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Preliminary communication

Docosahedral carbaboranetungsten-alkylidyne complexes: synthesis of compounds with heteronuclear metal–metal bonds

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Abstract

The salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ ($R = C_6H_4Me$-4 (Ia) or $C_6H_3Me_2$-2,6 (Ib)) have been prepared and used to synthesise complexes with bonds between tungsten and gold, rhodium, and iron. The structure of Ib has been established by X-ray diffraction, demonstrating the docosahedral nature of the $C_2B_{10}W$ framework.

We have successfully employed salts of the anionic complexes $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ (R = alkyl or aryl) as reagents for preparing a variety of hetero-di- and tri-nuclear metal complexes [1]. The W≡C bonds in these salts readily add metal ligand fragments, thereby forming metal–metal bonds bridged by alkylidyne groups. In some of the products the $\eta^5\text{-}C_2B_9H_9Me_2{}^{2-}$ ligand, isolobal with $\eta^5\text{-}C_5H_5{}^-$, adopts a spectator role, as in the compounds $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, prepared by treating $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $[AuCl(PPh_3)]$ and $[Rh(cod)(PPh_3)_2][PF_6]$ (cod = cycloocta-1,5-diene), respectively [1b]. However, in the majority of the reactions novel complexes result as a consequence of the icosahedral $C_2B_9H_9Me_2$ fragment bridging the heteronuclear metal–metal linkages while remaining η^5-coordinated to the tungsten atom. This bridge bonding is accomplished through the formation of exopolyhedral B–H→metal or B–metal bonds. The net result has been the synthesis of cluster compounds with unprecedented structures.

The involvement of the $\eta^5\text{-}C_2B_9H_9Me_2$ ligand in reactions of the species $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ prompted us to prepare the related salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ ($R = C_6H_4Me$-4 (Ia) or $C_6H_3Me_2$-2,6 (Ib)). In these salts the tungsten atom occupies a vertex in a docosahedral $C_2B_{10}W$ cage, in contrast with its occupation of an icosahedral site in the C_2B_9W group present in the anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$. It was anticipated that the

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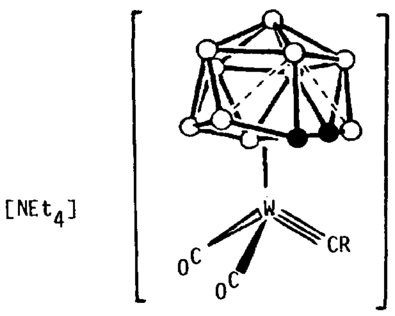

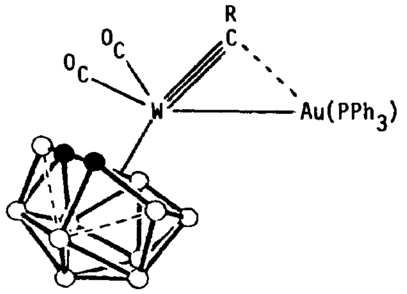

○ BH ● CMe

	R
Ia	C_6H_4Me-4
Ib	$C_6H_3Me_2$-2,6

	R
IIa	C_6H_4Me-4
IIb	$C_6H_3Me_2$-2,6

reagents I would also be useful precursors in the synthesis of compounds with metal–metal bonds and that the properties of the products containing $C_2B_{10}W$ cages would differ from those with a C_2B_9W framework isolated previously [1].

Treatment of the alkylidyne compounds $[W(\equiv CR)Cl(CO)_2(py)_2]$ (R = C_6H_4Me-4 or $C_6H_3Me_2$-2,6) with $Na_2[C_2B_{10}H_{10}Me_2]$ [2] in thf (tetrahydrofuran) at room temperature, with addition of NEt_4Cl, affords the yellow salts I in ca. 70% yield [3*]. The structure of Ib was established [4*] by X-ray diffraction, and the anion is shown in Fig. 1. The η^6-coordination mode of the C_2B_{10} cage results in a decidedly non-planar $\overline{B(3)C(40)B(5)B(6)B(7)C(20)}$ face ligating the tungsten atom. The C(20)–W (2.26(1) Å) and C(40)–W (2.56(1) Å) distances are distinctly different. The occurrence of the six atom face above the B(8)–B(12) five-membered ring results in deviations in the $C_2B_{10}W$ framework from the triangular faces observed in icosahedral cage structures. Thus the long B(3)–B(8) (1.99(2) Å) and B(7)–B(8) (1.98(2) Å) connectivities lead to the presence of two essentially square faces $\overline{B(3)C(20)B(8)B(9)}$ and $\overline{B(7)C(20)B(8)B(12)}$. This effect has been observed previously in docosahedral metallacarbaborane complexes [5]. The tungsten atom in Ib is also ligated by two CO groups, and the alkylidyne fragment. The C(1)≡W separation (1.84(1) Å) may be compared with that found for the C≡W bond (1.826(7) Å) in the salt $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [6], and it is noteworthy that in Ib C(1) is transoid to C(40), the carbon atom in the cage furthest from the tungsten atom.

Compounds I undergo fluxional behaviour as revealed by NMR studies; but limiting spectra are observed at −80 °C. The data obtained at this temperature are in accord with the structure observed for Ib in the solid state. Thus in the room temperature ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of Ib the carbaborane C*Me* groups display one broad signal at δ 2.20 (^1H) and 36.7 ppm ($^{13}C\text{-}\{^1H\}$). However, at −80 °C two C*Me* resonances in each spectrum are observed [3*]. Moreover, the $^{13}C\text{-}\{^1H\}$ spectrum at this temperature shows two CO signals, whereas at ambient

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* Reference number with asterisk indicates a note in the list of references.

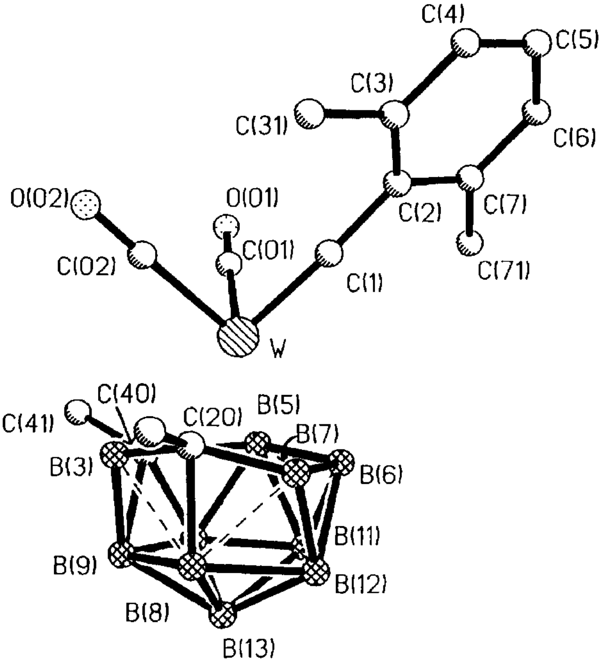
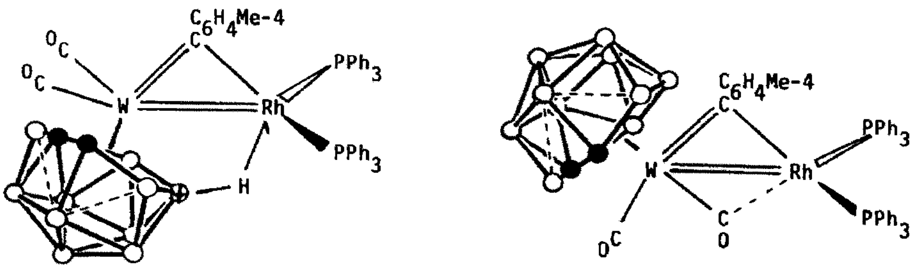


Fig. 1. The structure of the anionic complex $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]^-$. Structural parameters W–C(1) 1.84(1), W–C(01) 2.00(1), W–C(02) 2.01(1), W–C(20) 2.26(1), W–C(40), 2.56(1), B(3)–B(8) 1.99(2), B(7)–B(8) 1.98(2), B(3)–B(9) 1.81(2), B(5)–B(10) 1.80(2) Å; C(40)–W–C(1) 164.7(4), C(20)–W–C(01) 156.9(5), W–C(1)–C(2) 175.6(9)°.

temperatures only one peak is observed. The dynamic behaviour is attributed to a rotation of the $W(\equiv CR)(CO)_2$ fragment about an axis through the tungsten atom and the mid-point of the open carbaborane face. This process would be accompanied by a diamond-square-diamond rearrangement within the $C_2B_{10}W$ cage which exchanges the two cage-carbon atoms between long and short connectivities with the tungsten atom. The 'square' faces revealed by the X-ray study would be re-orientated with respect to the CMe vertices [2,7].

Reactions between $[AuCl(PPh_3)]$ and I in thf, in the presence of KPF_6, afford the complexes $[WAu(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ ($R = C_6H_4Me\text{-}4$ (IIa) or $C_6H_3Me_2\text{-}2,6$ (IIb) [8*]. Both compounds are formed as a mixture of two isomers, with each isomer undergoing fluxional behaviour of the type similar to that discussed above. Based on peak intensities in the NMR spectra, the isomer ratios are 2/3 for IIa, and 1/4 for IIb. Interestingly, only one isomer exists for $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$, containing the icosahedral C_2B_9W cage [1b]. We suggest that the two isomers of II arise as a consequence of the CR group being either transoid to a carbon atom in the face of the $\eta^6\text{-}C_2B_{10}H_{10}Me_2$ cage or transoid to a boron vertex.

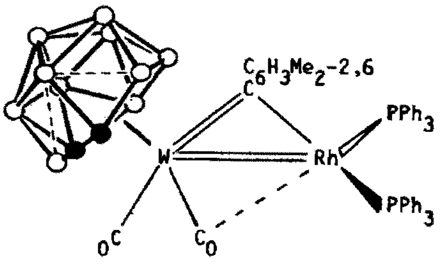
Treatment of Ia or Ib with $[Rh(cod)(PPh_3)_2][PF_6]$ affords the complexes $[WRh(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ ($R = C_6H_4Me\text{-}4$ (IIIa) or $C_6H_3Me_2\text{-}2,6$ (IIIb)). Both species undergo a fluxional process on the NMR time scale involving the core atoms of the cage similar to the salts I. However, compound IIIa is formed as a mixture of two isomers ((i) and (ii)) [9*]. The $^{11}B\text{-}\{^1H\}$ NMR spectrum of the major isomer (i) (75%) showed a diagnostic resonance at δ 21.8



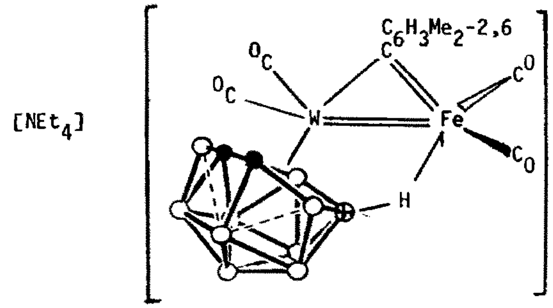
(i) (ii)

IIIa

○ BH ⊕ B ● CMe



IIIb



IV

ppm (rel. $BF_3 \cdot Et_2O$ external) for the presence of a B–H→Rh group [1a,d], and as expected in a coupled ^{11}B spectrum this signal appeared as a doublet (*J*(HB) 73 Hz). The existence of two isomers of IIIa is in contrast with the existence of single isomers of IIIb and the previously prepared compound $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [1b]. The structure of the latter has been established by X-ray diffraction and the structures of IIIa (ii) and IIIb are presumably similar, except for substitution of the $\eta^6\text{-}C_2B_{10}H_{10}Me_2$ group for the fragment $\eta^5\text{-}C_2B_9H_9Me_2$.

Finally, Ib undergoes a novel reaction with $[Fe_2(CO)_9]$ in thf giving the green crystalline complex $[NEt_4][WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_4(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ (IV). The structure has been established by X-ray diffraction [10*], the presence of the $Fe(CO)_2$ group and the three-centre two-electron B–H→Fe bond thereby being confirmed. Reactions between salts of the anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ and $[Fe_2(CO)_9]$ yield products with structures very different from that of IV [1c,d]. Thus $[NEt_4]$ $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[Fe_2(CO)_9]$ afford the pentacarbonyl tungsten-iron complex $[NEt_4][WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ in which the carbaborane group plays a spectator role, and an $Fe(CO)_3$ group is present.

The dimetal compounds reported herein provide the first examples of complexes containing the docosahedral $C_2B_{10}W$ group linked to another metal–ligand fragment, and their isolation indicates that the salts I are likely to have an extensive chemistry.

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3 Selected spectroscopic data (IR measured in CH_2Cl_2; NMR measurements at $-80\,°C$ for ^1H (in CD_2Cl_2) and ^{13}C-{^1H} (in CD_2Cl_2-CH_2Cl_2), with chemical shifts (δ) in ppm). Compound Ia: ν(CO)(max) 1990vs and 1930s cm^{-1}. NMR: ^1H, δ 1.51 (s, 3H, CMe), 2.28 (s, 3H, Me-4), 2.84 (s, 3H, CMe); ^{13}C-{^1H}, δ 302.6 (C≡W), 213.9, 212.9 (CO), 95.8, 63.9 (br, CMe), 37.9, 35.5 (CMe), 22.2 (Me-4). Compound Ib: ν(CO)(max) 1989vs and 1930s cm^{-1}. NMR: ^1H, δ 1.53 (s, 3H, CMe), 2.59 (s, 6H, Me_2-2,6), 2.87 (s, 3H, CMe); ^{13}C-{^1H}, δ 299.8 (W≡C), 215.1, 213.5 (CO), 95.3, 63.6 (br, *C*Me), 37.5, 35.5 (*CMe*), 21.2 (Me_2-2,6).

4 *Crystal data*: $C_{23}H_{45}B_{10}NO_2W$, $M = 659.57$, orthorhombic, $a = 13.380(3)$, $b = 19.381(6)$, $c = 23.357(7)$ Å, U 6057 Å^3, $Z = 8$, D_c 1.45 g cm^{-3}, $F(000)$ 2212, space group *Pbca*, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ 0.71069 Å, μ(Mo-K_α) 38.88 cm^{-1}. $R = 0.051$ ($R_w = 0.046$) for 3052 absorption corrected intensites (293 K, $\theta/2\theta$ scans, $3 \leqslant 2\theta \leqslant 50°$, $F \geqslant 3\sigma(F)$). Data were collected on a Nicolet *P3m* diffractometer, and the structure was solved by Patterson and Fourier methods with refinement by blocked-cascade least squares.Atomic coordinates, bond lengths and angles, and thermal parameters have been been deposited at the Cambridge Crystallographic Data Centre.

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8 Selected spectroscopic data (NMR measurements at $-80\,°C$ for ^1H (in CD_2Cl_2) and ^{13}C-{^1H} (in CD_2Cl_2/CH_2Cl_2 (IIa), CD_2Cl_2/thf (IIb)), with chemical shifts (δ) in ppm, and coupling constants in Hz). Compound IIa: ν(CO)(max) 2028s and 1981s cm^{-1} (in thf). NMR: ^1H, δ (major isomer) 2.02 (s, 3H, CMe), 2.44 (s, 3H, Me-4) 2.66 (s, 3H, CMe); δ (minor isomer), 1.84 (s, 3H, CMe), 2.44 (s, 3H, Me-4), 2.51 (s, 3H, CMe); ^{13}C-{^1H}, δ (major isomer) 280.5 (d, μ-C, J(PC) 27), 206.3, 204.3 (CO), 87.7, 76.6 (br, *C*Me), 37.9, 35.9 (*CMe*); δ (minor isomer) 296.8 (d, μ-C, J(PC) 34), 207.3, 206.0 (CO), 102.2, 76.1 (br, *C*Me), 40.5, 35.7 (*CMe*). Compound IIb: ν(CO)(max) 2034s and 1986s cm^{-1} (in CH_2Cl_2). NMR: ^1H, δ (major isomer) 1.97, 2.23, 2.49, 2.71 (s×4, 12H, CMe and Me_2-2,6); δ (minor isomer) 1.78, 2.38, 2.46, 2.98 (s×4, 12H, CMe and Me_2-2,6); ^{13}C-{^1H}, δ (major isomer) 276.8 (d, μ-C, J(PC) 29), 208.1, 203.5 (CO), 88.5 (*C*Me), 38.3, 35.8 (*CMe*), 22.6, 21.9 (Me_2-2,6); δ (minor isomer) 282.9 (d, μ-C, J(PC) 26), 206.6 (CO), 38.7 (*CMe*), 22.4, 22.3 (Me_2-2,6); other signals obscured.

9 Selected spectroscopic data for compound IIIa (IR in thf; NMR measurements at $-80\,°C$ for ^1H (in CD_2Cl_2) and ^{31}P-{^1H} (in CD_2Cl_2/CH_2Cl_2), chemical shifts (δ) (for ^{31}P-{^1H} rel. 85% H_3PO_4 external) in ppm and coupling constants in Hz). ν(CO)(max) 2001s, 1987sh, 1962s, and 1808m cm^{-1}. NMR: ^1H, δ (major isomer) 1.65, 1.99, 2.42 (s×3, 9H, CMe and Me-4); δ (minor isomer) 1.93, 2.46, 2.84 (s×3, 9H, CMe and Me-4); ^{31}P-{^1H}, δ (major isomer) 52.2 (d of d, PPh_3, J(PP) 29, J(RhP) 162), 38.5 (d of d, PPh_3, J(PP) 28, J(RhP) 148); δ (minor isomer) 41.3 (d of d, PPh_3, J(PP) 26, J(RhP) 172), 27.8 (d of d, PPh_3, J(PP) 25, J(RhP) 146).

10 (a) S. Crennell and J.A.K. Howard, unpublished results; (b) Selected spectroscopic data for compound IV; ν(CO)(max) 2002m, 1950vs and 1900m cm^{-1} (in CH_2Cl_2). NMR ($-40\,°C$): ^1H, δ -0.40 (br, q, 1 H, B–H→Fe, J(BH) 84), 1.62, 1.71, 1.87, 2.17 (s×4, 12H, CMe and Me_2-2,6); ^{13}C-{^1H}, δ 369.2 (μ-C, J(WC) 113), 219.6, 216.8 (FeCO), 213.3 (WCO, J(WC) 130), 202.5 (WCO, J(WC) 153), 76.9, 63.4 (br, *C*Me), 36.5, 34.5 (*CMe*), 21.1, 21.0 (Me_2-2,6).