Carbaborane Dimetal Complexes of Molybdenum and Tungsten: Insertion of a Bridging Alkylidyne Ligand into a Boron–Hydrogen Bond

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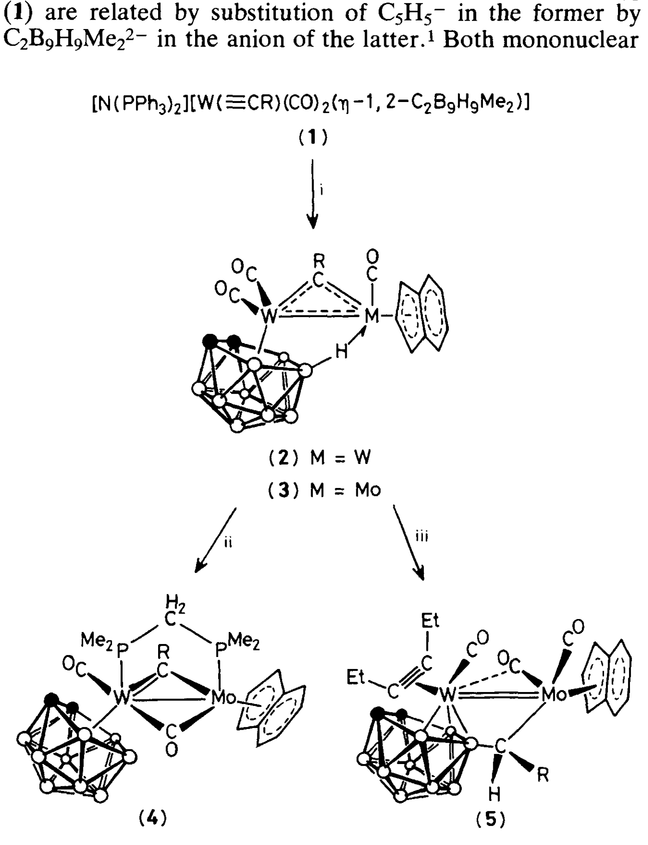
The salt $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (R = $C_6H_4Me\text{-}4$) reacts with the compounds $[M(CO)_2(NCMe)_2(\eta\text{-}C_9H_7)][BF_4]$ (M = Mo or W, $\eta\text{-}C_9H_7$ = indenyl) to afford dimetal complexes $[MW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_9H_7)(\eta\text{-}C_2B_9H_9Me_2)]$; treatment of the molybdenum–tungsten species with hex-3-yne affords $[MoW\{\mu\text{-}\sigma,\eta^3\text{-}CH(R)(C_2B_9H_8Me_2)\}(CO)_3(\eta\text{-}EtC_2Et)(\eta\text{-}C_9H_7)]$, structurally identified, as was its precursor, by *X*-ray diffraction.

The compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$) and the salt $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (**1**) are related by substitution of $C_5H_5^-$ in the former by $C_2B_9H_9Me_2^{2-}$ in the anion of the latter.[1] Both mononuclear tungsten species are isolobal[2] with alkynes, and may be used to prepare compounds containing metal–metal bonds spanned by tolylmethylidyne ligands. The various syntheses resemble reactions of alkynes, following the isolobal model.[3] Herein we report reactions of (**1**) with the salts $[M(CO)_2(NCMe)_2(\eta\text{-}C_9H_7)][BF_4]$ (M = W or Mo, $\eta\text{-}C_9H_7$ = indenyl).[4] The latter react with alkynes yielding products in which the alkynes



Scheme 1. i, $[M(CO)_2(NCMe)_2(\eta\text{-}C_9H_7)][BF_4]$ in CH_2Cl_2; ii, $Me_2PCH_2PMe_2$ in $(CH_2)_4O$; iii, EtC_2Et in PhMe.

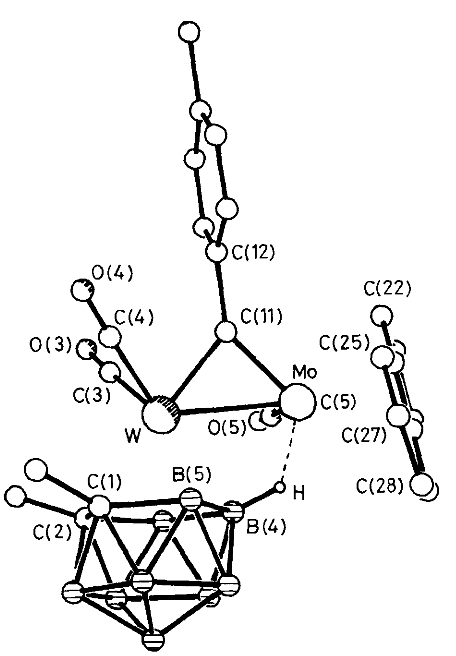


Figure 1. Molecular structure of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_9H_7)(\eta\text{-}C_2B_9H_9Me_2)]$ (**3**). Dimensions: Mo–W 2.658(2), Mo–C(11) 1.943(17), W–C(11) 2.025(13), W–C(1) 2.456(13), W–C(2) 2.451(14), W–B(3) 2.354(20), W–B(4) 2.264(19), W–B(5) 2.351(16), Mo–B(4) 2.500(16), Mo–H 1.720, B(4)–H 1.02 Å.

function as four-electron donors, as does $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ in certain instances.[5]

In CH_2Cl_2 at room temperature, (**1**) and either of the two salts $[M(CO)_2(NCMe)_2(\eta\text{-}C_9H_7)][BF_4]$ (M = Mo or W) yield green crystalline neutral dimetallic complexes (**2**) or (**3**) (Scheme 1). In their n.m.r. spectra these compounds† show characteristic signals for B(μ-H)M and μ-*C*R groups.‡ *X*-Ray diffraction studies§ established the presence of these features and also that both complexes are essentially isostructural. Figure 1 shows the molybdenum–tungsten species (**3**).

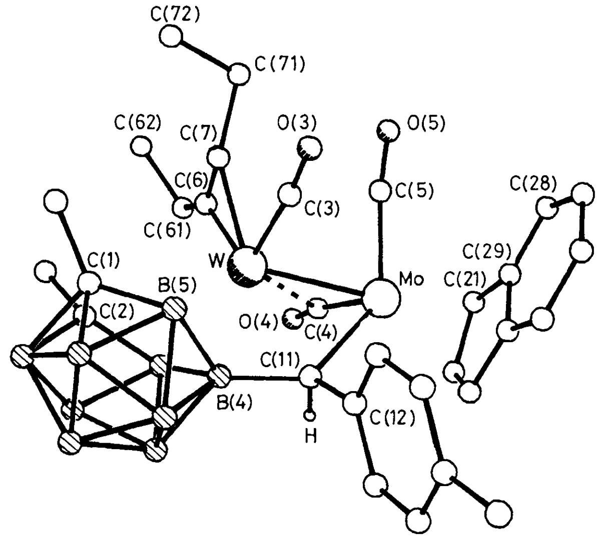


Figure 2. Molecular structure of $[MoW\{\mu\text{-}\sigma,\eta^3\text{-}CH(C_6H_4Me\text{-}4)(C_2B_9H_8Me_2)\}(CO)_3(\eta\text{-}EtC_2Et)(\eta\text{-}C_9H_7)]$ (**5**). Dimensions: Mo–W 2.604(1), Mo–C(11) 2.317(4), W–C(11) 2.339(4), W–C(6) 2.079(4), W–C(7) 2.119(6), W–B(3) 2.463(5), W–B(4) 2.174(4), W–B(5) 2.450(5), W----C(1) 3.038, W----C(2) 3.054, C(11)–H 1.02(4) Å; Mo–C(4)–O(4) 168.1(4)°.

The Mo–W bond [2.658(2) Å] is bridged by the CC_6H_4Me-4 group [μ-C–Mo 1.943(17), μ-C–W 2.025(13) Å]. The Mo–W and μ-C–Mo distances are appreciably shorter than those found[6] in $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [Mo–W 2.938(1), μ-C–Mo 2.196(12) Å], a complex having two dimetallacyclopropene ring systems in which the metal atoms have 18 valence-electron configurations. The smaller dimensions of the $\overline{Mo\{\mu\text{-}C(11)\}W}$ ring in (**3**) reflect multiple bond character in all three linkages, associated with the complex being a 32 rather than a 34 valence-electron dimetal species. The $\eta\text{-}C_2B_9H_9Me_2$ ligand is essentially symmetrically bonded to the tungsten atom, but with the hydrogen atom attached to B(4) forming a three-centre two-electron B–H ⇀ Mo interaction. This is the first example of such *exo*-polyhedral bridge-bonding in a heteronuclear dimetal compound, but has been previously observed[7] in the homonuclear dimetal compounds $[Rh_2(PR_3)_2(\eta\text{-}C_2B_9H_{11})_2]$ ($PR_3 = PPh_3$, PEt_3, or PMe_2Ph). In their ^1H n.m.r. spectra, the latter show resonances for B–H ⇀ Rh in the range δ −4.0 to −9.0. The corresponding signal in the spectrum of (**3**) is at δ −7.98 p.p.m.

A study of the reactivity of (**2**) and (**3**) shows that the carbaborane cage is not just a spectator ligand, the B(μ-H)M sites being the focus of interesting reactions. Thus with $Me_2PCH_2PMe_2$, compound (**3**) affords the brown crystalline complex (**4**)‡ which no longer contains a B–H ⇀ Mo bond. With hex-3-yne, (**3**) gives a red-purple compound (**5**)‡ (Scheme 1); the nature of which was established by *X*-ray diffraction.§ The structure is unprecedented; it is shown in Figure 2. The alkylidyne group in (**3**) has inserted into the cage B(4)–H bond with resulting 'slippage' of the carbaborane ligand, so that in (**5**) it is η^3-bound to the tungsten. This slippage is accompanied by a general tilting of the C_2B_3 face away from the metal centre, and by a slight fold across B(3)–B(5) (dihedral angle 6.7°). The very short metal–metal distance [2.604(1) Å] probably corresponds to a Mo=W bond. The EtC_2Et molecule is co-ordinated to the W atom, and the

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† In solution, both (**2**) and (**3**) exist as a mixture of two isomers one of which predominates, as was revealed by the observation of additional peaks in the n.m.r. spectra. Isomers could result from two different orientations of the $M(CO)(\eta\text{-}C_9H_7)$ groups with respect to the $\overline{W(\mu\text{-}CR)M}$ rings.

‡ *Selected spectroscopic data* [i.r. measured in CH_2Cl_2, n.m.r. measured in CD_2Cl_2 (^1H, $^{11}B\{^1H\}$, $^{31}P\{^1H\}$) or CD_2Cl_2—CH_2Cl_2 ($^{13}C\{^1H\}$), coupling constants in Hz, chemical shifts are to high frequency and relative to $BF_3 \cdot Et_2O$ (external) for $^{11}B\{^1H\}$ and to 85% H_3PO_4 (external) for $^{31}P\{^1H\}$, only n.m.r.signals for major isomer of each species listed]; Compound (**2**), ν_{CO} (max.) at 2 002s, 1 952s, and 1 929sh cm^{-1}, ν_{BH} (max.) at 2 566m cm^{-1}. N.m.r.: ^1H, δ 7.32—6.72 (m, 8 H, C_6H_4 and C_9H_7), 6.00 (m, 1 H, C_9H_7), 5.80 [t, 1 H, *J*(HH) 3], 5.48 (m, 1 H, C_9H_7), 2.60 (s, 3 H, Me-4), 2.10 (s, 3 H, CMe), 2.02 (s, 3 H, CMe), and −8.50 [q, 1 H, B(μ-H)W, *J*(BH) 65]; $^{13}C\{^1H\}$ (at −40 °C), δ 367.6 (μ-C), 221.1 [WCO, *J*(WC) 153], 213.8, 211.4 (WCO), 32.0, 31.1 (C*Me*), and 20.6 p.p.m. (Me-4); $^{11}B\{^1H\}$, δ 16.2 [*B*(μ-H)W] and −9.5 p.p.m. ($C_2B_8H_8Me_2$). Compound (**3**), ν_{CO} (max.) at 2 002s, 1 956s, and 1 933m cm^{-1}, ν_{BH} (max.) at 2 566m cm^{-1}. N.m.r.: ^1H, δ −7.98 [q, 1 H, B(μ-H)Mo, *J*(BH) 84]; $^{13}C\{^1H\}$, δ 381.7 (μ-C), 226.2, 222.5, and 212.9 p.p.m. (CO); $^{11}B\{^1H\}$, δ 14.1 [*B*(μ-H)Mo] and −10.9 p.p.m. ($C_2B_8H_8Me_2$). Compound (**4**), ν_{CO} (max.) at 1 923s and 1 765s cm^{-1}, ν_{BH} (max.) at 2 546m cm^{-1}. N.m.r.: $^{13}C\{^1H\}$, δ 375.1 (μ-C), 274.8 (μ-CO), and 242.1 [d, WCO, *J*(PC) 18], and 56.3 p.p.m. [d of d, CH_2, *J*(PC) 31 and 31]; $^{31}P\{^1H\}$, δ 21.6 [d, PMo, *J*(PP) 40] and −3.9 p.p.m. [d, PW, *J*(PP) 40, *J*(WP) 389]. Compound (**5**), ν_{CO} (max.) at 1 994m, 1 942s, and 1 886m cm^{-1}, ν_{BH} (max.) at 2 561m cm^{-1}. N.m.r.: ^1H, δ 5.01 (s br, 1 H, μ-C*H*); $^{13}C\{^1H\}$, δ 233.9, 229.4, 223.5 (CO), 178.2, 172.0 (EtC_2Et), and 73.1 p.p.m. (br, μ-C); $^{11}B\{^1H\}$, δ 34.0 (μ-CB), −3.0 (5 B), −16.9 (2 B), and −21.1 p.p.m. (1 B).

§ *Crystal data for* (**3**): $C_{24}H_{29}B_9O_3MoW$, $M = 742.6$, monoclinic, $a = 14.178(5)$, $b = 16.346(7)$, $c = 14.526(8)$ Å, $\beta = 113.62(4)°$, $U = 3\,084(3)$ Å^3, $Z = 4$, $D_c = 1.60$ g cm^{-1}, $F(000) = 1\,431$, space group $P2_1/c$ (no. 14), $\mu(Mo\text{-}K_\alpha) = 42.3$ cm^{-1}, $R = 0.053$ ($R' = 0.054$) for 2 481 absorption corrected reflections (293 K, $2\theta \leqslant 40°$) measured on a Nicolet *P*3*m* diffractometer [$I \geqslant 2\sigma(I)$]; Mo-K_α *X*-radiation, graphite monochromator ($\lambda = 0.710\,69$ Å). The structure was solved by heavy atom (Patterson) and Fourier methods and refined using blocked-cascade least squares. Atom μ-H located, but positional parameters were not refined.

Crystal data for (**2**): $C_{24}H_{29}B_9O_3W_2$, $M = 830.5$, monoclinic, $a = 14.187(11)$, $b = 16.321(5)$, $c = 14.560(12)$ Å, $\beta = 113.76(6)°$, $U = 3\,086(3)$ Å^3, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,559$, space group $P2_1/c$ (no. 14), $\mu(Mo\text{-}K_\alpha) = 76.4$ cm^{-1}, $R = 0.065$ ($R' = 0.066$) for 3 135 absorption corrected reflections, [$2\theta \leqslant 45°$, $I \geqslant 2\sigma(I)$], measured as for (**3**). Parameters: W–W 2.660(2), μ-C–W 1.935(20) and 2.082 (16), μ-H–W 1.665, B(4)–H 1.37 Å.

Crystal data for (**5**): $C_{30}H_{39}B_9O_3MoW$, $M = 824.7$, triclinic, $a = 14.779(8)$, $b = 11.435(5)$, $c = 10.020(3)$ Å, $\alpha = 82.36(3)$, $\beta = 99.95(3)$, $\gamma = 104.39(3)°$, $U = 1\,608(1)$ Å^3, Z = 2, $D_c = 1.70$ g cm^{-3}, $F(000) = 808$, space group $P\bar{1}$ (no. 2), $\mu(Mo\text{-}K_\alpha) = 40.6$ cm^{-1}. $R = 0.038$ ($R' = 0.039$) for 6 913 absorption corrected reflections [190 K, $2\theta \leqslant 55°$, $I \geqslant 4\sigma(I)$] measured and refined as for (**3**). Atoms C(71) and C(72) show 50:50 positional disorder. Atom *H*–C(11) was located and refined isotropically.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$^{13}C\{^1H\}$ n.m.r. chemical shifts‡ for the ligated carbon nuclei are in the range expected for an alkyne donating three or four electrons to a metal centre.[8] Several canonical forms may be written for complexes (**2**)—(**5**), all four species being formally unsaturated.

We have shown previously[9] that heteronuclear dimetal compounds with bridging alkylidyne ligands undergo insertion reactions with alkynes, affording allyl-bridged complexes. Formation of (**5**) contrasts with the earlier work, and emphasizes the ready involvement of the carbaborane ligand.

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