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Synthesis and Structural Characterization of the Compounds $[WCoAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ and $[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ and Studies on Related Mixed-Metal Complexes

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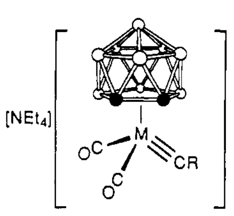
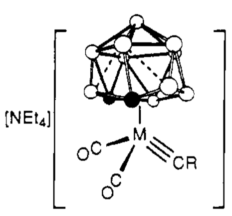
The compounds $[Co(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ and $[NEt_4][M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (M = Mo, W) react in CH_2Cl_2 to afford the salts $[NEt_4][MCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$. Protonation ($HBF_4{\cdot}Et_2O$) of these species yields the dimetal compounds $[MCo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^6\text{-}C_2B_{10}H_9Me_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$, while treatment with $[AuCl(PPh_3)]$ in tetrahydrofuran in the presence of $TlBF_4$ yields the trimetal complexes $[MCoAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$. The structure of the species with M = W has been established by X-ray diffraction. Crystals are triclinic, space group $P\bar{1}$ (No. 2) with a = 10.007 (4) Å, b = 10.791 (3) Å, c = 21.642 (7) Å, α = 87.81 (2)°, β = 84.58 (3)°, γ = 73.10 (2)°, and Z = 2. The core of the molecule consists of a metal triangle [Au–W 2.855 (2), Au–Co 2.603 (3), W–Co 2.576 (3) Å] that is asymmetrically capped by the *p*-tolylmethylidyne group [μ_3-C–Au 2.39 (2) Å, μ_3-C–W 2.01 (2) Å, μ_3-C–Co 1.91 (2) Å]. The gold and cobalt atoms carry PPh_3 and $\eta^4\text{-}C_4Me_4$ ligands, respectively. The tungsten atom is η^6 coordinated by the open face of the *nido*-$C_2B_{10}H_{10}Me_2$ fragment and by the two carbonyl groups. One carbonyl ligand semibridges the W–Co bond [W–C–O 166 (2)°]. The cobalt complex $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ reacts with the salts $[NEt_4][M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ in CH_2Cl_2 to afford the compounds $[MCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$. An X-ray diffraction study on the dimetal complex with M = Mo revealed that the crystals were monoclinic, space group $P2_1/c$ (No. 14) with a = 16.276 (2) Å, b = 11.870 (2) Å, c = 15.791 (4) Å, β = 112.60 (2)°, and Z = 4. The metal–metal bond [2.540 (1) Å] is bridged on one side by the alkylidyne group [μ-C–Mo 1.914 (7), μ-C–Co 1.915 (6) Å] and on the other by the *nido*-$C_2B_{10}H_{10}Me_2$ cage. The open face of the latter is η^6 coordinated to the Mo atom, while the BH group, which is in the β site with respect to the carbon atoms in the $\overline{\text{CBCB}\mathit{B}\text{B}}$ ring, forms an exo-polyhedral B–H → Co bond. The cobalt atom carries the $\eta^4\text{-}C_4Me_4$ ligand, and the molybdenum atom is ligated by two CO groups, as expected. Reactions between $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ and the salts $[NEt_4][M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ afford the dimetal compounds $[MCo(\mu\text{-}CR)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Mo, W, R = C_6H_4Me-4; M = W, R = Me).

Introduction

The alkylidyne–metal salts $[NEt_4][\mathit{closo}\text{-}1,2\text{-}Me_2\text{-}3\text{-}(\equiv CR)\text{-}3,3\text{-}(CO)_2\text{-}3,1,2\text{-}MC_2B_9H_9]$ (**1**: M = Mo, W; R = alkyl, aryl, alkynyl) and $[NEt_4][\mathit{closo}\text{-}1,3\text{-}Me_2\text{-}4\text{-}(\equiv CC_6H_4Me\text{-}4)\text{-}4,4\text{-}(CO)_2\text{-}4,1,3\text{-}WC_2B_{10}H_{10}]$ (**2**) are proving to be versatile reagents for preparing compounds containing heteronuclear metal–metal bonds.[1] The C≡M linkages present in these salts readily add metal–ligand fragments to give species in which an alkylidyne group bridges a bond between tungsten or molybdenum and another metal center. An interesting feature of this chemistry, however, is that the products formed initially often undergo further transformations as a result of the carbaborane fragments adopting nonspectator roles. This latter behavior results in the cages forming exo-polyhedral B–H → metal or B–metal bonds, or in some instances boron–carbon linkages.





●CMe ○BH

	M	R
1a	W	C_6H_4Me-4
1b	Mo	C_6H_4Me-4
1c	W	Me

	M	R
2a	W	C_6H_4Me-4
2b	Mo	C_6H_4Me-4

In this paper[2] we describe studies employing the salts **1** and **2** as precursors to species with bonds between cobalt and tungsten or molybdenum. We have previously reported[3] that the salt **1a** reacts with $[Co_2(CO)_8]$ to afford the hexacarbonyl–trimetal compound $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ via the intermediacy of a labile octacarbonyl–trimetal complex $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$. The anions of both trimetal salts have μ_3-$CWCo_2$ core structures, but whereas in the octacarbonyl species the $C_2B_9H_9Me_2$ cage ligates the W atom in the usual η^5 fashion, in the hexacarbonyl the cage slips to form two exo-polyhedral B–H → Co bonds across one face of the WCo_2 triangle, while the opposite face is capped by the alkylidyne group. The two three-center B–H → Co linkages in the hexacarbonyl complex are readily lifted upon treatment with CO so as to regenerate the octacarbonyl compound.

Results

Treatment of **2a** with $[Co(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ in CH_2Cl_2 affords the deep purple salt $[NEt_4][WCo(\mu\text{-}CC_6H_4Me\text{-}$

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(1) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53.

(2) This article is part 113 of a series on the synthesis and structures of complexes containing bonds between different transition elements. For part 112 see: Pilotti, M. U.; Stone, F. G. A.; Topaloğlu, I. *J. Chem. Soc., Dalton Trans.* **1991**, 1621.

(3) Baumann, F.-E.; Howard, J. A. K.; Musgrove, R. J.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1891.

0276-7333/91/2310-2718$02.50/0

Table I. Analytical and Physical Data for the Complexes

	compd	color	yield/%	$\nu_{max}(CO)^a/cm^{-1}$	analysis[b]/% C	analysis[b]/% H
(**3a**)	$[NEt_4][WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	purple	83	1926 (s), 1756 (s, br)	45.18[c] (45.78)	6.56 (6.96)
(**3b**)	$[NEt_4][MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]^d$	purple		1939 (s), 1759 (s, br)		
(**4a**)	$[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^6\text{-}C_2B_{10}H_9Me_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$	green	70	2024 (s), 1985 (m)	40.50 (40.69)	5.87 (5.26)
(**4b**)	$[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^6\text{-}C_2B_{10}H_9Me_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$	green	62	2031 (s), 1997 (m)	46.85 (46.46)	5.76 (6.01)
(**5a**)	$[WCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	brown	86	1967 (s), 1832 (m, br)	42.65 (43.17)	4.83 (4.57)
(**5b**)	$[MoCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	brown	64	1976 (s), 1826 (m, br)	46.13 (46.68)	5.29 (4.94)
(**7a**)	$[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	brown	88	2020 (s), 1977 (m)	37.94 (38.72)	5.43 (5.17)
(**7b**)	$[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$	brown	80	2026 (s), 1990 (m)	44.36 (44.45)	5.75 (5.93)
(**8a**)	$[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)]$	brown	42	2025 (m), 1980 (s), 1906 (s)	38.93 (39.55)	5.08 (4.91)
(**8b**)	$[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)]$	brown	58	2026 (m), 1987 (s), 1916 (s)	44.47 (45.24)	5.29 (5.61)
(**8c**)	$[WCo(\mu\text{-}CMe)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)]$	brown	57	2028 (m), 1977 (s), 1902 (s)	32.41 (32.80)	5.07 (4.86)

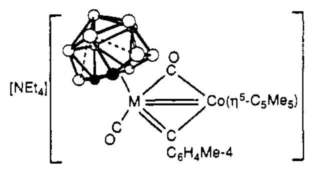
[a] Measured in CH_2Cl_2; medium intensity bands observed at ca. 2550 cm^{-1} in the spectra of all the compounds are due to B-H absorptions. [b] Calculated values are given in parentheses. [c] N 1.84 (1.67%). [d] Not isolated due to instability of compound (see text). However, i.r. bands in the CO region could be measured from reaction mixtures.

Table II. Hydrogen-1 and Carbon-13 NMR Data for the Complexes

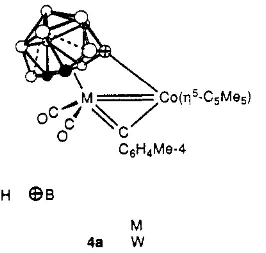
compd	$^1H/\delta^b$	$^{13}C/\delta^c$
3a[d]	1.20 (br, 12 H, *Me*CH_2N), 1.25 (s, 15 H, C_5Me_5), 2.25 (s, 6 H, CMe), 2.49 (s, 3 H, Me-4), 3.08 (br, 8 H, Me*CH_2*N), 6.74, 7.25 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) = 8 Hz]	388.2 (μ-C), 163.1 [$C^1(C_6H_4)$], 134.1, 127.1, 120.7 (C_6H_4), 95.3 (C_5Me_5), 53.2 (Me*CH_2*N), 35.4 (C*Me*), 21.5 (Me-4), 8.9 (C_5*Me_5*), 8.1 (*Me*CH_2N)
4a[e]	1.15 (s, 15 H, C_5Me_5), 1.68 (s, 6 H, CMe), 2.45 (s, 3 H, Me-4), 6.62, 7.08, 7.38 (m × 3, 4 H, C_6H_4)	349.5 (μ-C), 204.3, 197.2 (CO), 157.6 [$C^1(C_6H_4)$], 136.3, 127.7, 127.5, 120.8, 119.4 (C_6H_4), 95.7 (*C_5*Me_5), 75.8, 65.7 (br, *C*Me), 34.4, 34.3 (C*Me*), 20.9 (Me-4), 9.9 (C_5*Me_5*)
4b[e]	1.18 (s, 15 H, C_5Me_5), 1.37, 1.57 (s × 2, 6 H, CMe), 2.44 (s, 3 H, Me-4), 6.66, 7.17, 7.34, 7.40 (m × 4, 4 H, C_6H_4)	363.9 (μ-C), 211.8, 205.4 (CO), 156.2 [$C^1(C_6H_4)$], 136.3, 128.0, 127.8, 120.7, 119.0 (C_6H_4), 96.1 (*C_5*Me_5), 85.3, 69.2 (br, *C*Me), 34.4, 33.8 (C*Me*), 20.9 (Me-4), 9.3 (C_5*Me_5*)
5a	1.05 (s, 15 H, C_5Me_5), 2.26, 2.29 (s × 2, 6 H, CMe), 2.42 (s, 3 H, Me-4), 7.02–7.58 (19 H, Ph and C_6H_4)	255.8[f] (μ-C), 202.7 (br, CO), 159.2–135.8 (Ph and C_6H_4), 98.1 (*C_5*Me_5), 35.2, 34.7 (C*Me*), 21.1 (Me-4), 8.7 (C_5*Me_5*)
5b	1.06 (s, 15 H, C_5Me_5), 1.89, 2.29 (s × 2, 6 H, CMe), 2.39 (s, 3 H, Me-4), 7.01–7.51 (19 H, Ph and C_6H_4)	263.8[f] (μ-C), 213.3 (br, CO), 158.2–128.2 (Ph and C_6H_4), 99.1 (*C_5*Me_5), 34.7, 34.2 (C*Me*), 21.2 (Me-4), 8.8 (C_5*Me_5*)
7a[e]	−8.73 (vbr, 1 H, B–H–Co), 1.00 (s, 12 H, C_4Me_4), 1.62, 2.10 (s × 2, 6 H, CMe), 2.35 (s, 3 H, Me-4), 7.07, 7.12 [(AB), 2 H, C_6H_4, *J*(AB) = 8 Hz], 7.26, 7.29 [(AB), 2 H, C_6H_4, *J*(AB) = 9 Hz]	323.2 (μ-C), 205.7, 199.6 (CO), 157.3 [$C^1(C_6H)_4$], 136.3, 127.9, 127.7, 122.5, 121.9 (C_6H_4), 93.0 (*C_5*Me_5), 82.8, 63.5 (br, *C*Me), 35.7, 34.5 (C*Me*), 20.8 (Me-4), 10.1 (C_5*Me_5*)
7b[e,g]	1.03 (s, 12 H, C_4Me_4), 1.54, 1.86 (s × 2, 6 H, CMe), 2.37 (s, 3 H, Me-4), 7.11, 7.16 [(AB), 2 H, C_6H_4, *J*(AB) = 7 Hz], 7.27, 7.29 [(AB), 2 H, C_6H_4, *J*(AB) = 7 Hz]	337.1 (μ-C), 213.5, 208.2 (CO), 154.7 [$C^1(C_6H_4)$], 136.4, 128.1, 127.9, 122.4, 122.0 (C_6H_4), 93.9 (*C_4*Me_4), 93.2, 67.5 (br, *C*Me), 35.5, 33.9 (C*Me*), 20.9 (Me-4), 10.2 (C_4*Me_4*)
8a	−7.70 [q, 1 H, B–H–Co, *J*(BH) = 77 Hz], 1.32 (s, 12 H, C_4Me_4), 2.08, 2.23, 2.29 (s × 3, 9 H, CMe and Me-4), 7.18, 7.34 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) = 6 Hz]	288.7 (μ-C), 226.9, 220.5 (WCO), 201.4 (br, CoCO), 154.8 [$C^1(C_6H_4)$], 137.7, 129.4, 126.5 (C_6H_4), 97.0 (*C_4*Me_4), 63.4, 60.7 (br, *C*Me), 30.9, 30.1 (C*Me*), 21.7 (Me-4), 10.1 (C_4*Me_4*)
8b	−8.19 (q, 1 H, B–H–Co, *J*(BH) = 76 Hz], 1.30 (s, 12 H, C_4Me_4), 1.95, 2.05, 2.35 (s × 3, 9 H, CMe and Me-4), 7.22, 7.33 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) = 7 Hz]	303.4 (μ-C), 231.9, 224.0 (WCO), 201.0 (br, CoCO), 151.9 [$C^1(C_6H_4)$], 138.2, 129.4, 126.4 (C_6H_4), 97.3 (*C_4*Me_4), 66.1, 62.7 (br, *C*Me), 30.2, 29.6 (C*Me*), 21.6 (Me-4), 10.1 (C_4*Me_4*)
8c	−7.67 [q, 1 H, B–H–Co *J*(BH) = 75 Hz], 1.54 (s, 12 H, C_4Me_4) 2.02, 2.24, 2.56 (s × 3, 9 H, CMe and μ-CMe)	296.0 (μ-C), 226.5, 220.8 (WCO), 201.5 (br, CoCO), 95.7 (*C_4*Me_4), 63.4, 60.0 (br, *C*Me), 45.2 (μ-C*Me*), 30.9, 30.0 (C*Me*), 10.2 (C_4*Me_4*)

[a] Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2. [d] Compound is fluxional at ambient temperatures resulting in nonobservation of signals due to the CO and *C*Me nuclei. Low solubility prevented satisfactory spectra being observed at reduced temperatures. [e] Measured at −80 °C. [f] Signals arising from *C*Me nuclei not observed due to low solubility of the compound. [g] Signal due to B–H–Co linkage not observed in ^1H spectrum.

4)$(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)$] (**3a**), data for which are given in Tables I and II. Although this complex is relatively unstable, both in solution and in the solid state, analytical and spectroscopic data were obtained. There are two CO bands in the IR spectrum (1926 and 1756 cm^{-1}); the absorption at lowest frequency suggests that one carbonyl ligand bridges or semibridges the Co–W bond. The ^1H NMR spectrum revealed the expected peaks, but in the $^{13}C\{^1H\}$ NMR spectrum signals due to the CO ligands and CMe cage nuclei were not observed. It is likely that this is due to dynamic behavior in solution. However, attempts to obtain spectra of **3a** at low temperatures were frustrated by the insolubility of the complex.



	M
3a	W
3b	Mo



	M
4a	W
4b	Mo

It is interesting to compare the chemical shift for the μ-C resonance at δ 388.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **3a** with that observed for the corresponding but appreciably less deshielded signal at δ 341.0 ppm in the spectrum of the related complex [WCo(μ-CC_6H_4Me-4)-

Table III. Selected Internuclear Distances (Å) and Angles (deg) for the Complex $[WCoAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (5a) with Estimated Standard Deviations in Parentheses

Au–W	2.855 (2)	Au–Co	2.603 (3)	W–Co	2.576 (3)	Au–P	2.313 (6)
Au–C(7)	2.39 (2)	W–C(7)	2.01 (2)	Co–C(7)	1.91 (2)	W–C(5)	1.98 (2)
W–C(6)	1.92 (3)	Co–C(6)	2.36 (3)	W–C(1)	2.53 (2)	W–C(2)	2.31 (2)
W–B(3)	2.46 (2)	W–B(4)	2.53 (3)	W–B(5)	2.45 (3)	W–B(6)	2.41 (3)
Co–C(C_5Me_5)	2.087 (2)[a]	P–C(C_6H_5)	1.81 (3)[a]	C(1)–B(3)	1.67 (4)	C(1)–B(6)	1.65 (3)
C(1)–B(8)	1.70 (3)	C(1)–B(9)	1.72 (3)	C(2)–B(3)	1.62 (4)	C(2)–B(4)	1.53 (3)
C(2)–B(10)	1.75 (4)	B(3)–B(9)	1.78 (4)	B(3)- - -B(10)	1.98 (4)	B(4)–B(5)	1.84 (4)
B(4)- - -B(10)	1.98 (4)	B(4)–B(11)	1.80 (4)	B(5)–B(6)	1.76 (4)	B(5)–B(7)	1.70 (4)
B(5)–B(11)	1.73 (3)	B(6)–B(7)	1.77 (3)	B(6)–B(8)	1.73 (3)	B(7)–B(8)	1.70 (4)
B(7)–B(11)	1.69 (5)	B(7)–B(12)	1.71 (4)	B(8)–B(9)	1.78 (4)	B(8)–B(12)	1.74 (5)
B(9)–B(10)	1.84 (5)	B(9)–B(12)	1.74 (4)	B(10)–B(11)	1.92 (4)	B(10)–B(12)	1.79 (5)
B(11)–B(12)	1.75 (4)	C(5)–O(5)	1.17 (3)	C(6)–O(6)	1.23 (4)	C(7)–C(8)	1.44 (3)

Au–W–Co	57.0 (1)	Au–Co–W	66.9 (1)	W–Au–Co	56.1 (1)
W–Au–P	141.2 (1)	Co–Au–P	149.4 (2)	W–Au–C(7)	43.9 (5)
Co–Au–C(7)	44.7 (5)	Au–W–C(7)	55.6 (5)	Au–Co–C(7)	61.7 (5)
W–Co–C(7)	50.6 (6)	Co–W–C(7)	47.2 (6)	Au–C(7)–W	80.5 (7)
Au–C(7)–Co	73.6 (6)	W–C(7)–Co	82.3 (9)	Au–C(7)–C(8)	112 (1)
W–C(7)–C(8)	152 (1)	Co–C(7)–C(8)	125 (1)	W–C(5)–O(5)	173 (2)
W–C(6)–O(6)	166 (2)				

[a] Average distances between Co and C atoms of C_5Me_5 ring, and between P and C^1 atoms of Ph rings, respectively.

$(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$.[4a] The latter is an electronically saturated 34 valence electron dimetal species, whereas **3a** is an unsaturated 32 valence electron complex. We have drawn attention previously[4b] to the interesting feature that the ^{13}C resonances attributable to μ-C nuclei in dimetal complexes are significantly more deshielded in 32 valence electron species than in comparable 34 valence electron compounds. The species **3a** and the compound $[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ evidently also follow this increasingly useful but empirical rule.

The reaction between **2b** and $[Co(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ affords a very unstable species formulated as $[NEt_4][MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (**3b**), by analogy with **3a**. Although microanalytical and NMR data could not be obtained for this product, as described below, it can be prepared in situ and used to prepare other compounds.

Protonation of the salts **3** was next investigated. Treatment of **3a** in CH_2Cl_2 with $HBF_4\cdot Et_2O$ at low temperatures affords the complex $[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^6\text{-}C_2B_{10}H_9Me_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$ (**4a**), characterized by the data given in Tables I and II and by its $^{11}B\{^1H\}$ NMR spectrum. The latter (see Experimental Section) showed a deshielded resonance of intensity corresponding to one boron nucleus at δ 69.0 ppm. This resonance remained a singlet in a fully coupled ^{11}B spectrum, indicating that the boron atom does not carry a hydrogen atom. Other signals in the spectrum corresponded to nine boron nuclei and occurred as overlapping broad bands in the range δ 0.1 to −21.7 ppm. The resonance at δ 69.0 ppm may be assigned to an exo-polyhedral B–Co bond, on the basis of data obtained previously for several species containing cage boron–metal σ bonds.[5] However, isomers are possible since the B–Co bond in **4a** could involve boron atoms that are in alternative sites in the $\overline{\text{CBCBBB}}$ ring forming the open face of the *nido*-$C_2B_{10}H_9Me_2$ cage. Only one isomer of **4a** was formed on protonation of **3a**, and the data available do not allow a decision to be made as to whether the species formed is as depicted or whether the B–Co linkage involves a boron adjacent to a cage CMe group in the face of the cage. Unfortunately, crystals suitable for an X-ray diffraction study were not obtained.

Generation of **3b** in situ followed by treatment with $HBF_4\cdot Et_2O$ gave the compound $[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^6\text{-}C_2B_{10}H_9Me_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$ (**4b**), the spectroscopic properties of which are similar to those of **4a**. In particular, the $^{11}B\{^1H\}$ NMR spectrum of **4b** revealed a resonance for the B–Co group at δ 72.1 ppm. The ^1H NMR spectra of the complexes **4** displayed the expected peaks, and the $^{13}C\{^1H\}$ spectra showed diagnostic signals for the ligated carbon atoms of the bridging *p*-tolylmethylidyne groups at δ 349.5 (**4a**) and 363.9 ppm (**4b**). Other peaks in the $^{13}C\{^1H\}$ NMR spectra were as expected, but the observation of six rather than four resonances for the C_6H_4 ring indicates that rotation about the $\mu\text{-}C\text{–}C^1(C_6H_4Me\text{-}4)$ bonds is restricted on the NMR time scale, a feature also observed in some other systems discussed earlier.[6]

Formation of the compounds **4** by protonation of the salts **3** probably occurs through the intermediacy of a hydridocobalt species. On the basis of model systems reported earlier,[5d,e,7] it is also probable that in such an intermediate there is a BH group in the open face of the $C_2B_{10}H_{10}Me_2$ ligand which is activated by formation of a B–H → Co bond. Reductive elimination of molecular hydrogen from this linkage and a hydride ligand at the cobalt center could then afford the compounds **4**.

The isolobal relationship between a proton and a $AuPPh_3^+$ fragment[8] prompted study of reactions between the salts **3** and $[AuCl(PPh_3)]$ in tetrahydrofuran, in the presence of $TlBF_4$. The latter reagent is added to remove chloride as insoluble TlCl. In this manner the trimetal compounds $[MCoAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (**5a**, M = W; **5b**, M = Mo) were obtained, data for which are given in Tables I and II. Discussion of the spectroscopic properties is deferred,

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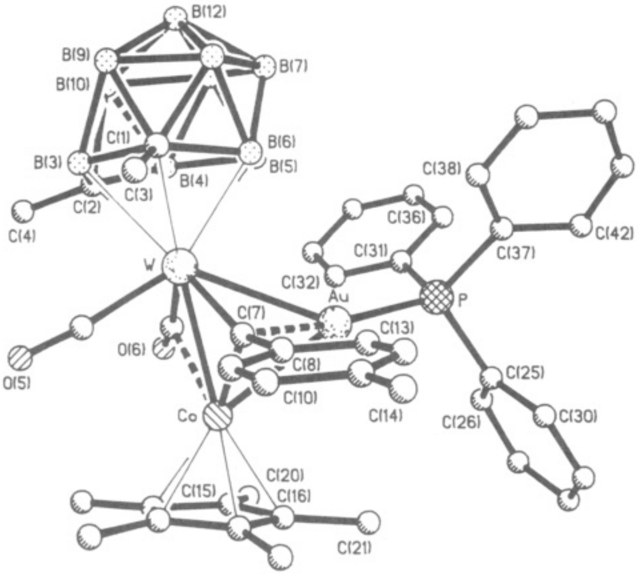
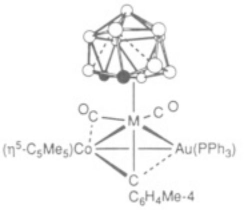
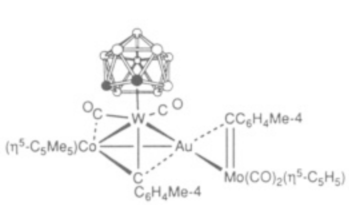


Figure 1. Structure of [WCoAu(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η^5-C$_5$Me$_5$)(η^6-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**5a**), showing the crystallographic numbering system.

however, until after the results of an X-ray diffraction study on **5a** are given.





● CMe ○ BH

	M
5a	W
5b	Mo

6

The structure of **5a** is shown in Figure 1, and selected bond lengths and angles are given in Table III. The core of the molecule consists of a metal triangle [Au–W 2.855 (2) Au–Co 2.603 (3), W–Co 2.576 (3) Å] asymmetrically capped by the *p*-tolylmethylidyne group [Au–C(7) 2.39 (2), W–C(7) 2.01 (2), Co–C(7) 1.91 (2) Å]. A similar μ_3-CWCoAu core structure is found in the cluster compound [MoWCoAu(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**6**), which has comparable metal–metal distances [Au–W 2.826 (1), Au–Co 2.580 (2), W–Co 2.597 (2) Å].[9] The two structures are closely related. In the tetranuclear metal species **6** an η^5-C$_2$B$_9$H$_9$Me$_2$ group replaces the η^6-C$_2$B$_{10}$H$_{10}$Me$_2$ cage present in **5a**, while an (η^5-C$_5$H$_5$)(OC)$_2$Mo≡CC$_6$H$_4$Me-4 fragment ligates the gold atom instead of a PPh$_3$ molecule. Moreover, as in complex **5a**, in compound **6** the μ_3-alkylidyne group asymmetrically caps the WCoAu triangle [Au–C(7) 2.30 (1), W–C(7) 1.97 (1), Co–C(7) 1.86 (1) Å]. The μ_3-CC$_6$H$_4$Me-4 groups in these two molecules are evidently more tightly bound to the W and Co atoms than to the Au atom. It is noteworthy that in the compound [WRh$_2$Au$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)$_2$], which contains a μ_3-CWAu$_2$ core, there is a more symmetrical arrangement with the μ_3-C–Au and μ_3-C–W distances at 2.06 (2) and 2.02 (2) Å, respectively.[10]

The W–C(7) and Co–C(7) separations in **5a** and in **6** are similar (see above) and are comparable with those in the dimetal complex [WCo(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)] [μ-C—W 1.913 (7), μ-C—Co 1.939 (8) Å].[4a] However, whereas in the latter species the W—Co bond is 2.758 (1) Å, in **5a** and in the tetrametal compound **6** these bonds are appreciably shorter, at 2.576 (3) and 2.597 (2) Å, respectively. This suggests appreciable electron delocalization within the $\overline{\mathrm{C(7)WCo}}$ rings in compounds **5a** and **6**. Indeed, the tungsten–cobalt separations may imply a degree of W═Co bonding. It is noteworthy that in the complex [PPh$_4$][WCo$_2$(μ_3-CPh)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)] the W—Co distances (average 2.768 Å) are significantly longer.[3]

As expected, in compound **5a** the gold atom carries the PPh$_3$ group and the cobalt and tungsten atoms are coordinated by the C$_5$Me$_5$ ring and the C$_2$B$_{10}$H$_{10}$Me$_2$ cage, respectively. The tungsten atom is also ligated by two CO molecules, but C(6)O(6) semibridges the W–Co bond [W–C(6)–O(6) 166 (2)°]. Within the 13-vertex WC$_2$B$_{10}$ cage there are different connectivities between the metal atom and the ligating atoms of the cage and there are also distorted triangular faces within the carbaborane fragment. Such features were first noted by Hawthorne and coworkers[11] and subsequently by others[12,13] in several mononuclear metal species having MC$_2$B$_{10}$ core structures. These cage distortions are discussed further below.

Formally, compound **5a** can be regarded as having 44 cluster valence electrons, in contrast with the 48 required for an electronically saturated triangular metal species. As found frequently with metal clusters, assignment of valence-electron counts to the individual metal centers of **5a** does not lead to a satisfactory bond representation, and this is not unexpected in view of the distortions in the μ_3-CWCoAu core discussed above.

Having established the nature of **5a** the spectroscopic properties of this compound are readily interpreted, as are those of **5b**, which must have a similar structure. Both complexes display two CO stretching bands in their IR spectra (Table I). The absorption at ca. 1830 cm^{-1} in each spectrum may be assigned to the semibridging carbonyl group. In the ^{13}C{^{1}H} NMR spectra of **5a** and **5b** only one broad CO resonance is observed (Table II), suggesting site-exchange of the two ligands on the NMR time scale. Limiting low-temperature spectra could not be measured. Diagnostic signals for the μ_3-C nuclei are seen at δ 255.8 (**5a**) and 263.8 ppm (**5b**). Bands in the ^{1}H NMR spectra are expected.

Reactions between the salts **2** and the compound [Co(CO)$_2$(NCMe)(η^4-C$_4$Me$_4$)][PF$_6$] were next investigated, and the dimetal complexes [MCo(μ-CC$_6$H$_4$Me-4)(CO)$_2$(η^4-C$_4$Me$_4$)(η^6-C$_2$B$_{10}$H$_{10}$Me$_2$)] (**7a**, M = W; **7b**, M = Mo) were thereby isolated. The ^{1}H NMR spectrum of **7a** showed a broad resonance at δ −8.73 ppm, corresponding in intensity to a single proton. This signal is strongly indicative of the presence of a B–H ⇀ Co bond. Thus similar peaks are observed at δ −7.72 and −7.15 ppm in the spectrum of [NEt$_4$][WCo$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$], which as mentioned earlier, contains two exo-polyhedral B–H ⇀ Co linkages.[3] The presence of the B–H ⇀ Co group in **7a**

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Table IV. Selected Internuclear Distances (Å) and Angles (deg) for the Complex $[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (7b) with Estimated Standard Deviations in Parentheses

Mo–Co	2.540 (1)	Mo–C(7)	1.914 (7)	Co–C(7)	1.915 (6)	Co–B(5)	2.24 (1)
Co–H(5)	1.74 (7)	Mo–C(5)	2.030 (8)	Mo–C(6)	2.020 (6)	Mo–C(1)	2.255 (7)
Mo–C(2)	2.555 (7)	Mo–B(3)	2.491 (9)	Mo–B(4)	2.378 (8)	Mo–B(5)	2.308 (8)
Mo–B(6)	2.457 (7)	Co–C(C_4Me_4)	2.026 (6)[a]	C(1)–B(3)	1.56 (1)	C(1)–B(6)	1.55 (1)
C(1)–B(8)	1.78 (1)	C(2)–B(3)	1.71 (1)	C(2)–B(4)	1.70 (1)	C(2)–B(9)	1.69 (1)
C(2)–B(10)	1.68 (1)	B(3)- - -B(8)	2.02 (1)	B(3)–B(9)	1.80 (1)	B(4)–B(5)	1.78 (1)
B(4)–B(10)	1.78 (1)	B(4)–B(11)	1.80 (1)	B(5)–H(5)	1.08 (6)	B(5)–B(6)	1.81 (1)
B(5)–B(7)	1.74 (1)	B(5)–B(11)	1.76 (1)	B(6)–B(7)	1.80 (1)	B(6)- - -B(8)	1.98 (1)
B(7)–B(8)	1.91 (1)	B(7)–B(11)	1.74 (1)	B(7)–B(12)	1.74 (1)	B(8)–B(9)	1.88 (1)
B(8)–B(12)	1.80 (1)	B(9)–B(10)	1.72 (1)	B(9)–B(12)	1.74 (1)	B(10)–B(11)	1.76 (1)
B(10)–B(12)	1.77 (1)	B(11)–B(12)	1.79 (1)	C(5)–O(5)	1.13 (1)	C(6)–O(6)	1.14 (1)
C(7)–C(8)	1.47 (1)						

Mo–Co–C(7)	48.4 (2)	Mo–C(7)–Co	83.1 (3)	Mo–C(7)–C(8)	143.7 (4)
Co–Mo–C(7)	48.5 (2)	Co–C(7)–C(8)	133.2 (4)	Co–H(5)–B(5)	102 (4)
Mo–C(5)–O(5)	176 (1)	Mo–C(6)–O(6)	178 (1)		

[a] Average distance between Co and C atoms of the C_4Me_4 ring.

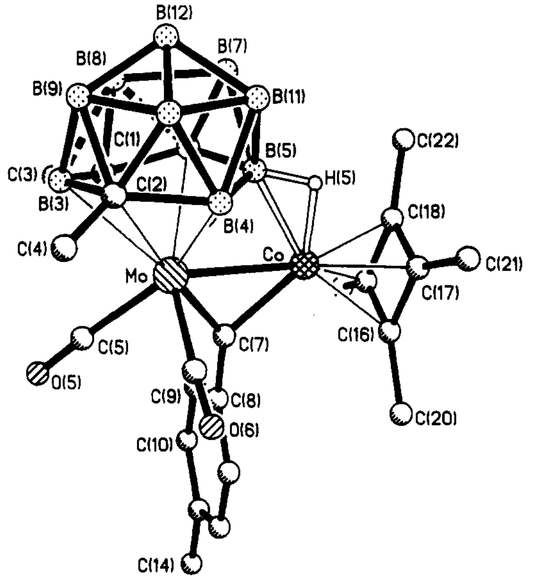
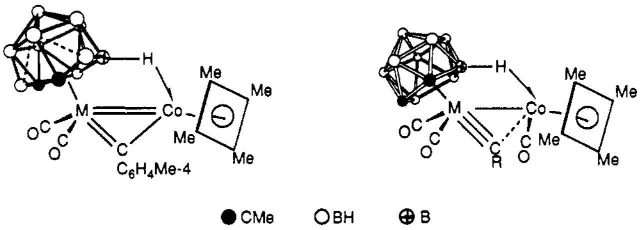


Figure 2. Structure of $[MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (**7b**), showing the crystallographic numbering system.

was confirmed by the appearance in the $^{11}B\{^1H\}$ NMR spectrum of a very broad resonance at δ 15.5 ppm of intensity corresponding to one boron nucleus. It was evident from the spectroscopic data that compound **7b** was an analogue of **7a**, although a B–H → Co signal could not be detected in its ^1H NMR spectrum. Such resonances are, however, often difficult to resolve, but the presence of the B–H → Co group was indicated by a fully coupled ^{11}B NMR spectrum, which revealed a diagnostic doublet signal at δ 16.5 ppm (J_{BH} = 78 Hz). In the ^{11}B NMR spectrum of $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ the two nonequivalent B–H → Co groups give rise to ^{11}B resonances at δ 15.00 (J_{BH} = 98 Hz) and 10.58 ppm (J_{BH} = 78 Hz).[3]



	M
7a	W
7b	Mo

	M	R
8a	W	$C_6H_4Me\text{-}4$
8b	Mo	$C_6H_4Me\text{-}4$
8c	W	Me

Fortunately, compound **7b** formed crystals suitable for an X-ray crystallographic study, so that the molecular structure could be fully established. Selected bond distances and angles are given in Table IV, and the molecule is shown in Figue 2. The Mo–Co bond [2.540 (1) Å] is spanned symmetrically on one side by the *p*-tolylmethylidyne group [C(7)–Mo 1.914 (7), C(7)–Co 1.915 (6) Å]. Indeed, the dimensions of the $\overline{\mathrm{MoC(7)Co}}$ ring are very similar to those of the $\overline{\mathrm{W(\mu\text{-}C)Co}}$ ring in $[WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$ [μ-C–W 1.913 (7), μ-C–Co 1.939 (8) Å].[4a]

Interest centers on the bonding of the *nido*-$C_2B_{10}H_{10}Me_2$ cage, which is η^6 coordinated to the molybdenum atom but is also linked to the cobalt center via the B(5)–H(5)–Co bridge. The atom H(5) was directly located in the X-ray study and its position refined. It is noteworthy that it is the BH group which is β to the carbon atoms of the $\overline{\mathrm{CBCB}\mathit{B}\mathrm{B}}$ ring which forms the three-center 2-electron bond with the cobalt atom. It is interesting to compare the ligating properties of the η^6-$C_2B_{10}H_{10}Me_2$ group in **7b**, formed as a single isomer, as determined by NMR spectroscopy, with the situation pertaining in $[NEt_4][WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_4(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$[13] and in $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$.[14] These two compounds are also each formed as a single isomer and contain B–H → Fe and B–H → Mo bonds, respectively. X-ray diffraction studies reveal that for each molecule it is the unique β BH group in the $\overline{\mathrm{CBCB}\mathit{B}\mathrm{B}}$ ring which forms the exo-polyhedral B–H → M (Fe or Mo) bond, as occurs in **7b**. A similar configuration for the B–H → Mo group probably occurs also in $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$,[6] although for this compound the structure has not been established by X-ray diffraction.

The nonplanar character of the $\overline{\mathrm{CBCBBB}}$ face of the ligand in **7b** is well evidenced by the appreciable variations in the distances of the six ring atoms from the molybdenum [Mo–C(1) 2.255 (7), Mo–C(2) 2.555 (7), Mo–B(3) 2.491 (9), Mo–B(4) 2.378 (8), Mo–B(5) 2.308 (8), Mo–B(6) 2.457 (7) Å]. The longest and shortest connectivities are associated with the two carbon atoms. Moreover, as expected, C(1), associated with the shortest separation, is the cage vertex with the lowest connectivity in the framework.[11-13] Additionally, the long connectivities (shown in Figure 2 by dotted lines) B(3)- - -B(8) [2.02 (1) Å] and B(6)- - -B(8)

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(14) Brew, S. A.; Carr, N.; Mortimer, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 811.

[1.98 (1) Å] involve the high-coordinate B(8) vertex and result in two square faces sited about C(1). The high connectivity associated with B(8) is manifested in the long B(8)–B(9) [1.88 (1) Å] and B(8)–B(12) [1.80(1) Å] separations. Moreover, the low-coordinate C(1) atom displays relatively short distances to B(3) [1.56 (1) Å] and B(6) [1.55 (1) Å]. These parameters are no doubt influenced by slippage of the cage leading to Mo–B(5) and Co–B(5) separations of 2.308 (8) and 2.24 (1) Å, respectively.

The molybdenum atom carries two terminally bound CO groups, and the cobalt atom is ligated by the η^4-C_4Me_4 ring. Indeed, the B–H → Co (η^4-C_4Me_4) unit present in compound **7b** has been found previously in [$CoRh(CO)_2(PPh_3)(\eta^4$-$C_4Me_4)(\eta^5$-$C_2B_9H_{11})$].[7]

The ^1H and $^{13}C\{^1H\}$ NMR data for **7a** and **7b** are in accord with the structure of the latter established by X-ray diffraction. In the $^{13}C\{^1H\}$ spectrum characteristic resonances for the μ-C nuclei of the alkylidyne groups occur at δ 323.2 (**7a**) and 337.1 ppm (**7b**). The spectra of both complexes reveal two CO ligands and six signals for the C_6H_4 rings. This latter feature is in accord[6] with restricted rotation about the μ-C–C^1(C_6H_4Me-4) bond, with the ring lying orthogonal to the Co–Mo bond (Figure 2).

During the course of the work described herein, we investigated reactions of the salts **1** with [$Co(C_2H_4)_2(\eta^5$-$C_5Me_5)$] but we were unable to isolate stable products akin to the complexes **3** and **4**. However, as with the reagents **2**, the salts **1** did afford stable dimetal species upon treatment with [$Co(CO)_2(NCMe)(\eta^4$-$C_4Me_4)$][PF_6]. The complexes [$MCo(\mu$-CR$)(CO)_3(\eta^4$-$C_4Me_4)(\eta^5$-$C_2B_9H_9Me_2)$] (**8a**, M = W, R = C_6H_4Me-4; **8b**, M = Mo, R = C_6H_4Me-4; **8c**, M = W, R = Me) were characterized by the data given in Tables I and II. The IR spectrum of each complex shows three CO stretching bands. In further agreement with the presence of three carbonyl ligands, the $^{13}C\{^1H\}$ NMR spectra of these products display three CO resonances. The $^{13}C\{^1H\}$ NMR spectra also display diagnostic peaks for the μ-C nuclei at δ 288.7 (**8a**), 303.4 (**8b**), and 296.0 ppm (**8c**). These chemical shifts, however, are in the region for semibridging rather than fully bridging alkylidyne groups, as discussed elsewhere.[5d,f,10]

The presence of the exo-polyhedral B–H → Co bonds is established by the ^1H, $^{11}B\{^1H\}$, and ^{11}B NMR spectra. In the ^1H spectra high-field quartet resonances are seen at δ −7.70 (**8a**), −8.19 (**8b**), and −7.67 ppm (**8c**), with J_{BH} values of 77, 76, and 75 Hz, respectively. The $^{11}B\{^1H\}$ NMR spectra show diagnostic signals for B–H → Co groups at δ 13.9 (**8a**), 15.4 (**8b**), and 12.4 ppm (**8c**), which in fully coupled ^{11}B spectra display ^1H–^{11}B couplings of 77, 76, and 75 Hz, respectively. These data, however, do not establish whether the B–H → Co bonds involve a BH group in the face of the *nido*-C_2B_9 fragment that is α or β to a CMe fragment. With either structure there is no mirror plane through the metal atoms, the β-BH group, and the midpoint of the connectivity between the two CMe groups. The absence of such a mirror plane results in nonequivalence of the CMe groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra, as is observed (Table II). These spectra, therefore, cannot be used to distinguish between the two possibilities. We have chosen arbitrarily to depict structures where it is a BH group α to a carbon in the $\overline{\mathrm{CC}\mathit{B}\mathrm{BB}}$ ring which forms the B–H → Co bridge system, because this arrangement has been established by X-ray diffraction in the related molecule [$CoRh(CO)_2(PPh_3)(\eta^4$-$C_4Me_4)(\eta^5$-$C_2B_9H_{11})$].[7]

It is interesting to note that whereas the dimetal species **8** are formally 34 valence electron dimetal compounds, the dimetal complexes **7** are electronically unsaturated with 32 valence electrons. For both types of compounds the cages can be regarded as contributing 6 electrons to the dimetal systems. It was mentioned earlier that the Mo–Co distance in **7b** is 2.540 (1) Å. In agreement with the unsaturation of this complex, this metal–metal distance is unusually short. Allowing for the covalent radii of Mo and W being the same, it is interesting to compare the Mo–Co separation in **7b** with the W–Co bond length [2.758 (1) Å] in the electronically saturated 34 valence electron complex [$WCo(\mu$-CC_6H_4Me-4$)(CO)_3(\eta^5$-$C_5H_5)(\eta^5$-$C_5Me_5)$].[4a]

The new compounds described in this paper add significantly to the range of mixed-metal complexes accessible via the salts **1** or **2**. This is especially true of the compounds derived from the reagent **2**, where it is now established that the C_2B_{10} cage ligand can adopt either a spectator role in the polynuclear metal species, as found in complexes **3** or **5**, or form exo-polyhedral B–metal or B–H → metal bonds, as in the species **4** and **7**, respectively.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk-line techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. Petroleum ether refers to that fraction of bp 40–60 °C. Chromatography columns (ca. 15 cm in length and 2 cm in diameter) were packed with either alumina (Brockman activity II) or Florisil (BDH, 100–200 mesh). The reagents **1** and **2a** were prepared as previously described.[13-15] The salt **2b** was obtained from [$Mo(\equiv CC_6H_4$Me-4$)Cl(CO)_2(NC_5H_4$Me-4$)_2$] by using the procedure employed to obtain **2a**.[13] The compounds [$Co(C_2H_4)_2(\eta^5$-$C_5Me_5)$],[16] [$Co(CO)_2(NCMe)(\eta^4$-$C_4Me_4)$][PF_6],[17] and [$AuCl(PPh_3)$][18] were prepared by literature methods. The $HBF_4 \cdot Et_2O$ used for protonation was purchased from Aldrich (85% HBF_4 in Et_2O). Analytical and other data for the new compounds are given in Table I.

Instrumentation. NMR spectra were recorded at ambient temperatures, unless otherwise stated, on JEOL JNM FX90Q, GX270, and GX400 spectrometers. The chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra are referenced to $SiMe_4$, and those for the $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ spectra, measured in CD_2Cl_2–CH_2Cl_2, are positive to high frequency of $BF_3 \cdot Et_2O$ (external) and 85% H_3PO_4 (external), respectively. The J_{BH} values listed below were obtained from fully coupled ^{11}B spectra. IR spectra were measured with a Perkin-Elmer FT1600 spectrometer.

Synthesis of the Salts [NEt_4][$MCo(\mu$-CC_6H_4Me-4$)(CO)_2(\eta^5$-$C_5Me_5)(\eta^6$-$C_2B_{10}H_{10}Me_2)$] (M = Mo, W). (i) A mixture of **2a** (0.30 g, 0.47 mmol) and [$Co(C_2H_4)_2(\eta^5$-$C_5Me_5)$] (0.12 g, 0.48 mmol) in CH_2Cl_2 (15 mL) was stirred for 3 h. After filtration through a Celite pad (4 cm), the resulting purple solution was reduced in volume in vacuo to ca. 5 mL. Addition of petroleum ether (ca. 30 mL) and cooling to ca. −20 °C afforded purple *microcrystals* of [NEt_4][$WCo(\mu$-CC_6H_4Me-4$)(CO)_2(\eta^5$-$C_5Me_5)(\eta^6$-$C_2B_{10}H_{10}Me_2)$] (**3a**) (0.32 g).

(ii) A mixture of **2b** (0.34 g, 0.61 mmol) and [$Co(C_2H_4)_2(\eta^5$-$C_5Me_5)$] (0.16 g, 0.64 mmol) in CH_2Cl_2 (25 mL) was stirred until the IR spectrum showed no bands due to the salt **2b** (ca. 3 h). The volume of solvent was reduced in vacuo to ca. 5 mL, and petroleum ether (ca. 25 mL) was added to precipitate [NEt_4][$MoCo(\mu$-CC_6H_4Me-4$)(CO)_2(\eta^5$-$C_5Me_5)(\eta^6$-$C_2B_{10}H_{10}Me_2)$] (**3b**) as a deep purple powder, slightly contaminated with decomposition products.

Protonation of the Compounds [NEt_4][$MCo(\mu$-CC_6H_4Me-4$)(CO)_2(\eta^5$-$C_5Me_5)(\eta^6$-$C_2B_{10}H_{10}Me_2)$] (M = Mo, W). (i) A CH_2Cl_2 (15 mL) solution of **3a** (0.17 g, 0.26 mmol) was cooled to ca. −50 °C, and $HBF_4 \cdot Et_2O$ (42 μL, 0.24 mmol) was added. The solution was warmed to room temperature and solvent removed in vacuo.

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Table V. Crystallographic Data for 5a and 7b[a]

	5a	**7b**
cryst dimens/mm	0.25 × 0.20 × 0.10	0.70 × 0.20 × 0.15
formula	$C_{42}H_{53}AuB_{10}CoO_2PW$	$C_{22}H_{35}B_{10}CoMoO_2$
M_r	1168.7	594.5
cryst color, shape	brown prisms	brown plates
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	10.007 (4)	16.276 (2)
b/Å	10.791 (3)	11.870 (2)
c/Å	21.642 (7)	15.791 (4)
α/deg	87.81 (2)	
β/deg	84.58 (3)	112.60 (2)
γ/deg	73.10 (2)	
V/Å^3	2226 (1)	2817 (1)
Z	2	4
d_{calcd}/g cm^{-3}	1.74	1.40
μ(Mo Kα)/cm^{-1}	63.5	10.4
F(000)/e	1132	1208
T/K	298	298
no. of reflns measd	7769	5372
no. of unique reflns	7570	4927
no. of obsd reflns	4185	3006
criterion for obsd n [$F_o \geq n\sigma(F_o)$]	$n = 3$	$n = 4$
R (R')[b]	0.072 (0.057)	0.045 (0.041)
final electron density diff features (max/min)/e Å^{-3}	1.3/-2.4	0.4/-0.4

[a] Data collected on a Siemens R3m/V four-circle diffractometer operating in the θ-2θ scan mode in the range $4 \leq 2\theta \leq 50°$; graphite monochromated Mo Kα X radiation, $\bar{\lambda} = 0.71069$ Å. Refinement was by full-matrix least-squares with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ with $g = 0.0007$ (**5a**), 0.0005 (**7b**); $\sigma^2(F_o)$ is the variance in F_o due to counting statistics; g was chosen so as to minimize variation in $\sum w(|F_o| - |F_c|)^2$ with $|F_o|$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R' = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$.

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 5a

atom	x	y	z	U(eq)[a]
Au	1614 (1)	−2060 (1)	2645 (1)	34 (1)
W	1200 (1)	329 (1)	1971 (1)	27 (1)
Co	3144 (3)	−1748 (3)	1643 (1)	29 (1)
P	1463 (7)	−2865 (6)	3646 (3)	39 (2)
O(5)	2680 (18)	1025 (17)	711 (8)	71 (8)
O(6)	4047 (17)	100 (14)	2514 (7)	49 (7)
B(3)	−188 (32)	2495 (24)	1655 (12)	46 (11)
B(4)	741 (32)	1983 (22)	2821 (12)	45 (11)
B(5)	−289 (30)	823 (24)	2947 (12)	40 (11)
B(6)	−1218 (27)	575 (24)	2335 (11)	37 (10)
B(7)	−2046 (31)	1531 (22)	2986 (12)	36 (11)
B(8)	−2658 (24)	1913 (24)	2274 (13)	39 (10)
B(9)	−1978 (26)	3156 (23)	1930 (11)	35 (10)
B(10)	−742 (38)	3388 (26)	2463 (13)	57 (14)
B(11)	−1016 (29)	2403 (24)	3197 (12)	47 (11)
B(12)	−2375 (32)	3098 (28)	2729 (15)	65 (13)
C(1)	−1264 (23)	1555 (19)	1729 (10)	40 (9)
C(2)	919 (25)	2492 (18)	2156 (11)	44 (9)
C(3)	−1567 (23)	1211 (19)	1093 (9)	41 (9)
C(4)	1989 (26)	3195 (22)	1957 (12)	67 (12)
C(5)	2220 (21)	723 (18)	1192 (10)	29 (5)
C(6)	3027 (31)	42 (22)	2256 (12)	61 (12)
C(7)	1166 (22)	−1343 (18)	1606 (8)	32 (8)
C(8)	477 (20)	−2125 (16)	1305 (9)	27 (7)
C(9)	280 (22)	−1906 (19)	686 (9)	36 (8)
C(10)	−412 (23)	−2580 (22)	376 (9)	46 (9)
C(11)	−1023 (22)	−3502 (20)	687 (11)	39 (9)
C(12)	−844 (24)	−3640 (19)	1286 (10)	41 (9)
C(13)	−100 (22)	−3026 (19)	1600 (10)	37 (8)
C(14)	−1776 (25)	−4196 (23)	336 (12)	61 (11)
C(15)	5218 (25)	−2726 (21)	1828 (11)	44 (10)
C(16)	4479 (22)	−3624 (19)	1690 (12)	40 (10)
C(17)	4032 (22)	−3329 (22)	1073 (10)	39 (9)
C(18)	4494 (23)	−2283 (23)	863 (10)	43 (10)
C(19)	5252 (22)	−1906 (18)	1301 (10)	36 (9)
C(20)	5968 (25)	−2721 (23)	2409 (11)	63 (11)
C(21)	4281 (25)	−4696 (20)	2110 (11)	58 (11)
C(22)	3399 (25)	−4214 (21)	753 (12)	66 (12)
C(23)	4340 (26)	−1804 (24)	211 (10)	64 (12)
C(24)	5953 (25)	−877 (23)	1208 (11)	61 (12)
C(25)	2718 (32)	−4434 (24)	3804 (10)	54 (12)
C(26)	3813 (29)	−4497 (23)	4134 (12)	61 (12)
C(27)	4813 (25)	−5713 (25)	4197 (11)	57 (11)
C(28)	4623 (27)	−6825 (24)	3984 (13)	57 (11)
C(29)	3469 (36)	−6753 (29)	3689 (13)	79 (16)
C(30)	2496 (33)	−5569 (29)	3575 (15)	85 (16)
C(31)	1928 (24)	−1816 (20)	4167 (9)	40 (9)
C(32)	2746 (26)	−1067 (19)	3966 (11)	49 (10)
C(33)	3168 (36)	−291 (26)	4387 (16)	89 (17)
C(34)	2597 (43)	−188 (28)	4978 (17)	107 (20)
C(35)	1823 (34)	−908 (29)	5187 (13)	82 (16)
C(36)	1408 (27)	−1728 (25)	4794 (12)	65 (12)
C(37)	−256 (25)	−2951 (26)	3892 (10)	50 (10)
C(38)	−1385 (27)	−2168 (24)	3626 (12)	55 (11)
C(39)	−2698 (27)	−2166 (24)	3818 (12)	54 (11)
C(40)	−3013 (31)	−2995 (31)	4264 (14)	81 (15)
C(41)	−1906 (37)	−3728 (35)	4510 (17)	117 (20)
C(42)	−541 (31)	−3858 (32)	4352 (17)	119 (18)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The residue was extracted with CH_2Cl_2–petroleum ether (3 mL, 1:2) and chromatographed on alumina. Elution with the same solvent mixture gave a deep green eluate, which upon removal of solvent in vacuo and crystallization from CH_2Cl_2–petroleum ether (20 mL, 1:10) gave green *microcrystals* of [WCo(μ-CC_6H_4Me-4)(μ-σ:η^6-$C_2B_{10}H_9Me_2$)$(CO)_2$(η^5-C_5Me_5)] (**4a**) (0.10 g). $^{11}B\{^1H\}$ NMR: δ 69.0 (1 B, B–Co), +0.1 to −21.7 ppm (br, 9 B, BH).

(ii) Compound **3b** was prepared in situ from **2b** (0.26 g, 0.46 mmol) and [Co$(C_2H_4)_2$(η^5-C_5Me_5)] (0.12 g, 0.48 mmol) in CH_2Cl_2 (20 mL). The solution was cooled to ca. −50 °C, and HBF_4·Et_2O (80 μL, 0.46 mmol) was added. After warming to room temperature, solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2–petroleum ether (8 mL, 1:2) and chromatographed at 0 °C on alumina. Elution with the same solvent mixture gave a green eluate, which upon removal of solvent in vacuo yielded green *microcrystals* of [MoCo(μ-CC_6H_4Me-4)(μ-σ:η^6-$C_2B_{10}H_9Me_2$)$(CO)_2$(η^5-C_5Me_5)] (**4b**) (0.18 g). $^{11}B\{^1H\}$ NMR: δ 72.1 (1 B, Co–B), −3.2 to −21.1 ppm (br, 9 B, BH).

Reactions with [AuCl(PPh$_3$)]. (i) A THF (15 mL) solution containing **3a** (0.15 g, 0.18 mmol), [AuCl(PPh_3)] (0.09 g, 0.18 mmol), and $TlBF_4$ (0.07 g 0.24 mmol) was stirred for 2 h. Solvent was removed in vacuo, the residue was extracted with CH_2Cl_2 (10 mL), and the extracts were filtered through a Celite pad (3 cm). Removal of solvent in vacuo gave a brown oily residue, which was dissolved in CH_2Cl_2–petroleum ether (5 mL, 1:1) and chromatographed on alumina. Elution with the same solvent mixture removed a brown eluate, which after removal of solvent in vacuo yielded brown *microcrystals* of [WCoAu(μ_3-CC_6H_4Me-4)$(CO)_2$(PPh_3)(η^5-C_5Me_5)(η^6-$C_2B_{10}H_{10}Me_2$)] (**5a**) (0.18 g). $^{31}P\{^1H\}$ NMR: δ 54.3 ppm.

(ii) A mixture of the salt **2b** (0.13 g, 0.23 mmol) and [Co$(C_2H_4)_2$(η^5-C_5Me_5)] (0.06 g, 0.24 mmol) was dissolved in CH_2Cl_2 (15 mL), and the solution was stirred for 4 h, after which solvent was removed in vacuo and replaced by THF (10 mL). This solution was added to a suspension of [AuCl(PPh_3)] (0.12 g, 0.24 mmol) and $TlBF_4$ (0.08 g, 0.27 mmol) in THF (10 mL), and the resulting mixture was stirred for 1 h. After removal of solvent in vacuo, the product was extracted with CH_2Cl_2 (10 mL) and the extracts were filtered through a Celite pad (3 cm). The volume of solvent was reduced in vacuo to ca. 5 mL, and the solution was chromatographed on alumina. Elution with CH_2Cl_2 removed a brown band, which after removal of solvent in vacuo afforded brown *microcrystals* of [MoCoAu(μ_3-CC_6H_4Me-4)$(CO)_2$(PPh_3)(η^5-C_5Me_5)(η^6-$C_2B_{10}H_{10}Me_2$)] (**5b**) (0.16 g), after crystallization from CH_2Cl_2–petroleum ether (10 mL, 1:4) at −20 °C. $^{31}P\{^1H\}$ NMR: δ 51.9 ppm.

Reactions of the Salt [Co(CO)$_2$(NCMe)(η^4-C$_4$Me$_4$)][PF$_6$] with the Reagents 1 and 2. (i) A CH_2Cl_2 (20 mL) solution of **2a** (0.28 g, 0.44 mmol) and [Co$(CO)_2$(NCMe)(η^4-C_4Me_4)][PF_6] (0.18 g, 0.44 mmol) was stirred for 24 h, after which time solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2–petroleum

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 7b

atom	x	y	z	U(eq)[a]
Mo	2173 (1)	4555 (1)	6785 (1)	36 (1)
Co	2745 (1)	6003 (1)	8064 (1)	38 (1)
O(5)	870 (4)	2537 (5)	6680 (5)	97 (3)
O(6)	503 (4)	5981 (5)	5556 (4)	89 (3)
B(3)	2849 (5)	3208 (7)	6028 (5)	49 (3)
B(4)	2821 (5)	5692 (6)	5967 (5)	44 (3)
B(5)	3475 (5)	5570 (7)	7160 (5)	45 (3)
B(6)	3756 (5)	4206 (7)	7701 (5)	49 (3)
B(7)	4492 (5)	4961 (8)	7293 (5)	56 (3)
B(8)	4149 (5)	3493 (8)	6785 (5)	58 (4)
B(9)	3582 (5)	3764 (7)	5523 (5)	52 (3)
B(10)	3477 (6)	5200 (7)	5364 (5)	52 (3)
B(11)	4002 (5)	5920 (7)	6408 (5)	54 (3)
B(12)	4453 (5)	4620 (8)	6205 (5)	61 (4)
C(1)	3229 (4)	3213 (6)	7101 (4)	49 (3)
C(2)	2631 (4)	4433 (5)	5411 (4)	44 (2)
C(3)	3225 (5)	2075 (6)	7567 (5)	76 (4)
C(4)	1860 (4)	4321 (6)	4478 (4)	57 (3)
C(5)	1341 (5)	3243 (6)	6691 (5)	61 (4)
C(6)	1099 (4)	5448 (6)	5986 (5)	54 (3)
C(7)	1780 (4)	4951 (5)	7744 (4)	39 (2)
C(8)	1115 (4)	4696 (5)	8136 (4)	39 (2)
C(9)	1304 (4)	3924 (6)	8853 (5)	53 (3)
C(10)	675 (5)	3644 (6)	9208 (5)	59 (3)
C(11)	−168 (4)	4119 (6)	8859 (5)	52 (3)
C(12)	−364 (4)	4860 (6)	8150 (5)	51 (3)
C(13)	254 (4)	5145 (5)	7783 (4)	46 (3)
C(14)	−828 (5)	3828 (8)	9279 (5)	79 (4)
C(15)	2922 (4)	6431 (5)	9381 (4)	47 (3)
C(16)	2286 (4)	7139 (6)	8737 (4)	46 (3)
C(17)	2969 (4)	7604 (5)	8466 (4)	47 (3)
C(18)	3614 (4)	6883 (5)	9137 (4)	41 (2)
C(19)	2968 (5)	5708 (7)	10169 (4)	72 (4)
C(20)	1364 (4)	7500 (6)	8561 (5)	63 (3)
C(21)	3011 (5)	8551 (6)	7862 (4)	62 (3)
C(22)	4608 (4)	6799 (6)	9546 (4)	63 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ether (10 mL, 1:2), and the solution was chromatographed on alumina. Eluting with the same solvent mixture removed a trace of unidentified material, followed by a brown fraction. Removal of solvent in vacuo from the latter and crystallization from CH_2Cl_2–petroleum ether (10 mL, 1:4) gave brown *microcrystals* of [$WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)$] (**7a**) (0.26 g). $^{11}B\{^1H\}$ NMR: δ 15.5 (vbr, 1 B, B–H → Co, J_{BH} not resolved), +3.5 to −21.0 ppm (br, 9 B, BH).

(ii) With a similar procedure, **2b** and [$Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)$][$PF_6$] (0.10 g, 0.24 mmol) gave brown *crystals* of [$MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta^4\text{-}C_4Me_4)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)$] (**7b**) (0.12 g). $^{11}B\{^1H\}$ NMR: δ 16.5 (br, 1 B, B–H → Co, J_{BH} = 78 Hz), +0.1 to −15.9 ppm (br, 9 B, BH).

(iii) The compounds **1a** (0.39 g, 0.61 mmol) and [$Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)$][$PF_6$] (0.25 g, 0.61 mmol) were dissolved in THF (40 mL), and the mixture was stirred for 10 h. Solvent was removed in vacuo, and the residue dissolved in CH_2Cl_2–petroleum ether (10 mL, 1:4) and chromatographed at −40 °C on Florisil. Elution with the same solvent mixture removed a trace of unidentified material, followed by a brown fraction. Removal of solvent in vacuo from the latter afforded brown *microcrystals* of [$WCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)$] (**8a**) (0.18 g). $^{11}B\{^1H\}$ NMR: δ 13.9 (1 B, B–H → Co, J_{BH} = 77 Hz), −5.1 to −19.0 ppm (br, 8 B, BH).

(iv) The compound [$MoCo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)$] (**8b**) (0.17 g) was similarly obtained from **1b** (0.26 g, 0.48 mmol) and [$Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)$][$PF_6$] (0.20 g, 0.49 mmol). $^{11}B\{^1H\}$ NMR: δ 15.4 (1 B, B–H → Co, J_{BH} = 76 Hz), −6.1 to −20.2 ppm (br, 8 B, BH).

(v) Similarly, the reagents **1c** (0.37 g, 0.68 mmol) and [$Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)$][$PF_6$] (0.27 g, 0.66 mmol) in THF (50 mL) afforded brown *microcrystals* of [$WCo(\mu\text{-}CMe)(CO)_3(\eta^4\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_9Me_2)$] (**8c**) (0.24 g) after a similar workup. $^{11}B\{^1H\}$ NMR: δ 12.4 (1 B, B–H → Co, J_{BH} = 75 Hz), −5.3 to −19.6 ppm (br, 8 B, BH).

Crystal Structure Determinations. The crystal data and other experimental details for the compounds **5a** and **7b** are summarized in Table V. Crystals of **5a** were grown from CH_2Cl_2–petroleum ether (1:4, ca. −20 °C), and those of **7b**, by the slow diffusion of petroleum ether into a CH_2Cl_2 solution of the complex at ambient temperatures. All data were corrected for Lorentz, polarization, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[19] The structures were solved by Patterson and difference Fourier methods, by which all non-hydrogen atoms were located and refined anisotropically except the atom C(5) of compound **5a**, which would not refine anisotropically and was therefore refined with an isotropic thermal parameter. For compound **7b** the hydrogen atom of the B–H → Co linkage [H(5)] was directly located and refined with a fixed thermal parameter (ca. $1.2U_{eq}$ of the parent boron atom) but without positional constraints. All other hydrogen atoms were included at calculated positions (C–H 0.96, B–H 1.10 Å)[20] with fixed isotropic thermal parameters (ca. $1.2U_{eq}$ of the parent carbon or boron atom).

Calculations were performed on a Digital micro-vax II computer with the SHELXTL PLUS system of programs.[19] Scattering factors with corrections for anomalous dispersion were taken from ref 21. Atomic coordinates for **5a** and **7b** are given in Tables VI and VII, respectively.

Supplementary Material Available: Complete tables of bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **5a** and **7b** (13 pages); lists of observed and calculated structure amplitudes for **5a** and **7b** (45 pages). Ordering information is given on any current masthead page.

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(19) Sheldrick, G. M. SHELXTL PLUS programs used with the Siemens R3m/V X-ray system.

(20) Sherwood, P. BHGEN, a program used for the calculation of idealized H positions for carbaborane fragments. University of Bristol, 1986.

(21) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.