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DICARBOLLIDE COMPLEXES OF RHODIUM AND RUTHENIUM

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Summary

The 7,8-$B_9C_2H_{11}^{2-}$ ion reacts with $(Ph_3P)_2Rh(CO)Cl$ to form $(B_9C_2H_{11})Rh(Cl)(Ph_3P)_2$. This rhodacarborane reacts with $NaBPh_4$ to produce $(B_9C_2H_{11})Rh(Ph_3P)(Ph_4B)$. The new metallocarboranes $[(B_9C_2H_{11})Rh(Ph_3P)(C_6H_6)]_2$ and $(B_9C_2H_{11})Rh(H)(Ph_3P)$ were obtained from the reaction of $B_9C_2H_{11}^{2-}$ and $(Ph_3P)_3RhCl$. The ruthenacarboranes $(B_9C_2H_{11})Ru(CO)(Ph_3P)_2$ and $(B_9C_2H_{11})Ru(CO)_3 \cdot 0.5C_6H_6$ were prepared from $(Ph_3P)_2Ru(CO)_2Cl_2$ and $[Ru(CO)_3Cl_2]_2$ respectively.

Introduction

Since the discovery in 1965 by Hawthorne and coworkers of the first metallocarboranes [1], it has been found that the isomeric 7,8- and 7,9-$B_9C_2H_{11}^{2-}$ ions form *closo*-π complexes with a very wide variety of transition metals [2-6] as well as *closo* derivatives in which such main group elements as B [7], Be [8], Al [9], Ga [9], Sn [10] and Pb [10] complete the icosahedral boron—carbon framework. Synthesis of dicarbollide complexes of the late second and third row transition metals by reaction of 7,8-$B_9C_2H_{11}^{2-}$ with the appropriate metal halide is complicated by reduction of the metal to the zero valent state. Examples of compounds prepared by this method include $(B_9C_2H_{11})_2Pd^{n-}$ (n = 0,1) [11], $(C_8H_{12})Pt(B_9C_2H_{11})$ [12] and $(Ph_4C_4)Pd(B_9C_2H_{11})$ [13]. An alternate approach, involving oxidative addition to smaller *closo* carboranes, has been used by Stone and coworkers to prepare $(R_3P)_2Pt[(CH_3)_2B_9C_2H_9]$ and $(t\text{-}C_4H_9NC)_2Pd[(CH_3)_2B_9C_2H_9]$ [14]. This work describes the synthesis of rhodium and

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ruthenium complexes of the $7,8\text{-}B_9C_2H_{11}^{2-}$ ion employing low valent derivatives of these metals as starting materials. Interest in such materials is accentuated by their potential for use as catalysts. Indeed, Hawthorne et al. have recently prepared $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhB_9C_2H_{11}$ and $2,2\text{-}(Ph_3P)_2\text{-}2\text{-}H\text{-}2,1,7\text{-}RhB_9C_2H_{11}$ [15] and found that these compounds function in homogenous catalytic reactions [16].

Results and discussion

Addition of a tetrahydrofuran solution of $Na_2\text{-}7,8\text{-}B_9C_2H_{11}$ to a suspension of $(Ph_3P)_2Rh(CO)Cl$ in benzene afforded a deep orange solution which, on exposure to air, turned green and then brown. This series of color changes is likely due to oxidation of some initially formed Rh^I species to Rh^{III} derivatives and could be duplicated, under oxygen-free conditions, with ferric chloride or *p*-quinone. In view of this observed air sensitivity, no deliberate effort was made to isolate low valent rhodacarborane complexes from this system. The brown reaction mixture was quite complex and thin layer chromatographic analysis indicated the presence of ten components. Concentration of this mixture caused the separation of orange, crystalline $(B_9C_2H_{11})Rh(Cl)(PPh_3)_2$ (I). The residue contained a small amount of a purple compound (III) which will be described later. The orange material was very soluble in benzene, moderately soluble in chloroform and only sparingly soluble in acetone. The infrared spectrum contained a sharp band at 295 cm^{-1}, attributed to $\nu(Rh{-}Cl)$ for a study of the far infrared spectra of a series of Rh^{III} halide derivatives showed that this absorption occurs in the range 350-250 cm^{-1} [17]. This information suggests that the chlorine is covalently bonded to rhodium and argues against an ionic formulation. Like many other metalloboranes containing triarylphosphine ligands, I exhibited a broad, amorphous ^{11}B NMR spectrum which provided no useful structural information. Similar effects have been observed in the ^{11}B NMR spectrum of $3\text{-}[(PPh_3)_2IrHCl]\text{-}1,2\text{-}B_{10}C_2H_{11}$ [18]. The ^1H NMR spectrum, however, contained aromatic and carborane C—H resonances in the expected ratio of 15/1. If the $7,8\text{-}B_9C_2H_{11}^{2-}$ ion is considered to be a six electron donor, the d^6 Rh^{III} in this metallocarborane has an eighteen electron configuration. It is of interest to note that $7,8\text{-}B_9C_2H_{11}^{2-}$ displaces carbon monoxide from $(PPh_3)_2Rh(CO)Cl$ whereas the carbonyl ligand is retained in reactions with $B_{10}H_{13}^-$ to form $[(B_{10}H_{12})Rh(CO)(PPh_3)_2]^-$ [19] and with $n\text{-}B_{18}H_{20}^{2-}$ to form $[(n\text{-}B_{18}H_{20})Rh(CO)(PPh_3)]^-$ [20]. As in these reactions, displacement of triphenylphosphine, to form $[(B_9C_2H_{11})_2Rh]^{n-}$ ($n = 1, 3$) was not observed. The proposed structure of I is shown in Fig. 1a.

Although the Rh—Cl bond in I is evidently highly covalent, the compound reacted with sodium tetraphenylborate in refluxing benzene—methanol to afford $(B_9C_2H_{11})Rh(PPh_3)(BPh_4)$ (II). The two most conspicuous features of this yellow, crystalline material are its lack of electrical conductivity in acetone solution and its proton magnetic resonance spectrum. The ^1H NMR spectrum revealed two overlapping multiplets at -7.6 and -7.3 ppm, each of relative area six, and two smaller multiplets of relative area one at -6.9 and -6.8 ppm. An upfield shift of one seventh of the aromatic protons is expected for an arene ring bonded to a transition metal via a π (h_n) interaction [21] and similar shifts have

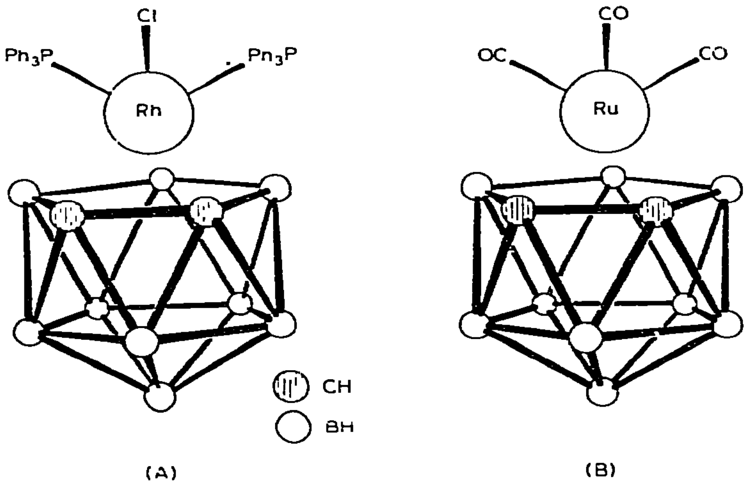

Fig. 1. Proposed structure of (a) $(B_9C_2H_{11})Rh(Cl)(PPh_3)_2$ and (b) $(B_9C_2H_{11})Ru(CO)_3$.

been reported by Schrock and Osborn [22] for π-bonded tetraphenylborate complexes of Rh^I and Ir^I. An analysis of the higher field multiplets, which, in a π-bonded tetraphenylborate complex, would represent the AB_2C_2 portion of an AB_2C_2X pattern (X = ^{11}B, ^{10}B), was not pursued. Infrared absorptions in II were observed at 6.95 and 7.30 μm; bands at ca. 6.85 and 7.20 μm, due to in-plane C—C skeletal vibrations, have been reported to be indicative of a π-bonded tetraphenyl borate moiety [22]. Since Rh^{III} is more electronegative than Rh^I, these bands might be expected to shift to somewhat lower frequencies. This spectroscopic evidence suggests that one of the arene rings of the Ph_4B^- moiety in II is coordinated to the rhodium atom. The arene ring could function either as a h_4 or h_2 ligand, resulting in an eighteen or sixteen electron configuration respectively for the transition metal. Since II was not observed to react with triphenylphosphine or dioxygen, a coordinatively saturated eighteen electron configuration seems more realistic. It should be noted that, in complexes such as diolefinrhodium tetraphenylborate [22], as in II, the tetraphenylborate group could conceivably function as a four rather than a six electron donor.

The reaction of Na_2-7,8-$B_9C_2H_{11}$ with $(Ph_3P)_3RhCl$ under strictly oxygen-free conditions afforded useful amounts of the purple compound (III) referred to above. III was easily purified by preparative scale thin layer chromatography. Elemental analyses indicated that this material was $(B_9C_2H_{11})Rh(PPh_3)(C_6H_6)$. The ^1H NMR spectrum in 100 atom percent $CDCl_3$ revealed a complex pattern of sharp resonances in the aromatic region and a sharp spike at —7.4 ppm due to the solvated benzene. Two broad signals were observed at —3.6 and —3.4 ppm and assigned to dicarbollide C—H protons; they were each of relative area one and the relative area of the aromatic proton signals was 21. The reason for the apparent nonequivalence of the signals assigned to the dicarbollide protons is not known; spin coupling with ^{31}P or ^{103}Rh is unlikely since the chemical shifts change to —3.9 and —3.3 ppm in C_6D_6 solution. The purple color of III is unusual for Rh^I or Rh^{III}, for derivatives prepared here and reported elsewhere [15] are yellow or orange. The dicarbollide—rhodium ratio determined from the analytical data indicates that the metal is in a formal +2 oxidation state. Since a species containing d^7 Rh^{II} would be paramagnetic, the purple compound is likely aggregated, for the ^1H NMR spectrum showed no evidence for broadened or shited resonances. An osmometric molecular weight determination in benzene gave a value of 788; the calculated molecular weight of the monomer is 575 and of the dimer, 1150. A value lower than that expected for a dimer may be caused by dissociation of the triphenylphosphine ligands. The data at hand suggest a dimeric structure for III, i.e. $[(B_9C_2H_{11})Rh(PPh_3)(C_6H_6)]_2$, in which a rhodium—rhodium bond would lead to a diamagnetic 16 electron configuration for the transition metal; they do not constitute a proof of structure and an X-ray diffraction study of III is needed to provide additional information.

An orange crystalline product which analyzed for $(B_9C_2H_{11})Rh(H)(PPh_3)$ (IV) was isolated in 1% yield from the reaction of $B_9C_2H_{11}^{2-}$ with $(Ph_3P)_3RhCl$. The infrared spectrum of IV contained a band at 4.50 μm attributed to Rh—H stretching. The ^1H NMR spectrum showed an apparent 1/2/1 triplet at +10.5 ppm. This high field resonance is also indicative of a rhodium hydride species. The triplet pattern may result from overlap of two doublets due to J(Rh—H) and ^2J(H—Rh—P). This rhodacarborane hydride derivative presumably has a sixteen electron configuration about the metal. Because IV was obtained in such low yield by the present method, its chemistry has not yet been extensively studied. It may be an intermediate in reactions catalyzed [16] by $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhB_9C_2H_{11}$ [15].

The reaction of $Na_2\text{-}7,8\text{-}B_9C_2H_{11}$ with $(Ph_3P)_2Ru(CO)_2Cl_2$ led to the displacement of both chlorines and one molecule of carbon monoxide to form $(B_9C_2H_{11})Ru(CO)(PPh_3)_2$ (V). The ^1H NMR spectrum of V contained a broad singlet at -3.6 ppm, attributed to the dicarbollide C—H protons, and a complex multiplet due to the triphenylphosphine protons, in a ratio of 1/15. The infrared spectrum contained a single ν(CO) absorption at 5.22 μm, consistent with the presence of only one carbonyl group.

Another neutral ruthenium dicarbollide complex, $(B_9C_2H_{11})Ru(CO)_3 \cdot 0.5C_6H_6$ (VI) was prepared from $Na_2\text{-}7,8\text{-}B_9C_2H_{11}$ and $[Ru(CO)_3Cl_2]_2$. The ^1H

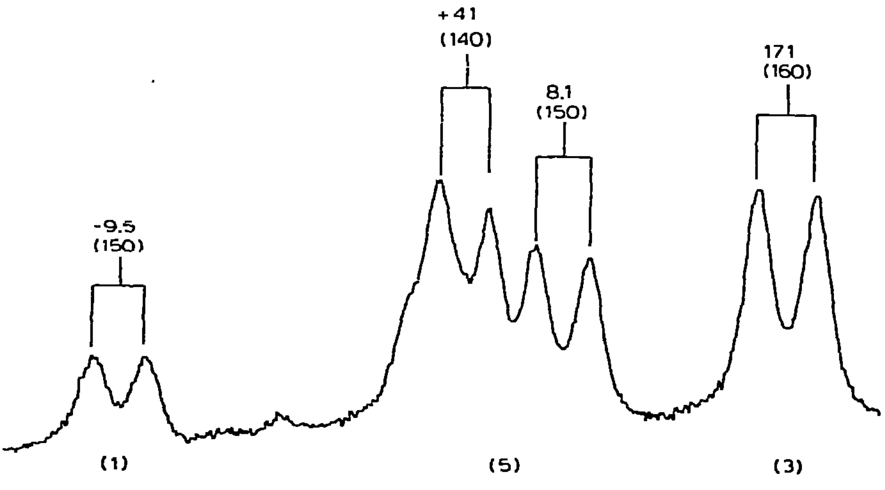

Fig. 2. ^{11}B NMR spectrum of $(B_9C_2H_{11})Ru(CO)_3 \cdot 0.5C_6H_6$ in 1,2-dichloroethane.

NMR spectrum of this material in CD_3CN contained a broad singlet at −3.7 ppm due to the dicarbollide C—H protons and a spike at −7.27 ppm due to the solvated benzene. The mass spectrum of VI revealed polyisotopic clusters of peaks due to $(B_9C_2H_{11})Ru(CO)_n$ ($n = 0, 1, 2$) but a parent ion was not observed. However, the infrared spectrum of a benzene solution of VI contained three carbonyl stretching bands indicative of a ruthenium tricarbonyl moiety with effective C_{3v} symmetry. The ^{11}B NMR spectrum of this ruthenacarborane, shown in Fig. 2, resembles that of $[(7,8\text{-}B_9C_2H_{11})_2Co]^-$ [23] and is consistent with a *closo*-$B_9C_2H_{11}Ru$ structure for this compound (Fig. 1b).

Experimental

Na_2-7,8-$B_9C_2H_{11}$ was prepared from $(CH_3)_3NH$-7,8-$B_9C_2H_{12}$ and sodium hydride in tetrahydrofuran [2]. Literature methods were used to prepare $(Ph_3P)_3RhCl$ [24] and $(Ph_3P)_2Rh(CO)Cl$ [25]; $(Ph_3P)_2Ru(CO)_2Cl_2$ and $[Ru(CO)_3Cl_2]_2$ were used as received from Strem Chemical Co. Tetrahydrofuran and benzene were dried by distillation from lithium aluminum hydride. All reactions were run under a nitrogen atmosphere. ^1H and ^{11}B NMR spectra were obtained at 220 and 70.6 MHz respectively and are referenced to internal tetramethylsilane and external $BF_3 \cdot O(C_2H_5)_2$ respectively. Melting points were measured in evacuated, sealed capillaries. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N.Y.

$(B_9C_2H_{11})Rh(Cl)(Ph_3P)_2$. A solution of 1 mmol Na_2-7,8-$B_9C_2H_{11}$ in 20 ml tetrahydrofuran was added with stirring to 0.9 g $(Ph_3P)_2Rh(CO)Cl$ in 30 ml benzene. The reaction mixture was stirred for three days, then opened to the air and poured into aqueous sodium chloride. The orange organic phase turned green, then, more slowly, to brown. The benzene layer was separated and dried over calcium chloride, then taken to dryness under reduced pressure. Addition of a small amount of benzene to the residue caused the separation of the orange product which was recrystallized from benzene—acetonitrile. The yield was 0.19 g (16%), m.p. 195-196° (dec.). A thin layer chromatogram (silica gel, acetone) revealed only one component. Anal. Found: C, 57.23; H, 5.29; B, 12.52; Cl, 4.01; Rh, 11.60. $C_{38}H_{41}B_9ClP_2Rh$ calcd.: C, 57.43; H, 5.16; B, 12.22; Cl, 4.41; Rh, 12.97%. Osmometric molecular weight (C_6H_6): found, 549, calcd., 794. Ir (KBr): 3.35w, 3.95s, 5.87w, 6.80m, 7.05s, 8.50w, 9.25s, 10.10m, 13.35s, 14.50s μm. Electronic spectrum (C_6H_6): λ_{max} at 287 (5.7×10^4), 380 nm (6.3×10^3). ^1H NMR ($CDCl_3$): multiplets at −7.6, −7.2, −7.1 ppm (15H); broad singlet at −3.7 ppm (1H). ^{11}B NMR (C_6H_6): three broad, overlapping resonances at −9.9, 4.8 and 18.1 ppm.

$(B_9C_2H_{11})Rh(PPh_3)BPh_4$. A mixture of 0.02 g $(B_9C_2H_{11})Rh(Cl)(PPh_3)_2$, 0.1 g $NaBPh_4$, 7.5 ml methanol and 2.5 ml benzene was refluxed with stirring for 16 hours. The reaction mixture was evaporated to dryness and chromatographed on a 3.5 × 0.5 in. column of silica gel. Dichloromethane eluted the product as a yellow band. The product was purified by recrystallization from dichloromethane—ethanol to give 0.017 g of yellow needles which decomposed without melting at 300°. A thin layer chromatogram (silica, dichloromethane) revealed only one component. Anal. Found: C, 64.45; H, 5.81; B, 14.05; Rh, 12.30. $C_{44}H_{46}B_{10}PRh$ calcd.: C, 64.71; H, 5.64; B, 13.24; Rh, 12.62%. IR(KBr):

3.30w, 3.95s, 6.30m, 7.00s, 9.20s, 10.00w, 10.15w, 13.25m, 14.40s μm. Electronic spectrum (acetone): λ_{max} at 332 nm (5.8×10^2). ^{1}H NMR (acetone-d_6): two overlapping multiplets at —7.6 and —7.3 ppm (30H), two multiplets at —6.9 and —6.8 ppm (5H), broad singlet at —3.5 ppm (2H, carborane C—H). ^{11}B NMR (1,2-$C_2H_4Cl_2$): three broad, overlapping resonances at —0.9, —5.9, +5.7 ppm. Conductivity: Λ_M (8.4×10^{-4} *M* in acetone): 20.2 ohm^{-1} cm^2 mol^{-1}.

Reaction of $Na_2B_9C_2H_{11}$ with $(Ph_3P)_3RhCl$. This reaction was conveniently carried out in an H-shaped vessel consisting of two separate reaction flasks connected by a medium porosity glass frit. Tetrahydrofuran and benzene were degassed by three freeze-pump-thaw cycles. A solution of 1 mmol $Na_2B_9C_2H_{11}$ in 10 ml tetrahydrofuran was filtered into 0.93 g (1 mmol) $(Ph_3P)_3RhCl$ in 30 ml benzene. After stirring for 3 days, the vessel was opened to the air and the contents poured into aqueous NaCl. The deep orange solution turned green and then very dark. The organic layer was separated, dried over sodium sulfate, and then evaporated under reduced pressure to a small volume. This mixture was chromatographed on a 4 × 1.5 in. column of silica gel, eluting with benzene. The dark colored, fast moving band was collected and taken to dryness on a rotary evaporator. The residue was dissolved in a minimum amount of benzene and applied to an 8 × 8 in. preparative TLC plate coated with silica gel, then developed with 2/1 benzene—cyclohexane. A fast moving purple band, followed by a slower moving orange band were visualized. The purple band was eluted with benzene and purified by an additional cycle of thin layer chromatography as described above, then recrystallized from benzene—isooctane to afford 0.045 g (6%) of deep purple microcrystals. The orange band was eluted with benzene and the product recrystallized from acetonitrile—benzene to give 0.009 g (1%) of product as orange needles.

$[(B_9C_2H_{11})Rh(Ph_3P)(C_6H_6)]_2$. M.p. 155° (dec.). Anal. Found: C, 54.53; H, 5.59; B, 16.47; Rh, 17.63. $C_{26}H_{32}B_9PRh$ calcd.: C, 54.26; H, 5.57; B, 16.87; Rh, 17.91%. IR(KBr): strong bands occurred at 3.90, 7.00, 9.20, 13.50, and 14.60 μm. Electronic spectrum (C_6H_6): λ_{max} at 440 (6.8×10^4) and 612 nm (6.8×10^4). ^{1}H NMR (100 atom percent $CDCl_3$): a complex multiplet containing many sharp peaks was seen in the aromatic region. Rising from this structure was a sharp peak at —7.35 ppm. Two broad singlets occurred at —3.56 and —3.44 ppm. The relative areas of the aromatic and the two carborane C—H protons were 21/1/1. ^{11}B NMR spectrum (1/1 C_6H_6/CH_2Cl_2): four broad resonances centered at —24.9, —14.2, +3.7 and +13.5 ppm. Osmometric molecular weight (benzene): found: 788; monomer calcd.: 575; dimer calcd.: 1150.

$(B_9C_2H_{11})Rh(H)(PPh_3)$. In an evacuated, sealed tube, the compound blackened but did not melt up to 300°. Anal. Found: C, 48.48; H, 5.64. $C_{20}H_{27}B_9PRh$ calcd.: C, 48.19; H, 5.43%. IR(KBr): 3.30w, 3.95s, 4.50m, 6.80m, 7.00s, 9.20m, 10.20w, 13.45m, 14.40s μm. Electronic spectrum (C_6H_6): λ_{max} at 283 (2.9×10^4), 330 nm (sh, 7.2×10^3). ^{1}H NMR (C_6D_6): complex multiplet centered at —7.4 ppm; a triplet was observed at +10.5 ppm with a spacing of 20 cps. ^{11}B NMR (acetone): broad hump at +8.5 ppm.

$(B_9C_2H_{11})Ru(CO)(Ph_3P)_2$. To a solution of 1 mmol $Na_2B_9C_2H_{11}$ in 15 ml tetrahydrofuran was added 0.95 g $(Ph_3P)_2Ru(CO)_2Cl_2$ and 5 ml benzene. The reaction mixture was stirred at room temperature for six hours, then refluxed for six hours, after which time, it was filtered and evaporated under reduced

pressure. Water and dichloromethane were added. The organic layer was separated and dried over sodium sulfate, then evaporated to dryness. Addition of acetone caused the separation of 0.15 g (20%) of fine yellow crystals. A 0.1 g portion of this product was recrystallized from 100 ml boiling acetone to afford the analytical sample, m.p. 315-316° (dec.). Anal.: Found: C, 59.71; H, 5.48; Ru, 12.50; Cl, < 0.1. $C_{39}H_{41}B_9OP_2Ru$ calcd.: C, 59.62; H, 5.22; Ru, 12.87; Cl, 0.00%. Osmometric molecular weight (1,2-$C_2H_4Cl_2$): found 614, calcd.: 788. IR(KBr): 3.35w, 3.97s, 6.80m, 7.05s, 9.26s, 9.83w, 10.10m, 13.45s and 14.45s μm. ^{1}H NMR (CD_2Cl_2): complex multiplet centered at −7.4 ppm (15H); broad singlet at −3.6 ppm (1H, carborane C—H).

$(B_9C_2H_{11})Ru(CO)_3 \cdot 0.5C_6H_6$. A solution of 4 mmol $Na_2B_9C_2H_{11}$ in 15 ml tetrahydrofuran was added to 2 mmol, 0.62 g, of $[Ru(CO)_3Cl_2]_2$ in 10 ml tetrahydrofuran. The orange reaction mixture was stirred overnight under reflux then filtered through Celite. The filtrate was evaporated under reduced pressure. Water and methylene chloride were added to the residue. The organic layer was dried over magnesium sulfate, evaporated and chromatographed on a 12 × 1 in. silica gel column. Benzene eluted a yellow band. The yellow eluent was evaporated to a small volume. Slow addition of cyclohexane caused the product to separate as yellow flakes. The yield was 0.1 g. The crystals appeared to decompose on heating but did not melt up to 350°. Anal. Found: C, 27.30; H, 3.91; B, 26.84; Cl, < 0.5; Ru, 28.13. $C_8H_{14}B_9O_3Ru$ calcd.: C, 26.97; H, 3.93; B, 27.25; Cl, 0.00; Ru, 28.37%. Molecular weight (osmometric, C_6H_6): found, 347, calcd. 356. Electronic spectrum (CH_3CN): λ_{max} at 231 (7.1×10^3), 282 (2.2×10^3) and 350 nm (sh, 5.6×10^2). IR(KBr): 3.32w, 3.95s, 7.15w, 8.32w, 9.05m, 9.82m, 10.07m, 11.32 w, 13.45m, and 13.7m μm. The infrared spectrum in the carbonyl region was examined using a spectrometer with grating optics; absorptions in a benzene solution at 2082, 2070 and 2020 cm^{-1} were observed.

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