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[15] Other compounds, which at first glance appear similar, such as the fullerene-analogous In_{74} in the Zintl phase $Na_{96}In_{97}Ni_2$ are fundamentally different to the metalloid clusters: In such Zintl phases[23] the metallic structure of the metals is broken by reduction with electropositive elements, resulting in negatively charged cluster units containing negative average oxidation numbers. In contrast, the molecular metalloid cluster intermediates lie on the path from monomeric or oligomeric oxidized species to the metals, that is, the average oxidation numbers for example within the metalloid Ga clusters are between +1 and 0.

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[21] The Al and Ga cluster compounds that we have already structurally characterized show that the bulkiness of the ligand has an effect on the maximum cluster size, that is for clusters with the same number of ligands a bulky ligand leads to a smaller metal cluster than a less bulky ligand. Indirectly, this principle becomes clear on comparing the Ga_{84} cluster with the Al_{77} cluster, which is surrounded by the same ligand shell (see above). Analogous conclusions regarding the influence of the ligands can not yet be drawn for the metalloid precious metal clusters, since for the larger clusters hardly any detailed structure information is available due to the lack of single-crystal structure determinations.

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$[\{Rh(\eta^5\text{-}Ph_2C_2B_9H_9)(\mu_3\text{-}OH)\}_4]$: A Tetrameric Icosahedral Metallacarborane Containing an $\{Rh(OH)\}_4$ Cubane Cluster[**]

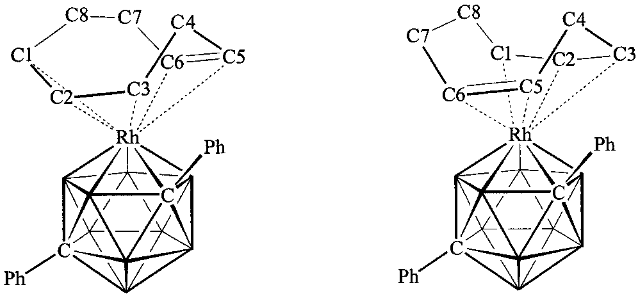
Bruce E. Hodson, David Ellis, Thomas D. McGrath,
John J. Monaghan, Georgina M. Rosair, and
Alan J. Welch[*]

We are currently investigating the mechanism of isomerization of metalladiphenylcarboranes by inducing low-temperature isomerizations through steric crowding.[1] Our strategy uses vertex-substitution to follow the movement of specific cluster vertices through the isomerization process since the integrity of the vertex-substituent bond is reasonably assured at low temperatures and thus eventually should provide a complete experimental mapping of the process. Although our initial studies have involved platina-,[2] molybda-,[3] and nickeladiphenylcarboranes[4] we have begun to investigate rhodium species. This has led, fortuitously, to the isolation and characterization of the novel rhodacarborane tetramer described herein.

When $Na_2[7,8\text{-}Ph_2\text{-}7,8\text{-}\mathit{nido}\text{-}C_2B_9H_9]$ (prepared in situ from $[HNEt_3][7,8\text{-}Ph_2\text{-}7,8\text{-}\mathit{nido}\text{-}C_2B_9H_{10}]$ and excess NaH in THF under reflux) is allowed to react with $[\{Rh(C_8H_{12})Cl\}_2]$ in THF, two new compounds are formed which may be separated by chromatography. The major species **1**, is

$$[1,8\text{-}Ph_2\text{-}2\text{-}(1\text{-}3\text{-}\eta^3\text{-}:5,6\text{-}\eta^2\text{-}C_8H_{11})\text{-}\mathit{closo}\text{-}2,1,8\text{-}RhC_2B_9H_9]\ \mathbf{1}$$

characterized by ^1H and ^{11}B NMR spectroscopy and by a crystallographic study. The $^{11}B\text{-}\{^1H\}$ NMR spectrum of **1** contains eleven peaks instead of the expected nine between $\delta = +10$ and -15, the range usually associated with resonance signals from closo metallacarboranes. This apparent anomaly was resolved by analysis of ^1H, $^1H-{}^1H$ correlated (COSY), and $^1H-{}^1H$ nuclear Overhauser effect (nOe) NMR spectra, which show clear evidence for two conformers (**1a** and **1b**, Scheme 1) which differ in the disposition of the η^3:η^2-C_8H_{11} ring relative to the carborane cage. Unfortunately it is not possible to establish which conformer is the major component in solution. Subsequent exhaustive thin layer chromatography (tlc) with a variety of eluents could not separate **1a** and **1b**.



1a **1b**

Scheme 1. The two conformers of compound **1**. The relative amounts of **1a**:**1b** are approximately 3:1 in the solid state (by X-ray diffraction). In solution (by NMR) there are also two conformers in a 3:1 ratio, but it is not possible to establish which is the major form.

A structural study of **1**[5] (Figure 1) establishes that low-temperature isomerization has occurred, separating the cage carbon atoms in a net 1,2 →1,7 manner[1] as in $\mathit{closo}\text{-}C_2B_{10}H_{12}$. In the crystal the η^3:η^2-C_8H_{12} ligand is partially disordered (atoms C23 and C25) corresponding to an effective superimposition of conformers **1a** and **1b** in the approximate ratio 3:1.

The direct synthesis of compound **1** is unexpected. Jeffery et al.[6] have previously obtained the related (but nonisomerized) species $[1,2\text{-}Me_2\text{-}3\text{-}(1\text{-}3\text{-}\eta^3\text{-}:5,6\text{-}\eta^2\text{-}C_8H_{11})\text{-}\mathit{closo}\text{-}3,1,2\text{-}$

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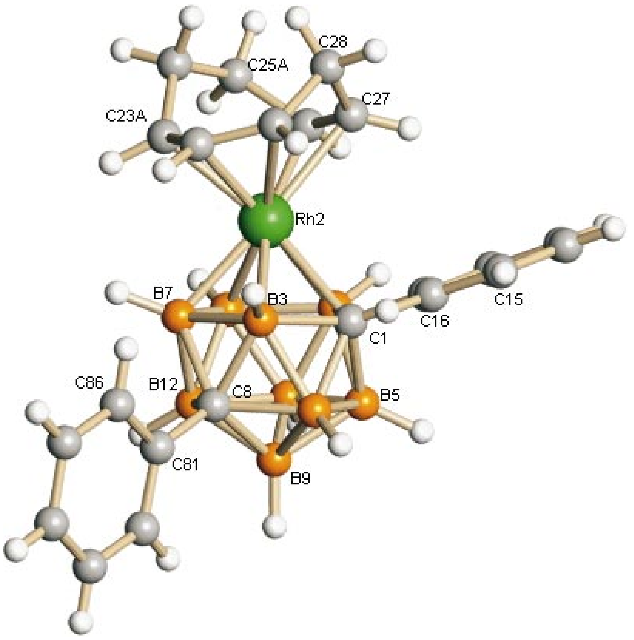

Figure 1. Perspective view of the structure of the major isomer **1a** as determined crystallographically. Selected bond distances [Å] and angles [°]: Rh2-C1 2.268(4), Rh2-B3 2.137(4), Rh2-B7 2.176(4), Rh2-B6 2.189(5), Rh2-B11 2.224(5), Rh2-C21 2.310(4), Rh2-C22 2.196(4), Rh2-C23A 2.217(7), Rh2-C26 2.296(4), Rh2-C27 2.302(4); C21-C22-C23A 123.0(4). C23A and C25A have 76% occupancy. In the minor isomer (**1b**) C23B and C25B (24% occupancy) are nonbonding and bonding to Rh2, respectively; Rh2-C25B 2.215(18), C25B-C26-C27 123.2(8).

$RhC_2B_9H_9$] by deliberate H^- abstraction from the ion [1,2-Me_2-3-(1,2-η^2-:5,6-η^2-C_8H_{12})-*closo*-2,1,8-$RhC_2B_9H_9$]$^-$. We believe that **1** also forms from a (nonisolable) η^2:η^2-C_8H_{12} containing anionic intermediate but by spontaneous loss of an H^- ion, presumably to the medium.

Compound **2** forms as a minor by-product in the preparation of compound **1**. The ^{11}B-{^1H} NMR spectrum of **2** in $CDCl_3$ at 298 K shows only five broad, overlapping peaks between $\delta = +15$ and -15, but there is some sharpening and resolution of the spectrum (into seven components) at 333 K. The ^1H NMR spectrum shows only resonance signals assignable to Ph rings which indicates the loss of the C_8 ligand.

The structure of compound **2** was revealed by a crystallographic study (Figure 2).[7] The molecule is the tetramer [{(HO)$RhPh_2C_2B_9H_9$}$_4$] composed of four 2,1,8-RhC_2B_9 icosahedra bridged by four μ_3-OH units to give a cubanelike {$Rh_4(OH)_4$} central core. The tetramer has effective S_4 symmetry (of which C_2 is crystallographically imposed) with alternating 2,1,8-RhC_2B_9 cages of opposite chirality. The results of the crystallographic study suffer from partial disorder of the [{(HO)$RhPh_2C_2B_9H_9$}$_4$] tetramer parallel to the crystallographic *b* axis ("ghosts" with a 4% occupancy factor ca. 1 Å above and below the major component) and from disordered CH_2Cl_2 and C_5H_{12} solvate molecules. However, because of mass spectrometric evidence[8] we are confident that **2** is correctly formulated as [{(HO)$RhPh_2C_2B_9H_9$}$_4$]; **2** can be prepared deliberately by stirring compound **1** with NaOH in THF.[9]

Compound **2** is the first tetrameric icosahedral metallacarborane,[10] extending in logical sequence this family of compounds from simple monomer (e.g. [$CpFeC_2B_9H_{11}$][11]) through dimer (e.g. [{$(CO)_2FeC_2B_9H_{11}$}$_2$]$^{2-}$,[12]) and trimer (e.g. [{$Cu(NC_5H_4CO_2Me)C_2B_9H_{10}$}$_3$][13]). It is, moreover, the first example of a species with an {$M_4(OH)_4$} cubanelike core in which M is a Group 9 metal. Structurally and electronically **2** is analogous to the well known species $Cp^*_4Rh_4S_4$[14] ($Cp^* = C_5Me_5$) illustrating further the potential for new chemistry afforded by formal replacement of the five-electron Cp/Cp* ligand with the four-electron carborane ligand.

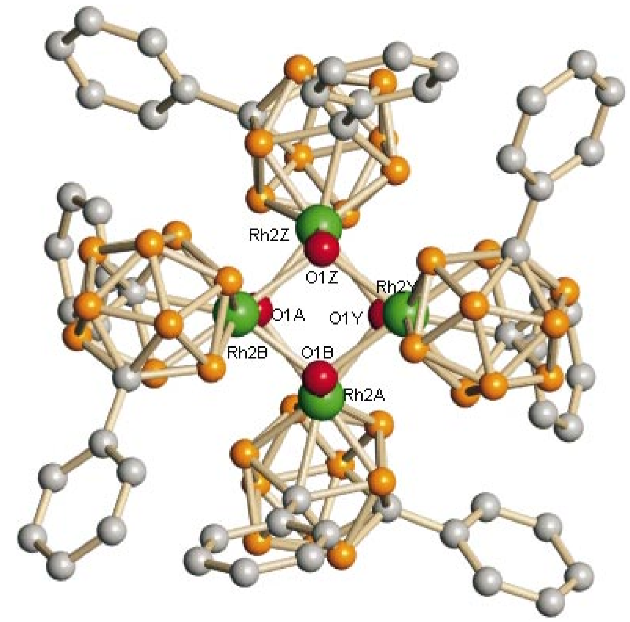

Figure 2. The tetramer **2** viewed down its approximate S_4 axis (crystallographic C_2). For clarity the H atoms are not shown. Selected bond lengths [Å]: Rh2A-O1A 2.249(7), Rh2A-O1B 2.194(9), Rh2A-O1Y 2.142(8), Rh2B-O1A 2.190(8), Rh2B-O1B 2.169(8), Rh2B-O1Z 2.202(9).

Experimental Section

[{$Rh(C_8H_{12})Cl$}$_2$] (0.54 mmol) in THF (30 mL) was added to a frozen solution of Na_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (1.08 mmol) in THF (40 mL). After 24 h stirring under N_2 at room temperature solvent was removed in vacuo and the resultant brown powder was dissolved in dichloromethane (5 mL). Initial column chromatography (silica) with dichloromethane : 60/80 petroleum ether (1:1) as the eluent afforded a crude mixture of compounds **1** and **2** as an orange solid (28% yield). Subsequent preparative tlc (silica) of this crude product with 60/80 petroleum ether : dichloromethane (3:2) afforded **1** as yellow ($R_f = 0.55$) and **2** as orange ($R_f = 0.63$) products in the approximate ratio 5:1. For **1**; IR (CH_2Cl_2) $\tilde{\nu}_{max} = 2574$ cm^{-1} (s, br; B-H); ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 7.7-7.0$ (m, Ph), major conformer: 5.86 (ddd, C6-H), 5.28 (ddd, C1-H), 5.00 (dd, C2-H), 3.83 (ddd, C3-H), 3.17 (ddd, C4-H), 2.87 (ddd, C5-H), 2.64 (dddd, C7-H), 2.59 (ddd, C4-H), 2.37 (dddd, C7-H); minor conformer: 5.82 (ddd, C6-H), 5.48 (ddd, C1-H), 4.77 (dd, C2-H), 3.79 (ddd, C3-H), 3.12 (ddd, C5-H), 2.67 (ddd, C4-H), below $\delta = 2.5$ impossible to assign; ^{11}B-{^1H} NMR (128.4 MHz, $CDCl_3$, 298 K): $\delta = 5.10$, 3.61, 2.50, 0.48, -2.22 -3.26, -4.65, -11.01, -11.70, -12.87, -14.20.

2: IR (CH_2Cl_2) $\tilde{\nu}_{max} = 2586$ cm^{-1} (s, br) (B-H); ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 7.5-6.9$ (m, Ph); ^{11}B-{^1H} NMR (128.4 MHz, $CDCl_3$, 333 K): $\delta = 12.15$, 8.74, 5.13, 4.20, -0.68, -3.83, -10.81.

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[5] For both structure determinations: Crystals grown by diffusion of a CH_2Cl_2:40/60 petroleum ether (1:5) solution at 263 K, Bruker $P4$ diffractometer, 160(1) K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $2\theta_{max} = 50°$, corrections for absorption effects (Ψ-scans), Lorentz and polarisation effects, structure solved by direct methods and refined (against F^2) by full-matrix least-squares methods. Crystal data for **1**: $C_{22}H_{30}B_9Rh$, $M_r = 494.66$: crystal size $0.15 \times 0.32 \times 0.22$ mm, triclinic, $P\bar{1}$, $a = 9.7270(14)$, $b = 10.7460(12)$, $c = 12.1641(17)$ Å, $\alpha = 106.834(9)$, $\beta = 105.519(10)$, $\gamma = 98.800(9)°$, $V = 1135.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.447$ g cm^{-3}, $F(000) = 504$, $\mu = 0.761$ mm^{-1}, of 3896 unique reflections 3289 were observed $[F_o > 4\sigma(F_o)]$, 308 parameters, $R_1 = 0.0385$, $wR_2 = 0.0824$ (for observed data), $S = 1.033$, max. and min. residual electron density: 0.398 and -0.557 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149160 (**1**) and -149161 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[7] Crystal data for **2**: $(C_{14}H_{20}B_9ORh)_4 \cdot \mathbf{1} \cdot x\,CH_2Cl_2 \cdot C_5H_{12}$, $M_r = 1811.10^*$, crystal size $0.55 \times 0.52 \times 0.24$ mm, monoclinic, $C2/c$, $a = 20.830(5)$, $b = 28.683(8)$, $c = 15.916(3)$ Å, $\beta = 106.84(2)°$, $V = 9101(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.322^*$ g cm^{-3}, $F(000) = 3640^*$, $\mu = 0.813^*$ mm^{-1}, of 7849 unique reflections 4003 were observed $[F_o > 4\sigma(F_o)]$, 541 parameters, $R_1 = 0.0973$, $wR_2 = 0.2140$ (for observed data), $S = 0.984$, max. and min. residual electron density: 1.188 and -2.667 e Å^{-3}. See ref. [5]. ($^*M_r$, ϱ_{calcd}, $F(000)$ and μ calculated on the basis of modeling the fractional CH_2Cl_2 solvate as an approximate triangle of 50% occupancy carbon atoms in general space).

[8] mass spectrometry: CH_2Cl_2 solution diluted with CH_3OH and $N(CH_2CH_2OH)_3$, Thermoquest LCQ ion trap mass spectrometer, negative ion MS, mass range m/z 100–2000. MS/MS product ion spectra were obtained using a precursor ion mass window of 14 amu and collision energy between 24% and 30% of maximum. Molecular ion range m/z 1611–1623, centered on m/z 1616. Successive product-ion MS/MS scans, starting from m/z 1616, showed consecutive losses of $2 \times OH$.

[9] Stirring of a THF solution of **1** overnight with excess NaOH under N_2 affords compound **2** in ca. 40% yield (not yet optimised). Full details will be reported later.

[10] a) The compound $[\{Ru(Et_2C_2B_4H_4)Co(Et_2C_2B_3H_3Bu)\}_4]$ is tetrameric with cobaltacarborane sandwiches linked by exopolyhedral Ru atoms. K. G. Parker, J. M. Russell, M. Sabat, R. N. Grimes, *Collect. Czech. Chem. Commun.* **1999**, *64*, 819; b) The compound $[\{Hg(C_2B_{10}H_{10})\}_4]$ is tetrameric and icosahedral but is not a metallacarborane in the sense that the metal atom is not part of the heteroborane cage. X. Yang, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **1991**, *103*, 1519; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1507.

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Structure and Dynamics of the Host–Guest Complex of a Molecular Tweezer: Coupling Synthesis, Solid-State NMR, and Quantum-Chemical Calculations**

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Felix Koziol, Christian Ochsenfeld, Frank-Gerrit Klärner, and Hans Wolfgang Spiess*

Supramolecular chemistry and noncovalent interactions are of major importance in many biological systems, for example in enzyme–substrate binding or antigen–antibody recognition, as well as in the design of new materials by molecular self-assembly.[1] An example is receptor **1**, which belongs to a family of molecules termed "molecular tweezers", due to their concave–convex topology and their propensity to selectively form complexes with electron-deficient aromatic and aliphatic compounds as well as with organic cations.[2] This high selectivity has been correlated with a markedly negative electrostatic potential, by using semiempirical and quantum-chemical calculations, for the concave side of the molecular tweezer.[3]

Hunter and Packer described a supramolecular structure determination, based on the empirical calculation of complexation-induced ^1H NMR shifts in solution[4] employing the empirical methods[5] developed for the prediction of ^1H NMR shifts of proteins. As further illustrated by, for example, the study of the dimerization of formic acid in a matrix at 7 to 40 K using IR spectroscopy,[6] a quantitative elucidation of the structure, dynamics, and electronic properties of such complex systems requires the coupling of advanced techniques of physical characterization and theoretical chemistry. The results of such an endeavour, which we describe here, can then provide guidelines for generating new structures.

Central to our approach are advances in high-resolution ^1H solid-state NMR based on fast magic-angle spinning (MAS).[7] At rotation frequencies above 30 kHz, sufficient line narrowing is achieved such that ^1H resonances due to chemically distinct protons can be distinguished.[8] Moreover, fast MAS can be combined with double-quantum (DQ) spectroscopy[9]

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