Chemistry of $[NEt_4][10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}nido\text{-}C_2B_9H_9Me_2]$: Carborane Cage Transfer from Gold to Rhodium and Iridium

Judith A. K. Howard, John C. Jeffery, Paul A. Jelliss, Thomas Sommerfeld and F. Gordon A. Stone*†
School of Chemistry, The University, Bristol BS8 1TS, UK

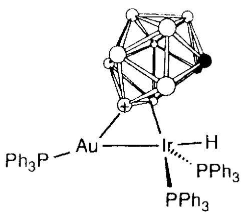
The salt $[NEt_4][10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}nido\text{-}C_2B_9H_9Me_2]$ has been used to synthesise several complexes in which gold forms bonds with rhodium and iridium, including $[IrAuH(\mu\text{-}\sigma,\eta^3\text{-}C_2B_9H_8Me_2)(PPh_3)_3]$, $[exo\text{-}nido\text{-}5,10\text{-}\{Rh(PPh_3)_2\}\text{-}5,10\text{-}\mu\text{-}(H)_2\text{-}10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}C_2B_9H_7Me_2]\cdot CH_2Cl_2$, and $[RhAu_2(\mu\text{-}H)(PPh_3)_3(\eta^5\text{-}C_2B_9H_9Me_2)]\cdot 2(CH_2Cl_2)$.

Salts of the anionic carboranes $[7,8\text{-}C_2B_9H_{10}R_2]^-$ (R = H or Me) are versatile precursors for the synthesis of transition element complexes in which metal centres are ligated by the open pentagonal faces of *nido*-icosahedral $C_2B_9H_9R_2$ fragments.[1] Given the isolobal relationship[2] between the anions $[10\text{-}endo\text{-}H\text{-}7,8\text{-}nido\text{-}C_2B_9H_9R_2]^-$ and $[10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}nido\text{-}C_2B_9H_9R_2]^-$, recently highlighted by structural studies for R = H,[3] it seemed likely that the gold–carborane species would be useful reagents for preparing polynuclear metal compounds in which gold is bonded to other metals. This methodology has afforded a variety of metal complexes, some of which have unprecedented structures.

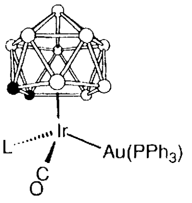
The salt $[NEt_4][10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}nido\text{-}C_2B_9H_9Me_2]$ **1** has been prepared by treating $[AuCl(PPh_3)]$ in thf (tetrahydrofuran) with $Na_2[7,8\text{-}C_2B_9H_9Me_2]$, followed by

---

† *Present address*: Department of Chemistry, Baylor University, Waco, Texas 76798-7348, USA.

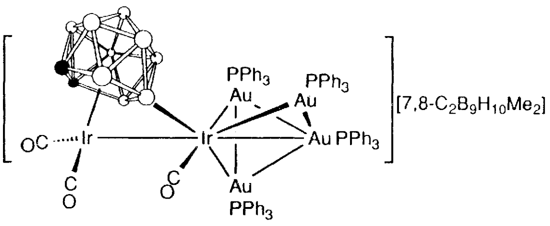


2



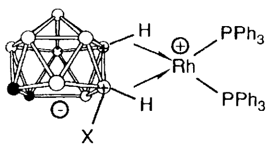
L

3a PPh3
3b CO



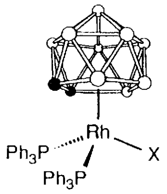
[7,8-$C_2B_9H_{10}Me_2$]

4



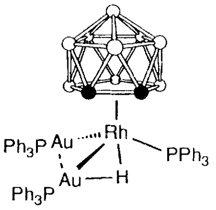
X

5a Au(PPh3)
6a H



X

5b Au(PPh3)
6b H



7

● CMe ○ BH ⊕ B

addition of NEt_4Cl. In thf the reagent **1** reacts with $[IrCl(PPh_3)_3]$, in the presence of $TlBF_4$, to afford the bimetal complex $[IrAuH(\mu\text{-}\sigma,\eta^3\text{-}C_2B_9H_8Me_2)(PPh_3)_3]$ **2** in *ca.* 90% yield.‡ The molecular structure of this complex was established by X-ray diffraction, and is shown in Fig. 1.§ The Au–Ir bond is spanned by the $C_2B_9H_8Me_2$ cage in such a manner that it is σ-bonded to the gold *via* B(4) and η^3-coordinated to the iridium through B(3), B(4) and B(5). The structure may be viewed as one in which there is an incipient transfer of the C_2B_9 cage from gold to iridium. Complete cage transfer occurs

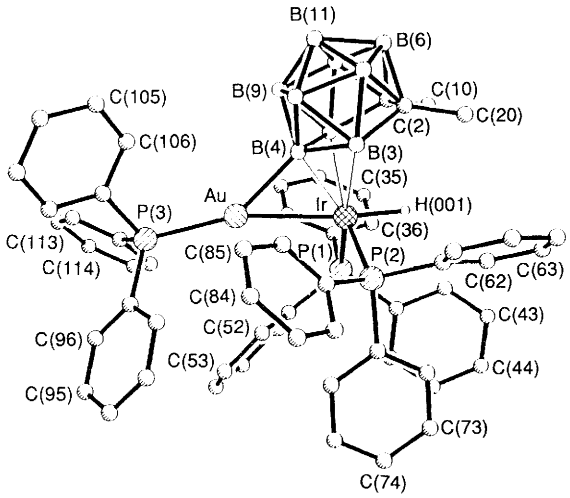


Fig. 1 Molecular structure of $[IrAuH(\mu\text{-}\sigma,\eta^3\text{-}C_2B_9H_8Me_2)(PPh_3)_3]$ **2**. Dimensions: Ir–Au 2.739(1), Ir–H(001) 1.58(9), Au–B(4) 2.20(1), Ir–B(3), 2.33(1), Ir–B(4) 2.03(1), Ir–B(5) 2.42(1) Å; P(3)–Au–Ir 164.6(1), H(001)–Ir–Au 168(3)°.

---

‡ *Selected spectroscopic data* [IR spectra recorded in CH_2Cl_2; NMR measurements in CD_2Cl_2 at room temperature unless otherwise stated, with chemical shifts (δ) in ppm and coupling constants in Hz. The $^{31}P\text{-}\{^1H\}$ and $^{11}B\text{-}\{^1H\}$ shifts are relative to 85% H_3PO_4 (external) and $BF_3\cdot Et_2O$ (external), respectively]. Compound **2** (orange), ^1H NMR, δ −15.21 (d of t, 1 H, IrH, J_{PH} 22 and 22); $^{31}P\text{-}\{^1H\}$, δ 58.3 (br, 1 P, PAu) and 18.8 (br, 2 P, PIr); $^{11}B\text{-}\{^1H\}$, δ 66.5 (br, 1 B, BAu). Compound **3a** (yellow), IR, $\nu_{max}(CO)$ at 1971vs cm^{-1}; $^{31}P\text{-}\{^1H\}$ NMR, δ 37.4 (d, PAu, J_{PP} 10) and 11.0 (d, PIr, J_{PP} 10). Compound **3b** (pale orange), IR, $\nu_{max}(CO)$ at 2051vs and 2002s cm^{-1}; $^{31}P\text{-}\{^1H\}$ NMR, δ 42.3 (s, PAu). Compound **4** (yellow), IR, $\nu_{max}(CO)$ at 2043s, 1996s and 1956m cm^{-1}; $^{31}P\text{-}\{^1H\}$ NMR, δ 51.2 (s, PAu); $^{11}B\text{-}\{^1H\}$, δ 38.3 (br, 1 B, BIr), −3.2 (br, 1 B), −9.2 (vbr, 6 B) and −12.9 (br, 1 B). Compound **5** (red); NMR (resonances due to minor isomer **5b** marked with an asterisk), ^1H, δ −5.4 (br, 2 H, BHRh), 1.18 and 1.27* (2 × s, 6 H, CMe); $^{31}P\text{-}\{^1H\}$, δ 46.9 (d, 2 P, PRh, J_{RhP} 184), 43.3 (m, vbr, 1 P, PAu), 42.1* (d, 1 P, PAu, J_{RhP} 20), and 37.3* (d, 2 P, PRh, J_{RhP} 133). Compound **7** (yellow); ^1H NMR (−60 °C), δ −3.90 (mbr, 1 H, μ-H), 1.29 and 2.05 (s × 2, 6 H, CMe); $^{31}P\text{-}\{^1H\}$ (−60 °C), δ 46.2 (d of d of d, PRh, J_{RhP} 140, J_{PP} 14 and 10), 39.5 (d of d of d, PAu, J_{RhP} 20, J_{PP} 7 and 14), and 29.5 (d of d of d, PAu, J_{RhP} 17, J_{PP} 7 and 10).

§ *Crystal data* for **2**: $C_{58}H_{60}AuB_9IrP_3$, M = 1336.5, monoclinic, space group $P2_1/c$, a = 21.507(4), b = 12.508(2), c = 20.669(4) Å, β = 91.24(2)°, U = 5557(2) Å^3, Z = 4, D_c = 1.60 g cm^{-3}, $F(000)$ = 2616, μ(Mo-Kα) = 51.4 cm^{-1}, R = 0.032 (R_w = 0.031) for 4609 unique data [293 K, θ–2θ scans, 2θ ≤ 40°, $F \geq 2\sigma(F)$]. For **5a**. $C_{58}H_{60}AuB_9P_3Rh\cdot CH_2Cl_2$, M = 1332.2, triclinic, space group $P\bar{1}$, a = 12.575(5), b = 13.472(3), c = 19.975(5) Å, α = 84.89(2), β = 77.34(3), γ = 64.35(2)°, U = 2976(2) Å^3, Z = 2, D_c = 1.49 g cm^{-3}, $F(000)$ = 1328, μ(Mo-Kα) = 29.4 cm^{-1}, R = 0.061 (R_w = 0.056) for 3949 unique data [293 K, Wyckoff ω scans, 2θ ≤ 45°, $F \geq 5\sigma(F)$]. For **7**: $C_{58}H_{61}Au_2B_9P_3Rh\cdot 2(CH_2Cl_2)$, M = 1615.0, monoclinic, space group $P2_1/c$, a = 20.516(9), b = 14.373(7), c = 22.739(8) Å, β = 106.18(3)°, U = 6440(5) Å^3, Z = 4, D_c = 1.67 g cm^{-3}, $F(000)$ = 3144, μ(Mo-Kα) = 50.8 cm^{-1}, R = 0.063 (R_w = 0.066) for 3262 unique data [293 K, Wyckoff ω scans, 2θ ≤ 40°, $F \geq 5\sigma(F)$]. Data were collected using a Siemens R3m/V diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, λ = 0.71069 Å). The data were corrected for Lorentz, polarisation and X-ray absorption effects. The structures were solved by conventional heavy atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. Final refinements by full-matrix least-squares procedures were performed on a Micro Vax computer with the SHELXTL system of programs.[5] Scattering factors with corrections for anomalous dispersion were taken from ref. 6. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

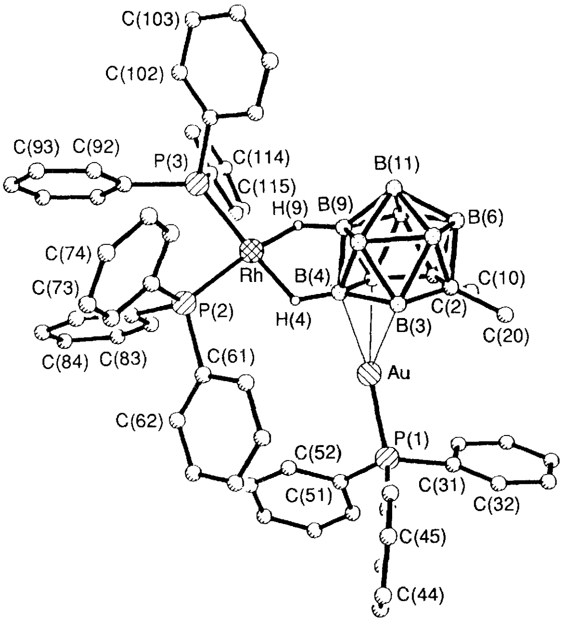


Fig. 2 Molecular structure of [*exo-nido*-5,10-{Rh(PPh$_3$)$_2$}-5,10-μ-(H)$_2$-10-*endo*-{Au(PPh$_3$)}-7,8-C$_2$B$_9$H$_7$Me$_2$]·CH$_2$Cl$_2$ **5a**. Dimensions: Au–B(3) 2.48(2), Au–B(4) 2.22(2), Au–B(5) 2.60(3), Au–P(1) 2.262(6), Rh–P(2) 2.214(6), Rh–P(3) 2.241(4), Rh–B(4) 2.41(2), Rh–B(9) 2.37(2) Å; P(1)–Au–B(4) 172.1(7)°. The atoms H(4) and H(9) were located in a difference map but their positions were not refined: Rh–H(4) 1.67, Rh–H(9) 1.57, B(4)–H(4) 1.11, and B(9)–H(9) 1.25 Å.

in the reaction between **1** and [*trans*-IrCl(CO)(PPh$_3$)$_2$] in thf, in the presence of TlBF$_4$, which gives [IrAu(CO)(PPh$_3$)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] **3a**, in essentially quantitative yield.¶

In contrast with these results, treatment of [IrCl(CO)$_2$(NH$_2$C$_6$H$_4$Me-4)] with **1** in CH$_2$Cl$_2$, in the presence of TlBF$_4$, affords a chromatographically separable mixture (*ca.* 1:2) of [IrAu(CO)$_2$(PPh$_3$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] **3b**‡ and the cluster compound **4**.¶ The latter displays dynamic behaviour in solution at room temperature, as evidenced by the appearance of a single resonance in the ^{31}P-{^{1}H} NMR spectrum.‡ Formation of **3b** from **1** involves transfer of the C$_2$B$_9$H$_9$Me$_2$ cage from Au to Ir. However, **3b** may also be obtained as the sole product from the reaction between [NEt$_4$][Ir(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] and [AuCl(PPh$_3$)] in CH$_2$Cl$_2$.

Treatment of [RhCl(PPh$_3$)$_3$] with **1** in thf, in the presence of TlBF$_4$, affords compound **5**,‡ which in solution exists as an equilibrium mixture of two isomers **5a** and **5b** (*ca.* 6:1). Solutions afford crystals of the major isomer **5a**, the structure of which was established by X-ray crystallography (Fig. 2).§ The molecule may be regarded as an ion-pair complex of the cationic rhodium fragment [Rh(PPh$_3$)$_2$]$^+$ and the anion of the salt **1**. In this respect, **5a** is isolobal with [*exo-nido*-5,10-{Rh(PPh$_3$)$_2$}-5,10-μ-(H)$_2$-10-*endo*-H-7,8-C$_2$B$_9$H$_7$Me$_2$] **6a**.[4] The latter in solution exists in equilibrium with its tautomer **6b** which has a *closo*-icosahedral structure similar to that proposed for **5b**. The relationship between the species **5** and **6** provides a remarkable example of isolobal mapping involving the groups H$^+$ and [Au(PPh$_3$)]$^+$.

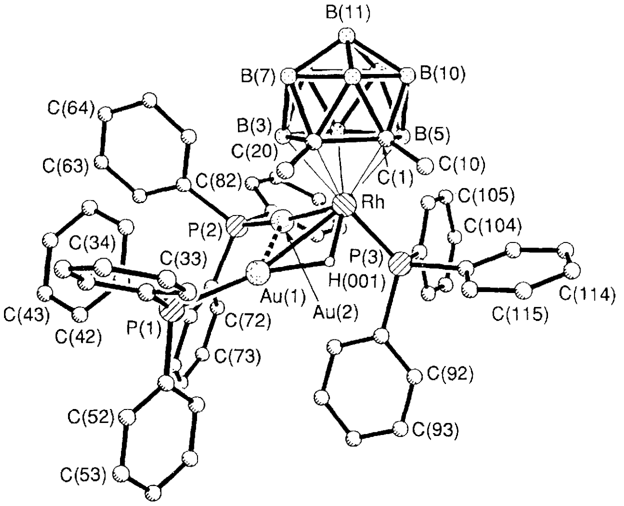


Fig. 3 Molecular structure of [RhAu$_2$(μ-H)(PPh$_3$)$_3$(η^5-C$_2$B$_9$H$_9$Me$_2$)]·2(CH$_2$Cl$_2$) **7**. Dimensions: Au(1) · · · Au(2) 2.905(2), Au(1)–Rh 2.695(2), Au(2)–Rh 2.601(3), Au(1)–P(1) 2.270(7), Au(2)–P(2) 2.269(8), Rh–P(3) 2.279(8) Å; Au(1)–Rh–Au(2) 66.5(1), P(3)–Rh–Au(1) 99.4(2), P(3)–Rh–Au(2) 85.2(2), P(1)–Au(1)–Rh 163.7(2), P(2)–Au(2)–Rh 173.0(2)°. Atom H(001) in calculated position: Au(1)–H(001) 1.82, Rh–H(001) 1.79 Å.

If hydrogen-saturated CH$_2$Cl$_2$ solutions of [Rh(PPh$_3$)$_2$(cod)][PF$_6$] (cod = cycloocta-1,5-diene) are treated with **1** at −20 °C, a mixture of **5** and the μ-hydride trimetal complex **7**‡ is formed in *ca.* 2:1 ratio. The structure of the latter is shown in Fig. 3,§ and provides a further example of cage transfer from gold to another metal centre.

These reactions demonstrate the versatility of the reagent **1** in the synthesis of compounds with metal–metal bonds involving gold.

Received, 2nd September 1991; Com. 1/04548E

¶ Single crystal X-ray diffraction studies have been carried out on compounds **3a** and **4**, and the results will be reported in a full paper. For compound **4** only the positions of the metal atoms have been located: Ir–Ir 2.82(2), Au–Au (range) 2.69(1)–3.13(1), and Au–Ir (range) 2.60(1)—2.75(1) Å.

References

1 K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, 1976, **14**, 145; M. F. Hawthorne, *J. Organomet. Chem.*, 1975, **100**, 97; M. F. Hawthorne and G. B. Dunks, in *Boron Hydride Chemistry*, ed. E. Muetterties, Academic Press, NYC, 1975, pp. 383–430.
2 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 771.
3 J. Buchanan, E. J. M. Hamilton, D. Reed and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1990, 677; E. J. M. Hamilton and A. J. Welch, *Polyhedron*, 1990, **9**, 2407.
4 J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2979.
5 G. M. Sheldrick, SHELXTL programs for use with a Nicolet X-ray System, Cambridge, 1976, updated Göttingen, 1981.
6 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.