SYNTHESES AND STRUCTURAL CHARACTERIZATIONS OF *closo* AND *nido* 10-VERTEX METALLATRICARBANONABORANES

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Dedicated to our friend Bohumil Štíbr on the occasion of his 70th birthday.

Deboronation of the 11-vertex metallatricarbadecaboranes 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ [M = Ru, Fe] and 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ [M = Re] with tetrabutylammonium fluoride (TBAF) produced the first examples of the 10-vertex families of *closo* and *nido* metallatricarbanonaborane complexes, 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-M-$C_3B_6H_8$ [M = Ru (**1**), Fe (**2**)] and 5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9^-$ (**3**). Crystallographic characterizations of **1** and **3** confirmed geometries, based on a bicapped square antiprism for **1** and a bicapped square antiprism with one missing vertex for **3**, that are consistent with their respective 22 (*closo*) and 24 (*nido*) skeletal-electron counts.

Keywords: Boron clusters; Metallatricarbaborane; Tricarbaborane; Carboranes; Boranes; Sandwich complexes; Deboronation; Ten-vertex cluster.

Although the first metallatricarbaboranyl complex, (2-$CH_3C_3B_3H_5$)$Mn(CO)_3$, was synthesized by Grimes more than forty years ago[1], it has only been in recent years that systematic studies of the chemistry and properties of larger-cage metallatricarbaboranes have become possible. The high yield syntheses of the 10-vertex *nido*-6-R-5,6,9-$C_3B_7H_{10}$ and *arachno*-5,6,10-$C_3B_7H_{10}$ tricarbadecaboranes by Kang[2] and Su[3] have enabled the production of a wide variety of 11-vertex metallatricarbadecaboranyl clusters based on the R-$C_3B_7H_9^-$ anions[4]. Likewise, the development by Štíbr and coworkers[5] of efficient routes to the tricarbollide *nido*-$C_3B_8H_{11}^-$ anions has provided access to numerous 12-vertex metallatricarbaboranes[6]. We have recently been exploring routes to the unknown families of the intermediate sized 8-, 9- and 10-vertex metallatricarbaboranes and we report in this paper the syntheses and structural characterizations of the first examples of *closo* and

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nido 10-vertex metallatricarbanonaborane complexes, 2-(η^5-C_5H_5)-10-Ph-2,1,6,10-M-$C_3B_6H_8$ (M = Ru, Fe) and 5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9^-$.

EXPERIMENTAL

Materials

The 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ (M = Fe, Ru)[4h,4i] and 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ (M = Re)[4l] were prepared by the reported methods. Tetrabutylammonium fluoride (TBAF, 1 M in THF (Aldrich)) was used as received. THF was dried by passing through an activated alumina column. All other solvents were used as received unless otherwise noted. Silica gel (Fisher) was used as received.

Physical Measurements

^{11}B NMR at 128.4 MHz and ^{1}H NMR at 400.1 MHz were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories (δ, ppm; *J*, Hz). All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to internal residual protons or carbons in the lock solvents and are referenced to Me_4Si (0.0 ppm). High- and low-resolution mass spectra employing chemical ionization with negative ion detection were obtained on a Micromass AutoSpec high-resolution mass spectrometer. IR spectra (ν, cm^{-1}) were obtained on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out at Robertson Microlit Laboratories in Madison (NJ). Melting points were determined using a standard melting point apparatus and are uncorrected.

X-ray intensity data were collected on Rigaku Mercury CCD (for **1**) or Bruker APEXII CCD (for **3**) area detectors. Both collections used graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SIR97 [7] or SHELXS97 [8]). Refinement was by full-matrix least squares based on F^2 using SHELXL97.

CCDC 777396 (for **1**) and 777397 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Synthesis of 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-Ru-$C_3B_6H_8$ (**1**)

A 1 M solution of TBAF in THF (0.25 ml, 0.25 mmol) was added dropwise to a sample of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Ru-$C_3B_7H_9$ (90 mg, 0.25 mmol) dissolved in 6 ml of THF. The solution was stirred at 0 °C for 19 h and then flash filtered through a short plug of silica gel with CH_2Cl_2. The solvent was removed in vacuo and the orange residue separated by thin layer chromatography using 2:1 hexanes/CH_2Cl_2 as eluent to yield orange crystals of **1** (R_F 0.73). Yield 32.6 mg (37%). Orange. M.p. 129 °C. For $C_{14}H_{18}B_6Ru$ (352.24) calculated: 47.74% C; 5.15% H; found: 48.58% C, 5.45% H. HRMS: *m/z* calculated for $^{12}C_{14}{}^1H_{18}{}^{11}B_6{}^{103}Ru^-$ 356.1017, found 356.1022. ^{11}B NMR (128.4 MHz, CD_2Cl_2): 8.4 d, 1 B, *J* = 190; –2.4 d, 1 B, *J* = 173; –7.6 d, 1 B, *J* = 139; –23.4 d, 1 B, *J* = 173; –27.2 d, 2 B, *J* = 156. ^{1}H NMR (400.1 MHz, $CDCl_3$): 9.10 s, 1 H (CH); 7.72–7.39 m, 5 H (Ph); 5.19 s, 5 H (Cp);

4.54 s, 1 H (CH). IR (KBr): 3060 (w), 2548 (s), 1597 (w), 1494 (m), 1446 (m), 1412 (m, br), 1076 (m, br), 1040 (m), 1002 (m, br), 897 (m), 838 (w), 814 (m), 757 (m), 693 (m), 612 (w), 515 (w), 493 (m).

Synthesis of 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-Fe-$C_3B_6H_8$ (**2**)

A 1 M solution of TBAF in THF (0.50 ml, 0.50 mmol) was added dropwise to a sample of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Fe-$C_3B_7H_9$ (50 mg, 0.16 mmol) dissolved in 6 ml of THF. The solution was stirred at 0 °C for 5 h and then flash filtered through a short plug of silica gel with CH_2Cl_2. The solvent was removed in vacuo and the dark blue residue chromatographed on silica gel plates using 2:1 hexanes/CH_2Cl_2 as eluent to yield **2** as a pink-purple solid (R_F 0.67). Yield 22.6 mg (46%). Pink. M.p. 85–88 °C. HRMS: *m/z* calculated for $^{12}C_{14}{}^{1}H_{18}{}^{11}B_6{}^{57}Fe^-$ 309.1316, found 309.1373. ^{11}B NMR (128.4 MHz, CD_2Cl_2): 4.6 d, 1 B, J = 187; –4.9 d, 1 B, J = 153; –8.2 d, 1 B, J = 153; –21.7 d, 1 B, J = 170; –28.9 d, 1 B, J = 153; –30.8 d, 1 B, J = 170. ^{1}H NMR (400.1 MHz, $CDCl_3$): 9.21 s, 1 H (CH); 7.89–7.48 m, 5 H (Ph); 5.54 s, 1 H (CH); 4.63 s, 5 H (Cp). IR (KBr): 2959 (s), 2925 (s), 2873 (s), 2731 (w), 2669 (w), 2632 (w), 2600 (w), 1466 (s), 1378 (m), 1301 (w), 1136 (w), 931 (w), 722 (w).

Synthesis of Bu_4N^+[5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9$]$^-$ (**3**)

A 1 M solution of TBAF in THF (0.35 ml, 0.35 mmol) was added dropwise to a sample of 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-Re-$C_3B_7H_9$ (50 mg, 0.11 mmol) dissolved in 6 ml of THF. The solution was stirred at 0 °C for 5 h and then flash filtered through a short plug of silica gel with CH_2Cl_2. The solvent was removed in vacuo and the dark golden residue was then chromatographed on silica gel plates using CH_2Cl_2 as eluent (R_F 0.84). Recrystallization from heptane gave **3** as a golden yellow solid. Yield 17.5 mg (35%). M.p. 103–105 °C. HRMS: *m/z* calculated for $^{12}C_{12}{}^{1}H_{13}{}^{11}B_6{}^{187}Re^{2-}$ (P-1) 458.0979, found 458.1022. ^{11}B NMR (128.4 MHz, CD_2Cl_2): 20.1 d, 1 B, J = 139; –0.2 d, 1 B, J = 121; –3.0 d, 1 B, J = 121; –7.4 d, 1 B, J = 139; –23.6 d, 1 B, J = 173; –33.1 d, 1 B, J = 139. ^{1}H NMR (400.1 MHz, $CDCl_3$): 7.57–7.03 m, 5 H (Ph); 5.48 s, 1 H (CH); 3.16 s, 1 H (CH); 3.14 m, 8 H (TBA); 1.61 m, 8 H (TBA); 1.43 q, 8 H, J = 7.02 (TBA); 1.03 t, 12 H, J = 7.02 (TBA). IR (KBr): 3515 (s), 2960 (s), 2925 (vs), 2541 (vs), 2308 (w), 1944 (w), 1640 (m, br), 1496 (m), 1467 (m), 1418 (m), 1343 (m), 1323 (m), 1261 (vs), 1096 (vs), 1080 (vs), 1021 (vs), 898 (w), 879 (w), 802 (vs), 758 (m), 695 (m), 498 (m).

RESULTS AND DISCUSSION

As early as the 1960s it was demonstrated that strong nucleophiles, such as hydroxides, alkoxides, and amines, are capable of deboronating carboranes[9]. These types of polyhedral contraction reactions have now been widely employed as routes to smaller-cage polyborane clusters[10]. Polyborane deboronations induced by reactions with the fluoride anion, using either tetrabutylammonium fluoride (TBAF)[11] or CsF [12], have been shown to be especially useful. As described below, we have now used such fluoride induced deboronation of metallatricarbadecaboranyl clusters to produce the

first examples of the 10-vertex families of *closo* and *nido* metallatricarbanonaborane complexes.

*Syntheses and Structural Characterizations of 2-(η^5-C_5H_5)-10-Ph-closo-2,1,6,10-M-$C_3B_6H_8$, M = Ru (**1**) and Fe (**2**)*

As shown in Eq. (*1*), the 11-vertex metallatricarbadecaboranes 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ (M = Ru and Fe) reacted at 0 °C with TBAF in THF to form the new 10-vertex 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-M-$C_3B_6H_8$ (M = Ru (**1**) and Fe (**2**)) tricarbanonaboranyl complexes.

$$\text{1-}(\eta^5\text{-}C_5H_5)\text{-2-Ph-}closo\text{-1,2,3,4-M-}C_3B_7H_9 \xrightarrow[0\ ^\circ C]{\text{TBAF, THF}} \text{2-}(\eta^5\text{-}C_5H_5)\text{-10-Ph-}closo\text{-2,1,6,10-M-}C_3B_6H_8 \quad (1)$$

M = Ru (**1**), Fe (**2**)

The best yields were obtained employing 3 equivalents of TBAF. While the reaction with 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Fe-$C_3B_7H_9$ was complete in only a few hours, the reaction with 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Ru-$C_3B_7H_9$ required much longer times (~19 h). Both **1** and **2** were separated by preparative TLC and recrystallized from CH_2Cl_2. While **1** was both air and moisture stable, **2** proved slightly unstable to air while in solution.

Both the mass spectral and ^{11}B NMR data for **1** and **2** confirmed the loss of one cage boron to produce cage-contracted metallatricarbanonaborane frameworks. The ^{11}B NMR spectra of **1** and **2** were similar, but quite different from those of their 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ precursors (Fig. 1). Instead of the seven-boron patterns of the starting metallatricarbadecaboranes, the spectrum of **1** showed 5 doublets, with the upfield resonance having intensity 2, and that of **2** showed 6 equal-intensity doublets. The ^{1}H NMR spectra of both **1** and **2** showed two cage C-H resonances, with one appearing at midfield (4.54 ppm for **1** and 5.54 ppm for **2**) and the other at a lower field shift (9.10 ppm for **1** and 9.21 ppm for **2**).

Crystallographic data and structure refinements for **1** and **3** are presented in Table I. A crystallographic determination of **1** confirmed the closo bicapped square antiprism geometry shown in Fig. 2, which is consistent with the predicted *closo*-electron count of its M-$C_3B_6H_8$ fragment (22 skeletal electrons with the CpRu group donating one electron). The observed cage geometry of **1** is similar to those that have been determined for the isoelectronic 2-(η^6-$(CH_3)_3C_6H_3$)-*closo*-Fe-1,6-$C_2B_7H_9$ [13], 2-(η^6-C_6Me_6)-*closo*-

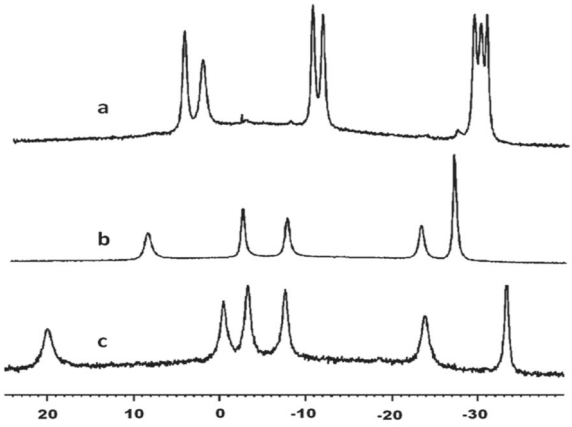

FIG. 1
The $^{11}B\{^1H\}$ NMR spectra of: a 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Ru-$C_3B_7H_9$, b 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-Ru-$C_3B_6H_8$ (**1**) and c 5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9^-$ (**3**)

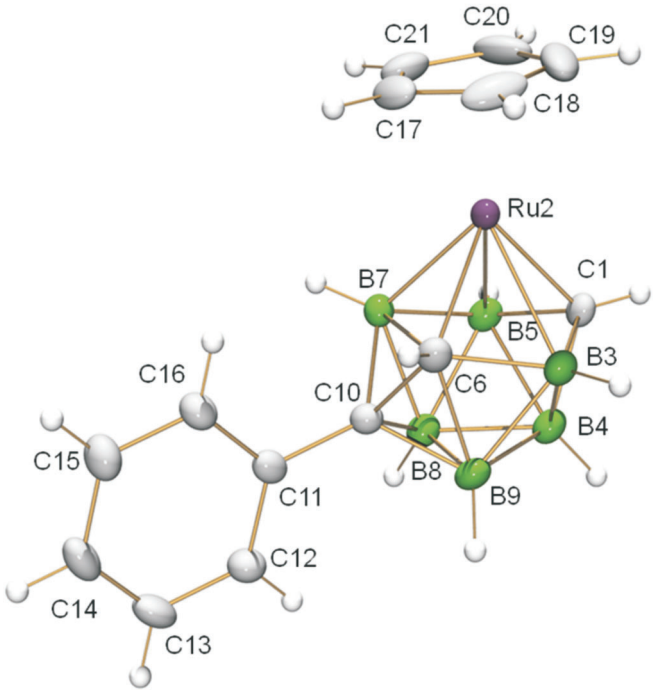

FIG. 2
Crystallographically determined structure of 2-(η^5-C_5H_5)-10-Ph-*closo*-2,1,6,10-Ru-$C_3B_6H_8$ (**1**)

TABLE I
Crystallographic data collection and structure refinement information

Parameter	**1**	**3**
Empirical formula	$C_{14}H_{18}B_6Ru$	$C_{28}H_{50}B_6NO_3Re$
Formula weight	352.21	699.75
Crystal class	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
a, Å	7.5357(8)	10.8688(7)
b, Å	7.9813(7)	16.4930(10)
c, Å	12.8095(13)	19.0988(12)
α, °	75.607(5)	
β, °	89.016(7)	106.150(2)
γ, °	81.380(6)	
V, Å^3	737.65(13)	3288.5(4)
D_{calc}, g/cm^3	1.586	1.413×10^3
μ, cm^{-1}	10.44	37.23
λ(MoKα), Å	0.71073	0.71073
Crystal size, mm^3	0.30 × 0.15 × 0.08	0.22 × 0.07 × 0.03
F(000)	352	1416
2θ angle, °	5.32–54.98	1.96–27.62
Temperature, K	143	100(1)
hkl collected	$-9 \le h \le 9$; $-9 \le k \le 10$; $-12 \le l \le 16$	$-14 \le h \le 14$; $-21 \le k \le 20$; $-24 \le l \le 22$
No. of reflections measured	8721	57018
No. of unique reflections	3330 (R_{int} = 0.0176)	7587 (R_{int} = 0.0315)
No. of observed reflections ($F > 4\sigma$)	3193	6404
No. of reflections used in refinement	3330	57018
No. of parameters	233	408
R^a indices ($F > 4\sigma$)	$R1$ = 0.0217, $wR2$ = 0.0519	$R1$ = 0.0302, $wR2$ = 0.0686
R^a indices (all data)	$R1$ = 0.0230, $wR2$ = 0.0528	$R1$ = 0.0409, $wR2$ = 0.0733
GOF^b	1.080	1.162
Final difference peaks, e/Å^3	+0.767, –0.604	+1.480, –0.865

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n = no. of reflections; p = no. of parameters refined.

2,1,6-Ru-$C_2B_7H_9$ [14] and 2,2,2-$(PPh_3)_2$-H-*closo*-2,1-6-Rh-$C_2B_7H_9$ [15] clusters. In **1**, two of the cage carbons (C1 and C10) occupy the low-coordinate capping positions (Fig. 2) of the bicapped square antiprism, while the third carbon (C6) is situated in a five-coordinate site. In agreement with the one low-field C-H shift observed in the ^{1}H NMR, only one of the low-coordinate carbons (C1) has a hydrogen substitutent and this carbon is directly bonded to the metal. The phenyl group is attached to the other four-coordinate C10 carbon, but, unlike in 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-Ru-$C_3B_7H_9$, this carbon is not bonded to the ruthenium.

Selected bond distances for **1** are presented in Table II. The ruthenium is η^5-coordinated to the puckered five-membered (C1–B3–C6–B7–B5) face with the closest metal-cage interaction being with C1, Ru2–C1 2.0297(18) Å. Somewhat longer distances are observed between Ru2–C6 2.1075(18) Å and Ru2–B7 2.121(2) Å, and then even longer distances from Ru2–B5 2.269(2) Å and Ru2–B3 2.258(2) Å. The B7–B5 1.777(3), B5–C1 1.630(3), C1–B3

TABLE II
Selected intramolecular distances and bond angles in **1**

Bond	Distance, Å	Bond	Distance, Å
Ru2–C1	2.0297(18)	B4–B9	1.782(3)
Ru2–B3	2.258(2)	B4–B5	1.856(3)
Ru2–B5	2.269(2)	B5–B7	1.777(3)
Ru2–C6	2.1075(18)	C6–B7	2.019(3)
Ru2–B7	2.121(2)	C6–B9	1.784(3)
Ru2–Cp	1.865	C6–C10	1.561(3)
C1–B3	1.625(3)	B7–B8	1.810(3)
C1–B4	1.619(3)	B7–C10	1.632(3)
C1–B5	1.630(3)	B8–B9	1.810(3)
B3–B4	1.862(3)	C10–C11	1.489(2)
B3–C6	1.733(3)		
Bonds	**Angle, °**	**Bonds**	**Angle, °**
C10–C6–Ru2	113.59(12)	C6–C10–B7	78.38(12)
C10–B7–Ru2	109.86(12)		

1.625(3) and B3–C6 1.733(3) Å distances in the five-membered ring all fall in the expected ranges, but the C6–B7 distance 2.019(3) Å is substantially longer. This lengthening has the effect of generating an open four-membered Ru2–C6–C10–B7 face. Similar cage-opening distortions have been observed in other formally *closo* 10-vertex metallaborane, metallamonocarbaborane and dimetalladicarbaborane systems[14,16]. Kennedy[16b] has described the structures of these clusters as closo, isonido or isocloso depending upon the geometric properties of their four-membered faces. For **1**, the long C6–B7 and Ru2–C10 (3.804(2) Å) distances and the low +8.7° fold angle observed between the Ru2–B7–C10 and Ru2–C6–C10 planes seem most consistent with a structure tending toward the Kennedy isonido classification.

Synthesis and Structural Characterization of Bu_4N^+*[5,5,5-(CO)*$_3$*-10-Ph-nido-5,6,9,10-Re-*$C_3B_6H_9]^-$

In contrast to the reactions observed with the 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ complexes, 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-Re-$C_3B_7H_9$ reacted with three equivalents of TBAF in THF to form the Bu_4N^+[5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9]^-$ salt. The product was purified via preparative TLC using dichloromethane as eluent, and recrystallized from heptane to yield air and moisture stable golden-yellow crystals.

$$\text{1,1,1-(CO)}_3\text{-2-Ph-}\textit{closo}\text{-1,2,3,4-Re-C}_3\text{B}_7\text{H}_9 \xrightarrow[0\ ^\circ\text{C}]{\text{TBAF, THF}} \text{5,5,5-(CO)}_3\text{-10-Ph-}\textit{nido}\text{-5,6,9,10-Re-C}_3\text{B}_6\text{H}_9^- \ (\mathbf{3}) \qquad (2)$$

The observed spectral data suggested that **3** had a very different structure than those found for **1** and **2**. Thus, as can be seen in Fig. 1c, the ^{11}B NMR spectrum of **3** showed six resonances, but at significantly different chemical shifts than those observed for **1** and **2**. The ^{1}H NMR spectrum again showed two C-H resonances, but in this case, both resonances appeared in the mid-field range (3.16 and 5.48 ppm).

The crystallographic determination of **3** depicted in Fig. 3 showed that, in agreement with a *nido*-electron count of the Re-$C_3B_6H_9^-$ fragment (24 skeletal electrons with the $(CO)_3$Re group donating one electron), the cage adopts a geometry based on a bicapped square antiprism with one missing vertex. Selected bond distances for **3** can be found in Table III. The rhenium is η^4-coordinated to the cage with approximately equivalent val-

ues between the Re and the four bonded cage atoms Re5–C6 2.319(5), Re5–B1 2.388(6), Re5–B2 2.347(7) and Re5–C10 2.365(4) Å. The Re and all three of the cage carbons occupy positions on the six-membered open face of the cluster with two of the cage carbons occupying the lowest coordinate 6 and 9 positions.

The average Re–C (carbonyl) distance (1.909(4) Å) in **3** is significantly shorter than the average Re–C (carbonyl) distance in the neutral starting material 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-Re-$C_3B_7H_9$ (1.943(4) Å)[4l]. This difference is consistent with an increased Re–CO back-bonding in **3** that is enhanced by its negative charge and, accordingly, the CO stretching adsorptions in **3** are at significantly lower energies (2004, 1890 and 1884 cm^{-1}, KBr) than those in the starting material 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-Re-$C_3B_7H_9$ (2055, 1997 and 1947 cm^{-1}, KBr)[4l].

At first glance, it is perhaps surprising that two different types of cage products resulted from the deboronation reactions given in Eqs (*1*) and (*2*). Nucleophilic polyhedral deboronation would be expected to be directed at the most electropositive cage borons. Previous studies[9e,12] have shown that the most electropositive borons in dicarbaboranes are those situated be-

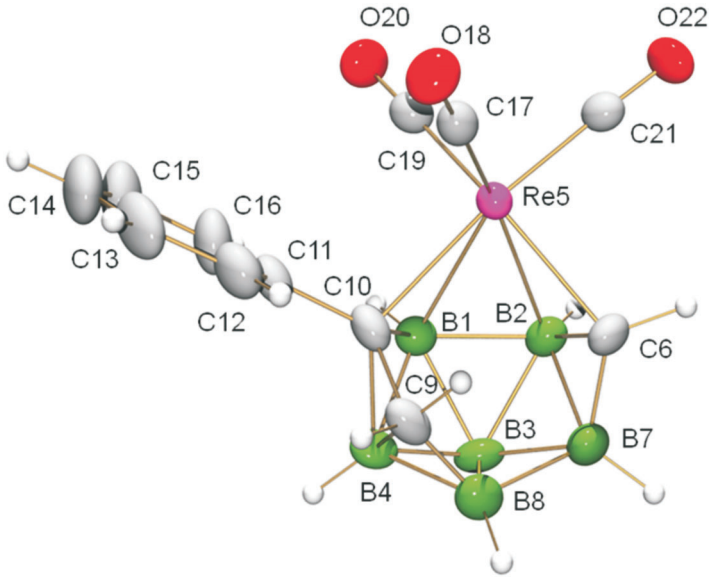

FIG. 3
Crystallographically determined structure of 5,5,5-$(CO)_3$-10-Ph-*nido*-5,6,9,10-Re-$C_3B_6H_9^-$ (**3**)

TABLE III
Selected intramolecular distances and bond angles in **3**

Bond	Distance, Å	Bond	Distance, Å
Re5–B1	2.388(6)	B1–B2	1.849(10)
Re5–B2	2.347(7)	B2–C6	1.659(9)
Re5–C6	2.319(5)	C10–C11	1.499(6)
Re5–C10	2.365(4)	Re5–C17	1.913(4)
C6–B7	1.546(9)	Re5–C19	1.911(5)
B7–B8	1.851(11)	Re5–C21	1.902(4)
B8–C9	1.520(9)	C17–O18	1.151(5)
C9–C10	1.531(7)	C19–O20	1.144(5)
B1–C10	1.611(7)	C21–O22	1.164(5)
Bonds	**Angle, °**	**Bonds**	**Angle, °**
O18–C17–Re5	178.0(4)	C6–Re5–C10	87.5(2)
O20–C19–Re5	178.1(4)	C11–C10–Re5	111.4(3)
O22–C21–Re5	178.0(4)	B2–Re5–B1	46.0(3)

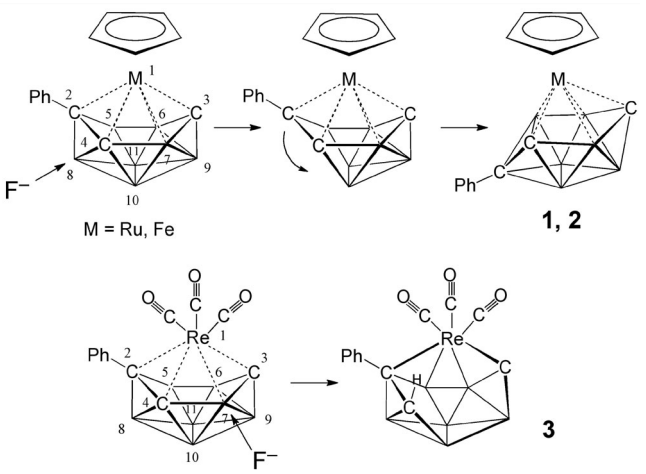

FIG. 4
Possible pathways for the fluoride induced deboronation reactions of 1-(η^5-C_5H_5)-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ (M = Fe, Ru) and 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-Re-$C_3B_7H_9$

tween the two carbons. Only the borons in the 8 and 7 positions of the 2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ starting clusters are attached to two carbons and therefore both of these borons would be expected to be preferred deboronation sites. As illustrated in Fig. 4, fluoride abstraction of the B8 position of **1** and **2** would initially generate an open five-membered face. The structures observed for **1** and **2** can be obtained in a straightforward manner from the intially deboronated structure by the simple movement indicated in the figure of the Ph–C to a four-coordinate position off of the metal-bonding face of the new *closo*-tricarbanonanborane framework. Likewise, as also indicated in the figure, fluoride abstraction of the B7 position of 1,1,1-$(CO)_3$-2-Ph-*closo*-1,2,3,4-M-$C_3B_7H_9$ would generate the structure observed for **3**. The relative deboronation reactivity of the B7 and B8 sites in the metallatricarbadecaboranes may simply result from the relative bonding properties of the (η^5-C_5H_5)M (M = Ru, Fe) and $(CO)_3$Re units.

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