Boron–Carbon Bond Formation at an Interstitial Boron Atom: Molecular Structure of [$HRu_4(CO)_{12}B(H)C(Ph)CHPh$]

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Upon photolysis, the tetraruthenaborane butterfly cluster [$HRu_4(CO)_{12}BH_2$] reacts with diphenylacetylene to produce [$HRu_4(CO)_{12}B(H)C(Ph)CHPh$] in good yield and insertion of the alkyne into the cluster is accompanied by (i) B–H bond activation, (ii) B–C bond formation and (iii) Ru_{hinge}–Ru_{wing} bond cleavage; the crystallographic structural characterisation and solution NMR spectroscopic properties of [$HRu_4(CO)_{12}B(H)C(Ph)CHPh$] are reported.

One of the interests of tetrametal butterfly clusters is that they frequently possess an interstitial atom or a bridging group which supports the butterfly framework. Unsupported M_4-butterfly skeletons are quite rare.[1] The geometry of the butterfly framework replicates that of a step site on a metal surface; reactions mediated by this M_4-array, but carried out at the molecular level, should give insight into the activity of the stepped-surface site.[1—4] The most actively explored area is that of the chemistry of M_4-cluster carbides,[1,4,5] and recently, Lewis *et al.* have reported the coupling of an alkyne to the interstitial carbide atom in [$H_2Ru_4(CO)_{12}C$], [Figure 1(a)].[6] The reaction path observed for this carbide cluster with diphenylacetylene contrasts with that observed by Gladfelter *et al.* for the isoelectronic cluster nitride, [$HRu_4(CO)_{12}N$].[7] In this case, the acetylene is inserted into the hinge of the metal butterfly with concomitant generation of a μ_4-NH ligand, [Figure 1(b)]. We now extend this series of reactions to that of PhC≡CPh with [$HRu_4(CO)_{12}BH_2$],[8—10] a cluster which is

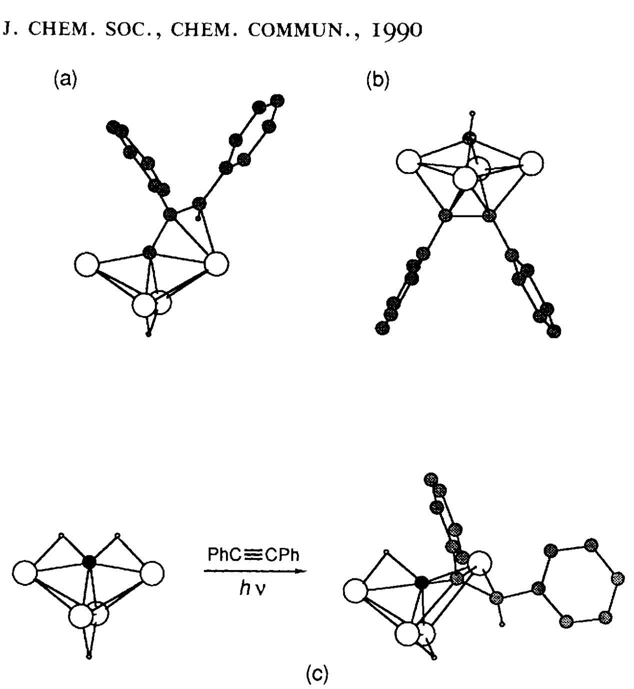

Figure 1. Schematic representations of (a) structure of $[HRu_4(CO)_{12}CC(Ph)CHPh]$;[6] (b) structure of $[(PhCCPh)Ru_4(CO)_{12}NH]$;[7] and (c) the formation of $[HRu_4(CO)_{12}B(H)C(Ph)CHPh]$, (**2**).

isoelectronic with both $[H_2Ru_4(CO)_{12}C]$ and $[HRu_4(CO)_{12}N]$ but which possesses additional *endo*-hydrogen atoms.

The photolysis of PhC≡CPh (0.6 mmol) with $[HRu_4(CO)_{12}BH_2]$, (**1**) (0.2 mmol),[8-10] in chloroform solution for 22 h at room temperature leads to a colour change from yellow–orange to red. Chromatographic separation using hexane as the eluting solvent, gives two coloured bands; the first (yellow) band is due to residual $[HRu_4(CO)_{12}BH_2]$. The second (orange) band yields (*ca.* 60%) $[HRu_4(CO)_{12}B(H)C(Ph)CHPh]$, (**2**).† The ^{11}B NMR spectrum of (**2**) shows a signal at δ +93.7 compared with δ +109.9 ppm for (**1**).[8,9] This change in shift is relatively small and suggests that the boron atom remains in contact with four ruthenium atoms. Crystals of (**2**) suitable for *X*-ray analysis were obtained from hexane solution.‡ The structure of (**2**) is illustrated in Figure 2 and exhibits an open Ru_4-cluster which may be envisioned as a 64-electron spiked triangular framework supporting a C_2B-fragment. The boron atom, originally interstitial within the Ru_4-butterfly of (**1**), retains four Ru–B bonding contacts in (**2**) and is also bonded to one carbon atom of the unsaturated hydrocarbon. Compared with the original butterfly skeleton of (**1**), one Ru_{hinge}–Ru_{wing} is cleaved as the alkyne inserts to form (**2**); Ru(1)···Ru(4) = 4.007(1) Å. The B(1)–C(14) bond length of 1.612 (17) Å lies towards the extreme end of the range observed for B–C single bonds[11] but is within the range of distances determined by *X*-ray diffraction for multicentre B–C interactions in carbaborane clusters.[12] The connectivity of atom C(14) is five, and this may be rationalised by recognising that atom C(14) bridges the Ru(1)–B(1) edge; the distance of 2.387(11) Å for C(14)–Ru(1) is rather long for a Ru–C σ-bond and is actually longer than either C(14)–Ru(4) or C(13)–Ru(4), the two interactions which comprise an alkene-to-ruthenium π-bond [Figures 1(c) and 2]. The carbon–carbon bond length of the unsaturated hydrocarbon is 1.466(14) Å, a distance which indicates[13] a significant loss of π-character as the alkyne interacts with the ruthenaborane; this C–C distance compares with 1.402(5) Å in $[HRu_4(CO)_{12}CC(Ph)CHPh]$[6] and 1.416(3) Å in $[Ru_4(CO)_{12}(NH)C_2Ph_2]$.[7]

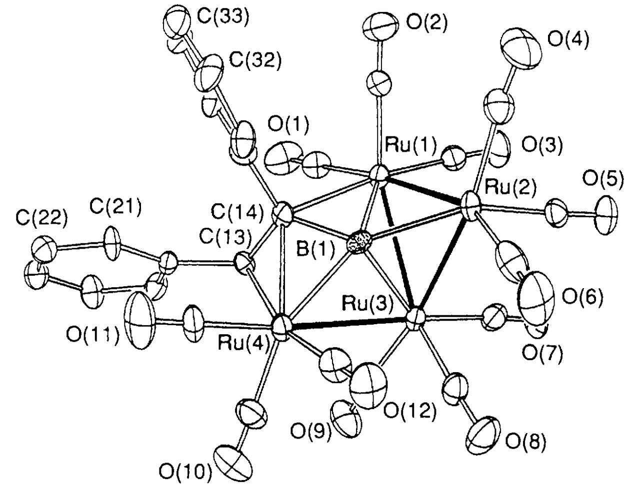

Figure 2. Molecular structure of (**2**) (one of two independent, but chemically similar structures shown): Ru(1)–Ru(2), 2.794(1); Ru(1)–Ru(3), 2.922(1), Ru(2)–Ru(3), 2.807(1); Ru(3)–Ru(4), 2.950(1); B(1)–Ru(1), 2.236(14); B(1)–Ru(2), 2.178(13); B(1)–Ru(3), 2.193(12); B(1)–Ru(4), 2.152(13) Å.

The *endo*-hydrogen atoms in (**2**) were not located directly, but ^{11}B and ^{1}H NMR spectral data indicate population of Ru–H–Ru and Ru–H–B sites. Inspection of the carbonyl ligand orientations provides indirect evidence that the *endo*-H atoms bridge edges Ru(1)–Ru(3) and Ru(2)–B(1). Ru(1)–Ru(3) represents the original hinge of the Ru_4-butterfly in (**1**) and is *ca.* 0.12 Å longer than the other two Ru–Ru distances in the Ru_3-triangle. Ru(4)–Ru(1) and Ru(2)–B(1) correspond to the original Ru_{wing}–B edges in (**1**); in (**2**), Ru(2)–B is slightly longer than Ru(4)–B, consistent with the presence of a bridging H atom.[14] All carbonyl ligands in (**2**) are terminally bonded and this is in contrast to those in the isoelectronic cluster $[HRu_4(CO)_{12}CC(Ph)CHPh]$.[6] The room temperature ^{13}C NMR spectrum of (**2**) is consistent with the persistence of a static structure in solution, although three of the resonances (δ 195.7, 191.9, and 188.6) are somewhat broader than the remaining nine. This implies that the barrier for localized carbonyl ligand rotation for one $Ru(CO)_3$ unit is lower than for the other three, and we propose that this site is Ru(2) since it is the least sterically hindered.

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† $[HRu_4(CO)_{12}B(H)C(Ph)CHPh]$: 400 MHz ^{1}H NMR ($CDCl_3$) δ 7.4—7.0 (m Ph), 5.04 (s, CH), −7.3 (br B–H–Ru), −19.06 (s Ru–H–Ru); 128 MHz ^{11}B NMR ($CDCl_3$) δ +93.7 (d J_{BH} 40 Hz); 100 MHz ^{13}C NMR ($CDCl_3$) δ 200.4 (1 CO), 197.6 (1 CO), 197.4 (1 CO), 196.4 (1 CO), 195.7 (1 CO), 194.2 (1 CO), 192.0 (1 CO), 191.9 (1 CO), 189.9 (1 CO), 188.6 (1 CO), 188.1 (1 CO), 187.3 (1 CO), 147.3 (1 C_{Ph}), 143.8 (1 C_{Ph}), 129.7 (br C_B), 128.5 (4 C_{Ph}), 128.0 (4 C_{Ph}), 127.3 (1 C_{Ph}), 125.6 (1 C_{Ph}), 74.2 (CH, J_{CH} 160 Hz); IR (hexane, ν_{CO}) 2098w, 2073vs, 2060s, 2049vs, 2027m, 2018m, 2012w, 1997w; FAB-MS in 3-NBA matrix, *m/z* 934 (P^+) with 12 CO losses observed; isotopic pattern agrees with that simulated for (**2**).

‡ *Crystal data* for (**2**): $C_{26}H_{13}BO_{12}Ru_4$, mol. wt. = 932.44, monoclinic, $P2_1/c$, a = 9.758(2), b = 36.653(8), c = 17.131(4) Å, β = 101.92(2)°, U = 5996(3) Å^3, Z = 8 (two independent, but chemically similar, molecules), D_x = 2.066 g cm^{-3}, μ(Mo-K_α) = 20.0 cm^{-1}, T = 294 K. Of 12 843 data collected (Nicolet R3m diffractometer) and corrected for absorption ($4° \leq 2\theta \leq 52°$), 11 764 were independent and 7001 with $F_o \geq 4\sigma(F_o)$ were observed. With all non-hydrogen atoms anisotropic, non-bridging hydrogen atoms idealized, and phenyl rings constrained to rigid hexagons: R_F = 5.56%, $R_{(wF)}$ = 6.57%, GOF = 1.197, $\Delta(\rho)$ = 1.27 e Å^{-3}, N_o/N_v = 9.63. SHELXTL software (5.1), G. Sheldrick, Nicolet XRD, Madison, WI (USA). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

During the reaction of diphenylacetylene with (**1**), one B–H bond is activated and an *endo*-hydrogen atom is transferred from a Ru–H–B bridge site to a C–H terminal position generating an alkene ligand with concomitant B–C bond formation. The organic fragment donates one σ- and two π-electrons to the tetraruthenium framework, while the boron atom provides all of its valence electrons; thus, with two *endo*-hydrogen atoms still present in (**2**), the net electron count is 64 and the butterfly cluster, therefore, opens in going from (**1**) to (**2**). This phenomenon appears to be in response to the fact that the boron atom maintains its interstitial role and is not drawn out of the cluster as B–C bond formation occurs; *i.e.* C(14) lies *endo* to the cluster rather than *exo*. This contrasts with the bonding in [$HRu_4(CO)_{12}CC(Ph)CHPh$] in which the carbon atom corresponding to C(14) is in an *exo*-position, thus, permitting the cluster to retain the 62 electron count of the starting cluster [$H_2Ru_4(CO)_{12}C$].[6] The bonding in (**2**) is currently being examined in detail.

Acknowledgement is made to the Donors of the PRF, administered by the ACS, for support of this research (grant #19155-AC3), to the Royal Society for a 1983 University Research Fellowship (to C. E. H.), and to the NSF for a grant towards the purchase of a diffractometer at the University of Delaware. Johnson–Matthey is thanked for generous loans of $RuCl_3$.

Received, 10th April 1990; Com. 0/01624A

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