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Synthesis of Charge-Compensated Octacarbonyltriruthenium Monocarbollide Complexes[†]

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The charge-compensated monocarbon carboranes *nido*-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{12}}$ react with $[\mathrm{Ru_3(CO)_{12}}]$ in toluene at reflux temperatures to give the triruthenium complexes $[\mathrm{Ru_3(CO)_8}(\eta^5$-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{10}})]$ [$\mathrm{NR_3} = \mathrm{NMe_3}$ (**1a**), $\mathrm{NH_2Bu^t}$ (**1b**), and $\mathrm{NMe_2Bu^t}$ (**1c**)]. The molecular structure of **1a** has been established by X-ray crystallography. The metal atoms form an essentially isosceles triangle. One Ru atom carries two terminal CO groups and the *nido*-7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_{10}}$ cage, coordinated in a pentahapto manner. The two boron atoms in the β-sites with respect to the carbon in the $\overline{\mathrm{CB}BB\mathrm{B}}$ ring form exopolyhedral three-center, two-electron B−H⇀Ru bonds to the other two Ru atoms. These metal atoms also carry three essentially terminally attached CO ligands. Treatment of **1a** with $\mathrm{PPh_3}$ in toluene gave, after column chromatography of the mixture, $[\mathrm{Ru_3}(\mu\text{-H})(\mu_3\text{-}\sigma\text{:}\,\eta^5$-7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_9})(\mathrm{CO})_7(\mathrm{PPh_3})]$ (**2**), whereas reaction with $\mathrm{CNBu^t}$ affords $[\mathrm{Ru_3(CO)_7(CNBu^t)}(\eta^5$-7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_{10}})]$ (**3**). The structure of **2** has been established by X-ray crystallography. The molecule has a triangular array of ruthenium atoms. As in **1a**, one metal center Ru(1) carries two CO groups and forms a *closo*-icosahedral $\mathrm{RuCB_{10}}$ framework by coordination in a pentahapto manner to the open face of a *nido*-$\mathrm{CB_{10}}$ fragment. A second Ru atom is ligated by two CO molecules and the $\mathrm{PPh_3}$ group, the latter being transoid to Ru(1), while the third Ru atom is terminally attached to three CO molecules. The Ru(2)−Ru(3) connectivity is bridged by a hydrido ligand, and in addition both of these metal atoms are linked to the $\mathrm{CB_{10}}$ framework through boron atoms in the β-sites of the $\overline{\mathrm{CB}BB\mathrm{B}}$ ring coordinated to Ru(1). Atom Ru(2) forms a three-center, two-electron B−H⇀Ru bond, while atom Ru(3) forms an Ru−B σ-bond, with the result that the *nido*-7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_9}$ group bridges the $\mathrm{Ru_3}$ triangle via η^5-$\overline{\mathrm{CBBBB}}$, B−H⇀Ru, and B−Ru interactions. The NMR data for the new compounds are reported and discussed in relation to their structures.

Introduction

The number of known transition metal complexes with carborane ligands continues to increase rapidly as the variety of the bonding modes of the cage systems to metals becomes apparent.[1] Much work has focused on the C- and B-substituted derivatives of the anions [*nido*-7,*n*-$\mathrm{C_2B_9H_{11}}]^{2-}$ (n = 8 or 9), but species in which metal ions are incorporated into $\mathrm{C_2B_4}$ and $\mathrm{C_2B_{10}}$ frameworks have also attracted considerable attention. In contrast, studies on monocarbon metallacarboranes have been much more limited, even though the first examples of such species were reported as long ago as the mid-1960s.[2] Herein we report the synthesis and some reactions of the triruthenium cluster compounds $[\mathrm{Ru_3(CO)_8}(\eta^5$-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{10}})]$ (**1**, $\mathrm{NR_3} = \mathrm{NMe_3}$, $\mathrm{NH_2Bu^t}$, and $\mathrm{NMe_2Bu^t}$). This work was stimulated by the recent observation that *nido*-7,8-$\mathrm{C_2B_9H_{13}}$ readily reacts with $[\mathrm{Ru_3(CO)_{12}}]$ to yield $[\mathrm{Ru(CO)_3}(\eta^5$-7,8-$\mathrm{C_2B_9H_{11}})]$.[3] It seemed possible, therefore, that the monocarbon carboranes *nido*-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{12}}$, which are isolobal with *nido*-7,8-$\mathrm{C_2B_9H_{13}}$, would undergo a similar reaction to afford mononuclear ruthenium complexes $[\mathrm{Ru(CO)_3}(\eta^5$-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{10}})]$. However, trinuclear rather than mononuclear ruthenium species were obtained unexpectedly.

Results and Discussion

The *nido*-carborane 7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_{12}}$ reacts with $[\mathrm{Ru_3(CO)_{12}}]$ in toluene at reflux temperatures to give the cluster complex $[\mathrm{Ru_3(CO)_8}(\eta^5$-7-$\mathrm{NMe_3}$-7-$\mathrm{CB_{10}H_{10}})]$ (**1a**). Similar reactions between ruthenium carbonyl and the *nido*-carboranes 7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{12}}$ afford the species $[\mathrm{Ru_3(CO)_8}(\eta^5$-7-$\mathrm{NR_3}$-7-$\mathrm{CB_{10}H_{10}})]$ (**1b,** $\mathrm{NR_3} = \mathrm{NH_2}$-

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[†] The complexes described in this paper have three ruthenium atoms disposed in a triangle, one metal atom of which is incorporated into a *closo*-1-carba-2-ruthenadodecaborane structure. However, to avoid an impossibly complex nomenclature for the various molecules reported, we treat the cages as *nido*-11-vertex ligands with numbering as for an icosahedron from which the 12th vertex has been removed. This has the added convenience of relating the ruthenacarborane complexes to the many species that are known to have cyclopentadienyl ligands η^5- coordinated to one or more metal centers in metal clusters.

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Table 1. Physical and Infrared Absorption Data

cmpd	color	yield (%)	ν_{max}(CO)^a (cm^{-1})	anal. (%)^b C	H	N
[Ru$_3$(CO)$_8$(η^5-7-NMe$_3$-7-CB$_{10}$H$_{10}$)] (**1a**)	deep yellow	50	2086 s, 2052 s, 2014 s	19.3 (20.1)	2.5 (2.6)	1.5 (1.9)
[Ru$_3$(CO)$_8$(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**1b**)	yellow	20	2086 s, 2052 s, 2014 s	21.4 (21.3)	3.4 (2.9)	2.1 (2.0)
[Ru$_3$(CO)$_8$(η^5-7-NMe$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**1c**)	deep yellow	35	2086 s, 2052 s, 2014 s	23.5 (23.7)	3.5 (3.3)	2.1 (1.8)
[Ru$_3$(μ-H)(μ_3-σ:η^5-7-NMe$_3$-7-CB$_{10}$H$_9$)(CO)$_7$(PPh$_3$)] (**2**)	orange	90	2062 s, 2042 s, 2000 s, 1980 s, 1958 m,1918 m	41.3 (41.3)	1.8 (3.4)	1.1 (1.4)^c
[Ru$_3$(CO)$_7$(CNBu^t)(η^5-7-NMe$_3$-7-CB$_{10}$H$_{10}$)] (**3**)	dark yellow	85	2176 s,^{d} 2086s, 2064 s, 2016 s, 1994 m, 1928 m	23.5 (23.8)	3.5 (3.4)	3.1 (3.2)^e

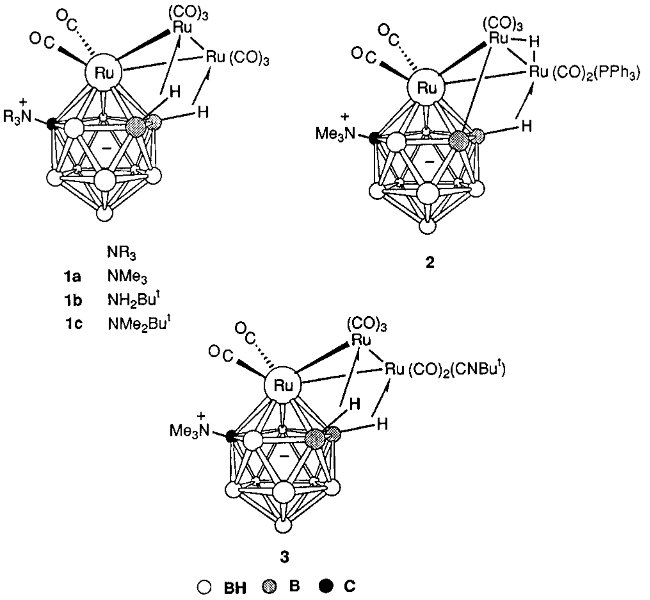
^{a} Measured in CH$_2$Cl$_2$; broad medium-intensity bands observed at ca. 2550 cm^{-1} in the spectra of all the compounds are due to B−H absorptions. ^{b} Calculated values are given in parentheses. ^{c} Crystallizes with one molecule of PhMe. ^{d} ν_{max}(NC). ^{e} Crystallizes with one molecule of CH$_2$Cl$_2$.

Table 2. Hydrogen-1, Carbon-13, and Boron-11 NMR Data^a

cmpd	^{1}H (δ)^b	^{13}C (δ)^c	^{11}B (δ)^d
1a	−10.76 [br q, 2 H, B−H$\rightharpoonup$Ru, J(BH) = 70], 3.17 (s, 9 H, Me)	203.1, 201.0 193.1, 189.2 (CO), 59.8 (cage C), 57.3 (Me)	21.7 (2 B), −5.1 (2 B), −7.4 (2 B), −12.8 (2 B), −16.9 (2 B)
1b	−10.60 [br q, 2 H, B−H$\rightharpoonup$Ru, J(BH) = 69], 1.59 (s, 9 H, Bu^t), 6.17 (br s, 2 H, NH$_2$)	201.7, 199.3, 191.1, 187.7(CO), 68.3 (cage C), 54.2 (*C*Me$_3$), 29.7 (C*Me$_3$*)	21.7 (2 B), −5.1 (2 B), −7.4 (2 B), −12.8 (2 B), −16.9 (2 B)
1c	−10.75 [br q, 2 H, B−H$\rightharpoonup$Ru, J(BH) = 75], 1.60 (s, 9 H, Bu^t) 2.80 (s, 6 H, Me)	205.9, 203.3, 197.8, 195.8 (CO), 57.9 (cage C), 50.1 (Me, *C*Me$_3$), 29.6 (C*Me$_3$*)^e	21.5 (2 B), −4.2 (1 B), −6.6 (1 B), −8.9 (2 B), −13.2 (2 B), −15.5 (2 B)
2^f	−17.71 (s br, 1 H, μ-H), −10.20 [br q, 1 H, B−H$\rightharpoonup$Ru, J(BH) = 65], 3.15 (s, 9 H, Me), 7.20−7.60 (m, 15 H, Ph)	202.9, 195.3 (CO), 135.2−130.5 (Ph), 60.0 (cage C), 56.1 (Me)	53.3 (1 B), 31.6 (1 B), −2.5 (4 B), −7.7 (1 B), −8.8 (1 B), −14.6 (2 B)
3	−10.80 (br q, 2 H, B−H$\rightharpoonup$Ru, J(BH) = 69], 3.16 (s, 9 H, Me), 1.45 (s, 9 H, Bu^t)	201.5, 194.9 (CO), 189.4 (*C*N), 59.9 (cage C), 59.6 (Me), 58.2 (*C*Me$_3$), 30.2 (C*Me$_3$*)	−20.4 (2 B), −6.1 (2 B), −7.2 (2 B), −13.8 (2 B), −17.5 (2 B)

^{a} Chemical shifts (δ) are in ppm, and coupling constants (J) are in hertz; measurements were in CD$_2$Cl$_2$ unless otherwise stated. ^{b} Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. −1 to 2.5. ^{c} Hydrogen-1 decoupled; chemical shifts are positive to high frequency of SiMe$_4$. ^{d} Hydrogen-1 decoupled; chemical shifts are positive to high frequency of BF$_3$·Et$_2$O (external). ^{e} Measured in CD$_3$CN. ^{f} NMR ^{31}P, δ = 44.5, chemical shifts are positive to high frequency of 85% H$_3$PO$_4$ (external).

Chart 1



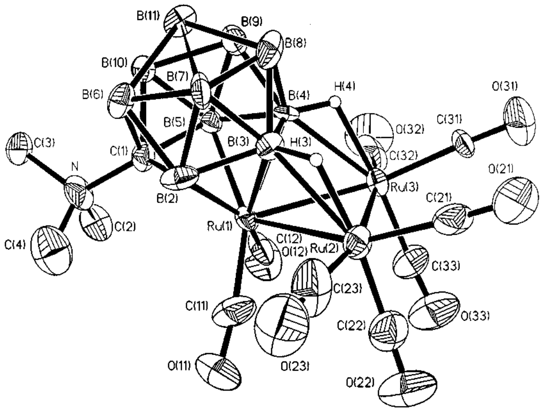


Figure 1. Structure of [Ru$_3$(CO)$_8$(η^5-7-NMe$_3$-7-CB$_{10}$H$_{10}$)] (**1c**), showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms, except for H(3) and H(4), have been omitted for clarity.

Bu^t; **1c,** NR$_3$ = NMe$_2$Bu^t) (Chart 1). These products were characterized by the data given in Tables 1 and 2. However, discussion of the NMR spectra is deferred until after a description of the molecular structure of **1a** has been given, which was established by X-ray crystallography.

Compound **1a** crystallizes in the orthorhombic space group *Pccn* and contains eight molecules per unit cell. The structure is shown with the atom labeling scheme in Figure 1. Selected bond distances and angles are collected in Table 3. The molecule is based on a triangular core of ruthenium atoms [Ru(1)−Ru(2) = 2.764(2), Ru(1)−Ru(3) = 2.756(2), and Ru(2)−Ru(3) = 2.793(2) Å], which is bridged by the *nido*-7-NMe$_3$-7-CB$_{10}$H$_{10}$ group. The bonding of the carborane cage to the metal atoms involves pentahapto coordination to Ru(1) and formation of three-center, two-electron B−H$\rightharpoonup$Ru interactions between atoms B(3) and Ru(2) and between atoms B(4) and Ru(3). The positions of hydrogen atoms H(3) and H(4) were determined by using the steric potential energy minimization technique,[4] and their presence was further established from the ^{1}H NMR spectrum discussed in the following.

Although the 7-NMe$_3$-7-CB$_{10}$H$_{10}$ ligand is neutral, it is zwitterionic with a cationic nitrogen atom attached to the carbon vertex of the monoanionic CB$_{10}$H$_{10}$ group. The C(1)−N bond length is 1.58(2) Å and the mean N−C(2,3,4) bond distance is 1.49 Å (range 1.47−1.50 Å). The Ru(1)−C(1) distance [2.31(2) Å] is somewhat

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Table 3. Selected Internuclear Distances (Å) and Angles (deg) for [$Ru_3(CO)_8(\eta^5$-7-NMe_3-7-$CB_{10}H_{10})$] (1a)

Ru(1)−C(1)	2.31(2)	Ru(1)−B(2)	2.24(2)	Ru(1)−B(3)	2.19(2)	Ru(1)−B(4)	2.19(2)
Ru(1)−B(5)	2.28(2)	Ru(1)−C(11)	1.85(2)	Ru(1)−C(12)	1.92(2)	Ru(1)−Ru(2)	2.764(2)
Ru(1)−Ru(3)	2.756(2)	C(1)−B(2)	1.72(2)	C(1)−B(5)	1.82(2)	C(1)−B(6)	1.67(2)
C(1)−B(10)	1.71(2)	C(1)−N	1.58(2)	B(2)−B(3)	1.74(3)	B(2)−B(6)	1.77(3)
B(2)−B(7)	1.75(3)	B(3)−B(4)	1.68(3)	B(3)−B(7)	1.75(3)	B(3)−B(8)	1.78(3)
B(3)−Ru(2)	2.38(2)	B(3)−H(3)	1.10	B(4)−B(5)	1.85(3)	B(4)−B(8)	1.71(3)
B(4)−B(9)	1.77(3)	B(4)−Ru(3)	2.39(2)	B(4)−H(4)	1.10	B(5)−B(9)	1.78(3)
B(5)−B(10)	1.78(3)	B(6)−B(7)	1.73(3)	B(6)−B(10)	1.74(2)	B(6)−B(11)	1.81(3)
B(7)−B(8)	1.79(3)	B(7)−B(11)	1.78(3)	B(8)−B(9)	1.72(3)	B(8)−B(11)	1.73(3)
B(9)−B(10)	1.82(3)	B(9)−B(11)	1.79(3)	B(10)−B(11)	1.77(2)	N−C(2)	1.51(2)
N−C(3)	1.47(2)	N−C(4)	1.49(2)	C(11)−O(11)	1.18(2)	C(12)−O(12)	1.17(2)
Ru(2)−C(21)	1.85(2)	Ru(2)−C(22)	1.84(2)	Ru(2)−C(23)	1.87(2)	Ru(2)−Ru(3)	2.793(2)
Ru(2)−H(3)	1.75	C(21)−O(21)	1.17(2)	C(22)−O(22)	1.17(2)	C(23)−O(23)	1.17(3)
Ru(3)−C(31)	1.85(1)	Ru(3)−C(32)	1.89(2)	Ru(3)−C(33)	1.82(2)	Ru(3)−H(4)	1.82
C(31)−O(31)	1.17(2)	C(32)−O(32)	1.17(2)	C(33)−O(33)	1.17(2)		

C(1)−Ru(1)−B(2)	44.5(6)	C(1)−Ru(1)−B(5)	46.9(6)	B(2)−Ru(1)−B(3)	46.2(7)	B(3)−Ru(1)−B(4)	45.1(7)
B(4)−Ru(1)−B(5)	48.9(6)	Ru(2)−Ru(1)−Ru(3)	60.8(1)	Ru(1)−Ru(2)−Ru(3)	59.5(1)	Ru(1)−Ru(3)−Ru(2)	59.7(1)
Ru(2)−Ru(1)−B(3)	55.9(5)	Ru(3)−Ru(1)−B(4)	56.4(5)	Ru(1)−B(3)−Ru(2)	74.4(6)	Ru(1)−B(4)−Ru(3)	73.9(5)
B(3)−Ru(2)−Ru(3)	76.4(4)	B(4)−Ru(3)−Ru(2)	76.5(4)	Ru(2)−B(3)−B(4)	104(1)	Ru(3)−B(4)−B(3)	103(1)
Ru(2)−B(3)−H(3)	43.6(4)	B(3)−Ru(2)−H(3)	25.7(3)	B(3)−H(3)−Ru(2)	110.7(6)	Ru(3)−B(4)−H(4)	46.6(4)
B(4)−Ru(3)−H(4)	26.1(3)	B(4)−H(4)−Ru(3)	107.3(6)	C(11)−Ru(1)−C(12)	88.2(8)	Ru(1)−Ru(2)−C(21)	152.0(5)
Ru(1)−Ru(2)−C(22)	100.8(6)	Ru(1)−Ru(2)−C(23)	104.1(6)	Ru(1)−Ru(3)−C(31)	150.9(6)	Ru(1)−Ru(3)−C(32)	108.6(5)
Ru(1)−Ru(3)−C(33)	101.4(6)	C(21)−Ru(2)−C(22)	91.5(8)	C(21)−Ru(2)−C(23)	100.6(8)	C(22)−Ru(2)−C(23)	91.8(8)
C(21)−Ru(2)−Ru(3)	95.3(5)	C(21)−Ru(2)−H(3)	94.1(8)	C(31)−Ru(3)−C(32)	94.7(7)	C(31)−Ru(3)−C(33)	94.7(8)
C(32)−Ru(3)−C(33)	92.0(8)	C(31)−Ru(3)−Ru(2)	97.2(5)	C(31)−Ru(3)−H(4)	91.4(8)	H(3)−Ru(2)−Ru(3)	90.1(6)
H(4)−Ru(3)−Ru(2)	95.4(6)	C(1)−N−C(2)	114(1)	C(1)−N−C(3)	115(1)	C(1)−N−C(4)	109(1)
C(2)−N−C(3)	106(1)	C(2)−N−C(4)	107(1)	C(3)−N−C(4)	106(1)	Ru(1)−C(11)−O(11)	172(2)
Ru(1)−C(12)−O(12)	169(1)	Ru(2)−C(21)−O(21)	177(2)	Ru(2)−C(22)−O(22)	174(2)	Ru(2)−C(23)−O(23)	175(1)
Ru(3)−C(31)−O(31)	176(1)	Ru(3)−C(32)−O(32)	179(2)	Ru(3)−C(33)−O(33)	177(2)		

longer than those [2.19(2)−2.28(2) Å] between Ru(1) and the other atoms in the pentahapto-bonded $\overline{\mathrm{CBBBB}}$ ring. When considering the relationship of Ru(1) to the centroid of the pentahapto $\overline{\mathrm{CBBBB}}$ ring, the slippage (0.050 Å) is insignificant. However, the near-symmetrical bonding of the Ru(1) to the open face of the cage is accompanied by a folding (5.0°) of the $\overline{\mathrm{CBBBB}}$ plane about B(2)···B(5). Similar structural features have been observed in the zwitterionic compound [RhBr-(PPh_3){η^5-7-NH($CH_2CH{=}CHMe)_2$-7-$CB_{10}H_{10}$}].[5] The dihedral angle between the C(1)B(2,3,4,5) and B(6,7,8,9,-10) belts of the cage is 0.28°, and that between the former plane and the Ru_3 plane is 1.81°.

Atom Ru(1) carries two CO groups, and atoms Ru(2) and Ru(3) are each coordinated by three such groups. The mean Ru−C≡O bond angle is 174.8°; however, the carbonyls attached to Ru(1) deviate slightly from linearity [Ru(1)-C(11)−O(11) = 172(1)°, Ru(1)−C(12)−O(12) = 169(1)°]. Since the carbonyl ligands contribute 16 electrons to the metal triangle, and the monocarbon carborane *nido* cage fragment formally donates 8 electrons, 4 to Ru(1) and 2 each to Ru(2) and Ru(3), the overall cluster valence electron count, including the 24 electrons from the ruthenium atoms, is 48. The species thus is electronically saturated.

With the molecular structure of compound **1a** established, the NMR data (Table 2) can be readily interpreted, as can those for **1b** and **1c** since the spectra of all three species display similar features. In the ^1H NMR spectra there are diagnostic quartet resonances at δ ca. −10.7 [J(BH) = ca. 70 Hz] for the $B-H\rightharpoonup Ru$ bonds. The appearance of only one such signal in each spectrum is as expected, in accord with the symmetrical structure revealed by the X-ray diffraction study of **1a**. The $B-H\rightharpoonup Ru$ groups are equivalent since they lie on either side of a mirror plane in the molecule through C(1) and the midpoints of the B(3)−B(4) and Ru(2)−Ru(3) connectivities. The dimetal complexes [WRu(μ-CR)$(CO)_3(\eta^5$-$C_5H_5)(\eta^5$-7,8-Me_2-7,8-$C_2B_9H_9$)] have exopolyhedral $B-H\rightharpoonup Ru$ linkages and display quartet signals at δ −11.48 [J(BH) = 70 Hz] when R = C_6H_4Me-4[6a] and at δ −12.0 [J(BH) = 76 Hz] when R = $C_6H_3Me_2$-2,6.[6b] The presence of the $B-H\rightharpoonup Ru$ linkages in the complexes **1** is also revealed by the $^{11}B\{^1H\}$ NMR spectra, which show resonances at δ ca. 21.7 corresponding in intensity to two boron nuclei, and these peaks become doublets in fully coupled ^{11}B spectra [J(HB) = ca. 70 Hz]. In the $^{13}C\{^1H\}$ NMR spectra the resonances for the cage carbon atoms occur at δ 57.3 (**1a**), 68.3 (**1b**), and 57.9 (**1c**). Other resonances in the ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra are as expected.

It is interesting that the *nido*-carboranes 7-NR_3-7-$CB_{10}H_{12}$ react with [$Ru_3(CO)_{12}$)] to afford triruthenium cluster complexes, whereas *nido*-7,8-$C_2B_9H_{13}$ reacts to give the mononuclear ruthenium species [$Ru(CO)_3(\eta^5$-7,8-$C_2B_9H_{11}$)].[3] Attempts to obtain complexes of the formulation [$Ru(CO)_3(\eta^5$-7-NR_3-7-$CB_{10}H_{10}$)] by adjusting the conditions for the reaction between 7-NR_3-7-$CB_{10}H_{12}$ and [$Ru_3(CO)_{12}$)] so far have been unsuccessful. Further studies are in progress to determine whether substituents on the carbon atoms in the *nido*-carborane precursors influence the nuclearity of the ruthenium in the products.

Molecules incorporating *closo*-3,1,2-MC_2B_9 frameworks with BH vertices in the η^5-$\mathrm{C}\overline{\mathrm{CBBB}}$ face, and which form intramolecular $B-H\rightharpoonup M'$ bonds to other metal centers, often function as intermediates on the pathway to products with B−M′ and M(μ-H)M′ linkages.[7] Such processes occurring at the M' center are readily understood, since the $B-H\rightharpoonup M'$ bonds represent

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Table 4. Selected Internuclear Distances (Å) and Angles (deg) for $[Ru_3(CO)_7(PPh_3)(\eta^5\text{-}7\text{-}NMe_3\text{-}7\text{-}CB_{10}H_{10})]$ (2)

Ru(1)−C(1)	2.291(9)	Ru(1)−B(2)	2.23(1)	Ru(1)−B(3)	2.22(1)	Ru(1)−B(4)	2.217(9)
Ru(1)−B(5)	2.24(1)	Ru(1)−C(11)	1.870(8)	Ru(1)−C(12)	1.863(9)	Ru(1)−Ru(2)	2.770(1)
Ru(1)−Ru(3)	2.806(1)	C(1)−B(2)	1.71(1)	C(1)−B(5)	1.78(1)	C(1)−B(6)	1.75(2)
C(1)−B(10)	1.75(2)	C(1)−N(1)	1.59(1)	B(2)−B(3)	1.83(1)	B(2)−B(6)	1.81(2)
B(2)−B(7)	1.77(2)	B(3)−B(4)	1.81(1)	B(3)−B(7)	1.76(2)	B(3)−B(8)	1.81(2)
B(3)−Ru(3)	2.15(1)	B(4)−H(4)	1.08	B(4)−B(5)	1.78(1)	B(4)−B(8)	1.78(2)
B(4)−B(9)	1.69(2)	B(4)−Ru(2)	2.37(1)	B(5)−B(9)	1.78(2)	B(5)−B(10)	1.82(2)
B(6)−B(7)	1.75(2)	B(6)−B(10)	1.79(1)	B(6)−B(11)	1.74(2)	B(7)−B(8)	1.78(1)
B(7)−B(11)	1.78(2)	B(8)−B(9)	1.76(2)	B(8)−B(11)	1.890(2)	B(9)−B(10)	1.80(1)
B(9)−B(11)	1.79(2)	B(10)−B(11)	1.72(2)	N(1)−C(2)	1.54(1)	N(1)−C(3)	1.46(1)
N(1)−C(4)	1.50(1)	C(11)−O(11)	1.17(1)	C(12)−O(12)	1.19(1)	Ru(2)−Ru(3)	2.982(1)
Ru(2)−C(13)	1.876(8)	Ru(2)−C(14)	1.86(1)	Ru(2)−H(4)	1.76	Ru(2)−H(1)	1.76
Ru(3)−H(1)	1.683	Ru(3)−C(15)	1.846(7)	Ru(3)−C(16)	1.98(1)	Ru(3)−C(17)	1.85(1)
C(13)−O(13)	1.16(1)	C(14)−O(14)	1.17(1)	C(15)−O(15)	1.162(9)	C(16)−O(16)	1.16(1)
C(17)−O(17)	1.18(1)	Ru(2)−P(1)	2.327(2)	P(1)−C(21)	1.829(8)	P(1)−C(31)	1.84(1)
P(1)−C(41)	1.850(8)						

C(1)−Ru(1)−B(2)	44.4(3)	C(1)−Ru(1)−B(5)	46.2(3)	B(2)−Ru(1)−B(3)	48.4(3)	B(3)−Ru(1)−B(4)	48.2(3)
B(4)−Ru(1)−B(5)	47.2(4)	Ru(2)−Ru(1)−Ru(3)	64.7(1)	Ru(1)−Ru(2)−Ru(3)	58.3(1)	Ru(1)−Ru(3)−Ru(2)	57.1(1)
Ru(2)−Ru(1)−B(4)	55.4(3)	Ru(3)−Ru(1)−B(3)	49.0(3)	Ru(1)−B(3)−Ru(3)	79.8(4)	Ru(1)−B(4)−Ru(2)	74.2(3)
B(3)−Ru(3)−Ru(2)	76.8(2)	B(4)−Ru(2)−Ru(3)	73.2(2)	Ru(3)−B(3)−B(4)	108.8(6)	Ru(2)−B(4)−B(3)	101.3(6)
Ru(2)−Ru(3)−H(1)	30.6(1)	Ru(3)−Ru(2)−H(1)	29.2(1)	Ru(2)−H(1)−Ru(3)	120.1(1)	Ru(2)−B(4)−H(4)	44.0(2)
B(4)−Ru(2)−H(4)	25.2(1)	B(4)−H(4)−Ru(2)	110.8(2)	C(11)−Ru(1)−C(12)	86.9(4)	Ru(1)−Ru(3)−C(15)	99.3(3)
Ru(1)−Ru(3)−C(16)	110.9(3)	Ru(1)−Ru(3)−C(17)	143.1(3)	Ru(1)−Ru(2)−C(13)	96.6(2)	Ru(1)−Ru(2)−C(14)	96.8(2)
Ru(1)−Ru(2)−P(1)	167.6(1)	C(15)−Ru(3)−C(16)	96.0(4)	C(15)−Ru(3)−C(17)	88.6(4)	C(16)−Ru(3)−C(17)	103.9(4)
C(17)−Ru(3)−Ru(2)	109.5(2)	C(17)−Ru(3)−H(1)	79.5(2)	P(1)−Ru(2)−H(1)	86.8(1)	P(1)−Ru(2)−C(13)	89.7(2)
C(13)−Ru(2)−C(14)	95.1(4)	P(1)−Ru(2)−Ru(3)	115.3(1)	P(1)−Ru(2)−H(4)	94.2(3)	H(4)−Ru(2)−Ru(3)	87.5(3)
Ru(2)−P(1)−C(21)	116.8(2)	Ru(2)−P(1)−C(31)	116.2(3)	Ru(2)−P(1)−C(41)	111.6(3)	C(21)−P(1)−C(31)	102.8(4)
C(21)−P(1)−C(41)	104.3(4)	C(31)−P(1)−C(41)	103.5(4)	C(1)−N(1)−C(2)	114.1(8)	C(1)−N(1)−C(3)	111.0(6)
C(1)−N(1)−C(4)	111.3(6)	C(2)−N(1)−C(3)	105.0(7)	C(2)−N(1)−C(4)	106.2(7)	C(3)−N(1)−C(4)	108.8(8)

phenyl rings	mean	range	mean	range
C(21)−C(26)	1.37(2)	1.34−1.39	120(2)	116.8−122.9
C(31)−C(36)	1.37(2)	1.35−1.40	120(2)	117.6−123.2
C(41)−C(46)	1.38(1)	1.37−1.40	120(2)	117.8−122.5

a state of incipient oxidative addition. In an attempt to promote conversion of the B−H$\rightharpoonup$Ru linkages in **1a** into a new structure with B−Ru and Ru(μ-H)Ru bonds, reactions with the donor molecules PPh_3 and $CNBu^t$ were investigated.

Treatment of **1a** with 1 equiv of PPh_3 in toluene at 60 °C for a few minutes gave $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\eta^5\text{-}7\text{-}NMe_3\text{-}7\text{-}CB_{10}H_9)(CO)_7(PPh_3)]$ (**2**) after purification by column chromatography. Examination of the NMR spectra, which will be discussed further later, revealed that complex **2** contained both Ru(μ-H)Ru and B−Ru groups. To fully establish the molecular architecture, an X-ray diffraction study was carried out.

The crystals are triclinic space group $P\bar{1}$ with two molecules in the unit cell. Selected structural parameters are listed in Table 4, and the molecule is shown in Figure 2. As in **1a**, atom Ru(1) shows no appreciable slippage (0.066 Å) in relation to the centroid of the $\overline{\mathrm{CBBBB}}$ ring to which it is coordinated, but despite the almost symmetrical bonding of the $\overline{\mathrm{CBBBB}}$ plane, there is a folding (6.0°) along the B(2)···B(5) vector. The dihedral angle between the CB(2,3,4,5) plane and the Ru_3 plane is 6.3°, and that between the planes defined by the atoms CB(2,3,4,5) and B(6,7,8,9,10) is 0.8°.

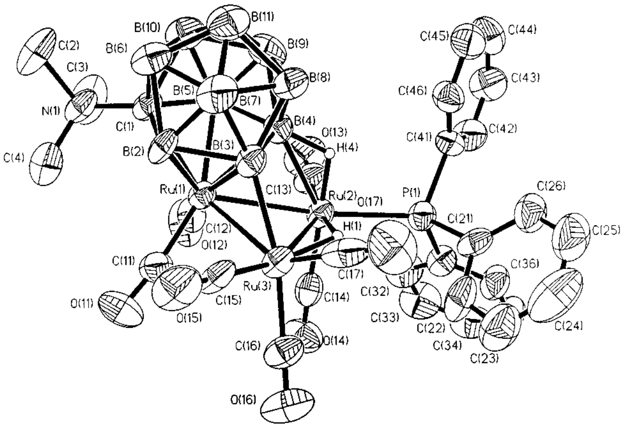

Figure 2. Structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\ \eta^5\text{-}7\text{-}NMe_3\text{-}7\text{-}CB_{10}H_9)\text{-}(CO)_7(PPh_3)]$ (**2**), showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms, except for H(1) and H(4), have been omitted for clarity.

As expected, the PPh_3 group in **2** results from the substitution of a CO ligand in **1a** and is coordinated to Ru(2) in a site that lies transoid [P(1)−Ru(2)−Ru(1) = 167.6(1)°] to the Ru(1)−Ru(2) connectivity [2.770(1) Å]. The Ru(2)−P(1) distance [2.327(2) Å] is in excellent agreement with the data for such bonds in related structures.[8] Hydrogen atoms H(1) and H(4) were located from difference Fourier mapping. The latter forms part of a B(4)−H(4)$\rightharpoonup$Ru(2) three-center, two-electron bond linking B(4) and Ru(2), while H(1) bridges the Ru(2)−Ru(3) linkage [2.982(2) Å, μ-H−Ru(mean) = 1.72 Å]; these distances are comparable with those found in other molecules with Ru(μ-H)Ru bonds.[9] The Ru(1)−Ru(3) bond [2.806(1) Å] is bridged by the cage atom B(3) [B(3)−Ru(1) = 2.22(1), B(3)−Ru(3) = 2.15(1) Å], so that in the reaction between **1a** and PPh_3, one of the B−H$\rightharpoonup$Ru groups in the former has undergone an oxidative addition process to form a B−Ru and a Ru-(μ-H)Ru linkage. The bonding of the *nido*-7-NMe₃-7-

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CB_{10} fragment to the Ru_3 group in **2** is reminiscent of that of the 7,8-Me_2-7,8-C_2B_9 cage to the metal triangle in [$WRh_2(\mu\text{-}H)(\mu\text{-}\sigma\text{:}\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_2(\eta^5\text{-}C_5Me_5)_2$].[10] In the latter the tungsten atom is attached to the carborane framework in an η^5-bonding mode, while the rhodium atoms in the WRh_2 triangle are linked to the cage by B−Rh and B−H$\rightharpoonup$Rh bonds, respectively.

Replacement of a CO group in **1a** by PPh_3, a better electron donor, would increase the electron density at the ruthenium center to which it is attached, thus promoting oxidative addition at that center. It is somewhat surprising, therefore, that the PPh_3 molecule is attached to Ru(2), the metal atom involved in the B−H$\rightharpoonup$Ru linkage, rather than to Ru(3), the atom that forms the B−Ru σ-bond. This suggests that complex **2** is a thermodynamically stable product resulting from an intermediate that is kinetically unstable. This intermediate might undergo rearrangement of its B−Ru and B−H$\rightharpoonup$Ru groups between the adjacent boron atoms [B(3) and B(4)] in the $\overline{\text{CBBBB}}$ ring and atoms Ru(2) and Ru(3). This would be facilitated by the migration of hydrogen between Ru(μ-H)Ru and B−H$\rightharpoonup$Ru sites, an exchange process for which there is precedent from related systems[10,11]

The NMR data for **2** are in complete accord with the structure established in the solid state by X-ray diffraction. In the ^1H NMR spectrum, there is a diagnostic resonance for the Ru(μ-H)Ru group at δ −17.71.[12] The presence of the B−H$\rightharpoonup$Ru group is revealed in both the ^1H and $^{11}B\{^1H\}$ NMR spectra. In the former there is a quartet signal at δ −10.20 [J(BH) = 65 Hz], and in the latter there is a signal corresponding in intensity to one boron atom at δ 31.6, which in a fully coupled ^{11}B spectrum becomes a doublet [J(HB) = 65 Hz]. The existence of the B−Ru σ-bond is shown by the resonance at δ 53.3 in the $^{11}B\{^1H\}$ NMR spectrum, which remains a singlet in the fully coupled ^{11}B spectrum. In the $^{11}B\{^1H\}$ NMR spectrum of [$WRu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma\text{:}\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_3(\eta^5\text{-}C_5H_5)$], the peak for the B−Ru group is observed at δ 45.9.[6a] In the $^{13}C\{^1H\}$ NMR spectrum of **2**, the resonance for the cage carbon vertex occurs at δ 60.0. The remaining peaks in the NMR spectra (Table 2) are as expected, although the observation of only two CO resonances in the $^{13}C\{^1H\}$ spectrum indicates site exchange of these ligands on the NMR time scale.

Compound **3**, in contrast with **2**, retains the structural features present in **1a**. This is apparent from the NMR spectra and is not surprising since $CNBu^t$ is not as strong a σ-donor as PPh_3 and, moreover, has good π-acceptor properties, a situation conducive to retaining the integrity of the B−H$\rightharpoonup$Ru bonds. The ^1H NMR spectrum of **3** displays a characteristic quartet for these bonds at δ −10.80 [J(BH) = 69 Hz]. The relative intensity of this signal indicated that it was due to two protons. Correspondingly, a peak at δ −20.4 in the $^{11}B\{^1H\}$ NMR spectrum lies in the chemical shift region for a B−H$\rightharpoonup$Ru linkage[6a,7] with a relative intensity for two boron nuclei. As expected, it becomes a doublet in a fully coupled ^{11}B spectrum. The $^{11}B\{^1H\}$ NMR spectrum showed no resonance in the chemical shift region expected for a B−Ru σ-bond. In the $^{13}C\{^1H\}$ spectrum, the resonance for the cage carbon atom is at δ 59.9, while that for the ligated carbon of the *C*NBu^t molecule is at δ 189.4.

Conclusions

Several metal complexes are known to have either charge-compensated C-substituted monocarbollide ligands or charge-compensated B-substituted dicarbollide groups.[1,5,13] However, as far as we are aware, the species **1** are the first ruthenium complexes with C-substituted zwitterionic monocarbollide groups, although a B-substituted charge-compensated dicarbollide complex [$RuH(PPh_3)_2(\eta^5\text{-}9\text{-}NC_5H_5\text{-}7,8\text{-}C_2B_9H_{10})$] has been described.[14] The compounds **1** are also the first examples of triruthenium clusters with a bridging monocarbollide moiety. Several molecules are known in which a dicarbollide ligand bridges a metal triangle by virtue of being η^5-coordinated to one metal center while also forming B−H$\rightharpoonup$M bonds with the other two metal centers, and examples include [NEt_4][$WCo_2(\mu\text{-}CPh)(CO)_6(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$],[15] [$NEt_4$][$Mo_2W(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(\mu\text{-}CO)(CO)_7(PPh_3)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$],[16] and [$Co_2Ni(\mu\text{-}CO)(CO)_5(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$].[17] The two B−H$\rightharpoonup$M bonds are nonequivalent in these dicarbollide trimetal compounds because one boron atom is in the α-site and the other is in the β-position with respect to the two carbon atoms in the $\overline{\text{CCBBB}}$ face bonded in an η^5-mode to the third metal center. In contrast, and as discussed earlier, the compounds **1** have B−H$\rightharpoonup$Ru bridges that lie on the opposite side of a plane of symmetry.

The reactions between **1a** and the donor molecules PPh_3 and $CNBu^t$ lead to the replacement of one CO group, but afford products of a very different nature. Reactions of other donor molecules with the species **1** remain to be studied and should afford new complexes of structural interest.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen, using Schlenk line techniques. Solvents were distilled under nitrogen from the appropriate drying agents before use. Light petroleum refers to that fraction of boiling point 40−60 °C. Chromatography columns (ca. 40 cm in length and 1 cm in diameter) were packed with Florisil (Aldrich, 100−200 mesh). The reagents *nido*-7-NR_3-7-$CB_{10}H_{12}$ (NR_3 = NMe_3, NH_2Bu^t, NMe_2Bu^t) were prepared by procedures previously reported.[18] Dodecacarbonyltriruthenium was used as supplied by Aldrich. The NMR spectra were measured at the following frequencies: ^1H at 360.13 MHz, ^{13}C at 90.56 MHz, ^{31}P at 145.78 MHz, and ^{11}B at 115.55 MHz.

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Table 5. Data for X-ray Crystal Structure Analyses[a]

	1a	**2a**
cryst dimens (mm)	0.13 × 0.21 × 0.26	0.12 × 0.26 × 0.39
formula	$C_{12}H_{19}B_{10}NO_8Ru_3 \cdot 0.125CH_2Cl_2$	$C_{29}H_{34}B_{10}NO_7PRu_3 \cdot C_7H_8 \cdot 0.25\ CH_2Cl_2$
M_r	727.2	1064.2
cryst color, shape	red, parallelepiped	red, irregular shape
cryst system	orthorhombic	triclinic
space group (no.)	*Pccn* (no. 56)	$P\bar{1}$ (no. 14)
a (Å)	17.817 (4)	10.246(2)
b (Å)	30.418(7)	13.974(4)
c (Å)	9.599(2)	17.885(5)
α (deg)	90.0	112.19(2)
β (deg)	90.0	92.32(2)
γ (deg)	90.0	98.93
V (Å^3)	5202(2)	2328.5(9)
Z	8	2
d_{calcd} (g cm^{-3})	1.857	1.518
μ(Mo Kα)/cm^{-1})	17.49	10.47
F(000)/e	2794	1057
2*θ* range/deg)	3.0−40.0	3.0−40.0
T (K)	292	292
no. of reflns measd	3038	4662
no. of unique reflns	2418	4331
no. of observed reflns	2015	3891
criterion for observed *n* [$F_o \leq n\sigma(F_o)$]	$n = 4$	$n = 4$
R_{int}	0.021	0.025
data-to-parameter ratio	6.3:1	7.3:1
$R(R')$[b]	0.059 (0.070)	0.049 (0.059)
final electron density diff features (max/min) (e Å^{-3})	1.21/−0.94	1.66/−0.55
S (goodness-of-fit)	1.45	1.26

[a] Data were collected on an Enraf-Nonius CAD4-F automated diffractometer operating in the $\omega-2\theta$ scan mode (*h*, −4 to 17, *k* −7 to 29, *l*, −2 to 9 for **1a**; *h* 0 to 9, *k*, −13 to 13, *l*, −17 to 17 for **2**); graphite-monochromated Mo Kα X-radiation, $\bar{\lambda} = 0.710\ 73$. Refinement was block full-matrix least-squares on *F* with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ ($g = 0.0046$ for **1a**, 0.0043 for **2**), where $\sigma_c{}^2(F_o)$ is the variance in F_o due to counting statistics. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$.

Synthesis of the Compounds [$Ru_3(CO)_8(\eta^5$-7-NR_3-7-$CB_{10}H_{10})$] (NR_3 = NMe_3, NH_2Bu^t, and NMe_2Bu^t). (i) A mixture of the compounds [$Ru_3(CO)_{12}$] (2.0 g, 3.13 mmol) and *nido*-7-NMe_3-7-$CB_{10}H_{12}$ (0.60 g, 3.13 mmol) was refluxed in toluene (30 mL) for 5 h, during which period the color slowly changed from orange to brown, and IR measurements showed complete consumption of the starting reagents. Solvent was removed in vacuo, CH_2Cl_2 (10 mL) was added to the residue, and the suspension formed was absorbed on Florisil (ca. 2 g). The latter was transferred to the top of a chromatography column. Elution with light petroleum initially removed a trace of [$Ru_4(\mu$-$H)_4(CO)_{12}$], identified by IR spectroscopy.[19] Further elution with CH_2Cl_2−light petroleum (1:3) removed a yellow fraction containing the desired product. Evaporation of the solvent in vacuo from the eluant gave deep yellow *microcrystals* of [$Ru_3(CO)_8(\eta^5$-7-NMe_3-7-$CB_{10}H_{10})$] (**1a**) (1.12 g).

(ii) By using a similar procedure, [$Ru_3(CO)_{12}$] (1.0 g,1.56 mmol) and *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ (0.32 g, 1.56 mmol), after being refluxed together in toluene (30 mL), afforded yellow *microcrystals* of [$Ru_3(CO)_8(\eta^5$-7-NH_2Bu^t-7-$CB_{10}H_{10})$] (**1b**) (0.22 g) after recrystallization from CH_2Cl_2−light petroleum (1:4).

(iii) Similarly, [$Ru_3(CO)_{12}$] (1.4 g, 2.23 mmol) and *nido*-7-NMe_2Bu^t-7-$CB_{10}H_{12}$ (0.52 g, 2.23 mmol) refluxed in toluene (30 mL) gave yellow *microcrystals* of [$Ru_3(CO)_8(\eta^5$-7-NMe_2Bu^t-7-$CB_{10}H_{10})$] (**1c**) (0.59 g).

Reactions of [$Ru_3(CO)_8(\eta^5$-7-NMe_3-7-$CB_{10}H_{10})$]. (i) A mixture of **1a** (0.20 g, 0.28 mmol) and PPh_3 (0.07 g, 0.28 mmol) was stirred in toluene (5 mL) at 60 °C for 30 min. Solvent was then removed in vacuo, and the residue was dissolved (ca. 5 mL) and chromatographed. Elution with CH_2Cl_2−light petroleum (1:1, 3 cm^3) gave orange *microcrystals* of [$Ru_3(\mu$-$H)(\mu_3$-σ:η^5-7-NMe_3-7-$CB_{10}H_9)(CO)_7(PPh_3)$] (**2**) (0.24 g).

(ii) A solution of **1a** (0.14 g, 0.19 mmol) in CH_2Cl_2 (10 mL) was treated with $NCBu^t$ (0.016 g, 0.012 mL, 0.19 mmol), and the mixture was stirred for 15 min. Solvent was then reduced in vacuo to ca. 5 mL and the solution was chromatographed. Elution with CH_2Cl_2−light petroleum (1:2) gave a yellow fraction. Solvent was removed in vacuo and crystallization of the residue from CH_2Cl_2−light petroleum (1:3, 5 mL) gave dark yellow *microcrystals* of [$Ru_3(CO)_7(CNBu^t)(\eta^5$-7-$NMe_3$-*nido*-7-$CB_{10}H_{10})$] (**3**) (0.13 g).

Crystal Structure Determination and Refinement. The crystal data and other experimental parameters for compounds **1a** and **2** are presented in Table 5. Crystals of compound **1a** were grown as opaque red parallelepipeds from toluene, and those of **2** were obtained as clear red irregularly shaped specimens from toluene−light petroleum (1:1). However, the diffraction studies revealed that the unit cells of both molecules contained CH_2Cl_2 derived from the initial purification procedure involving chromatography with this solvent. Conoscopic examinations of **1a** and **2**, by using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II, verified the biaxial nature and optical purity of the studied systems. Data were obtained on an Enraf-Nonius CAD4-F diffractometer equipped with a dense graphite monochromator (take-off angle 2.8°), and for each data set, final lattice constants were derived from the setting of 25 accurately centered high *θ* angle values, >20°. The crystal stabilities and electronic hardware reliability were verified by monitoring three standard reflections as a function of time (every 2 h of exposure time). All intensity data were corrected for Lorentz and polarization effects, after which empirical absorption corrections based on high-angle ψ scans[20] were performed (min, max transmission factors = 0.9522, 0.9999 for **1a** and 0.9652, 0.9998 for **2**). An examination of each data set using an *N*(*Z*) analysis (cumulative probability distribution test) provided evidence that both complexes were centrosymmetric.[21]

The phase problem for each compound was solved by the heavy atom Patterson method, which located the three Ru atoms in both **1a** and **2**. Difference Fourier mapping found all other non-hydrogen atoms. Boron hydrogen atoms and the bridging H-atoms in **1a** and **2** were located by using the

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Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Paramters (Å^2 $\times$ 10^3) for 1a

name	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	4750(1)	1208(1)	−2914(1)	26(1)
C(1)	5776(8)	863(5)	−3887(16)	30(5)
B(2)	5996(10)	1279(6)	−2743(21)	34(7)
B(3)	5544(10)	1166(6)	−1181(19)	30(6)
B(4)	5009(10)	715(6)	−1327(18)	30(7)
B(5)	5095(10)	490(6)	−3107(18)	29(7)
B(6)	6608(10)	834(5)	−3082(19)	32(6)
B(7)	6486(10)	1020(6)	−1395(18)	35(7)
B(8)	5862(11)	650(7)	−525(19)	39(7)
B(9)	5571(10)	248(7)	−1670(19)	38(7)
B(10)	6067(10)	361(6)	−3285(17)	27(6)
B(11)	6521(11)	443(6)	−1667(17)	38(7)
N	5837(8)	900(4)	−5520(12)	44(5)
C(2)	5111(10)	816(6)	−6274(16)	45(7)
C(3)	6387(10)	603(6)	−6167(17)	44(6)
C(4)	6082(13)	1352(5)	−5897(20)	72(9)
C(11)	4636(12)	1772(5)	−3605(21)	65(10)
O(11)	4579(10)	2109(5)	−4198(15)	97(8)
C(12)	3823(8)	1056(6)	−3804(17)	41(6)
O(12)	3318(8)	907(5)	−4430(12)	75(6)
Ru(2)	4682(1)	1728(1)	−558(1)	36(1)
C(21)	4512(11)	1809(5)	1327(15)	50(7)
O(21)	4426(10)	1844(4)	2533(14)	82(6)
C(22)	3895(10)	2095(6)	−1013(20)	58(8)
O(22)	3440(8)	2361(5)	−1268(18)	86(6)
C(23)	5383(12)	2171(7)	−895(21)	72(9)
O(23)	5772(10)	2470(6)	−1150(17)	99(7)
Ru(3)	3780(1)	981(1)	−794(1)	30(1)
C(31)	3566(10)	918(5)	1079(14)	41(6)
O(31)	3438(8)	902(5)	2268(14)	79(7)
C(32)	3229(10)	481(6)	−1349(16)	54(7)
O(32)	2892(9)	168(5)	−1673(16)	87(7)
C(33)	2992(9)	1344(6)	−1142(19)	50(7)
O(33)	2474(9)	1577(4)	−1301(16)	83(6)
Cl(1)	7158(12)	2062(8)	1125(21)	78(8)
C(41)	7500	2500	1960(23)	83(28)

[a] Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

programs BHGEN[22] and XHYDEX,[4] respectively. The boron hydrogen atoms were then fixed at 1.10 Å. In complex **2**, the bridging H-atoms [H(1) and H(4)] were not positionally fixed. All carbon-bonded hydrogen atoms were placed in calculated positions (C−H, 0.96 Å), and all types of H-atoms were constrained to ride on their connected atoms with fixed isotropic thermal factors (B−H and C−H, $U_{iso} = 60$ and 80×10^{-3} Å^2, respectively). The structural models were refined by the full-matrix least-squares method,[23] and after secondary extinction corrections were applied [$7(3) \times 10^{-5}$ and $2.0(8) \times 10^{-4}$ e^2, **1a** and **2**, respectively], the anisotropic refinement of all non-hydrogen atoms yielded final residual indices (Table 5). Final respective electron density maps (**1a** and **2**) revealed some density in the region of the metal atomic positions, as is usual for heavy metal compounds. Elsewhere, the density maps were virtually featureless, displaying only random fluctuating backgrounds. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors and associated anomalous dispersion correction factors were taken from the usual source.[24] Final atomic positional parameters for non-hydrogen atoms with equivalent isotropic displacement coefficients for complexes **1a** and **2** are given in Table 6 and 7, respectively.

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Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Paramters (Å^2 $\times$ 10^3) for 2

name	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	−394(1)	1507(1)	3960(1)	37(1)
C(1)	−1664(7)	2730(5)	3987(5)	43(3)
B(2)	2(9)	3151(7)	4016(6)	45(4)
B(3)	615(9)	2198(7)	3153(5)	43(4)
B(4)	−816(9)	1170(7)	2650(5)	44(4)
B(5)	−2214(8)	1466(7)	3201(6)	45(4)
B(6)	−1192(9)	3708(7)	3610(6)	52(4)
B(7)	185(11)	3343(8)	3098(7)	59(5)
B(8)	−301(10)	2128(8)	2242(7)	58(5)
B(9)	−1983(11)	1664(9)	2286(6)	61(5)
B(10)	−2560(10)	2657(8)	3110(7)	60(5)
B(11)	−1417(11)	3044(9)	2557(7)	68(5)
N(1)	−2427(6)	3110(5)	4773(4)	52(3)
C(2)	−3011(10)	4108(8)	4900(7)	89(5)
C(3)	−3563(10)	2310(8)	4725(7)	84(5)
C(4)	−1525(10)	3359(8)	5529(6)	77(5)
C(11)	742(8)	1919(6)	4916(5)	51(4)
O(11)	1352(7)	2230(6)	5557(4)	83(3)
C(12)	−1370(8)	521(6)	4288(5)	52(4)
O(12)	−2057(7)	−108(5)	4466(4)	87(3)
Ru(2)	−56(1)	−321(1)	2708(1)	40(1)
C(13)	−1796(8)	−1058(6)	2593(5)	55(4)
O(13)	−2883(6)	−1501(5)	2496(5)	84(4)
C(14)	657(8)	−927(6)	3354(5)	49(4)
O(14)	1122(7)	−1308(5)	3757(4)	75(3)
P(1)	338(2)	−1618(2)	1508(1)	44(1)
C(21)	1925(8)	−1371(6)	1119(5)	48(4)
C(22)	3062(9)	−1057(7)	1666(6)	75(5)
C(23)	4307(10)	−862(9)	1438(9)	90(6)
C(24)	4375(12)	−986(10)	663(11)	113(9)
C(25)	3266(14)	−1325(10)	96(7)	98(7)
C(26)	2052(10)	−1536(7)	320(5)	66(5)
C(31)	291(8)	−2932(6)	1520(5)	50(4)
C(32)	−462(10)	−3264(7)	2030(6)	74(5)
C(33)	−479(12)	−4275(8)	2021(7)	85(6)
C(34)	255(11)	−4933(8)	1509(7)	86(6)
C(35)	991(11)	−4603(7)	1009(6)	80(5)
C(36)	967(10)	−3619(6)	1011(6)	66(5)
C(41)	−927(8)	−1850(6)	660(4)	51(4)
C(42)	−1766(9)	−2812(6)	291(5)	69(4)
C(43)	−2680(9)	−2951(8)	−339(6)	74(5)
C(44)	−2849(10)	−2150(8)	−582(6)	75(5)
C(45)	−2015(11)	−1200(9)	−201(6)	78(6)
C(46)	−1029(8)	−1035(7)	424(5)	54(4)
Ru(3)	2172(1)	1505(1)	3469(1)	44(1)
C(15)	2976(7)	2848(6)	4157(5)	51(4)
O(15)	3520(6)	3686(6)	4581(5)	85(3)
C(16)	3191(8)	768(7)	3970(5)	56(4)
O(16)	3896(7)	407(5)	4263(5)	88(4)
C(17)	3188(8)	1659(7)	2676(6)	67(5)
O(17)	3843(8)	1743(6)	2170(5)	95(4)
Cl(1)	4955(18)	5659(14)	569(10)	287(8)[b]
C(99)	6099(35)	4527(29)	538(21)	62(9)[b]
C(91)	4453(13)	6604(10)	3036(8)	148(11)
C(92)	5689(10)	6644(10)	3383(7)	112(8)
C(93)	6100(11)	5723(14)	3318(10)	162(15)
C(94)	5214(19)	4778(10)	2960(12)	160(13)
C(95)	3960(17)	4751(10)	2663(11)	188(15)
C(96)	3575(9)	5672(13)	2681(8)	124(9)
C(97)	4001(18)	7574(13)	3060(10)	175(14)

[a] Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Cl(1) and C(99) were refined isotropically.

Supporting Information Available: Complete tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1a** and **2** (22 pages). Ordering information is given on any current masthead page.

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