

Hydrotris(methimazolyl)borato Alkylidyne Complexes of Tungsten¹

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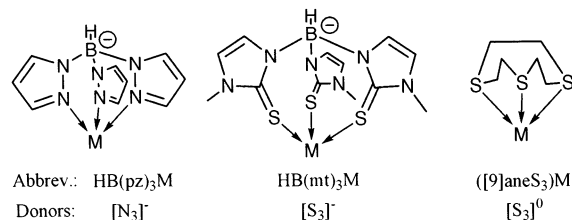
The syntheses of the alkylidyne complexes $[W(\equiv CR)(CO)_2\{HB(mt)_3\}]$ ($R = N^iPr_2$ **1a**, C_4H_3S-2 **1b**, $C\equiv CMe_3$ **1c**, C_6H_4Me-4 **1d**, $C_6H_3Me_2-2,6$ **1e**, $C_5H_4Mn(CO)_3$ **1f**; $mt = 2$ -mercapto-3-methylimidazolyl) are reported. The crystal structures of three examples (**1a**, **1b**, and **1c**) reveal a progressive distortion of the alkylidyne ligand from octahedral coordination at tungsten, and in addition have a chiral C_3 -symmetric conformation for the $B(mt)_3W$ cage, which is also implicit from solution NMR data. A set of parameters is suggested for describing the geometry of $HB(mt)_3M$ cages.

Introduction

The hydrotris(methimazolyl)borate chelate $HB(mt)_3$ ($mt = N$ -methyl-2-mercaptoimidazol-1-yl, "methimazolyl") introduced by Reglinski (Chart 1)²¹ presents three sulfur donors for *facial* coordination to a transition metal, in a manner reminiscent of both Trofimenko's hydrotris(pyrazolyl)borates^{3,4} and the cyclic thioether 1,4,7-trithiacyclononane.⁵

Since the original report,^{2a} $HB(mt)_3$, the related $H_2B(mt)_2$ chelate, and N -functionalized derivatives of each have attracted considerable attention,^{1,2,5–10} with the primary focus of many studies being in bioinorganic

Chart 1. Facially Tridentate Ligands



metalloenzyme modeling.^{9,10} The first reported examples of organotransition metal derivatives of the $HB(mt)_3$ ligand, viz., $[RuR(CO)(PPh_3)\{HB(mt)_3\}]$ ($R =$ aryl, alk- enyl), proved to be unstable due to the transfer of the bridgehead borohydride to the ruthenium center followed by elimination of arene or alkene and formation of novel metallaboratranes (Scheme 1).¹

We reasoned that if alkylidyne complexes¹¹ co-ligated by $HB(mt)_3$ could be prepared, they might be prone to similar hydrogen migrations, but with the hydrogen atom remaining bound to the resulting alkylidene ligand, rather than being lost as hydrocarbon. Alterna-

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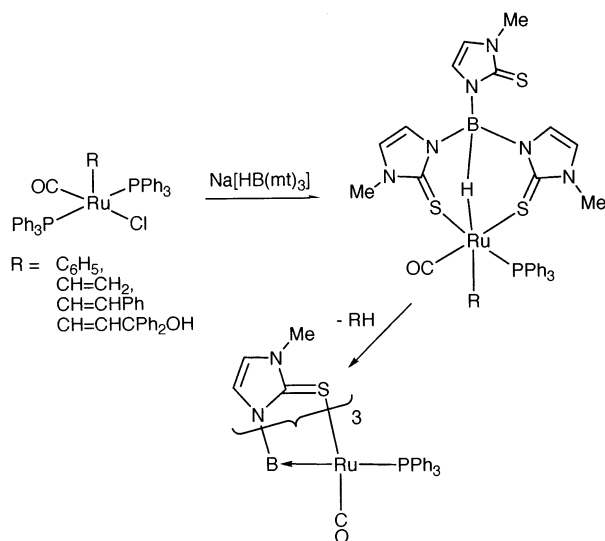
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Scheme 1



Scheme 2

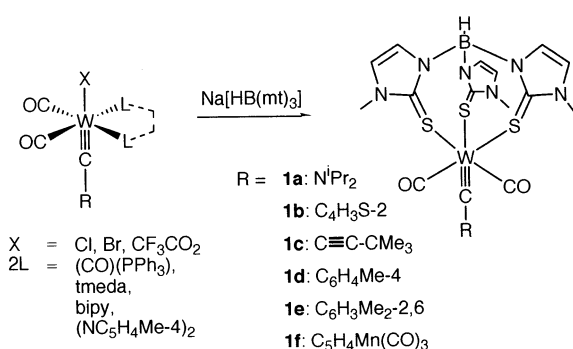


Table 1. Selected Infrared and ¹³C NMR Data for Alkyldiyne Complexes^a

complex	$\nu(\text{CO})/\text{cm}^{-1}$	$k_{\text{CK}}/\text{N m}^{-1}$	$\delta(^{13}\text{C}\equiv\text{W})$
1a : [W]≡CN ⁱ Pr ₂	1926, 1822	14.19	249.7
1b : [W]≡CC ₄ H ₃ S-2	1970, 1880	14.97	264.0
1c : [W]≡CC≡CMe ₃	1975, 1885	15.05	250.1
1d : [W]≡CC ₆ H ₄ Me-4	1967, 1875	14.91	281.1
1e : [W]≡CC ₆ H ₃ Me ₂ -2,6	1967, 1877	14.93	283.3
1f : [W]≡CC ₅ H ₄ Mn(CO) ₃	1970, 1880 ^a	14.97	266.6

^a [W] = W(CO)₂{HB(mt)₃}; $k_{\text{CK}} = 2.0191 \times 10^{-6} \text{ N m}^{-1} \times (\nu_{12} + \nu_{22})$; $\nu(\text{CO})$ measured in CH₂Cl₂ solution; $\delta(^{13}\text{C}\equiv\text{W})$ measured in CDCl₃ solution.

tively α -addition of the B–H bond to the alkyldiyne carbon might occur in a manner recalling Stone's demonstration of alkyldiyne hydroboration, either intermolecularly with B₂H₆ or (9-BBN)₂¹² or intramolecularly by carbaborane co-ligands.¹³ We have shown previously that alkyldiyne ligands may serve intramolecularly as hydrogen acceptors in the condensation of triboronate (B₃H₈) ligands to form the dodecaboronate [B₁₂H₁₂]²⁻ dianion.¹⁴

Herein we report the synthesis of a range of alkyldiyne complexes of tungsten bearing the HB(mt)₃ ligand, which reveal an unusual trend in alkyldiyne deformation. The modest deformations (ca. 0–10°) of alkyldiyne ligands from linearity that are sometimes observed in the solid state have been addressed from a theoretical perspective.¹⁵ The general conclusion, however, has been that these deformations arise from crystal packing forces or hyperconjugative effects in the case of the ethyldiyne complex [Cr(≡CMe)Cl(CO)₄].

Results and Discussion

The complexes [W(≡CR)(CO)₂{HB(mt)₃}] (R = NⁱPr₂ **1a**, C₄H₃S-2 **1b**, C≡CMe₃ **1c**) were obtained via the reactions of Na[HB(mt)₃]^{2a,5} with various preformed alkyldiyne complexes: [W(≡CNⁱPr₂)I(CO)₃(PPh₃)],¹⁶ [W(≡CNⁱPr₂)Cl(CO)₃(PPh₃)],¹⁶ [W(≡CC₄H₃S-2)Cl(CO)₂(tmeda)],¹⁶ [W(≡CC₄H₃S-2)Cl(CO)₂(py)₂],^{16,17} and

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[W(≡C–C≡CMe₃)(O₂CCF₃)(CO)₂(tmeda)]¹⁸ (Scheme 2). In contrast to the reactions of these substrates with, for example, NaC₅H₅ or K[HB(pz)₃] (pyrazol-1-yl), which often proceed at room temperature, the incorporation of the HB(mt)₃ ligand generally requires more elevated temperatures and was most conveniently achieved in refluxing tetrahydrofuran over periods of 5–18 h, depending on the substrate. The complexes **1a**, **1b**, and **1c** have been characterized crystallographically and will be discussed in detail below. The complexes [W(≡CR)(CO)₂{HB(mt)₃}] [R = C₆H₄Me-4 **1d**, C₆H₃Me₂-2,6 **1e**, C₅H₄Mn(CO)₃ **1f**] were prepared in a similar manner from [W(≡CC₆H₄Me-4)Br(CO)₂(tmeda)],¹⁹ [W(≡CC₆H₃Me₂-2,6)Br(CO)₂(bipy)],¹⁶ [W(≡CC₆H₃Me₂-2,6)Br(CO)₂(NC₅H₄Me-4)₂],²⁰ and [W(≡CC₅H₄Mn(CO)₃)(O₂CCF₃)(CO)₂(tmeda)],²¹ respectively. Their formulations follow unambiguously from spectroscopic and elemental microanalytical data, supported by analogy with the structurally characterized examples **1a–c**.

Routine spectroscopic data for all the new complexes are consistent with their formulation; however, a number of points are worthy of note. First, the retention of the intact alkyldiyne groups is confirmed by the characteristic low-field ¹³C resonances [**1a**, 249.7; **1b**, 264.0; **1c**, 250.1 ppm] in the NMR spectra. Second, the infrared data (Tables 1 and 2, vide infra) for the W(CO)₂ unit reflect a sensitivity toward the π -acidity of the alkyldiyne group, as indicated by the Cotton–Kraihanzel force constants (k_{CK}),²² which increase in the order **1a** < **1d** ≤ **1e** < **1b** = **1f** < **1c** (Table 1).

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Table 2. IR and NMR Data for Alkyldiyne Complexes $[LW(CO)_2(=CC_6H_4R-4)]^{x+}$ ^a

L	R	x	$\nu(CO)/cm^{-1}$	$k_{CK}/N\ m^{-1}$	$\delta(^{13}C\equiv W)$	ref
κ^3 -CpCo(PO ₃ Me ₂) ₃	CH ₃	0	1961, 1859	14.74	279.1	42
η^5 -C ₂ B ₉ H ₉ Me ₂	CH ₃	1-	1956, 1874	14.82	298.3	43
κ^3 -HB(mt) ₃	CH ₃	0	1967, 1875	14.91	281.1	
η^5 -C ₂ B ₉ H ₁₁	CH ₃	1-	1965, 1880	14.93	293.9	43
κ^3 -Me ₃ [9]aneN ₃	H	1+	1975, 1879	15.00	288.0 ^e	44
κ^3 -HB(pzMe ₂) ₃	CH ₃	0	1974, 1888 ^c	15.07	279.6	45
κ^3 -HB(pzPh) ₃	CH ₃	0	1982, 1897	15.20	282.3	45
κ^3 -HC(py) ₃ ⁺	H	1+	1988, 1894 ^b	15.22	288.1	31
κ^3 -[9]aneS ₃	H	1+	1984, 1899 ^b	15.23	293.1 ^d	31
η -C ₅ H ₅	CH ₃	0	1982, 1902	15.24	300.1	41
κ^3 -F ₅ C ₆ AuC(pz) ₃	CH ₃	0	1985, 1899	15.24	290.0	46
η -C ₅ H ₅	H	0	1984, 1905	15.28	300.1	41
κ^3 -HB(pz) ₃	CH ₃	0	1986, 1903	15.28	284.8	47
κ^3 -F ₃ BC(pz) ₃	CH ₃	0	1988, 1902	15.28	290.8	48
η -C ₅ Me ₅	CH ₃	0	1981, 1910 ^c	15.29	301.3	49
κ^3 -HC(pz) ₃	CH ₃	1+	1995, 1912	15.42	292.6	50
η^6 -C ₂ B ₁₀ H ₁₀ Me ₂	CH ₃	1-	1990, 1930	15.52	302.6	51
κ^3 -P(py) ₃	H	1+	2007, 1925 ^b	15.62	286.3 ^d	31
κ^3 -MeC(CH ₂ Ph) ₂	H	1+	1999, 1934 ^b	15.62	294.8	31
κ^3 -PhP(C ₂ H ₄ PPh ₂) ₂	CH ₃	1+	2005, 1941	15.72	300.4 ^d	52

^a Unless otherwise indicated, measurements in CH₂Cl₂ solution. ^b In KBr. ^c In hexane. ^d In CD₃CN. ^e In acetone.

The most curious spectroscopic features however involve the ¹³C{¹H} NMR data associated with the W(CO)₂ group and the ¹H or ¹³C{¹H} NMR data associated with the N-CH₃ groups. In all cases *two* carbonyl resonances are observed in the ¹³C{¹H} NMR spectrum, while both the ¹H and ¹³C{¹H} NMR spectra indicate *three* chemically distinct environments for the "mt" heterocycles. The related complexes [W(=CR)(CO)₂{HB(pz)₃}]¹¹ possess molecular planes of symmetry that bisect the W(CO)₂ group such that two pyrazolyl environments (ratio 1:2) are generally evident from NMR studies. The complexes **1a–f** however are clearly devoid of this element of symmetry. Variable-temperature ¹H NMR studies of the complexes **1a** and **1d** reveal that at higher temperatures [**1a**, 15 °C (Figure 1); **1d**, 90 °C] the signals for the three N-CH₃ groups coalesce. The origin of this behavior lies in geometric constraints that are incumbent upon HB(mt)₃ coordination, but absent for HB(pz)₃ coordination. This is most readily visualized with reference to the molecular structures depicted in Figures 2–4 (discussed below) and Scheme 3. While a HB(pz)₃M unit typically comprises a bicyclo[2.2.2] cage with *local* C_{3v} symmetry, each methimazolyl buttress of a HB(mt)₃M cage has one more atom than a pyrazolyl bridge, and accordingly the bicyclo[3.3.3] cage twists to assume a chiral C₃ local symmetry. This renders the carbonyl ligands diastereotopic and places each N-CH₃ group in a distinct chemical environment.

The coalescence behavior at elevated temperatures (Figure 1) could arise from two possible fluxional processes. The simplest would be an untwisting of the intact cage through a C_{3v}-W(mt)₃BH transition state (path a, Scheme 3). Alternatively, dissociation of one mt arm would also allow interconversion via a 16-electron coordinatively unsaturated intermediate capable of Berry pseudorotation (path b, Scheme 3). Although we have no definitive evidence to discriminate between these possibilities, the nature of the ¹H NMR coalescence behavior points toward a dissociative mechanism. Since all three N-CH₃ environments become chemically equilibrated (collapse of three signals to a singlet), a three-site exchange must operate. The alternative torsional twist (Scheme 3a) proceeds via a transition state that equilibrates *two* of the mt arms straddling a

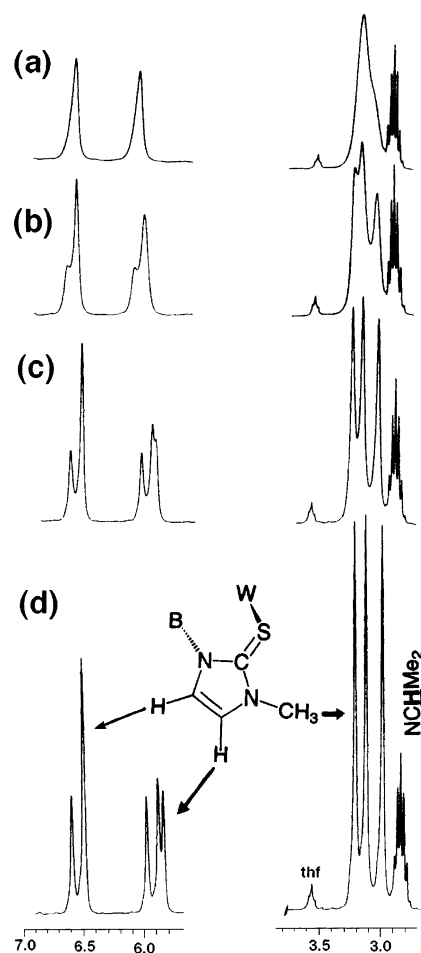


Figure 1. Variable-temperature ¹H NMR (*d*₈-toluene) spectra (extracts) for [W(=CNⁱPr₂)(CO)₂{HB(mt)₃}], **1a**: (a) 20 °C; (b) 10 °C; (c) 0 °C; (d) -10 °C.

molecular plane of symmetry and should be manifest as two singlet resonances (ratio 2:1). In further support of the dissociative mechanism is the well-documented *trans*-labilizing effect of alkyldiyne ligands (presaged in a *trans* influence apparent in the ground state structures of **1b** and **1c**, vide infra). Unlike the dissociative mechanism, the torsional twist mechanism would not

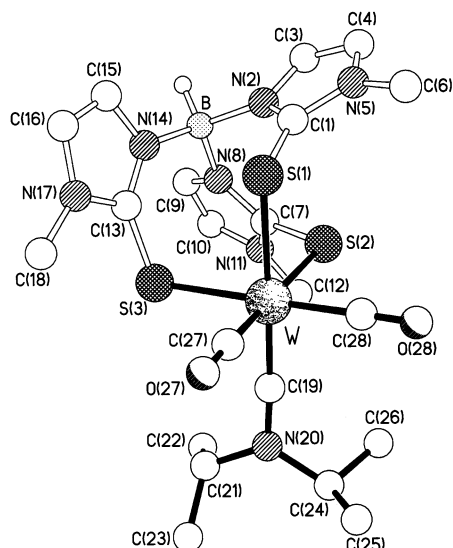


Figure 2. Molecular structure of one of the two independent molecules in the structure of **1a**. The B···W separation is 4.295(10) Å [4.291(10) Å].

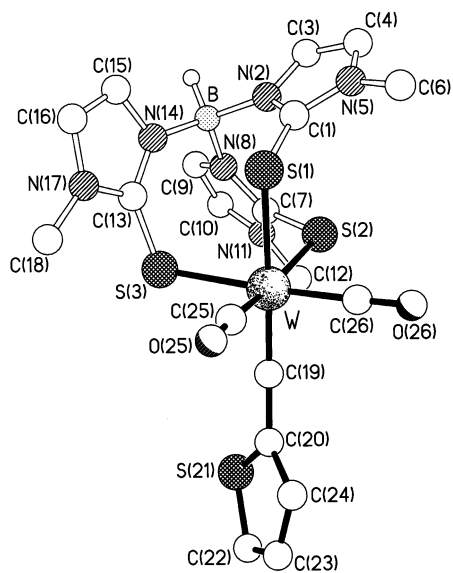


Figure 3. Molecular structure of **1b**. The B···W separation is 4.264(8) Å.

be expected to be strongly dependent on the nature of the alkylidene substituent (variable *trans* effect): A difference of 75 °C in coalescence temperature for **1a** and **1d** indicates that the alkylidene substituent plays a very significant role. Chart 2 suggests how intermediates of reduced coordination number might be stabilized by aminomethylidene ligands for which a 2-azavinylidene canonical form contributes to the resonance bonding description. It should be noted that the superlative *trans* influence and *trans* effect of the alkylidene ligand should facilitate a dissociative mechanism in this instance. However, for other systems with different types of ligands the nondissociative twist mechanism may well operate.

Three examples of the above complexes were characterized crystallographically, and their structures are illustrated in Figures 2–4, with their geometric parameters presented in Table 3. Complex **1a** crystallizes with two independent molecules in the asymmetric unit. The HB(mt)₃W(CO)₂ cores of each complex are similar and

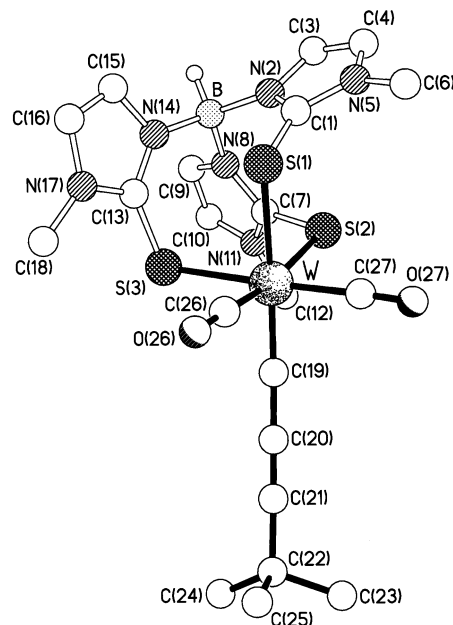


Figure 4. Molecular structure of **1c**. The B···W separation is 4.258(10) Å.

Scheme 3. Mechanisms for the Chemical Equilibration of mt Sites in the Complexes 1 via (a) Torsional Twist about the B···W Vector and (b) Dissociation–Berry Pseudorotation

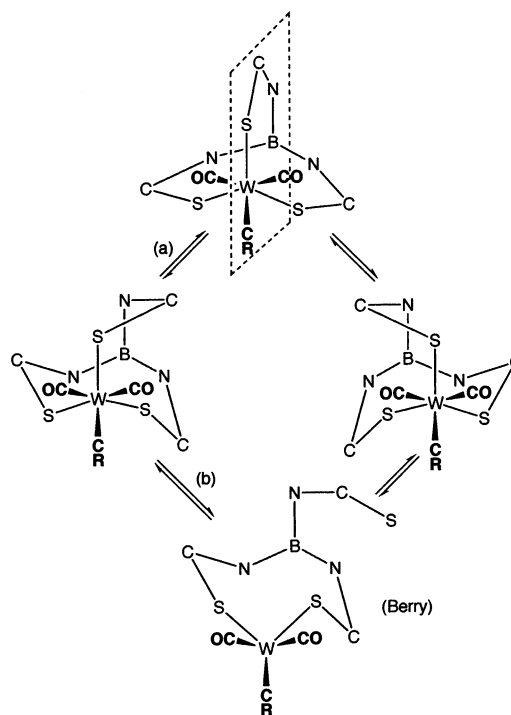


Chart 2. Aminomethylidene Resonance Forms



may be discussed generically. In each case the three sulfur donors and two carbonyl carbons assume a square-pyramidal geometry within the constraints imposed by the tris(chelate) HB(mt)₃ unit, the sixth octahedral site being occupied by the alkylidene ligand. A point of contrast between HB(mt)₃ and HB(pz)₃M coordination is immediately apparent: HB(pz)₃M coordination

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 1a (two independent molecules, A and B), 1b, and 1c^a

Complex 1a					
	mol. A	mol. B		mol. A	mol. B
W–S(1)	2.618(2)	2.619(2)	W–S(2)	2.614(3)	2.595(3)
W–S(3)	2.577(3)	2.589(3)	W–C(19)	1.859(9)	1.842(9)
W–C(27)	1.941(10)	1.948(11)	W–C(28)	1.995(11)	1.966(10)
S(1)–C(1)	1.706(10)	1.721(10)	S(2)–C(7)	1.722(9)	1.716(10)
S(3)–C(13)	1.723(9)	1.731(10)	B–N(2)	1.563(13)	1.552(13)
B–N(8)	1.569(13)	1.531(12)	B–N(14)	1.540(14)	1.556(13)
C(19)–N(20)	1.294(12)	1.301(12)			
S(1)–W–S(2)	87.14(8)	88.62(8)	S(1)–W–S(3)	91.47(8)	91.58(9)
S(2)–W–S(3)	89.09(8)	88.29(7)	S(1)–W–C(19)	176.2(3)	174.3(3)
S(1)–W–C(27)	90.2(3)	90.7(3)	S(1)–W–C(28)	87.0(4)	85.7(4)
S(2)–W–C(19)	96.6(3)	93.2(3)	S(2)–W–C(27)	176.0(3)	177.9(3)
S(2)–W–C(28)	91.8(4)	91.3(3)	S(3)–W–C(19)	88.7(3)	93.9(3)
S(3)–W–C(27)	93.9(3)	93.7(3)	S(3)–W–C(28)	178.2(3)	177.2(4)
C(19)–W–C(27)	86.1(4)	87.3(4)	C(19)–W–C(28)	92.8(5)	88.9(5)
C(27)–W–C(28)	85.1(5)	86.7(4)	W–C(19)–N(20)	176.9(9)	176.3(8)
			Compound 1b		
W–S(1)	2.644(2)		W–S(2)	2.530(2)	
W–S(3)	2.563(2)		W–C(19)	1.819(7)	
W–C(25)	1.995(9)		W–C(26)	1.953(10)	
S(1)–C(1)	1.717(7)		S(2)–C(7)	1.708(8)	
S(3)–C(13)	1.709(7)		B–N(2)	1.542(12)	
B–N(8)	1.562(9)		B–N(14)	1.548(11)	
S(1)–W–S(2)	88.15(6)		S(1)–W–S(3)	91.42(6)	
S(2)–W–S(3)	90.07(6)		S(1)–W–C(19)	165.6(2)	
S(1)–W–C(25)	81.3(2)		S(1)–W–C(26)	86.7(3)	
S(2)–W–C(19)	105.4(2)		S(2)–W–C(25)	168.5(2)	
S(2)–W–C(26)	88.1(3)		S(3)–W–C(19)	93.4(2)	
S(3)–W–C(25)	94.6(3)		S(3)–W–C(26)	177.4(3)	
C(19)–W–C(25)	84.8(3)		C(19)–W–C(26)	88.9(3)	
C(25)–W–C(26)	86.8(4)		C(1)–S(1)–W	108.0(2)	
C(7)–S(2)–W	110.8(2)		C(13)–S(3)–W	105.8(3)	
C(20)–C(19)–W	169.8(6)				
			Compound 1c		
W–S(1)	2.635(2)		W–S(2)	2.534(2)	
W–S(3)	2.577(2)		W–C(19)	1.837(7)	
W–C(26)	1.983(7)		W–C(27)	1.998(9)	
S(1)–C(1)	1.716(8)		S(2)–C(7)	1.723(9)	
S(3)–C(13)	1.730(7)		B–N(2)	1.55(2)	
B–N(8)	1.554(13)		B–N(14)	1.552(11)	
C(19)–C(20)	1.371(9)		C(20)–C(21)	1.207(11)	
C(21)–C(22)	1.472(11)				
S(1)–W–S(2)	88.83(6)		S(1)–W–S(3)	92.24(7)	
S(2)–W–S(3)	88.17(6)		S(1)–W–C(19)	161.1(2)	
S(1)–W–C(26)	80.6(2)		S(1)–W–C(27)	86.4(2)	
S(2)–W–C(19)	108.8(2)		S(2)–W–C(26)	169.4(2)	
S(2)–W–C(27)	90.4(2)		S(3)–W–C(19)	95.1(2)	
S(3)–W–C(26)	91.4(2)		S(3)–W–C(27)	178.1(2)	
C(19)–W–C(26)	81.8(3)		C(19)–W–C(27)	86.6(3)	
C(26)–W–C(27)	89.7(3)		W–C(19)–C(20)	167.4(6)	
C(19)–C(20)–C(21)	179.5(8)		C(20)–C(21)–C(22)	179.5(10)	

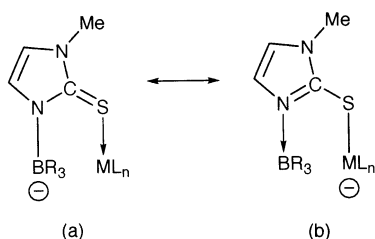
^a Estimated standard deviations are given in parentheses.

dination within an octahedron usually involves acute N–M–N angles⁴ (ca. 80° in [W(≡CC₆H₄Me-4)(CO)₂{B(pz)₄}]²³); however, the inter-sulfur angles of the HB-(mt)₃W cages are close to ideal for octahedral coordination and lie in the ranges 87.14(8)–91.47(8)° [88.29(7)–91.58(9)°] for **1a**, 88.15(6)–91.42(6)° for **1b**, and 88.17(6)–92.24(7)° for **1c**. Complexes **1b** and **1c** reveal the expected *trans* influence of the alkylidyne relative to the carbonyl ligands, manifest in a lengthening of the W–S bond *trans* to the alkylidyne [**1b**, 2.644(2); **1c**, 2.635(2) Å] with W–S bonds *trans* to the carbonyl ligands lying in the range 2.530(2)–2.577(2) Å. This pattern is

however less pronounced in the case of the two crystallographically independent molecules of **1a** with W–S(1) 2.618(2) Å [2.619(2) Å], cf. the remaining W–S bond lengths of 2.577(3) and 2.614(3) Å [2.589(3) and 2.595(3) Å].

The nature of the W–S bonding calls for comment, in that the sulfur can be viewed as either a thioketone/thiourea type of (neutral two-electron) donor or as a (one-electron anionic) thiolate depending on the relative contributions of the various canonical forms (Chart 3). From the thiourea perspective, the complex [W{S=C(NMeCH₂)₂}(CO)₅] provides a point of reference with W–S and S–C bond lengths of 2.617(2) and 1.716(7) Å, respectively,²⁴ both of these being longer than observed in the thiobenzaldehyde complex [W(S=CHPh)-

(23) Green, M.; Howard, J. A. K.; James, A. P.; De M. Jelfs, A. N.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1623.

Chart 3. B(mt)M Resonance Forms: (a) Thiourea; (b) Thiolate

(CO)₅] [2.479(3), 1.62(1) Å]²⁵ and the thiocarboxamide [W{S=C(NPh₂)CH₂NPh₂}(CO)₅] [2.572(1), 1.692(6) Å].²⁶ Mononuclear thiolate complexes of tungsten for comparison include both 16- and 18-electron examples, and Angelici has noted that the former typically show W–S separations ca. 0.1 Å shorter²⁷ than the latter, reflecting π -donation from sulfur to the otherwise coordinatively unsaturated metal center(s). Within alkyldiyne chemistry this W–S bond contraction is exemplified by the complexes [W(≡CSMe)(SMe)₂{HB(pz)₃}] [formally 16-electron, W–S 2.343(2), 2.338(2) Å]²⁷ and *trans,mer*-[W(≡CPh)(SC₆H₁₁)(CO)(PMe₃)₃] [18-electron, W–S 2.576(2) Å],²⁸ whereas the binuclear complex [W₂(μ -SPh)₂(≡CNEt₂)₂(CO)₈] [Et₂NCW–S 2.621(6), 2.598(7) Å *trans*; 2.553(6), 2.541(6) Å *cis*] illustrates metal–sulfur bond lengthening typical of a bridging thiolate.²⁹ The bonding of the mt groups to tungsten in **1a**, **1b**, and **1c** would appear to involve contributions from both canonical forms in that comparatively long W–S bonds are observed [2.530(2)–2.644(2) Å], and these are in general lengthened by coordination *trans* to the more strongly π -acidic alkyldiyne. The metal centers in **1a–1c** are coordinatively saturated (18-electron), reducing the significance of π -dative interactions between sulfur and the approximately (t_{2g})⁶ tungsten. The thiourea C=S bond lengths fall in the range 1.706(10)–1.730(7) Å, values comparable to that found [1.716(7) Å] in the thiourea complex [W{S=C(NMeCH₂)₂}(CO)₅],²⁴ longer than in Fischer's thiobenzaldehyde complex [1.62(1) Å],²⁵ and shorter than in the simple thiolates [W(≡CSMe)(SMe)₂{HB(pz)₃}] [WS–C 1.81(1), 1.831(8) Å]²⁷ and *trans,mer*-[W(≡CPh)(SC₆H₁₁)(CO)(PMe₃)₃] [WS–C 1.836(8) Å].²⁸ Although alkyldiyne thioether complexes are known, e.g., [Re(CH₂R)(=CHR)(≡CR)([9]aneS₃)⁺ (R = CMe₃)³⁰ and [W(≡CPh)(CO)₂([9]aneS₃)⁺ ([9]aneS₃ = 1,4,7-trithiacyclononane),³¹ structural data are not yet available for comparison. Thus the bonding between the mt groups and tungsten is best considered a hybrid of thiolate and thiourea coordination with partial C–S multiple bonding, akin to dithiocarbamate or dithioacetate chelation. In this respect the S–W and C–S bond lengths observed for [W(S₂CMe)(CO)₄][−] [W–S 2.557(5), 2.565(5) Å; C–S 1.67(2), 1.71(2) Å]³² correlate well with those for **1a–c**.

(24) Mak, T. C.; Jasim, K. S.; Chieh, C. *Inorg. Chim. Acta* **1985**, *99*, 31.

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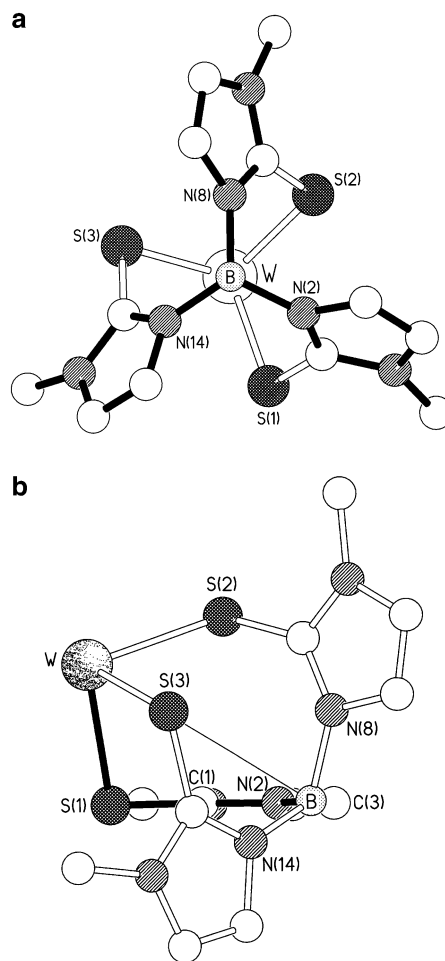


Figure 5. Alternative views of the HB(mt)₃W unit of **1a** corresponding to the schematic representations in Chart 4 (a) along the B···W vector; (b) normal to the B···W vector and edge on the plane of one of the mt rings.

The chiral twist of the HB(mt)₃ ligand has already been alluded to in the discussion of the NMR data above and is clear in the representations of the HB(mt)₃W core of **1a** depicted in Figure 5. Since this type of twist is likely to emerge in many future structural studies of HB(mt)₃ complexes, it is perhaps useful at this point to introduce a unified set of parameters to expediently denote this type of deformation. To avoid confusion with the geometric parameters α and β already used to describe the steric features of HB(pz*)₃M coordination,⁴ the new parameters will be denoted by θ and ω (Chart 4). We first suggest that θ denote the N–B–M–S torsional angle for each mt buttress (with θ^m the mean angle). Notably, this parameter also implicitly contains the chirality of the molecule such that $\theta < 0$ implies the $\lambda\lambda\lambda$ stereochemistry of the three buttresses, while $\theta > 0$ indicates the $\delta\delta\delta$ absolute configuration. Clearly, since no mixtures of δ and λ configuration could be geometrically accommodated within the one cage, the sign of θ alone suffices to denote the absolute configuration.

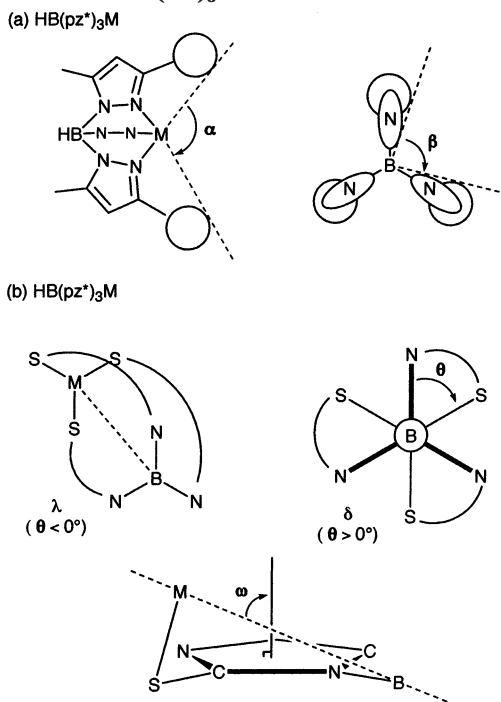
The second feature of this twisting is that the metal is displaced from the mt plane. Such a deformation would not be favorable in the case of HB(pz)₃ chelation by virtue of the requisite sp² hybridization at nitrogen.

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Table 4. Parametrization of HB(mt)₃M (LM) Fragment Geometry (see Chart 4)

complex	θ^1	θ^2	θ^3	θ^m	ω^1	ω^2	ω^3	ω^m	CCDC ^{ref}
1a ^a	44.2	45.8	49.8	46.6	58.5	56.1	58.0	57.5	b
	45.9	45.8	47.7	46.5	57.7	58.3	56.1	57.4	b
1b	43.9	45.1	47.6	45.5	58.8	60.2	58.4	59.1	b
1c	45.1	46.5	49.4	47.0	57.6	59.8	57.4	58.3	b
[L ₂ BiCl ₂] ₂	48.5	48.4	47.3	48.1	57.5	53.7	55.1	55.4	HIXNAD ^{2c}
LCuP(C ₆ H ₄ Me-3) ₃ ^c				45.5				58.7	RIYLOA ^{6e}
LCuP(C ₆ H ₄ Me-4) ₃ ^c				40.2				59.0	RIYNES ^{6e}
[L ₂ Bi] ^{+d}	47.1	48.7	48.6	48.1	54.9	54.2	55.1	54.7	HIXNEH ^{2c}
[L ₂ Tl] ^{+c,e}				47.9				55.1	LIQYIT ^{2d}
				-49.4				-55.0	LIQYIT ^{2d}
[L ₂ Tl] ^{+d}	47.7	46.6	46.4	46.9	55.4	56.0	56.1	55.8	LIQYEP ^{2d}
LRe(CO) ₃ ^{a,c}				47.2				59.0	QUSNOH ^{8b}
				42.8				61.7	QUSNOH ^{8b}
LZnCl	47.6	47.7	43.8	46.4	55.9	53.4	56.1	55.1	AGEZAN ^{2f}
LZnBr ^c				-45.6				-57.3	TODHID ^{2a}
LznI	45.3	45.4	41.9	44.2	56.9	57.1	61.6	58.5	AGEZER ^{2f}
LHgBr	47.7	48.1	46.6	47.5	51.6	50.6	54.0	52.1	AGEZIV ^{2f}
LCdBr	46.8	46.7	47.4	47.0	52.7	51.7	53.2	52.5	AGEZOY ^{2f}
LMo(CO) ₂ (C ₃ H ₅)	49.2	45.6	47.6	47.5	56.9	58.8	60.3	58.7	ICUCOY ^{2e}
LW(CO) ₃ I	48.7	47.2	43.9	46.6	58.8	56.8	59.2	58.3	ICUCUE ^{2e}

^a Two independent molecules. ^b This work. ^c Crystallographically imposed C₃ symmetry. ^d Crystallographically imposed inversion center. ^e Two independent ligands.

Chart 4. Parametrization of (a) HB(pz*)₃M⁴ and (b) HB(mt)₃M Geometries

The more flexible hybridization offered by sulfur, however, easily accommodates this folding. We suggest that this be denoted ω as the angle that the normal to the plane of an mt ring makes with the B→M vector (with ω^m the mean angle of all three). This makes the reasonable assumption that the sulfur remains effectively coplanar with the mt ring. Thus C_{3v} HB(mt)₃M symmetry if achievable would be indicated by $\theta^m = 0^\circ$, $\omega^m = 90^\circ$. Table 4 compares these parameters for complexes **1a**, **1b**, and **1c** together with those for other published complexes of the HB(mt)₃ ligand. From this table it is immediately apparent that the parameters are remarkably invariant for a range of metal centers from different sections of the periodic table. The structural chemistry of the HB(mt)₃ ligand is still in its infancy; however the narrow ranges for θ (42.8–49.8°) and ω (50.6–61.7°) so far observed suggest a substantial

degree of rigidity; that is, the HB(mt)₃ ligand may well be less flexible than might have been imagined. The comparatively high barriers to inversion of the HB(mt)₃W cages in **1** which are apparent from NMR spectroscopy (vide supra) would be an obvious corollary, in favor of a dissociative mechanism, rather than untwisting through a C_{3v} transition state.

While the introduction of bulky substituents onto the 5(N)-position of pyrazolylborates significantly alters the steric profile of the scorpionates,⁴ this appears to be less apparent in the chemistry of HB(mt^R)₃ ligands,^{9,10} where the steric influence of an introduced N-substituent is less felt at the metal center because the substituent points away from the coordination sphere. This may be quantified by comparison of the θ^m and ω^m values derived from the range of four-coordinate complexes included in Table 5. These values fall essentially within the range for the octahedral complexes in Table 4, and so it may be surmised that replacing the NCH₃ groups with larger substituents (R = CMe₃, C₆H₅, C₆H₂Me₃-2,4,6) does not lead to significant deformation of the HB(mt^R)₃M cage.

The alkylidyne ligands provide a further focus for interest, with each showing characteristically short W–C separations [**1a** 1.859(9) [1.842(9)]; **1b** 1.819(7); and **1c** 1.837(7) Å] typical of tungsten–carbon triple bonds.¹¹ The longest of these, **1a**, reflects the π -donative role of the N⁴Pr₂ group which compromises the W≡C bond order (Chart 2). The only other structurally characterized alkynylalkylidynes (propargylidynes) are the tricarbide compound [(^tBuO)₃W≡C–C≡C–Re(NO)-(PPh₃)₃](η -C₅Me₅)₂ reported by Gladysz [W≡C 1.769(8) Å]^{33–35} and Fischer's complexes [W(≡C–C≡CPh)(CO)₂–{HB(pzMe₂)₃}] and [W(≡C–C≡CCMe₃)Cl(CO)₂(tmeda)]³⁶

(33) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824.

(34) Weng, W.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 891.

(35) NB: Although structural data are not yet available, the complex [HB(pzMe₂)₃(CO)₂W≡C–C≡C–Mo(=O)₂{HB(pzMe₂)₃}] has been described, arising from the aerial oxidation of the anionic complex [HB(pzMe₂)₃(CO)₂W=C–C≡C–Mo(CO)₂{HB(pzMe₂)₃}][–]; Woodward, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418.

(36) Schwenzer, B.; Schlu, J.; Burzlaff, N.; Karl, C.; Fischer, H. *J. Organomet. Chem.* **2002**, *641*, 134.

Table 5. Steric Perturbation of θ and ω Parameters for $\text{HB}(\text{mt}^{\text{R}})_3\text{ZnX}$ (see Chart 4)

X	R	θ^1	θ^2	θ^3	θ^m	ω^1	ω^2	ω^3	ω^m	CCDC ^{ref}
F	CMe_3^a				43.7				56.6	NEBNUD ^{9b}
Cl	CMe_3	45.6	45.4	46.9	46.0	55.6	54.8	56.2	55.5	NEBNOX ^{9b}
Cl	$\text{C}_6\text{H}_2\text{Me}_3^b$	48.4	43.8	46.8	46.3	54.2	57.6	54.7	55.5	LEYQUB ^{10b}
		46.0	45.6	44.5	45.4	55.9	56.2	57.2	56.4	LEYQUB ^{10b}
Cl	Me	47.6	47.7	43.8	46.4	55.9	53.4	56.1	55.1	AGEZAN ^{2f}
Br	Me^a				-45.6				-57.3	TODHID ^{2a}
I	Me	45.3	45.4	41.9	44.2	56.9	57.1	61.6	58.5	AGEZER ^{2f}
I	Ph	47.8	45.7	48.0	47.2	56.3	56.9	56.8	56.7	LEYROW ^{10b}
I	$\text{C}_6\text{H}_2\text{Me}_3$	45.8	45.8	44.8	45.5	55.7	54.6	55.3	55.2	LEYQIP ^{10b}
Br	CH_2Ph^a				46.5				56.8	MEVLUU ⁵⁴
Br	CMe_3	46.4	47.1	48.3	47.3	55.4	55.6	52.1	54.4	XOTPAX ^{7b}

^a Crystallographically imposed C_3 symmetry. ^b Two independent molecules.

for which $\text{W}\equiv\text{C}$ separations of 1.839(13) and 1.834(5) Å were found, comparable to that for **1c**. Each of these displays essentially linear WC_3 spines within the range ascribed to crystal packing forces. Only one example of a structurally characterized thienylmethylidyne has been reported, viz., $[\text{W}(\equiv\text{CC}_4\text{H}_3\text{S}-2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [$\text{W}\equiv\text{C} = 1.828(10)$ Å],¹⁷ though this complex exhibited rotational disorder of the thiophene ring, a feature not present in **1b**.

The feature of **1c** that calls for comment, however, is the severe deformation of the $\text{W}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}$ spine both from linear geometry and also from octahedral coordination at tungsten. Thus the $\text{S}(1)-\text{W}-\text{C}(19)$ angle of $161.1(2)^\circ$ is strongly contracted from the expected 180° . A similar but smaller deformation is observed in the case of **1b** [$\text{S}(1)-\text{W}-\text{C}(19)$ $165.6(2)^\circ$], whereas the corresponding angle for **1a** is essentially linear [$176.2(3)^\circ$ [$174.3(3)^\circ$]]. The steric bulk of these alkylidyne ligands decreases in the order $\text{N}^i\text{Pr}_2 > \text{C}_4\text{H}_3\text{S}-2 > \text{C}\equiv\text{C}-\text{CMe}_3$, allowing simple steric factors to be excluded. In the case of **1c** it transpires that the deformation possibly arises in part from an intermolecular hydrogen-bonding interaction between one of the imidazole methine hydrogen atoms, $\text{C}(9)-\text{H}$, in one molecule and the π -system of the alkylidyne ligand of another; $\text{H}\cdots\text{C}(20)$ 2.86 Å, $\text{C}(9)-\text{H}\cdots\text{C}(20)$ 150° . This interaction is reminiscent of hydrogen bonding to the triple bond of conventional alkynes.³⁷ The enthalpies of interaction for both methane and HCN hydrogen bonding to ethyne in the gas phase have been estimated using a density functional theory approach^{37b} to be ca. -5.5 and -13 kJ mol⁻¹, respectively. Thus the substantial deformation of the $\text{W}\equiv\text{C}-\text{C}\equiv\text{C}$ spine that results from these weak noncovalent interactions suggests that $\text{M}\equiv\text{C}-\text{R}$ deformations in this system require little energy. With this deformation of **1c** accounted for, at least in part, the curiosity that nevertheless remains to be explained is the marked deformation in **1b**. We have been unable to identify any intra- or intermolecular contacts that might be responsible. Accordingly, if such a deformation is a genuine (and more general) phenomenon, it may well be also contributing to the deformation observed in **1c**.

Infrared Spectroscopy. There now exists a particularly wide range of complexes of the form " $\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_2\text{L}$ " where L is a facially tridentate ligand (the majority of which arise from Stone's pioneering work on their use in the strategic synthesis

of heteropolymetallic clusters³⁸⁻⁴⁰), which constitute perhaps the largest series of isoelectronic complexes for which solution IR data exist for comparison of the donor abilities of various facial ligands. Tables 1 and 2 give $\nu(\text{CO})_2$ infrared data for these alkylidyne complexes, in addition to the derived Cotton-Kraihanzel parameter.²² Carbonyl infrared data have long been used as an indicator of retrodonative capacity of transition metal centers, and accordingly, Table 2 allows an order of net ligand basicity to be compiled for this range of facial ligands. Table 2 is therefore ordered with respect to increasing k_{CK} . A number of points need to be made: First, some entries are for benzyldiyne rather than toulidyne complexes, and the benzyldiyne data arise from solid state measurements which are by their nature less reliable, given the peculiarities of crystal packing effects on $\nu(\text{CO})$ values. Nevertheless, the difference between $\nu(\text{CO})$ for benzyldiyne versus toulidyne complexes should be modest; for example, k_{CK} for $\text{W}(\equiv\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ⁴¹ is calculated to be 15.28 N m⁻¹, i.e., only 0.04 N m⁻¹ higher than the toulidyne analogue.⁴¹ Accordingly, this difference can reasonably be neglected, given the more dubious nature of the solid state data. From the table a few points emerge: Perhaps the most striking is that the charge on the complex is not the over-riding factor for, for example, $\text{Me}_3[9]\text{-aneN}_3$ lying well above $\text{C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2$ and the lowest value of k_{CK} being observed for the neutral complex of Kauai's $\text{CpCo}(\text{PO}_3\text{Me}_2)_3$ tripod. Table 2 reveals that the $\text{HB}(\text{mt})_3$ ligand central to this paper is particularly electron releasing, surpassed only by the anionic $\text{CpCo}(\text{PO}_3\text{Me}_2)_3$ and dianionic $\text{C}_2\text{B}_9\text{H}_9\text{Me}_2$ ligands. Counter-intuitively, what Table 2 fails to reveal is any obvious correlation between k_{CK} (or $\nu(\text{CO})_2$) and the chemical shift of the alkylidyne carbon. One might have expected that both would reflect, at least in part, the π -basicity of the metal center.

Each of the complexes **1** show two weak bands in the area $2200-2300$ cm⁻¹, e.g. 2316 and 2222 cm⁻¹ for **1e**. While the higher of these might in principle be an overtone for the strong absorptions of the $\text{HB}(\text{mt})_3$ ligand typically observed around 1200 cm⁻¹, this does not account for the second lower band. The structural

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studies on **1a**, **1b**, and **1c** allow us to exclude the presence of agostic B–H...W interactions. We are therefore at a loss to explain these bands, but report their appearance since they are a recurrent feature of the solid state spectra of each complex.

Concluding Remarks. The isolation of alkylidyne complexes **1** of the HB(mt)₃ ligand for low-valent tungsten is noteworthy inasmuch as there is no indication of a tungstaboratrane alkylidene tautomerism. This is despite the possibility of the alkylidyne serving as an internal hydrogen “sink” or undergoing hydroboration. Thus metallaboratranes remain at present limited to those based on ruthenium(0),¹ osmium(0), and rhodium(I).⁵⁵ Each of these involves octahedrally coordinated d⁸-metal centers, and simple electron counting and isolobal considerations⁵⁶ would suggest that for formally d⁶ metals (i.e., W(0)), seven-coordinate metallaboratranes should be accessible.

Experimental Section

Conventional Schlenk and vacuum line techniques were employed for the exclusion of air. However, once isolated, the complexes **1** were generally air-stable as dry solids. Solvents were distilled under nitrogen from appropriate drying agents. The salt Na[HB(mt)₃] has been obtained by heating solid Na[BH₄] and Hmt as a melt.^{2a,53} In our experience samples prepared in this way are prone to contamination with Hmt and Na[H₂B(mt)₂] (each of which reacts with the tungsten precursors) and often brown due to charring, which results from inhomogeneous heating. For this study, our alternative procedure⁵ was employed, which makes use of refluxing xylenes as a means of moderating the reaction, controlling temperature, and maintaining homogeneity. This provided colorless samples of high purity and a means of easily recovering unreacted Hmt for future use. The alkylidyne complexes [W(=CC₆H₃Me₂-2,6)Br(CO)₂(pic)₂], [W(=CNⁱPr₂)X(CO)₃(PPh₃)] (X = Cl, Br, I), [W(=CC₄H₃S-2)Cl(CO)₂(tmeda)], [W(=CC₄H₃S-2)Cl(CO)₂(γ-pic)₂], [W(=CC₆H₃Me₂-2,6)Br(CO)₂(bipy)], and [W(=C–C≡CCMe₃)(O₂CCF₃)(CO)₂(tmeda)] are described elsewhere.^{1,16–21} Elemental microanalytical data were obtained commercially from the University of North London Analytical Service.

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Synthesis of [W(=CNⁱPr₂)(CO)₂{HB(mt)₃}] **1a. A mixture of [W(=CNⁱPr₂)Br(CO)₃(PPh₃)] (6.33 g, 8.76 mmol) and Na[HB(mt)₃] (3.60 g, 9.62 mmol) in tetrahydrofuran (60 mL) was stirred for 18 h. During this time the mixture darkened from yellow to orange, and the progress was monitored (IR) by observing the replacement of bands due to the starting complex (2045, 1973, 1929 cm⁻¹) with those for **1a** (1930, 1832 cm⁻¹) and by TLC (silica gel, CH₂Cl₂). The mixture was evaporated to dryness and the resulting residue extracted with dichloromethane (2 × 20 mL). The combined extracts were filtered through a short plug of diatomaceous earth, which was then washed with further dichloromethane until the washings were colorless. The combined filtrates were diluted with light petroleum (60 mL), and the resulting mixture was filtered once again through diatomaceous earth. The filtrate was concentrated to the point at which crystallization began to commence and then cooled to -20 °C overnight. The resulting orange crystals were isolated by decantation of the cold mother liquor and dried in vacuo. Yield 1.59 g (2.26 mmol, 26%, not optimized). NB: This complex is not stable to chromatography on silica gel under ambient conditions. IR CH₂Cl₂: 2401 [ν(BH)], 1925, 1822 [ν(CO)] cm⁻¹. Nujol: 2433w, 2404w [ν(BH)], 2316w, 2225w, 1920vs, 1816vs [ν(CO)], 1529s, 1460s, 1311s, 1205s, 1148w, 1125w, 1095w cm⁻¹. FAB-MS: *m/z* (%) 703(29)[M]⁺, 675(100)[M - CO]⁺, 647(62)[M - 2CO]⁺, 535(75)[M - 2CO - mt]⁺, 422(25)[M - 2CO - 2mt]⁺. NMR (CDCl₃, 25 °C) ¹H: δ 1.24, 1.34 [d × 2, 6 H, CCH₃, ³J(HH) = 6.5], 3.20 [h, 2 H, NCH, ³J(HH) = 6.5 Hz], 3.62 [s(br), 9 H, NCH₃], 6.76 [s(br), 6 H, CH=CH] (see also Figure 1). ¹³C{¹H}: 249.7 [W=C], 229.4, 220.8 [W(CO)₂], 160.6 (br, C=S), 122.5, 119.4 (C₂H₂), 52.3(NCHMe₂) 34.7 (NCH₃), 23.2, 23.1 (CCH₃) ppm. ¹¹B: -2.59 ppm. Anal. Found: C, 35.9; H, 4.3; N, 13.9. Calcd for C₂₁H₃₀N₇O₂S₃W: C, 35.9; H, 4.30; N, 13.94. The complex was also characterized crystallographically: *Crystal data*: C₂₁H₃₀N₇O₂BS₃W·0.5CH₂Cl₂, *M* = 745.8, monoclinic, *P*₂/c (no. 14), *a* = 16.569(2) Å, *b* = 16.121(1) Å, *c* = 22.212(2) Å, β = 90.01(7)°, *V* = 5933.1(9) Å³, *Z* = 8 (two independent molecules), *D*_c = 1.670 g cm⁻³, μ(Mo Kα) = 4.23 mm⁻¹, *T* = 293 K, orange blocks; 10 397 independent measured reflections, *F*² refinement, *R*₁ = 0.047, *wR*₂ = 0.088, 6441 independent observed absorption corrected reflections [|*F*_o| > 4σ(*F*_o)], 2θ ≤ 50°, 703 parameters.**

Synthesis of [W(=CC₄H₃S-2)(CO)₂{HB(mt)₃}] **1b. [W(=CC₄H₃S-2)Cl(CO)₂(γ-pic)₂] (0.43 g, 0.53 mmol) was dissolved in dichloromethane (100 mL), and to this was added Na[HB(mt)₃] (0.32 g, 0.86 mmol). The resulting mixture was stirred for 15 h. The reaction was monitored by observing the disappearance of ν(CO) absorptions (1988, 1901 cm⁻¹) due to [W(=CC₄H₃S-2)Cl(CO)₂(γ-pic)₂] and the appearance of bands due to the product (1970, 1880 cm⁻¹) and by TLC (silica gel, CH₂Cl₂). The mixture was concentrated under reduced pressure to ca. 5 mL and then diluted with diethyl ether (50 mL). The resulting red solution was filtered through diatomaceous earth and then concentrated, resulting in the formation of crystals of **1b**. Yield: 0.25 g (0.37 mmol, 69%). Similar yields were obtained beginning with [W(=CC₄H₃S-2)Cl(CO)₂(tmeda)]. IR CH₂Cl₂: 1970, 1880 [ν(CO)] cm⁻¹. Nujol: 2435w, 2410w [ν(BH)], 2316w, 2223w, 1959vs, 1865vs [ν(CO)], 1604w, 1561w, 1413w, 1325w, 1300m, 1203s, 1154w, 1123w, 1086w, 1043w cm⁻¹. FAB-MS: *m/z* (%) 686(53)[M]⁺, 658(73)[M - CO]⁺, 630(49)[M - 2CO]⁺. NMR (CDCl₃, 25 °C) ¹H: δ 3.60, 3.70, 3.74 [s × 3, 9 H, NCH₃], 6.77–6.81, 6.87 [m, 7 H, NCH=CH, H⁴-(C₄H₃S)], 6.95, 7.08 [dd × 2, 1 H × 2, H^{3,5}-(C₄H₃S)], ²J(H⁴H⁵) = 5.1, 3.6. ³J(H³H⁵) = ca. 1.1 Hz. ¹³C{¹H}: 264.0 (W=C), 223.7, 218.7 [W(CO)₂], 160.8, 159.0, 158.5 (C=S), 155.2 [C²-(C₄H₃S)] 128.1, 126.3, 125.5 [C³⁻⁵-(C₄H₃S)], 122.9, 122.8, 122.7 [C⁵-(C₃N₂)], 120.1(1C), 120.0 (2C) [C⁴-(C₃N₂)], 34.93, 34.83, 34.79 (NCH₃) ppm. ¹B: -2.22 ppm. Anal. Found: C, 33.4; H, 2.70; N, 12.02. Calcd for C₁₉H₁₉N₆O₂S₄W: C, 33.25; H, 2.79; N, 12.25. The complex was also characterized crystallographically: *Crystal data*: C₁₉H₁₉N₆O₂BS₄W, *M* = 686.3, monoclinic,**

$P2_1/n$ (no. 14), $a = 11.716(1) \text{ \AA}$, $b = 15.620(1) \text{ \AA}$, $c = 14.012(1) \text{ \AA}$, $\beta = 96.98(1)^\circ$, $V = 2545.3(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.791 \text{ g cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 11.72 \text{ mm}^{-1}$, $T = 293 \text{ K}$, orange blocks; 3773 independent measured reflections, F^2 refinement, $R_1 = 0.041$, $wR_2 = 0.088$, 3047 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 120^\circ$], 299 parameters.

Synthesis of $[\text{W}(\equiv\text{C}-\text{C}\equiv\text{CCMe}_3)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ 1c. A mixture of $[\text{W}(\equiv\text{C}-\text{C}\equiv\text{CCMe}_3)(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})]$ (4.00 g, 7.11 mmol) and $\text{Na}[\text{HB}(\text{mt})_3]$ (2.80 g, 7.48 mmol) in tetrahydrofuran (50 mL) was heated under reflux for 8 h. The solvent was removed and the residue extracted with dichloromethane (2 \times 20 mL), and the combined extracts were filtered through a short plug of silica gel, which was subsequently washed with further dichloromethane (2 \times 10 mL). The combined filtrates were diluted with petroleum ether (40 mL) and then concentrated slowly under reduced pressure to a volume of ca. 30 mL to produce a red precipitate. The mother liquor was removed by cannula filtration and the solid washed with petroleum ether and dried in vacuo. The crude product was dissolved in a minimum of dichloromethane (70 mL), layered with petroleum ether (70 mL), and stored at -20°C for 3 days to provide an orange-red solid. Yield: 2.82 g (4.12 mmol, 58%). IR CH_2Cl_2 : 2127 $[\nu(\text{C}\equiv\text{C})]$, 1975, 1885 $[\nu(\text{CO})]$ cm^{-1} . Nujol: 2430w, 2405w $[\nu(\text{BH})]$, 2318w, 2219w, 2123w $[\nu(\text{C}\equiv\text{C})]$, 1970vs, 1883vs $[\nu(\text{CO})]$, 1696w, 1562m, 1415m, 1299w, 1275w, 1205s, 1149w, 1123w, 1086w, 1045w, 1014w cm^{-1} . FAB-MS: m/z (%) 684(32) $[\text{M}]^+$, 656(55) $[\text{M} - \text{CO}]^+$, 628(45) $[\text{M} - 2\text{CO}]^+$. NMR ^1H (CDCl_3 , 25 $^\circ\text{C}$): δ 1.18 (s, 9 H, CMe_3), 3.57, 3.69, 3.75 (s \times 3, 9 H, NCH_3), 6.75–6.79, 6.85 (m \times 2, 6 H, $\text{NCH}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$: 250.1 ($\text{W}=\text{C}$), 224.7, 220.2 $[\text{W}(\text{CO})_2]$, 160.0, 158.4, 158.0 ($\text{C}=\text{S}$), 122.8, 120.0, 119.9 $[\text{NCH}=\text{CH}]$, 97.33 $[\text{W}=\text{C}-\text{C}\equiv\text{C}]$, 86.97 $[\text{W}=\text{C}-\text{C}\equiv\text{C}]$, 34.87, 34.64, 34.53 (NCH_3), 30.17 (CCH_3), 28.06 (CCH_3) ppm. ^{11}B : -2.65 ppm. Anal. Found: C, 36.9; H, 3.78; N, 12.35. Calcd for $\text{C}_{21}\text{H}_{30}\text{BN}_6\text{O}_2\text{S}_3\text{W}$: C, 36.86; H, 3.68; N, 12.28. The complex was also characterized crystallographically: *Crystal data*: $\text{C}_{21}\text{H}_{25}\text{N}_6\text{O}_2\text{BS}_3\text{W}\cdot\text{C}_4\text{H}_{10}\text{O}$, $M = 758.4$, monoclinic, $P2_1/n$ (no. 14), $a = 9.861(1) \text{ \AA}$, $b = 17.424(3) \text{ \AA}$, $c = 19.781(3) \text{ \AA}$, $\beta = 104.27(1)^\circ$, $V = 3293.8(9) \text{ \AA}^3$, $Z = 4$, $D_c = 1.529 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 3.73 \text{ mm}^{-1}$, $T = 293 \text{ K}$, orange plates; 5802 independent measured reflections, F^2 refinement, $R_1 = 0.041$, $wR_2 = 0.087$, 4371 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 50^\circ$], 384 parameters.

Synthesis of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ 1d. A suspension of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)\text{Br}(\text{CO})_2(\text{tmeda})]$ (5.66 g, 10.50 mmol) and $\text{Na}[\text{HB}(\text{mt})_3]$ (4.12 g, 11.00 mmol) in tetrahydrofuran (250 mL) was heated under reflux for 18 h. The mixture was filtered through diatomaceous earth and the solvent removed from the filtrate under reduced pressure to provide an orange solid. This solid was recrystallized from a mixture of dichloromethane and diethyl ether at -20°C to provide an orange solid, which was isolated by filtration, washed with petroleum ether, and dried in vacuo. Yield: 6.48 g. (9.33 mmol, 89%). IR CH_2Cl_2 : 1967, 1875 $[\nu(\text{CO})]$ cm^{-1} . Nujol: 2426w, 2395w $[\nu(\text{BH})]$, 2314w, 2214w, 1962vs, 1876vs $[\nu(\text{CO})]$, 1561m, 1414m, 1324w, 1299m, 1204s, 1149w, 1120w, 1086w, 1042w, 1013w, 818 $[\delta(\text{C}_6\text{H}_4)]$ cm^{-1} . FAB-MS: m/z (%) $[\text{M}]^+$ not observed, 666(12) $[\text{M} - \text{CO}]^+$, 638(55) $[\text{M} - 2\text{CO}]^+$. NMR (CDCl_3 , 25 $^\circ\text{C}$) ^1H : δ 2.22 [s, 3 H, $\text{C}-\text{CH}_3$], 3.60, 3.78, 3.74 (s \times 3, 9 H, NCH_3), 6.77–6.81 (m, 3 H, $\text{NCH}=\text{CH}$), 6.86 (d, 2 H, $\text{NCH}=\text{CH}$), 6.98, 7.17 $[(\text{AB})_2]$, 4 H, $^3J(\text{AB}) = 8.00$, C_6H_4], 7.25 [d, 1 H, $\text{NCH}=\text{CH}$, $^3J(\text{HH}) = 1.08 \text{ Hz}$]. $^{13}\text{C}\{^1\text{H}\}$: 281.1 ($\text{W}=\text{C}$), 223.4, 218.6 $[\text{W}(\text{CO})_2]$, 161.1, 159.2, 158.9 ($\text{C}=\text{S}$), 148.2 $[\text{C}^1(\text{C}_6\text{H}_4)]$, 136.9 $[\text{C}^4(\text{C}_6\text{H}_4)]$, 128.9, 128.3 $[\text{C}^{2,3,5,6}(\text{C}_6\text{H}_4)]$, 122.8, 122.7, 122.6 $[\text{C}^4(\text{C}_3\text{N}_2)]$, 120.0(1C), 119.9(2C) $[\text{C}^5(\text{C}_3\text{N}_2)]$, 34.91, 34.83, 34.80 (NCH_3), 21.8 (CCH_3) ppm. ^{11}B : -2.62 ppm. Anal. Found: C, 38.19; H, 3.43; N, 11.96. Calcd for $\text{C}_{22}\text{H}_{23}\text{BN}_6\text{O}_2\text{S}_3\text{W}$: C, 38.06; H, 3.34; N, 12.10.

Synthesis of $[\text{W}(\equiv\text{CC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ 1e. (a) $[\text{W}(\equiv\text{CC}_6\text{H}_3\text{Me}_2-2,6)\text{Br}(\text{CO})_2(2,2'\text{-bipy})]$ (2.97 g, 5.00 mmol) was dissolved in tetrahydrofuran (60 mL) and treated with

$\text{Na}[\text{HB}(\text{mt})_3]$ (1.95 g, 5.20 mmol), and the resulting mixture was heated under reflux for 18 h. The reaction was monitored (IR) by the disappearance of absorptions due to the starting complex (1984, 1900 cm^{-1}), which are replaced by those of the product (1966, 1877 cm^{-1}). The mixture was allowed to cool, before being filtered through diatomaceous earth. The solvent was removed under reduced pressure, and the residue was then extracted with dichloromethane (3 \times 20 mL). The combined extracts were filtered through a short plug of silica pad and then diluted with light petroleum. The solution was concentrated under reduced pressure to ca. 15 mL to provide a red microcrystalline solid, which was isolated by filtration and dried in vacuo. Yield: 1.47 g (2.08 mmol, 42%). (b) The complex $[\text{W}(\equiv\text{CC}_6\text{H}_3\text{Me}_2-2,6)\text{Br}(\text{CO})_2(\text{pic})_2]$ may be employed in place of $[\text{W}(\equiv\text{CC}_6\text{H}_3\text{Me}_2-2,6)\text{Br}(\text{CO})_2(\text{bipy})]$ with a similar reaction time; however it is not necessary to heat the reaction mixture since the reaction progresses at room temperature. IR CH_2Cl_2 : 1967, 1876 $[\nu(\text{CO})]$ cm^{-1} . Nujol: 2435m, 2409m $[\nu(\text{BH})]$, 2316w, 2222w, 1960vs, 1865vs $[\nu(\text{CO})]$, 1667w, 1561m, 1414m, 1323w, 1300m, 1205s, 1150w, 1124w, 1090w, 1042w, 1012w, 844 $[\delta(\text{C}_6\text{H}_4)]$ cm^{-1} . FAB-MS: m/z (%) 708(21) $[\text{M}]^+$, 680(45) $[\text{M} - \text{CO}]^+$, 652(28) $[\text{M} - 2\text{CO}]^+$. NMR (CDCl_3 , 25 $^\circ\text{C}$) ^1H : δ 2.57 (s, 6 H, $\text{C}-\text{CH}_3$), 3.60 (s, 6 H, $\text{N}-\text{CH}_3$), 3.76 (s, 3 H, NCH_3), 6.79–6.87 (m, 9 H, $\text{NCH}=\text{CH}$ and C_6H_3). $^{13}\text{C}\{^1\text{H}\}$: 283.3 ($\text{W}=\text{C}$), 225.2, 220.8 $[\text{W}(\text{CO})_2]$, 160.6, 159.2, 159.1 ($\text{C}=\text{S}$), 147.4 $[\text{C}^1(\text{C}_6\text{H}_3)]$, 140.4 $[\text{C}^{2,6}(\text{C}_6\text{H}_3)]$, 126.8 $[\text{C}^{3,5}(\text{C}_6\text{H}_3)]$, 126.6 $[\text{C}^4(\text{C}_6\text{H}_3)]$, 123.1, 122.7, 122.5 $[\text{C}^4(\text{C}_3\text{N}_2)]$, 119.8(2C), 119.7(1C) $[\text{C}^5(\text{C}_3\text{N}_2)]$, 34.8(1C), 34.7(2C) $[\text{NCH}_3]$, 20.8 ($\text{C}-\text{CH}_3$) ppm. ^{11}B : -2.07 ppm. Anal. Found: C, 38.9; H, 3.51; N, 11.75. Calcd for $\text{C}_{23}\text{H}_{25}\text{BN}_6\text{O}_2\text{S}_3\text{W}$: C, 39.00; H, 3.56; N, 11.86.

Synthesis of $[\text{W}\{\equiv\text{CC}_5\text{H}_4\text{Mn}(\text{CO})_3\}(\text{CO})_2\{\text{HB}(\text{mt})_3\}]$ 1f. A mixture of $[\text{W}\{\equiv\text{CC}_5\text{H}_4\text{Mn}(\text{CO})_3\}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})]$ (0.73 g, 1.06 mmol) and $\text{Na}[\text{HB}(\text{mt})_3]$ (0.45 g, 1.20 mmol) in tetrahydrofuran (50 mL) was heated under reflux for 18 h. The reaction was monitored (IR) by observing the disappearance of $\nu(\text{CO})$ (2021, 1990, 1935, 1905 cm^{-1}) and $\nu(\text{CO}_2)$ (1717 cm^{-1}) due to $[\text{W}\{\equiv\text{CC}_5\text{H}_4\text{Mn}(\text{CO})_3\}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})]$ and the appearance of bands due to the product [2019, 1967, 1931, 1882 $\nu(\text{CO})$, 1688 $\nu(\text{CO}_2)$ cm^{-1}]. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (2 \times 20 mL). The combined extracts were filtered through diatomaceous earth and then diluted with light petroleum (20 mL). The solvent volume was then reduced in vacuo to ca. 10 mL, resulting in a red-brown solid, from which the supernatant was decanted. The residue was ultrasonically triturated with a 1:1 mixture of diethyl ether and light petroleum to improve the crystallinity. Yield: 0.54 g (0.67 mmol 63%). IR CH_2Cl_2 : 2021, 1934 $[\nu(\text{MnCO})]$, 1970, 1880 $[\nu(\text{WCO})]$ cm^{-1} . Nujol: 2436w $[\nu(\text{BH})]$, 2020vs, 1964vs, 1946vs, 1919vs, 1876vs $[\nu(\text{CO})]$, 1561w, 1413w, 1299m, 1204s, 1151w, 1087m, 1042w cm^{-1} . FAB-MS: m/z (%) 806(21) $[\text{M}]^+$, 778(52)- $[\text{M} - \text{CO}]^+$, 748(9) $[\text{M} - 3\text{CO}]^+$, 666(57) $[\text{M} - 5\text{CO}]^+$. NMR (CDCl_3 , 25 $^\circ\text{C}$) ^1H : δ 3.58, 3.70, 3.73 (s \times 3, 9 H, NCH_3), 4.48, 4.51, 4.92, 4.98 [s(br) \times 4, 4 H, $\text{C}_5\text{H}_4\text{Mn}$], 6.79, 6.85 [s(br) \times 2, 6 H, $\text{NCH}=\text{CH}$]. $^{13}\text{C}\{^1\text{H}\}$: 266.6 ($\text{W}=\text{C}$), 224.8 $[\text{Mn}(\text{CO})_3]$, 223.2, 218.1 $[\text{W}(\text{CO})_2]$, 160.8, 159.1, 158.5 ($\text{C}=\text{S}$), 122.7(3C), 120.0(1C), 119.9(2C) $[\text{NCH}=\text{CH}]$, 110.2 $[\text{C}^1(\text{C}_5\text{H}_4)]$, 80.52, 80.38, 79.78, 79.67 $[\text{C}^{2-5}(\text{C}_5\text{H}_4)]$, 34.83(1C), 34.74(2C) (NCH_3) ppm. ^{11}B : -2.65 ppm. Satisfactory elemental microanalytical data were not obtained.

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Supporting Information Available: Full details of the crystal structure determinations of **1a**, **1b**, and **1c** including positional and thermal parameters and thermal ellipsoid plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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