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Electrochemical evidence for electronic interactions through the *para*-carborane skeleton in the novel tricluster [{$Co_2C_2(SiMe_3)(CO)_4$(dppm)}$_2$(μ-$CB_{10}H_{10}C$)]

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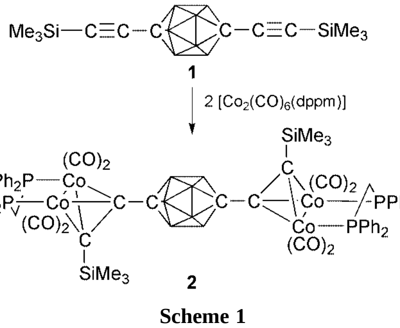
The electrochemical properties of the title compound reveal electronic interactions between two dicobalt–dicarbon clusters *via* a 1,12-*para*-carborane cage.

Conjugated molecular and polymeric compounds with delocalised π-electron frameworks and rigid-rod geometries are a source of immense contemporary interest, with potential for application in the construction of photonic and molecular electronic devices.[1] The unusual electronic properties of *closo*-carborane cages, which display three-dimensional aromaticity,[2] and the abilities of *para*-carboranes to form rod-like structures have raised considerable interest in the synthesis of novel conjugated materials that contain this motif.[3–7] The capacity for polyhedral transition metal clusters to act as 'electron sinks', accepting or releasing electrons in response to the demands of the environment (*i.e.* an electrode) or pendant groups, suggests molecular assemblies which feature these moieties may be of use in molecular electronics applications.[8]

However, compounds which feature both carborane and transition metal clusters are rare,[9] and the transmission of electronic effects between these different types of polyhedra has not yet been demonstrated. We have taken advantage of the availability of 1,12-bis(trimethylsilylethynyl)-*para*-carborane **1**[10] and the redox properties of Co_2(alkyne) complexes[11,12] to demonstrate, using electrochemical methods, the capacity for the 12-vertex *para*-carborane fragment to transmit electronic information between two transition metal clusters. Aryl, alkynyl and ferrocenyl based spacing groups have already been shown to permit such interactions between cobalt-containing tetrahedral clusters.[12]

The reaction of **1** with [$Co_2(CO)_6$(dppm)][13] in refluxing benzene afforded a dark red solution from which the novel tricluster compound **2** was isolated as the major product (60 mg, 40%) by preparative TLC and crystallisation (CH_2Cl_2–MeOH) (Scheme 1). The composition of the complex was established from the spectroscopic data,† and confirmed by X-ray analysis.‡ The structure (Fig. 1) clearly shows the *para*-C_2B_{10} icosahedron and the two Co_2C_2 tetrahedra, which are related by a crystallographic inversion centre at the centre of the carborane cage. The carborane cage in **2** is the most spherical example of a *para*-carborane structurally characterised to date, with a cage C···C separation of 3.176 Å and an average tropical B–B bond length of 1.776 Å. This contrasts sharply with the distorted cage geometry found in 1,12-bis(ethynyl)-*para*-carborane [C···C 3.104(2) Å, tropical B–B 1.793(3) Å].[10] These variations in the geometry of the carborane cage are probably a consequence of the different interactions between the carborane C_{sp} atom and the carbon centre of the pendant ethynyl group [C_{sp}, C–C 1.451(2) Å] or cobalt cluster [**2**, C_{sp^3}, C(1)–C(2) 1.497(2) Å]. The parameters associated with the cobalt(alkyne) cluster cores fall in the range established for aryl substituted clusters.[14] While the description of carborane clusters as analogues of benzene is not intended to be literal, we note here that the C(1)–C(2) bond in **2** is longer than the C(aryl)–C(cluster) separations in conjugated Co_2(μ-η^2-$RC_2C_6H_4$-X-*p*)$(CO)_4$(dppm) systems [1.458(3)–1.463(3) Å],[14] due to the high coordination number of the carborane cage carbon atoms.



Scheme 1

The Co_2C_2 tetrahedral cluster core offers a filled a_2-type fragment orbital suitable for interaction with π-systems of adjacent groups bonded at a carbon vertex of the tetrahedron.[15] The carbon atoms of the carborane cage offer tangential fragment orbitals with considerable p-character suitable for such an interaction.[16] Of course, good orbital overlap requires matching of fragment orbital energy as well as symmetry. The concept of a degree of π-bonding between the cobalt/carbon and boron/carbon cluster cores in the neutral tricluster **2** is supported, although by no means proven, by the geometry adopted by the complex in the solid state. Semi-empirical MO calculations (LANL2MB)[17] revealed the frontier orbitals (HOMO and LUMO) of **2** to be largely centred on the cobalt clusters.

The cyclic voltammogram of complex **2** revealed both oxidation and reduction processes which were better resolved using semi-derivative[18] and square wave voltammetry (SWV) (Fig. 2). Digital simulation of the CV and SWV responses was employed to confirm the four redox potentials [+0.87, +0.77, −1.58, −1.66 V (*vs.* decamethylferrocene, Fc*/Fc*⁺ 0.084 V); ΔE^0(ox) *ca.* 105 mV, $K_C = e^{\Delta E^\circ F/RT} = 60$; ΔE^0(red) *ca.* 80

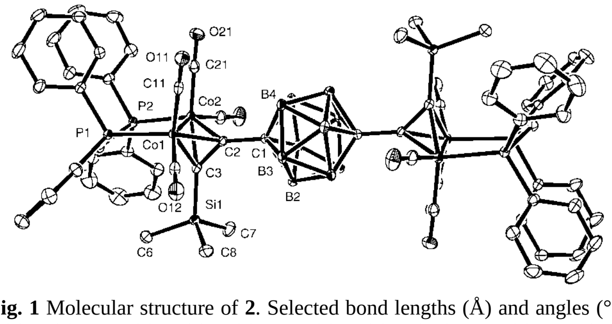


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.497(2), C(2)–C(3) 1.359(2), C(1)–B(av.) 1.728(3), B–B(av.) 1.771(3), Co(1)–Co(2) 2.4804(4), C(1)–C(2)–C(3) 139.3(2), C(2)–C(3)–Si(1) 138.9(1), Co(1)–Co(2)–P(2) 98.41(2), Co(2)–Co(1)–P(1) 95.14(2).

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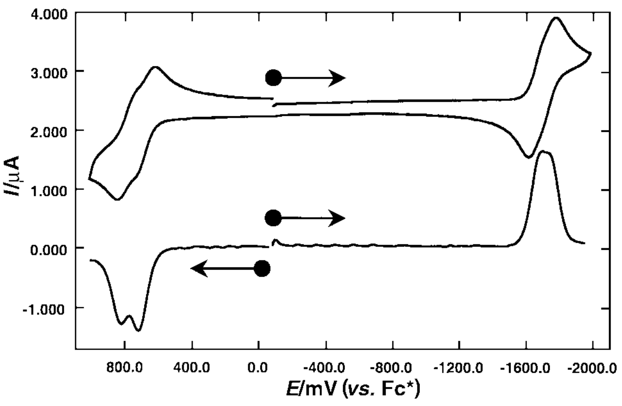

Fig. 2 Cyclic voltammogram (upper trace) and corresponding semi-derivative voltammogram of a THF solution of 2 (0.5 mM), containing 0.1 M $[NBu_4]PF_6$ as supporting electrolyte, at 0.2 V s^{-1}. Data obtained at 298 K, glassy carbon working electrode *vs.* SCE reference electrode.

mV, K_C = 5].[19] No redox processes were found within the accessible potential window when **1** was subjected to a similar electrochemical study. For comparison, the phenyl-bridged complex $[\{Co_2C_2(H)(CO)_4(dppm)\}_2(\mu\text{-}1,4\text{-}C_6H_4)]$ gave also gave two oxidation and reduction processes with ΔE^0(ox) 110 mV, ΔE^0(red) 80 mV.[12c]

The splitting of redox waves associated with otherwise chemically identical redox sites contained within a single molecular unit is often cited as evidence of electronic interaction (or communication) between these sites.[11,12,20] These interactions may be transmitted between the bonding framework or through-space.[21] While ion-pairing effects may be expected to play a role in the magnitude of the coulombic interaction between remote intramolecular sites, a through-space interaction should affect both oxidation and reduction processes more or less equally. In the present example, the difference in oxidation potentials observed is significantly large, especially given the > 6 Å separation of the cobalt cluster cores, and is indicative of a moderate degree of extended electronic communication between the cobalt clusters in the radical cation $\mathbf{2}^{\cdot+}$. The separation of the reduction events is somewhat smaller, but is still larger than the statistical limit (*ca.* 36 mV at 298 K) predicted for non-interacting redox centres.[20] The voltammetric studies reported here therefore suggest that the unpaired electron in both the radical cation $\mathbf{2}^{\cdot+}$ and the radical anion $\mathbf{2}^{\cdot-}$ is delocalised through the bonding framework. These studies clearly indicate that the bonding framework of the *para*-carborane cage can offer an efficient conduit for electronic effects, and may participate in π-type delocalised bonding with substituents in the 1 and 12 positions. Further studies on the scope of these interactions and a thorough molecular orbital description of assemblies derived from *para*-carboranes, including $\mathbf{2}^{\cdot+}$ and $\mathbf{2}^{\cdot-}$ are in progress.

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Notes and references

† *Selected spectral data*: NMR ($CDCl_3$): ^1H, δ 7.10–6.30 (m, 20H, Ph), 3.09, 3.25 (2 dt, $J_{HP} = J_{HH}$ = 11 Hz, 2 × 1H, CH_2), 1.28 (br, 5H, BH), 0.00 (s, 9H, $SiMe_3$). ^{11}B, δ −11.0. FAB-MS (*m/z*) 1454, 1426, 1342 $[M - nCO]^+$ (n = 4, 5, 7). IR (cyclohexane): ν(BH) 2659; ν(CO) 2026m, 2002s, 1976s, 1964m cm^{-1}. Found: C, 52.15; H, 4.56. $C_{70}H_{72}B_{10}O_8Si_2P_4Co_4\cdot 0.5CH_2Cl_2$ requires C, 52.64; H, 4.42%.

‡ *Crystal data*: $C_{73}H_{78}B_{10}O_8Si_2P_4Cl_6Co_4$, M = 1819.93, triclinic, space group $P\bar{1}$, a = 12.287(2), b = 13.004(2), c = 13.545(2) Å, α = 103.15(1), β = 95.82(1), γ = 96.04(1)°, V = 2078.1(6) $Å^3$, T = 100(2) K, Z = 1, μ(Mo-Kα) = 1.135 mm^{-1}, 23469 reflections measured, 9578 unique (R_{int} = 0.0396) which were used in all calculations. The final $wR(F^2)$ = 0.0789 (all data). All phenyl group hydrogen atoms were placed in calculated positions and refined using a riding model. Three disordered molecules of CH_2Cl_2 were found per formula unit. CCDC reference number 167400. See http://www.rsc.org/suppdata/cc/b1/b104307m/ for crystallographic data in CIF or other electronic format.

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