2548 *Organometallics* **2003,** *22,* 2548−2550

Metal Insertion into the Open Face of an *isonido*-Metallathiaborane Cluster: Formation and Characterization of [2-PPh_3-2,3-Cl_2-2,3-(μ-Cl)-3,7-(μ-dppm)-*closo*-2,3,1-$Rh_2SB_9H_8$] from [1-PPh_3-{1,3-(μ-dppm)}-*isonido*-1,2-$RhSB_9H_8$]

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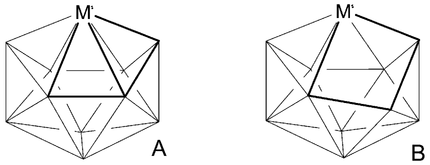
Received February 20, 2003

Summary: The isonido cluster [1-PPh_3-{1,3-(μ-dppm)}-isonido-1,2-$RhSB_9H_8$] reacts with [$RhCl(PPh_3)_3$] to afford the icosahedral cluster [2-PPh_3-2,3-Cl_2-2,3-(μ-Cl)-3,7-(μ-dppm)-closo-2,3,1-$Rh_2SB_9H_8$] in a reaction wherein the metal reagent inserts into the quadrilateral face of the isonido 11-vertex cluster. The structure of the product is explained in terms of a diamond−square−diamond rearrangement and ligand exchange which follows insertion.

Chart 1



The isonido, isocloso nomenclature for heteroborane clusters was first introduced by the Greenwood and Kennedy group[1] to describe systems that deviate from the Wade/Williams formalism[2] in terms of either structural or electron-counting considerations. This communication addresses the 11-vertex isonido system. Several years ago Jung and Hawthorne[3,4] described a series of metalladicarbaboranes with the general formula *nido*-9,9-L_2-9,7,8-$MC_2B_8H_{11}$, where M = Rh, Ir and L = PR_3, AsR_3, SbR_3. The species are two electrons short of the formal electron count required by the polyhedral skeletal electron pairs theory (PSEPT) for nido structures.[3] Thus, for example, *nido*-$L_2MC_2B_8H_{11}$, where L_2M = $Ir(PPh_3)_2$, $Rh(PEt_3)_2$, will readily add 1 mol of ligand to the metal, thereby providing an additional two electrons to the cluster, affording a nido species with the "correct" electron count. These species also thermally rearrange to form closo clusters of the general, formula *closo*-1,1-L_2-1-H-1,2,4-$M_2C_2B_8H_{10}$.[3] NMR data for the latter were consistent with a structure involving a regular octadecahedron expected for a regular 11-vertex closo system, shown as A in Chart 1. Later Greenwood, Kennedy, et al. described the structure of a novel species, [1-(η^6-*p*-cym)-2,4-Me_2-1,2,4-$RuC_2B_8H_8$],[5] which featured a quadrilateral open face, and since then the structures of two of the Jung/Hawthorne-type species, [1,1-$(PPh_3)_2$-1-H-1,2,4-$MC_2B_8H_{10}$], were investigated and shown to have the same isonido structure with an open quadrilateral face.[6] This structural motif is also shown (as B) in Chart 1. Since then a number of metalladicarbaboranes have been discovered which contain the four-membered open face.[7] All of these species and those described above are reminiscent of a "frozen" intermediate or transition state proposed by Lipscomb et al.[8] for the known fluxional process, which renders all the vertexes in the closo 11-vertex borane $[B_{11}H_{11}]^{2-}$ equivalent on the NMR time scale.[9] The process is thought to involve diamond−square−diamond rearrangements, and the square-faced species is the transition state or intermediate for such processes. All of these 11-vertex isonido species[7a] were from the metalladicarbaundecaborane class, but recently we reported the first example of an isonido 11-vertex rhodathiaborane cluster, [1-PPh_3-{1,3-(μ-dppm)}-*isonido*-1,2-$RhSB_9H_8$] (**1**), where dppm is $[CH_2(PPh_2)_2]$.[10] Further chemistry of these 11-vertex isonido clusters has not been developed to any extent. The only report

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10.1021/om0301177 CCC: $25.00
Publication on Web 05/17/2003

of their chemistry involves the high-temperature thermolysis of type B structures to form type A structures.[7b,c] Herein we describe the first example of the insertion of a metal-containing moiety into the open face of an isonido 11-vertex cluster.

The reaction between $[RhCl(PPh_3)_3]$ and $[1\text{-}PPh_3\text{-}\{1,3\text{-}(\mu\text{-dppm})\}\text{-}\textit{isonido}\text{-}1,2\text{-}RhSB_9H_8]$ (**1**) in CH_2Cl_2, under N_2 at room temperature, leads to the formation of a red crystalline solid which was characterized as $[2\text{-}PPh_3\text{-}2,3\text{-}Cl_2\text{-}2,3\text{-}(\mu\text{-}Cl)\text{-}3,7\text{-}(\mu\text{-dppm})\text{-}\textit{closo}\text{-}2,3,1\text{-}Rh_2SB_9H_8]$ (**2**) in 39% yield.[11] NMR spectra[12] suggested the formulation, which was confirmed by elemental analysis.[13] Recrystallization from CH_2Cl_2/pentane allowed a crystal structure determination,[14] which is illustrated in Figure 1. The structure of **2** is a *closo*-icosahedral Rh_2SB_9 cluster containing adjacent phosphine-ligated $RhCl_2$ moieties. Each Rh bears a Cl ligand, and another Cl bridges the two metals. In addition, one Rh atom bears a PPh_3 ligand and the other bears a dppm moiety which bridges to a boron atom adjacent to both metal atoms.

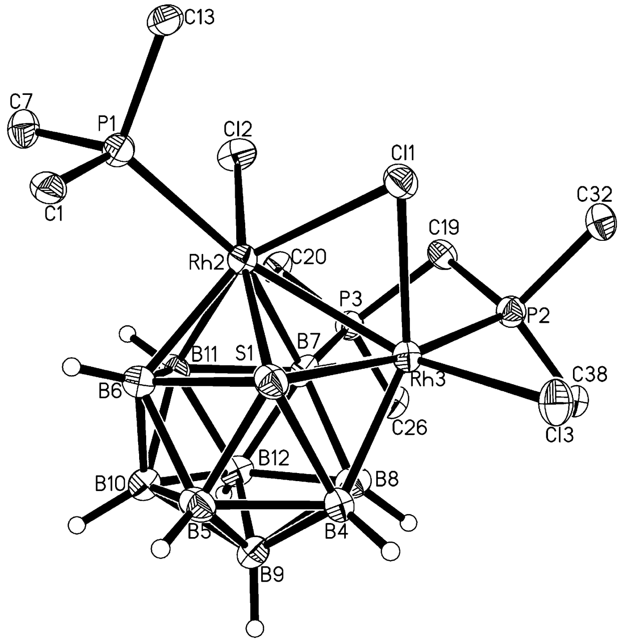
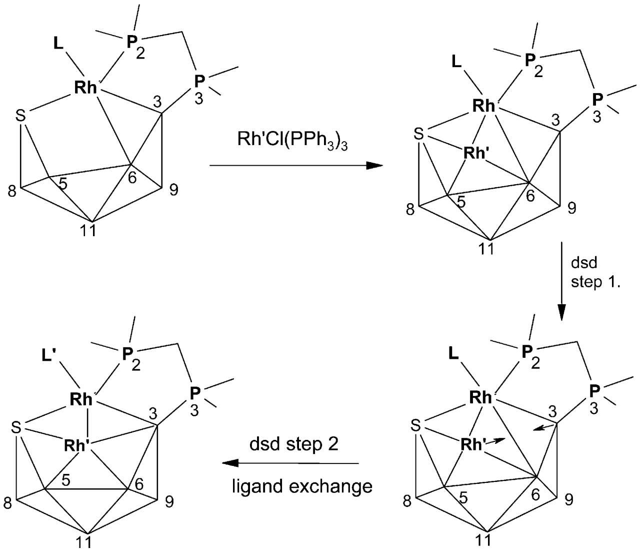


Figure 1. Molecular structure of **2** with displacement ellipsoids drawn at the 50% level. The phenyl rings on phosphorus, ipso carbon atoms excepted, are omitted for clarity, as are all the H atoms on carbon. Bond lengths (Å): Rh(2)−Rh(3) = 2.592(1), Rh(2)−S(1) = 2.351(1), Rh(2)−P(1) = 2.331(1), Rh(2)−Cl(2) = 2.342(1), Rh(2)−Cl(1) = 2.474(1), Rh(2)−B(7) = 2.410(6), Rh(2)−B(6) = 2.195(6), Rh(2)−B(11) = 2.201(6), Rh(3)−S(1) = 2.427(1), Rh(3)−P(2) = 2.778(1), Rh(3)−Cl(1) = 2.440(1), Rh(3)−Cl(3) = 2.405(1), Rh(3)−B(7) = 2.228(6), Rh(3)−B(4) = 2.666(6), Rh(3)−B(8) = 2.215(6), S(1)−B(4) = 2.091(6), S(1)−B(5) = 1.968(6), S(1)−B(6) = 2.129(7), P(3)−B(7) = 1.946(6). Intercage B−B distances range from 1.730(9) Å for B(6)−B(4) to 1.864(8) Å for B(7)−B(11). Angles (deg): Rh(2)−Cl(1)−Rh(3) = 63.66(3), P(3)−B(7)−Rh(3) = 114.3(3), B(7)−Rh(3)−P(2) = 86.37(1).

Scheme 1



Although there are some examples of oxidative insertion of zerovalent metal and other metal moieties into both small and larger *closo*-metallacarboranes and -carboranes,[15] organometallic reagents do not normally react with closed metallaborane clusters, since the latter are typically quite stable. We are unaware of instances where a $[RhCl(PPh_3)_3]$ moiety oxidatively inserts into *closo*-borane or -carborane clusters. Thus, our assumption is that the metal inserts into the open quadrilateral face of **1**. The formation of the 12-vertex icosahedral cluster **2**, from the insertion of the metal moiety into the square face of **1**, involves the conversion of a species with different cluster vertex connectivities into one in which all the connectivities are 5. Our explanation for this is illustrated in Scheme 1, in which we describe the reaction by showing only the “front” half of the cluster. An 11-vertex closed polyhedron, an octadecahedron which is illustrated as A in Chart 1, consists of 1 6-connected vertex, 2 of connectivity 4, and 8 of connectivity 5. The distorted isonido cluster, shown as structure B, has 8 5-connected vertexes and 3 4-connected vertexes. The metal moiety inserts into the quadrilateral face, as indicated in Scheme 1, to generate

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(11) $[RhCl(PPh_3)_3]$ (37 mg, 0.040 mmol) was added to a solution of $[1\text{-}PPh_3\text{-}\{1,3\text{-}(\mu\text{-dppm})\}\text{-}\textit{closo}\text{-}1,2\text{-}RhSB_9H_8]$ (12 mg, 0.013 mmol) in CH_2Cl_2 (ca. 10 mL) under N_2. The reaction mixture was stirred at room temperature for 6 days. After this time, the solution was filtered over silica gel and a red component was collected. Recrystallization in CH_2Cl_2/pentane gave rise to the isolation of crystals characterized as $[2\text{-}PPh_3\text{-}2,3\text{-}Cl_2\text{-}2,3\text{-}(\mu\text{-}Cl)\text{-}3,7\text{-}(\mu\text{-dppm})\text{-}\textit{closo}\text{-}2,3,1\text{-}Rh_2SB_9H_8]\cdot C_5H_{12}$ (6 mg, 0.005 mmol; 39%).

(12) NMR data (CD_2Cl_2, 25 °C). ^{11}B (160.5 MHz): δ 41.7(d, J(P,B) = 131 Hz, 1B), 13.7 (d, J(H,B) = 123 Hz, 1B), 6.9 (d, J(H,B) = 128 Hz, 1B), 1.1 (d, J(H,B) = 132 Hz, 1B), −6.5 (v br, 2B), −11.6 (v br, 2B), −23.6 (v br, 1B). ^1H (500 MHz): δ 7.79−7.02 (m, 35H; C_6H_5), 4.74 (br m, 1H; $Ph_2PCH_2PPh_2$), 3.97 (br m, 1H; $Ph_2PCH_2PPh_2$). $^1H\{^{11}B\}$ NMR (500 MHz): δ 4.36 (1H, BH), 3.67 (1H, BH), 3.55 (2H, BH), 3.28 (1H, BH), 2.41 (2H, BH), 2.15 (1H, BH).

(13) Anal. Calcd for $C_{43}H_{45}B_9Cl_3P_3Rh_2S\cdot C_5H_{12}$: C, 49.34; H, 4.92. Found: C, 48.62; H, 4.64.

(14) Crystal data for **2**: $C_{43}H_{47.50}B_9Cl_3O_{2.50}P_3Rh_2S$, M_r = 1138.74, monoclinic, space group $C2/c$, a = 34.637(3) Å, b = 14.5946(12) Å, c = 23.865(2) Å, β = 116.387(5)°, V = 10807.2(16) Å^3, Z = 8, D_c = 1.400 Mg/m^3, F(000) = 4580, Bruker SMART CCD using Mo Kα radiation (λ = 0.710 73 Å), T = 110(2) K, R1 = 0.0521, wR2 = 0.1294, GOF = 1.053. Two and a half molecules of H_2O were located in the lattice. All cage hydrogen atoms were located and refined freely, except for B(10) (Riding model).

(15) See for example: (a) Paxson, T. E.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 1604. (b) Green, M.; Spencer, J. L.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 179. (c) Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1974**, *96*, 3090. (d) Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1679. (e) Miller, V. R.; Barker, G. K.; Green, M.; Garcia, M. P.; Stone, F. G. A.; Bassett, J.-M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1266. (f) Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1981**, 933. (g) Stibr, B.; Kennedy, J. D.; Thornton-Pett, M.; Drdakova, E.; Jelinek, T.; Plesek, J. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1439.

a species in which all the vertexes have intracluster connectivities of 5, except for the Rh and B(6) positions, which are 6, and the Rh′ and B(3) atoms, which are 4. A diamond−square−diamond rearrangement involving these same positions would render all vertexes 5-connected, as is observed in the final product **2**. Except for some exchange reactions between PPh_3 and Cl on the metal, the structure of the product is exactly what is predicted from the process indicated in the scheme. Such ligand exchange involving chloride and phosphine ligands in the presence of $[RhCl(PPh_3)_3]$ has been observed previously in related systems.[10] There are clearly unanswered questions about this proposed mechanism. Exactly how the Rh moiety inserts into the cages is one of them. Presumably, loss of at least one PPh_3 ligand, well-known for $[RhCl(PPh_3)_3]$, precedes insertion, and since the species is fluxional in solution, the specific location of insertion cannot be completely described except that it is likely to be one of four possible sites adjacent to the existing metal center.

The cluster **2,** although the cage is distorted somewhat, conforms structurally to the PSEPT[2a] and has the correct 26-skeletal-electron count for a 12-vertex closo system.[2,16] There are two other systems known which have structures similar to that of **2**. They are [7-Cl-2,3-$\{\eta^5$-$C_5Me_5\}_2$-*closo*-2,3,1-$Rh_2SB_9H_8$] (**3**), formed in the reaction between $Cs[SB_9H_{12}]$ and $[RhCl_2(\eta^5$-$C_5Me_5)]_2$,[17] and [2,3-$(PPh_3)_2$-3-(Cl)-2,3-(μ-Cl)-2-$(Ph_2PC_6H_4)$-*closo*-2,3,1-$Rh_2SB_9H_8$] (**4**), from [8,8-$(PPh_3)_2$-8,7-*nido*-$RhSB_9H_{10}$] and $[RhCl(PPh_3)_3]$ in the presence of Me_4NCl.[18] All three systems **2**−**4** contain an adjacent pair of Rh atoms both bonded to a S atom and a unique B atom. Also in the three compounds the boron atom has another unique feature. In **3** the B atom bears a Cl ligand; in **4** the B atom is connected to an ortho carbon atom from a PPh_3 group on Rh, and in **2** the dppm ligand bridges the B atom and Rh(3). The three Rh−Rh distances are 2.592(1), 2.778(1) and 2.601(1) Å, respectively, for **2**−**4**. In **2** and **4** the Rh atoms are bridged by a Cl moiety, which serves as a three-electron donor to the cluster,[16] and in these cases the metal−metal bond is somewhat shorter than in **3**. Also, the bridged Rh−B distances, those involving the dppm ligand in **2** and ortho boronation in **4**, are the shortest of the bonds to the unique boron atom and shorter than either of the bonds in **3**. In addition to **3** and **4**, there is a related *closo*-Co_2SB_9 system, [7-I-2,3-$(\eta^5$-$C_5Me_5)_2$-2,3,1-*closo*-$Co_2SB_9H_8$], containing an analogous SCo_2B motif, prepared in a metal atom reactor.[19]

The nature of cluster **2** is thus not novel, but the nature of its formation is certainly novel, and this suggests that the use of these isonido clusters to form bimetallaboranes may allow tailoring of the metal pair in such species so as to allow a study of metal−metal interactions in metallaborane clusters. We intend to pursue this topic.

Acknowledgment. We acknowledge the NSF (Grant No. CHE-9727570), the Missouri Research Board, and UM−St. Louis for research grants to L.B. and the NSF, the UM−St. Louis Center for Molecular Electronics, and the Missouri Research Board for funds which helped purchase the NMR, XRD, and MS facilities.

Supporting Information Available: X-ray structural data for **2**, including tables giving a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters; data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Skeletal electron count for **2**: S (4e) + $B_9H_8PPh_3$ (19e) + $2RhPPh_2Cl$ (0e) + μ-Cl (3e) = 26e.

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