A NOVEL HETEROOCTAMETALLIC METALLACARBORANE TETRAMER+

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.

The synthesis and X-ray crystal structure determination of $[(2,3\text{-}Et_2C_2B_4H_4)\text{-}Co(2,3\text{-}Et_2C_2B_3H_3\text{-}5\text{-}Bu)Ru]_4$ (**3**) are reported. Complex **3** was obtained serendipitously in low yield from a reaction of $[(\eta^4\text{-}C_8H_{12})Ru(MeCN)_4][PF_6]_2$ with the $(Et_2C_2B_4H_4)\text{-}Co(Et_2C_2B_3H_3Bu)^{2-}$ anion in THF solution at room temperature. The molecular geometry of **3**, isolated as a yellow-orange crystalline solid, is without precedent in boron cluster chemistry and consists of an array of four $(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_3Bu)Ru$ units linked *via* intercluster Ru–B covalent bonds. Each cluster moiety contains a double-decker $(C_2B_4)Co(C_2B_3)$ sandwich with an exo-polyhedral ruthenium atom occupying a "wedging" position in which it is bound to the C_2B_3 and the C_2B_4 ligands as well as to a neighboring sandwich unit.
Key words: Boranes; Carboranes; Metallacarboranes; Ruthenium; Cobalt clusters; Sandwich complexes.

Synthetic routes to stable, isolable multidecker metallacarborane sandwich complexes and larger systems derived from them, have been described in a series of papers from this laboratory[2]. Most of these complexes contain internal $RR'C_2B_3H_3^{4-}$ planar rings while the end ligands are cyclic hydrocarbons such as $C_5H_5^-$, $C_5Me_5^-$, or arenes; Scheme 1 outlines the general strategy employed in the preparation of triple- and tetradecker sandwiches of this type.

In recent work[3,4], our group has developed synthetic pathways to multidecker sandwiches in which one or both of the end ligands are other than hydrocarbons, *e.g.*, $(CO)_n$ or small carboranes ($Et_2C_2B_4H_4^{2-}$, $Et_2C_2B_3H_5^{2-}$). In

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+ Part 53 in the series Organotransition-Metal Metallacarboranes. For Part 52 see ref.[1]
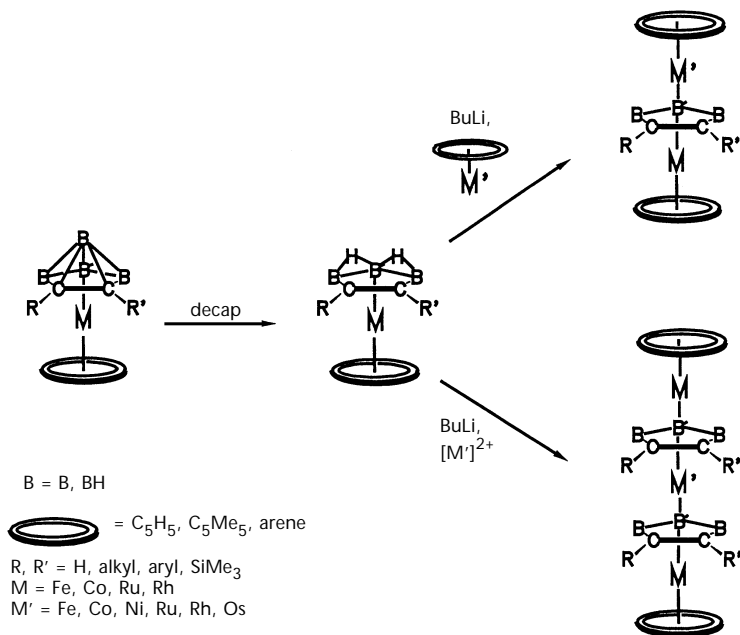
the latter class, carborane-endcapped dicobalt triple-decker anions of the type $Cp^*Co(Et_2C_2B_3H_3)Co(Et_2C_2B_3H_3)^{2-}$ serve as precursors to penta- and hexadecker complexes *via* complexation of their open C_2B_3 faces with transition metal ions[3a]. A synthetic goal of interest to us has been the construction of complexes having open carborane ring ligands at both ends, as building blocks for assembling polydecker systems.

RESULTS AND DISCUSSION

In an effort to synthesize the ruthenium-centered tetradecker **2** (Scheme 2), we treated the *nido,closo*-dianion **1**$^{2-}$ (obtained by deprotonation of neutral **1**, an analogue of previously reported[3–5] *nido,closo*-complexes $(R_2C_2B_4H_4)$-$CoH(R_2C_2B_3H_4R')$ (R = Me, Et; R' = Me, Et, Bu) with $[(COD)Ru(MeCN)_4]^{2+}$ in THF solution (COD = η^4-cyclooctadiene) at room temperature. However, the expected complex **2** was not found in the product mixture. The only isolated and characterized species was **3**, obtained in low ($\approx$3%) yield as yellow-orange crystals. The solid is air-stable, but in solution the compound on exposure to air slowly reverts to the neutral starting monomer **1**.
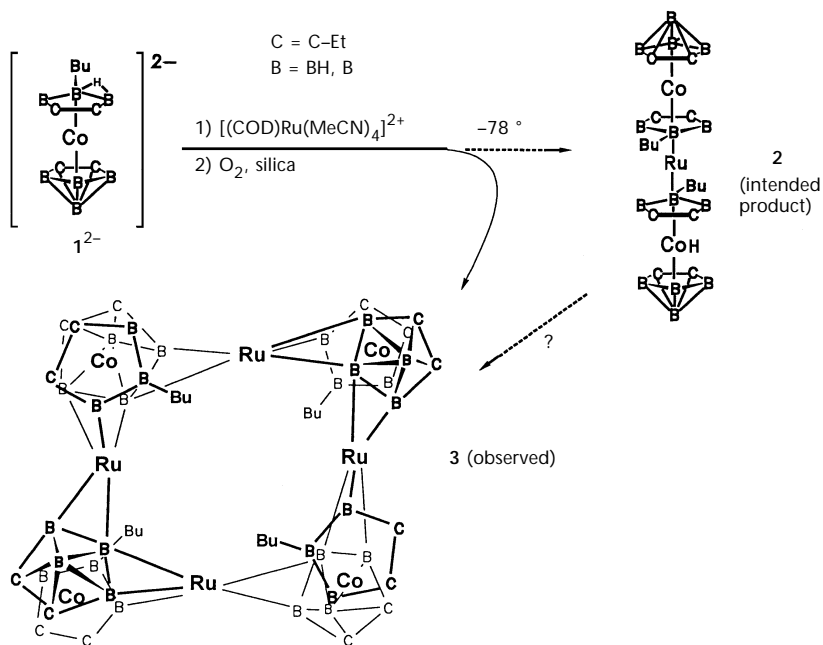
Scheme 2

The CI positive ion mass spectrum of **3** exhibits a strong envelope centered at m/z 366 corresponding to the $(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_3–C_4H_9)$ unit; no parent ion is observed. The 300-MHz ^1H NMR spectrum in $CDCl_3$ and in acetone-d_6 shows multiplets arising from the carborane ethyl and butyl protons as well as a broad singlet at δ –6.1 ppm assigned to the B–H–B bridging hydrogen atoms. These spectral data do not establish the molecular geometry, but the structure was determined *via* a single crystal X-ray crystallographic analysis, the data for which are summarized in Tables I and II.

As illustrated in Scheme 2 and in more detail in Figs 1–3, the solid-state structure of **3** is a cyclic tetramer consisting of four crystallographically equivalent $(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_3–C_4H_9)Ru$ cluster units that are related *via* a four-fold inversion axis in the tetragonal $I4_1/a$ space group. Each monomeric unit consists of a $(C_2B_4)Co(C_2B_3)$ double-decker sandwich to which a ruthenium atom is covalently bound *via* interaction with both carborane ligands and an adjacent sandwich, as shown. The carborane faces coordinated to cobalt [C(2)–C(3)–B(4)–B(5)–B(6) and C(4)–C(5)–B(7)–B(8)–B(9)] are planar but not quite parallel, as they are bent away from the ruthenium atom with a dihedral angle of 6.6°; the Co–C and Co–B distances are typical

for cobalt-small carborane sandwiches, falling within the range 2.05 to 2.18(1) Å.

Metallacarboranes exhibiting external atoms that are "wedged" between two small carborane ligands have been observed previously[6,7], although the only prior examples in which the wedging atom is a transition metal are afforded by the diiron complexes $[(Me_2C_2B_4H_4)]_2Fe_2L_2$ [L_2 = $(OMe)_2C_2H_4$ or 2 THF], the first of which was crystallographically established[6]. These species contain a low-spin Fe(II) center sandwiched between the two ligands

TABLE I
Crystallographic data of compound **3**

Empirical formula	$Co_4Ru_4C_{64}B_{28}H_{144}$
Formula weight	1 856.56
Crystal color and habit	orange plate
Crystal dimensions	$0.27 \times 0.18 \times 0.41$ mm
Crystal system	tetragonal
Lattice parameters	a = 28.152(8) Å
	c = 11.329(4) Å
	V = 8 979(8) Å^3
Space group	$I4_1/a$(No. 88, origin No.2)
Z	4
D_{calc}	1.37 g cm^{-3}
Radiation	MoKα (λ = 0.71069 Å
μ(MoKα)	13.95 cm^{-1}
Absorption corr.	Ψ scans (transm. factors 0.94–1.00)
Temperature	–120 °C
$2\theta_{max}$	46°
No. of reflections measured	Total: 3 474
	Unique: 3 320(R_{int} = 0.034)
No. of reflections $I > 3\sigma(I)$	1 722
No. of variables	226
Residuals R; R_w	0.049; 0.065
Goodness of fit	1.60
Maximum peak in final diffr. map	0.8 e Å^{-3}

and an external high-spin Fe(II)L$_2$ group. In other cases, the wedging atom is germanium, tin, or boron[7].

In **3**, the Ru and Co atoms are separated by 2.806 (2) Å, a distance that suggests little or no metal–metal interaction; in the above-mentioned diiron complex, the metal–metal distance is much shorter at 2.414 (4) Å, although in this case there is no evidence of spin-spin coupling[6]. In **3**, the agents binding the tetramer together are the four ruthenium atoms, each of

TABLE II
Selected bond distances (Å) and angles (°) for [(2,3-Et$_2$C$_2$B$_4$H$_4$)Co(2,3-Et$_2$C$_2$B$_3$H$_3$-5-Bu)Ru]$_4$ (**3**)

Atoms	Distances	Atoms	Angles
Ru–Co	2.806(2)	C3–C2–B6	115(1)
Ru–B6	2.47(1)	C2–C3–B4	115(1)
Ru–B8	2.45(1)	C3–B4–B5	106(1)
Ru–B9	2.43(1)	B4–B5–B6	97(1)
Ru–B7*	2.58(1)	C2–B6–B5	107(1)
Ru–B8*	2.50(1)	C4–C5–B7	114(1)
Co–C2	2.10(1)	B7–B8–B9	108(1)
Co–C3	2.10(1)	C4–B9–B8	103(1)
Co–C4	2.05(1)	B6–Ru–B8	92.0(4)
Co–C5	2.06(1)	B6–Ru–B9	90.8(5)
Co–B4	2.05(1)	B8–Ru–B8*	134.6(5)
Co–B5	2.05(1)	C5–B7–B8	103(1)
Co–B6	2.10(1)	B8–Ru–B7*	135.4(5)
Co–B7	2.10(1)	B4–H45–B5	90.8(5)
Co–B8	2.16(1)		
Co–B9	2.18(1)		
C2–C3	1.43(1)		
C6–C7	1.41(2)		
C7–C8	1.57(2)		
C8–C9	1.48(2)		
B4–H45	1.37(13)		
B5–H45	1.18(13)		
<B–H(term)>	1.13(2)		

which is linked to B(8), B(9), and B(6) within its own $(C_2B_4)Co(C_2B_3)Ru$ cluster unit and is also bonded to the atoms B(7*) and B(8*) on the C_2B_4 ligand of its neighboring cluster (*vide infra*). For purposes of discussion these interactions will be labeled "intracluster" and "intercluster", respectively. As Table II indicates, the latter (intercluster) distances are slightly longer (*ca* 0.05–0.10 Å) than the intracluster Ru–B bonds, and hence are presumably weaker than the latter; moreover, there is no bonding interaction between Ru and the open C_2B_3 ring of its neighbor. There is no evidence of an agostic Ru–H–B interaction in **3** in either the solution or solid state.

The NMR spectra of **3** are consistent with an essentially diamagnetic species. On this basis the monomeric unit may be described, to a first approximation, as a complex of formal d^6 Co^{3+} and d^6 Ru^{2+} metal centers with $Et_2C_2B_3H_3Bu^{3-}$ and $Et_2C_2B_4H_4^{2-}$ ligands. Filled eighteen-electron valence shells are achieved for both metals if the cobalt acquires six electrons from each carborane ligand (in the usual metallocene-like sandwich-bonding pattern), and if the ruthenium ion is involved in a four-electron interaction with each of the three carborane units to which it is bound. This admittedly hypothetical formulation is at least consistent with the observed molecular geometry.

The mechanistic origin of this product is unknown at present. As we suggest in Scheme 2, there is a possibility that the original target sandwich **2**
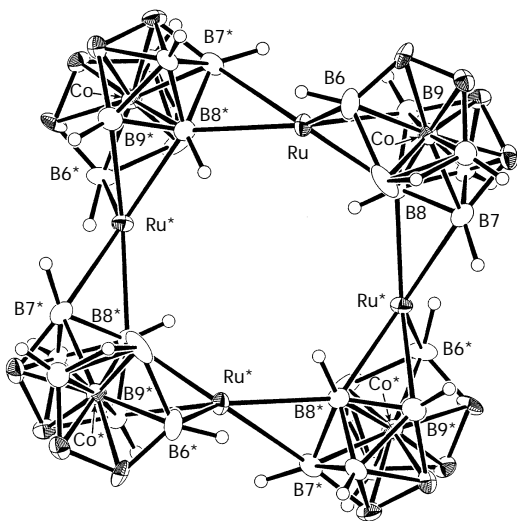

Fig. 1

Molecular structure of $[(2,3\text{-}Et_2C_2B_4H_4)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}5\text{-}Bu)Ru]_4$ (**3**), drawn with 30% thermal ellipsoids, with ethyl and butyl groups omitted for clarity

may actually have formed but subsequently converted to **3** under the reaction conditions; however, this is speculative and there is no direct evidence to support it. In view of the fact that **3** is a low-yield product that was isolated from a complex mixture, little can be said at this time about the nature of the reaction. Of primary interest here is the cyclic tetramer architecture of **3**, which has not previously been seen in metallacarborane chemistry although Hawthorne and coworkers have prepared trimeric and tetrameric species involving icosahedral C_2B_{10} carborane cages linked by
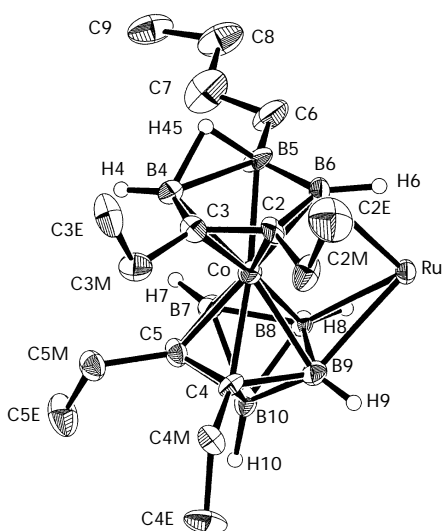

FIG. 2

Molecular structure of the $(2,3\text{-Et}_2C_2B_4H_4)$-$Co(2,3\text{-Et}_2C_2B_3H_3\text{-}5\text{-Bu})Ru$ monomer unit, with ethyl and butyl hydrogen atoms omitted
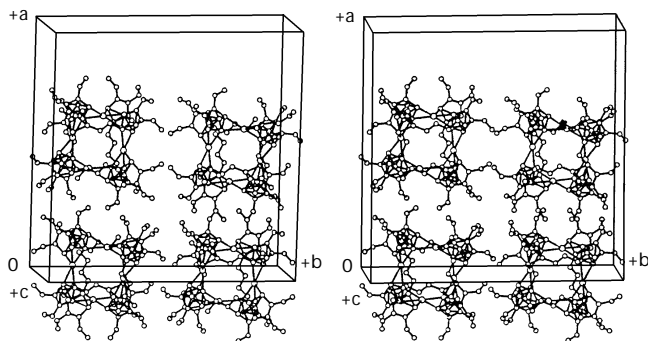

FIG. 3
Unit cell packing in **3**

exo-polyhedral mercury atoms[8]. In the small metallacarborane area, trimers composed of Mn–C_2B_4 and Gd–C_2B_4 clusters have been synthesized by Hosmane *et al.*[9]. The isolation of **3** further expands the scope of metallaborane/metallacarborane-based polycluster structures that are shown to be capable of stable existence, and that may eventually be accessible by controlled synthetic routes.

EXPERIMENTAL

Instrumentation and Procedures

^{1}H NMR (300 MHz) NMR spectra were recorded on a GE QE-300 spectrometer in $CDCl_3$ and acetone-d_6 solution. Unit resolution mass spectra were obtained on a Finnegan MAT 4600 spectrometer using perfluorotributylamine (FC43) as a calibration standard. All operations were conducted under an inert atmosphere unless otherwise indicated. Workup of products was carried out in air using benchtop procedures. Column chromatography was performed on silica gel 60 (Merck) and on silica gel 60 plates (ICN). Solvents were distilled from appropriate drying agents under an inert atmosphere.

Synthesis of $(Et_2C_2B_4H_4)CoH(Et_2C_2B_3H_4Bu)$ (1)

A 0.493 g (1.60 mmol) sample of $(Et_2C_2B_4H_4)CoH(Et_2C_2B_3H_5)$ (ref.[3c]) was dissolved in tetrahydrofuran (20 ml). 1.6 M *t*-butyllithium (1.99 ml, 3.2 mmol) was added dropwise to the solution. After the mixture was stirred at room temperature for 45 min, 1-bromobutane (0.17 ml, 1.58 mmol) was added dropwise and the mixture was stirred overnight at room temperature. An excess of acetic acid (*ca* 2 ml) was added to the solution, which was then stirred for 45 min. The reaction mixture was washed twice with 200 ml of a saturated solution of sodium hydrogencarbonate in water and was dried by stirring over anhydrous magnesium sulfate for one hour. The solution was filtered and the solvent was removed on a rotary evaporator to yield a yellow oil that was extracted with hexane, loaded onto a silica plug, and eluted with hexane, affording **1** (0.376 g, 65%) as a pure yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.56 (m, 2 H, ethyl CH_2); 2.30 (m, 2 H, ethyl CH_2); 2.16 (m, 2 H, ethyl CH_2); 2.01 (m, 2 H, ethyl CH_2); 1.35 (m, 2 H, B-butyl); 1.12 (m, 2 H, B-butyl); 1.00 (m, 2 H, B-butyl); 1.19 (t, 6 H, ethyl CH_3); 1.08 (t, 6 H, ethyl CH_3); 0.90 (t, 3 H, butyl CH_3); –4.95 (br s, BHB); –6.20 (br s, Co-H).

Synthesis of 3

A sample of **1** (228 mg, 0.623 mmol) was dissolved in tetrahydrofuran (25 ml). 1.6 M *t*-butyllithium (0.78 ml, 1.2 mmol) was added dropwise to the yellow solution. The reaction mixture was stirred at room temperature for one hour, during which time the color changed from yellow to orange. The reaction vessel was cooled to –78 °C, and $[(\eta^4\text{-}C_8H_{12})Ru(MeCN)_4][PF_6]_2$ (207 mg, 0.312 mmol) was added to the solution under nitrogen flow. The reaction mixture rapidly became brown. The solution was allowed to stir 18 h at room temperature. An excess of acetic acid (*ca* 2 ml) was added to the solution, which was then stirred for one hour. The reaction mixture was washed twice with 200 ml of a saturated solution of sodium hydrogen carbonate in water and was dried by stirring over anhy-

drous magnesium sulfate for one hour. The solvent was removed in air on a rotoevaporator, and the resultant brown oil was extracted with hexane and loaded onto a silica plug. The silica was washed with hexane (yielding unreacted starting material as a yellow band), and the product **3** was eluted with dichloromethane. Preparative TLC on this band (silica plates, hexane eluent) yielded *ca* 10 mg (3%) of the compound as a yellow-orange solid. X-Ray quality crystals were obtained by the slow evaporation of a dichloromethane–hexane solution (*ca* 1 : 1) under nitrogen flow. ^{1}H NMR (acetone-d_6, 300 MHz): 2.59 (m, 8 H, ethyl CH$_2$); 2.38 (m, 8 H, ethyl CH$_2$); 2.13 (m, 8 H, ethyl CH$_2$); 1.99 (m, 8 H, ethyl CH$_2$); 1.26 (m, 24 H, B-butyl); 1.17 (t, 24 H, ethyl CH$_3$); 1.03 (t, 24 H, ethyl CH$_3$); 0.84 (t, 12 H, butyl CH$_3$); –6.13 (br s, 1 H, BHB).

X-Ray Crystallographic Analysis of **3**

Diffraction data were collected at –120 °C on a Rigaku AFC6S diffractometer using MoKα radiation (λ = 0.71069 Å). Details of data collection and structure determination are listed in Table I.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-114485. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

The unit cell dimensions were determined by applying the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored during the data collection showing ψ scans of several reflections with the transmission factor ranging from 0.94–1.00. Calculations were performed on a VAX station 3520 computer by using TEXSAN 5.0 software[10] and in the later stages on a Silicon Graphics Personal Iris 4D35 computer using the teXsan 1.7 package[11]. The structure was solved by Patterson techniques. Full matrix least-squares refinement with anisotropic thermal displacement parameters was carried out for all nonhydrogen atoms. The hydrogen atoms were found from the difference Fourier maps and included in the calculation without further refinement. The final difference map was essentially featureless with the highest peak of 0.8 e/Å^3.

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