The Synthesis and Reactions of an Anionic Tungsten–Carbyne Complex Stabilised by the Carbaborane Ligand 1,2-$C_2B_9H_9Me_2$; Evidence for a Novel Cage Hydroboration Reaction
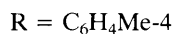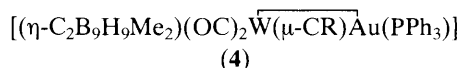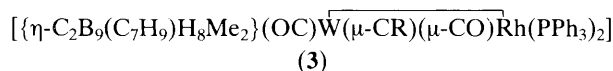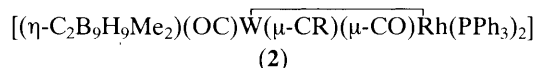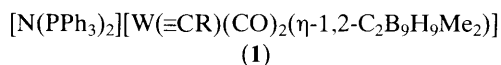
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The salt [N(PPh$_3$)$_2$][W($\equiv$CR)(CO)$_2$(η^5-1,2-C$_2$B$_9$H$_9$Me$_2$)] (R = C$_6$H$_4$Me-4) reacts with the compounds [RhCl(PPh$_3$)$_3$], [Rh(PPh$_3$)$_2$(diene)][BF$_4$] (diene = cyclo-octa-1,5-diene or norbornadiene), and [AuCl(PPh$_3$)] to give products with tungsten–rhodium or tungsten–gold bonds, the structures of which were determined by X-ray diffraction; that from the norbornadiene complex contains a nortricyclane moiety bonded to a boron atom of the C$_2$B$_9$ cage.

The synthesis of the iron complex [Fe(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^{2-}$ and the recognition of the structural relationship between this species and ferrocene led to the development of metallacarbaborane chemistry.[1] There is evidence[2] to suggest that the electron donor ability and steric requirements of the *nido*-C$_2$B$_9$H$_{11}$$^{2-}$ anion are similar to those of η-C$_5$Me$_5$, although the notional replacement of a cyclopentadienyl ligand in a metal complex by the carbaborane cage places a negative charge on any resultant compound. There is thus an isolobal relationship between the groups W(CO)$_2$(η-C$_5$R'$_5$) and W(CO)$_2$(η-C$_2$B$_9$H$_9$R'$_2$)$^-$ (R' = H or Me) suggesting[3] that salts of the anion [W($\equiv$CR)(CO)$_2$(η-C$_2$B$_9$H$_9$Me$_2$)]$^-$ might be prepared. It was anticipated that the carbaborane ligand would focus electron density on the tungsten centre, resulting in the carbyne–metal species undergoing unusual reactions.

The compound Na$_2$[7,8-C$_2$B$_9$H$_9$Me$_2$][4] in tetrahydrofuran (thf) reacts with [W($\equiv$CR)Br(CO)$_4$] (R = C$_6$H$_4$Me-4)[5] (-40 °C, warming to room temperature) with CO evolution. Addition of [N(PPh$_3$)$_2$]Cl gives an orange salt (1), spectroscopic data† for which are in accord with the formulation

[N(PPh$_3$)$_2$][W($\equiv$CR)(CO)$_2$(η-1,2-C$_2$B$_9$H$_9$Me$_2$)]

(1)

[(η-C$_2$B$_9$H$_9$Me$_2$)(OC)$\overline{W(\mu$-CR)(μ-CO)}Rh(PPh$_3$)$_2$]

(2)

[{η-C$_2$B$_9$(C$_7$H$_9$)H$_8$Me$_2$}(OC)$\overline{W(\mu$-CR)(μ-CO)}Rh(PPh$_3$)$_2$]

(3)

[(η-C$_2$B$_9$H$_9$Me$_2$)(OC)$_2\overline{W(\mu$-CR)}Au(PPh$_3$)]

(4)

R = C$_6$H$_4$Me-4

proposed. Treatment of dichloromethane solutions of (1) with either [RhCl(PPh$_3$)$_3$] or [Rh(PPh$_3$)$_2$(cod)][BF$_4$] (cod = cyclo-octa-1,5-diene) affords the green-black complex (2),† the structure of which (Figure 1) was established by X-ray diffraction.‡ The molecule has a Y-shaped WRhP$_2$ core in which μ-CR and μ-CO ligands bridge opposite sides of the WRhP$_2$ plane. The Rh–W [2.681(1) Å] and μ-C–W [1.880(6) Å] separations in (2) are distinctly shorter than those in the related dimetal compound [RhW(μ-CR)(CO)$_2$(PMe$_3$)(η-C$_5$H$_5$)(η-C$_9$H$_7$)] [Rh–W 2.796(1), μ-C–W 1.913(14) Å],[6] in accord with both metal centres being formally electronically unsaturated. As expected, the C$_2$B$_9$ cage in the precursor has remained intact in the product.

In contrast with the formation of (2) from [Rh(PPh$_3$)$_2$(cod)][BF$_4$] and (1), the latter reacts with [Rh(PPh$_3$)$_2$(nbd)][BF$_4$] (nbd = norbornadiene) to afford a black crystalline product (3) which has a structure (Figure 2)‡ with a nortricyclane unit bonded to a boron atom in the open face of the carbaborane cage. Thus an apparent unprecedented hydroboration reaction has occurred in which a cage B–H adds 1,4 to the homodiene with concomitant C–C bond formation. The overall geometry of the central core of (3) is remarkably similar to that of (2), the most noticeable difference being a shortening of the Rh–W distance [2.662(2) Å] in the former. In the two molecules the two bridging carbon atoms (CR and CO) are not coplanar, the dihedral angle between the planes $\overline{Rh(\mu$-CO)}W and $\overline{Rh(\mu$-CR)}W being 13° in (2) and 20° in (3). Attachment of the nortricyclane fragment

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† Selected spectroscopic data [i.r. measured in CH$_2$Cl$_2$, n.m.r. measured in CD$_2$Cl$_2$ (^{1}H, ^{11}B-{^{1}H}) or CD$_2$Cl$_2$–CH$_2$Cl$_2$ (^{13}C-{^{1}H}), coupling constants in Hz, chemical shifts are to high frequency and relative to BF$_3$·Et$_2$O (external) for ^{11}B-{^{1}H} and to 85% H$_3$PO$_4$ (external) for ^{31}P-{^{1}H}: Compound (1), ν_{CO} (max) at 1956s and 1874s cm^{-1}, ν_{BH} (max) at 2516m cm^{-1}. N.m.r. ^{1}H, δ 7.70—7.25 (m, 34 H, Ph), 2.18 (s, 3 H, Me-4), and 2.07 (s, 6 H, Me-cage); ^{11}B-{^{1}H}, δ -10.9 (5 B), -20.2 (3 B), and -38.3 p.p.m. (1 B); ^{13}C-{^{1}H}, δ 298.3 [CR, J(WC) 198] and 226.8 p.p.m. [CO, J(WC) 182]. Compound (2), ν_{CO} (max) at 1961s and 1767s cm^{-1}, ν_{BH} (max) at 2555m cm^{-1}. N.m.r.: ^{1}H, δ 7.12 (m, 34 H, Ph), 2.44 (s, 3 H, Me-4), and 1.90 (s, 6 H, Me-cage); ^{13}C-{^{1}H}, δ 343.1 [d, μ-CR, J(RhC) 30] and 236.1 p.p.m. [d, CO, J(RhC) 17]; ^{31}P-{^{1}H}, δ 32.2 p.p.m. [d, J(RhP) 166]. Compound (3), ν_{CO} (max) at 1961s and 1756s cm^{-1}, ν_{BH} (max) at 2553m cm^{-1}. N.m.r.: ^{13}C-{^{1}H}, δ 338.2 [d, μ-CR, J(RhC) 28], 256.2 (br, μ-CO), and 222.5 p.p.m. (br, CO); ^{31}P-{^{1}H}, δ 33.9 p.p.m. [d, J(RhP) 166], at -60 °C, δ 32.5 [d of d of d, ABX system, J(PP) 32, J(RhP) 180 and 152]. Compound (4), ν_{max} (CO) at 2002s and 1933s cm^{-1}, ν_{max} (BH) 2554m cm^{-1}. N.m.r.: ^{13}C-{^{1}H}, δ 292.9 [d, μ-CR, J(PC) 28] and 220.0 p.p.m. [CO, J(WC) 162]; ^{31}P-{^{1}H}, δ 56.1 p.p.m.

Figure 1. Molecular structure of [RhW(μ-CO)(μ-CC₆H₄Me-4)(CO)(PPh₃)₂(η-C₂B₉H₉Me₂)] (2). Dimensions: Rh–W 2.681(1), W–C(a) 1.880(6), Rh–C(a) 2.068(5), W–C(01) 2.032(6), Rh–C(01) 2.105(6), Rh–P(1) 2.346(2), Rh–P(2) 2.281(2) Å; W–C(01)–O(01) 160.2(5), Rh–C(01)–O(01) 118.9(4), W–C(a)–Rh 85.4(2), W–C(02)–O(02) 176.9(5), P(1)–Rh–P(2) 98.8(1)°.
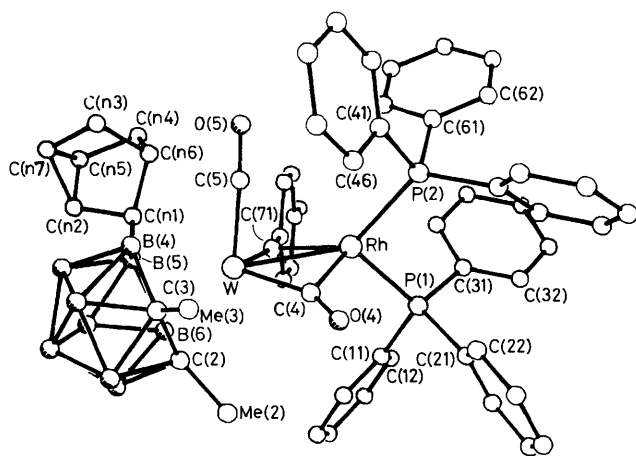

Figure 2. Molecular structure of [RhW(μ-CO)(μ-CC₆H₄Me-4)-(CO)(PPh₃)₂{η-C₂B₉(C₇H₉)H₈Me₂}] (3). Dimensions: Rh–W 2.662(2), W–C(71) 1.84(2), Rh–C(71) 2.12(2), W–C(4) 2.07(2), Rh–C(4) 2.05(2), Rh–P(1) 2.287(4), Rh–P(2) 2.351(5), W–B(4) 2.39(2), W–B(5) 2.47(2), W–B(6) 2.38(2), W–C(2) 2.36(2), W–C(3) 2.46(2), B(5)–C(n1) 1.64(4) Å; W–C(4)–O(4) 156(1), Rh–C(4)–O(4) 124(1), W–C(71)–Rh 84.1(7), W–C(5)–O(5) 175(2), P(1)–Rh–P(2) 98.7(2)°.

increases the W–B(5) distance by *ca.* 0.085 Å compared with the other two W–B separations (Figure 2).

A reaction of this kind has not been observed previously and raises the question as to whether this is an example of a metal promoted hydroboration reaction. In this context it is particularly interesting that (2) does not react with norbornadiene to form (3).

Compounds (2) and (3) also show interesting dynamic behaviour. Only one ³¹P resonance is observed in the n.m.r. spectra† at room temperature; however, at −60 °C the spectrum of (3) has an ABX pattern suggesting that rotation of the RhP₂ unit about the Rh–W axis is slow on the n.m.r. time scale at this temperature. In addition, there is a process
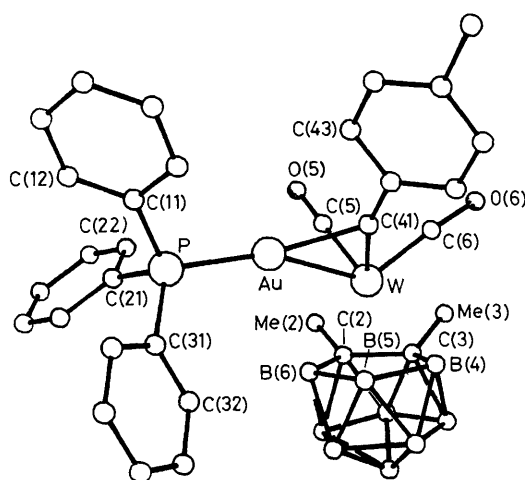

Figure 3. Molecular structure of [AuW(μ-CC₆H₄Me-4)(CO)₂(PPh₃)-(η-C₂B₉H₉Me₂)] (4). Dimensions: Au–W 2.780(8), Au–C(41) 2.19(3), W–C(41) 1.88(3), Au–P 2.27(1) Å; Au–C(41)–W 86(1), P–Au–C(41) 162.7(7), W–C(5)–O(5) 177(3), W–C(6)–O(6) 174(2)°.

associated with CO site exchange. The ¹³C-{¹H} spectrum of (2) shows only one CO environment at room temperature, whereas the spectrum of (3) exhibits two broad signals which diverge on cooling to −60 °C. This implies a rocking movement of the two CO groups between bridging and terminal sites, so that in (2) only one signal is observed as a result of the exchange, whereas in (3) the asymmetry of the molecule causes one carbonyl to spend more time bridging than the other.

The orange gold–tungsten compound (4)† was prepared from (1) and [AuCl(PPh₃)] in thf, in the presence of TlPF₆. The structure is shown in Figure 3.‡ The Au–W distance [2.780(8) Å] is similar to that observed⁷ [2.752(1) Å] in the cation [AuW₂(μ-CR)₂(CO)₄(η-C₅H₅)₂]⁺. The μ-C–W separation [1.88(3) Å] is similar to those in (2) and (3), implying multiple bond character. However, in contrast with the two rhodium complexes, the CO ligands in (4) show no tendency to adopt a bridge bonding mode.

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