space group $Fm3m$ with $a_0 = 9.944$ Å, and all the "extra" reflections in the Cs profile (Figure 1a) are described by the tetragonal space group $I4_1/amd$ with $a_0 = 10.309$ Å and $c_0 = 20.729$ Å. Refinement of each profile by the Rietveld technique[13] using the POWDER system[14] on the SERC Interactive Computing Facility leads to the fits shown in Figure 1 and the unit cell parameters and bond lengths listed in Table I. In refining the Cs_2SbCl_6 profile, account was taken of the $Cs_3Sb_2Cl_9$ impurity by using a multiphase fitting procedure.[15] An absorption correction was applied to all the powder diffraction profiles by Hewat's method.[16]

The proposed ordering of $M^{III}Cl_6^{3-}$ and $Sb^VCl_6^-$ in the tetragonal salts is similar to that postulated in a single-crystal X-ray diffraction study of $(NH_4)_2SbBr_6$.[17] Each $M^{III}Cl_6^{3-}$ is surrounded by eight $SbCl_6^-$ and four $M^{III}Cl_6^{3-}$, the latter at the corners of a tetrahedron. The $Fm3m$ unit cell (that of the K_2PtCl_6 structure) is doubled along one axis. In contrast to $(NH_4)_2SbBr_6$[17] we find less than 0.5° angular distortion of the $SbCl_6^-$ but a small (2.5°) D_{2d} distortion of $SbCl_6^{3-}$ and $BiCl_6^{3-}$, to be compared with $TlCl_6^{3-}$, which showed an angular distortion of 1.5°. In the cubic salts the space group constrains all anions to be octahedral. An important parameter in theories of electron transfer in mixed-valency compounds is the difference in bond lengths around the ions of different oxidation state. In the present case we find Sb^{III}–Cl is 2.646 and Sb^V–Cl 2.384 Å compared with 2.63 and 2.35 Å in $(C_3H_7NH_3)_4Sb_{0.5}{}^{III}\,Sb_{0.5}{}^{V}Cl_6(Cl)_2$,[16] which has a rather different structure. Of the nine salts $A_2M_{0.5}{}^{III}Sb_{0.5}{}^{V}Cl_6$ investigated, three were found to have superlattice ordering of $M^{III}Cl_6^{3-}$ and $Sb^VCl_6^-$, the rest being disordered. All the Rb salts were disordered, and among the Cs salts ordering was found in both salts in which M^{III} had an ns^2 electron configuration and one where M^{III} was an ns^0 ion (Tl^{III}). To identify the reasons for this result, we note that the average (M^{III},Sb^V)–Cl bond lengths span a range from 2.541 to 2.361 Å (Table I). The change from order to disorder occurs between 2.472 ($Cs_2Tl_{0.5}Sb_{0.5}Cl_6$) and 2.448 Å ($Rb_2Tl_{0.5}Sb_{0.5}Cl_6$). Salts with an average (M^{III},Sb^V)–Cl bond length greater than 2.472 Å are ordered while all those where it is less than 2.448 Å are disordered. Thus the difference in size between MCl_6^{3-} and $SbCl_6^-$ appears to be the dominant factor. Unfortunately $Rb_2Sb_{0.5}{}^{III}Sb_{0.5}{}^{V}Cl_6$ is very unstable and transforms easily to the monoclinic salt $Rb_{2.67}SbCl_6$, but we are continuing powder neutron diffraction work on the hexabromoantimonates(III,V) and related mixed-metal salts to clarify the structural principles governing this class of compound.

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Registry No. $Cs_2Bi^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 12441-33-7; $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 17805-64-0; $Cs_2Tl^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 41875-61-0; $Cs_2In^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 41875-60-9; $Cs_2Fe^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 61269-02-1; $Rb_2Tl^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 12432-76-7; $Rb_2In^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 85370-04-3; $Rb_2Fe^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 61269-01-0; $Rb_2Rh^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, 85370-05-4.

Supplementary Material Available: Table of positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Syntheses and Structures of Anionic *closo*-Rhodacarborane Clusters That Contain a Formal Rhodium(I) Vertex

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Structural characterization of electron-rich metallacarboranes has been of interest since the earliest crystallographic studies showed that some late transition-metal metallacarboranes adopt significantly distorted polyhedral structures.[1] The importance of the electronic configuration of the metal was immediately recognized,[2] but more recent structural studies of 12-vertex platinum and palladium metallacarboranes have shown that the degree of polyhedral distortion is also a sensitive function of the ancillary ligands, the relative positions of the carbon atoms present in the carborane ligand and the metal itself.[3] Prompted by these unique structural findings, Mingos has completed extended Hückel calculations on model icosahedral platinacarboranes and has explained the conformations and polyhedral distortions adopted by late transition-metal metallacarboranes.[3e,4] While there are many examples of icosahedral d^8 L_2M^{II} (L = CO, RNC, PR_3; M = Ni,[5] Pd,[3] Pt[3]) metallacarboranes, isolation of isoelectronic L_2M^I (M = Co, Rh, Ir) metallacarboranes has proven to be more elusive. Only one example of the latter, namely, 3-(Ph_3P)-3-CO-4-(C_5H_5N)-3,1,2-$RhC_2B_9H_{11}$, has been structurally characterized,[6] and the conformation of the metal vertex proved to be incompatible with molecular orbital predictions. Thus, in order to evaluate structural consequences of icosahedral d^8 rhodium(I) metallacarboranes, we have synthesized and structurally characterized salts of $[3,3\text{-}(Ph_3P)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$ and $[2,2\text{-}(Ph_3P)_2\text{-}2,1,7\text{-}RhC_2B_9H_{11}]^-$. Structures of these two anions provide the first opportunity to evaluate the effects of introducing identical d^8 metal centers into isomeric 7,8- and 7.9-$C_2B_9H_{11}{}^{2-}$ ligands. Furthermore, we are not aware of any other structurally characterized monometallic anions that contain both formal Rh(I) and PPh_3 ligands.

Isomeric hydridorhodacarborane clusters 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$[7a] (**1a**), 2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$[7a] (**1a**), 2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$[7a] (**1b**), and 2,2-$(Ph_3P)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$[7b] (**1c**) react with many bases (e.g., KOH, NaH, K-Selectride) at the rhodium vertex to generate air-sensitive anionic rhodacarboranes **2a–c**, respectively. On the basis of analytical and spectroscopic data,[8] each of these anions was formulated as $[(Ph_3P)_2RhC_2B_9H_{11}]^-$, available (85% yield) as crystalline tetraalkylammonium salts or potassium 18-crown-6 salts. Ethanol suspensions of complexes **2a–c** reacted with dilute

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[8] Supplementary material.

0002-7863/83/1505-3368$01.50/0

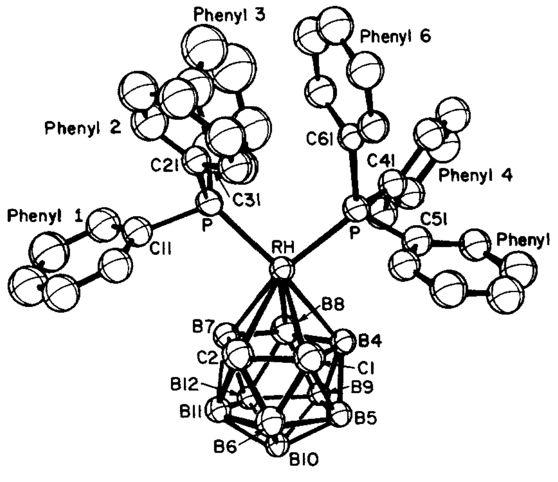

Figure 1. Anion of **2a**.

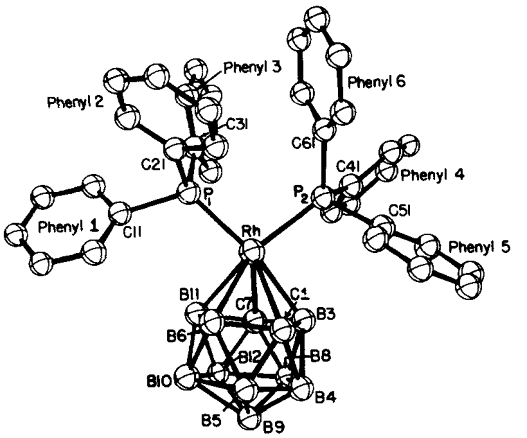

Figure 2. Anion of **2b**.

mineral acids to quantitatively regenerate the respective parent hydrido complexes **1a–c**.

Dichloromethane solutions of complexes **2a–c** were found to react readily with CO (1 atm, 25 °C) to produce tetraethylammonium salts of $[(Ph_3P)(CO)RhC_2B_9H_{11}]^-$ (**3a–c**, respectively; 80–95% yields).[8] Similarly, **2a** and **2b** react with ethylene to produce (65–75% yield) the corresponding isomeric species $[(Ph_3P)\text{-}(\eta^2\text{-}C_2H_4)RhC_2B_9H_{11}]^-$ [**4a**, NEt_4 cation; **4b**, K[18-crown-6]].[8c] Complexes **3a–c** were quite stable in the absence of air, but **4a** and **4b** slowly dissociated ethylene in solution.

To determine the nature and the extent of distortion produced by the electron-rich $(Ph_3P)_2Rh^I$ vertex in **2a** and **2b**, X-ray structure determinations were carried out on the potassium 18-crown-6 salt (**2a**)[9] and the tetramethylammonium salt (**2b**).[9]

A projection of **2a** is shown in Figure 1. Contrary to initial expectations of a slipped or distorted polyhedral structure, as in $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}PtC_2B_9H_{11}$,[3c] the rhodium vertex in **2a** was found to be symmetrically bonded to the planar C_2B_3 face of the carborane ligand.

In accord with the molecular orbital predictions,[4] the P1–Rh–P2 plane is nearly perpendicular to the mirror plane in the carborane ligand passing through B8, the midpoint between C1 and C2, and B10, the apical boron atom.

Bond distances and angles within the carborane framework are not unusual; overall icosahedral geometry closely resembles that found in **1a**.[10]

The molecular structure of $NMe_4^+\cdot$**2b** is shown in Figure 2. Unlike **2a**, the C_2B_3 bonding face of ion **2b** shows significant deviation from planarity, with carbon atoms bent back into the cage, away from the metal. The nonplanarity of this C_2B_3 face can be further described in terms of the angle between the normals to planes C1–B6–B11–C7 and C1–B3–C7, 15.7°. The P1–Rh–P2 plane is nearly parallel to the mirror plane in the carborane ligand passing through B3, the midpoint between B6 and B11 and the apical boron atom B9. This is the same metal vertex conformation found in $2,2\text{-}(PPhMe_2)_2\text{-}1,7\text{-}(CH_3)_2\text{-}2,1,7\text{-}PtC_2B_9H_9$[3c] and is calculated to be the preferred conformation.[4]

In the solid state, **2b** adopts the metal conformation predicted by Mingos;[4] however, it is fluxional in solution. The variable-temperature 81.02-MHz $^{31}P\{^1H\}$ NMR (acetone-d_6) of **2b** (room temperature) consists of a doublet centered at 51.7 ppm (downfield of external D_3PO_4) with a rhodium-phosphorus coupling constant of 212 Hz. At 240 K, this resonance collapses to a broad featureless peak centered at 52.5 ppm, which at 190 K sharpens into two separate doublets of doublets centered at 58.5 ($J_{Rh\text{-}P}$ = 241 Hz, $J_{P\text{-}P}$ = 42 Hz) and 44.3 ppm ($J_{Rh\text{-}P}$ = 186 Hz, $J_{P\text{-}P}$ = 42 Hz). This behavior is consistent with hindered rotation about the metal vertex–carborane axis.[11] The low-temperature limiting spectrum represents a fixed metal conformation which is probably the one observed in the crystal. The $^{31}P\{^1H\}$ NMR behavior of **2a** and **2c** show no temperature dependence; we assume that the barrier to rotation in these complexes is much smaller.

Qualitatively, polyhedral distortions of late transition-metal metallacarboranes have been explained in terms of electron population of low-lying antibonding orbitals involving the metal and the carborane ligand.[4] This notion, coupled with the structures of **2a** and **2b**, suggests that the HOMO in **2b** has greater antibonding character than the HOMO in **2a**, precisely the conclusion derived from molecular orbital calculations. Similarly, one might expect complex **2c** to adopt a structure similar to that found in $2,2\text{-}(\textit{tert}\text{-}C_4H_9NC)_2\text{-}1\text{-}NMe_3\text{-}2,1\text{-}PdCB_{10}H_{10}$[3b] with the plane defined by the $(Ph_3P)_2Rh$ fragment being perpendicular to the mirror plane of the carborane ligand and the carbon atom in the bonding face of the carborane ligand bent back into the cage away from rhodium. Verification awaits structural characterization of **2c**.

The anionic, five-coordinate nature of the new complexes reported here has been exploited in a variety of ways. The accompanying communication describes novel cycloaddition reactions of arylnitrile *N*-oxides with the rhodium–carbonyl carbon bond in complexes **3a** and **3b**.[12]

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Registry No. 1a, 53687-46-0; **1b**, 53754-45-3; **1c**, 82848-97-3; $[Et_4N]$**2a**, 85422-26-0; K[18-crown-6]**2a**, 85422-35-1; $[Me_4N]$**2b**, 85422-36-2; $[Et_4N]$**2b**, 85422-28-2; K[18-crown-6]**2b**, 85422-37-3; $[Et_4N]$**2c**, 85422-30-6; $[Et_4N]$**3a**, 85369-53-5; $[Et_4N]$**3b**, 85369-55-7; $[Et_4N]$**3c**, 85422-32-8; $[Et_4N]$**4a**, 85422-34-0; K[18-crown-6]**4b**, 85442-20-2; ethylene, 74-85-1.

Supplementary Material Available: IR and NMR spectral and analytical data (1 page). Ordering information is given on any current masthead page.

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