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Synthesis, Structural Characterization, and Reactions of *closo*-Rhodacarborane Anions Containing a Formal d^8 Metal Vertex[1,2]

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Deprotonation of three neutral closo hydrido complexes $[(L)_2\text{–H–RhC}_2B_9H_{11}]$ under carefully controlled reaction conditions yields the corresponding isomeric $[closo\text{-}L_2RhC_2B_9H_{11}]^-$ species. Two of these have been structurally characterized. K[18-crown-6][*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]·C_4H_8O·H_2O (**2a**) crystallized in the monoclinic space group $P2_1/c$ with $a = 13.931$ (4) Å, $b = 19.954$ (5) Å, $c = 21.665$ (7) Å, $\beta = 100.97$ (2)°, $V = 5913$ Å^3, and $Z = 4$. Data were collected on a Syntex $P\bar{1}$ diffractometer (Mo Kα radiation) to a maximum $2\theta = 50°$, giving 10521 unique reflections, and the structure was solved by conventional heavy-atom techniques. The final discrepancy index was $R = 0.062$, $R_w = 0.072$ for 6149 independent reflections. The d^8-rhodacarborane anion adopts a closo structure similar to that found in the parent hydrido complex. The Rh–P_2 plane lies almost perpendicular to the least-squares plane that passes through the bonding face of the carborane ligand and lies parallel to a line joining the two ortho carbon atoms of this ligand, in accord with theoretical studies. $[Me_4N]$[*closo*-2,2-$(PPh_3)_2$-2,1,7-$RhC_2B_9H_{11}$] (**2b**) crystallized in the triclinic space group $P\bar{1}$ with $a = 12.355$ (13) Å, $b = 14.896$ (16) Å, $c = 15.186$ (22) Å, $\alpha = 68.00$ (9)°, $\beta = 102.86$ (6)°, $\gamma = 112.17$ (5)°, $V = 2389$ Å^3, and $Z = 2$. Data were collected on a Picker FACS-1 diffractometer (Mo Kα radiation) to a maximum in 2θ of 45°, giving 6180 unique reflections, and the structure was solved by conventional heavy-atom techniques. The final discrepancy index was $R = 0.063$, $R_w = 0.067$ for 4761 independent reflections. Unlike **2a**, this d^8-rhodacarborane anion adopts a significantly distorted icosahedral structure. Carbon atoms of the significantly nonplanar C_2B_3 face are bent back into the cage and away from the metal. Rh–C bonds in **2b** are 2.340 (9) and 2.442 (9) Å, while those in **2a** are 2.314 (8) and 2.301 (7) Å. The plane containing RhP_2 is nearly perpendicular to the C_2B_3 face and nearly parallel to the noncrystallographic mirror plane in the carborane ligand (the calculated preferred conformation). Salts of **2a**$^-$, **2b**$^-$, and [*closo*-2,2-$(PPh_3)_2$-2,1,12-$RhC_2B_9H_{11}]^-$ (**2c**) were treated with dilute mineral acids in ethanol to produce the neutral hydrido closo complexes and with π-acceptor ligands L = CO or C_2H_4 to produce the corresponding [*closo*-(PPh_3)(L)-$RhC_2B_9H_{11}$] salts. Anions [*closo*-3,3-$(PPh_3)_2$-3,1,2-$IrC_2B_9H_{11}]^-$, [*closo*-3-(PPh_3)-3,3-$(H)_2$-3,1,2-$IrC_2B_9H_{11}]^-$, and [*closo*-3-(PPh_3)-3-(CO)-3,1,2-$IrC_2B_9H_{11}]^-$ have also been prepared.

Introduction

Recent studies in metallacarborane chemistry that have emanated from this laboratory have been principally concerned with the reactivity of metal vertices found in these polyhedral clusters. As examples, one finds a set of isocahedral rhodacarboranes of general formula $(PPh_3)_2Rh(H)C_2B_9H_{11}$ that serve as precursors for novel exo-nido Rh(1+) catalysts generated by reductive elimination of the rhodium vertex.[3] Similarly, the various reactions of [*closo*-3-PPh_3-3-X-3,1,2-$RhC_2B_9H_{11}$] (X = bidentate NO_3^- and CH_3COO^-) and [*closo*-3,3-$(PPh_3)_2$-3-HSO_4-3,1,2-$RhC_2B_9H_{11}$] provide further examples of Rh(3+) chemistry at a polyhedral vertex.[4]

Very early crystallographic studies[5] demonstrated that electron-rich metal centers, such as those found in the late transition metals, very often provided examples of distorted polyhedral metallacarborane structures. The importance of metal electron configuration,[6] the identity of ancillary ligands, and the relative positions of the polyhedral carbon atoms have been recognized as factors that determine the nature and degree of distortion.[7] In fact, such factors have been treated in some depth by Mingos[7e,8] and employed in predicting metallacarborane structures. Such species as the d^8-$L_2M(2+)$ (L = CO, RNC, PR_3; M = Ni,[9] Pd,[7] Pt[7]) icosahedral metallacarboranes have been treated by this means, but the corresponding isoelectronic $L_2M(1+)$ (M = Rh, Ir) metallacarboranes have only recently been prepared and Rh species structurally characterized.[2,10] A single example of this class of compound had been previously characterized,[11] [*closo*-3-PPh_3-3-CO-4-C_5H_5N-3,1,2-$RhC_2B_9H_{11}$], and the conformation of the metal vertex was found to be structurally incompatible with molecular orbital predictions then extant.

Combination of a d^8-$L_2Rh(1+)$ vertex with the three known isomeric [*nido*-$C_2B_9H_{11}]^{2-}$ ions generates a set of three isomeric [*closo*-$L_2RhC_2B_9H_{11}]^-$ species. Anions of this sort, in which L = PPh_3, CO, and C_2H_4, provide the subject of the synthesis and structural studies described in this and the succeeding paper.[12] Figure 1 presents a summary of the structures of these species.

Results and Discussion

Syntheses and Characterization of Salts of [*closo*-$(PPh_3)_2RhC_2B_9H_{11}]^-$. Conceptually, one can envision three different synthetic routes to salts of the anionic species [*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}]^-$ (**2a**$^-$). (1) The reaction of $RhCl(PPh_3)_3$ with Na_2[*nido*-7,8-$C_2B_9H_{11}$] should produce the sodium salt of **2a**$^-$. A similar reaction of $RhCl(PPh_3)_3$ and NaC_5H_5 produced $(PPh_3)_2Rh(\eta^5\text{-}C_5H_5)$ in 75% yield after column chromatography.[13] Although $RhCl(PPh_3)_3$ does react with Na_2[*nido*-7,8-$C_2B_9H_{11}$] in THF, attempts to isolate pure salts from these reactions were frustrated by their air-sensitive nature. A more convenient source of the [*nido*-7,8-$C_2B_9H_{11}]^{-2}$ ligand, namely, Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] was also found to react with $RhCl(PPh_3)_3$ in benzene to produce a burgundy-colored rhoda-

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(1) Taken in part from: Walker, John A. Ph.D. Thesis, The University of California, Los Angeles, 1983.

(2) Previously communicated: Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3368.

(3) (a) Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024. (b) Baker, R. T.; Delaney, M. S.; King, R. E.; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G. Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2965. (c) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979. (d) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990. (e) Long, J. A.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3004. (f) Behnken, P. E.; Belmont, J. A.; Busby, D. C.; Delaney, M. S.; King, R. E.; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3011.

(4) Kalb, W. C.; Demidowicz, Z.; Speckman, D. M.; Knobler, C. B.; Teller, R. G.; Hawthorne, M. F. *Inorg. Chem.* **1982**, *21*, 4027.

(5) (a) Wing, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 4701. (b) Wing, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4828. (c) Wing, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 1187.

(6) Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *90*, 4823.

(7) (a) Green, M.; Spencer, J. L.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 179. (b) Carroll, W. E.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2263. (c) Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1473. (d) Colquoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1978**, 322. (e) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

(8) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602.

(9) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 786.

(10) Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370.

(11) Teller, R. G.; Wilczynski, J. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472.

(12) Walker, J. A.; Knobler, C. B.; Soto, J.; Zheng, L.; Hawthorne, M. F., to be submitted for publication in *Inorg. Chem.*

(13) Wakatusuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1974**, *64*, 393.

0020-1669/85/1324-2688$01.50/0

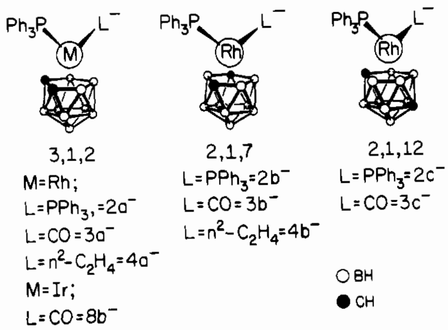


Figure 1. Schematic representation of closo anions derived from a combination of a d^8-L_2Rh^I vertex with the three known isomeric [*nido*-$C_2B_9H_{11}]^{2-}$ ions.

carborane. Since the elemental analyses of this product indicated a Tl:Rh:P:B ratio of 1:1:1:9, further characterization of this product was not pursued. (2) A second potential route to salts of **2a**⁻ would be the chemical reduction of the dimeric Rh(II) species[14] $[(PPh_3)RhC_2B_9H_{11}]_2$ in the presence of triphenylphosphine. The reduction of neutral binuclear complexes is a well-established method of producing singly charged anionic metal carbonyl complexes (e.g., $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow 2[\eta^5\text{-}C_5H_5)Fe(CO)_2]^-)$.[15] The aforementioned rhodium dimer does indeed react with Na(Hg) in THF in the presence of excess triphenylphosphine, but attempts to isolate the anionic species produced in this reaction by the addition of salts of large cations, e.g., [PPN]Cl, $[Ph_4As]Cl$, or $[Et_4N]Br$ only produced intractable solids. It was found, however, that treatment of the solutions formed after the reduction described above with a slight excess of CF_3CO_2H produced the known hydrido complex [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**) in 60% yield after chromatography. This observation supported the existence of **2a**⁻, but superior methodologies were still required to produce crystalline salts of **2a**⁻. (3) A third and more direct route to salts of **2a**⁻ would be deprotonation of **1a**.[16] Indeed, many moderate to strong bases were found to react with **1a** to produce solutions containing **2a**⁻. Because these solutions were air-sensitive, isolation of crystalline solids required carefully controlled reaction conditions, which will be more fully described below.

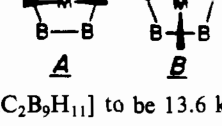
The reaction of complex **1a** in THF at room temperature with a solution of K[18-crown-6]OH in ethanol rapidly produced a deep red solution. The addition of absolute ethanol and evaporation of the THF in vacuo produced air-sensitive golden crystalline flakes of K[18-crown-6][*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$] (K[18-crown-6][**2a**]) in good yields. Although totally satisfactory elemental analyses were not obtained for this salt, elemental ratios clearly supported the formulation of **2a**⁻ and subsequent X-ray crystallographic characterization of this salt (vide infra) unequivocally established its identity. The ^1H NMR spectrum of acetone-d_6 solutions of this salt displayed the expected resonances and intensities for the triphenylphosphine ligands, the cation, and the two equivalent carboranyl C–H protons. The 25 °C $^{31}P\{^1H\}$ NMR spectrum of Na[**2a**] displayed one sharp doublet at 47.3 ppm (J_{Rh-P} = 197 Hz) in 10% benzene-d_6/THF, which remained essentially unchanged at temperatures as low as −30 °C. The $^{11}B\{^1H\}$ NMR spectrum of Na[**2a**], in THF consisted of four broad absorptions with relative intensities 1:2:4:2 (low field to high field).

Further elaboration of **2a**⁻ sometimes required a simple alkali metal cation; thus it was necessary to develop routes to such crystalline salts. It was found that a benzene/ether slurry of **1a** reacted with butyllithium to produce brown crystalline flakes of Li[**2a**]. The potassium salt of **2a**⁻ could be produced in THF from **1a** and potassium-tri-*sec*-butylborohydride (K-Selectride, Aldrich) and quantitatively precipitated from solution as golden brown microcrystals by the slow addition of dry pentane. This salt is slightly more stable than Li[**2a**]. The greater ease of handling of K-Selectride over butyllithium coupled with the enhanced stability of K[**2a**] over Li[**2a**] made the latter procedure the method of choice to produce a simple salt of **2a**⁻.

Figure 2. Variable-temperature 81.02-MHz $^{31}P\{^1H\}$ FT-NMR spectra of $[Et_4N]$[**2b**] in acetone-d_6.

The 2,1,7-isomer of **1a**, namely **1b**,[3b] was also found to react with a variety of bases to produce salts of **2b**⁻. For example, THF solutions of **1b** react with ethanol solutions of $[Et_4N]OH$ to produce $[Et_4N]$[**2b**], which is isolable in high yield by the addition of absolute ethanol to the reaction and removal of the THF in vacuo. The orange salt so produced could be recrystallized several times from acetone/ether to produce red crystals analyzing as $[Et_4N]$[**2b**]$\cdot 2(CH_3)_2CO$. The $[Me_4N]^+$ and $[n\text{-}Bu_4N]^+$ salts of **2b**⁻ could be similarly prepared and purified as could K[**2b**] via the K-Selectride procedure.

The IR and ^1H NMR spectra of $[Et_4N]$[**2b**] were as expected and were unexceptional. The $^{31}P\{^1H\}$ NMR spectrum of $[Et_4N]$[**2b**] in 10% acetone-d_6/acetone displayed a slightly broadened doublet at 51.7 ppm (J_{Rh-P} = 212 Hz) at room temperature. Unlike **2a**⁻, cooling this solution of **2b**⁻ to −33 °C collapses the doublet to a broad featureless peak centered at 51.5 ppm and further cooling to −73 °C produced two separate doublets of doublets centered at 58.5 ppm (J_{Rh-P} = 242 Hz; J_{P-P} = 42 Hz) and 41.8 ppm (J_{Rh-P} = 186 Hz; J_{P-P} = 42 Hz). These spectral features are illustrated in Figure 2 and are consistent with the well-established phenomenon of hindered rotation about the metal–carborane ligand axis.[17] The room-temperature spectrum indicates an average triphenylphosphine ligand environment created by rapid rotation of the metal vertex with respect to the carborane ligand while the low-temperature limiting spectrum represents a fixed metal vertex conformation, most likely the one observed in the crystal structure (vide infra). From the NMR data presented above it is possible to estimate the barrier to rotation in this complex to be approximately 10 kcal·mol⁻¹. Interestingly, Mingos has calculated[8] the energy difference between conformations A and B for the hypothetical complex [*closo*-2,2-$(PH_3)_2$-2,1,7-$PtC_2B_9H_{11}$] to be 13.6 kcal·mol⁻¹, with B the more stable.



A *B*

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[14] Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F.; *J. Am. Chem. Soc.* **1978**, *100*, 8266.

[15] For reviews, see: (a) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (b) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157.

[16] Deprotonation of neutral and cationic transition-metal hydrides is certainly not a new reaction; see: Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

[17] Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988.

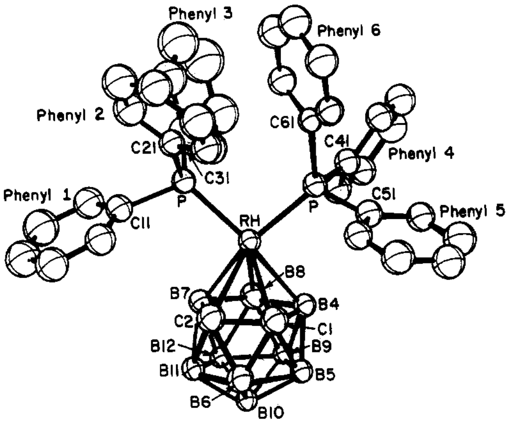

Figure 3. Structure of the anion present in K[18-crown-6][**2a**]·$C_4H_8O{\cdot}H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

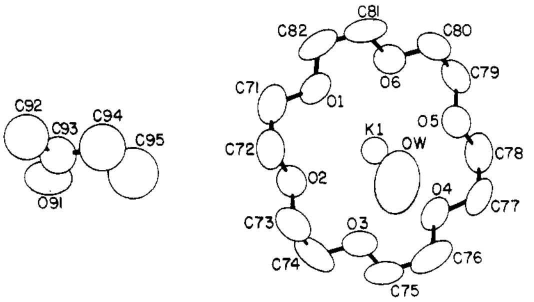

Figure 4. Structure of the cation and solvates present in K[18-crown-6][**2a**]·$C_4H_8O{\cdot}H_2O$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

While salts of **2b**⁻ were quite air sensitive, they were qualitatively observed to be more stable than the corresponding salts of **2a**⁻. The same trend in stability was observed in the 3,1,2- and 2,1,7-isomers of $Ni[C_2B_9H_{11}]_2^{-2}$.[18]

A THF solution of the hydrido complex, [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (**1c**),[19] was found to react with ethanolic $[Me_4N]OH$ to produce analytically pure $[Me_4N]$[**2c**]·$(CH_3)_2CO$ after recrystallization of the reaction product. The spectral data are consistent with the formulation and are given in the Experimental Section. Because of the reduced availability of [*closo*-1,12-$C_2B_{10}H_{12}$] from which complex **1c** is derived, detailed investigations of the behavior of $[Me_4N]$[**2c**] were not performed.

Description of the Molecular Structure of K[18-crown-6][2a]·$C_4H_8O{\cdot}H_2O$. The compound K[18-crown-6][**2a**] crystallizes from $CH_3COC_2H_5/(CH_3)_2CHOH$ as red prisms containing one methyl ethyl ketone and one water solvate per K[18-crown-6]⁺ cation. An ORTEP projection of the anion is shown in Figure 3, and an ORTEP projection of the cation is shown in Figure 4. Table I lists selected interatomic distances, and Table II gives some of the interatomic angles in this salt.

The structural analysis shows that this d^8-rhodacarborane anion adopts a closo structure similar to that found in the parent hydrido complex, **1a**. Thus, this salt is a member of a relatively small class of structurally characterized d^8-metallacarboranes that do not display significant polyhedral distortions. A regular closo structure was also found in a related d^8-rhodacarborane, namely [*closo*-3-(PPh_3)-3-(CO)-4-(C_5H_5N)-3,1,2-$RhC_2B_9H_{10}$].[11] In contrast, the neutral isoelectronic complex [3,3-$(PEt_3)_2$-3,1,2-$PtC_2B_9H_{11}$][7c] adopts a significantly distorted icosahedral structure. The electronic factors that encourage polyhedral distortions in electron-rich metallacarboranes have been previously discussed,[7c,8] and it has generally been found that increasing the electron density at the metal center promotes these distortions while decreasing the electron density at the metal center with π-acid ligands favors regular closo structures. This trend is clearly illustrated by the structures observed for [3,3-$(C_2H_4(NMe_2)_2)$-3,1,2-$PdC_2B_9H_{11}$] and [3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$].[7d] The palladium complex bearing the moderate π-acceptor ligand PMe_3 adopts a slightly distorted icosahedral structure, the distortion being quantitatively described by the "slip parameter",[7d] $\Delta = 0.26$ Å, while the palladium complex with the chelating amine ligand, a ligand devoid of π-acid character, adopts a significantly distorted structure, $\Delta = 0.52$ Å (the slip parameter is defined as the displacement of the metal atom from the perpendicular passing through the centroid of the lower pentagonal face). The degree of polyhedral distortion has been found to be a function of the d–p promotion energy of the metal. This trend is illustrated by comparing the

Table I. Selected Distances (Å) in K[18-crown-6][*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]·$C_4H_8O{\cdot}H_2O$

from	to	dist[a]	from	to	dist[a]
Rh	P(1)	2.257 (2)	B(10)	B(12)	1.742 (13)
Rh	P(2)	2.233 (2)	B(10)	B(11)	1.751 (13)
Rh	C(B1)	2.314 (8)	B(11)	B(12)	1.769 (12)
Rh	B(4)	2.240 (8)	C(71)	O(1)	1.408 (12)
Rh	C(B2)	2.301 (7)	C(71)	C(72)	1.474 (16)
Rh	B(C7)	2.273 (8)	C(72)	O(2)	1.413 (12)
Rh	B(C8)	2.324 (8)	C(73)	O(2)	1.381 (12)
C(B1)	C(B2)	1.640 (11)	C(73)	C(74)	1.485 (15)
C(B1)	B(6)	1.761 (11)	C(74)	O(3)	1.413 (12)
C(B1)	B(5)	1.777 (11)	C(75)	O(3)	1.398 (13)
C(B1)	B(4)	1.783 (11)	C(75)	C(76)	1.486 (16)
C(B2)	B(C7)	1.685 (10)	C(76)	O(4)	1.405 (12)
C(B2)	B(11)	1.737 (11)	C(77)	O(4)	1.418 (12)
C(B2)	B(6)	1.739 (11)	C(77)	C(78)	1.472 (15)
B(4)	B(C8)	1.767 (11)	C(78)	O(5)	1.415 (11)
B(4)	B(5)	1.796 (11)	C(79)	O(5)	1.427 (12)
B(4)	B(9)	1.807 (11)	C(79)	C(80)	1.483 (15)
B(5)	B(6)	1.759 (12)	C(80)	O(6)	1.393 (12)
B(5)	B(10)	1.777 (13)	C(81)	O(6)	1.406 (11)
B(5)	B(9)	1.801 (12)	C(81)	C(82)	1.470 (15)
B(6)	B(11)	1.744 (13)	C(82)	O(1)	1.413 (12)
B(6)	B(10)	1.754 (12)	K	O(1)	2.791 (6)
B(C7)	B(C8)	1.659 (11)	K	O(2)	2.797 (7)
B(C7)	B(11)	1.748 (11)	K	O(3)	2.809 (7)
B(C7)	B(12)	1.756 (11)	K	O(4)	2.815 (6)
B(C8)	B(12)	1.753 (11)	K	O(5)	2.754 (6)
B(C8)	B(9)	1.762 (11)	K	O(6)	2.787 (6)
B(9)	B(12)	1.724 (12)	K	O(W)	2.823 (12)
B(9)	B(10)	1.776 (12)	K	O(91)	2.688 (8)

[a] Standard deviations in parentheses.

Table II. Selected Angles (deg) in K[18-crown-6][*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]·$C_4H_8O{\cdot}H_2O$

from	through	to	angle[a]
P(2)	Rh	B(4)	90.19 (22)
P(2)	Rh	P(1)	97.57 (7)
P(2)	Rh	B(C7)	157.16 (20)
P(2)	Rh	C(B2)	147.08 (19)
P(2)	Rh	C(B1)	107.14 (20)
P(2)	Rh	B(C8)	114.94 (20)
B(4)	Rh	P(1)	166.20 (21)
B(4)	Rh	B(C7)	73.38 (28)
B(4)	Rh	C(B2)	73.66 (29)
B(4)	Rh	C(B1)	46.07 (28)
B(4)	Rh	B(C8)	45.51 (28)
P(1)	Rh	B(C7)	95.82 (19)
P(1)	Rh	C(B2)	104.58 (21)
P(1)	Rh	C(B1)	139.79 (20)
P(1)	Rh	B(C8)	120.69 (20)
B(C7)	Rh	C(B2)	43.24 (26)
B(C7)	Rh	C(B1)	72.96 (27)
B(C7)	Rh	B(C8)	42.28 (27)
C(B2)	Rh	C(B1)	41.63 (26)
C(B2)	Rh	B(C8)	73.78 (27)
C(B1)	Rh	B(C8)	76.77 (28)

[a] Standard deviations in parentheses.

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(18) Hawthorne, M. F.; Young, D. C.; Andrews, T. J.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

(19) Busby, D.; Hawthorne, M. F. *Inorg. Chem.* **1982**, *21*, 4101.

Table III. Selected Distances (Å) in [Me$_4$N][*closo*-2,2-(PPh$_3$)$_2$-2,1,7-RhC$_2$B$_9$H$_{11}$]

from	to	dist^a	from	to	dist^a
Rh	P(1)	2.220 (2)	B(12)	B(11)	1.813 (15)
Rh	P(2)	2.266 (2)	B(12)	B(10)	1.775 (15)
Rh	C(7)	2.442 (9)	B(12)	B(9)	1.748 (17)
Rh	B(3)	2.269 (11)	B(12)	H(12)	1.06 (9)
Rh	B(11)	2.221 (10)	B(11)	B(6)	1.827 (14)
Rh	C(1)	2.340 (9)	B(11)	B(10)	1.792 (15)
Rh	B(6)	2.229 (10)	B(11)	H(11)	0.93 (7)
P(1)	C(11)	1.837 (5)	C(1)	B(6)	1.665 (14)
P(1)	C(21)	1.836 (5)	C(1)	B(4)	1.665 (14)
P(1)	C(31)	1.837 (5)	C(1)	B(5)	1.716 (14)
P(2)	C(41)	1.843 (5)	C(1)	H(1)	1.14 (8)
P(2)	C(51)	1.843 (5)	B(6)	B(10)	1.774 (14)
P(2)	C(61)	1.827 (5)	B(6)	B(5)	1.800 (16)
C(7)	B(3)	1.651 (14)	B(6)	H(6)	1.13 (7)
C(7)	B(8)	1.663 (15)	B(10)	B(9)	1.782 (16)
C(7)	B(12)	1.675 (13)	B(10)	B(5)	1.768 (16)
C(7)	B(11)	1.641 (13)	B(10)	H(10)	0.85 (8)
C(7)	H(7)	0.93 (7)	B(9)	B(4)	1.765 (17)
B(3)	B(8)	1.801 (15)	B(9)	B(5)	1.730 (17)
B(3)	C(1)	1.700 (14)	B(9)	H(9)	0.94 (6)
B(3)	B(4)	1.810 (16)	B(4)	B(5)	1.761 (17)
B(3)	H(3)	1.16 (8)	B(4)	H(4)	1.06 (10)
B(8)	B(12)	1.743 (15)	B(5)	H(5)	1.18 (8)
B(8)	B(9)	1.756 (17)	N	CMe(1)	1.47 (2)
B(8)	B(4)	1.759 (17)	N	CMe(2)	1.52 (2)
B(8)	H(8)	0.86 (9)	N	CMe(3)	1.47 (2)
			N	CMe(4)	1.51 (2)

^{a}Standard deviations in parentheses.

slip parameters of the aforementioned Pt complex and the (PMe$_3$)$_2$Pd complex. The respective values of Δ = 0.42 and 0.26 Å are in accord with the larger d–p promotion energy of Pt compared to that of Pd. Seen in the light of the foregoing structural observations and structural predictions based on theory, it is possible to rationalize the closo structure adopted by **2a**$^-$ (Δ = 0.05 Å) on the basis of the smaller d–p promotion energy of Rh compared to those of Pt and Pd and the combined effects of the greater π-acid strength and weaker σ-donating capabilities of triphenylphosphine ligands compared to those of trialkylphosphine ligands.

The Rh–P(1) bond length, 2.257 Å, and the Rh–P(2) bond length, 2.233 (2) Å, in **2a**$^-$ can be compared to other Rh(I)–P bond lengths of 2.304 (4) and 2.338 (4) Å found for the mutually trans triphenylphosphine ligands in the orange allotrope of [RhCl(PPh$_3$)$_3$][20] and to values of 2.225 (4) Å for a triphenylphosphine ligand trans to a chloride ligand in the same crystal. The Rh–P bond lengths of **2a**$^-$ are shorter than the average Rh–P bond length found in complex **1a** of 2.329 Å[21] and reflect the increased rhodium–phosphorus back-bonding in **2a**$^-$ as a result of its lower formal oxidation state and negative charge. The Rh–P$_2$ plane lies almost perpendicular to the least-squares plane that passes through the bonding face of the carborane ligand, and the Rh–P$_2$ moiety is found to be parallel to a line joining the two ortho carbon atoms of the carborane ligand, an observation that is strictly in accord with the theoretical studies by Mingos[7e] briefly reiterated below.

The crystal displays an unusual disorder in which the carborane ligand adopts one of two orientations in a 54:46 ratio corresponding to a rotation of this ligand by an angle of $4\pi/5$ rad about an axis through the rhodium atom and the apical boron atom. On the basis of thermal parameters and bond lengths, one of the atoms of the C$_2$B$_3$ bonding face was identified as B(4) and each orientation was constrained so that the Rh atom is bound to the same B(4) atom; additionally, the carbon atom positions were constrained to be identical with those of the remaining disorder-related boron atoms in the bonding face of the carborane ligand in the two orientations.

Table IV. Selected Angles (deg) in [Me$_4$N][*closo*-2,2-(PPh$_3$)$_2$-2,1,7-RhC$_2$B$_9$H$_{11}$]

from	through	to	angle^a
P(1)	Rh	P(2)	98.2 (1)
P(1)	Rh	C(7)	123.7 (2)
P(2)	Rh	C(7)	116.4 (2)
P(1)	Rh	B(3)	164.5 (3)
P(2)	Rh	B(3)	91.1 (3)
C(7)	Rh	B(3)	40.8 (3)
P(1)	Rh	B(11)	94.8 (3)
P(2)	Rh	B(11)	156.7 (3)
C(7)	Rh	B(11)	40.9 (3)
B(3)	Rh	B(11)	72.4 (3)
P(1)	Rh	C(1)	142.8 (3)
P(2)	Rh	C(1)	105.5 (2)
C(7)	Rh	C(1)	69.8 (3)
B(3)	Rh	C(1)	43.3 (4)
B(11)	Rh	C(1)	74.1 (4)
P(1)	Rh	B(6)	103.7 (3)
P(2)	Rh	B(6)	143.8 (3)
C(7)	Rh	B(6)	73.9 (3)
B(3)	Rh	B(6)	74.8 (4)
B(11)	Rh	B(6)	48.5 (4)
C(1)	Rh	B(6)	42.6 (4)
Rh	P(1)	C(11)	119.8 (2)
Rh	P(1)	C(21)	119.0 (2)
Rh	P(1)	C(31)	114.2 (2)
C(11)	P(1)	C(21)	96.7 (3)
C(11)	P(1)	C(31)	99.2 (3)
C(21)	P(1)	C(31)	104.7 (3)
Rh	P(2)	C(41)	117.6 (2)
Rh	P(2)	C(51)	108.7 (2)
Rh	P(2)	C(61)	125.7 (2)
C(41)	P(2)	C(51)	102.2 (3)
C(41)	P(2)	C(61)	97.6 (3)
C(51)	P(2)	C(61)	101.8 (3)
CMe(1)	N	CMe(2)	109 (1)
CMe(1)	N	CMe(3)	114 (1)
CMe(1)	N	CMe(4)	102 (1)
CMe(2)	N	CMe(3)	113 (1)
CMe(2)	N	CMe(4)	110 (1)
CMe(3)	N	CMe(4)	109 (1)

^{a}Standard deviations in parentheses.

The six oxygen atoms of the crown ether lie alternately 0.16–0.21 Å above and below their mean plane so that the coordination polyhedron around K$^+$ is a very flat octahedron (K···O = 2.754–2.815 (6) Å), very similar to that found in the potassium thiocyanate complex of 1,4,7,10,13,16-hexaoxacyclooctadecane (K···O = 2.770–2.833 Å).[22] Potassium is 0.3 Å away from this plane. The coordination sphere of potassium is completed by oxygen from water (K···O = 2.82 (1) Å) and oxygen from the methyl ethyl ketone solvate (K···O = 2.688 (8) Å), completing a distorted hexagonal bipyramid. Within the crown ether the C–C distances are somewhat short (1.47–1.49 (2) Å), probably because of internal motion in the ring. Bond angles at O (112.6–114.5 (9)°) are larger than those at C (108.1–110 (9)°).

The source of the water solvate in this crystal is not known. Although the crystallization solvents, methyl ethyl ketone and 2-propanol, were ostensibly distilled from appropriate drying agents, these particular solvents are well-known for their hygroscopic nature. Moreover, the 18-crown-6, which is known to complex many small neutral polar molecules containing acidic H atoms such as H$_2$O, was not rigorously purified prior to its use. In any case the presence of these solvates in conjunction with the K[18-crown-6]$^+$ cation was instrumental in the isolation of this single crystal inasmuch as single crystals of **2a**$^-$ were not available with other cations. In general, it was observed that the presence of moisture in the solutions containing **2a**$^-$ lead to decomposition, but in this case the affinity of the cation for the water solvate and the rapid rate of single-crystal growth (5 min) apparently attenuated the ruinous effects of moisture in these solutions and

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(20) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655.

(21) Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 264.

(22) Seiler, P.; Dobler, M.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, B30, 2744.

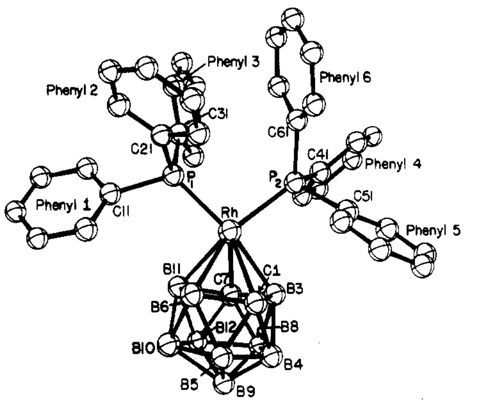

Figure 5. Structure of the anion of $[Me_4N][\mathbf{2b}]$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

favorably contributed to the lattice energy of this single crystal.

Description of the Molecular Structure of $[Me_4N][\mathbf{2b}]$. The salt $[Me_4N][\mathbf{2b}]$ crystallizes from acetone/ether as unsolvated red prisms. An ORTEP projection of the anion is shown in Figure 5. Tables III and IV, respectively, list selected interatomic distances and selected interatomic angles in this salt.

The structural analysis shows that this d^8-rhodacarborane anion adopts a significantly distorted icosahedral structure unlike its 3,1,2 counterpart. The C_2B_3 face shows a significant deviation from planarity with the carbon atoms bent back into the cage and away from the metal. This geometry allows the cage carbon atoms to bond only weakly to the rhodium and to tend toward their preferred cage coordination number of four.[23] The Rh–C(1) bond length, 2.340 (9) Å, and the Rh–C(7) bond length, 2.442 (9) Å, compare with 2.269 (11), 2.229 (10), and 2.221 (10) Å for the Rh–B(3), Rh–B(6) and Rh–B(11) bond lengths, respectively, and the slip parameter,[7d] Δ, equals -0.13 Å. The nonplanarity of this C_2B_3 face can be further described in terms of the angle between the normals to the planes C(1)–B(6)–B(11)–C(7) and C(1)–B(3)–C(7), 15.7°. The plane containing the RhP_2 moiety intersects the C_2B_3 face nearly perpendicularly, and the RhP_2 plane is nearly parallel to the (noncrystallographic) mirror plane in the carborane ligand passing through B(3), the midpoint between B(6) and B(11), and B(9), the apical boron atom. This is the same metal vertex conformation found in $[\textit{closo}\text{-}2,2\text{-}(PPhMe_2)_2\text{-}1,7\text{-}(CH_3)_2\text{-}2,1,7\text{-}PtC_2B_9H_{11}]$[7c] and is calculated to be the preferred conformation.[7e] Thus, the coordination of the rhodium atom can be described in terms of an approximately square-planar geometry with the mutually cis phosphorus atoms lying trans to B(3) and the midpoint of the B(6) and B(11) bond. The Rh–P(1) bond length, 2.220 (2) Å, and the Rh–P(2) bond length, 2.266 (2) Å, reflect an appreciable difference in the trans influence of a single boron atom compared to that of a boron–boron bond. This difference is also seen in the low-temperature $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{2b}^-$ (see Figure 2). It is likely that the more strongly bound P(1) atom gives rise to the lower field doublet with the large coupling constant, $J_{Rh-P} = 242$ Hz, while the lower field doublet with the smaller coupling constant, $J_{Rh-P} = 186$ Hz, is due to P(2).

The crystal structures of $\mathbf{2a}^-$ and $\mathbf{2b}^-$, for the first time, present the opportunity to compare the effects of introducing identical d^8 metal fragments into the isomeric $[\textit{nido}\text{-}7,8\text{-}$ and $\textit{nido}\text{-}7,9\text{-}C_2B_9H_{11}]^{2-}$ ligands. The results obtained from these studies indicate that larger polyhedral distortions will occur for d^8-metallacarboranes derived from $[\textit{nido}\text{-}7,9\text{-}C_2B_9H_{11}]^{2-}$ than will occur for the corresponding metallacarboranes derived from $[\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$. This view is supported by a theoretical comparison[7e] of the electronic structures of the hypothetical molecules $[3,3\text{-}(PH_3)_2\text{-}3,1,2\text{-}PtC_2B_9H_{11}]$ and $[2,2\text{-}(PH_3)_2\text{-}2,1,7\text{-}PtC_2B_9H_{11}]$, which are isoelectronic with $\mathbf{2a}^-$ and $\mathbf{2b}^-$, respectively. In addition, the observed rotational orientation of the $(PPh_3)_2Rh$ vertex with respect to the bonding faces of the 7,8- and 7,9-dicarbollide ligands is precisely that predicted from the LUMO–HOMO interactions described by Mingos.[7e]

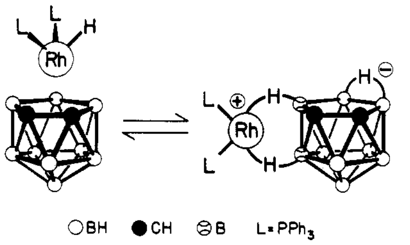

Figure 6. Representation of exo-nido–closo equilibrium associated with $[\textit{closo}\text{-}3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$.

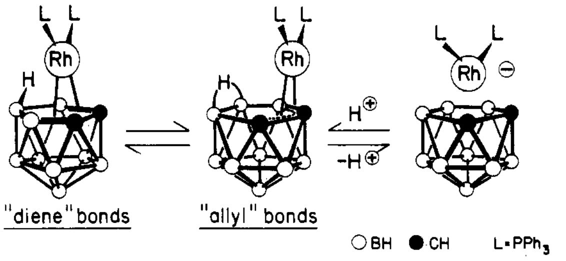

Figure 7. Representation of possible thermodynamically unstable tautomers of **1a** generated by kinetically controlled protonation of $\mathbf{2a}^-$ at low temperature.

Protonation and Deuteration of $\mathbf{2a}^-$, $\mathbf{2b}^-$, and $\mathbf{2c}^-$. Recently published results[3f] have shown that species such as **1a–c** are efficient catalyst precursors for alkene hydrogenation and other reactions. The effective catalysts in these systems were demonstrated to be Rh(1+)-containing tautomers derived from the closo Rh(3+) precursors by rapid and reversible reductive elimination. The Rh(1+) tautomers were formulated[3] as exo-nido species in which a $(PPh_3)_2Rh^+$ center was firmly attached to a $[\textit{nido}\text{-}C_2B_9H_{12}]^-$ ion through a pair of B–H–Rh bridge bonds as shown in Figure 6. Conceivably, other less stable Rh(1+) tautomers, based upon prototropic reactions, could have been involved as the true catalyst species as shown in Figure 7. Thus, it was of interest to protonate salts of $\mathbf{2a}^-$ to determine whether any neutral Rh(1+) rhodacarborane intermediates could be detected prior to the formation of **1a**. Accordingly, we have treated salts of $\mathbf{2a}^-$ and $\mathbf{2b}^-$ with protio and deuterio acids at room temperature and low temperatures.

Salts of $\mathbf{2a}^-$, $\mathbf{2b}^-$, and $\mathbf{2c}^-$ each react with dilute mineral acids in ethanol to quantitatively produce the respective hydrido complexes **1a**, **1b**, and **1c**. It was further observed that salts of $\mathbf{2c}^-$ reacted with ethanol in the absence of excess hydroxide ion to produce **1c** while salts of $\mathbf{2a}^-$ and $\mathbf{2b}^-$ each reacted with methanol in the absence of excess hydroxide ion to regenerate **1a** and **1b**, respectively. It appears that complexes **1a**, **1b**, and **1c** are comparable in acid strength to primary alcohols and $\mathbf{2c}^-$ is slightly more basic than $\mathbf{2a}^-$ or $\mathbf{2b}^-$. Salts of complexes $\mathbf{2a}^-$, $\mathbf{2b}^-$, and $\mathbf{2c}^-$ each react in ethanol-*d* with excess D_3PO_4 to produce the respective deuterio complexes. The IR spectra of the deuterio complexes so produced show weak absorptions at 1520 cm^{-1} corresponding to ν_{Rh-D}. Furthermore, the ^1H NMR spectra of these products do not display any high-field rhodium hydride resonances.

Treatment of solutions of $[Et_4N][\mathbf{2a}]$ (THF or CH_2Cl_2 solution) with CF_3CO_2H at -73 °C immediately and quantitatively produced **1a** as judged by the ^1H and $^{31}P\{^1H\}$ NMR spectra of these solutions, and there was no indication of formation of B–H–B bonds. Thus, we were unable to observe neutral Rh(I) species in these protonation reactions although these experiments established an expedient route to isotopically pure Rh–D catalyst precursors.

In a further attempt to establish whether the carborane ligand in $\mathbf{2a}^-$ could compete with the rhodium vertex for an electrophile at very low temperatures, $K[\mathbf{2a}]$ was treated with 0.97 molar equiv

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(23) Evans, W. J.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 4565.

of Br_2 in CH_2Cl_2 at −78 °C for 3 h. After the solution was allowed to warm to room temperature, the known complex [*closo*-3,3-$(PPh_3)_2$-3-(Br)-3,1,2-$RhC_2B_9H_{11}$][4] was isolated in 90% yield as determined from its characteristic $^{31}P\{^1H\}$ NMR and IR spectra. Since B–Br bonds, if once formed under these conditions, should remain intact, this again demonstrates that the metal vertex of **2a**$^-$ is the most nucleophilic center of this anion. It is noteworthy that the preparation of the bromo complex mentioned here is currently the preferred route to this species.

Reactions of Salts of 2a$^-$, 2b$^-$, and 2c$^-$ with π-Acceptor Ligands L (L = CO, C_2H_4). Treatment of THF or CH_2Cl_2 solutions of $[Et_4N]$[**2a**] with carbon monoxide (1 atm, 25 °C) produced orange solutions of $[Et_4N]$[*closo*-3-(PPh_3)-3-(CO)-3,1,2-$RhC_2B_9H_{11}$] ($[Et_4N]$[**3a**]). This salt can be isolated in good yields as a crystalline analytically pure orange salt. The same salt is directly produced by the reaction of complex **1a** with $[Et_4N]OH$ in THF/ethanol under a carbon monoxide atomosphere. The IR spectrum of $[Et_4N]$[**3a**] displays absorptions expected to arise from the cation, the dicarbollide ligand, and the triphenylphosphine ligand. Additionally, an intense absorption at 1910 cm^{-1} is assigned to ν_{CO}. This frequency is rather low and suggests significant back-bonding from the anionic rhodium (1+) vertex to π^* orbitals on the carbonyl ligand. In comparison, the neutral rhodium (1+) species *trans*-$RhCl(CO)(PPh_3)_2$ exhibits ν_{CO} at 1974 cm^{-1}[24] and the anionic species [*n*-Bu_4N][$Rh(CO)(PEt_3)$(mnt)] (mnt = maleonitriledithiolate) exhibits ν_{CO} at 1945 cm^{-1}.[25] The ^1H, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectral data are not unusual and are given in the Experimental Section. The isomeric, crystalline, analytically pure salts $[Et_4N]$[**3b**] and $[Et_4N]$[**3c**] can be similarly prepared from the respective isomeric hydrido complexes **1b** and **1c** and display comparable spectral features.

Dilute solutions of **1a** in THF/ethanol also react with ethylene (1 atm, 25 °C) in the presence of $[Et_4N]OH$ to produce $[Et_4N]$[*closo*-3-(PPh_3)-3-$(\eta^2$-$C_2H_4)$-3,1,2-$RhC_2B_9H_{11}$] ($[Et_4N]$[**4a**]) in good yields as a crystalline analytically pure salt. Similarly, complex **1b** reacts with K[18-crown-6]OH in THF/ethanol to produce the crystalline analytically pure salt K[18-crown-6][*closo*-2-(PPh_3)-2-$(\eta^2$-$C_2H_4)$-2,1,7-$RhC_2B_9H_{11}$] (K[18-crown-6][**4b**]) in good yields. Other salts of **4a**$^-$ and **4b**$^-$ could be similarly prepared, and in order to simplify the interpretation of the ^1H NMR spectra of these salts, [PPN][**4a**] and [PPN][**4b**] were prepared. The ^1H NMR spectra of CD_2Cl_2 solutions of [PPN][**4a**] displays the resonances expected to arise from the phenyl protons of the cation and triphenylphosphine ligands and the two equivalent carboranyl C–H protons. Additionally, one observes an apparent triplet at 1.46 ppm (H_1) and a doublet at 2.40 ppm (H_2). These resonances are assigned to the coordinated olefin. Cooling this solution to −73 °C did not change the ^1H NMR spectrum. Decoupling experiments showed that H_2 was coupled to H_1 ($J_H - J_H = 9$ Hz) while H_1 was coupled to H_2 and the phosphorus nucleus ($J_{P-H} = 7$ Hz). It is noteworthy that the olefinic resonances of the related complex $(\eta^5$-$C_5H_5)Rh(\eta^2$-$C_2H_4)(PMe_3)$ give rise to a very similar spectrum.[26] The ^1H NMR spectrum of [PPN][**4b**] at −23 °C is qualitatively similar to the room-temperature spectrum of [PPN][**4a**]; however, warming a CD_2Cl_2 solution of [PPN][**4b**] to 37 °C causes a complete disappearance of the olefinic resonances, indicating that an exchange process is occurring and that this temperature is very near the coalescence temperature. Attempts to obtain a high-temperature limiting spectrum were frustrated by sample decomposition at slightly elevated temperatures. From the low-temperature limiting spectrum of [PPN][**4b**] and the estimated coalescence temperature of 310 K, one calculates an activation barrier for the process to be 14.3 ± 0.5 kcal·mol^{-1}. Due to sample decomposition of [PPN][**4a**] at slightly elevated temperatures it was not possible to reliably measure the coalescence temperature for the same process in this salt, but this barrier is qualitatively greater than that observed in [PPN][**4b**] and is probably larger than 15 kcal·mol^{-1}.

Dynamic solution behavior is commonly observed in transition-metal–ethylene complexes and has generally been rationalized in terms of a propeller-like rotation of the olefin about the metal–olefin σ-bond axis. The magnitude of the barrier is a function of the π-bond strength between the metal and olefin, which in turn is expected to increase with the electron density at the metal atom. For example, the activation barrier observed for olefin rotation in the neutral complex $(\eta^5$-$C_5H_5)Rh(\eta^2$-$C_2H_4)_2$ is 15.7 kcal·mol^{-1},[27] while the barrier to olefin rotation observed in the cationic complex $[Os(CO)(NO)(\eta^2$-$C_2H_4)(PPh_3)_2][PF_6]$ is 9.5 kcal·mol^{-1}.[28] The activation barriers observed in **4a**$^-$ and **4b**$^-$ indicate the presence of a moderately strong π bond and indicate that this bond is slightly stronger in **4a**$^-$ than in **4b**$^-$. That the ethylene ligand is more tightly bound in **4a**$^-$ than **4b**$^-$ is a reflection of the greater electron density at the metal center of **4a**$^-$ than the metal center of **4b**$^-$ and is consistent with the idea that the 7,9-dicarbollide ligand has greater π-electron acceptor properties compared to those of its 7,8-isomer and competes more effectively with ethylene for π-electron density.

Iridacarborane Anions. In light of the observed reactivity of complexes **1a**, **1b**, and **1c** with moderately strong Brønsted–Lowry bases it was of interest to examine the reactivity of the iridium congener of **1a**, namely **5a**,[29] toward several Brønsted–Lowry bases. On the basis of the stronger bond strengths found in third-row transition-metal complexes compared to those in their second-row counterparts, **5a** would be expected to be less acidic than **1a**. Moreover, it is anticipated that anions derived from **5a** might exhibit enhanced nucleophilicity due to the greater radial extension of an electron pair in a 5d orbital compared to that of electrons in lower lying 4d orbitals. Described briefly below are some preliminary observations on the reactivity of **5a**.

Tetrahydrofuran solutions of **5a** were unreactive toward ethanolic KOH at room temperature. It was observed that **5a** reacts with potassium hydride in THF at room temperature to produce a red anionic species, **6a**$^-$. The addition of excess ethanol to these red solutions rapidly regenerates **5a**. On the basis of these observations, this red anion is formulated as [*closo*-3,3-$(PPh_3)_2$-3,1,2-$IrC_2B_9H_{11}]^-$. A crude $[PPN]^+$ salt of **6a**$^-$ can be obtained by metathesis of [PPN]Cl and K[**6a**] in THF, but an analytically pure salt was not obtained.

While complex **1a** reacts with K-Selectride in THF to produce H_2 and **2a**$^-$, complex **5a** exhibits a different reactivity towards K-Selectride. The addition of a slight excess of a THF solution of K-Selectride to a THF solution of **5a** containing 1 molar equiv of dibenzo-18-crown-6 at 0 °C rapidly gives rise to a colorless solution, which over a period of several hours turns to red. If this reaction is quenched before the solution darkens, by the addition of dry pentane to the reaction, a white solid precipitates from solution. The ^1H NMR spectrum of freshly prepared acetone-d_6 solutions of this product displays a double Ir–H resonance at −11.7 ppm ($J_{P-H} = 29$ Hz) and resonances expected to arise from the triphenylphosphine ligand and a K[dibenzo-18-crown-6]$^+$ cation. These data suggest that this white material should be formulated as K[dibenzo-18-crown-6][*closo*-3-(PPh_3)-3,3-$(H)_2$-3,1,2-$IrC_2B_9H_{11}$] (K[dibenzo-18-crown-6][**7a**]). The rhodium analogue of **7a**$^-$ is apparently unstable.

The iridium congener of **3a**$^-$, namely [*closo*-3-(PPh_3)-3-(CO)-3,1,2-$IrC_2B_9H_{11}]^-$, can be isolated from the reaction of PPN[*closo*-3,1,2-$TlC_2B_9H_{11}$] and *trans*-$IrCl(CO)(PPh_3)_2$ in THF as an analytically pure yellow crystalline salt, [PPN][**8a**]. A similar reaction of sodium cyclopentadienide and Vaska's complex in refluxing benzene produced $(\eta^5$-$C_5H_5)Ir(PPh_3)(CO)$ in 60% yield.[30] The IR spectrum (Nujol) of [PPN][**8a**] displays an intense terminal carbonyl absorption at 1875 cm^{-1}, which is, as expected, lower in frequency than the corresponding absorption

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[24] Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun. J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430.

[25] Cheng, C. H.; Eisenberg, R. *Inorg. Chem.* **1979**, *18*, 1418.

[26] Werner, H.; Feser, R. *Angew. Chem.* **1979**, *91*, 171.

[27] Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.

[28] Segal, J. A.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1975**, 677.

[29] Paxson, T. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 4674.

[30] Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2653.

in **3a**$^-$ and much lower than the value of 1944 cm^{-1} recorded for the corresponding absorption in the cyclopentadienyl-iridium complex mentioned above.

Conclusions

Thus far, this study has developed the syntheses of formal 18 e, Rh^{I} *closo*-metallacarborane monoanions that contain LL′Rh vertices with L = L′ = PPh$_3$, L = PPh$_3$ and L′ = CO, and L = PPh$_3$ and L′ = η^2-C$_2$H$_4$. Structural correlations were made with theory by means of X-ray diffraction studies, and the fluxional character of representative systems was established. In the following paper we describe the use of the *closo*-rhodacarborane anions described here as reagents for the further synthesis[12] of representative alkyl, acyl, and η^3-allyl Rh(3+) *closo*-metallacarboranes.

Experimental Section

General Techniques. All manipulations were carried out under an atmosphere of high-purity nitrogen in standard Schlenk apparatus or in a Vacuum Atmospheres inert-atmosphere glovebox. All solvents were purified and distilled from appropriate drying agents.[31] Complexes **1a**, **1b**,[29] **1c**,[19] and **5a**[29] were prepared as previously described. The complex *trans*-IrCl(CO)(PPh$_3$)$_2$ was prepared by using Collman's procedure.[32] 18-crown-6 was purchased from Aldrich Chemical Co. and used as received. [PPN]Cl[33] and Tl[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$][34] were prepared by using literature procedures. K-Selectride was available as a 1 M THF solution from Aldrich Chemical Co. Carbon monoxide and ethylene were obtained from Air Products and used directly from the cylinder. IR spectra were obtained as Nujol mulls on a Perkin-Elmer 137 instrument. The 200.133 MHz ^{1}H and 81.02 MHz ^{31}P{^{1}H} FT NMR spectra were recorded on a Bruker WP-200 spectrometer. ^{11}B NMR spectra were recorded at 80.5, 111.80, and 127.01 MHz on an instrument designed and constructed by Professor F. A. L. Anet and co-workers at UCLA. ^{11}B chemical shifts were referenced to external BF$_3$·OEt$_2$ where positive shifts refer to lower field. ^{31}P chemical shifts were referenced to external 85% D$_3$PO$_4$ and are uncorrected. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Li[2a]. To a suspension of 0.806 g (1.06 mmol) of **1a** in 25 mL of benzene and 25 mL of diethyl ether was added 2.0 mL of butyllithium (2.5 M solution in hexane; 5.00 mmol). After 2 h, the initial yellow suspension was replaced by a red-brown solution and brown crystalline flakes of Li[**2a**]. The air-sensitive solid was isolated by filtration, washed with dry ether followed by pentane, and dried in vacuo. ^{11}B{^{1}H} NMR (THF, 25 °C): −9.57 (1), −13.97 (2), −15.45 (4), −25.2 (2) ppm.

Preparation of K[2a]. To a solution of 0.350 g (0.46 mmol) of **1a** in 25 mL of THF was added 1.0 mL of K-Selectride (1 M in THF; 1.0 mmol), instantly producing a deep red solution. After 30 min, 40 mL of dry pentane was slowly added, quantitatively precipitating an air-sensitive brown microcrystalline solid. The crystals were isolated by filtration, washed several times with pentane, and then dried in vacuo.

Preparation of K[18-crown-6][2a]. To a homogeneous solution of 1.5 g (5.6 mmol) of 18-crown-6 and 1.0 g (15.1 mmol) of KOH in 250 mL of THF and 30 mL of absolute ethanol was added 3.00 g (3.94 mmol) of **1a**. After 2 h, the resultant dark red solution was concentrated in vacuo to 75 mL. An additional 200 mL of absolute ethanol was then added, producing a large crop of air-sensitive golden crystalline flakes. The crystals were isolated by filtration and thoroughly washed with ethanol and ether. Yield: 3.1 g (74%). Mp: 95–97 °C dec. ^{31}P{^{1}H} NMR (THF/benzene-d_6, 25 °C): 47.3 (d, $J_{\text{Rh-P}}$ = 197 Hz) ppm.

Preparation of [R$_4$N][2b] (R = Me, Et, *n*-Bu). To a solution of 1.0 g of KOH dissolved in 100 mL of THF and 30 mL of absolute ethanol was added 0.407 g (0.53 mmol) of **1b**, instantly producing a cherry red solution. After 4 h, the red solution was filtered into a solution of 5.0 g of [R$_4$N]X (R = Me, Et, *n*-Bu; X = Cl, Br) in 300 mL of O$_2$-free, distilled water. The resultant orange precipitate was isolated and thoroughly washed with absolute ethanol and water. Yield: 85%. A crystalline analytically pure sample of the [Et$_4$N]$^+$ salt of **2b**$^-$ was obtained by recrystallizing the reaction product two times from acetone/ether and was found to contain approximately two acetone solvates per molecule of complex. Anal. Calcd for C$_{52}$H$_{73}$N$_1$Rh$_1$P$_2$B$_9$O$_2$: C, 62.06; H, 7.30; N, 1.39; Rh, 10.22; P, 6.15; B, 9.67. Found: C, 62.13; H, 7.17; N, 1.64; Rh, 10.21; P, 6.44; B, 9.68. ^{31}P{^{1}H} NMR (acetone/benzene-d_6, 25 °C): 51.7 (d, $J_{\text{Rh-P}}$ = 212 Hz) ppm.

Table V. Details of Crystallographic Data Collection

compd	[Me$_4$N][**2b**]	K[18-crown-6][**2a**]·C$_4$H$_8$O·H$_2$O
temp/C	25	25
cryst size/mm	0.4 × 0.4 × 0.8	0.16 × 0.35 × 0.33
normal to faces	110, 1$\bar{1}$0, 001	01$\bar{1}$, 011, $\bar{2}\bar{1}\bar{1}$
appearance	dark red parallelepipeds	red prisms
diffractometer	Picker FACS-1	Syntex P$\bar{1}$
radiation	Mo Kα (Zr filter)	Mo Kα (graphite monochromator)
wavelength/Å	0.71069	0.71069
space group	$P\bar{1}$	$P2_1/c$
a/Å	12.355 (13)	13.931 (4)
b/Å	14.896 (16)	19.954 (5)
c/Å	15.186 (22)	21.665 (7)
α/deg	68.00 (9)	
β/deg	102.86 (6)	100.97 (2)
γ/deg	112.17 (5)	
V/Å^3	2389	5913
Z	2	4
ρ(calcd)/g·cm^{-3}	1.16	1.26
ρ(measd)/g·cm^{-3}	1.23	
μ/cm^{-1}	3.99	4.5
range of transmission factors	0.8468–0.9220	0.9272–0.9668
scan width	2.0(1 + 0.692 tan θ)	1.0 below Kα_1, 1.0 above Kα_2
scan rate/deg·*min*$^{-1}$	2	6
no. of unique reflcns	6180	10521
no. of observed ($I > 3\sigma(I)$) reflcns	4761	6149
2θ max/deg	45	50
data collcd	$\pm h,\pm k,l$	$h,k,\pm l$
no. of params refined	266	418
R	0.0632	0.062
R_w	0.0668	0.072
GOF	1.64	1.81

Preparation of [Me$_4$N][2c]. To a solution of 0.300 g (0.39 mmol) of complex **1c** in 30 mL of THF was added 0.02 g (0.5 mmol) of KH. One drop of absolute ethanol was then added to the reaction mixture, producing an immediate color change from yellow to red. After 12 h, 0.3 g (1.8 mmol) of [Me$_4$N]OH·5H$_2$O was added as a solid and the reaction was stirred an additional 12 h. The solution was then filtered, and all of the solvent was removed in vacuo. The orange semisolid substance remaining was then dissolved in 15 mL of CH$_3$CN and filtered. Addition of ether precipitated an orange powder and some red crystals. The solvent was then decanted off, and the solid material remaining was washed with benzene and ether. Recrystallization of this material from acetone/ether gave 0.3 g (85%) of beautiful red crystals that contain one acetone solvate per molecule of complex. Mp: 121–123 °C dec. Anal. Calcd for C$_{45}$H$_{59}$N$_1$Rh$_1$P$_2$B$_9$O$_1$: C, 60.57; H, 6.66; N, 1.57; Rh, 11.53; P, 6.94; B, 10.90. Found: C, 60.83; H, 6.74; N, 1.82; Rh, 11.08, P 7.26; B, 11.14. ^{11}B{^{1}H} NMR (acetone, 25 °C): −10.87 (2), −14.60 (1), −17.12 (2), −23.87 (2), −25.08 (2) ppm. ^{31}P{^{1}H} NMR (THF/acetone-d_6, 25 °C): 48.9 (d, $J_{\text{Rh-P}}$ = 185 Hz) ppm.

Preparation of [Et$_4$N][3a]. To a suspension of 1 g (15 mmol) of KOH and 0.5 g (2.4 mmol) of tetraethylammonium bromide in 200 mL of THF and 20 mL of absolute ethanol was added 1.50 g (1.97 mmol) of **1a**. The reaction mixture was then saturated with CO and stirred under a CO atmosphere for 24 h. The orange solution was filtered and concentrated to 40 mL. An additional 200 mL of ethanol was added, producing an air-sensitive orange precipitate. This solid was isolated, washed successively with ethanol, benzene, and ether, and dried in vacuo. Yield: 1.5 g (78%). Analytically pure, unsolvated material was obtained by several recrystallizations of the reaction product from CH$_2$Cl$_2$/absolute ethanol. Anal. Calcd for C$_{29}$H$_{46}$NRhB$_9$O: C, 53.11; H, 7.06; N, 2.13; Rh, 15.69; P, 4.72; B, 14.83. Found: C, 52.82; H, 7.36; N, 2.38; Rh, 15.23; P, 4.95; B, 14.89. ^{11}B{^{1}H} NMR (THF, 25 °C): −10.75 (1), −13.75 (5), −24.34 (3) ppm. ^{31}P{^{1}H} NMR (THF/benzene-d_6, 25 °C): 34.1 (d, $J_{\text{Rh-P}}$ = 156 Hz) ppm. IR: ν_{CO} 1910 cm^{-1}.

Preparation of [Et$_4$N][3b]. This complex was obtained in 81% yield from **1b** by using the procedure described for the preparation of [Et$_4$N][3a]. Anal. Calcd for C$_{29}$H$_{46}$NRhPB$_9$O: C, 53.11; H, 7.06; N, 2.13; Rh, 15.69; P, 4.72; B, 14.83. Found: C, 53.08; H, 7.24; N, 2.34;

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(31) Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley-Interscience: New York, 1972; p 434.

(32) Collman, J. P.; Sears, C. T.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

(33) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(34) Smith, H. D., Jr.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 2312.

Table VI. Positions of Atoms for K[18-crown-6][**2a**]·$C_4H_8O \cdot H_2O$[d]

(a) Refined with Anisotropic Thermal Parameters

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
B(4)	0.2054 (6)	0.0267 (4)	0.1742 (4)	C(80)	0.1283 (8)	0.8343 (6)	0.9857 (6)
B(5)	0.1935 (7)	−0.0042 (4)	0.2503 (4)	C(81)	0.1290 (8)	0.7521 (6)	0.9095 (5)
B(6)	0.2051 (7)	0.0645 (5)	0.3019 (4)	C(82)	0.1783 (10)	0.6901 (7)	0.8962 (5)
B(9)	0.0857 (6)	0.0092 (4)	0.1910 (4)	O(1)	0.1541 (5)	0.6392 (3)	0.9360 (3)
B(10)	0.0881 (7)	0.0340 (5)	0.2700 (4)	O(2)	0.2020 (5)	0.5404 (3)	1.0301 (4)
B(11)	0.1104 (7)	0.1204 (5)	0.2743 (4)	O(3)	0.1867 (5)	0.5734 (4)	1.1538 (3)
B(12)	0.0355 (7)	0.0847 (5)	0.2072 (4)	O(4)	0.2051 (5)	0.7101 (4)	1.1905 (3)
C(71)	0.1975 (9)	0.5772 (7)	0.9267 (6)	O(5)	0.1527 (4)	0.8057 (3)	1.0943 (3)
C(72)	0.1627 (9)	0.5261 (6)	0.9664 (6)	O(6)	0.1679 (4)	0.7736 (3)	0.9710 (3)
C(73)	0.1756 (9)	0.4947 (5)	1.0717 (7)	O(91)	0.6243 (5)	0.3397 (4)	0.9192 (4)
C(74)	0.2232 (10)	0.5112 (6)	1.1372 (7)	O(W)	−0.0018 (8)	0.6190 (6)	0.0744 (6)
C(75)	0.2239 (10)	0.5939 (7)	1.2154 (6)	K(1)	0.1804 (1)	0.6744 (1)	0.0628 (1)
C(76)	0.1809 (9)	0.6591 (8)	1.2295 (5)	P(1)	0.2761 (1)	0.2375 (1)	0.1303 (1)
C(77)	0.1602 (8)	0.7724 (7)	1.1987 (5)	P(2)	0.3512 (1)	0.0848 (1)	0.0919 (1)
C(78)	0.1918 (9)	0.8230 (6)	1.1574 (6)	Rh(3)	0.25984 (4)	0.12900 (3)	0.15577 (2)
C(79)	0.1753 (9)	0.8539 (5)	1.0505 (6)				

(b) Not Refined with Anisotropic Thermal Parameters

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2	atom	*x/a*	*y/b*	*z/c*
C(B1)	0.2777 (6)	0.0611 (4)	0.2438 (4)	3.88 (17)	H(73B)	0.1923	0.4469	1.0619
B(C1)	0.2777 *a*	0.0611	0.2438	3.88	H(74A)	0.2992	0.5140	1.1394
C(B2)	0.2249 (5)	0.1322 (4)	0.2554 (3)	3.51 (15)	H(74B)	0.2160	0.4736	1.1685
B(C2)	0.2249 *a*	0.1322	0.2554	3.51	H(75A)	0.2186	0.5596	1.2484
B(C7)	0.1250 (6)	0.1443 (4)	0.1990 (4)	3.25 (16)	H(75B)	0.3012	0.6021	1.2206
C(B7)	0.1250 *a*	0.1443	0.1990	3.25	H(76A)	0.2020	0.6717	1.2747
B(C8)	0.1059 (6)	0.0812 (4)	0.1482 (4)	3.82 (17)	H(76B)	0.1077	0.6521	1.2205
C(B8)	0.1059 *a*	0.0812	0.1482	3.82	H(77A)	0.0855	0.7686	1.1861
C(92)	0.5094 (12)	0.3092 (8)	0.8281 (8)	14.6 (5)	H(77B)	0.1749	0.7878	1.2438
C(93)	0.5477 (11)	0.3484 (7)	0.8846 (6)	9.3 (3)	H(78A)	0.2667	0.8248	1.1648
C(94)	0.4753 (13)	0.3933 (10)	0.8969 (9)	15.3 (6)	H(78B)	0.1706	0.8708	1.1675
C(95)	0.4922 (16)	0.4203 (11)	0.9553 (11)	19.9 (8)	H(79A)	0.1531	0.8999	1.0605
H(1)	0.3670 (62)	0.0461 (42)	0.2591 (38)	*b*	H(79B)	0.2482	0.8553	1.0524
H(8)	0.0579 (61)	0.0893 (42)	0.1009 (41)		H(80A)	0.1352	0.8700	0.9547
H(12B)	−0.0409 (61)	0.1016 (45)	0.1918 (40)		H(80B)	0.0541	0.8283	0.9846
H(11)	0.0839 (63)	0.1568 (44)	0.3048 (40)		H(81A)	0.0551	0.7420	0.9048
H(2)	0.2629 (63)	0.1654 (46)	0.2823 (41)		H(81B)	0.1341	0.7883	0.8773
H(9)	0.0407 (60)	−0.0356 (44)	0.1683 (38)		H(82A)	0.2514	0.7001	0.9051
H(7)	0.1058 (66)	0.1774 (48)	0.1896 (43)		H(82B)	0.1592	0.6784	0.8503
H(10)	0.0380 (59)	0.0082 (44)	0.2985 (39)		H(92)	0.5607	0.3181	0.8062
H(4)	0.2272 (63)	−0.0082 (45)	0.1479 (39)		H(95)	0.4557	0.4083	0.9888
H(6)	0.2431 (60)	0.0605 (44)	0.3488 (39)		H(92A)	0.4432	0.3216	0.8011
H(5)	0.2147 (61)	−0.0523 (44)	0.2648 (40)		H(92B)	0.5053	0.2582	0.8358
H(71A)	0.1850	0.5640	0.8806	*c*	H(95A)	0.4940	0.4721	0.9593
H(71B)	0.2735	0.5812	0.9395		H(95B)	0.5639	0.4068	0.9788
H(72A)	0.1834	0.4810	0.9531		H(94A)	0.4067	0.3769	0.8815
H(72B)	0.0900	0.5293	0.9566		H(94B)	0.4762	0.4367	0.8630
H(73A)	0.1025	0.4960	1.0716					

[a] Positional and thermal parameters of this atom are constrained to be equal to those of the preceding atom. [b] Thermal parameters for hydrogen atoms on the carborane cage were set at 6.0 Å^2. [c] Thermal parameters for other nongroup hydrogen atoms were set at 9.0 Å^2. [d] Standard deviation in parentheses.

Rh, 15.37; P, 4.85; B, 14.57. $^{11}B\{^1H\}$ NMR (CH_2Cl_2, 25 °C): −10.75 (1), −13.27 (5), −24.34 (3) ppm. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 25 °C): 42.7 (d, J_{Rh-P} = 165 Hz) ppm. IR: ν_{CO} 1915 cm^{-1}.

Preparation of [Et_4N][3c]. This complex was obtained in 80% yield from **1c** by using the procedure described for the preparation of [Et_4N][**3a**]. Anal. Calcd for $C_{29}H_{46}NRhB_9O$: C, 53.11; H, 7.06; N, 2.13; Rh, 15.69; P, 4.72; B, 14.83. Found: C, 53.11; H, 7.26; N, 2.12; Rh, 14.85; P, 4.82; B, 14.46. $^{31}P\{^1H\}$ NMR (THF/acetone-d_6, 25 °C): 40.3 (d, J_{Rh-P} = 165 Hz) ppm. IR: ν_{CO} 1910 cm^{-1}.

Preparation of [Et_4N][4a]. To a solution of 0.500 g (0.657 mmol) of **1a** in 130 mL of THF and 60 mL of absolute ethanol were added 0.5 g (8 mmol) of KOH and 0.5 g (2.4 mmol) of [Et_4N]Br. The mixture was then stirred under an atmosphere of ethylene for 24 h, slowly producing an orange solution and white solids. The solution was filtered and concentrated in vacuo to 75 mL. An additional 150 mL of absolute ethanol was then added, precipitating an air-sensitive orange solid. This solid was isolated, washed with ethanol, benzene, and ether, and dried in vacuo. Yield: 0.30 g (70%). The analytical sample was obtained by recrystallization of this material several times from ethylene-saturated acetone/pentane solvent mixtures. Anal. Calcd for $C_{30}H_{50}NRhPB_9$: C, 54.94; H, 7.50; N, 2.14; Rh, 15.69; P, 4.72; B, 14.84. Found: C, 55.03; H, 7.50; N, 2.29; Rh, 15.25; P, 4.81; B, 15.23. $^{11}B\{^1H\}$ NMR (acetone, 25 °C): −4.51 (1), −12.42 (2), −13.54 (3), −24.16 (3) ppm. $^{31}P\{^1H\}$ NMR (THF/benzene-d_6, 25 °C): 48.0 (d, J_{Rh-P} = 183 Hz) ppm.

Preparation of K[18-crown-6][4b]. To a solution of 0.420 g (0.55 mmol) of **1b** in 40 mL of THF were added 0.32 g (4.9 mmol) of KOH and 0.5 g (1.9 mmol) of 18-crown-6 dissolved in 80 mL of absolute ethanol. The solution was then stirred under an atmosphere of ethylene for 6 h, producing a lemon yellow solution. The solution was then concentrated in vacuo to 25 mL, producing a yellow microcrystalline solid. An additional 150 mL of absolute methanol was added, causing further precipitation of the product. The yellow air-sensitive solid was isolated and dried. Yield: 0.29 g (65%). The analytical sample was obtained by recrystallizing the reaction product from CH_2Cl_2/MeOH under an atmosphere of ethylene and was found to contain approximately one methanol solvate per molecule of complex. Anal. Calcd for $C_{35}H_{58}RhPKB_9O_7$: C, 48.82; H, 6.78; Rh, 11.85; P, 3.59; K, 4.54; B, 11.30. Found: C, 48.89; H, 6.49; Rh, 11.95; P, 3.81; K, 4.88; B, 11.32. $^{11}B\{^1H\}$ NMR (CH_2Cl_2, 25 °C): −11.80 (2), −13.98 (1), −15.51 (2), −21.81 (1), −23.60 (1), −25.70 (2) ppm. $^{31}P\{^1H\}$ NMR (THF/benzene-d_6, 25 °C): 48.9 (d, J_{Rh-P} = 162 Hz) ppm.

Preparation of [PPN][8a]. To a suspension of 0.30 g (0.55 mmol) of $Tl_2C_2B_9H_{11}$ and 0.33 g (0.57 mmol) of [PPN]Cl in 100 mL of THF was added 0.440 g (0.56 mmol) of *trans*-$IrCl(CO)(PPh_3)_2$, producing a lemon yellow solution after 3 h and a precipitate of TlCl. After the solid material was allowed to settle, the solution was filtered several times to remove all of the undissolved material. The clear yellow solution was concentrated in vacuo to 25 mL.

The addition of 200 mL of absolute ethanol then produces a clean yellow solid. Yield: 0.55 g (84%). The analytical sample was obtained by recrystallization from CH_2Cl_2/ethanol and CH_2Cl_2/pentane. Anal. Calcd for $C_{57}H_{56}NP_3IrB_9O$: C, 59.35; H, 4.89; N, 1.21; P, 8.05; Ir, 16.66; B, 8.44. Found: C, 59.57; H, 5.03; N, 1.41; P 7.92; Ir, 17.00; B, 8.79. $^{31}P\{^1H\}$ NMR (acetone-d_6, 25 °C): 26.8 (s), 18.5 (s) ppm. IR: ν_{CO} 1875 cm^{-1}.

Preparation of 1a Containing Rh–D. To a suspension of 0.200 g (0.19 mmol) of K[18-crown-6][**2a**], in 15 mL of ethanol-*d* was added approximately 0.3 mL of 85% D_3PO_4, producing a yellow solid, which was isolated and washed with 3 mL of D_2O and 3 mL of ethanol-*d* and then Et_2O. The IR and ^1H NMR spectra showed that this solid is 100% Rh–D **1a** (ν_{Rh-D} = 1520 cm^{-1}). Similar procedures using salts of $\mathbf{2b}^-$ or $\mathbf{2c}^-$ produce the respective deuterio complexes.

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$]. The salt prepared from 0.500 g (0.66 mmol) of **1a** and K-Selectride was isolated, dried, and placed in a 250-mL Schlenk flask. The flask was fitted with a vacuum adapter and evacuated on a high-vacuum line. A mixture of 75 mL of CH_2Cl_2 and 32 μL (0.63 mmol) of Br_2 was freeze–pump–thaw degassed three times and then co-distilled into the liquid-nitrogen-cooled Schlenk flask. The mixture was then allowed to gradually warm to −78 °C and maintained at this temperature for 3 h. After the flask was allowed to warm to room temperature, the reactor was removed from the vacuum line and filled with dry nitrogen. The dark orange solution was filtered to remove the KBr produced and then evaporated in vacuo. The residue was then purified by a literature procedure, producing 0.49 g (90% based on **1a**) of authentic *closo*-3,3-$(PPh_3)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$.[4]

Collection and Reduction of X-ray Data for K[18-crown-6][2a]·$CH_3COC_2H_5$·H_2O. An air-stable crystal, obtained from methyl ethyl ketone/2-propanol was mounted along the *a* axis on a thin glass fiber. Preliminary oscillation and Weissenberg photographs revealed systematic absences for reflections $0k0$, $k = 2n + 1$, and for $h0l$, $h + l = 2n + 1$. The crystal was transferred to a Syntex $P\bar{1}$ diffractometer. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections ($18 < 2\theta < 24°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected in the θ–2θ scan mode. Three intense reflections (308, 323, $23\bar{3}$) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±2%, during the course of the experiment. A total of 10 521 unique reflections were measured. Of these, 6149 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects.[35]

Solution and Refinement of the Structure of K[18-crown-6][2a]·C_4H_8O·H_2O. Atoms were located by use of the heavy-atom method. In the course of refinement, all cage C and B atoms were assigned boron scattering factors and full-matrix least-squares refinement of positional and vibrational parameters for these atoms led to identification of the carbon atoms. On the basis of vibrational parameters and bond lengths, one of the atoms in the C_2B_3 face coordinated to Rh was identified as boron and the other four atoms were assigned variable occupancies of x and $1 - x$, representing pairs of C and pairs of B atoms with statistical disorder. This occupancy refined to 0.54 (4). The vibrational parameters of each of these four atoms were tied to the corresponding disorder-related atom. Because of this disorder, distances C(1)–C(2) and C(7)–C(8) are 1.64 and 1.66 Å, respectively, while the distance between C(2) and B(7) is 1.68 Å.

All calculations were performed on the VAX 11/780 of the chemistry department. All cage hydrogen atoms were located and included in the structure factor calculation. All phenyl and methylene hydrogen atoms were included in calculated positions, C–H = 1.0 Å. 418 parameters were refined, including the aforementioned occupancy parameter, positional and anisotropic thermal parameters for Rh, P, K, O, C (crown ether), and non disordered B, positional and isotropic thermal parameters for the disordered atoms and for C (solvate), positional parameters for terminal H on the icosahedron, and group and isotropic thermal parameters (C only) for the phenyl groups. The six phenyl rings of the two triphenylphosphine ligands were treated as rigid groups with C–C and C–H set at 1.39 and 1.0 Å, respectively, and all C–C–C and C–C–H angles set at 120°. Scattering factors for H were obtained from Stewart et al.[36] and for other atoms were taken from ref 37. Anomalous dispersion terms were applied to the scattering of Rh, P, and K. A final difference electron density map was essentially featureless, the maximum peak being about $^3/_4$ e/$Å^3$. Least-squares refinement converged to a final agreement factor $R = 0.062$, $R_w = 0.072$, GOF = 1.81.[38,39] Final positional and thermal parameters are given in Table VI. A table of structure factors is available.[40]

Table VII. Positional Parameters for $[Me_4N]$[**2b**]

atom	x/a	y/b	z/c	B, $Å^2$
Rh	0.29722 (6)	0.20106 (5)	0.12309 (5)	2.6^b
P(1)	0.3832 (2)	0.1274 (2)	0.2619 (2)	3.0^b
P(2)	0.2377 (2)	0.3002 (2)	0.1714 (2)	3.1^b
C(1)	0.3268 (8)	0.2892 (7)	−0.0381 (7)	3.6^b
B(3)	0.1830 (10)	0.2317 (8)	−0.0170 (8)	3.5^b
B(4)	0.2342 (11)	0.2713 (9)	−0.1328 (9)	4.4^b
B(5)	0.3681 (10)	0.2472 (9)	−0.1122 (8)	4.4^b
B(6)	0.3962 (9)	0.2034 (8)	0.0157 (8)	3.3^b
C(7)	0.1527 (8)	0.1062 (7)	0.0236 (6)	3.6^b
B(8)	0.1226 (9)	0.1534 (8)	−0.0936 (8)	4.1^b
B(9)	0.2408 (9)	0.1602 (9)	−0.1449 (8)	4.5^b
B(10)	0.3402 (11)	0.1152 (10)	−0.0489 (9)	4.0^b
B(11)	0.2780 (11)	0.0834 (10)	0.0591 (9)	3.1^b
B(12)	0.1860 (11)	0.0565 (9)	−0.0451 (9)	4.0^b
N	0.240 (1)	0.751 (1)	0.103 (1)	5.6 (2)
CMe(1)	0.216 (2)	0.780 (2)	0.177 (2)	14.5 (7)
CMe(2)	0.281 (2)	0.658 (2)	0.151 (1)	13.3 (6)
CMe(3)	0.321 (2)	0.835 (2)	0.036 (2)	14.9 (7)
CMe(4)	0.120 (2)	0.721 (2)	0.050 (2)	16.0 (8)
H(1)	0.365 (6)	0.373 (5)	−0.043 (5)	5.9 (16)
H(3)	0.124 (7)	0.279 (6)	−0.023 (6)	2.0 (19)
H(4)	0.235 (8)	0.342 (7)	−0.185 (6)	6.0 (23)
H(5)	0.444 (6)	0.301 (6)	−0.162 5)	5.1 (5)
H(6)	0.492 (7)	0.227 (7)	0.043 (6)	3.0 (19)
H(7)	0.088 (7)	0.067 (5)	0.058 (5)	3.1 (16)
H(8)	0.047 (7)	0.140 (6)	−0.105 (6)	2.0 (21)
H(9)	0.240 (5)	0.150 (4)	−0.202 (5)	4.7 (13)
H(10)	0.367 (8)	0.080 (8)	−0.065 (7)	4.2 (24)
H(11)	0.285 (7)	0.022 (6)	0.104 (5)	1.2 (18)
H(12B)	0.142 (7)	−0.018 (7)	−0.045 (6)	2.7 (21)

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. [b] Equivalent *B*.

Collection and Reduction of X-ray Data for $[Me_4N]$[2b]. A dark red crystal, obtained from acetone/ether, was mounted along the *c* axis on a glass fiber. Unit cell dimensions were determined from a least-squares fit of 12 accurately centered reflections ($10 < 2\theta < 27°$). These and other parameters, including conditions of data collection, are summarized in Table V. Data were collected on a Picker FACS-1 diffractometer, using the $\theta - 2\theta$ scan mode. Two reflections, ($32\bar{1}$) and (063), were measured every 100 reflections to check stability. Intensities of these reflections fluctuated only slightly, a maximum of ±6% during the course of the experiment. A total of 6180 reflections were measured. Of these, 4764 were considered observed ($I > 3\sigma(I)$) and were used in analysis of the structure. Data were corrected for Lorentz, polarization, and absorption effects.[35]

Solution and Refinement of the Structure of $[Me_4N]$[2b]. Atoms were located by use of the heavy-atom method. All calculations were performed on the IBM 3033 of the UCLA Office of Academic Computing. Refinement converged at $R = 0.0632$ and $R_w = 0.0668$.[38] The standard deviation of an observation of unit weight was 1.64. All phenyl groups were treated as rigid C_6H_5 hexagons, C–C = 1.395 Å, C–H = 1.08 Å. All terminal hydrogen atoms on the C_2B_9 icosahedron were located on different electron density maps and were included in the least-squares calculations. No hydrogen atoms on methyl groups were included. A total of 266 parameters were refined, including positional and anisotropic thermal parameters for Rh, P, and the C and B atoms of the C_2B_9 icosahedron, positional and isotropic thermal parameters for N and C of the cation and for the terminal H, and group and isotropic thermal

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[35] Programs used in this work include locally written data reduction and absorption programs and locally revised versions of ORFLS, ORFFE, ORTEP, MULTAN, and SHELX-76.

[36] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[37] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[38] The function $\sum w|F_o| - |F_c|^2$ was minimized in the least-squares refinements, and the discrepancy indices were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [1/\sigma(F_o)]^2$.

[39] The final "goodness of fit" is defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observed reflections and N_v is the number of variable parameters.

[40] Supplementary materials.

parameters (C only) for phenyl groups. Three values for thermal parameters of phenyl H were also refined, for those attached to ortho, meta, or para carbons (with respect to the linkage to P), respectively. Scattering factors[36,37] and anomalous dispersion terms[37] were applied. A final difference electron density map was essentially featureless, the maximum peak being about $^2/_3$ e/Å^3. Final positional and thermal parameters are given in Table VII. A table of structure factors is available.[40]

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Registry No. **1a**, 53687-46-0; **1a**-d_1, 82808-04-6; **1b**, 53754-45-3; **1c**, 76287-18-8; Li[**2a**], 97112-45-3; K[**2a**], 97112-46-4; K[18-crown-6][**2a**], 85422-35-1; K[18-crown-6][**2a**]$CH_3COC_2H_5\cdot H_2O$, 97112-47-5; [Et_4N][**2b**], 85422-28-2; [Me_4N][**2b**], 85422-36-2; [Me_4N][**2c**], 97112-49-7; [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; [PPN][**8a**], 97112-44-2; [*closo*-3,3-$(PPh_3)_2$-3-Br-3,1,2-$RhC_2P_9H_{11}$], 97112-48-6; $Tl_2C_2B_9B_{11}$, 97102-40-4; *trans*-IrCl(CO)$(PPh_3)_2$, 59246-46-7.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, and parameters for atoms treated as rigid groups, a complete listing of interatomic angles, and a listing of least-squares planes for **2a** and **2b** (66 pages). Ordering information is given on any current masthead page.

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Vapor Pressures and Enthalpies of Sublimation and Evaporation of Trifluoroacetylacetonates in Helium and Helium Containing the Ligand Vapor

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The vapor pressures of 21 metal trifluoroacetylacetonates were determined in helium and in helium containing the ligand vapor by using transpiration techniques. The vapor pressure of hydrated chelates can be measured only in helium containing the ligand vapor because considerable thermal decomposition occurs in helium. The volatility is mainly dependent on their structure. The predominant factor that decides volatility of coordination-saturated trifluoroacetylacetonates such as octahedral and tetrahedral chelates is van der Waals forces, while other strong forces are apparent in square-planar and square-pyramidal chelates. From the Clausius–Clapeyron equation, sublimation enthalpies and evaporation enthalpies of coordination-saturated chelates are generally 28 ± 2 and 19 ± 2 kcal mol^{-1}, respectively, and those of cobalt(II), nickel(II), and rare-earth-metal trifluoroacetylacetonates are larger than these values. The values measured by the Freeman–Carroll method for some chelates agreed well with those of the Clausius–Clapeyron equation.

Introduction

The study of volatile metal chelates has been extended into the field of gas chromatography and other practical techniques. Particularly, β-diketonates are important and of wide range of use. However, the vapor pressures of β-diketonates are not well studied, and there are few systematic data. Berg and Truemper[1] reported the vapor pressure of various metal β-diketonates, but they found no correlation with sublimation temperature or heat of sublimation for a series of chelates. It was later pointed out that the results were erroneous because thermal decomposition accompanied the measurement by an isoteniscope. Sicre et al.[2] reported the vapor pressure of rare-earth metal 2,2,6,6-tetramethyl-3,5-heptanedionates by a spoon gauge and discussed the relation between the ionic radius and the heats of sublimation and vaporization. Wolf et al.[3] reported the vapor pressure of aluminum and chromium β-diketonates and some other thermally stable β-diketonates and discussed the volatility on the basis of the difference of ligands. Reliable data are limited to these few chelates, and other studies are often discrepant. This is because many β-diketonates are subject to partial thermal decomposition, and the products often are more volatile than chelates and interfere in the determination of vapor pressure by static methods.

The authors have reported[4] that the β-diketonates are stabilized at high temperatures and are quantitatively eluted from gas chromatographic columns by using a carrier gas containing the ligand vapor. This technique was effectively applied to measurements of vapor pressure by the transpiration method.[5] In this paper, the vapor pressures of 21 metal trifluoroacetylacetonates ($M(tfa)_n$) were measured by this method, and the results were discussed as to the structure and the volatility of the chelates.

Experimental Section

Reagents and Preparation of Chelates. Commercial 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone) was purified by refluxing in the presence of disodium hydrogenphosphate, which was added to remove trifluoroacetic acid contained as a major impurity, and distilled at 107 °C.

The following chelates were prepared: $Al(tfa)_3$, $Sc(tfa)_3$, $Fe(tfa)_3$, $Ni(tfa)_2$, $Cu(tfa)_2$, $Zn(tfa)_2$, $Ga(tfa)_3$, $In(tfa)_3$ $Er(tfa)_3$, $Tm(tfa)_3$, $Yb(tfa)_3$, and $Lu(tfa)_3$. About 1 g of metal, oxide, or salt was dissolved in acid or water, the acid used depending on the sample characteristics. For example, gallium metal and indium oxide were dissolved in hot concentrated nitric acid, scandium and rare-earth oxides in hot concentrated hydrochloric acid, and aluminum chloride, iron chloride, nickel nitrate, copper sulfate, and zinc sulfate in water. These solutions were neutralized with 1 M aqueous ammonia or, for nickel, copper, and zinc solutions, with 1 M sodium hydroxide. The precipitated metal hydroxides were centrifuged and washed twice with distilled water. A small excess over the calcualted amount of H(tfa) was added to the precipitate, and the mixture was warmed to about 80 °C. The supernatant liquid was removed by decantation, and the chelate was filtered off on a glass filter and washed successively with water and hexane. The nickel, copper, and zinc chelates were dissolved in diethyl ether, heavy rare-earth-metal chelates in diisopropyl ether, and the other chelates in benzene. The insoluble materials, if any, were removed by filtration, and the chelates were recovered by the evaporation of the organic solvent in a clean dry air stream. The other chelates used were prepared according to previously reported procedures.[6]

Vapor Pressure Measurements. A Shimadzu Model GC-6A gas chromatograph equipped with a ligand vapor generator was used. The

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(1) (a) Berg, E. W.; Truemper, J. T. *J. Phys. Chem.* **1960**, *64*, 487. (b) Berg, E. W.; Truemper, J. T. *Anal. Chim. Acta* **1965**, *32*, 245.

(2) Sicre, J. E.; Dubois, J. T.; Eisentraut, K. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 3476.

(3) Wolf, W. R.; Sievers, R. E.; Brown, G. H. *Inorg. Chem.* **1972**, *11*, 1995.

(4) (a) Fujinaga, T.; Kuwamoto, T.; Murai, S. *Talanta* **1971**, *18*, 429. (b) Fujinaga, T.; Kuwamoto, T.; Murai, S. *Anal. Chim. Acta* **1974**, *71*, 141. (c) Fujinaga, T.; Kuwamoto, T.; Kimoto, T. *Talanta* **1976**, *23*, 753. (d) Fujinaga, T.; Kuwamoto, T.; Sugiura, K.; Matsubara, N. *Anal. Chim. Acta* **1982**, *136*, 175.

(5) Matsubara, N.; Kuwamoto, T. *Thermochim. Acta* **1985**, *83*, 193.

(6) (a) Fay, R. C.; Piper, T. S. *J. Am. Chem. Soc.* **1963**, *85*, 500. (b) Morris, M. L.; Moshier, R. W.; Sievers, R. E. *Inorg. Synth.* **1967**, *9*, 50. (c) Ellern, J. B.; Ragsdale, R. O. *Inorg. Synth.* **1968**, *11*, 82. (d) Dilli, S.; Patsalides, E. *Aust. J. Chem.* **1976**, *29*, 2369. (e) Dilli, S.; Patsalides, E. *Aust. J. Chem.* **1976**, *29*, 2389. (f) Okeya, S.; Ooi, S.; Matsumoto, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085.

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