

structure of 1 may not be the ground-state geometry of the molecule, even though no specific intermolecular contacts are found in the crystal lattice. Similar molecules such as $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Si}$ have very shallow bending potentials and, therefore, exist as independent linear and bent forms in the same lattice.¹³

Although the tin atom adopts an essentially η^5 -bonding posture with respect to each of the C_2B_3 faces with the Sn-centroid distances of 2.105 and 2.087 Å, the average Sn-C distances (2.708 (6) Å) are significantly longer than the average Sn-B distances (2.355 (8) Å), thus making the metal slipped toward the three boron atoms with concomitant tightening of the C-C bond (1.453 (8) and 1.478 (7) Å in 1 vs 1.494 (7) Å in 2) on the C_2B_3 face in each ligand. Such slip distortions of the metallacarborane cages have been observed previously.⁴ The (ring centroid 1)-Sn-(ring centroid 2) angle of 142.5° in 1 is comparable to the corresponding angles in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}^{\text{II}}$ (145.8°)¹ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sn}^{\text{II}}$ (144.1°),^{2a} and thus the bent geometry of 1 resembles those of the stannocene derivatives despite the

2- charge on each carborane ligand. Nonetheless, compound 1 represents the first tin(IV) sandwich complex ever to be reported.

The results of this investigation suggest that a number of novel complexes containing higher oxidation states, that are not normally produced by conventional synthetic approaches, can be synthesized by oxidizing the metal in the complex with an oxidizing metal reagent stronger than the complexed metal itself. We are currently exploiting this synthetic strategy in the preparation of hitherto unexplored carborane sandwich complexes of main-group elements and early transition metals.

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Supplementary Material Available: Tables of positional and thermal parameters, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

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$\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$: A Novel Boride Cluster Formed by the Degradation of $\text{Ru}_6(\text{CO})_{17}\text{B}(\text{AuPPh}_3)$

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Summary: Under a pressure of CO (55 atm), $\text{Ru}_6(\text{CO})_{17}\text{B}(\text{AuPPh}_3)$ extrudes one ruthenium vertex and forms $\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$ (2) as the only product. Crystallographic characterization of 2 confirms the presence of a square-pyramidal Ru_5 core with an interstitial boron atom lying 0.375 Å below the square face. 2 is the first structurally elucidated example of a boride cluster built upon an M_5B core.

The emerging area of discrete molecular boride clusters has provided examples of boron atoms encapsulated within hexametallic cages; structurally characterized clusters are octahedral ($\text{HRu}_6(\text{CO})_{17}\text{B}$,^{1,2} $[\text{Fe}_4\text{Rh}_2(\text{CO})_{16}\text{B}]^-$,³ and $\text{H}_2\text{Fe}_3\text{Rh}_3(\text{CO})_{16}\text{B}^3$) and trigonal prismatic ($[\text{H}_2\text{Ru}_6(\text{CO})_{18}\text{B}]^-$).⁴ During the reaction to form $[\text{Fe}_4\text{Rh}_2(\text{CO})_{16}\text{B}]^-$, Fehlner has observed the formation of an intermediate species proposed to possess an Fe_4RhB core.³ Pentanuclear

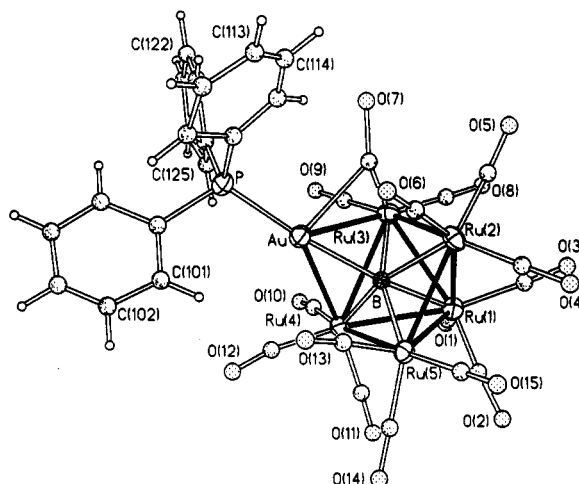


Figure 1. Molecular structure of $\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$ (2).

species are well exemplified for molecular transition-metal carbonyl carbides⁵⁻⁸ and nitrides.^{5,9,10} Our own work in

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the area of borides has concentrated on ruthenium-based clusters. We now report the successful synthesis of a pentaruthenium boride cluster via the degradation of a hexaruthenium species.

The anion $[\text{Ru}_6(\text{CO})_{17}\text{B}]^-$ was prepared from $[\text{Ru}_3(\text{C}-\text{O})_3\text{B}_2\text{H}_5]^-$ as previously described.⁴ Treatment of a CH_2Cl_2 solution of $[\text{Ru}_6(\text{CO})_{17}\text{B}]^-$ with Ph_3PAuCl in the presence of TlPF_6 gave red-brown $\text{Ru}_6(\text{CO})_{17}\text{B}(\text{AuPPh}_3)$ (1) in >90% yield.¹¹ A solution of 1 in CH_2Cl_2 was placed in an autoclave under 55 atm of carbon monoxide for 14.5 h with constant stirring at room temperature. Upon chromatographic separation (with 2:1 hexane- CH_2Cl_2 as eluent) two fractions were obtained. The first to be collected was bright blue and was identified as $\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$ (2),¹² formed in approximately 50% yield with respect to 1. The second fraction was unreacted 1.

A comparison of the ^{11}B NMR spectral data for 1 and 2 indicates that the environments about the boron atom are significantly different in the two compounds.^{13,14} For 1, the ^{11}B NMR spectral shift of $\delta +194.4$ is close to that of the parent hydrido cluster $\text{HRu}_6(\text{CO})_{17}\text{B}^{1,2}$ and its conjugate base $[\text{Ru}_6(\text{CO})_{17}\text{B}]^-$,¹⁴ implying that an octahedral core (crystallographically confirmed for $\text{HRu}_6(\text{CO})_{17}\text{B}^{1,2}$) is present in 1. Consistent with this is the fact that the ^{11}B NMR signal for 1 is sharp¹¹ (fwhm 25 Hz). Compound 2 is characterized by an ^{11}B NMR spectral resonance at $\delta +172.5$ with fwhm 175 Hz. In comparison to 1, the higher field shift and the broader line width for 2 suggest that the boron atom resides in a metal cage which is more open and less symmetrical¹³ than that in 1. This proposition has been confirmed crystallographically.

A crystal of 2 suitable for X-ray analysis was grown from CH_2Cl_2 layered with hexane.¹⁶ The molecular structure

of 2 is shown in Figure 1. The five ruthenium atoms define a square-based pyramid, a core geometry that is consistent with the 74-valence-electron count of $\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$ provided that the AuPPh_3 unit functions as a pseudo-hydride ligand. Distances from the apical atom Ru(1) to the basal atoms Ru(2), Ru(3), Ru(4), and Ru(5) are 2.804 (7), 2.836 (7), 2.851 (5), and 2.870 (6) Å, respectively. The boron atom resides 0.375 Å below the square face defined by atoms Ru(2), Ru(3), Ru(4), and Ru(5) and is within bonding contact of all five ruthenium atoms: Ru(1)-B = 2.28 (6) Å, Ru(2)-B = 2.16 (4) Å, Ru(3)-B = 2.16 (4) Å, Ru(4)-B = 2.03 (5) Å, and Ru(5)-B = 2.09 (4) Å. The position of the AuPPh_3 fragment is unprecedented. It caps the basal triangle defined by atoms Ru(3), Ru(4), and B and is asymmetrically placed with respect to and pendant from the square face of the Ru_5 framework; Au-B = 2.26 (5) Å, Au-Ru(3) = 2.775 (4) Å, and Au-Ru(4) = 2.821 (5) Å and $\angle\text{Ru}(1)\text{-B-Au} = 151.4$ (3)°. The presence of the AuPPh_3 unit lengthens one of the edges of the square face of the Ru_5 core; Ru(3)-Ru(4) = 3.054 (4) Å compared to an average of 2.898 (4) Å for the remaining three edges. With the exception of C(7)O(7), the carbonyl ligands are terminally bound. Ligand C(7)-O(7) is bridging along the edge Ru(3)Au with Au-C(7) = 2.56 (2) Å and $\angle\text{Ru}(3)\text{-C}(7)\text{-O}(7) = 146$ (3)°.

Several carbido clusters related to 2 have been structurally characterized. However, the location of the AuPPh_3 group in 2 contrasts with the sites noted in these carbides. $\text{Ru}_5(\text{CO})_{13}(\text{NO})\text{C}(\text{AuPEt}_3)^{18}$ and $\text{Os}_5(\text{CO})_{14}\text{C}(\text{AuPPh}_3)_2^{19}$ exhibit either M-M edge bridging or M_3 face capping (M = Ru, Os) gold(I) phosphine fragments, leaving the carbon atom exposed in the middle of the basal plane of the M_5 skeleton. In $\text{M}_5(\text{CO})_{14}\text{C}(\text{AuPEt}_3)_2$ (M = Fe,^{20,21} Ru²¹), one AuPEt_3 unit bridges one basal Fe-Fe edge while the second unit caps the entire basal plane, rendering the carbon atom fully interstitial. The preference shown by the gold atom in 2 to be associated with the boron atom follows a trend that we have previously observed in a series of M_4 -butterfly-based M_4BAu_x clusters (M = Fe, Ru; $x = 1-3$).²² The preference for the unusual μ_3 - AuPPh_3 group in 2 over the μ_4 site observed in $\text{M}_5(\text{CO})_{14}\text{C}(\text{AuPEt}_3)_2$ (M = Fe, Ru) may be due to steric effects, perhaps the extra carbonyl ligand present in 2.

The transformation of 1 to 2 involves the extrusion of one ruthenium vertex from an octahedral Ru_6 cage. Corresponding changes in cluster nuclearity have been

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(12) $\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)$ (2): 400-MHz ^1H NMR (CDCl_3) δ 7.8-7.4 (m, Ph); 128-MHz ^{11}B NMR (CDCl_3 ; $\text{BF}_3\cdot\text{OEt}_2$ reference) δ +172.5; 162-MHz ^{31}P NMR (CDCl_3 ; H_3PO_4 reference) δ +63.1; IR (hexane, cm^{-1}) 2086 w, 2048 vs, 2032 m (sh), 2018 s, 1995 m, 1965 m, 1915 w; FAB-MS in 3-NBA matrix m/z 1395 (P^+) with 5 CO losses (calcd for $^{12}\text{C}_{33}^{1}\text{H}_{15}^{197}\text{Au}^{11}\text{B}^{16}\text{O}_{15}^{31}\text{P}^{101}\text{Ru}_5$ 1395).

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observed in the conversions of $[\text{Ru}_6(\text{CO})_{16}\text{N}]^-$ to $[\text{Ru}_5(\text{C}-\text{O})_{14}\text{N}]^-$ (quantitative with 1 atm of CO at 25 °C)⁹ and $\text{Ru}_6(\text{CO})_{17}\text{C}$ to $\text{Ru}_5(\text{CO})_{15}\text{C}$ (quantitative with 80 atm of CO at 70 °C).⁶ We are currently studying methods of forming the anionic cluster $[\text{Ru}_5(\text{CO})_{15}\text{B}]^-$, initially by removing the gold(I) phosphine group from 2.

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Supplementary Material Available: Tables of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters, and H atom fractional coordinates (8 pages). Ordering information is given on any current masthead page.

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New Simple Route to Allylstannanes by Zinc-Mediated Coupling of Allyl Bromides with Bu_3SnCl or Bu_2SnCl_2 in an H_2O (NH_4Cl)/THF Medium

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Summary: A new zinc-mediated coupling reaction of allyl and allyl-like bromides with Bu_3SnCl (1) or Bu_2SnCl_2 (2), performed in H_2O (NH_4Cl)/THF medium, represents an easy route to the following organostannanes: $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ (3) and $\text{Bu}_2\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ (4), $\text{Bu}_3\text{Sn}(\text{C}_4\text{H}_7)$ (5) and $\text{Bu}_2\text{Sn}(\text{C}_4\text{H}_7)_2$ (6) (where C_4H_7 stands for *trans*-crotyl, *cis*-crotyl, or α -methylallyl), and $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ (7). This striking one-pot procedure successfully improves the already general routes where Grignard or other conventional organometallic reagents are used.

Allylstannanes have been shown to be versatile reagents in organic synthesis¹ in (i) *allylstannation*² of carbonyl compounds, (ii) allylations promoted by $\text{BF}_3\cdot\text{Et}_2\text{O}^3$ or by scrambling reagents⁴ such as Bu_2SnCl_2 , Bu_3SnCl , SnCl_4 , BCl_3 , BBr_3 , TiCl_4 , and Cp_2TiCl_2 , and (iii) catalyzed cross-coupling reactions of allyl halides with triorganoallylstannanes.⁵

The various approaches provide convenient methods for C-C bond formation via stoichiometric or catalyzed reactions. Even reactions leading to C-O-C formation, by means of a thermal condensation of two molecules of aldehydes with allyltin substrates, have been considered.⁶ Furthermore, it has been demonstrated that allylstannations by means of allyltin halides occur under mild conditions, with very short reaction times and without the use of organic solvents and an inert-gas atmosphere.^{2,6} In fact, allylstannations leading to C-C bond formation can be performed in the presence of water⁷ and even in aqueous acid media.⁸

Synthetic routes to allylstannanes are based on the following procedures: (a) preparation of a conventional organometallic compound (Grignard, RLi , etc.) which will react with an organotin halide or oxide,⁹ (b) reactions of

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