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Synthesis of *nido*-[1-OMe-2,3-(Cp*Ru)$_2${μ-P(OMe)$_2$}B$_3$H$_5$]: Methoxy Transfer from Phosphorus to Boron and Cluster Core Rearrangement

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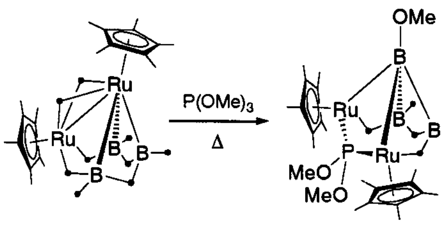
The chemistry of ruthenaboranes has been described as “rich and varied” because of its ability to show various cluster structures and for its unique sensitivity in responding to kinetic control during cluster expansion or degradation.[1,2] Indeed, in the degradation reaction of *nido*-[1,2-(Cp*Ru)$_2$(μ-H)$_2$B$_3$H$_7$] (**1**) (7 skeltal electron pairs, sep) through the action of tertiary phosphines, we previously showed the formation of an electron-deficient metallaborane complex [(Cp*Ru)$_2$(μ-H)($\parallel$-μ-η^4-B$_2$H$_5$)(PMe$_2$Ph)] (**3**) and its thermolytic conversion to tetrahedral *nido*-[(Cp*Ru)$_2$(μ-PMe$_2$)($\perp$-μ-η^4-B$_2$H$_5$)] (**4**), both of which possess 6 sep (Scheme 1).[1,3] During the course of study on the reactivity of **1** to P-donor ligands, we found that P(OMe)$_3$ induces a different type of reaction: cluster core rearrangement with preservation of 7 sep.

A 1:2 mixture of **1** and P(OMe)$_3$ in toluene was flame-sealed in a Pyrex glass tube and heated to 60 °C for 3 days. The resulting brownish red solution was concentrated and chromatographed on a silicagel column using a 1:4 mixture of toluene and hexane as eluent. Cluster *nido*-[1-OMe-2,3-(Cp*Ru)$_2${μ-P(OMe)$_2$}B$_3$H$_5$] (**2**) was isolated as orange crystals.[4] This reaction includes the rearrangement of 1,2-disubrogated cluster **1** to 2,3-disubrogated **2** with concomitant formation of a phosphido bridge and an apical BOMe group through methoxy transfer from phosphorus to boron.



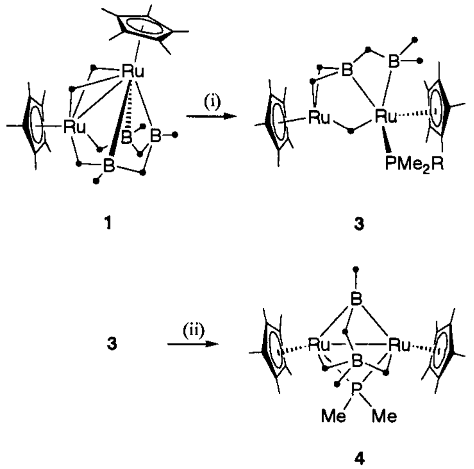
1 **2**

Cluster **2** is a *nido*-diruthenaborane, formally derived from pentaborane(9) by the isolobal replacement of a B$_2$H$_3$ moiety by the [(Cp*Ru)$_2$P(OMe)$_2$] fragment. It belongs to the series of square-based pyramidal clusters having a M$_2$B$_3$ core. NMR spectroscopy indicates 50% conversion to **2**; however, considerable decomposition on silicagel occurs, reducing the isolated yield of **2** (ca. 5%).

In the ^{1}H NMR spectrum of **2**, the Cp* groups gave a sharp doublet at 1.88 ppm while the two methoxy substituents of the bridging phosphido group were observed at inequivalent positions (2.82 and 3.69 ppm). The methoxy group bonded to the apical boron gave a low-field signal at 3.85 ppm. For the B$_2$H$_5$ fragment, three broad peaks were observed at 5.46, −3.37, and −14.40 ppm with integral intensities of two, one, and two protons, respectively. The first signal appeared as a broad quartet and is assigned to the terminal B*H* protons of the basal boron atoms. The second and third are attributed to the bridging B−*H*−B and Ru−*H*−B protons, respectively. All these protons are part of the basal B$_2$H$_5$ fragment of the cluster, which exhibited a similar mode of coordination to the metal-rich ruthenaborane cluster *nido*-[1,2,3-{Ru(CO)$_3$}$_3$(μ-H)(B$_2$H$_5$)] and its phosphine derivatives.[5] The apical and two basal boron atoms were observed at 66.93 and 19.53 ppm, respectively, in the ^{11}B NMR spectrum. The large downfield shift of the apical boron atom reflects the highly metallic environment and the presence of a methoxy group. The bridging phosphido gave a downfield-shifted peak at 362.5 ppm in the ^{31}P NMR spectrum. This value is characteristic of a phosphido group bridging across a metal−metal bond.[3,6]

The molecular structure of **2** along with selected bond distances and angles is shown in Figure 1.[7] The cluster core maintains a

Scheme 1



• = H; (i) 2 PMe$_2$R (R = Me, Ph), (ii) R = Ph, Δ, - C$_6$H$_6$

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(4) Data for **2**. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ −14.40 (br, 2H, Ru*H*B), −3.37 (br, 1H, B*H*B), 1.88 (d, 15H × 2, $J_{\text{PH}} = 1$ Hz, Cp*), 2.82 (d, 3H, $J_{\text{PH}} = 13.5$ Hz, PO*Me*), 3.69 (d, 3H, $J_{\text{PH}} = 11.0$ Hz, PO*Me*), 3.85 (s, 3H, BO*Me*), 5.46 (br q, 2H, $J_{\text{BH}} = 169.0$ Hz, ter B*H*). ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ 19.53 (2B, B$_{\text{basal}}$), 66.93 (1B, B$_{\text{apical}}$). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ 362.5. ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 95.62 (s, *C*$_5$-Me$_5$), 59.79 (s, BO*Me*), 54.28 (d, $J_{\text{PC}} = 11$ Hz, PO*Me*), 52.21 (d, $J_{\text{PC}} = 3$ Hz, PO*Me*), 10.67 (s, C$_5$*Me*$_5$). IR (KBr, cm^{-1}): 2479 (s) ν(BH); 2363 (m) ν(BHB); 1785 (w), 1748 (w) ν(RuHB). MS (EI): *m/z* 634 (2, M$^+$), 589 (5, M$^+$ − (BOMe) − 3H), 503 (17, Cp*$_2$Ru$_2$P), 134 (100, Cp* − H).

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(7) Crystal data for **2**. C$_{23}$H$_{44}$B$_3$O$_3$PRu$_2$, MW = 634.18, monoclinic, space group *C*2/*c* (No. 15), $a = 28.212(3)$ Å, $b = 15.058(1)$ Å, $c = 15.700(2)$ Å, $\beta = 123.255(9)$°; $V = 5577(1)$ Å^3, $T = 293$ K, $Z = 8$, μ(Mo Kα) = 1.145 mm^{-1}. Of the 3456 reflections measured, 3412 were observed [$I > 3\,\sigma(I)$]. R1 = 0.0335, wR2 = 0.1028 for observed unique reflections and R1 = 0.0341, wR2 = 0.1048 for all 3456 reflections. H(1)−H(5) were found by the difference Fourier synthesis and refined isotropically. Methyl hydrogen atoms were idealized.

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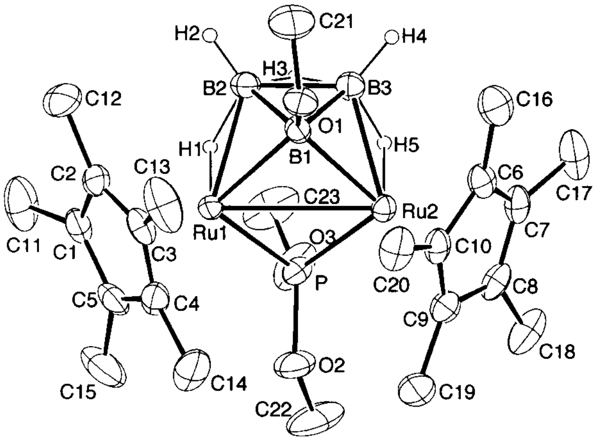
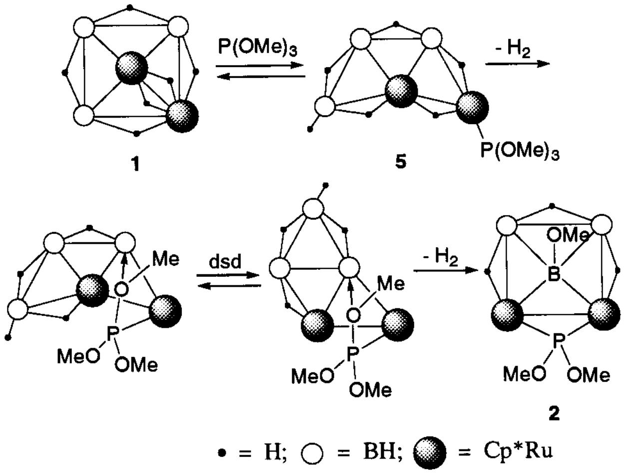


Figure 1. Molecular structure of **2**, with the following selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(2) 2.893(1), Ru(1)−P 2.220(2), Ru(2)−P 2.223(2), Ru(1)−B(1) 2.163(6), Ru(1)−B(2) 2.242(7), Ru(2)−B(1) 2.155(7), Ru(2)−B(3) 2.221(7), B(1)−B(2) 1.77(1), B(1)−B(3) 1.761(9), B(2)−B(3) 1.76(1), B(1)−O(1) 1.397(8); Ru(1)−P−Ru(2) 81.27(6), Ru(1)−B(1)−Ru(2) 84.2(3), Ru(1)−B(1)−B(2) 68.7(3), Ru(1)−B(1)−B(3) 107.4(4), Ru(2)−B(1)−B(2) 107.4(4), Ru(2)−B(1)−B(3) 68.3(3), Ru(1)−B(2)−B(3) 104.4(4), Ru(2)−B(3)−B(2) 105.2(4), B(1)−B(2)−B(3) 59.6(4), B(2)−B(1)−B(3) 59.9(4).

highly distorted square pyramidal geometry containing three boron and two ruthenium atoms. The metallic centers occupy the 2,3-positions and are bridged by a dimethoxyphosphido group. The five-membered core is characterized by a trapezoidal base due to a long Ru−Ru side (2.893(1) Å), a short B_{basal}−B_{basal} distance (1.76(1) Å), and Ru−B_{basal} bond lengths of 2.242(7) and 2.221(7) Å. The B_{apical}−B_{basal} bonds in cluster **2** are between 1.76 and 1.77 Å, which are far longer than the corresponding component in the parent borane *nido*-B_5H_9 (1.66(2) Å)[8] and are comparable to those in related *nido*-2,3-dimetallapentaborane clusters: *nido*-[2,3-$(Cp^*Rh)_2B_3H_7$] (1.72 Å),[2] *pileo*-[2,3-$(Cp^*Ru)_2(\mu\text{-}H)B_4H_7$] (1.718 Å),[2] and *nido*-[2-(Cp*Ir)-3-{$(PPh_3)_2$(CO)Os}(μ-H)B_3H_6] (1.749 Å).[9] The intermetallic distance is 2.893(1) Å, which is within the range of usual Ru−Ru single bond lengths.

A possible mechanism for the formation of **2** is presented in Scheme 2.

Scheme 2



Scheme 2. The coordination of $P(OMe)_3$ with cleavage of a B−H−Ru three-center−two-electron (3c2e) bond is quite plausible. The resulting vital arachno intermediate **5** was not isolated but was spectroscopically observed in a related reaction of **1** with $PHPh_2$. It is presumed that the intermediate **5** is also involved in the reaction of **1** with PMe_2R, described in Scheme 1. In contrast to that system, the five-membered core is preserved because of the weaker nucleophilicity of $P(OMe)_3$ compared to that of PMe_2R. Subsequent H_2 loss and diamond−square−diamond (dsd) rearrangement produce the observed product. A relevant heat-induced skeletal rearrangement has been observed in the thermolysis of a dicobaltaborane cluster *nido*-[1-(Cp*Co)-2-(η^4-C_5Me_5HCo)(μ-H)B_3H_7].[10] Likewise, the 1,2-dirhodapentaborane cluster, [3-Cl-1,2-$(Cp^*Rh)_2B_3H_6$],[2] converts to the 2,3-isomer on heating. Moreover, phenyl migration from phosphorus to boron has been observed in the formation of [$(CpCo)_3$(μ_3-PPh)(μ_3-BPh)].[11] The high affinity between boron and oxygen is suspected as one of the driving forces in the activation of the P−O bond.

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Supporting Information Available: Tables furnishing the positional parameters and anisotropic thermal parameters of the non-hydrogen atoms, bond lengths, and bond angles for *nido*-[1-OMe-2,3-$(Cp^*Ru)_2$\{μ-$P(OMe)_2$\}-B_3H_5] (**2**) and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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