ 0.03) and agostic (δ −3.61) B–H groups. These are of comparable intensity and so it might be assumed that both protons reside on the same boron atom, with the remaining free BH_2 being to lower field and typically broadened beyond recognition. The positions of these two resonances are essentially invariant over the temperature range 30–70 °C and at this temperature and above, significant albeit clean decomposition ensues. The decomposition product was identified as free methimazole and the (^1H NMR silent) fate of the tungsten remains unknown. Since the complex was initially obtained from refluent thf (b.p. 69 °C) it may be assumed that thermal sensitivity is not the issue, but rather that the dmso is responsible for the decomposition, possibly acting as an oxygen transfer agent. Thus fluxional interconversion of the two coordination modes does not therefore appear to occur beneath the temperature at which decomposition commences. This result is in contrast to the typical behavior of poly(pyrazolyl)borates: Whilst these ligands are occasionally observed to fragment during attempts to introduce them into the coordination sphere of transition metals [19], once successfully chelated they tend to be robust.

Crystals of **2** suitable for crystallographic analysis were obtained by slow diffusion of diethylether vapor into a dilute dichloromethane solution of the compound over a period of two weeks. The results of the study are summarized in Fig. 1 and confirm both the gross formulation and the distinct rôles adopted by the two $H_2B(mt)_2$ ligands. Although agostic coordination of hydropoly(azolyl)chelates has not been structurally authenticated for tungsten, it is well established for molybdenum from the early studies of Trofimenko [20], Kosky et al. [21] and Cotton et al. [22]. Furthermore, other types of agostic B–H–W interactions have been observed in a range of compounds. Chart 2 provides a selection of such situations that is illustrative rather than exhaustive. The simplest cases involve the coordination of borane–Lewis base adducts to the '$W(CO)_5$' fragment [14,23] and such complexes provide a benchmark for non-constrained coordination, to which we will return. The remaining examples involve some type of tethering of the B–H group, as part of either a more complicated ligand or cluster arrangement. The tetrahydroborate anion has been shown to act as either a monodentate [10] [3], [4] or bidentate ligand [24] and their interconversion has been demonstrated. The triboronate anion

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[1] The alternative formulation *trans*-$[W(CO)_2\{H_2B(mt)_2\}_2]$, whilst also only having one ν(CO) absorption, would not give rise to two methimazolyl environments.

[2] The relative insignificance of retrodonation from tungsten(0) to the σ* BH) orbital of agostically coordinated B–H bonds has been discussed [14] and is presumably similarly negligible in this instance.

[3] In a sense, κ^1-H-BH_4 coordination [4] might be viewed as analogous to the coordination of borane–Lewis base adducts, with 'H^-' serving the role of Lewis base.

[4] Examples of $W(\kappa^1\text{-}H\text{-}BH_4)$ complexes include $[W(HBH_3)(NO)(CO)(PMe_3)_3]$ [8] and the thermally unstable alkylidyne complexes $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(HBH_3)(CO)L_3]$ ($L = PMe_3, P(OMe)_3$) [10].

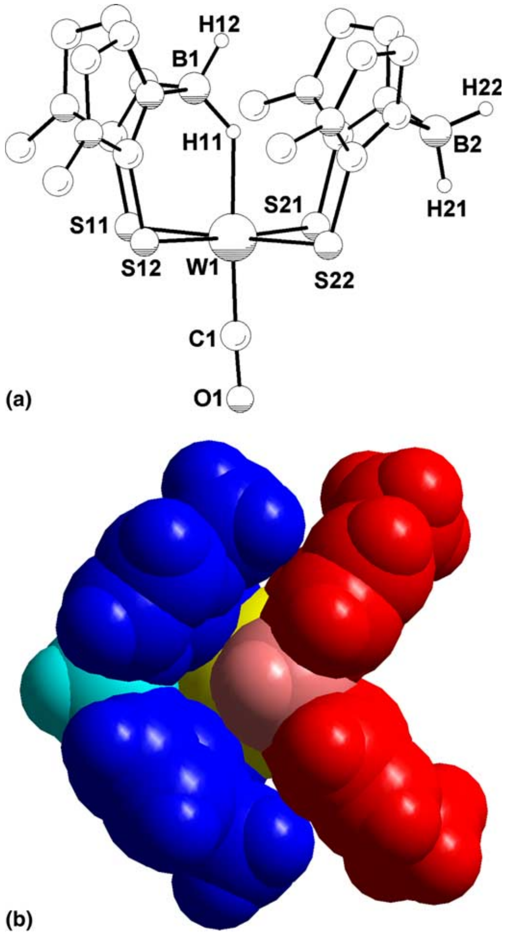


Fig. 1. Molecular structure of $[W(CO)\{H_2B(mt)_2\}_2]$. (a) Ball and spoke. (b) Space filling. Selected bond lengths (Å) and angles (deg): W1–S11 2.4479(10), W1–S12 2.4736(9), W1–S21 2.4084(9), W1–S22 2.4179(10), W1–C1 1.864(4), W1–H11 1.99(4), S11–W1–S12 86.58(3), S11–W1–S21 92.02(3), S12–W1–S22 89.26(3), S21–W1–S22 92.07(3), S11–W1–C1 91.32(11), S12–W1–C1 94.79(11), S21–W1–C1 88.08(11), S22–W1–C1 90.39(11), W1–C1–O1 176.5(3), N111–B1–N121 110.2(3), N211–B2–N221 108.3(3), B1–H11–W1 138(3)°.

$[B_3H_8]^-$ binds through two B–H–W interactions [25,26] and is in some respects akin to the topology of the diborane-4 complex $[W\{B_2H_4(PMe_3)_2\}(CO)_4]$ [23]. Stone first demonstrated the hydroboration of alkylidynes to provide ditungsten bora-alkyne complexes in which the B–C bond transversely bridges the W–W bond, supported by an agostic B–H–W interaction [27]. Finally, an increasingly recurrent feature to emerge from the bi- and polymetallic chemistry of dicarbollide and monocarbollide complexes is the prevalence for one or more exo-icosohedral B–H bonds of a bi- or trimetallacarbaborane to bridge a metal-metal bond and this has now been observed in a number of tungsten complexes [28,29].

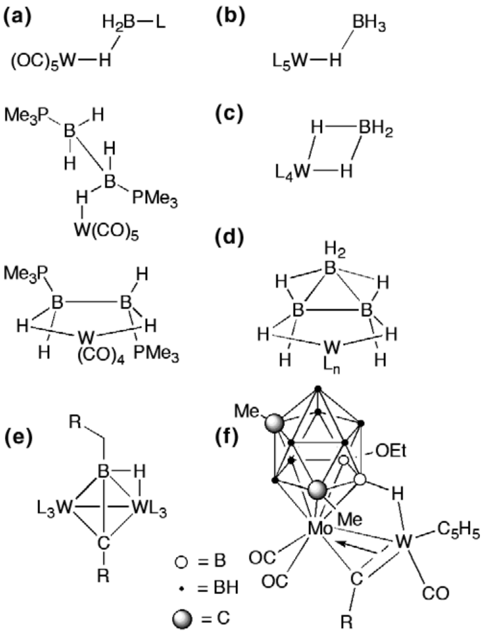


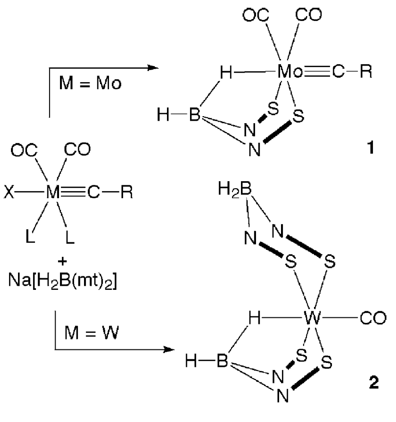
Chart 2. Representative examples of agostic B–H–W interactions. (a) Borane–Lewis base adducts[14,23]. (b) Monodentate tetrahydroborate [10,24] 3 4. (c) Bidentate tetrahydroborate [10,24]. (d) Bidentate triboronate [25,26]. (e)Bora-alkyne [27]. (f) *Exo*-polyhedral dimetalladicarbollides [28,29].

The agostic B(1)–H–W interaction in **2** involves B1–H(11), H(11)–W1 and B1–W1 separations of 1.08(4), 1.99(4) and 2.893(4) Å, respectively. These values and the W1–H11–B1 angle of 138(3)° may be compared with those reported for the borane–Lewis base complexes $[W(H_3B\leftarrow PR_3)(CO)_5]$, (R = Me, Ph; Table 1). Although the position of H(11) was located and refined, it was naturally modeled with less precision than those of W1 or B1 [30]. Accordingly, we will limit comparison of geometric parameters to the W–B separation and with appropriate caution, the W1–H11–B1 angle. The W1–B1 bond length in **2** is within statistical equivalence of those found for $[W(H_3B \leftarrow PMe_3)(CO)_5]$ and the two crystallographically independent molecules of $[W(H_3B \leftarrow PPh_3)(CO)_5]$. The W1–H11–B1 bond angle of 138(3)° falls inside the large range (27°!) of values observed for $[W(H_3B \leftarrow PR_3)(CO)_5]$ however this also most likely reflects the lack of precision in locating the hydrogen atom in these structures. It may therefore be surmised that although the agostic B–H–W interaction in **2** forms part of a cage structure, any attendant geometric constraints do not prevent the adoption of a geometry close to those for non-constrained systems. Indeed the geometry of the cage may well be ideal for such interactions, a possibility that could underpin the prevalence of the κ^3-*H*,*S*,*S*′ coordination mode for $H_2B(mt)_2$ complexes.

Table 1
Comparative geometric features for agostic B–H–W interactions

Complex	B–H (Å)	H–W (Å)	B–W (Å)	B–H–W (°)
2	1.08(4)	1.99(4)	2.893(4)	138(3)
$[W(H_3B \leftarrow PMe_3)(CO)_5]$	1.14(10)	2.01(9)	2.86(2)	128(7)
$[W(H_3B \leftarrow PPh_3)(CO)_5]$	1.38	1.91	2.85(1)	119.0
(2 independent molecules)	1.19	1.75	2.81(1)	146.3

The interpretative value of the molecular structure of **2** lies in the coexistence of both coordination modes within the same molecule. However this is itself noteworthy in that for a formally 18-electron tungsten center, both $H_2B(mt)_2$ ligands would be required to adopt the trihapto mode of coordination. Homoleptic complexes $[M\{H_2B(mt^R)_2\}_2]$ ($mt^R = NC_2H_2NRCS$; R = Me, CH_2Ph, CMe_3, C_6H_4Me-4; M = Cd [4a], Hg [4a], Zn [2b,4a], Ni [4b]; not all variants) are known and for the M/R = Cd/Me, Zn/CMe_3, Cd/CMe_3, Hg/CMe_3, Ni/Me combinations the κ^3-*H*,*S*,*S*′ coordination mode is adopted in the solid state whilst for the Zn/Me combination, the κ^2-*S*,*S*′ coordination mode is adopted. This selection of metals spans the ranges for covalent metallic radii and Pauling electronegativities, (1.154(Ni)–1.440(Hg) Å and 1.6(Zn)–1.9(Hg), respectively) that includes those for tungsten (1.304 Å, 1.7) [31]. Thus steric factors are not sufficient to explain the lack of a second agostic B–H–W interaction, especially when 7-coordination is common for tungsten(II) [32,33]. Thus the adoption of only one agostic B–H–W interaction would appear to be electronic in origin and might be traced to the high π-basicity of the methimazolyl donors, reducing the requirement for coordinative saturation and 18-electron rule adherence. A second contributing factor may however be the nestling of the κ^3-*H*,*S*,*S*′ bound ligand within the cleft provided by the κ^2-*S*,*S*′ bound ligand as illustrated in the space-filling representation (Fig. 1(b)). Such an accommodation would not be provided if both ligands were trihapto coordinated. The homoleptic bis(κ^3-*H*,*S*,*S*′) cases noted above place the two agostic B–H–M interactions in a mutually *cis* orientation. A comparison of the W–S bonding in the two chelates reveals that for the trihapto mode, the S11–W1–S12 angle (85.58(3)°) is compressed, somewhat, relative to that for the bidentate ligand (92.07(3)°) and that this is accompanied by an elongation of the W–S bond lengths (2.4479(10), 2.4736(9) Å) when compared with those for the bidentate chelate (2.4084(9), 2.4179(10) Å). The angles at each sulfur lie in the narrow range 105.21(12)–106.60(12)° whilst the angles between the *cis* coordinated ligands on tungsten fall within the expected range for regular octahedral coordination [85.58(3)–94.79(11)°]. Thus it appears that the two sulfur donors of the $H_2B(mt)_2$ ligand can coordinate comfortably to *cis*-octahedral sites in either coordination mode Scheme 1.



Scheme 1. Reactions of alkylidyne complexes with $Na[H_2B(mt)_2]$ (X = Cl, Br; L = py, Hpz*; R = $C_6H_2Me_3$-2,4,6).

3. Conclusions

The isolation of the alkylidyne complex **1** further illustrates the prevalence of agostic B–H–M interactions in the chemistry of $H_xB(mt)_{4-x}$ ligands. However, the formation of the tungsten complex **2**, is somewhat surprising given that alkylidyne complexes of tungsten are generally more robust than the molybdenum analogues. Complex **2** does however provide a novel situation where both modes of $H_2B(mt)_2$ coordination coexist within the same complex. The mechanism by which **2** is obtained remains obscure, however the complex $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2\{\kappa^3\text{-}H,S,S'\text{-}H_2B(mt)_2\}]$ (analogous to **1**) seems a likely intermediate, given that thermolysis of the complexes $[Cr(\equiv CR)Br(CO)_4]$ (R = Me, Ph) provides the alkynes RC≡CR and by inference, chromium(II) bromide [34,35]. The failure of either the $H_2B(mt)_2$ ligand or the sterically encumbered alkylidyne substituent to stabilise the intermediate is surprising.

4. Experimental

4.1. General procedures

Conventional Schlenk and vacuum line techniques were employed for the exclusion of air. The salt $Na[H_2B(mt)_2]$ was prepared as described previously [5]. 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 from the A.N.U. Analytical Service.

4.2. Synthesis of $[Mo(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(Hpz^*)_2]$

A mixture of lithium (1.39 g, 0.20 mol) and bromomesitylene (12.3 ml, 0.10 mol) were suspended in diethyl ether (200 ml) and stirred over 2 days to yield an off-white milky suspension. In a separate flask molybdenum hexacarbonyl (2.64 g, 10.0 mmol) was suspended in diethyl ether (100 ml), to which the lithium reagent was added in 30 ml aliquots. The solution was allowed to turn to a clear yellow solution (indicating the complete reaction of the lithium reagent) before each subsequent addition. The reaction was monitored *via* solution infrared spectroscopy. Once the amount of molybdenum carbonyl [ν(CO) = 1976 cm^{-1}] present was negligible (<5%), the solution was cooled (dry ice/propanone) and trifluoroacetic anhydride (1.41 ml, 10 mmol) was slowly added drop-wise to the solution. The solution was stirred for 10 min after which time 3,5-dimethylpyrazole (1.92 g, 20 mmol) was added in one portion. The solution was allowed to warm to room temperature slowly over 2 h with stirring. The resulting suspension was allowed to settle, and the supernatant liquor decanted off and discarded. The bright yellow solid was dried and recrystallised from a mixture of dichloromethane and light petroleum (40–60) to remove residual unreacted dimethylpyrazole. Yield = 2.62 g (47%). IR Nujol: 3313m, 3227m [ν(NH)], 2004vs, 1908vs [ν(CO)], 1602w, 1570m, 1291w, 1157w, 1026w, 853m, 794 cm^{-1}. Et$_2$O: 2001, 1921 [ν(CO)] cm^{-1}. THF: 1995, 1913 [ν(CO)] cm^{-1}. NMR ^{1}H (300 MHz, CDCl$_3$, 25 °C): δ = 2.19 [s, 3 H, C$_6$H$_2$CH$_3$-4], 2.22, 2.28, 2.43 [s × 3, 6 H × 3, CH$_3$(pz*) and C$_6$H$_2$CH$_3$-2,6], 5.86 [s, 2 H, H^4(pz*)], 6.70 [s, 2 H, H^{3,5}(C$_6$H$_2$)], 10.83 [s, 2 H, NH] ppm. ^{13}C{^{1}H} (68 MHz, CDCl$_3$, 25 °C): δ = 11.02, 14.92 [pz*-CH$_3$], 20.54 [C$_6$H$_2$CH$_3$-2,6], 21.36 [C$_6$H$_2$CH$_3$-4], 106.0 [C^4(pz*)], 128.3 [C^{3,5}(C$_6$H$_2$)], 138.3 [C^1(C$_6$H$_2$)], 140.5, 141.1 [C^{3,5}(pz*)], 151.7 [C^{2,6}(C$_6$H$_2$)], 224.7 (CO), 286.9 ($Mo{\equiv}C$). APCI-MS *m*/*z*(%) [assignment] = 973(10) [(M − HBr)$_2$ + Na]$^+$, 644(8) [M + 2Na + MeCN], 619(9) [M + Na + MeCN], 568(5) [M − Br − 2Hpz*]$^+$, 290(20) [Mo(pz*)$_2$]$^+$, 255(15) [M − Br − 2Hpz − CO]$^+$, 227(5) [M − Br − 2Hpz − 2CO]$^+$. Crystal data: $C_{22}H_{27}BrMoN_4O_2$; M_r = 555.33; triclinic; $P\bar{1}$ (No. 2); a = 8.7147(1); b = 10.9222(2); c = 13.7466(2) Å; α = 73.8988(7); β = 78.0343(6); γ = 75.4494(7)°; V = 1203.40(3) Å^3; Z = 2; D_x = 1.532 g cm^{-3}; μ(Mo Kα) = 2.23 mm^{-1}; T = 200 K, yellow rod 0.16 × 0.09 × 0.06 mm; 27108 measured reflections(2θ < 55°), F refinement, R = 0.024, wR = 0.025 for 4064 independent absorption corrected reflections [$I > 3\sigma(I)$], 353 parameters, CCDC 241835. The molecular geometry and selected geometric parameters are presented in Fig. 2(a). The geometry is as expected and typical of octahedrally coordinated alkylidyne complexes of molybdenum. A feature of note is the dimeric association that occurs in the solid state arising from hydrogen bonding interactions. There are

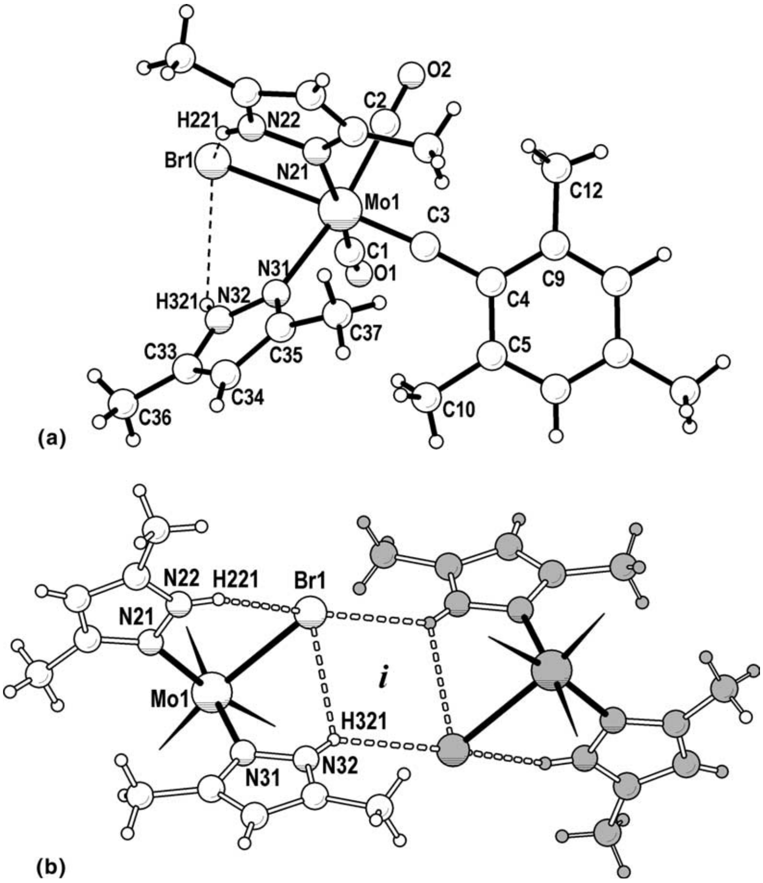


Fig. 2. Crystal structure of [Mo($\equiv$CC$_6$H$_2$Me$_3$-2,4, 6)Br(Hpz*)$_2$(CO)$_2$]. (a) Molecular geometry. (b) Hydrogen bonding in dimmer. Selected bond lengths (Å) and angles (°): Mo1–Br1 2.7692 (3), Mo1–N21 2.279 (2), Mo1–N31 2.250 (2), Mo1–C1 1.986 (3), Mo1–C2 2.012 (3), Mo1–C3 1.799 (2), C3–C4 1.453 (3), Br1–Mo1–N21 85.95 (5), Br1–Mo1–N31 83.68 (5), N21–Mo1–N31 83.35 (7), Br1–Mo1–C1 85.92 (8), Br1–Mo1–C3 168.19 (7), N21–Mo1–C3 105.73 (9), N31–Mo1–C3 99.18 (9), C1–Mo1–C3 82.34 (11), C2–Mo1–C3 88.72 (11), Mo1–C3–C4 172.46 (19).

two types of hydrogen bond present. The first is a simple intramolecular NH221···Br1 interaction whilst the second is a bifurcated hydrogen bond from the second pyrazole NH321 to both the intramolecular Br and to the Br of an adjacent symmetry related molecule. The latter gives rise to dimeric units (Fig. 2(b)). This hydrogen bond network may account for the comparatively low solubility that facilitates product recovery, without chromatography being necessary for purification.

4.3. Synthesis of [Mo($\equiv$CC$_6$H$_2$Me$_3$-2,4,6)Cl(CO)$_2$(py)$_2$]

A suspension of LiC$_6$H$_2$Me$_3$-2,4,6 was prepared as described above. Molybdenum hexacarbonyl (2.64 g, 10.0 mmol) was suspended in diethyl ether (100 ml), and the lithium reagent added in 30 ml aliquots. The solution was allowed to turn to a clear yellow solution (indicating the complete consumption of the lithium reagent) before each subsequent addition. The reaction was monitored via solution infrared spectroscopy as above. Once the amount of molybdenum carbonyl present was negligible (<5%), the solution was cooled to −78 °C treated dropwise with a solution of oxalyl chloride (5 ml, 2.0 mol dm^{-3}, 10 mmol) in dichloromethane. The solution was stirred for 10 min at −78 °C, warmed to −10 °C and stirred for a further 10 min. The solution was then cooled to −78 °C, and pyridine (2 ml) was slowly added to the reaction mixture, upon which the solution immediately becomes cloudy with evolution of gas (CO). The suspension was allowed to warm to room temperature slowly over 2 h with stirring. The resulting suspension was allowed to settle, and the supernatant decanted off and discarded (this contains further product, contaminated with [Mo(CO)$_6$]). The bright yellow solid was dried in vacuo and recrystallized from a mixture of dichloromethane and light petroleum (40–60). Yield = 2.26 g (47%). IR Nujol: 1991vs, 1908vs [ν(CO)], 1636w, 1602m, 1442w, 1213w, 1064m, 852w cm^{-1}. Et$_2$O: 2000, 1919 [ν(CO)]. CH$_2$Cl$_2$: 2000, 1919 [ν(CO)] cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 2.72$ [s, 3 H, C$_6$H$_2$CH_3-4], 2.97 [s, 6 H, C$_6$H$_2$CH_3-2,6], 7.24 [s, 2 H, H^{2,5}(C$_6$H$_2$)], 7.76–7.82 [m, 4 H, H^{3,5}(py)], 8.24–8.30 [m, 2 H, H^4(py)], 9.60–9.63 [m, 4 H, H^{2,6}(py)] ppm. ^{13}C{^{1}H} NMR (68 MHz, CDCl$_3$, 25 °C): $\delta = 20.41$ [C$_6$H$_2$$C$ H$_3$], 121.3 [C^4(C$_6$H$_2$)], 124.5 [C^3(py)], 128.3 [C^{3,5}(C$_6$H$_2$)], 138.0 [C^4(py)], 138.5 [C^1(C$_6$H$_2$)], 140.7 [C^2(py)], 152.8 [C^{2,6}(C$_6$H$_2$)], 224.7 (CO), 283.0 (Mo$\equiv$C). APCI-MS *m*/*z*(%) [assignment]: 476(10) [M]$^+$, 441(10) [Mo − Cl]$^+$.

4.4. Synthesis of [Mo($\equiv$CC$_6$H$_2$Me$_3$-2,4,6)(CO)$_2${(H$_2$B(mt)$_2$}]

(a) [Mo($\equiv$CC$_6$H$_2$Me$_3$-2,4,6)Cl(CO)$_2$(Hpz*)$_2$] (250 mg, 0.45 mmol) was dissolved in tetrahydrofuran (100 ml), and Na[H$_2$B(mt)$_2$] (118 mg, 0.45 mmol) was then added in one portion, with stirring. The solution was stirred at room temperature for 20 min and filtered through a short silica column to remove NaBr. The filtrate was freed of volatiles in vacuo, and the brown residue recrystallised from a mixture of dichloromethane and light petroleum to afford dark orange microcrystals. Yield = 157 mg (67%). (b) Similar treatment of [Mo($\equiv$CC$_6$H$_2$Me$_3$-2,4,6)Cl(CO)$_2$(py)$_2$] (215 mg, 0.45 mmol) provided the desired product. Yield 212 mg (90%). IR Nujol: = 1982, 1900 [ν(CO)], 1192, 1167, 1036 cm^{-1}. THF: 1981, 1905 [ν(CO)] cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 2.20$ [s, 3 H, C$_6$H$_2$CH$_3$-4], 2.52 [s, 6 H, C$_6$H$_2$CH$_3$-2,6], 3.55 (s, 6 H, NCH$_3$), 6.71 [s, 2 H, C$_6$H$_2$], 6.75, 6.79 [(AB)$_2$, 2 H × 2, ^{3}J(H$_A$H$_B$) = 2 Hz, C$_3$H$_2$N$_2$]. ^{13}C{^{1}H} NMR [68 MHz, d$_6$-dmso, 25 °C]: $\delta = 17.97$ (C$_6$H$_2$CH$_3$-2,6), 19.08 (C$_6$H$_2$CH$_3$-4), 32.48 (NCH$_3$), 120.4, 121.9 (NCN), 120.5 [C^{3,5}(C$_6$H$_2$)], 134.1 [C^4(C$_6$H$_2$)], 136.8, 139.3 [C^{2,6}(C$_6$H$_2$)], 151.4 [C^1(C$_6$H$_2$)], 157.5 (C=S), 222.7 (br, CO), 298.8 (br, Mo$\equiv$C). APCI-MS *m*/*z*(%) [assignment]: 464(10) [M − 2CO]$^+$, 385(60) [M − CC$_6$H$_2$Me$_3$]$^+$, 306(25) [Na + M − H$_2$B(mt)$_2$]$^+$, 279(5) [Na + M − H$_2$B(mt)$_2$ − CO]$^+$, 261(10) [NaH$_2$B(mt)$_2$]$^+$, 257(5) [M − H$_2$B(mt)$_2$-CO]$^+$. *Anal.* calc. for C$_{20}$H$_{23}$BMoN$_4$O$_2$S$_2$: 46.0; H, 4.44. Found: C, 46.6; H, 5.1%.

4.5. Synthesis of [W($\equiv$CC$_6$H$_2$Me$_3$-2,4,6)Cl(CO)$_2$(py)$_2$]

A mixture of lithium (1.39 g, 0.20 mol) and bromomesitylene (12.3 ml, 0.10 mol) were suspended in diethyl ether (200 ml) and stirred over 2 days to yield an off-white milky suspension. The reaction is not complete, with unreacted lithium still apparent. In a separate flask, tungsten hexacarbonyl (3.52 g, 10 mmol) was suspended in diethyl ether (100 ml), and the lithium reagent added in 30 ml aliquots. The solution was allowed to turn to a clear yellow solution (indicating the complete reaction of the lithium reagent) before each subsequent addition. The reaction of tungsten carbonyl was monitored via solution infrared spectroscopy [ν(CO) = 1974 cm^{-1}]. Once the amount of tungsten carbonyl present was negligible (<5%), the solution was cooled (dry ice/propanone) and a solution of oxalyl chloride in dichloromethane (5 ml, 2.0 mol dm^{-3}, 10 mmol) was slowly added drop-wise to the solution. The solution was stirred for 10 min before warming to −10 °C and stirring for a further 10 min. The solution was then recooled to −78 °C, and pyridine (2 ml) was slowly added to the reaction mixture (CO evolution). The solution was allowed to warm to room temperature slowly over 2 h with stirring. The resulting suspension was allowed to settle, and the liquor decanted off and discarded. The bright yellow solid was dried and recrystallised from dichloromethane-petrol. Yield = 3.56 g (63%). The compound was characterized by comparison of spectroscopic data with those previously reported [10].

4.6. Synthesis of $[W(CO)\{H_2B(mt)_2\}_2]$

A mixture of $[W(\equiv CC_6H_2Me_3\text{-}2,4, 6)Cl(CO)_2(py)_2]$ (2.00 g, 3.51 mmol) and $Na[H_2B(mt)_2]$ (1.86 g, 7.02 mmol) in tetrahydrofuran (150 ml) was heated under reflux for 24 h. The mixture was allowed to cool to room temperature over several hours, during which copious amounts of a brilliant green solid precipitated from the reaction mixture. The solid was filtered off and washed with dichloromethane (3×30 ml) and water (2×20 ml) to remove residual NaCl formed in the reaction. The solid was then washed with warm ethanol, and dried in vacuo, to yield the desired product as a dark green powder. Yield = 0.93 g (39%). IR Nujol: 2446, 2441 [ν(B-H)], 2246 [ν(BHMo)], 1765 [ν(CO)]; 1555, 1191, 1170 cm^{-1}. IR Solution: $\nu(CO) = 1785$ (CH_2Cl_2), 1764 (THF); 1771 (dmso) cm^{-1}. NMR ^1H (300 MHz, d_6-dmso, 25 °C): $\delta = -3.58$ (s.v.br, 1 H, B–H–W), 0.03 (s.v.br. 1 H, BH), 2.90, 3.45 (s × 2, 6 H × 2, NCH_3), 6.83, 7.27 [d × 2, 2 H × 2, $^3J(HH) = 1.5$, $C_3H_2N_2$], 6.94, 7.31 [d × 2, 2 H × 2, $^3J(HH) = 2.0$ Hz, CH=CH] ppm. $^{11}B\{^1H\}$ (96.2 MHz, d_6-dmso, 25 °C): $\delta = -4.97$ *Anal.* calc. for $C_{17}H_{24}B_2N_4OS_4W.2CH_2Cl_2$: C, 26.54; H, 3.28; N, 13.03. Found C, 26.6; H, 3.2; N, 13.4%. APCI-MS: m/z(%) [assignment] 691(40) $[M]^+$, 662(70) $[M - CO)]^+$. *Crystal data*: $C_{17}H_{24}B_2N_8OS_4W \cdot CH_2Cl_2$; $M_r = 775.10$; monoclinic; $P2_1/n$; $a = 9.5897(1)$; $b = 19.1292(2)$; $c = 15.0943(2)$ Å; $\beta = 91.5100$ (5)°; $V = 2767.99(5)$ Å^3; $Z = 4$; $D_x = 1.860$ g cm^{-3}; μ(Mo Kα) = 46.98 cm^{-1}; $T = 200$ K, green plate; 64499 measured reflections ($2\theta < 55°$), F refinement, $R = 0.023$, $wR = 0.016$ for 4431 independent absorption corrected reflections [$I > 3\sigma(I)$], 337 parameters, CCDC 235063.

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