Synthesis and molecular structure of dicarbaboryl ethenes and an unexpected dimetallated derivative

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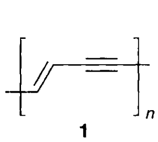
The first examples of molecules in which carbaborane clusters are linked *via* a simple C=C double bond, and which constitute model compounds for boronated polydiacetylenes, are reported; double metallation of one of these molecules affords a unique *closo–pseudocloso* bis(carbametallaborane).

Polydiacetylenes (PDAs) **1** are an important class of materials because of their third-order non-linear optical [$\chi^{(3)}$ NLO] properties.[1] Interestingly such NLO properties are retained when the alkyne units of PDAs are coordinated to transition-metal fragments such as $\{Co_2(CO)_6\}$.[2] Since an essential aspect of the $\chi^{(3)}$ NLO properties of PDAs is electron delocalisation along the molecular backbone, and since the electronic structures of carbaboranes are fully delocalised,[3] we reasoned that poly(carbaborane) species derived from PDAs might represent compounds with interesting and potentially useful electronic and optical properties. Herein we report the synthesis and characterisation of the first example of a polycarbaborane compound produced from an enyne (a model compound for a PDA) and a novel *closo–pseudocloso* bis(carbametallaborane) species derived from it.

Reaction of 1,6-diphenylhexa-1,5-diyn-3-ene with 2 equiv. of $B_{10}H_{14}$ in refluxing toluene in the presence of MeCN affords *trans*-1,2-bis(2′-phenyl-1′,2′-*closo*-dicarbadodecaboranyl)-ethene **2a** (Scheme 1). The bis(*p*-tolyl) analogue **2b** and the asymmetric Ph/*p*-tolyl analogue **2c** were prepared similarly. Compounds **2** were characterised by microanalysis and multinuclear NMR spectroscopy† and by a crystallographic study of **2a** (Fig. 1.)‡ The molecule resides on a crystallographic inversion centre, imposing a *trans* configuration about the central C=C double bond. The other cage carbon atom, C(2), is nearly coplanar with the C(1)C(11)C(11′)C(1′) sequence and positioned *trans* across the C(1)–C(11) bond affording a C(2)–C(1)–C(11)–C(11′) torsion angle of 154.5°. Overall, the entire molecule has nearly D_{2h} symmetry.

Decapitation of the bis(*closo*-carbaborane) **2a** with excess KOH in EtOH affords the bis(*nido*) species [*nido*-$PhC_2B_9H_9$–$\mu(C_2H_2)$–*nido*-$PhC_2B_9H_9]^{4-}$, isolated as its Tl^+ salt. Further reaction of this species with $[Ru(p\text{-cymene})Cl_2]_2$ (*p*-cymene = C_6H_4Me-1-Pr^i-4) in CH_2Cl_2 yields the bis(carbametallaborane) compound **3a** as an orange crystalline product, characterised by microanalysis and multinuclear NMR spectroscopy§ and by single-crystal X-ray diffraction (Fig. 2).‡

Although ^{11}B and ^1H NMR studies clearly show that, in solution at room temperature, **3a** is symmetric about the central C=C unit, in the solid state the two carbaruthenaborane units are clearly different. The cage of Ru(3A) has the expected *closo* icosahedral geometry previously established[4] for 1-Ph-2-Me-



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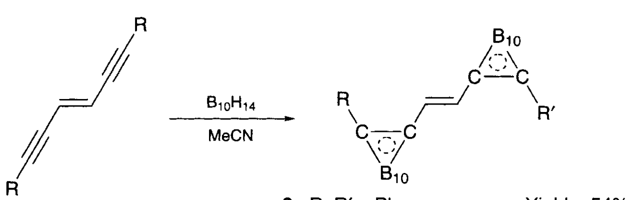

2a R, R′ = Ph Yield = 54%
b R, R′ = C_6H_4Me-*p* Yield = 45%
c R = Ph, R′ = C_6H_4Me-*p* Yield = 80%

Scheme 1

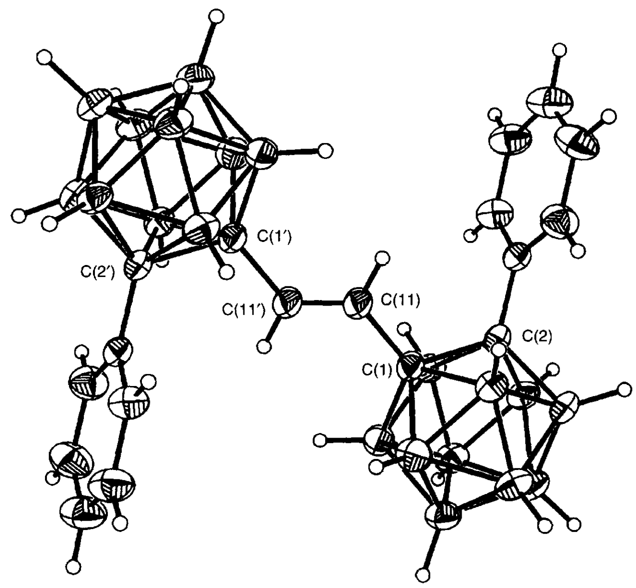

Fig. 1 Perspective view of compound **2a**; primed atoms are generated by crystallographically imposed inversion

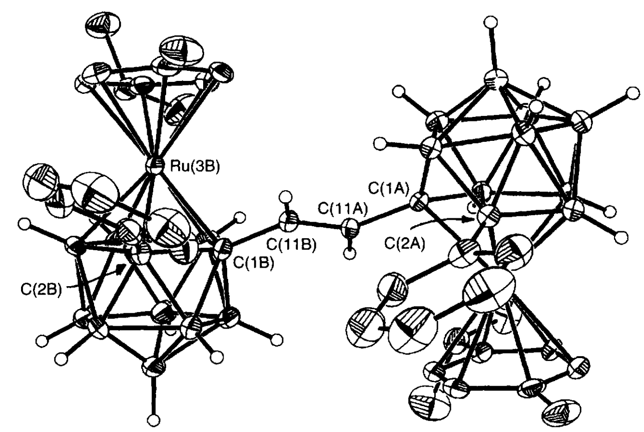

Fig. 2 Perspective view of compound **3a** with H atoms of the phenyl ring and *p*-cymeme ligand omitted for clarity; Ru(3A) is obscured by the phenyl group attached to C(2A)

3-(*p*-cymene)-3,1,2-*closo*-$RuC_2B_9H_9$, but the cage of Ru(3B) is deformed into the *pseudocloso* architecture very recently described[5] for 1,2-Ph_2-3-(*p*-cymeme)-3,1,2-*pseudocloso*-$RuC_2B_9H_9$. Thus, in **3a**, C(1B)–C(2B) has a normal length, 1.766(8) Å, whilst C(1A)–C(2A) is stretched to 2.361(8) Å. Compound **3a** represents the first example of *closo* and *pseudocloso* carbametallaboranes within the same molecule.

It is likely that the origin of the deformation of cage A of **3a** is repulsion between one of the *ortho*-H atoms of the phenyl ring and H(11B), which lies in a *cis* disposition to it (Fig. 3), by analogy with the cause of the *pseudocloso* deformation in related species[5] (no similar crowding exists for cage B). In cage A the congestion arises because the cage has undergone substantial rotation about the C(11A)–C(1A) bond relative to its position in **2a** [torsion angle C(2A)···C(1A)–C(11A)–C(11B) 56.5 °], presumably driven by the steric requirement of the two η-bonded *p*-cymene ligands to be far apart. This, in turn, implies that the double decapitation of **2** has unexpectedly involved the removal of boron vertices from the same side of the C(1)C(11)C(11′)C(1′) plane [*e.g.* B(3) and B(6′)].

Compounds **2a**, **2b** and **2c** constitute the first examples of a new class of compound (the dicarbaboryl ethenes) which are both model compounds for, and potential building blocks in the designed synthesis of, poly-boronated PDAs.¶ Such compounds clearly have potentially interesting derivative chemistries (exemplified by the unexpected structure of **3a**) and potentially useful materials properties.

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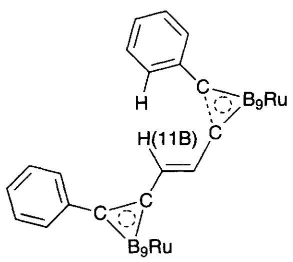

Fig. 3

Footnotes

† For compound **2a**: Anal. Found: C, 46.8; H; 7.13. Requires: C, 46.6; H, 6.91%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.6–7.3 (m, 10 H, Ph), 5.55 (s, 2 H, =CH–). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ −3.15 (2 B), −10.25 (8B). Compounds **2b** and **2c** similarly characterised.

‡ *Crystal data*: for **2a**, $C_{18}H_{32}B_{20}$, monoclinic, space group *C*2/*c*, a = 26.917(5), b = 6.8160(14), c = 19.465(4) Å, β = 129.50(3)°, U = 2755.6(10) Å^3, Z = 4. 2193 independent reflections were measured to θ_{max} 25° on a Siemens P4 diffractometer at 290 K. The structure was refined to R = 0.0568 for 1351 observed data [$F \geqslant 4\sigma(F)$].

For **3a**, $C_{38}H_{58}B_{18}Ru_2$, triclinic, space group $P\bar{1}$, a = 9.1640(10), b = 13.478(2), c = 19.064(2) Å, α = 104.766(9), β = 91.879(10), γ = 102.504(14)°, U = 2213.3(5) Å^3, Z = 2. 7660 independent reflections were measured as above. The structure was refined to R = 0.0442 for 5342 observed data [$F \geqslant 4\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/75.

§ Compound **3a**: Anal. Found: C, 48.2 H, 6.91. Requires: C, 48.6; H 6.75%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.4–7.0 (m, 10 H, Ph), 6.6 (s, 2 H, =CH–), 6.0–5.3 (m, 8 H, MeC_6*H_4*$CHMe_2$), 2.85 (spt, 2 H, $^3J_{HH}$ 7 Hz, MeC_6H_4C*H*Me_2), 1.9 (s, 6 H, *Me*$C_6H_4CHMe_2$), 1.2 (d, 12 H, $^3J_{HH}$ 7 Hz, MeC_6H_4CH*Me_2*). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ 20.4 (1B), 10.0 (1B), 4.2 (1B), −0.3 (2B), −2.4 (3B), −17.7 (1B).

¶ However, molecules containing vinyl and related groups attached to carbaboranes have been previously reported.[6]

References

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