5540 *Organometallics* **1998,** *17,* 5540−5548

Carborane Complexes of Ruthenium: Synthesis of the Bimetal Compounds [MRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo or W) and Their Reactions with Sulfur and Selenium[†,‡]

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Addition of the reagent [Ru(CO)$_2$(thf)(η^5-7,8-C$_2$B$_9$H$_{11}$)] (thf = tetrahydrofuran) to the compounds [M($\equiv$CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (M = Mo or W, HB(pz)$_3$ = hydrotris(pyrazol-1-yl)borato) in CH$_2$Cl$_2$ affords, respectively, the bimetal species [MRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo (**4a**), M = W (**4b**)). These complexes are readily cleaved by donor molecules, including thf, but they are stable in CH$_2$Cl$_2$ or toluene. X-ray diffraction studies established the molecular structures of **4b** and the related species [WRu(μ-CC$_6$H$_4$-Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)(η^5-C$_5$H$_5$)] (**2b**). In both molecules very long Ru−W bonds (ca. 3 Å) are asymmetrically bridged by the tolylmethylidyne groups (μ-C−W av 1.92 Å, μ-C−Ru av 2.21 Å). The complexes **4** react with sulfur or selenium in CH$_2$Cl$_2$ to give the compounds [MRu(μ-1κC^α,1:2κE-ECC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo, E = S (**6a**), Se (**6c**); M = W, E = S (**6b**), Se (**6d**)). The structure of **6b** was established by X-ray diffraction. The molecule possesses an unusual structure in which Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$) and W(CO)$_2${κ^3-HB(pz)$_3$} units are bridged by a thioacyl group which is η^2-coordinated to the tungsten through its carbon and sulfur atoms and bound to the ruthenium only through the sulfur atom. There is no metal−metal bond as both the W and Ru atoms have filled valence shells. The NMR data for the new compounds are reported and discussed.

Introduction

We have previously reported that treatment of the reagent [Ru(CO)$_2$(thf)(η^5-7,8-C$_2$B$_9$H$_{11}$)] (**1**, thf = tetrahydrofuran) (Chart 1) with the alkylidyne metal complexes [M($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] (M = Mo or W) affords the bimetallic compounds [MRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)(η^5-C$_5$H$_5$)] (M = Mo (**2a**), M = W (**2b**)).[1] These species are very labile and have a predilection for insertion of their tolylmethylidyne ligands into an adjacent B−H bond of the carborane group, forming the isomeric complexes [MRu{σ,η^5-9-CH(CC$_6$H$_4$Me-4)-7,8-C$_2$B$_9$H$_{10}$}(CO)$_4$(η^5-C$_5$H$_5$)] (M = Mo (**3a**), M = W (**3b**)). This transformation seemed to effectively inhibit use of the species **2** in further syntheses. Herein we describe the preparation of the complexes [MRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo (**4a**), M = W (**4b**), HB(pz$_3$)$_3$ = hydrotris(pyrazol-1-yl)borato). These compounds are analogues of **2** with the η^5-C$_5$H$_5$ ligands in the latter replaced by tridentate κ^3-HB(pz)$_3$ groups. Earlier studies had shown that low-valent metal species react readily with the molecules [M($\equiv$CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (M = Mo or W) to afford stable di- and trimetal complexes,[2] and it was anticipated that the reagent **1** would behave similarly. Moreover, introduction of the hydrotris(pyrazol-1-yl)borato ligand[3] could result in the complexes **4** being more stable than their cyclopentadienyl analogues **2** with respect to formation of species akin to **3**, thereby allowing their use in further syntheses.

Results and Discussion

Attempts to prepare the desired complexes [MRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo (**4a**), M = W (**4b**)) by adding the compounds [M($\equiv$CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] to the reagent **1** using thf as solvent were unsuccessful. It became apparent that this methodology failed because the species **4**

[†] Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

[‡] The compounds described in this paper have a ruthenium atom incorporated into a *closo*-1,2-dicarba-3-ruthenadodecaborane framework. However, to avoid a complicated nomenclature for the complexes reported and to relate them to the many known ruthenium species with η^5-coordinated cyclopentadienyl ligands, we treat the cages as *nido*-11-vertex ligands with numbering as for an icosahedron from which the 12th vertex has been removed.

(1) Anderson, S.; Jeffery, J. C.; Liao, Y.-H.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1997**, *16*, 958.

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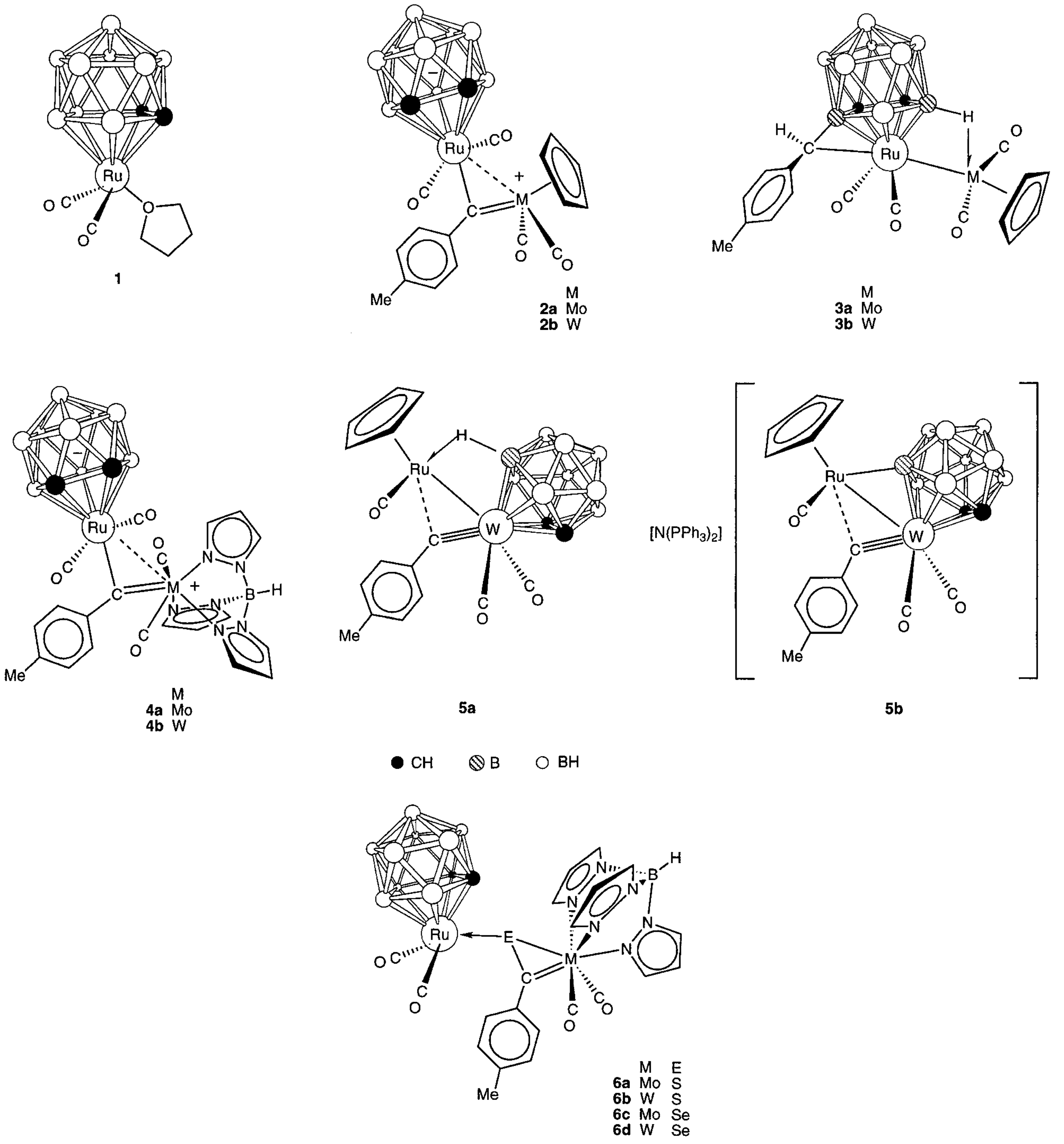
Chart 1



dissociated into their respective precursors when dissolved in thf. Removal of thf in vacuo followed by addition of CH_2Cl_2 re-formed the complexes **4**. Hence a successful synthesis in essentially quantitative yield was achieved, by adding CH_2Cl_2 solutions of [M($\equiv$$CC_6H_4Me$-4)$(CO)_2$\{$\kappa^3$-HB$(pz)_3$\}] to samples of **1** freshly prepared as a solid.[4a] In this way all but ruthenium-coordinated thf was excluded from the mixtures.

Physical data for the complexes **4** are given in Table 1. As expected the IR spectra show four CO stretching bands like their cyclopentadienyl analogues.[1] The ^{1}H NMR spectra (Table 2) were likewise unremarkable, displaying the expected resonances. In the $^{13}C\{^1H\}$ spectra diagnostic peaks for the cage carbons were seen at δ 47.2 and 57.7 (**4a**) and at δ 48.4 and 58.2 (**4b**).[5] The observation of two peaks for the cage carbon atoms in each spectrum implies asymmetry in the molecules in solution, a feature revealed in the solid-state structure of **4b** by an X-ray diffraction study discussed below.

The chemical shifts for the μ-CC_6H_4Me-4 nuclei (**4a** δ 303.2 and **4b** δ 287.4) were of immediate interest since they differ little from those of the terminal alkylidyne−carbon nuclei of [Mo($\equiv$$CC_6H_4Me$-4)$(CO)_2$\{$\kappa^3$-HB$(pz)_3$\}]

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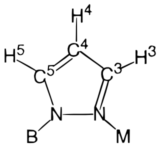
Table 1. Analytical and Physical Data

compd	color	yield (%)	$\nu_{max}(CO)^a$ (cm^{-1})	anal (%)[b] C	anal (%)[b] H
[MoRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**4a**)	red	85	2048 s, 2020 s, 1999 s, 1946 s	37.1 (36.5)[c]	4.2 (3.7)
[WRu(μ-CC$_6$H$_4$Me−4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**4b**)	red	88	2045 s, 2008 s, 1999 s, 1926 s	32.4 (32.7)[d]	3.5 (3.3)
[MoRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6a**)	black	77	2046 s, 2028 m, 1993 s, 1953 m	34.5 (34.9)[e]	3.5 (3.6)
[WRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6b**)	black	68	2044 s, 2020 s, 1991 s, 1935 m	31.5 (31.5)[f]	3.2 (3.3)
[MoRu(μ-1κC^{α},1:2κSe-SeCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6c**)	black	78	2044 s, 2028 m, 1990 s, 1958 m	29.8 (29.9)[g]	3.1 (3.1)
[WRu(μ-1κC^{α},1:2κSe-SeCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6d**)[h]	black	65	2041 s, 2019 s, 1998 s, 1939 s		

[a] Measured in CH_2Cl_2. A medium-intensity band observed at ca. 2550 cm^{-1} in the spectra of all compounds is due to B−H adsorptions. [b] Calculated values are given in parentheses. [c] N 10.6 (11.1). [d] N 9.4 (9.9). [e] N 10.1 (10.6); S 3.8 (3.6). [f] N 9.5 (9.6); S 3.6 (3.7). [g] N 9.0 (9.1). [h] Satisfactory microanalysis not obtained due to decomposition over 24 h. For FAB mass spectrum see Experimental Section.

Table 2. Hydrogen-1, Carbon-13, and Boron-11 NMR Data[a]



compd	$^1H/\delta^b$	$^{13}C/\delta^c$	$^{11}B/\delta^d$
4a	2.20 (s, 1 H, cage CH), 2.37 (s, 3 H, Me-4), 3.03 (s, 1 H, cage CH), 6.32, 6.36, 6.47 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.25, 7.34 ((AB)$_2$, 4 H, C$_6$H$_4$, J(AB) = 8), 7.29−8.00 (d × 6, 6 H, H^{3,5})	303.2 (*C*C$_6$H$_4$Me-4), 223.5 (MoCO × 2), 197.8, 197.2 (RuCO), 153.6−137.1 (C^{3,5} (pz), C$_6$H$_4$), 129.8 (C$_6$H$_4$), 107.7, 107.0, 106.8 (C^4 (pz)), 57.7, 47.2 (cage CH), 21.4 (Me-4)	3.8 (1 B), −3.4 (2 B), −4.4 (1 B), −6.6 (1 B), −8.1 (2 B), −16.8 (1 B), −18.3 (1 B), −19.5 (1 B)
4b	2.26 (s, 1 H, cage CH), 2.37 (s, 3 H, Me-4), 3.08 (s, 1 H, cage CH), 6.34, 6.41, 6.53 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.26 ((AB)$_2$, 4 H, C$_6$H$_4$, J(AB) = 8), 7.44−8.01 (d × 5, 6 H, H^{3,5})	287.4 (*C*C$_6$H$_4$Me-4)), 220.0, 218.8 (WCO), 197.6, 196.8 (RuCO), 155.4−136.9 (C^{3,5} (pz), C$_6$H$_4$), 129.7 (C$_6$H$_4$), 108.2, 107.7, 107.5 (C^4 (pz)), 58.2, 48.4 (cage CH), 21.4 (Me-4)	3.7 (1 B), −3.4 (2 B), −4.4 (1 B), −6.8 (1 B), −8.0 (2 B), −16.7 (1 B), −18.2 (1 B), −19.7 (1 B)
6a[e]	2.15 (s, 1 H, cage CH), 2.51 (s, 3 H, Me-4), 2.81 (s, 1 H, cage CH), 6.29, 6.34, 6.39 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.28−7.90 (m, 10 H, C$_6$H$_4$, H^{3,5})	270.0 (S*C*C$_6$H$_4$Me-4), 225.6, 225.2 (MoCO), 196.0, 195.7 (RuCO), 145.6−137.2 (C^{3,5} (pz), C$_6$H$_4$), 133.3, 130.1 (C$_6$H$_4$), 107.4, 107.2, 107.1 (C^4 (pz)), 49.1, 47.1 (cage CH), 22.2 (Me-4)	2.5 (1 B), −3.6 (1 B), −7.7 (3 B), −8.6 (2 B), −18.5 (1 B), −21.0 (2 B)
6b[e]	2.19 (s, 1 H, cage CH), 2.48 (s, 3 H, Me-4), 2.75 (s, 1 H, cage CH), 6.35, 6.40, 6.41 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.37−8.04 (m, 10 H, C$_6$H$_4$, H^{3,5})	252.1 (S*C*C$_6$H$_4$Me-4), 222.2, 221.1 (WCO), 196.0 (RuCO × 2), 146.3−137.0 (C^{3,5} (pz), C$_6$H$_4$), 132.7, 130.6 (C$_6$H$_4$), 107.9, 107.5, 107.4 (C^4 (pz)), 49.1, 46.7 (cage CH), 21.9 (Me-4)	2.1 (1 B), −3.5 (1 B), −7.7 (3 B), −8.9 (2 B), −18.5 (1 B), −20.9 (2 B)
6c[f]	2.21 (s, 1 H, cage CH), 2.51 (s, 3 H, Me-4), 2.68 (s, 1 H, cage CH), 6.32, 6.34, 6.41 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.41−7.93 (m, 10 H, C$_6$H$_4$, H^{3,5})	278.4 (Se*C*C$_6$H$_4$Me-4), 223.4 (MoCO × 2), 196.7, 196.6 (RuCO), 145.4−137.2 (C^{3,5} (pz), C$_6$H$_4$), 134.6, 130.4 (C$_6$H$_4$), 107.3, 107.1, 107.0 (C^4 (pz)), 47.2, 46.2 (cage CH), 21.4 (Me-4)	2.3 (1 B), −3.6 (1 B), −7.4 (3 B), −9.2 (2 B), −19.1 (1 B), −20.9 (2 B)
6d[f]	2.24 (s, 1 H, cage CH), 2.48 (s, 3 H, Me-4), 2.65 (s, 1 H, cage CH), 6.38, 6.40, 6.43 (*at* × 3, 3 H, H^4, J(HH) = 2, 2, 2), 7.45−8.06 (m, 10 H, C$_6$H$_4$, H^{3,5})	261.2 (Se*C*C$_6$H$_4$Me-4), 220.3, 219.3 (WCO), 197.1, 197.0 (RuCO), 146.5−137.3 (C^{3,5} (pz), C$_6$H$_4$), 134.1, 130.7 (C$_6$H$_4$), 108.2, 107.9, 107.8 (C^4 (pz)), 47.9, 46.0 (cage CH), 21.9 (Me-4)	1.9 (1 B), −3.6 (1 B), −7.5 (2 B), −8.1 (1 B), −9.4 (2 B), −19.0 (1 B), −20.9 (2 B)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in Hz, measurements in CD_2Cl_2, and at room temperature unless otherwise stated. [b] Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. −1 to 3.0. Signals for protons of the pyrazolyl ring appear as apparent triplets (*at*) due to overlap of peaks in doublets of doublets. [c] Hydrogen-1 decoupled; chemical shifts are quoted as positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $BF_3 \cdot Et_2O$ (external). [e] ^1H and $^{13}C\{^1H\}$ spectra recorded at −20 °C. [f] ^1H and $^{13}C\{^1H\}$ spectra recorded at 0 °C.

(δ 293.1)[2d] and [W(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (δ 284.8),[2a] the alkylidyne metal compounds from which complexes **4** are derived. A similar effect is seen when comparing the $^{13}C\{^1H\}$ NMR spectrum of **2b** (μ-C, δ 301.9)[1] with that of its precursor [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] (C≡W, δ 300.6).[6] These data are indicative of asymmetric bridging of the metal−metal bonds by the tolylmethylidyne ligands in the compounds **2** and **4**.[7] When alkylidyne groups bridge heteronuclear metal−metal bonds in a relatively symmetrical manner the chemical shifts for the μ-*C*C$_6$H$_4$Me-4 nuclei in the $^{13}C\{^1H\}$ NMR spectra are appreciably more deshielded, appearing in the range δ ca. 330−400.[7a,b]

While the bimetal compounds **4** are readily cleaved by oxygenated donor solvents, some dissociation is apparent even in CD_2Cl_2. Thus both the ^1H and $^{13}C\{^1H\}$ NMR spectra included peaks (ca. 2−5%) attributable to free [M(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}]. In further contrast with the complexes **2**, which readily form isomeric molecules **3**, prolonged thermolysis of toluene solutions of **4** did not result in the formation of new species in spectroscopically detectable amounts. These observations prompted single-crystal X-ray diffraction studies on **2b** and **4b** to determine if the variance in properties was attributable to any difference in their molecular structures.

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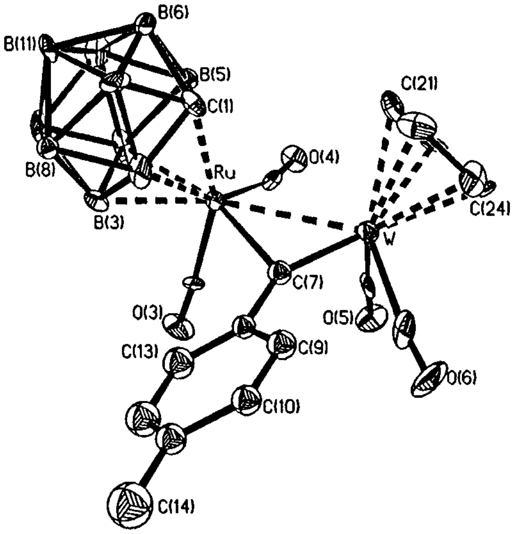

Figure 1. Molecular structure of [WRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)(η^5-C$_5$H$_5$)] (**2b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

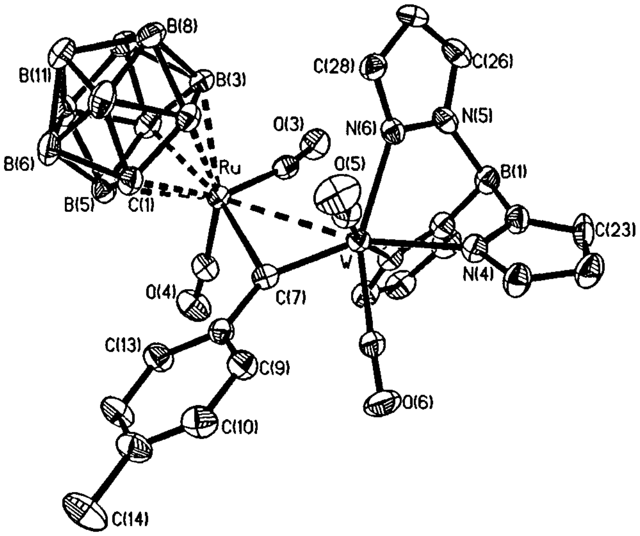

Figure 2. Molecular structure of [WRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**4b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

An X-ray diffraction study had not been carried out on **2b** at the time of its characterization.[1] Since it readily isomerizes to **3b**, data collection was made at 173 K. Unfortunately crystal quality was poor and some reflections, especially high-angle data, were weak, precluding a full analysis (see Experimental Section). Only the gross geometric parameters around the metal core are discussed below, and these data must be interpreted with caution. The crystal structure analysis revealed two molecules in the asymmetric unit, but the parameters for both are very similar, so those for only one of the molecules is mentioned.

Molecules **2b** and **4b** are shown in Figures 1 and 2. Bond lengths and angles from the X-ray diffraction study of **4b** are listed in Table 3; those for **2b** are included in the Supporting Information. The two structures are closely related, with the η^5-C$_5$H$_5$ group in **2b** replaced by the κ^3-HB(pz)$_3$ ligand in **4b**. As anticipated, in both **2b** and **4b** a Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$) moiety is joined to a W(CO)$_2$L (L = η^5-C$_5$H$_5$ or κ^3-HB(pz)$_3$) unit by the alkylidyne−carbon atom C(7) of the μ-CC$_6$H$_4$Me-4 group. In the two complexes the Ru−C(7) (2.19(2) Å (**2b**), 2.213(5) Å (**4b**)) and W−C(7) bond lengths (1.92(2) Å (**2b**), 1.921(5) Å (**4b**)) are very similar. So also are the separations between the two metal atoms (W−Ru 2.949(2) Å (**2b**), 3.0472(6) Å (**4b**)). It would appear that the metal−metal bonds in complexes **2b** and **4b** are weak since the metal−metal distances exceed the sum (2.70 Å) of the covalent radii for W and Ru. Nevertheless, it cannot be convincingly argued that there is no direct interaction between the metal atoms. Thus the X-ray diffraction study for molecule **3a**[1] also revealed a long metal−metal distance (2.976(1) Å), yet some Mo−Ru bonding is reasonable for this species since its presence allows both metal atoms formally to acquire closed valence shell configurations in accord with the diamagnetism.

It is interesting to compare the structures of **2b** and **4b** with those of the two previously characterized tungsten−ruthenium complexes [WRu(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)(η^5-C$_5$H$_5$)] (**5a**) and [N(PPh$_3$)$_2$][WRu(μ-CC$_6$H$_4$Me-4)(CO)$_3$(μ-σ,η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$)(η^5-C$_5$H$_5$)] (**5b**).[8] These species, like **2b** and **4b**, have asymmetrically bridging μ-CC$_6$H$_4$Me-4 groups; however, their W−Ru connectivities (2.803(2) Å **5a**, 2.748(1) Å **5b**) are shorter and thus unambiguously imply direct metal−metal bonding. The W−C(7) bond lengths in **2b** (1.92(2) Å) and **4b** (1.921(5) Å) are similar to the corresponding distances in **5a** (1.890(6) Å) and **5b** (1.941(5) Å). These separations are intermediate between those reported for the C═W distance in the complex [W(═CPh$_2$)(CO)$_5$] (2.14(2) Å)[9] and the C≡W distances in free [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] (1.82(2) Å)[6] or [W(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-B(pz)$_4$}] (1.821(7) Å).[2a]

Despite some similarities between the structures of the four bimetal compounds, there are significant differences. Thus the W−C(7)−C(8) angles in **2b** (147(2)°) and **4b** (144.3(4)°) are appreciably smaller than the corresponding angles in **5a** (152.6(5)°) and **5b** (149.3(4)°). Moreover, the W−C(7)−Ru angles in **2b** (91.4(9)°) and **4b** (94.7(2)°) are larger than the corresponding angles in **5a** and the anion of **5b**, which are the same at 85.6(2)°.[8] These variations in the structural parameters are likely due to the Ru atoms in **2b** and **4b** being ligated by the *nido*-C$_2$B$_9$ cage system, whereas in **5a** and **5b** it is the tungsten atoms that carry the carborane cages. Hence differences in bonding within the W(μ-CC$_6$H$_4$Me-4)Ru ring systems are probable as discussed further below.

Relevant to consideration of the bonding in the W(μ-CC$_6$H$_4$Me-4)Ru ring systems of the complexes under discussion are studies reported[10] on compounds containing [M(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] groups coordinated

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[8] Green, M.; Howard, J. A. K.; Jelfs, A. N. de M.; Johnson, O.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 73.

[9] Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

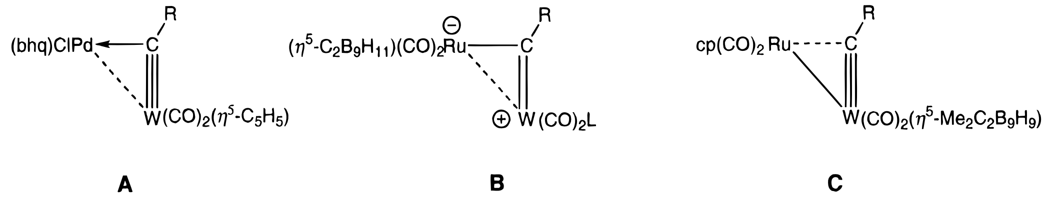
[10] Engel, P. F.; Pfeffer, M.; Dedieu, A. *Organometallics* **1995**, *14*, 3423.

Table 3. Selected Internuclear Distances (Å) and Angles (deg) for $[WRu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4\{\eta^5\text{-}7,8\text{-}C_2B_9H_{11}\}\{\kappa^3\text{-}HB(pz)_3\}]\cdot CH_2Cl_2$ (4b), with ESDs in Parentheses

Ru−C(4)	1.872(6)	Ru−C(3)	1.890(6)	Ru−C(7)	2.213(5)	Ru−B(4)	2.296(6)
Ru−C(2)	2.273(5)	Ru−C(1)	2.276(5)	Ru−B(5)	2.283(6)	Ru−B(3)	2.281(6)
Ru−W	3.0472(6)	C(3)−O(3)	1.131(6)	C(4)−O(4)	1.139(6)	C(7)−W	1.921(5)
W−C(5)	1.976(6)	W−C(6)	1.995(6)	W−N(2)	2.213(4)	W−N(4)	2.212(4)
W−N(6)	2.220(4)	C(6)−O(6)	1.131(6)	C(5)−O(5)	1.149(6)		

C(4)−Ru−C(3)	88.4(2)	C(4)−Ru−C(7)	86.4(2)	C(4)−Ru−B(3)	140.2(2)
C(3)−Ru−C(7)	107.6(2)	C(4)−Ru−C(2)	155.4(2)	C(7)−Ru−B(3)	133.3(2)
C(3)−Ru−C(2)	114.1(2)	C(7)-Ru-C(2)	95.5(2)	C(1)−Ru−B(3)	73.9(2)
C(4)−Ru−C(1)	114.3(2)	C(3)−Ru−C(1)	153.3(2)	C(3)−Ru−B(5)	133.1(2)
C(7)−Ru−C(1)	88.5(2)	C(2)−Ru−C(1)	41.5(2)	C(2)−Ru−B(5)	73.9(2)
C(4)−Ru−B(4)	95.8(2)	B(3)−Ru−B(5)	77.8(2)	C(3)−Ru−B(3)	79.7(2)
C(7)−Ru−B(4)	163.5(2)	C(3)−Ru−B(4)	88.9(2)	C(2)−Ru−B(3)	43.9(2)
C(1)−Ru−B(4)	75.6(2)	C(2)−Ru−B(4)	75.8(2)	C(4)−Ru−B(5)	83.5(2)
B(5)−Ru−B(4)	46.6(2)	B(3)−Bu−B(4)	46.7(2)	C(7)−Ru−B(5)	117.8(2)
C(1)−Ru−B(5)	43.7(2)	O(3)−C(3)−Ru	168.2(5)	O(4)−C(4)−Ru	175.3(5)
C(8)−C(7)−Ru	120.8(4)	W−C(7)−Ru	94.7(2)	C(8)−C(7)−W	144.3(4)
O(6)−C(6)−W	177.5(5)	O(5)−C(5)−W	178.4(5)	C(7)−W−C(5)	80.6(2)
C(7)−W−C(6)	75.1(2)	C(5)−W−N(2)	168.6(2)	C(5)−W−C(6)	95.2(2)
C(7)−W−N(4)	148.8(2)	C(7)−W−N(2)	110.8(2)	C(5)−W−N(4)	87.7(2)
C(6)−W−N(4)	77.4(2)	C(6)−W−N(2)	88.1(2)	C(7)−W−N(6)	129.2(2)
N(4)−W−N(2)	82.4(2)	N(2)−W−N(6)	85.4(2)	C(6)−W−N(6)	155.5(2)
C(5)−W−N(6)	87.1(2)	N(4)−W−N(6)	78.3(2)		

Chart 2. $R = C_6H_4Me\text{-}4$, bhq = Benzo(*h*)quinoline, $L = \eta^5\text{-}C_5H_5$ or $\kappa^3\text{-}HB(pz)_3$



in an η^1 manner to Pd(II). In the molecule $[WPdCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bhq)(\eta^5\text{-}C_5H_5)]$ (bhq = benzo(*h*)quinoline) the W−Pd distance is long (2.8001(6) Å), suggesting a weak bonding interaction, and the W−μ-C−Pd angle is 89.27(2)°. These structural features are similar to those for **2b** and **4b**. The $\overline{W(\mu\text{-}CC_6H_4Me\text{-}4)Pd}$ ring bonding in the palladium−tungtsen complex was interpreted in terms of the tungstacarbyne molecule being bound to the palladium essentially through the alkylidyne−carbon atom (Chart 2, **A**).[10] This maximizes the strong Lewis acid character of the Pd(II) center, while weak donation from the Pd d_{z^2} orbital into the π^* orbital of the tungstacarbyne is possible. There is little pertubation of the W≡C bond reflected in a bond distance of 1.897(7) Å and the resonance in the $^{13}C\{^1H\}$ NMR spectrum for the alkylidyne−carbon being seen at δ 303.3, parameters little different from those for $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ (1.82(2) Å and δ 300.6).[6] Interestingly in $[WPdCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bhq)(\eta^5\text{-}C_5H_5)]$ the tungstacarbyne moiety is weakly coordinated, readily exchanging with other donor ligands in solution, as occurs with **4b**.

While it is possible to interpret the bonding in molecules **2b** or **4b** in a fashion similar to that for $[WPdCl(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bhq)(\eta^5\text{-}C_5H_5)]$, we propose that the ylid formulation **B** might accord better with the properties of these tungsten−ruthenium species. The $Ru(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$ fragment present in the molecules **2** and **4** is electronically unsaturated by virtue of the 3,1,2-RuC_2B_9 cage. The latter readily accepts negative charge as in the anionic complexes $[RuX(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ (X = H, Cl, or I).[4a] More relevant to the present discussion is the existence of very stable zwitterionic complexes such as $[Ru\{C(Me){=}C(Ph)PEt_3\}(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$.[4b,11] With their $[\eta^5\text{-}C_2B_9H_{11}]^{2-}$ ligands the ruthenium atoms in the complexes **2** and **4** are formally Ru(II), and this would favor charge transfer from the tungsten or molybdenum centers to the *closo*-3,1,2-RuC_2B_9 cage. In the complexes **4** this transfer of electron density to the cage system would be enhanced by the strong donor properties of the κ^3-HB(pz)$_3$ groups.

In contrast with the complexes **2** and **4**, the bonding in the $\overline{W(\mu\text{-}CC_6H_4Me\text{-}4)Ru}$ rings in the compounds **5** is best interpreted by **C** in Chart 2. It was mentioned earlier that the W−Ru bond distances in **2b** (2.949(2) Å) or **4b** (3.047(2) Å) are appreciably longer than those in complexes **5a** (2.803(2) Å) and **5b** (2.748(1) Å), implying stronger metal−metal bonding in the species **5**. Especially significant are the differences in the angles at the bridging carbon atom. For **5a** and **5b** the W−C−$C^1(C_6H_4Me\text{-}4)$ angles have widened to 152.6(5)° and 149.3(4)°, respectively, from 147(2)° in **2b** and 144.3(4)° in **4b**. An extreme form of asymmetric bridge bonding of type **C** would result in the W−μ-C−C^1(aryl) angle being close to 180°, accompanied by a μ-C−W distance very similar to that for a C≡W bond. These features are found in the molecule $[WPt(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}\sigma,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_2(PEt_3)]$,[7c] where the W−C−$C^1(C_6H_3Me_2\text{-}2,6)$ angle is 175(1)° and the tungsten−alkylidyne carbon separation (1.88(2) Å) is essentially the same as that (1.82(2) Å) in $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$.[6] A less extreme example of asymmetric bonding of the alkylidyne group, similar to that of the species **5**, is shown by the complex $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_2(PMe_2Ph)_2]$,[7e] which

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(11) Jeffery, J. C.; Jelliss, P. A.; Psillakis, E.; Rudd, G. E. A.; Stone, F. G. A. *J. Organomet. Chem.* **1998**, *562*, 17.

Table 4. Selected Internuclear Distances (Å) and Angles (deg) for [WRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}${κ^3-HB(pz)$_3$}] (6b), with ESDs in Parentheses

Ru−C(3)	1.869(4)	Ru−C(4)	1.885(4)	Ru−C(2)	2.209(4)	Ru−C(1)	2.238(4)
Ru−B(3)	2.260(5)	Ru−B(5)	2.295(4)	Ru−B(4)	2.302(5)	Ru−S(1)	2.4238(13)
C(3)−O(3)	1.131(5)	C(4)−O(4)	1.130(5)	S(1)−C(7)	1.753(4)	S(1)−W	2.5002(10)
C(7)−W	1.970(4)	W−C(6)	2.001(4)	W−C(5)	2.002(4)	W−N(4)	2.193(3)
W−N(6)	2.201(3)	W−N(2)	2.207(3)	C(5)−O(5)	1.139(5)	C(6)−O(6)	1.135(5)

C(3)−Ru−C(4)	90.4(2)	C(3)−Ru−S(1)	92.74(13)	C(4)−Ru−B(3)	135.0(2)
C(3)−Ru−C(2)	110.2(2)	C(4)−Ru−S(1)	90.24(13)	C(2)−Ru−B(3)	45.4(2)
C(4)−Ru−C(2)	158.6(2)	C(2)−Ru−S(1)	94.61(11)	C(1)−Ru−B(3)	75.8(2)
C(3)−Ru−C(1)	152.6(2)	C(1)−Ru−S(1)	86.93(10)	C(3)−Ru−B(5)	150.7(2)
C(4)−Ru−C(1)	117.0(2)	B(3)−Ru−S(1)	134.66(12)	C(4)−Ru−B(5)	83.8(2)
C(2)−Ru−C(1)	42.76(14)	B(5)−Ru−S(1)	115.93(13)	C(2)−Ru−B(5)	75.3(2)
C(3)−Ru−B(3)	85.3(2)	B(4)−Ru−S(1)	161.92(13	C(1)−Ru−B(5)	43.7(2)
C(1)−Ru−B(4)	76.0(2)	C(4)−Ru−B(4)	92.2(2)	B(3)−Ru−B(5)	78.9(2)
B(3)−Ru−B(4)	46.7(2)	C(2)−Ru−B(4)	77.0(2)	C(3)−Ru−B(4)	105.1(2)
B(5)−Ru−B(4)	46.7(2)	Ru−S(1)−W	122.80(4)	C(7)−S(1)−Ru	122.40(13)
O(3)−C(3)−Ru	178.0(4)	O(4)−C(4)−Ru	175.1(4)	C(7)−S(1)−W	51.62(13)
S(1)−C(7)−W	84.1(2)	C(8)−C(7)−S(1)	126.0(3)	C(8)−C(7)−W	149.1(3)
C(7)−W−C(6)	76.2(2)	C(7)−W−S(1	44.24(11)	N(4)−W−N(2)	81.26(11)
C(7)−W−C(5)	79.5(2)	C(6)−W−S(1)	116.48(12)	N(6)−W−N(2)	83.82(11)
C(6)−W−C(5)	96.4(2)	C(5)−W−S(1)	92.78(12)	N(6)−W−S(1)	81.81(8)
C(7)−W−N(4)	150.87(14)	N(4)−W−S(1)	163.55(8)	N(2)−W−S(1)	97.10(8)
C(6)−W−N(4)	79.85(14)	C(7)−W−N(6)	123.48(13)	O(5)−C(5)−W	178.4(4)
C(5)−W−N(4)	87.02(14)	C(6)−W−N(6)	160.20(14)	O(6)−C(6)−W	175.6(4)
C(7)−W−N(2)	113.18(13)	C(5)−W−N(6)	89.79(14)	C(5)−W−N(2)	167.34(14)
C(6)−W−N(2)	86.3(2)	N(4)−W−N(6)	81.74(11)		

has a W−μ-C−C^1(C$_6$H$_4$Me-4) angle of 151(1)° and a μ-C−W bond length of 1.89(1) Å. It is evident that changes in the μ-C−W bond distances are less sensitive than those for the W−μ-C−C^1(aryl) angles. In [WPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_2$(η^5-C$_5$H$_5$)], where the alkylidyne ligand bridges the W−Pt bond symmetrically (μ-C−Pt 1.997(9), μ-C−W 1.967(6) Å), the W−μ-C−C^1(C$_6$H$_4$Me-4) angle is 137.9(7)°.[12] Moreover, in the ^{13}C{^{1}H} NMR spectrum of this platinum−tungsten complex the resonance for the *C*C$_6$H$_4$Me-4 nucleus occurs at δ 336.

Reactions between the complexes **4** and elemental sulfur and selenium were next investigated to determine if new species would result from a coupling of alkylidyne groups with the chalcogens. It had been previously established that iron−tungsten and −molybdenum compounds in which the metal−metal bonds are bridged by tolylmethylidyne groups react with sulfur to afford bimetal complexes with μ-SCC$_6$H$_4$Me-4 ligands.[13]

The compounds **4a** and **4b** reacted readily with stoichiometric amounts of sulfur in CH$_2$Cl$_2$ at room temperature to give the complexes **6a** and **6b**, respectively. These syntheses were accompanied by formation of appreciable amounts of the compounds [M(κ^2-S$_2$-CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}], previously obtained from the reaction between sulfur and the alkylidyne complexes [M(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}].[14] Since the nature of the products **6a** and **6b** could not be established solely from their microanalytical and spectroscopic data (Tables 1 and 2), an X-ray diffraction study was carried out on **6b**, suitable crystals of which could be obtained. The important structural information is given in Table 4, and the molecule is shown in Figure 3.

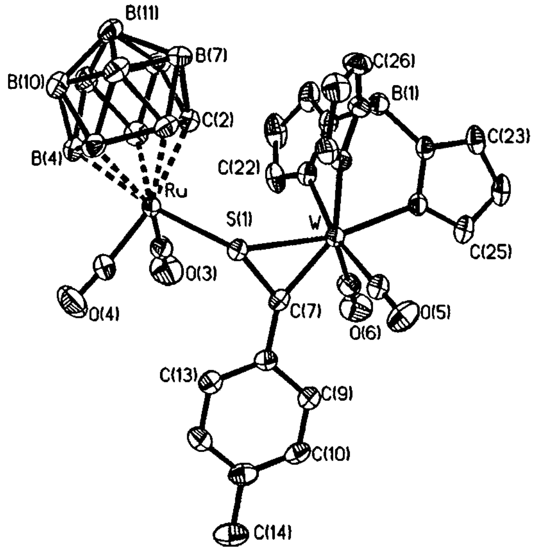

Figure 3. Molecular structure of [WRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

It will be seen that **6b** has the formulation [WRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB-(pz)$_3$}] and possesses an unusual structure in which Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$) and W(CO)$_2${κ^3-HB(pz)$_3$} units are bridged by a thioacyl group, but there is no metal−metal bond. The thioacyl group is η^2-coordinated to the tungsten and bound to the ruthenium only through the sulfur atom. Few structure determinations have been made on ruthenium(II) complexes with sulfur as an electron pair donor, but it appears that the Ru−S bond in **6b** (2.4238(13) Å) is somewhat long compared with that in thioether ruthenium complexes (2.262−2.333 Å).[15] However, in the η^2-silathioacyl complex [RuCl(CO)-

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[15] Lai, T.-F.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1982**, 1465.

(PPh$_3$)$_2$(η^2-C(S)SiMe$_2$OEt)] the Ru−S bond (2.545(2) Å) is longer than in **6b**.[16]

The dimensions of the W−C(7)−S three-membered ring in **6b** are of interest. Since the covalent radii of W and Os are the same, useful comparisons can be made with the crystallographic data for the molecule [Os(O$_2$CCF$_3$)(CO)$_2$(PPh$_3$)$_2$(η^2-SCC$_6$H$_4$Me-4)].[17] In the latter the bond lengths in the OsCS ring are Os−S 2.513(6), Os−C (thioacyl) 1.91(2), and C−S 1.72(2) Å. These parameters correspond very closely to those for **6b** (W−S 2.5002(10), W−C(7) 1.970(4), and S−C(7) 1.753(4) Å). The data for [Os(O$_2$CCF$_3$)(CO)$_2$(PPh$_3$)$_2$(η^2-SCC$_6$H$_4$Me-4)] were interpreted as implying pronounced multiple bond character for the Os−C connectivity and intermediacy between a C−S and C=S bond for the sulfur−carbon linkage.[17] The C(7)−W−S angle in **6b** is 44.24(11)° and may be compared with the C−Os−S "bite" angle of 43.0(5)° in the osmium compound.

Finally it is interesting to relate the structure of molecule **6b** to the cation in the salt [W(CO)$_2${η^2-S(Me)C(SMe)}{κ^3-HB(pz)$_3$}][SO$_3$CF$_3$].[18] If the Me$^+$ group of the η^2-S(*Me*)C(SMe) ligand in the cation is formally replaced by a Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$) moiety and the SMe group is substituted by C$_6$H$_4$Me-4, the molecule **6b** is derived. This results from the isolobal relationship between Me$^+$ and Ru(CO)$_2$(η^5-7,8-C$_2$B$_9$H$_{11}$).[19]

Data for complex **6a** (Tables 1 and 2) establish that it is the molybdenum analogue of **6b**. The spectroscopic data for both complexes are in full agreement with the X-ray diffraction results for **6b**. Four CO stretching bands are observed in their IR spectra (Table 1). However, these bands are considerably broader than those in the precursors **4**, a feature consistent with the occurrence of a dynamic process taking place in solution. Indeed when measured at ca. 30 °C, both the ^{1}H and ^{13}C NMR spectra were characteristic of a fluxional process under way near its coalesence temperature with broad unresolved peaks being observed. However, at −20 °C the resonances (Table 2) became sharp. The source of the dynamic behavior is likely to be pyramidal inversion at the sulfur atom due to its free lone pair, a process having ample precedent.[20] The ^{1}H NMR spectrum of **6b** displayed singlets at δ 2.19 and 2.75, each corresponding in relative intensity to one proton, and these are diagnostic for the nonequivalent cage CH groups.[5] Correspondingly in the ^{13}C{^{1}H} NMR spectrum resonances for the cage CH groups are seen at δ 46.7 and 49.1. The asymmetry in the molecule is further indicated by the observation of two signals for the CO ligands on W (δ 222.1, 222.2). Although only one resonance at δ 196.0 was attributable to RuCO, it was twice the intensity of those for WCO. Moreover, in the ^{13}C{^{1}H} NMR spectrum of **6a** four CO resonances are observed (Table 2). Resonances in the spectra of **6a** and **6b** at δ 270.0 and 252.1, respectively, may be ascribed to the S*C*C$_6$H$_4$Me-4 nuclei, shifts comparable with those for these nuclei in the complexes [M(CO)$_2$(η^2-SCR){κ^3-HB(pz)$_3$}] (R = aryl).[14]

The presence of the SC(C$_6$H$_4$Me-4) group ligating the molybdenum and tungsten atoms in the η^2 manner in **6a** and **6b** is of interest. Chalcogens generally add twice to the M≡C bonds of alkylidyne complexes of group 6 metals, yielding dichalcocarboxylate complexes, e.g., [Mo(κ^2-S$_2$CCH$_2$Bu^t)(CO)$_2$(η^5-C$_5$H$_5$)], [W(κ^2-S$_2$CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)],[21a] and [W(κ^2-S$_2$CMe)(CO)$_3${κ^2-H$_2$B(pz)$_2$}].[21b,c,22] Only by using 2-methylthiirane as the source of sulfur in reactions with the alkylidyne−molybdenum and −tungsten complexes have species such as [M(CO)$_2$(η^2-SCC$_6$H$_4$Me-4){κ^3-HB(pz)$_3$}] been obtained.[14]

Selenium reacts with the complexes **4** in a manner similar to sulfur, affording the compounds [MRu(μ-1κC^α,1:2κSe-SeCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo (**6c**), M = W (**6d**)) in high yield. Data characterizing **6c** and **6d** are given in Tables 1 and 2, and it is evident from their properties that they are similar in nature to **6a** and **6b**. Interestingly **6c** and **6d** showed less tendency to undergo dynamic behavior than their sulfur analogues. Thus the NMR spectra of **6d** were fully resolved at ca. 0 °C without recourse to cooling to −20 °C. At the former temperature the ^{13}C{^{1}H} NMR spectrum displayed four resonances for the inequivalent CO ligands in the Ru(CO)$_2$ and W(CO)$_2$ groups (Table 2), whereas at room temperature only two signals were seen. The ^{13}C{^{1}H} NMR spectrum for **6c** at 0 °C had probably not reached a low-temperature limit since only one peak was observed for the Mo(CO)$_2$ group and two signals for the Ru(CO)$_2$ group were barely separable. Nevertheless at 0 °C all the other peaks were sharp, in contrast with the broad peaks found in the NMR spectra of **6a** at this temperature. Higher barriers to inversion at the chalcogen atom for the selenium compounds compared with the sulfur complexes are to be anticipated.[20] In the ^{13}C{^{1}H} NMR spectra of **6c** and **6d** resonances for the Se*C*C$_6$H$_4$Me-4 nuclei occur at δ 278.4 and 261.2, respectively. Other peaks in the spectra are as expected (Table 2). A FAB mass spectrum of **6d** revealed the molecular ion at *m*/*z* 924.3 (calc 924.5, 7.9%). Most importantly the major observable species in the spectrum had a molecular envelope consistent with it being free W(η^2-SeCC$_6$H$_4$-Me-4)(CO)$_2${κ^3-HB(pz)$_3$} (*m*/*z* 636.1, calc 635.0, 100%). This peak was followed by sequential loss of both CO ligands.

Although the compounds **4** react readily with sulfur or selenium, surprisingly the complexes **2** do not. A possible explanation for this may lie in steric constraints and in the different behavior of the two classes of complex in solutions. For both classes of complex the potentially reactive C=M bonds are highly screened from attacking substrates by the ligands, and this is especially true for the molecules **4** with their HB(pz)$_3$ groups. This crowding is clearly revealed by space-filling models. However, as mentioned earlier, the molecules **4** completely dissociate in thf, and even in CH$_2$Cl$_2$ some partial dissociation is observed during NMR measure-

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Table 5. Data for X-ray Crystal Structure Analyses

	4b.CH_2Cl_2	**6b**
cryst dimens (mm)	0.20 × 0.20 × 0.05	0.31 × 0.20 × 0.08
formula	$C_{24}H_{30}B_{10}Cl_2N_6O_4RuW$	$C_{23}H_{28}B_{10}N_6O_4RuSW$
M_r	930.48	877.59
cryst color, shape	red-orange blocks	black needles
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.7703(17)	12.4593(59)
b (Å)	11.5609(16)	15.2357(20)
c (Å)	15.1758(31)	17.4836(23)
α (deg)	99.527(14)	
β (deg)	105.070(14)	99.820(20)
γ (deg)	102.996(12)	
V (Å$^{3)}$	1726.78(54)	3270.25(1.68)
Z	2	4
d_{calcd} (g cm^{-3})	1.790	1.782
μ(Mo Kα) (cm^{-1})	39.62	40.81
F(000) (e)	900	1696
T (K)	293	293
2θ range (deg)	3.7−48.0	3.3−50.0
no. of rflns coll (excld stds)	5721	5951
no. of unique rflns	5395	5744
no. of obsvd rflns	4689	4770
reflection limits: h, k, l	0 to 12; −13 to 12; −17 to 16	−14 to 14; 0 to 18; 0 to 20
no. of params refined	433	415
final residuals wR_2 (R_1) all data	0.0651 (0.0397)[a]	0.0540 (0.0348)[a]
weighting factors[a]	$a = 0.0285$, $b = 2.2709$	$a = 0.0282$, $b = 0.1628$
goodness of fit on F^2	1.046	1.034
final electron density diff features (max/min) (e Å$^{-3)}$	0.956, −0.938	0.703, −0.712

[a] Refinement was block full-matrix least-squares on all F^2 data: $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, where $w^1 = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. The value in parentheses is given for comparison with refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$ and $R_1 = \Sigma||F_o^2| - |F_c||/\Sigma|F_o|$ and $w^{-1} = [\sigma^2(F_o) + g(F_o^2)]$.

ments. In contrast there was no evidence of dissociation of the reagents **2** in these solvents. It may thus be that reactions between the chalcogens and the compounds **4** depend on their partial dissociation in CH_2Cl_2, affording [Ru(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$)]^{4a} and [M(≡CC_6H_4Me-4)(CO)$_2$-{κ^3-HB(pz)$_3$}]. The latter might then with the chalcogens give [M(CO)$_2$(η^2-ECC$_6H_4$Me-4){κ^3-HB(pz)$_3$}]. These intermediates could then react in one of two ways: (i) combination via their donor chalcogen atoms with free Ru(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$) would afford the products **6**, while further reaction with sulfur or selenium would yield dichalcocarboxylate complexes. As mentioned earlier, the compounds [M(κ^2-$S_2CC_6H_4$Me-4)(CO)$_2${κ^3-HB-(pz)$_3$}] are formed as byproducts in the syntheses of the species **6**; (ii) alternatively it is possible that the [Ru-(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$)] molecules produced by dissociation of **4** play a key role as carriers of the chalcogen atoms, forming intermediates [Ru(=E)(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$)], which subsequently react with the [M-(≡CC_6H_4Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] molecules in solution to give the products **6**. In this scenario the Ru(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$) fragments would have a role not unlike 2-methylthiirane in the synthesis of [W(CO)$_2$(η^2-SCC$_6H_4$-Me-4){κ^3-HB(pz)$_3$}].[14] Indeed when the Ru(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$) moiety is generated by addition of $AgBF_4$ to [NEt$_4$][RuI(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$)] in CH_2Cl_2^{4a} and subsequently treated with sulfur, a rapid reaction ensues, the nature of which is under investigation.

Conclusions

The compounds **4** are the first molecules to be reported in which tolylmethylidyne groups bridge Ru-(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$) and M(CO)$_2${κ^3-HB(pz)$_3$} fragments, the nature of the bridging alkylidyne system being of interest in the context of earlier studies.[7,10] The complexes [MRu(μ-1κC^{α},1:2κE-ECC$_6H_4$Me-4)(CO)$_4$(η^5-7,8-$C_2B_9H_{11}$){κ^3-HB(pz)$_3$}] (**6,** E = S or Se) have unique structures in which M(CO)$_2$(η^2-ECC$_6H_4$Me-4){κ^3-HB-(pz)$_3$} fragments are stabilized by attachment of Ru-(CO)$_2$(η^5-7,8-$C_2B_9H_{11}$) units to the sulfur and selenium atoms.

Experimental Section

General Considerations. Solvents were distilled from the appropriate drying agents under an inert gas (nitrogen or argon) and thoroughly purged with nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40−60 °C. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Preparative thin-layer chromatography plates were used as obtained from commercial sources (Analtech). The reagents [Ru(CO)$_2$(thf)-(η^5-7,8-$C_2B_9H_{11}$)]^{4a} and [M(≡C_6H_4Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (M = Mo, W)^{2a,d} were prepared according to previously described methods. The NMR measurements were recorded at the following frequencies: ^{1}H at 360.13 MHz, ^{13}C at 90.56 MHz, and ^{11}B at 115.55 MHz.

Synthesis of [MRu(μ-CC$_6H_4$Me-4)(CO)$_4$(η^5-7,8-$C_2B_9H_{11}$)-{κ^3-HB(pz)$_3$}] (M = Mo, W). (i) In a representative experiment, a CH_2Cl_2 (20 mL) solution of [Mo(≡CC_6H_4Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (70 mg, 0.15 mmol) was added to freshly prepared *solid* **1** (50 mg, 0.14 mmol), and the mixture was stirred for 30 s. Petroleum ether (30 mL) was added and the volume slowly reduced in vacuo to ca. 20 mL to afford [MoRu(μ-CC$_6H_4$-Me-4)(CO)$_4$(η^5-7,8-$C_2B_9H_{11}$){κ^3-HB(pz)$_3$}] (**4a**) (90 mg) as a highly crystalline red solid which was sufficiently pure for subsequent manipulations. Analytically pure samples were obtained by slow diffusion of a CH_2Cl_2 solution of **4a** into a pentane layer at 0 °C to obtain red blocks, which were washed with petroleum ether (1 × 5 mL) and dried in vacuo.

(ii) Similarly using [W(≡CC_6H_4Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] (83 mg, 0.15 mmol) and **1** afforded [WRu(μ-CC$_6H_4$Me-4)(CO)$_4$(η^5-7,8-$C_2B_9H_{11}$){κ^3-HB(pz)$_3$}] (**4b**) as a red microcrystalline solid (104 mg).

Synthesis of [MRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo, W). (i) In a representative experiment, compound **4a** (50 mg, 0.066 mmol) and sulfur (2 mg, 0.063 mmol) were placed in a Schlenk tube, which was evacuated for 2 h. After addition of CH$_2$Cl$_2$ (20 mL) and stirring for 12 h, the volume was reduced to ca. 2 mL in vacuo and the dark residue transferred to a preparative TLC plate. Development with Et$_2$O−petroleum ether (1:3) over a 12 h period separated two major eluates, one purple and one yellow-green band. Both were removed mechanically and extracted with acetone. After removal of solvent in vacuo the former was identified as [Mo(κ^2-S$_2$CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}] by comparison of its spectroscopic properties with those of an authentic sample.[23] The latter fraction, after crystallization of the residue by slow diffusion of a CH$_2$Cl$_2$ solution into a pentane layer, afforded black crystals of [MoRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6a**) (40 mg), which were dried in vacuo.

(ii) The procedure employed was as for **6a** substituting [WRu(μ-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (50 mg, 0.059 mmol), to afford [WRu(μ-1κC^{α},1:2κS-SCC$_6$H$_4$Me-4)(CO)$_4$-(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6b**) (35 mg) as black crystals.

Synthesis of [WRu(μ-1κC^{α},1:2κSe-SeCC$_6$H$_4$Me-4)(CO)$_4$-(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (M = Mo, W). (i) A sample of **4a** (40 mg, 0.053 mmol) and excess gray selenium (40 mg, 0.52 mmol) were placed in a Schlenk tube, which was evacuated for 2 h. The mixture was then treated with CH$_2$Cl$_2$ (20 mL) and the suspension stirred for 7 days. The volume of solvent was reduced in vacuo to ca. 2 mL and the dark residue transferred to preparative TLC plates. Development with Et$_2$O−petroleum ether (1:3) over a 12 h period separated a major dark green band, which was removed mechanically. Extraction with acetone, removal of solvent in vacuo, and subsequent crystallization of the residue by slow diffusion of a CH$_2$Cl$_2$ solution into a pentane layer afforded black crystals of [MoRu(μ-1κC^{α},1:2κSe-SeCC$_6$H$_4$Me-4)(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)-{κ^3-HB(pz)$_3$}] (**6c**) (34 mg), which were dried in vacuo.

(ii) A similar procedure was employed using **4b** (40 mg, 0.047 mmol) to afford [WRu(μ-1κC^{α},1:2κSe-SeCC$_6$H$_4$Me-4)-(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$){κ^3-HB(pz)$_3$}] (**6d**) (28 mg) as black crystals. FAB MS as a nitrobenzyl alcohol matrix *m*/*z*: 924.3 (M, calc 924.5, 7.9%), 810.2 (M-4 CO, calc 812.5, 7.1%), 636.1 ([W(η^2-SeCC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}], calc 635.0, 100%), 608.2 ([W(η^2-SeCC$_6$H$_4$Me-4)(CO){κ^3-HB(pz)$_3$}], calc 607.0, 38.5%), 580.3 ([W(η^2-SeCC$_6$H$_4$Me-4){κ^3-HB(pz)$_3$}], calc 579.0, 60.6%), 556.4 ([W(≡CC$_6$H$_4$Me-4)(CO)$_2${κ^3-HB(pz)$_3$}], calc 556.0, 35.7%), 530.4 ([W(≡CC$_6$H$_4$Me-4)(CO){κ^3-HB(pz)$_3$}], calc 528.0, 22.7%).

Crystal Structure Determinations and Refinements. Crystals of **2b**, **4b**, and **6b** were grown by diffusion of CH$_2$Cl$_2$ solutions into pentane. Experimental data for **4b** and **6b** are given in Table 5. That for **2b** is provided in the Supporting Information. All diffracted intensities were collected on Enraf-Nonius CAD-4 automated diffractometers using graphite-monochromated Mo Kα X-radiation operating in the $\omega-(2/3)\theta$ scan mode at low temperature for **2b** and at room temperature in the $\omega-2\theta$ scan mode for **4b** and **6b**. In all cases the final unit cell dimensions were determined from the setting angle values of 25 accurately centered reflections. The stability of the crystals during the period of the data collection was monitored by measuring the intensities of three standard reflections every hour for **2b** and every 2 h for **4b** and **6b**. Data were collected at varying scan speeds: 1.59−6.89 deg m^{-1} in ω for **2b** with a scan range of 0.90° + 0.35 tan θ; 4.13−5.17 deg m^{-1} in ω for **4b** with a scan range of 1.25° + 0.34 tan θ; and 0.54−5.17 deg m^{-1} in ω for **6b** with a scan range of 1.15° + 0.34 tan θ. Each data set was corrected for Lorentz, polarization, and X-ray absorption effects, the latter by a semiempirical method based on azimuthal scans of ψ data of several Euclerian angles (χ) near 90°.

The structure was solved by direct methods (**2b**) or conventional heavy-atom methods (**4b** and **6b**), and successive Fourier difference syntheses were used to locate all non-hydrogen atoms, using the SHELXTL-PC package.[24] Refinements were made by full-matrix least-squares on F^2 data, using SHELXL-93, with anisotropic thermal parameters for all non-hydrogen atoms except for some of those of **2b**. The data for the latter were very weak ($I/\sigma < 10$); the platelike crystal habit (dimensions 0.29 × 0.23 × 0.05 mm) and axial photos indicated the presence of a twin satellite crystal (TWIN law 1 0 0, 0 −1 0, 0 0 −1, and BASF parameter refined to 0.016(1)). The asymmetric unit contained two crystallographically independent molecules in general positions. The weak data precluded full anisotropic refinement of all non-hydrogen atoms; hence only the metal and CO ligand atoms (excluding C(5(A)) were assigned anisotropic thermal parameters. Carborane cage carbon atoms were identified from the magnitudes of their isotropic thermal parameters and from a comparison of bond lengths to adjacent boron atoms. All non-hydrogen atoms of molecules **4b** and **6b** were assigned anisotropic thermal parameters. All hydrogen atoms were included in geometrically calculated positions (C−H 0.96 Å and B−H 1.10 Å) and allowed to ride on their parent boron or carbon atom with fixed isotropic thermal parameters ($U_{\mathrm{iso}} = 1.2U_{\mathrm{iso}}$ of the parent atom except for methyl protons, where $U_{\mathrm{iso}} = -1.5U_{\mathrm{iso}}$). Atomic scattering factors were from ref 25. Significant residual electron density in the difference Fourier syntheses at convergence was found near the solvent molecule in **4b** and near the metal atoms of **2b** and **6b**.

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Supporting Information Available: Complete tables of bond lengths and angles, anisotropic thermal parameters, and atom positional and thermal parameters and crystal data for **2b**, **4b**, and **6b** (35 pages). Ordering information is given on any current masthead page.

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