Carborane Clusters

Heterometallic Cluster Assembly on a Rhenium–Monocarborane Substrate**

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The carborane ions [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ and [*nido*-7-$CB_{10}H_{11}$]$^{3-}$ may be compared with the ubiquitous cyclopentadienide ion [C_5H_5]$^-$, in that all three act as pentahapto, six-π-electron donor ligands to transition-metal centers.[1] However, compared to the relative wealth of information available on metal complexes of anionic dicarbon *nido*-carboranes, the corresponding complexes of monocarbon carboranes have scarcely been studied.[1] One aspect of particular interest derives from the monocarborane anions having a higher negative charge than their dicarbon analogues. Consequently their metal complexes also carry a higher negative charge, a property resulting in reactivity towards various electrophiles, which leads to functionalization at the carborane cage.[2] Moreover, cationic metal–ligand fragments react to give bimetallic species.[3,4] We have recently expanded our studies to non-icosahedral metal–monocarborane complexes with the rhenacarborane ion **1**$^{2-}$ (Scheme 1).[5] Herein we demonstrate that **1**$^{2-}$ may be used as

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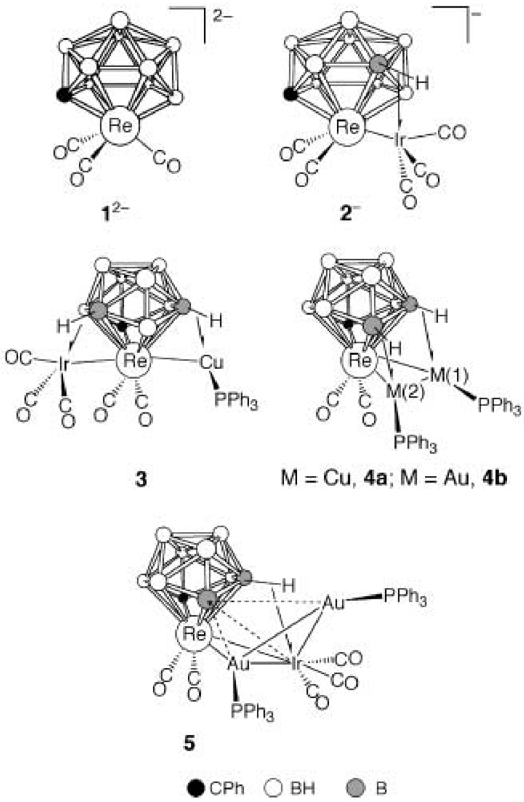

Scheme 1. Structures of the species 1^{2-}, 2^-, and 3–5.[7]

a scaffold for the stepwise assembly of heteropolymetallic clusters.

When $[N(PPh_3)_2][NEt_4]$-**1**[5] is treated in CH_2Cl_2 with $[IrCl(CO)_2(NH_2C_6H_4Me\text{-}1,4)]$[6] and $Tl[PF_6]$, the ionic rhenium–iridium complex $\mathbf{2}^-$ is formed. Its structure is reasonably inferred from its NMR spectra and from the known structures of compounds **3**–**5** (Scheme 1). Noting that $\mathbf{2}^-$ retains a single negative charge, it was of interest to establish whether a further, but different, cationic metal fragment could be added to the cage system. Accordingly, $\mathbf{2}^-$ was treated in CH_2Cl_2 with $[CuCl(PPh_3)]_4$[8] or $[AuCl(PPh_3)]$[9] in the presence of $Tl[PF_6]$, each reaction unexpectedly giving rise to two products.

In the copper system the anticipated product, a trimetallic Ir-Re-Cu species **3** was indeed observed and its structure was confirmed by a preliminary X-ray diffraction study. However, the major product was a rhenium–dicopper species **4a**, also characterized structurally. The metal atom arrangement in **3** resembles that of the Cu-Re-Cu compound formed by direct reaction of $\mathbf{1}^{2-}$ with $[CuCl(PPh_3)]_4/Tl[PF_6]$.[5] However, the latter trimetallic complex has a Cu-Re-Cu angle of 93.89(2)° (Cu–Re 2.7563(8), 2.7866(7) Å), whilst the Ir-Re-Cu angle in **3** is 164.27(4)° (Ir–Re 2.8860(12), Re–Cu 2.666(3) Å). These "V-shaped" trimetallic units contrast with **4a**, where there is an $\{ReCu_2\}$ triangle (Re–Cu(1) 2.6838(9), Re–Cu(2) 2.6117(9), Cu(1)–Cu(2) 2.9093(15) Å; Cu(1)-Cu(2)-Re 57.87(3), Cu(1)-Re-Cu(2) 66.64(3), Re-Cu(1)-Cu(2) 55.50(3)°). However, solution $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectral data for **4a** are consistent with a time-averaged symmetric structure, suggesting that the exopolyhedral $\{Cu(PPh_3)\}$ fragments are fluxional over the carborane surface.[4] Such a process might involve migration of the entire $\{Cu_2(PPh_3)_2\}$ unit, or else a breaking of the Cu–Cu connectivity to give an intermediate with a V-shaped trimetal unit akin to **3**.

The reaction of $\mathbf{2}^-$ with the source of $\{Au(PPh_3)\}^+$ also gives two products, namely complexes **4b** and **5** (Scheme 1). No Ir-Re-Au analogue of compound **3** was observed, but the major product **4b** is the rhenium-digold analogue of **4a** described above. Single crystals of **4b** were not available for an X-ray diffraction study but its structure is, nevertheless, reasonably assumed to be similar to that of **4a**: the $\{Au(PPh_3)\}_2$ derivative of $\mathbf{1}^{2-}$ is known to be isostructural with its dicopper analogue.[5] Although complex **5** is isolated in lesser amounts from this reaction its structure (Figure 1), confirmed by X-ray diffraction methods,[10] is of interest.

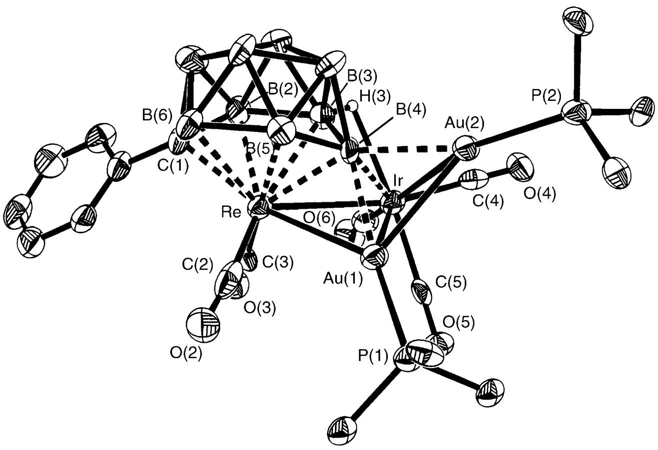

Figure 1. Molecular structure of **5** (thermal ellipsoids set at 40% probability). For clarity, only *ipso* C atoms of PPh3 ligands are shown and all H atoms are omitted except that in the B-H→Ir bridge. Selected interatomic distances [Å] and angles [°] are: Re-C(1) 2.165(13), Re-B(2) 2.434(18), Re-B(3) 2.346(16), Re-B(4) 2.236(15), Re-B(5) 2.362(16), Re-B(6) 2.385(17), Re-Au(1) 2.9126(8), Re-Ir 2.9540(9), B(3)⋯Ir 2.337(17), B(3)-H(3) 1.05(13), Ir-H(3) 2.21(13), B(4)-Au(1) 2.262(17), B(4)-Au(2) 2.270(14), B(4)-Ir 2.328(18), Ir-Au(1) 2.9765(8), Ir-Au(2) 2.8738(8), Au(1)-Au(2) 2.7723(8); Au(1)-Re-Ir 60.97(2), Au(2)-Ir-Re 96.53(2), Au(2)-Ir-Au(1) 56.54(2), Re-Ir-Au(1) 58.83(2), Au(2)-Au(1)-Re 99.79(2), Au(2)-Au(1)-Ir 59.86(2), Re-Au(1)-Ir 60.20(2), Au(1)-Au(2)-Ir 63.60(2).

In **5**, the $\{Ir(CO)_3\}$ and $\{Au(PPh_3)\}$ moieties are bonded to the rhenium center and to each other. The Au–Ir vector is bridged by a second $\{Au(PPh_3)\}$ fragment, so that overall an $\{ReIrAu_2\}$ "butterfly" has been assembled upon the starting rhenacarborane template. The iridium center is supported by an additional B–H→Ir interaction and the terminal hydrogen atom has been lost from one boron vertex. Note that this naked boron vertex B(4) is in contact with all four metal centers, in an arrangement reminiscent of $\{M_4B\}$ transition-metal boride clusters.[11] However, the ^{11}B NMR chemical shift of B(4) ($\delta = 37.9$ ppm) is substantially upfield of those of genuine borides.

Mechanistically, the mode of formation of **5** remains unclear. However, it seems likely that an Ir-Re-Au species akin to **3** might be its precursor. Moreover, it is conceivable that ejection of an iridium fragment from **5** and H capture from the medium would be sufficient to formally convert **5** into **4b**. Conversely, it is equally possible that a gold fragment simply displaces iridium from an Ir-Re-Au intermediate to give **4b** directly. Similar considerations would apply to the copper system.

Compound **5** represents a novel class of hybrid multiple cluster in which an {ReIrAu$_2$} butterfly has been constructed on a rhenacarborane substrate. Although carborane-supported heterometallic clusters have been reported,[12] we are not aware of three different metals being introduced in such a stepwise fashion, nor of any example of such intimate contact between the metal cluster and metallacarborane subunits. The ions **1**$^{2-}$ and **2**$^{-}$ appear to offer considerable potential for the synthesis of other new heteropolymetallic species. Complexes **2**$^{-}$, **3** and **4** are interesting in their own right and the details of their structures, and those of the many other species that are accessible by a similar synthetic methodology, will undoubtedly reveal yet further architectural novelty.

Experimental Section

[N(PPh$_3$)$_2$]-**2**:[13] Treatment (16 h) of [N(PPh$_3$)$_2$][NEt$_4$]-**1** in CH$_2$Cl$_2$ with [IrCl(CO)$_2$(NH$_2$C$_6$H$_4$Me-1,4)] and Tl[PF$_6$] (1 equiv each), followed by filtration, evaporation, and column chromatography of the residue, gave yellow [N(PPh$_3$)$_2$]-**2** (63%). Elemental analysis calcd (%) for $C_{48}H_{44}B_9IrNO_5P_2Re$: C 46.0, H 3.5, N 1.1; found: C 45.8, H 3.6, N 1.2; IR (CH$_2$Cl$_2$): $\tilde{\nu}_{max} = 2048$ s, 2011 s, 1985 s, 1915 br s cm^{-1} (CO); ^{1}H NMR (360.1 MHz, CD$_2$Cl$_2$, 298 K): $\delta =$ ca. −7.9 ppm (vbr, B-H$\rightharpoonup$Ir); ^{13}C{^{1}H} NMR (90.6 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 197.7$ (Ir-CO), 173.1 (br, Re-CO), 56.8 ppm (br, cage C); ^{11}B{^{1}H} NMR (115.5 MHz, CD$_2$Cl$_2$, 298 K; unit integral except where indicated): $\delta = 23.1$, 16.1, 4.2, −6.2 (br, B-H$\rightharpoonup$Ir), −16.4, −18.6, −22.8, −24.0, −35.8 ppm.

3 and **4a**:[13] Reaction (16 h) of [N(PPh$_3$)$_2$]-**2** with [CuCl(PPh$_3$)]$_4$ and Tl[PF$_6$] (equimolar ratio Re:Cu:Tl) in CH$_2$Cl$_2$ and workup as above gave, successively, pale yellow **3** (12%) and yellow **4a** (41% based on Re). For **3**: elemental analysis calcd (%) for $C_{30}H_{29}B_9CuIrO_5PRe\cdot C_5H_{12}$: C 37.8, H 3.7; found: C 37.4, H 3.5; IR (CH$_2$Cl$_2$): $\tilde{\nu}_{max} = 2067$ s, 2035 s, 2019 s, 1944 br s cm^{-1} (CO); ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = -6.73$ (br q, ^1J(B,H) ≈ 100 Hz, B-H$\rightharpoonup$Ir), −9.18 ppm (br q, ^1J(B,H) ≈ 110 Hz, B-H$\rightharpoonup$Cu); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta =$ 192.9, 192.5, 189.4 (Ir-CO), 176.4, 168.0 (Re-CO), 47.8 ppm (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 38.4$ (br), 6.9, 2.9, −9.4 (br), −13.9, −16.8 (br), −22.5, −23.7, −32.0 ppm; ^{31}P{^{1}H} NMR (145.8 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 9.2$ ppm (br). For **4a**: elemental analysis calcd (%) for $C_{45}H_{44}B_9Cu_2O_2P_2Re\cdot 0.5\,CH_2Cl_2$: C 48.3, H 4.0; found: C 48.2, H 4.1; IR (CH$_2$Cl$_2$): $\tilde{\nu}_{max} = 2023$ s, 1974 s cm^{-1} (CO); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 172.3$ (Re-CO), 63.5 ppm (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 7.6$, ca. 6.3 (vbr), −7.1, −10.4 (br, 2B), −28.8 (2B), −31.3 ppm (2B); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 9.2$ ppm (br).

4b and **5**[13] Similarly, [N(PPh$_3$)$_2$]-**2**, [AuCl(PPh$_3$)] and Tl[PF$_6$] in CH$_2$Cl$_2$ gave orange **5** (16% based on Re, not optimized) and then yellow **4b** (39% based on Re). For **4b**: elemental analysis calcd (%) for $C_{45}H_{44}Au_2B_9O_2P_2Re\cdot 0.5\,CH_2Cl_2$: C 39.1, H 3.2; found: C 39.1, H 3.2; IR (CH$_2$Cl$_2$): $\tilde{\nu}_{max} = 2044$ s, 2000 s cm^{-1} (CO); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 172.8$ (Re-CO), 54.2 ppm (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 11.1$, 9.2 (br), 0.5, −5.2 (br, 2B), −27.6 ppm (4B); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 44.7$ ppm. For **5**: elemental analysis calcd (%) for $C_{48}H_{43}Au_2B_9IrO_5P_2Re$: C 35.3, H 2.7; found: C 35.1, H 2.7; IR (CH$_2$Cl$_2$): $\tilde{\nu}_{max} = 2051$ s, 2009 vs, 1929 s, 1915 br s cm^{-1} (CO); ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta \approx -8.9$ ppm (vbr, B-H$\rightharpoonup$Ir); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 198.0$, 194.8, 192.6 (br, Ir-CO), 175.4, 171.0 (Re-CO), 56.1 ppm (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 37.9$ (B(4)), 18.3, 8.6 (br), −5.6 (vbr), −10.2 (br), −18.8 (br), −21.2 (2B), −33.6 ppm; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): $\delta = 58.7$ (br), 51.1 ppm (br).

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[10] Single crystals were grown by slow diffusion of 40–60 petroleum ether into a dichloromethane solution of **5** at −30 °C. Enraf-Nonius CAD-4 diffractometer, graphite monochromated Mo$_{K\alpha}$ X-ray radiation ($\lambda = 0.71073$ Å), 293(2) K, Lorentz and polarization corrections, numerical absorption correction based on measurement of crystal faces ($T_{max} = 0.087$, $T_{min} = 0.033$), solution by direct methods, refinement by full-matrix least-squares methods using all F^2 data. Crystal data for **5**·2 CH$_2$Cl$_2$: $C_{50}H_{47}Au_2B_9Cl_4IrO_5P_2Re$, $M_r = 1801.24$, crystal size 0.246 × 0.262 × 0.344 mm, monoclinic, $P2_1/n$, $a = 18.467(3)$, $b = 17.1872(14)$, $c = 19.797(2)$ Å, $\beta = 115.338(9)°$, $V = 5679.0(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.107$ g cm^{-3}, $F(000) = 3360$, $\mu = 9.900$ mm^{-1}. 10363 data collected ($\theta_{max} = 25.0°$), 10030 unique ($R_{int} = 0.0401$) and 6952 observed reflections [$F_o > 4\sigma(F_o)$], final $R_1 = 0.0534$ and $wR_2 = 0.1104$ (observed), $R_1 = 0.0931$ and $wR_2 = 0.1257$ (all data), max. and min. residual electron density: 1.661 (near Ir), −1.256 e Å^{-3}. CCDC 213812 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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