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Relative Hemilabilities of $H_2B(az)_2$ (az = pyrazolyl, dimethylpyrazolyl, methimazolyl) Chelates in the Complexes $[M(\eta\text{-}C_3H_5)(CO)_2\{H_2B(az)_2\}]$ (M = Mo, W)

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The reactions of $[M(\eta^3\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ (M = Mo, W) or $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(PMe_2Ph)_2]$ with $Na[H_2B(mt)_2]$ (mt = methimazolyl) affords the complexes $[M(\eta^3\text{-}C_3H_5)(CO)_2\{\kappa^3\text{-}H,S,S'\text{-}H2B(mt)_2\}]$, the 3-centre, 2-electron B–H–M interaction of which was found to be inert with respect to opening under mild conditions, while more forcing conditions (heating with PMe_2Ph) resulted in cleavage of the entire allyl and borate ligands to form $[Mo(CO)_3(PMe_2Ph)_3]$. In contrast, the reaction of $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ with $Na[H_2B(pz)_2]$ affords either $[Mo(\eta^3\text{-}C_3H_5)(CO)_2\{\kappa^3\text{-}H,N,N'\text{-}H_2B(pz)_2\}]$ or (more likely) $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)\{\kappa^2\text{-}N,N'\text{-}H_2B(pz)_2\}]$ which in turn reacts with phosphines to provide $[[Mo(\eta^3\text{-}C_3H_5)(CO)_2(PPhR_2)\{\kappa^2\text{-}N,N'\text{-}H_2B(pz)_2\}]$ (R = Me, Ph). The reactions discussed indicate the propensity for 3-centre, 2-electron B–H–Mo interactions to increase $H_2B(pz)_2 < H_2B(pz^*)_2 < H_2B(mt)_2$ (pz* = 3,5-dimethypyrazolyl).

Introduction

The chemistry of hydrotris(pyrazolyl)borates[1] is dominated by their use as innocent spectator ligands, by virtue of their strong tendency to form stable complexes in which they bind in a tridentate manner to the face of a coordination polyhedron. Further kinetic stability may be conferred by the use of 3,5-disubstitued pyrazoles, in which case the substituents are proximal to the coordination sphere of the metal offering steric shielding and influencing coordination number preferences ("octahedral and tetrahedral enforcers"). The dihydrobis(pyrazolyl)borates have not been as widely studied, although they offer many of the same features. However, one feature that distinguishes them from the tris(pyrazolyl)borates is their propensity to enter into 3-centre, 2-electron coordination of a bridgehead borohydride group to the metal center.[2] This behaviour was first encountered in the molybdenum allyl complex $[Mo(\eta^3\text{-}C_3H_5)(CO)_2\{H_2B(pz^*)_2\}]$ (hereafter pz = pyrazol-1-yl, pz* = 3,5-dimethylpyrazol-1-yl, mt = methimazolyl) for which a non-inert gas configuration was initially suspected.[2a] Subsequently, κ^3-*H,N,N'* coordination of the $H_2B(pz^*)_2$ ligand was established crystallographically for this[3] and the related η^3-cycloheptatrienyl analogue[4] confirming, at least in the solid state, that the inert gas configuration is achieved, at the expense of maximal C_7H_7 *hapticity*. In the interim such behaviour has been established for transition metals as diverse as zirconium,[2c] yttrium[2v,2w] and platinum.[2x]

The dihydrobis(methimazolyl)borate ligand (Chart 1)[5] is in some ways reminiscent of the dihydrobis(pyrazolyl)borate ligand in that it has been shown to readily adopt the κ^3-*H,S,S'* coordination mode for a wide range of metals including d-, p- and f-block examples.

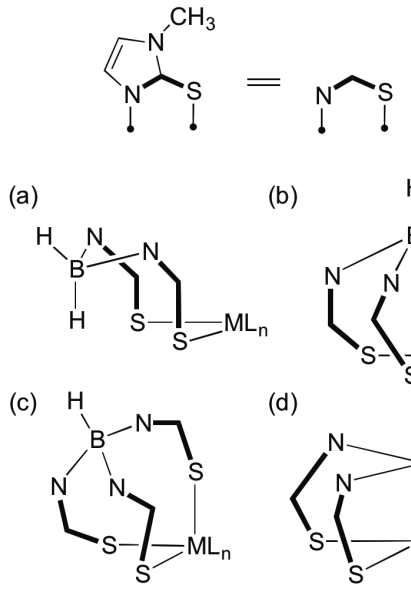

Chart 1. (a) κ^2-*S,S*-$H_2B(mt)_2$; (b) κ^3-*H,S,S*-$H_2B(mt)_2$; (c) κ^3-*S,S',S*-$HB(mt)_3$; (d) κ^4-*B,S,S',S''*-$B(mt)_3$ (metallaboratrane) Coordination Modes. mt = 2-mercapto-3-methyl-imidazol-1-yl (methimazolyl).

The inclusion of 3-atom bridges between boron and a metal so predisposes methimazolylborates to κ^3-*H,S,S'* coordination that a number of examples exist wherein this coordination mode is adopted even when a third classical door is available, *e.g.*, in complexes of bis(methimazolyl)pyrazolyl *and* tris(methimazolyl) borates.[6] Furthermore, this coordination mode can leave the two sulphur donors sufficiently nucleophilic

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[c] CCDC 1954561-1954565 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre

as to coordinate to a second metal.[7] Finally, complexes are known wherein two $H_2B(mt)_2$ ligands adopt distinct and non-interconverting κ^2-*S,S'* and κ^3-*H,S,S'* coordination modes (Chart 2b).[8]

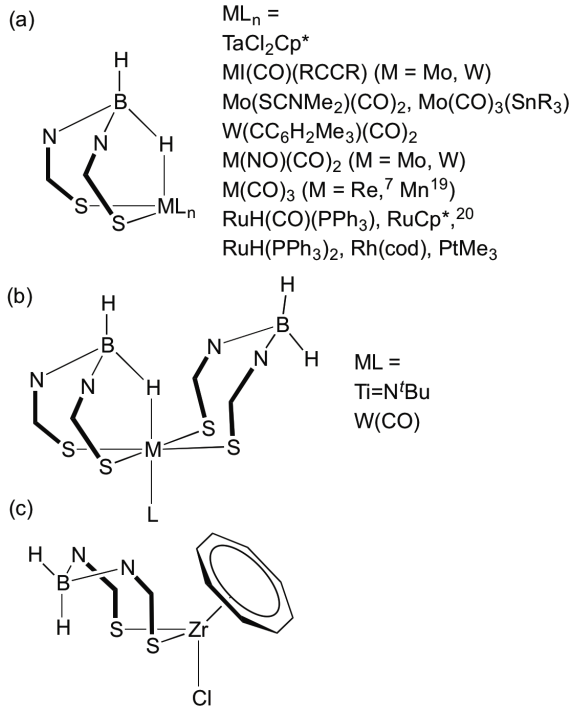


Chart 2. Coordinative flexibility of the $H_2B(mt)_2$ ligand: (a) Prevalent κ^3-*H,S,S'*-$H_2B(mt)_2$ coordination; (b) Disparate bonding modes in the same molecule; (c) A coordinatively unsaturated counter example of κ^2-*S,S'*-$H_2B(mt)_2$ coordination.

Santos and ourselves have encountered a similar propensity for this ligand to exhibit such behaviour, entering into κ^3-*H,S,S'* coordination to rhenium and molybdenum in the complexes $[Re(CO)_3\{\kappa^3\text{-}H_2B(mt)_2\}]$[9] and $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{\kappa^3\text{-}H_2B(mt)_2\}]$.[5b] Similar 3-centre, 2-electron (3c-2e) B–H–M interactions have been identified in the solid state structures of $[M\{H_2B(mt)_2\}_2]$ (M = Ru,[10] Ni,[11] Cd[12]) and the substituted derivatives $[M\{H_2B(mt^{tBu})_2\}_2]$ (M = Zn, Cd, Hg),[13] in contrast to the regular tetrahedral coordination of four sulfur donors to zinc observed in $[Zn\{H_2B(mt)_2\}_2]$ which is devoid of significant B–H–Zn interactions.[13] Notably, in the case of Santos' rhenium complex, it could be shown that the 3c-2e B–H–Re interaction could be readily opened by treating the complex with a variety of ligands to afford $[Re(CO)_3(L)\{\kappa^2\text{-}H_2B(mt)_2\}]$ (L = $CNCMe_3$, PPh_3, $pyNMe_2$-4),[9a] indicating the potential *hemilability* of such interactions, and calling to mind the similar behaviour of the manganese triboronate $[Mn(CO)_3(B_3H_8)]$, which possesses a similarly hemilabile B–H–Mn interaction.[14] There now exists a wide range of complexes of the $H_2B(mt)_2$ ligand in which it adopts the κ^3-*H,S,S'* bonding mode to a diversity of metals (Chart 2, Ti, Mo, W, Mn, Ru, Os, Rh, Ir, Pt)[5b,6a,7,8,15] including the examples $[ML\{H_2B(mt)_2\}_2]$ (ML = Ti=N^{t}Bu,[8b] WCO[8a]) with two $H_2B(mt)_2$ ligands each adopting different modes (κ^2-*S,S'* and κ^3-*H,S,S'*).

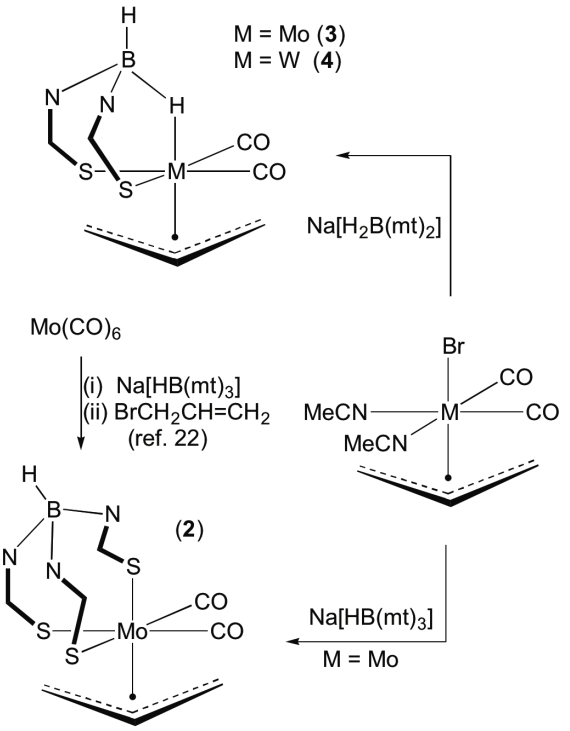
In the case of the tungsten complex, site exchange between the two disparately coordinated ligands could not be observed prior to the onset of thermal decomposition (*ca* 70 °C). In contrast, the 16-valence electron zirconium complex $[ZrCl(\eta^8\text{-}C_8H_8)\{H_2B(mt)_2\}]$[16a] adopts the κ^2-*S,S'* mode despite the coordinative unsaturation of the metal centre. Similar behaviour was observed for the hydrochlorobis(methimazolyl)borate ligand when bound (κ^2-*S,S'*) to niobium(V) and tantalum(V)[16b] whilst κ^3-*H,S,S'* coordination is observed for the tantalum(IV) complex $[TaCl_2(\eta\text{-}C_5Me_5)\{H_2B(mt)_2\}]$.[16c]

The molybdenum thiocarbamoyl and nitrosyl complexes $[Mo(L)(CO)_2\{\kappa^3\text{-}H_2B(mt)_2\}]$ (L = η^2-$SCNMe_2$,[5b] NO[15c]) form under particularly mild conditions from the reaction of the tetracarbonyl molybdate $[Mo(CO)_4\{H_2B(mt)_2\}]^-$ with dimethylthiocarbamoyl chloride or *N*-methyl-*N*-nitroso-4-toluenesulfonamide with spontaneous loss of *two* CO ligands, suggesting a strong tendency for the $H_2B(mt)_2$ ligand to adopt the *tridentate* coordination mode. We have a vested interest in understanding the nature of 3c-2e B–H–M interactions in the chemistry of poly(methimazolyl)borates, given our assertion[6a,17] that such interactions are mechanistically significant in the formation of metallaboratranes[17,18] via B–H activation. Such interactions are also relevant to the occasional *non-innocent* behaviour of $H_2B(mt)_2$ ligands, *e.g.* processes wherein boration of thiocarbonyl[19] and benzylidene[20] co-ligands have been observed. That said, the above observations would seem to suggest that definitive guidelines for the prediction of B–H–M hemilability are yet to emerge. We have now turned out attention to investigating the nature of this coordination relative to that of the more familiar $H_2B(pz)_2$ and $H_2B(pz^*)_2$ ligands and have therefore returned to the archetypal '$Mo(CO)_2(\eta\text{-}C_3H_5)$' fragment for comparative purposes.

Results and Discussion

Trofimenko's complex $[Mo(\eta\text{-}C_3H_5)(CO)_2\{H_2B(pz^*)_2\}]$ (**1**)[2a] is readily prepared either by reaction of $K[Mo(CO)_4\{H_2B(pz^*)_2\}]$ (prepared *in situ*) with allyl bromide or *via* the reaction of the pre-formed allyl complex $[Mo(\eta\text{-}C_3H_5)Cl(CO)_2(NCMe)_2]$[21] with $K[H_2B(pz^*)_2]$. Our initial studies began with a similar approach to the preparation of the hydrotris(methimazolyl)borato complex $[Mo(\eta\text{-}C_3H_5)(CO)_2\{HB(mt)_3\}]$ (**2**) which could be obtained in 92% yield from $Na[HB(mt)_3]$ and $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$. Complex **2** was reported previously by Reglinski[22] *via* a direct, albeit lower yielding (40%) route from $[Mo(CO)_6]$, $Na[HB(mt)_3]$ and allyl bromide (Scheme 1). From both the ^1H and $^{13}C\{^1H\}$ NMR spectra for **2**, it is clear that the molecule is fluxional on the NMR timescales in that (i) a single resonance is observed for the N-CH_3 groups in both spectra, (ii) a single (**AB**)$_3$ pattern is observed for the CH=CH unit of the three heterocycles in the ^1H NMR spectrum and (iii) a single resonance (δ = 226.1) is observed for the $Mo(CO)_2$ unit in the $^{13}C\{^1H\}$ NMR spectrum. The ground-state structure, as established crystallographically, has C_1 symmetry presenting three chemically distinct methimazolyl environments. Similar behaviour has been noted in the case of the alkylidyne tungsten complexes $[W(\equiv CR)(CO)_2\{HB(mt)_3\}]$ (R = N^{i}Pr$_2$, C_6H_4Me-4)[23] and attributed to a three-site mt exchange mechanism involving dissociation of one mt arm followed by Berry *pseudo*-rotation.

A similar fluxionality seems likely in the case of **2**, rather than the commonly encountered σ-π or *endo-exo* interconversion processes typically undergone by allyl ligands,[24] which would not chemically equilibrate all three methimazolyl environments. Each proton and carbon of the allyl ligand remains chemically distinct at room temperature as indicated by ^{1}H, $^{13}C\{^{1}H\}$ and ^{1}H-^{13}C correlated NMR spectroscopy. The methine ^{1}H resonance for the allyl ligand is somewhat obscured by the strong NCH_3 resonance, however its identity was unambiguously confirmed by COSY measurements (Figure 1).



Scheme 1. Synthesis of Poly(methimazolyl)borato Allyl Complexes of Molybdenum and Tungsten

The fluxionality of the complex was investigated by VT-^{1}H NMR spectroscopy (233 – 293 K, $CDCl_3$), with the spectra thus obtained indicating a broadening of the NCH_3 resonance at 283 K, a coalescence temperature of *ca* 270 K and three NCH_3 resonances that were sharp and well resolved below 250 K. The allyl resonances were essentially invariant throughout this temperature range and thus not intimately involved in the dynamic process. This is in accord with observations for the complex $[Mo(\eta\text{-}C_3H_5)(CO)_2\{HB(pz)_3\}]$[25] for which the allyl component of the spectrum is invariant over the range 233 – 323 K, with fluxionality being limited to the $HB(pz)_3Mo$ cage. In contrast, the complex $[Mo(\eta\text{-}C_3H_5)(CO)_2(\eta\text{-}C_5H_5)]$[26] is a text-book example of classical allyl fluxionality, between *endo* and *exo* conformations.

Treatment of $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ with $Na[H_2B(mt)_2]$ in dichloromethane provides high yields of the orange complex $[Mo(\eta\text{-}C_3H_5)(CO)_2\{H_2B(mt)_2\}]$ (**3**). Complex **3** was characterized by elemental microanalysis, spectroscopy

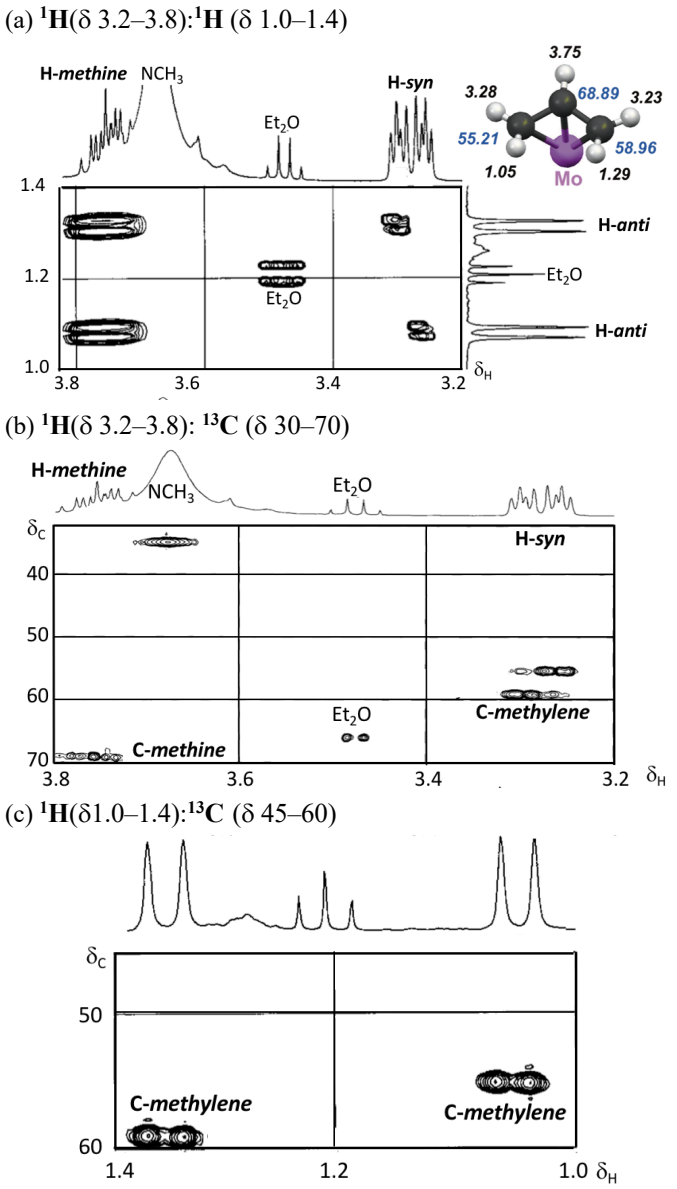


Figure 1. Truncated COSY NMR spectra for **2** (δ_H and δ_C).

and single-crystal X-ray diffraction. The molecular structure of **3** is depicted in Figure 2 and will be discussed below.

The feature of particular interest from the infrared spectrum is the appearance of two medium intensity absorptions at 2467 and 2287 cm^{-1} (Nujol) attributable to the terminal B–H and B–H–Mo bridge stretches. It would be premature to delineate a frequency range that is unequivocally diagnostic for B–H–M interactions in $H_2B(mt)_2$ complexes, however this value is comparable to those found for $[Re(CO)_3\{H_2B(mt)_2\}]$ (2140, 2060),[9] $[Mo(\eta^2\text{-}SCNMe_2)(CO)_2\{H_2B(mt)_2\}]$ (2261)[5b] and $[M\{H_2B(mt)_2\}]$ (M = Cd, 2355; Hg, 2360, 2287 cm^{-1}).[12] Furthermore the complex $[RuH(CO)(PPh_3)\{\kappa^3\text{-}H,S,S'\text{-}HB(mt)_3\}]$ which features a B–H–Ru interaction has an absorption at 2213 cm^{-1}.[6a] The 3c-2e coordination of one B–H group to molybdenum is also indicated by the appearance of a broadened resonance centred at δ_H = –5.7 ppm. At temperatures above 293 K thermal decoupling of

the boron quadrupole is sufficient to resolve a quartet structure with $^1J_{BH}$ ≈ 87 Hz (*cf.* 72 Hz for [RuCl(dmso)$_2${κ^3-*H,S,S'*-HB(mt)$_2$}][15d]). Throughout the

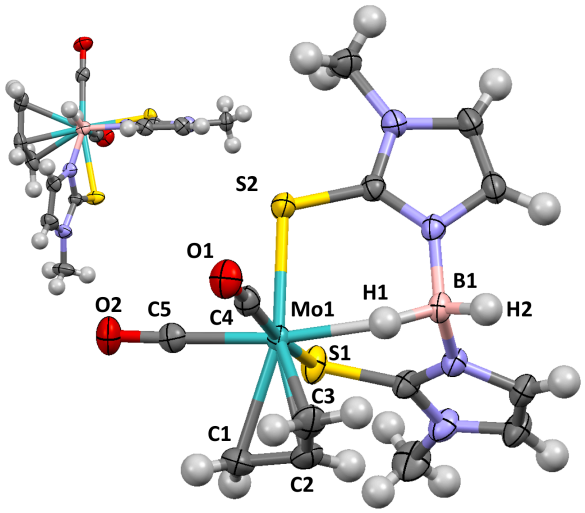


Figure 2. Molecular structure of **3** in a crystal of **3**.CH_2Cl_2 (50% probability ellipsoids) in the solid state. Selected bond lengths (Å) and angles (°): Mo1–S1 2.6047(8), Mo1–S2 2.4832, Mo1–C1, 2.365(3), Mo1–C2 2.231(3), Mo1–C3 2.326(3), Mo1–C4 1.956(3), Mo1–C5 1.943(3), Mo1–B1 3.003(3), Mo1–H 1.97(3), B1–H1 1.19(3), B1–H2 1.11(3), S1–Mo1–S2 85.27(3), S1–Mo–C1 79.34(11), S1–Mo–C2 86.5(1), C4–Mo–C5 80.00(11), Mo1–H1–B1 143(3), C1–C2–C3 117.0(3), N12–B1–N22 110.1. Inset = view along B···Mo vector.

temperature range 193 – 303 K the chemical shift of this resonance is invariant, suggesting that the B–H–Mo interaction is retained whilst other fluxional processes operate. Specifically, at ambient temperatures the mt heterocycles are chemically equivalent on the ^{1}H NMR timescale, however at lower temperatures (193 – 253 K, coalescence at ≈ 268 K) two distinct environments are observed, consistent with the structure adopted in the solid state (*vide infra*).

The corresponding tungsten complex [W(η^3-C_3H_5)(CO)$_2${H_2B(mt)$_2$}] (**4**) was obtained in 78% yield from the similar reaction of [W(η-C_3H_5)Br(CO)$_2$(NCMe)$_2$][27] and Na[H_2B(mt)$_2$]. Spectroscopic data for **4** were essentially comparable to those for **3** such that the ^{1}H and ^{13}C{^{1}H} NMR spectra were both indicative of fluxionality at room temperature. Nevertheless, the presence of a 3c-2e B–H–W coordination was evident from the appearance of a resonance in the ^{1}H NMR spectrum at δ = –4.9 the broadness of which precluded resolution of $^1J_{BH}$ or $^1J_{WH}$. This was further confirmed by the appearance of a ν(B–H–W) infrared absorption both in solution (THF: 2237 cm^{-1}) and in the solid state (Nujol: 2239 cm^{-1}). The identity of **4** was further confirmed by an X-ray crystallographic analysis, the results of which are summarized in Figure 3 and discussed below.

Given the inferred retention of the B–H…Mo interaction we were eager to assess the nature of this interaction in comparison with similar interactions for bis(pyrazolyl)borate complexes. The geometry of mt-derived borate chelates differs from those based on pyrazoles in that the arms of the former chelate are each one atom longer than in the latter. Thus, whilst quite flattened 6-membered B(pz)$_2$M rings are commonplace,[1] similar flattening of the corresponding 8-membered B(mt)$_2$M rings would be expected to be disfavoured, simply on geometric grounds. For bis(pyrazolyl)borate coordination, the introduction of 3,5-disubstitution appears to favour a deepening of the boat conformation with an attendant increase in the propensity for 3c-2e B–H–M coordination, thereby alleviating steric conflict between the 5-substitutents and the boron. We therefore considered it useful to compare the reactivity of **3** with that of [Mo(η-C_3H_5)(CO)$_2${H_2B(pz*)$_2$}] (**1**)[3] and the analogous complex [Mo(η-C_3H_5)(CO)$_2${H_2B(pz)$_2$}]. Trofimenko has already noted that complex **1** is unreactive towards acids and bases failing to display the electrophilicity expected for (what he presumed to be) a coordinatively unsaturated complex. The complex [Mo(η^3-C_3H_5)(CO)$_2${H_2B(pz)$_2$}] (**'5'**) appears to be unknown, and to pre-empt the following, remains so.

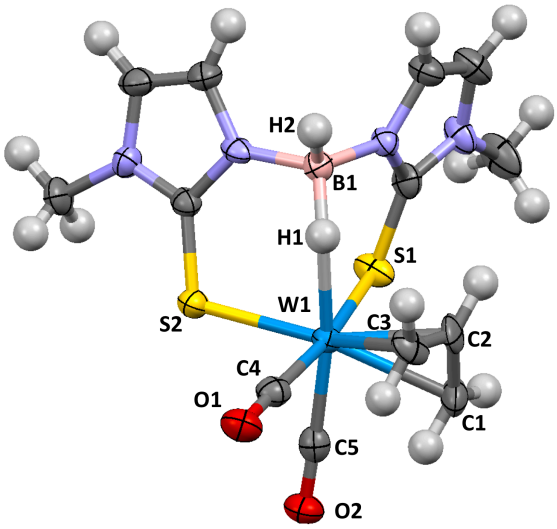
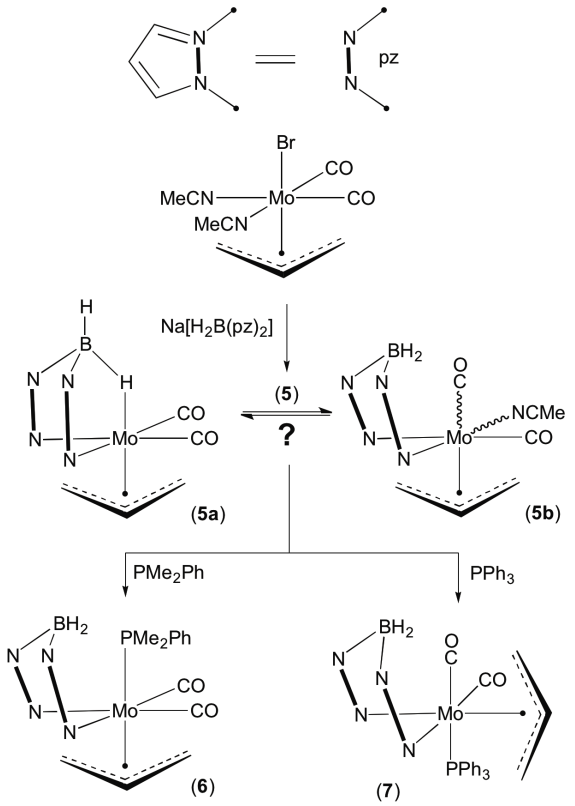


Figure 3. Molecular structure of **4** in a crystal of **4**.CH_2Cl_2 (50% probability ellipsoids) in the solid state. Selected bond lengths (Å) and angles (deg): W1–S1 2.587(2), W1–S2 2.473(2), W1–C1 2.378(8), W1–C2 2.236(7), 2.322(8), W1–C4 1.953(9), W1–B1 2.984(9), W1–H1 1.96(8), B1–H1 1.26(9), B1–H2 1.09(8), S1–W1–S2 84.87(7), S1–W1–C5 97.37(24), S2–W1–C4 85.36(26), C1–C2–C3 116.2(8).

In an attempt to prepare '**5**' a solution of [Mo(η-C_3H_5)Br(CO)$_2$(NCMe)$_2$] in dichloromethane was treated with Na[H_2B(pz)$_2$] resulting in the formation of a yellow solution of a thermally and air sensitive complex. The IR absorptions due to the starting complex [Nujol:[21] ν_{CO} = 1953, 1852 cm^{-1}] were replaced by bands at 1952 and 1861 cm^{-1} whilst the ν_{BH} region of the spectrum contained only weak equivocal absorptions. Attempts to isolate the thermally unstable product have so far met with failure and we are unable to say with certainty whether this species is [Mo(η-C_3H_5)(CO)$_2${κ^3-*H,N,N'*-H_2B(pz)$_2$}] (**'5a'**) or [Mo(η-C_3H_5)(CO)$_2$(NCMe){κ^3-*H,N,N'*-H_2B(pz)$_2$}] (**'5b'**, Scheme 2).

Solution infrared data (CH_2Cl_2) obtained after filtration through silica gel are not definitive: In addition to an absorption attributable to a terminal B–H stretch (2416 cm^{-1}), two slightly weaker bands (2286, 2254 cm^{-1}) appear in a region

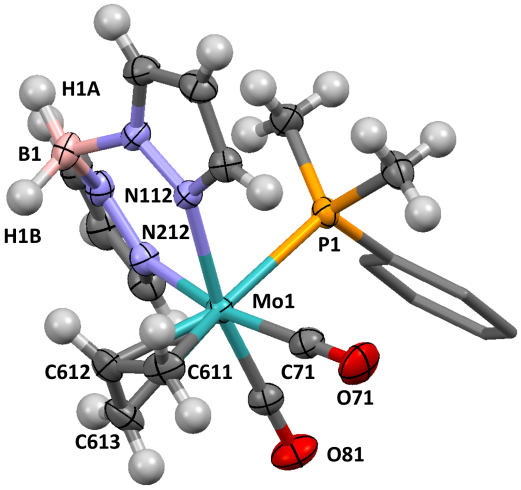


Scheme 2. Synthesis of Dihydrobis(pyrazolyl)borato Allyl Complexes of Molybdenum

that is consistent with either coordinated acetonitrile or a 3c-2e B–H–Mo interaction, whilst the higher of the two ν_{CO} absorptions (1946, 1853 cm^{-1}) appears to carry a shoulder to lower frequency. Thus solutions of '**5**' could well comprise mixtures of both '**5a**' and '**5b**'. The infrared spectrum calculated for '**5a**' (DFT: MO6-2X/6-31G*/LanL2DZ/gas phase) and scaled (0.977) to align calculated (1959, 1896 cm^{-1}) and observed ν_{CO} frequencies, has the agostic ν_{BHMo} absorption at 2098 cm^{-1}. Thus it seems likely that the absorptions at 2286, 2254 cm^{-1} correspond to coordinated and free acetonitrile, with formation of **5b** rather than **5a** (neat MeCN has ν_{CN} = 2252 cm^{-1}). It is worth noting in passing that the starting geometry used for geometry optimisation was that based on the published coordinates for **1** with pyrazolyl and allyl methyl substituents removed. For **1** the (albeit imprecise) Mo–H bond length is 2.13 Å, whilst the optimisation process for **5a** elongates this to 2.289 Å, providing further indirect circumstantial evidence for weaker B–H–M interactions in Bp *cf.* Bp* κ^3-*H,N,N'* coordination.

Nevertheless, the intermediate could be shown to be *synthetically equivalent* to "[Mo(η-C_3H_5)$(CO)_2${$H_2B(pz)_2$}]" in reactions with phosphines: Treating the solution of '**5**' with either PMe_2Ph or PPh_3 resulted in the formation of the simple adducts [Mo(η-C_3H_5)$(CO)_2$(L){$H_2B(pz)_2$}] (L = PMe_2Ph **6**, PPh_3 **7**), which by simple 18-electron rule arguments must have the $H_2B(pz)_2$ ligand adopting a κ^2-*N,N'* coordination mode. The solid state structures of both **6** and **7** were established crystallographically (Figures 4 and 5).

Figure 4. Molecular structure of **6** (50% probability ellipsoids) in the solid state. Phenyl



groups simplified. Selected bond lengths (Å) and angles (°): Mo1–C612 2.228(2), Mo1–C611 2.322(2), Mo1–C71 1.966(2), Mo1–C81 1.958(2), Mo1–N112 2.255(2), Mo1–N212 2.247(2), Mo1–P1 2.5563(7), Mo–C611 2.322(12), Mo–C612 2.23(2), Mo–C613 2.338(3), Mo–B1 3.63(1), B1–H1A 1.10(3), B1–H1B 1.10(3), C71–Mo1–C81 81.71(8), N112–Mo1–N212 86.50(5), P1–Mo1–N112 80.32(4), P1–Mo1–N212 81.27(4), P1–Mo1–C71 85.74(6), P1–Mo1–C81 89.27(6).

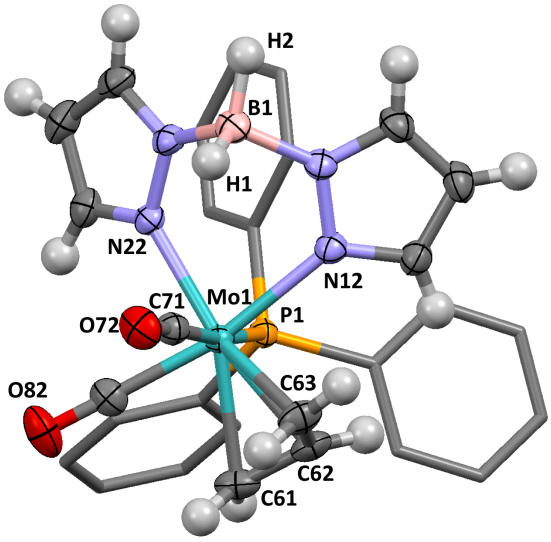


Figure 5. Molecular structure of **7** (50% probability ellipsoids) in the solid state. Phenyl groups simplified. Selected bond lengths (Å) and angles (°): Mo1–P1 2.7277(5), Mo1–N12 2.274(2), Mo–N22 2.226(2), Mo1–C61 2.315(2), Mo1–C62 2.218(2), Mo1–C63 2.325(2), Mo1–C71 1.971(2), Mo1–C81 1.950(2), C61–C62 1.405(3), C62–C63 1.410(3), P1–Mo1–C81 98.05, N12– Mo1–C71 96.54(7), N22– Mo1–C71 89.21(7), C71– Mo1–C81 78.97(8), N12–Mo–N22 83.28(6), C61–C62–C63 114.1(2), N21–B1–N11 108.23(16).

Spectroscopic features of note for **6** and **7** include (i) the absence of infrared absorptions in the region typical of 3c-2e B–H–Mo interactions; (ii) the absence of ^1H resonances to high field of $SiMe_4$, this being the region typical of B–H–M interactions. Both the ^1H and $^{13}C\{^1H\}$ NMR data for the complexes, however, show distinctions due to the formation of different isomers. In the case of **6**, $^{31}P\{^1H\}$ NMR spectroscopy indicates the presence of only one isomer (δ_P = 1.82) whilst in the case of **7** at room temperature two broad peaks are observed at δ_P 25.8 and δ_P –4.37, corresponding respectively to coordinated and free PPh_3 in equilibrium. This equilibrium is

also reflected in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **7**. In the latter, resonances attributable to the carbonyl (δ 226.7), pyrazolyl (δ 144.2, 136.0 and 106.0) and allyl-methylene (δ = *ca* 61) carbon nuclei are substantially broadened. One isomer is obtained on crystallization (Figure 4), however re-dissolution of this material (including the crystal used for diffractometry) regenerates the broadened spectrum. In the case of **6**, the $^{13}C\{^{1}H\}$ NMR spectrum clearly indicates C_s symmetry (ground-state or time-averaged) corresponding to the isomer with the phosphine *trans* to the allyl ligand and *cis* ($^{2}J_{PC}$ = 15.1 Hz) to the chemically equivalent carbonyl ligands, *i.e.*, the geometry corresponding to that adopted in the solid state (*vide infra*, Figure 4). Either the complex adopts the geometry in which the PMe_2 unit straddles a molecular plane of symmetry, or alternatively if free rotation occurs for this comparatively compact phosphine, it proceeds via such a geometry so as to render the halves of the molecule chemically equivalent. The dynamic processes apparent in the $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra of **7** prevent meaningful inferences about the stereochemistry at molybdenum, though in the solid state this involves a different stereochemistry to that of **6**. It therefore appears that the PMe_2Ph ligand of **6** does not dissociate in solution, whilst the PPh_3 ligand of **7** does.

Suspecting that the tungsten analogue of '**5**' might be more amenable to isolation, the reaction of $[W(\eta\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ with $K[H_2B(pz)_2]$ in tetrahydrofuran was investigated, however similar behaviour was observed. After 15 minutes, a compound with ν_{CO} = 1931, 1839 cm^{-1} and possibly $\nu_{BHW}/\nu_{C\equiv N}$ = 2289, 2252 cm^{-1} was observed. In dichloromethane, however upon standing (2 days) these converted to 1935 and 1837 cm^{-1} with loss of the albeit weak band attributed to ν_{BHW} or ν_{CN}. Slow crystallization of the product led to the gradual formation of a compound formulated as $[W(\eta\text{-}C_3H_5)(CO)_2(Hpz)\{H_2B(pz)_2\}]$ (**8**) on the basis of spectroscopic, microanalytical and crystallographic data.

The molecular structure of **8** is shown in Figure 6 and discussed below. Having carefully confirmed (^{1}H NMR, IR) the absence of free pyrazole in the sample of $K[H_2B(pz)_2]$ employed, it may be concluded that the formation of **8** proceed via metal-mediated cleavage of the $H_2B(pz)_2$ ligand. Furthermore, when the solution presumed to contain either $[W(\eta\text{-}C_3H_5)(CO)_2\{H_2B(pz)_2\}]$ or $[W(\eta\text{-}C_3H_5)(CO)_2(NCMe)\{H_2B(pz)_2\}]$ ('**9**') was treated with extraneous pyrazole, the immediate and spectroscopically quantitative conversion to **8** [ν_{CO} = 1927, 1830 cm^{-1}] was observed.

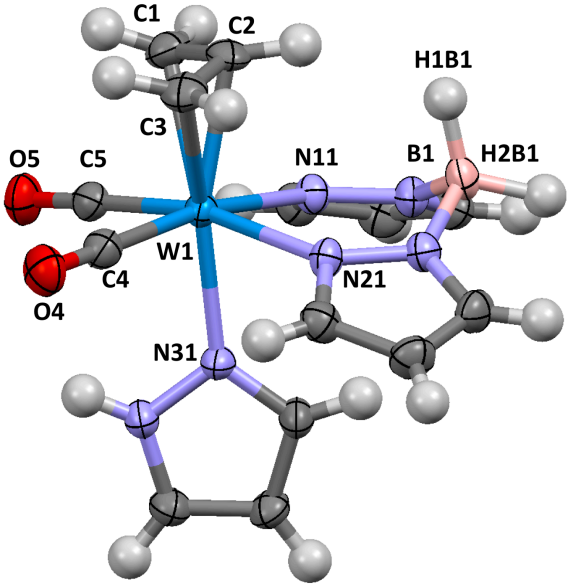
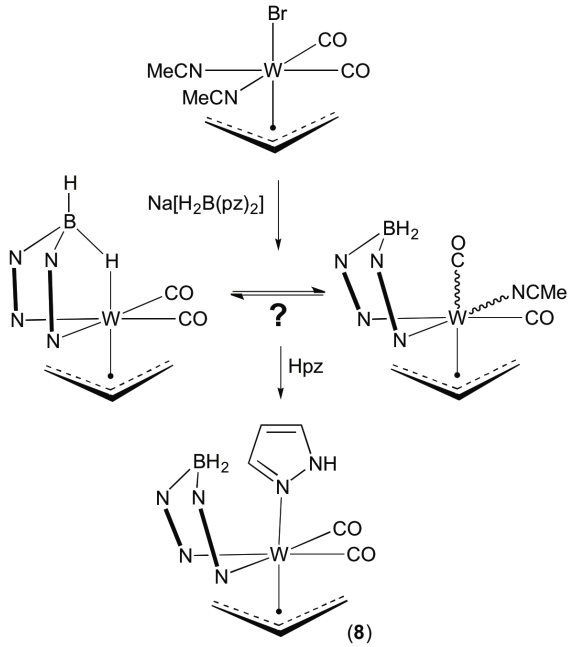


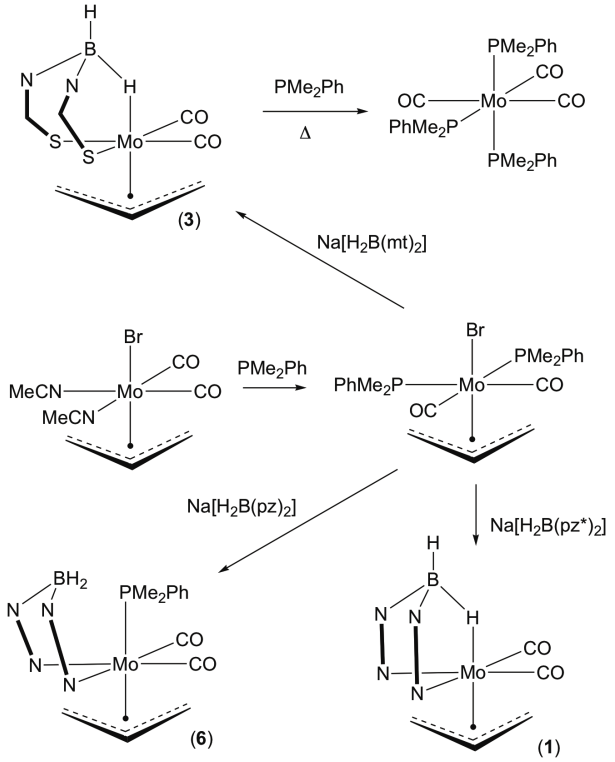
Figure 6. Molecular structure of **8** (50% probability ellipsoids) in the solid state. Selected bond lengths (Å) and angles (°): W1–C5 1.937(4), W1–C4 1.972(4), W1–C2 2.205(4), W1–C1 2.323(4), W1–C3 2.326(5), W1–N31 2.208(4), W1–N21 2.237(4), W1–N11 2.237(3), C1–C2 1.412(7), N22–B1 1.556(6), C2–C3 1.413(6), B1–H1B1 1.16(5), B1–H2B1 1.17(5), C5–W1–C4 83.57(17), C5–W1–N31 87.53(16), C4–W1–N31 90.50(16), C4–W1–N21 93.75(15), N31–W1–N21 78.45(13), C5–W1–N11 95.05(15), C4–W1–N11 169.28(15), N31–W1–N11 78.81(13), N21–W1–N11 84.98(12), N12–B1–N22 108.4(3), C1–C2–C3 115.2(4).

The cleavage or redistribution of pyrazolyl borates is not uncommon,[28] indeed pyrazole (Hpz) and dimethylpyrazole (Hpz*) adducts were reportedly obtained from the reactions of $K[Mo(CO)_4\{Et_2B(pz)_2\}]$ or $K[Mo(CO)_4\{H_2B(pz^*)_2\}]$, respectively with allyl or methyl halides.[3] Similarly, the complexes $Na[W(CO)_4\{R_2B(pz)_2\}]$ (R = Et, Ph) react with allylic electrophiles to provide compounds purported to be $[W(\eta\text{-}C_3H_5)(CO)_2(Hpz)\text{-}\{R_2B(pz)_2\}]$,[3] formulations that are now substantiated by the structural characterization of **8**.



Scheme 3. Synthesis of dihydrobis(pyrazolyl)borato allyl complexes of tungsten.

Given the facile formation of complexes **6** and **7**, the reactions of **3** and Trofimenko's complex **1** with phosphines were investigated to establish how easily the B–H–Mo interaction might be opened, *i.e.*, if it is *hemilabile* in a manner akin to Santos' complex $[Re(CO)_3\{H_2B(mt)_2\}]$.[7] Under the mild conditions that '**5**' reacts with phosphines (room temperature, CH_2Cl_2) no reaction was observed between either **1** or **3** and PMe_2Ph or PPh_3. Under more forcing conditions, the reaction of **3** with excess PMe_2Ph in refluxing tetrahydrofuran (b.p. 65 °C), benzene (b.p. 80 °C) or toluene (b.p. 110 °C) failed to provide any complexes bearing *both* the $H_2B(mt)_2$ and PMe_2Ph ligands. Rather, in all cases the only compound that could be isolated in appreciable amounts was $[Mo(CO)_3(PMe_2Ph)_3]$ (Scheme 4), which by comparison of IR and ^1H NMR data with those published by Shaw[29a] was found to form as the *mer* isomer (δ_P = 8.89d, –2.72t, $^2J_{PP}$ = 22 Hz). Further new characterisational data (MS, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR) are provided in the experimental section, further supporting Shaw's original geometry assignment.



Scheme 4. Phosphine substitution reactions.

The fate of the allyl and $H_2B(mt)_2$ ligands was not established however two possible interpretations present themselves. Either the complex is reduced by initial attack of PMe_2Ph at the coordinated allyl to liberate an allylphosphonium salt (not isolated) or alternatively, initial attack might occur at the metal centre to give an intermediate that is however unstable. The former route has precedent in the synthesis of $[Mo(CO)_2(NCMe)_2(PPh_3)_2]$ from $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ and PPh_3.[30] Indeed it has been reported that the reaction of -$[Mo(\eta\text{-}C_3H_4R\text{-}2)Cl(CO)_2(NCMe)_2]$ (R = H, Me) with PMe_2Ph also leads to reduction of the molybdenum center,[29a] as does the reaction with excess CNMe to provide $[Mo(CO)_2(CNMe)_4]$.[32] Mawby has shown that in the reaction of $[Mo(\eta\text{-}C_3H_4Me\text{-}2)Cl(CO)_2(NCMe)_2]$ with excess PMe_2Ph, the complex $[Mo(\eta\text{-}C_3H_4Me\text{-}2)Cl(CO)_2(PMe_2Ph)_2]$ could be isolated and shown to be an intermediate in the subsequent reduction to $[Mo(CO)_2(PMe_2Ph)_4]$, although the less stable parent allyl complex $[Mo(\eta\text{-}C_3H_5)Cl(CO)_2(PMe_2Ph)_2]$ eluded isolation.[31b] We find that a comparatively stable solution of $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(PMe_2Ph)_2]$ (ν_{CO} = 1940, 1848 cm^{-1} *cf.* 1936, 1808 for $[Mo(\eta\text{-}C_3H_4Me\text{-}2)Cl(CO)_2(PMe_2Ph)_2]$ in Nujol[31]) may be generated by addition of two equivalents of PMe_2Ph to a dichloromethane solution of $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$ (see Experimental; ν_{CO} = 1951, 1893 cm^{-1}). On the assumption that pre-coordination of PMe_2Ph might allow the synthesis of possible intermediates in the conversion of **3** to $[Mo(CO)_3(PMe_2Ph)_3]$, this solution was treated with $Na[H_2B(mt)_2]$. In a spectroscopically quantitative (IR) reaction, the instantaneous formation of **3** was observed, *i.e.*, liberation of *both* phosphine ligands rather than one or more carbonyls. Thus, under mild conditions we might surmise that the intermediate $[Mo(\eta\text{-}C_3H_5)(CO)_2(PMe_2Ph)\{H_2B(mt)_2\}]$ forms *en route* to **3**, but that expulsion of the remaining PMe_2Ph is rapid, irreversible and more facile than decarbonylation. We are therefore inclined to suspect that the conversion of **3** to $[Mo(CO)_3(PMe_2Ph)_3]$ occurs *via* direct attack by PMe_2Ph at the coordinated allyl, and that under these thermolytic conditions subsequent CO scrambling occurs. In a similar manner the reaction of solutions of $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(PMe_2Ph)_2]$ with $K[H_2B(pz^*)_2]$ provides **1**, whilst with $K[H_2B(pz)_2]$ complex **6** is obtained, both proceeding in spectroscopically quantitative yields. The formation of $[Mo(CO)_3(PMe_2Ph)_3]$ from **3** and PMe_2Ph is not clean, with other unidentified species being apparent when monitoring the reaction by infrared spectroscopy. Specifically, in tetrahydrofuran (4 days, reflux, 1 equivalent PMe_2Ph) although $[Mo(CO)_3(PMe_2Ph)_3]$ is by far the major product , a small amount (<5%) of a compound with ν_{CO} = 1936 cm^{-1} is apparent although this does not survive chromatographic purification in sufficient amounts for characterization. We suspect, however, that this corresponds to small amounts of the compound $[Mo_2(\mu\text{-}mt)_2(\eta\text{-}C_3H_5)_2(CO)_4]$ (ν_{CO} = 1935, 1872, 1852 cm^{-1}) which was previously obtained from the reaction of $Na[Me_2Ga(pz)(mt)]$ with $[Mo(\eta\text{-}C_3H_5)Br(CO)_2(NCMe)_2]$.[32]

The reluctance of the $H_2B(mt)_2$ ligand to adopt a bidentate coordination mode with divalent molybdenum appears incongruous given the results obtained by Santos for rhenium complexes. In further pursuit of a complex of reduced $H_2B(mt)_2$ denticity, the reaction of $Na[H_2B(mt)_2]$ with $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ was investigated, mindful that a similar reaction with $K[B(pz)_4]$ provides the complex $[Mo(CO)_2(\eta\text{-}C_5H_5)\{\kappa^2\text{-}B(pz)_4\}]$.[33] The crystal structure of this complex[33b] revealed a bidentate coordination for the $B(pz)_4$ ligand rather than increased denticity *via* further pyrazolyl coordination. We have been unable to identify the desired complex $[Mo(CO)_2\{H_2B(mt)_2\}(\eta\text{-}C_5H_5)]$ amongst the products of the reaction. Rather, the major product is the dimer $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ arising from a redox process in addition to a second compound (not obtained pure) which we formulate as $[Mo(\kappa^2\text{-}mt)(CO)_2(\eta\text{-}C_5H_5)]$. Cotton has

also observed the formation of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in reactions of $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ with either $K[HB(pz)_3]$[34] or $K[B(pz)_4]$[35] and it may be assumed that in serving as a reductant, the borate liberates Hmt for subsequent reaction with further $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$. The complex $[Mo(\kappa^2\text{-mt})(CO)_2(\eta\text{-}C_5H_5)]$ could more systematically be prepared independently from $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ and methimazole, however even in this case substantial amounts of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ were obtained, although the oxidation product of methimazole was not identified. Attempts to improve the yield of this complex by generating a solution of $[Mo(CO)_2(NCMe)_2(\eta\text{-}C_5H_5)]BF_4$ from the reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with $AgBF_4$ in acetonitrile were unsuccessful.

Infrared Data

There now exists a substantial range of allyl complexes of the general form $[Mo(\eta\text{-}C_3H_5)(CO)_2(L)]$ wherein the ligand L nominally occupies three sites of a *pseudo*-octahedron. Indeed, many more examples exist for substituted allyl derivatives,[36] with interest in such species arising from the deployment in a range of stoichiometic transformations within organic synthetic strategies.[36-40] Indeed it is within this context that the $HB(pz)_3$ ligand has most attracted the attention of synthetic organic chemists, offering demonstrable advantages over cyclopentadienyl based ligands. Since nucleophilic addition to the coordinated allyl ligand is often a key transformation (usually enhanced by CO/NO^+ substitution[36-40]), the electronic nature of the 'innocent' facial ligand "L" can play a moderating role. Due to the plethora of fluxional processes that may occur over different temperature ranges for such complexes, involving either the allyl (*endo-exo*, σ-π interconversion) or L ligands (rotations, variations in hapticity), NMR data are less robust indicators on which to base comparison. Accordingly, infrared data associated with ground-state structures (or isomers) provide the spectroscopic method of choice for useful comparison. Table 1 collates carbonyl associated infrared data for a range of the parent allyl complexes of the form $[Mo(\eta\text{-}C_3H_5)(CO)_2(\textit{fac}\text{-}L)]$.[3,21,30,36l,42-58]

Tungsten alkylidyne chemistry is somewhat more evolved than that of molybdenum and accordingly a similar analysis has been provided based on $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\textit{fac}\text{-}L)]$ which concluded that the $HB(mt)_3$ ligand was especially basic.[23] These data are ordered with respect to the decreasing π-basicity of the 'M(η-C_3H_5)L' fragment based on either the mean value of ν(CO) [$\nu_m = 0.5 \times (\nu_s + \nu_{as})$] or the Cotton-Kraihanzel force constant.[58] Each parameter involves attendant approximations, however since the ordering is identical for either parameter, in this qualitative use, either serves the purpose. Similarly, since both parameters assume that the two carbonyl ligands are equivalent and have similar interaction constants[59] the lowering of the local C_3 or C_{3v} symmetry of complexes involving ligands with two azolyl donors and one 3c-2e C–H–M or B–H–M interaction introduces uncertainty. Nevertheless, From Table 1 it is clear that the $HB(mt)_3$ ligand in a *trihapto* coordination mode (*vide infra*) is a particularly strong net donor to the molybdenum centre surpassed only by the dianionic dicarbaboranes $C_2B_9H_9R_2$ (R = H, Me, Ph) which by charge balance provide anionic complexes.[41,42] In contrast, the $H_2B(mt)_2$ ligand is seen to be intermediate in the series, indicating that whilst the 3c-2e B–H–Mo interaction might appear to be strong (or at least non-labile), it does not result in a substantial transfer of electron density to the molybdenum centre relative to the more conventional (2c-2e) donors in the series. Similarly, the $H_2B(pzBr_3)_2$ and $H_2B(pz')_2$ ligands (with crystallographically verified B–H–Mo interactions) lie further up the series. Notably,

Table 1. Carbonyl-associated Infrared data[a] for Selected Molybdenum Allyl Complexes $[Mo(\eta\text{-}C_3H_5)(CO)_2(\textit{fac}\text{-}L)]^{x+}$.[39,40,a]

fac-L[ref]	x	ν_s	ν_{as}	ν_m[b]	k_{CO}[c]
		cm^{-1}	cm^{-1}	cm^{-1}	Ncm^{-1}
$\eta^5C_2B_9H_9Me_2$	-1	1920[41]	1830	1875	14.20
η^5-$C_2B_9H_9Ph_2$	-1	1920[42]	1831	1876	14.21
η^5-$C_2B_9H_{11}$	-1	1928[41]	1832	1880	14.28
η^5-$C_2B_9H_{10}Ph$	-1	1924[42]	1833	1879	14.26
κ^3-HB(mt)$_3$	**0**	**1927**	**1835**	**1881**	**14.30**
η^5-C_9H_7	0	1931[43]	1845	1888	14.40
$H_2B(pz)_2(PMe_2Ph)$	**0**	**1933**	**1844**	**1891**	**14.41**
η^5-C_9Me_7	0	1933[44]	1846	1890	14.42
η^5-C_5Me_4Fc	0	1932[45]	1846	1889	14.42
$H_2B(pz)_2(PPh_3)$	**0**	**1939**	**1848**	**1894**	**14.49**
η^5-$C_2B_9H_8Me_2OEt_2$	0	1938[46,g]	1851	1895	14.50
κ^3-HB(indazolyl)$_3$	0	1939[47,h]	1852	1896	14.52
η^5-$C_2B_9H_{10}OEt_2$	0	1940[46,g]	1854	1897	14.54
κ^3-HB(pz*)$_3$	0	1944[21,e]	1850	1897	14.54
κ^3-HB(naphthopz)$_3$	0	1940[47,h]	1855	1898	14.55
κ^3-HB(pz)$_3$	0	1944[30]	1851	1898	14.55
η-C_5H_5	0	1942[43,48]	1855	1899	14.56
η-C_5Me_5	0	1945[43]	1855	1900	14.59
κ^3-$O_2P(pz^*)_2$	0	1950[49,f]	1850	1900	14.59
η^5-C_9H_6Fc	0	1944[45]	1861	1903	14.62
κ^3-$C_8H_{14}B(pz)_2$	0	1940[50,h]	1865	1903	14.62
κ^3-$H_2B(mt)_2$	**0**	**1948**	**1859**	**1904**	**14.64**
κ^3-MeGa(pz)$_3$	0	1948[51,e]	1860	1904	14.65
η^5-C_5H_4COMe	0	1949[53]	1867	1908	14.71
κ^3-HB(pzBr$_3$)$_3$	0	1958[52,e,h]	1870	1914	14.80
κ^3-N(CH_2py)$_3$	+1	1962[54]	1870	1916	14.83
κ^3-B(pz)$_4$	0	1958[30,e]	1875	1917	14.84
κ^3-HB(bta)$_3$	0	1960[55]	1874	1917	14.85
κ^3-$H_2B(pzBr_3)_2$	0	1958[52,e,h]	1878	1918	14.86
η^5-$MeBC_3H_3NCMe_3$	0	1953[56,h]	1872	1913	14.78
κ^3-$H_2B(pz^*)_2$	0	1963[3,d]	1874	1919	14.87
κ^3-MeN(CH_2pz')$_2$	+1	1966[57]	1874	1920	14.89
κ^3-$Ph_2B(pz)_2$	0	1961[3,d]	1878	1920	14.89
η^6-$C_2B_9H_9Ph_2$	-1	1954[42]	1893	1924	14.94
κ^3-MeN(CH_2pz)$_2$	+1	1976[57]	1879	1928	15.01
κ^3-$Et_2B(pz)_2$	0	1973[3]	1884	1929	15.03

[a]Unless otherwise indicated, data taken from CH_2Cl_2 solutions; [b]$(\nu_s + \nu_{as})/2$; [c]2.0191 x 10^{-6} x $(\nu_s^2 + \nu_{as}^2)$; [d]medium not reported; [e]cyclohexane; [f]Nujol; [g]10-substitution of the diethyl ether by SMe_2, PPh_3, py and bipy does not lead to significant changes in the infrared data for the CO ligands. [h]Methallyl derivative. [h]Petroleum Ether.

the examples with *agostic* C–H–Mo interactions [$Ph_2B(pz)_2$ and $Et_2B(pz)_2$] have ν_{CO} values comparable to or exceeding cationic examples, although these are known to display *hemi-labile* C–H–Mo interactions. Previously, we have compiled similar data for alkylidyne complexes of the form [W(≡CR)$(CO)_2$(L)].[23] Although the frontier orbitals of the 3-electron ligands C_3H_5 and CR fragments are essentially isolobal,[60,61] the alkylidyne ligand is a far superior π-acid as illustrated by comparison of IR data for [Mo(≡CC_6H_4Me-4)$(CO)_2${HB$(pz)_3$}][62] (ν_s,ν_{as} = 1998, 1921; ν^m = 1960) and [Mo(η-C_3H_5)$(CO)_2${HB$(pz)_3$}][3,6l] (ν_s,ν_{as} = 1942, 1855; ν^m = 1899 cm^{-1}). Perhaps the most remarkable feature of Table 1 is the smooth gradation that is now available in the net donor properties of the facial ligand. As with the Tollman electronic parameter *cf.* cone angle for phosphines, a gradation in steric profile is also available, though the two parameters are entirely independent.

Discussion of Crystal Structures

The molecular structures of the complexes [Mo(η-C_3H_5)$(CO)_2${H_2B(mt)$_2$}] (**3**) and [W(η-C_3H_5)$(CO)_2${H_2B(mt)$_2$}] (**4**) are depicted in Figures 2 and 3 respectively with selected geometric parameters provided in the captions. Assuming, as is generally accepted, that the covalent radii of molybdenum (154 pm) and tungsten (162 pm) are similar[63] and given that the two crystal structures are isomorphous within $P2_1/a$, both molecules will be discussed together. Based on the NMR data for **3**, a geometry with no element of symmetry would be expected and this is indeed the case in the solid state. The 3c-2e B–H–Mo or B–H–W interactions are seen to occupy coordination sites *trans* to one of the two chemically distinct carbonyl ligands. Considering the molybdenum centre in **3** to be approximately octahedrally hybridized, the observation that the Mo–C4 and Mo–C5 distances are not significantly different (5σ) indicates that there is no differential *trans* influence between the H1–Mo1 and S1–Mo1 donors despite the disparate nature of the bonding. In the case of **3** the allyl hydrogens were located and freely refined, however for **4** these did not satisfactorily refine and were included in calculated positions. For **3**, the allylic hydrogens adopt the usual distortions; the *anti* (and to a lesser extent the *methine*) protons are displaced away from the metal and the C1–C2–C3 plane, whilst the *syn* protons lie marginally towards the metal. The remaining features of **3** and **4** will be generically discussed below with those of **6**, **7** and **8**.

The molecular structures of the complexes [Mo(η-C_3H_5)$(CO)_2$(PMe_2Ph){H_2B(pz)$_2$}(PMe_2Ph)] (**6**) and [Mo(η-C_3H_5)$(CO)_2$(PPh_3){H_2B(pz)$_2$}(PPh_3)] (**7**) are depicted in Figures 4 and 5 respectively with selected geometric parameters provided in the captions. In addition to confirming the gross formulation, the most striking features are that whilst there are clearly no 3c-2e B–H–Mo interactions the two complexes adopt different stereochemistries with respect to the site of phosphine coordination. In the case of **6**, the PMe_2Ph ligand coordinates *trans* to the allyl group. This geometry was inferred from solution spectroscopic data which indicated a molecular plane of symmetry on the NMR timescales (implying free rotation of the phosphine). For **7**, the geometry with PPh_3 *trans* to one carbonyl is adopted in the solid state, however the apparent fluxionality precluded definitive assignment of the metal stereochemistry in solution. In both structures the $H_2B(pz)_2$Mo unit forms a somewhat shallow boat into which one phosphine substituent (PCH_3 for **6**, PPh for **7**) is cradled. However, the different steric profiles of these substituents is not dramatically reflected in the concavity of the cradle, with B1···Mo1 = 3.625 Å for **6** and 3.498 Å for **7**. In both structures the allylic hydrogen atoms were located and refined freely, adopting the expected displacements from coplanarity with the allyl carbon skeleton. In both structures which might be described as involving *pseudo*-octahedral molybdenum centres, the molybdenum atoms are marginally displaced towards the allyl ligand from the planes defined by the four donors *cis* to the allyl ligand (0.22 Å for **6**, 0.19 Å for **7**), reflecting presumably the steric constraints imposed by the *trihapto* allyl coordination. The remaining features of **6** and **7** will be generically discussed below with those of **3**, **4** and **8.**

The molecular structure of the complex [W(η-C_3H_5)$(CO)_2$(Hpz){H_2B(pz)$_2$}] (**8**) is depicted in Figure 6 which reveals that the molecule has an approximate but not crystallographically requisite plane of symmetry including the unique pyrazole and the boron and tungsten atoms, such that the pairs of W-pyrazolyl W–carbonyl bond lengths are comparable. As in the cases of **6** and **7** the $H_2B(pz)_2$W unit forms a shallow boat providing a cleft into which the unique pyrazole orients. The *pseudo*-octahedral geometry at tungsten is somewhat distorted in that the $H_2B(pz)_2$ ligand is skewed towards the unique pyrazole and away from the allyl ligand. Thus, as in the case of **6** and **7** above, the metal is displaced towards the allyl ligand and away from the plane defined by the four donor atoms *cis* to the allyl ligand (by 0.23 Å). Only two crystal structures of $H_2B(pz)_2$M (M = Mo, W) complexes have been previously described, those being the tungsten alkylidynes [W(≡$CC_6H_3Me_2$-2,6)$(CO)_2$(NC_5H_4Me-4){H_2B(pz)$_2$}] (**9**) and [W(≡$CC_6H_3Me_2$-2,6)$(CO)_2$(PMe_2Ph){H_2B(pz)$_2$}] (**10**u.[64] In the latter the phosphine coordinates *cis* to the alkylidyne such that (as in the case of **6**) one PCH_3 group nestles between the pyrazoles of the scorpionate. In the former, however the picoline ligand coordinates *trans* to the alkylidyne (although an alternative isomer is also present in solution), such that it orients within the $H_2B(pz)_2$W cleft akin to the geometry observed for **8**. Geometric parameters associated with the $H_2B(pz)_2$W groups for **8**, **9** and **10** are essentially similar with comparable W–N bond lengths and concavities.

The geometric features of the allyl ligands in the complexes **3**, **4**, **6**, **7** and **8** may be discussed at once. With over one hundred crystal structures having been reported for η^3-C_3H_5 complexes of group 6 metals and many more of substituted allyls, the behaviour of the allyl groups in the new complexes is unremarkable. The characteristic features of allyl coordination are observed in all cases. Thus (i) the facial arrangement of the allyl and carbonyl ligands is such that the allyl and M$(CO)_2$ units are essentially periplanar, with the *exo* geometry being adopted; (ii) in each case, the bond to the central carbon is slightly shorter (ca 4-5%) than to the peripheral carbons; (iii) the *anti* and unique methine hydrogen atoms are displaced from the allyl plane, away from the metal centre; (iv) the *syn* hydrogens are minimally displaced towards the metal centre.

The focus herein is the nature of the $H_2B(mt)_2$ ligand with respect to $H_2B(pz)_2$ and $H_2B(pz^*)_2$ ligands. With electronic comparisons resting on infrared data (Table 1), an impression of the steric profile (topographical steric maps[65]) is provided by Figure 7 which presents views along the metal-boron vector for complexes with κ^3-*S,S',S''*-HB(mt)$_3$, κ^3-*H,S,S'*-$H_2B(mt)_2$, κ^3-*H,N,N'*-$H_2B(pz)_2$ and κ^3-*H,N,N'*-$H_2B(pz^*)_2$ scorpionate ligands, the latter three involving B–H–M interactions, with the remaining co-ligands removed for clarity. The Tolman cone angle concept has for many decades enjoyed utility in quantifying the steric bulk of phosphine ligands,[66] not least because it reduces steric impact to a singular parameter reflecting the cone defined by a freely rotation phosphine. For more irregular ligands, *e.g.*, *N*-heterocyclic carbenes[67] and poly(azolyl)borates[68] a more immediately informative impression of the irregularity of the steric profile of the coordination sphere is provided by topographical steric maps arising from percentage buried volume calculations, which nevertheless also return a singular parameter (%V_{bur}). For simple conical phosphines this parameter reassuringly correlates directly with the Tolman cone angle,[67] but is more diversely applicable. In terms of buried percentage volume,[65] the $H_2B(pz)_2$ ligand is as expected the most compact. The $H_2B(pz^*)_2$ ligand is somewhat larger, with the N-CH_3 groups directed between adjacent co-ligands. The intrinsic local C_3 chirality offered by the HB(mt)$_3$ ligand is lost in the case of $H_2B(mt)_2$ coordination such that the more compact κ^3-*H,S,S'* coordination allows the metal to achieve essential co-planarity with one 'mt' heterocycle, with only a modest displacement from the second, reflecting the flexible hybridization offered by the sulfur donors. In the case of the $H_2B(pz^*)_2$ coordination, however, the metal is effectively coplanar with both pz* heterocycles, due to a combination of both the less flexible hydridization at nitrogen and the smaller

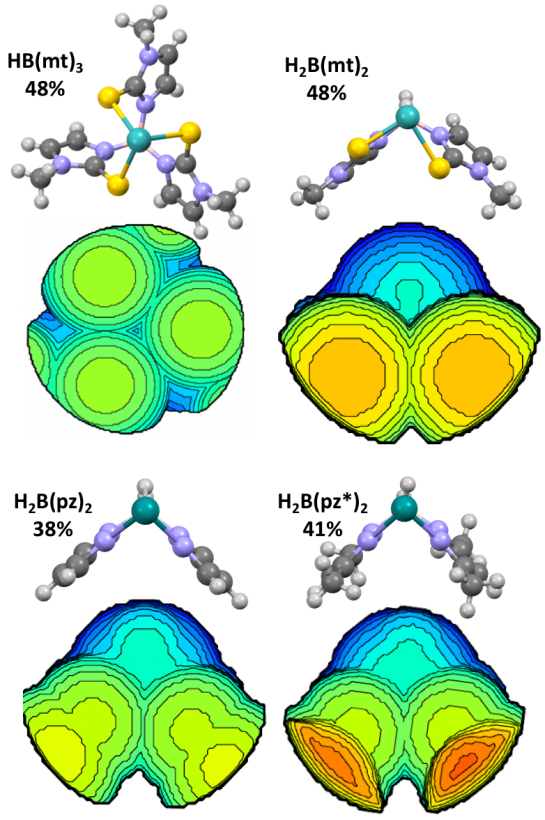


Figure 7. Views (co-ligands removed) along the metal-B vectors for κ^3-*S,S',S''*-HB(mt)$_3$, κ^3-*H,S,S'*-$H_2B(mt)_2$, κ^3-*H,N,N'*-$H_2B(pz)_2$ and κ^3-*H,N,N'*-$H_2B(pz^*)_2$ scorpionate complexes including topographic steric maps.[66]

chelate size. The interaction of interest is the 'agostic' B–H–M coordination and since there are variable degrees of certainty associated with the location of the hydrogen atom in such bridges, it is judicious to consider rather the more precise B···Mo or B···W distances. In the case of **3**, the BHMo hydrogen atom was located from a difference map and not refined, giving B–H and Mo–H bond lengths of 1.19(3) and 1.97(3) Å, respectively, with B–H–Mo = 142.8(25)°. Although with the 'eye of faith' the terminal B–H bond appears shorter (1.11(3) Å) than that involved in the 3-centre, 2-electron interaction, as would be expected, this difference is not within the precision limits of statistical significance for this light atom. It should be recalled that X-ray diffraction locates electron density maxima rather than nuclear positions. Both the X-ray and neutron diffraction analyses of a range of methallyl complexes [Mo(η^3-$H_2CCMeCH_2$)(CO)$_2$(κ^3-*H,N,N'*-H_2BR_2)] (R = $pzPh_2$-3,5, $pzMe_2Br$, $pzMe_3$, pz*) were investigated by Schultz[2s] who observed that for the terminal B–H bond, X-ray diffraction under-estimates this by ca 0.13 Å. However, there is closer correspondence between the X-ray and neutron results for the location of the BHMo hydrogen such that the Mo–H bond is marginally shorted (0.02-0.05 Å) and the B–H bond longer (0.03 – 0.16 Å) when determined by neutron diffraction. Geometrical optimisation of **3** at the DFT: MO6-2X/6-31G*/LanL2DZ level of theory reproduces reasonably the locations of the heavier elements and returns values of 2.046 (Mo-H), 1.229 (B-H···Mo) and 1.206 Å (B–H) that are closer to those that followed from the neutron diffraction studies. What distinguishes the Bm ligand, however, from the pyrazolyl based ligands, is the Mo-H-B angle

(calculated as 140.1°). Large B–H–metal angles for Bm ligands have been observed previously and whilst they typically fall in the range 120-150°, the complex [$TaCl_2(\kappa^3$-*H,S,S'*-$H_2B(mt)_2$}] has Ta-H-B = 163(3)°.

Conclusions

Tridentate κ^3-*H,S,S'* coordination of the $HB(mt)_3$ ligand has been observed *inter alia* for divalent ruthenium,[15] however for divalent molybdenum κ^3-*S,S',S"* appears to be preferred, possibly because the d^4 configuration allows an increase in the π-donor component of S–M bonding relative to the $(t_{2g})^6$ divalent ruthenium(II) centre. Nevertheless, κ^3-*H,S,S'* coordination to both molybdenum(II) and tungsten(II) could be demonstrated for the $H_2B(mt)_2$ ligand and initial comparisons with the $H_2B(pz)_2$ and $H_2B(pz^*)_2$ ligands would appear to suggest that this mode of coordination is particularly robust. Indeed the fluxionality apparent in the VT NMR spectra of [M(η^3-C_3H_5)$(CO)_2${$H_2B(mt)_2$}] (M = Mo, W) does not appear to involve dissociation of the B–H–M interaction, but rather, conventional rotation (*cf*. σ-π interconversion) of the allyl and CO ligands. Attempts to displace this B–H–Mo interaction by trapping with potential ligands (CO, PMe_2Ph) under mild conditions were unsuccessful and under more forcing conditions lead to products devoid of both the allyl and $H_2B(mt)_2$ ligands. We are therefore at present unable to provide evidence of B–H–Mo or B–H–W *hemilability*, a result that is in contrast with results obtained for rhenium complexes of this ligand.[9] Similarly robust B–H–Mo coordination was (re)confirmed for the $H_2B(pz^*)_2$ ligand whilst in marked contrast, unequivocal evidence of for κ^3-*H,N,N'* coordination of the $H_2B(pz)_2$ ligand could not be established in this system and if it occurs, the interaction is definitely labile. The difference between the predispositions of $H_2B(pz^*)_2$ *cf.* $H_2B(pz)_2$ ligands towards κ^3-*H,N,N'* coordination most likely arises from a *pseudo*-Thorpe-Ingold type of substituent congestion about boron whilst the proclivity of the $H_2B(mt)_2$ ligand to adopt and maintain κ^3-*H,S,S'* coordination is quite possibly a simple corollary of the geometric flexibility of the expanded $B(NCS)_2M$ *cf.* $B(NN)_2M$ cage. This does not however yet explain the *hemilability* of the $H_2B(mt)_2$ ligand in [$Re(CO)_3${$H_2B(mt)_2$}] which, as the field develops, appears increasingly anomalous.

Experimental

General Procedures. All manipulations were routinely carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk and vacuum line techniques or in an argon filled dry-box. 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). Petroleum spirit refers to that fraction with boiling point range 40-60 °C. ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian INOVA 300 or GEMINI 300 spectrometers (^1H 300.1 MHz; $^{31}P\{^1H\}$ 121.4 MHz; $^{13}C\{^1H\}$ 75.42 MHz) and calibrated against internal Me_4Si (^1H), $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using a Perkin-Elmar Spectrum One FT-IR spectrometer. APCI mass spectrometry was carried out by the R. S. C. Mass Spectrometry Service using acetonitrile or methanol. FAB-mass spectrometry was carried out using an Autospec-Q instrument with 3-nitrobenzyl alcohol as matrix. Assignments were confirmed by simulation of isotopic distributions. Elemental microanalyses were carried out by the R.S.C. microanalytical service and where solvates were inferred, this was confirmed by ^1H NMR integration. Data for X-ray crystallography were collected by the R. S. C. crystallography service with a Nonius Kappa CCD diffractometer. Structures were solved by direct methods and refined using a full-matrix least-squares procedure against *F* or F^2. The compounds [Mo(η-C_3H_5)$X(CO)_2(NCMe)_2$] (X = Cl, Br),[21] [W(η-C_3H_5)$Br(CO)_2(NCMe)_2$],[27] [$Mo(CO)_3(PMe_2Ph)_3$],[29] $K[H_2B(pz^*)_2]$,[68] $K[H_2B(pz)_2]$,[69] [$MoCl(CO)_3(\eta$-$C_5H_5)$],[70] $Na[H_2B(mt)_2]$,[5b] and $Na[HB(mt)_3]$[17a] were prepared according to published procedures. The complex [Mo(η-C_3H_5)$Br(CO)_2(PMe_2Ph)_2$] was generated *in situ* from [Mo(η-C_3H_5)$Br(CO)_2(NCMe)_2$] and PMe_2Ph but not isolated due to its subsequent further reaction with PMe_2Ph.

Synthesis of [W(η-C_3H_5)$Br(CO)_2(NCCH_3)_2$] - A suspension of tungsten hexacarbonyl (3.52 g, 10 mmol) in acetonitrile (50 mL) was refluxed for 50 hours to produce a yellow solution of $[W(CO)_3(NCMe)_3]$. The solution was allowed to cool to 60 °C, and allyl bromide (1.82 g, 15 mmol) slowly added. Once the evolution of carbon monoxide had ceased the solution was allowed to cool slowly to room temperature overnight without stirring. The light orange product was filtered from the reaction mixture to yield a fine powder. Yield = 2.56 g (57.8 %). The product identity was confirmed *via* comparison with literature values.[27]

Synthesis of [Mo(η-C_3H_5)$(CO)_2${$H_2B(mt)_2$}] (3) - A mixture of [Mo(η-C_3H_5)$(Br)(CO)_2(NCCH_3)_2$] (5.00 g, 14.1 mmol) and $Na[H_2B(mt)_2]$ (3.69 g, 14.1 mmol) was stirred in CH_2Cl_2 (100 mL) at room temperature for 4 hours to produce a cloudy yellow solution. The solution was filtered through silica gel, and the product crystallised from dichloromethane-petroleum spirit to yield bright orange crystals. Yield = 2.98 g (59.6 %). IR Nujol: 2460 ν_{BH}, 2269 ν_{BHMo}, 1927, 1837 ν_{CO}, 1556, 1419, 1195 cm^{-1}; IR CH_2Cl_2: 2413 ν_{BH}, 2278 ν_{BHMo}, 1948, 1859 ν_{CO} cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ_H = –5.47 [d.br, 1 H, $^1J_{BH}$ = 87 Hz, B–H–Mo], 1.42 [s.br, 4 H, $H^a H^{a'}(C_3H_5)$], 3.55 [s, 8 H, NCH_3, $H^s H^{s'}(C_3H_5)$], 3.84 (m, 1 H, $H^{meth}(C_3H_5)$], 6.66, 7.71 (s x 2, 2 H x 2, CH=CH). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 25 °C): δ_C = 35.15 (s, NCH_3), 75.79 (CH_2), 121.2, 122.3 (s x 2, CH=CH), 162.4 (C=S), 225.7 (br, CO). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 25°C): δ_B = –11.86. APCI-MS: *m/z*(%)[assignment] 403(40)[M-CO]$^+$, 376(40)[M-2(CO)]$^+$. Anal. Found C: 32.31, H: 3.52, N: 11.14%. Calcd for $C_{13}H_{17}BMoN_4O_2S_2.CH_2Cl_2$ C: 32.44, H: 3.70, N: 10.81%; CH_2Cl_2 solvent of crystallisation, confirmed by crystallography. *Crystal data:* $C_{13}H_{17}BMoN_4O_2S_2.CH_2Cl_2$; M_w = 517.12 $gmol^{-1}$; monoclinic; $P2_1/a$; *a* = 7.5475(1); *b* = 18.8361(2); *c* = 14.6355(2) Å; β = 101.6837(5)°; *V* = 2037.55(4) Å^3; *Z* = 4; D_{calcd} = 1.686 Mgm^{-3}; μ(Mo Kα) = 1.127 mm^{-1}; *T* = 200(2) K, orange needles; 37,832 measured reflections, *F* refinement, R_1 = 0.033, ωR_2 = 0.037 for 3,597 independent absorption corrected reflections [$I > 3\sigma(I)$, $2\theta < 55$] , 286 parameters, CCDC 1954561.

Synthesis of [W(η-C_3H_5)(CO)$_2${$H_2B(mt)_2$}] (4) - A mixture of [W(η-C_3H_5)(Br)(CO)$_2$($NCCH_3$)$_2$] (500 mg, 1.13 mmol) and Na[$H_2B(mt)_2$] (300 mg, 1.13 mmol) was stirred in tetrahydrofuran (50 mL) at room temperature for 1 hour to produce a dark green solution. The solution was filtered through silica gel, and the product crystallised from dichloromethane-petroleum spirit. Yield = 460 mg (78.0 %). IR Nujol: 2468 ν_{BH}, 2239 ν_{BHW}, 1916, 1838 ν_{CO} cm^{-1}; IR CH_2Cl_2: 2415 ν_{BH}, 2237 ν_{BHMo}, 1943, 1855 ν_{CO} cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ_H = –4.81 (d.br, 1 H, $^1J_{BH}$ = 92, BHW), 1.54 [s, 2 H, $H^{a,a'}(C_3H_5)$], 3.02 [m, 1 H, $H^{meth}(C_3H_5)$], 3.54 (s, 6 H, NCH_3) 6.69, 6.83 (s x 2, 2 H x 2, CH=CH) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C): δ_C = 35.13 (NCH_3), 68.51 (CH_2), 122.0 (s, CH=CH) ppm. ^{11}B{^{1}H} NMR (160.4 MHz, CD_2Cl_2, 25°C): δ_B = –8.06. APCI-MS: *m/z*(%)[assignment] 490(5)[M-CO]$^+$, 425(5)[Mo($H_2B(mt)_2$)]$^+$. Anal. Found C: 28.26, H: 3.06, N: 9.79%. Calcd for $C_{13}H_{17}BWN_4O_2S_2.CH_2Cl_2$ C: 27.79, H: 3.17, N: 9.26%. Solvent of crystallisation confirmed by crystallography. *Crystal data*: $C_{13}H_{17}BWN_4O_2S_2.CH_2Cl_2$; M_w = 605.03 $gmol^{-1}$; monoclinic; $P2_1/a$; a = 7.5455(1) Å; b = 18.7786(4) Å; c = 14.5838(2) Å; β = 101.4861(8)°; V = 2025.05(7) Å^3; Z = 4; D_{calcd} = 1.984 Mgm^{-3}; μ(Mo Kα) = 6.191 mm^{-1}; T = 200(2) K, orange plates; 4,638 independent reflections, F refinement, R_1 = 0.0299, ωR_2 = 0.0339 for 2210 independent absorption corrected reflections [$I > 3\sigma(I)$, $2\theta < 55°$], 236 parameters, CCDC 1954562.

Synthesis of [Mo(η-C_3H_5)(CO)$_2$(PMe_2Ph){$H_2B(pz)_2$}] (6) - A mixture of [Mo(η-C_3H_5)(Br)(CO)$_2$($NCCH_3$)$_2$] (500 mg, 1.41 mmol) and K[$H_2B(pz)_2$] (265 mg, 1.41 mmol) was stirred in dichloromethane (100 mL) at room temperature for 1 hour to produce a yellow solution. To this solution, PMe_2Ph (0.18 mL, 14.1 mmol) was added and stirred for 1 hour to give a light orange solution. The resulting yellow solution was filtered through silica gel, and the product crystallised from dichloromethane-petroleum spirit. Yield = 340 mg (50.4 %). IR Nujol: 1928, 1853, 1836 ν_{CO}, 1289, 1163, 1957; IR CH_2Cl_2: 1933, 1845 ν_{CO} cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ_H = 0.84, 0.87 (s x 2, 6 H, PCH_3), 1.79 [d, 2 H, $^3J_{HH}$ = 10.2, $H^a(C_3H_5)$], 3.24 [dd, 2 H, $^3J_{HH}$ = 6.9, $^2J_{HH}$ = 1.5, $H^s(C_3H_5)$], 5.00 [tt, 1 H, $^3J_{HH}$ = 10.2, 6.9 Hz, $H^{meth}(C_3H_5)$], 6.18 [dd, 2 H, $^3J_{HH}$ = 2.1, $H^4(pz)$], 7.19-7.25 (m, 2 H, C_6H_5), 7.28 (d, 2 H, $^3J_{HH}$ = 2.1, $H^{3,5}(pz)$], 7.38-7.41 (m, 2 H, C_6H_5), 7.55 [d, 1 H, $C^4(C_6H_5)$], 7.55 [d, 2 H, $^3J_{HH}$ = 2.1 Hz, $H^{3,5}$(pz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C): δ_C = 12.26 [d, $^1J_{PC}$ = 21, CH_3], 62.37 [$C^{a,a's,s'}(C_3H_5)$], 74.28 [d, $^2J_{PC}$ = 5.5, $C^{meth}(C_3H_5)$], 105.7 [$C^4(pz)$], 128.5 [d, $^2J_{PC}$ = 9.1, $C^{2,6}(C_6H_5)$], 129.6 [$C^4(C_6H_5)$], 130.5 [d, $^3J_{PC}$ = 8.3, $C^{3,5}(C_6H_5)$], 136.2 [d, $^1J_{PC}$ = 36, $C^1(C_6H_5)$], 137.3, 144.9 [s x 2, $C^{3,5}(C_6H_5)$], 225.5 (d, $^2J_{PC}$ = 15 Hz, CO). APCI-MS: *m/z*(%)[assignment] 331(40)[M-$H_2B(pz)_2$]$^+$, 303(10) [M-$H_2B(pz)_2$-CO]$^+$, 235(10)[Mo(PMe_2Ph)]$^+$. ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 25 °C) δ_P = 1.83. ^{11}B{^{1}H}NMR (160.4 MHz, $CDCl_3$, 25°C): δ_B = –10.81. Anal. Found, C: 47.45, H: 5.17, N: 11.46 %. Calcd. for $C_{19}H_{24}BMoN_4O_2P$ C: 47.73, H: 5.06, N: 11.72%. *Crystal data*: $C_{19}H_{24}BMoN_4O_2P$; M_w = 478.14 $gmol^{-1}$; monoclinic; $P2_1/n$; a = 15.393(3) ; b = 8.7520(18) ; c = 15.393(3) Å; β = 91.46(3)°; V = 2123.4(7) Å^3; Z = 4; D_{calcd} = 1.496 Mgm^{-3}; μ(Mo Kα) = 0.583 mm^{-1}; T = 200(2) K, yellow plates; 40,299 independent reflections, F refinement, R_1 = 0.0265, ωR_2 = 0.0631 for 4,871 independent absorption corrected reflections [$I > 3\sigma(I)$, $2\theta < 55$], 283 parameters, CCDC 1954563.

Synthesis of [Mo(η-C_3H_5)(CO)$_2$(PPh_3){$H_2B(pz)_2$}] (7) - A mixture of [Mo(η-C_3H_5)(Br)(CO)$_2$($NCCH_3$)$_2$] (500 mg, 1.41 mmol) and K[$H_2B(pz)_2$] (265 mg, 1.41 mmol) was stirred in dichloromethane (100 mL) at room temperature for 1 hour to produce a yellow solution. To this solution PPh_3 (370 mg, 1.41 mmol) was added and stirred for 10 mins. The resulting yellow solution was filtered through silica gel, and the product crystallised from dichloromethane-petroleum spirit. Yield = 450 mg (56.3 %). IR Nujol: 1956, 1857 ν_{CO}, 1153, 1058 cm^{-1}; IR CH_2Cl_2: 1939, 1848 ν_{CO} cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ_H = 1.27 [s, 2 H, $H^aH^{a'}(C_3H_5)$], 1.62 [s.br, 2 H, $H^{a,a'}(C_3H_5)$], 3.46 [s.br, 2 H, $H^{s,s'}(C_3H_5)$], 5.92 [s.br, 2 H, $H^4(pz)$], 7.12 [s.br, 4 H, $H^{3,5}(pz)$], 7.30-7.34 (m, 15 H, C_6H_5). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C): δ_C = 62.53 [$C^{meth}(C_3H_5)$], 75.40 [$C^{a,a',s,s'}$ (C_3H_5)], 106.0 [$C^4(pz)$], 128.7 [d, $C^{3,5}(C_6H_5)$, $^3J_{PC}$ = 7.5], 129.8 [$C^4(C_6H_5)$], 133.1 [d, $C^{2,6}(C_6H_5)$, $^2J_{PC}$ = 13.6], 136.0, 144.2 [$C^{3,5}(pz)$], 226.7 (CO) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 25 °C) δ_P = 25.65. ^{11}B{^{1}H}NMR (160.4 MHz, $CDCl_3$, 25°C): δ_B = –6.01. *Crystal data*: $C_{29}H_{28}BMoN_4O_2P$; M_W = 602.29 $gmol^{-1}$; monoclinic; $P2_1/c$; a = 10.2340(1); b = 14.6900(2); c = 18.1384(2) Å; β = 100.3843(6)°; V = 2682.22(5) Å^3; Z = 4; D_{calcd} = 1.491 Mgm^{-3}; μ(Mo Kα) = 0.583 mm^{-1}; T = 200(2) K, yellow plates; 58,929 independent reflections, F refinement, R_1 = 0.0213, ωR_2 = 0.0236 for 6,165 independent absorption corrected reflections [$I > 3\sigma(I)$, $2\theta < 55$], 427 parameters, CCDC 1954564.

Synthesis of [W(η-C_3H_5)(CO)$_2$(Hpz){$H_2B(pz)_2$}] (8). A mixture of [W(η-C_3H_5)(Br)(CO)$_2$($NCCH_3$)$_2$] (700 mg, 1.58 mmol) and K[$H_2B(pz)_2$] (294 mg, 1.58 mmol) was stirred in tetrahydrofuran (100 mL) at room temperature for 30 mins to produce a cloudy yellow solution. Pyrazole (108 mg, 1.58mmol) was then added, and the solution stirred for a further 2 hours at room temperature, before being filtered through a short silica gel plug. The product was then crystallised from dichloromethane-petrol to yield bright yellow crystals. Yield = 486 g (53.0%). IR Nujol: 1912, 1800 ν_{CO}, 1404, 1298, 1152, 1061 cm^{-1}; IR CH_2Cl_2: 1927, 1830 ν_{CO} cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ_H = 1.64 [d, 2 H, $^3J(H^{anti}H^{meth})$ = 8.8 Hz, $H^{a,a'}(C_3H_5)$], 3.05 [d, 2 H, $^3J(H^{syn}H^{meth})$ = 6.5 Hz, $H^{s,s'}(C_3H_5)$], 3.95 [m, 1 H, $H^{meth}(C_3H_5)$], 6.10 [t, 2 H, $^3J(H^4H^{3,5})$ = 2.2 Hz, $H^4(pz)$], 6.19 [s, 1 H, H^4(Hpz)], 7.20 [s, 2 H, $H^{3,5}$(Hpz)], 7.57 [d, 4 H, $^3J(H^{3,5}H^4)$ = 2.2, $H^{3,5}(pz)$], 8.57 [s(br), 1 H, NH] ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 25 °C): δ_C = 51.56 [s, $C^{s,s'a,a'}(C_3H_5)$], 60.15 [s, $C^{meth}(C_3H_5)$], 105.8 [s, $C^4(pz)$], 106.6 [s, C^4(Hpz)], 130.5 [s, $C^{3,5}$(Hpz)], 136.8 [s, $C^{3,5}(pz)$], 144.7 [s, $C^{3,5}$(Hpz)], 145.9 [s, $C^{3,5}(pz)$], 218.9 (CO) ppm. ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 25°C): δ_B = –12.4. APCI-MS: *m/z*(%)[assignment] 454(10)[M-(C_3H_5)]$^+$, 390(40)[M-(CO)$_2$-(C_3H_5)]$^+$, 373(90)[$WH_2B(pz)_2$-(NCMe)]$^+$. Anal. Found C: 34.03, H: 3.41, N: 17.02 %. Calcd. for $C_{14}H_{17}BN_6O_2W$: C: 33.90, H: 3.45, N: 16.94 %. *Crystal data:* $C_{14}H_{17}BN_6O_2W$; M_r = 496.00; monoclinic; $P2_1/c$; a = 14.288(10); b = 7.823(10); c = 15.337(10) Å; γ = 101.241(10)°; V = 1682(3) Å^3; Z = 4; D_x = 1.959 Mgm^{-3}; μ (Mo Kα) = 1.127 mm^{-1}; T = 200(2) K, orange needles; 31092 measured reflections, F refinement, R_1 = 0.0280, ωR_2 = 0.0686 for 3861 independent absorption corrected reflections [$I > 3\sigma(I)$, $2\theta < 55$] , 250 parameters, CCDC 1954565.

Reaction of [Mo(η-C_3H_8)(CO)$_2${$H_2B(mt)_2$}] (3) with PMe_2Ph. – A mixture of [Mo(η-C_3H_5)(CO)$_2${$H_2B(mt)_2$}] (**3**: 260 mg, 0.51 mmol) and PMe_2Ph (0.28 g, 2.0 mmol) in toluene (10 mL) was

heated under reflux for 12 hours and then freed of volatiles under reduced pressure. The residue was extracted with dichloromethane (2 x 10 mL) and the combined extracts were filtered through silica gel, concentrated and then diluted with petroleum spirit and cooled overnight (-18 °C). The crystalline product was isolated by filtration, dried in vacuo and identified as *mer*-$[Mo(CO)_3(PMe_2Ph)_3]$ on the basis of published spectroscopic data, supplemented by those that follow. Yield 0.143 g (47%). IR CH_2Cl_2: 1956, 1846 ν_{CO} cm^{-1}. THF: 1953, 1846 ν_{CO}, *cf.* $CHCl_3$: 1955, 1846 cm^{-1}.[29a] NMR (25 °C, CD_2Cl_2) ^1H (300 MHz): δ_H = 1.05 [d, 6 H, unique-PMe_2, $^2J_{PH}$ = 5.7], 1.63 [virtual-t, 12 H, *trans*-$(PMe_2)_2$, $^{2,4}J_{P2H}$ = 2.9 Hz], 7.10 – 7.46 (m x 8, 15 H, C_6H_5). [*cf.* $CDCl_3$: δ_H = 0.99 [d, 6 H, unique-PMe_2, $^2J_{PH}$ = 5.6], 1.64 [virtual-t, 12 H, *trans*-$(PMe_2)_2$, $^{2,4}J_{P2H}$ = 2.9 Hz].[27a] $^{13}C\{^1H\}$ (CD_2Cl_2, 75 MHz): 222.9 [dt, unique-MoCO, $^2J(PC)$ = 24.3], 215.6 [t, trans-$Mo(CO)_2$, $^2J(P_2C)$ = 14.4], 145.1 [pseudo-t, $C^1(C_6H_5)$, trans-$(PPh)_2$, $^{1,3}J(P_2C)$ = 12.9], 143.1 [d, unique-PPh, $C^1(C_6H_5)$, $^1J(PC)$ = 27.3], 130 – 128 [$C^{2\text{-}6}(C_6H_5)$], 22.00 [pseudo-t, trans-$(PMe_2)_2$, $^{1,3}J(P_2C)$ = 11.4], 19.56 [d, unique-PMe_2, $^1J(PC)$ = 19.8 Hz]. $^{31}P\{^1H\}$ (CD_2Cl_2, 121 MHz): δ 8.89 [d, 2 P, $^2J(PP)$ = 22.8], –2.72 [t, 1 P, $^2J(PP)$ = 22.2 Hz]. APCI-MS (+ve ion): *m/z*(%) = 566 (12) $[M\text{-}CO]^+$, 538 (24) $[M\text{-}2CO]^+$, 430 (48) $[M\text{-}PMe_2Ph]^+$, 402(13) $[M\text{-}2CO, PMe_2Ph]^+$, 289(4) $[M\text{-}CO,_2PMe_2Ph]^+$.

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The question of B–H–Mo hemilability in a range of dihydrobis(azolyl)borate scorpionate ligands is discussed with reference to η^3-allyl complexes $[Mo(\eta^3\text{-}C_3H_5)(CO)_2\{H_2B(az)_2\}]$ [az = pyrazolyl (pz), dimethylpyrazolyl (pz*), mercaptoimidazolyl (mt)].

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