Co(III), Cu(I) formulation would expect a yellow, diamagnetic product similar to the Cu(fdpp)I material.

The UV–visible spectra, Table IV, demonstrate the electronic changes that have occurred in the (cdpp)$^+$ fragment of the Cu(cdpp)Cl$_2$. In the spectrum of Cu(cdpp)Cl$_2$ there are no UV–visible absorptions which can clearly be attributed to the ligand [cdpp]$^+$. In contrast the high-energy portion of the UV–visible spectrum for [Co(cdpp)Cl$_2$]Cl matches the UV–visible spectrum of [cdpp]PF$_6$ exactly.

A more acceptable valence assignment is Co^{II}/Cu^{II}. This assignment accounts for the changes in the ligand part of the UV–visible spectrum and the paramagnetism of the compound. Since this material would have two paramagnetic centers, it could display magnetic concentration effects such as field-dependent paramagnetism. Nevertheless, magnetic concentration effects are complex, and more extensive study is needed before any realistic assignment can be made for this material.

Conclusion

1,1′-Bis(diphenylphosphino)cobaltocenium hexafluorophosphate has been prepared and its behavior is contrasted to the isoelectronic neutral 1,1′-bis(diphenylphosphino)-ferrocene. As a cationic phosphine ligand it is unique in that it has demonstrated an interaction of the positive charge with the complexed metal, in both the increased π-acid strength observed in the carbonyl stretching frequencies of the group 6 tetracarbonyl[1,1′-bis(diphenylphosphino)cobaltocenium] metal cations and the anomalous behavior of the Cu(cdpp)Cl$_2$ complex. In addition it has required fundamental changes in synthetic procedure such as the need for additional chloride ion to prepare the nickel(II) chloride complex Ni(cdpp)Cl$_3$. Cationic ligands using a quaternary ammonium or phosphonium ion as the source of the positive charge have failed to demonstrate either an extensive interaction of the positive charge with the complexed metal or a significant change in the reactivity of a cationic ligand over a neutral analogue.[20]

Registry No. Co(fdpp)Cl$_2$, 67292-36-8; Co(fdpp)Br$_2$, 67292-37-9; Co(fdpp)I$_2$, 67292-35-7; Ni(fdpp)Cl$_2$, 67292-34-6; Ni(fdpp)Br$_2$, 67292-33-5; Ni(fdpp)I$_2$, 67292-32-4; Cr(fdpp)(CO)$_4$, 67292-31-3; [Cr(cdpp)(CO)$_4$]PF$_6$, 67292-30-2; Mo(fdpp)(CO)$_4$, 67292-28-8; [Mo(cdpp)(CO)$_4$]PF$_6$, 67292-27-7; W(fdpp)(CO)$_4$, 67292-26-6; [W(cdpp)(CO)$_4$]PF$_6$, 67292-25-5; [cdpp]PF$_6$, 67292-48-2; [Co(cdpp)Cl$_2$]Cl, 67292-46-0; Cu(cdpp)Cl$_2$, 67292-45-9; Cu(fdpp)I, 67292-44-8; [NEt$_4$][V(fdpp)(CO)$_4$], 67292-43-7; [NEt$_4$][Ta(fdpp)(CO)$_4$], 67292-41-5; [Ni(cdpp)Cl$_2$]Cl, 67292-39-1; Cr(CO)$_6$, 13007-92-6; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; bis(diglyme)sodium hexacarbonylvanadate(–I), 15531-13-2; tetraethylammonium hexacarbonyltantalate(–I), 67292-38-0.

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Hydrido Complexes of Ruthenium with Carborane Ligands

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The synthesis and characterization of the complexes 2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$ and 3,3-(PPh$_3$)$_2$-3,3-H$_2$-3,-1,2-RuC$_2$B$_9$H$_{11}$ via the oxidative addition of 7,9- and 7,8-C$_2$H$_9$H$_{12}^-$, respectively, to (PPh$_3$)$_3$RuHCl are described. These complexes are formulated as seven-coordinate formal Ru(IV) compounds. The 2,1,7 isomer was found to reversibly eliminate one molecule of H$_2$ with heating in vacuo to give a five-coordinate d^6, formal Ru(II) complex. Both the 2,1,7 and 3,1,2 isomers readily lose hydrogen in their reactions with HCl and CO to give the corresponding substituted complexes. The pyridine-substituted complex 3,3-(PPh$_3$)$_2$-3-H-7-C$_5$H$_5$N-3,1,2-RuC$_2$B$_9$H$_{10}$ was also prepared and characterized.

The versatile homogeneous catalysts based on the rhodium and ruthenium metals include (PPh$_3$)$_3$RhCl and (PPh$_3$)$_3$RuHCl and many of their derivatives.[1,2] Recently, we reported the preparation and characterization of a novel class of homogeneous catalysts based on carborane ligands and rhodium and iridium metals.[3,4] These complexes are formed by the oxidative addition reaction of the isomeric C$_2$B$_9$H$_{12}^-$ anions to coordinatively unsaturated d^8 rhodium(I) and iridium(I) species. In two recent communications, we have further established that oxidative addition of *nido*- and *arachno*-carboranes to unsaturated transition-metal centers has proved to be a general reaction.[5,6] In this article we present details of the synthesis and characterization of several novel ruthenium complexes based on dicarbollide ligands and some of their reactions.

Results and Discussion

Synthesis. Both of the new ruthenium complexes were synthesized from the hydridotris(triphenylphosphine)ruthenium chloride complex (PPh$_3$)$_3$RuHCl. Oxidative addition of NHMe$_3^+$ salts of the carborane anions[7] 7,9- and 7,8-C$_2$B$_9$H$_{12}^-$ to (PPh$_3$)$_3$RuHCl·PhCH$_3$[8] in boiling ethanol gave

Table I. Infrared Data for Ruthenium–Carborane Complexes

no.	compound	absorptions,[a,b] cm^{-1}
I	2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$	3060 m, 2540 s, 2060 w, 2000 w, 1475 s, 1430 s, 1425 s, 1302 w, 1178 w, 1153 w, 1114 w, 1087 s, 1009 m, 996 m, 982 w, 915 w, br, 882 w, br, 748 s, 725 m, 693 s, br, 680 w
II	3,3-(PPh$_3$)$_2$-3,3-H$_2$-3,1,2-RuC$_2$B$_9$H$_{11}$	3040 m, 2540 s, 2060 w, 2040 w, 1475 s, 1425 s, 1302 w, 1198 w, 1178 m, 1148 w, 1087 s, 992 m, 920 w, 892 w, 845 w, br, 804 w, 746 s, br, 735 s, 700 s, 690 s, 652 w
III	2,2-(PPh$_3$)$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$	3050 w, 2515 s, br, 1470 s, 1423 s, 1298 w, 1175 w, 1150 w, 1114 w, 1083 s, 1033 w, 1021 w, 1004 m, 994 w, 976 w, 890 w, 868 w, 840 w, 738 s, 692 s, br
IV	2,2-(PPh$_3$)$_2$-2-H-2-Cl-2,1,7-RuC$_2$B$_9$H$_{11}$	3053 m, 2580 m, 2550 s, 2160 vw, 1472 m, 1427 s, 1183 w, 1152 w, 1081 s, br, 1010 m, 992 w, 928 w, 739 s, 695 m, 688 s, 330 w, br^c
V	2,2-(PPh$_3$)$_2$-2-CO-2,1,7-RuC$_2$B$_9$H$_{11}$	3055 w, 2585 s, 2560 m, 2520 s, 1957 s, 1475 m, 1427 s, 1310 w, 1154 w, 1050 w, 1082 s, 1010 m, 995 w, 976 w, 847 w, 745 s, 740 m, 696 s, br, 682 w
VI	3,3-(PPh$_3$)$_2$-3-H-3-Cl-3,1,2-RuC$_2$B$_9$H$_{11}$	3040 m, 2608 m, 2550 s, 2160 w, 1472 m, 1426 s, 1255 m, 1185 w, br, 1150 w, br, 1090 s, 1080 s, 1013 w, br, 990 m, br, 753 w, 735 s, br, 690 s, br, 330 w, br^c
VII	3,3-(PPh$_3$)$_2$-3-CO-3,1,2-RuC$_2$B$_9$H$_{11}$	3055 m, 2570 s, 2550 s, 1960 s, 1474 m, 1428 s, 1179 w, 1151 w, 1083 s, 1069 w, 1012 w, br, 994 w, br, 745 s, 694 s
VIII	3,3-(PPh$_3$)$_2$-3-H-7-C$_5$H$_5$N-3,1,2-RuC$_2$B$_9$H$_{10}$	3040 m, 2515 s, br, 2100 w, 1470 m, 1425 m, 1255 m, 1150 w, 1079 s, 1055 m, br, 1020 w, 1010 w, 978 w, 898 w, 850 w, 798 m, 752 m, 740 s, 692 s, br, 680 m, sh

^{a} Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad. ^{b} Spectrum from Nujol mull of sample except for peaks labeled c. ^{c} Spectrum from KBr pellet of sample.

Table II. Proton NMR Data for Ruthenium–Carborane Complexes in Tetrahydrofuran

no.	chemical shift^a	assignment
I	2.74	phenyl protons
	16.9	metal hydride triplet, J_{P-H} = 29 Hz
II	2.73	phenyl protons
	16.3	metal hydride triplet, J_{P-H} = 28 Hz
III	2.75	phenyl protons
VIII	1.55	pyridine protons
	2.74	phenyl protons
	19.6	metal hydride doublet, J_{P-H} = 31 Hz
	21.0	metal hydride doublet, J_{P-H} = 31 Hz

^{a} All chemical shifts are in τ.

Table III. 80.5-MHz ^{11}B NMR Data for Ruthenium–Carborane Complexes

no.	solvent	shifts^a
I	CH$_2$Cl$_2$	−1.2 (1), 7.6 (3), 13.1 (4), 18.3 (1)
II	CH$_2$Cl$_2$	−13.9 (2), −4.6 (5), 5.4 (2)
III	THF	−3.0 (1), 0.0 (1), 5.2 (2), 10.9 (2), 22.1 (3)
VIII	CD$_2$Cl$_2$	−5.2 (1), 11.1 (4), 13.4 (2), 23.4 (1), 29.4 (1)

^{a} Chemical shifts are ppm from BF$_3$·OEt$_2$. The relative areas are in parentheses.

2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$ (I) and 3,3-(PPh$_3$)$_2$-3,3-H$_2$-3,1,2-RuC$_2$B$_9$H$_{11}$ (II), respectively, in high yields.

Spectral Data. The IR spectra of I and II, shown in Table I, contain bands characteristic of neutral carborane complexes and also weak doublets (2060 and 2000 cm^{-1} (I), 2060 and 2040 cm^{-1} (II)) that were assigned to ν_{Ru-H} absorptions.

The 100-MHz ^{1}H NMR of I (tetrahydrofuran, THF) showed a 1:2:1 triplet centered at τ 16.9 (Table II) as expected for hydride ligands on a ruthenium with two equivalent

phosphorus nuclei (J_{P-H} = 29 Hz). This collapsed into a singlet upon ^{31}P decoupling. Similarly, II in THF exhibited a hydride triplet at τ 16.3 (J_{P-H} = 28 Hz).

The ^{31}P NMR of I (36.4 MHz, ^{1}H decoupled) in THF consisted of a singlet at −34.5 ppm from 85% H$_3$PO$_4$.[9]

The 80.5-MHz ^{11}B NMR of I in CH$_2$Cl$_2$ solution (^{1}H decoupled) as shown in Table III is consistent with a *closo*-metallocarborane of the 2,1,7 structure[3] and the ^{11}B spectrum of II is also reminiscent of analogous 3,1,2-rhoda- and similar metallocarboranes.[3]

Elemental analyses (Table IV) also support the characterization of these compounds as dihydridobis(triphenylphosphine)ruthenium(IV) complexes. If the dicarbollide moiety is regarded as a three-electron-pair donor analogous to cyclopentadienide anion, C$_5$H$_5^-$, we can formally describe the ruthenium centers to be d^4 and assign them a coordination number of seven.

To confirm the closo structure and to establish the stereochemistry of these complexes, a single-crystal X-ray diffraction study has been carried out with I.[5] The quality of the data plus refinement problems has so far precluded attempts at locating the hydride ligands.[10] Their positions, however, can be inferred to be symmetrically between the triphenylphosphine groups (Figure 1). The closo structure of the complex was confirmed.

Reversible Dehydrogenation of I. The light blue complex I turned grayish white upon exposure to a hydrogen atmosphere. The resulting complex had spectral and analytical properties identical with those of I. It was subsequently demonstrated that the blue coloration of I was due to traces of a new complex III. When crystals of I were slowly heated to 160 °C under vacuum, an intense blue color developed with concurrent elimination of hydrogen gas, 1 mol of H$_2$ being lost upon complete reaction. The resulting dark blue complex III

Table IV. Analytical Data for Ruthenium–Carborane Complexes

	analysis, %									
	calcd					found				
no.	C	H	P	B	other	C	H	P	B	other
I	60.08	5.66	8.15	12.81	13.30 (Rh)	60.00	5.70	8.26	12.77	12.60 (Rh)
II	60.08	5.66	8.15	12.81		60.15	5.85	7.85	12.51	
III	60.23	5.41	8.18	12.84		59.93	5.69	7.91	12.36	
IV	57.47	5.29	7.80		4.46 (Cl)	57.82	5.58	7.93		4.26 (Cl)
V	59.62	5.22	7.88			59.85	5.41	7.52		
VI	57.47	5.29	7.80	12.25	4.46 (Cl)	57.18	5.08	7.43	11.94	4.85 (Cl)
VII	59.62	5.22	7.88	12.38		59.98	5.34	7.98	12.59	
VIII	60.20	5.60	7.22			60.24	5.63	7.06		
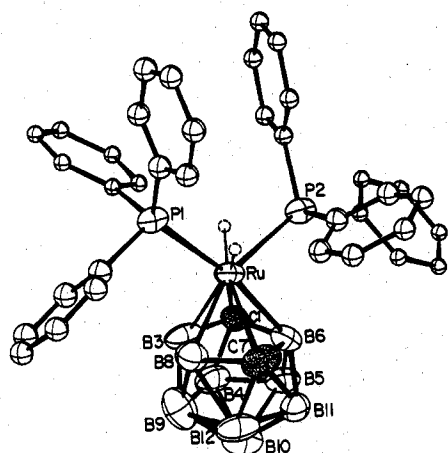
Figure 1. An ORTEP drawing (ref 5) of 2,2-(PPh₃)₂-2,2-H₂-2,1,7-RuC₂B₉H₁₁ (I). Hydride atoms, which were not located, are shown as dotted circles in calculated positions. Hydrogen atoms on the carborane ligand are omitted for clarity (see ref 10).

showed no metal–hydride bands in the IR spectra and the absence of high-field hydride resonances in the ¹H NMR spectra. Its ¹¹B NMR spectrum in THF consisted of resonances typical of *closo*-metallocarboranes and its ³¹P NMR spectrum contained a singlet (–60.8 ppm, ¹H decoupled). III readily added hydrogen at ambient temperature to regenerate I. Complex III is therefore formulated as 2,2-(PPh₃)₂-2,-1,7-RuC₂B₉H₁₁, a d⁶ Ru(II) complex. The equilibrium (PPh₃)₂H₂RuC₂B₉H₁₁ ⇌ H₂ + (PPh₃)₂RuC₂B₉H₁₁ appeared to lie far to the left at room temperature. III was sensitive to prolonged exposure to air both in solution and in the solid state. Being an unsaturated 16-electron complex, it rapidly reacted with carbon monoxide and hydrogen chloride to give coordinatively saturated products similar to that of I (vide infra).

Although II lost hydrogen at 160 °C under vacuum after prolonged heating, no tractable product was isolated and the dehydrogenation was found to be irreversible. The relative instability of a 3,1,2 isomer of (PPh₃)₂RuC₂B₉H₁₁ compared to the 2,1,7 isomer may account for this behavior.

Reactions of I. Although complex I in crystalline form was found to be air stable for at least a few hours, solutions of it were extremely air sensitive. All of the reactions of I were dominated by loss of hydrogen and were essentially those of complex III.

Dry HCl gas readily displaced the hydride ligands of I at 80 °C in the solid state and at room temperature in toluene or dichloromethane solution. A yellow complex, IV, was obtained that analyzed for 2,2-(PPh₃)₂-2-H-2-Cl-2,1,7-RuC₂B₉H₁₁. Its IR exhibited a weak ν_{Ru-H} band at 2160 cm⁻¹ and a broad ν_{Ru-Cl} band centered at 330 cm⁻¹. Although the complex was too insoluble to give any informative spectral data in solution, it seems reasonable to expect no gross structural changes in going from I to IV except for the larger steric requirements of a Cl ligand.

IV is more stable than I to decomposition and can be worked up with little loss in air.

Complex I readily reacted with carbon monoxide at 80 °C in the solid state and slowly at room temperature in CH₂Cl₂ solution. A yellow complex, V, was obtained that analyzed for 2,2-(PPh₃)₂-2-CO-2,1,7-RuC₂B₉H₁₁. A single, sharp ν_{CO} was observed in its IR spectrum at 1957 cm⁻¹. V is a formally six-coordinate, 18-electron d⁶ ruthenium(II) complex and this is reflected in its inertness and stability, even when in solution.

Reactions of Complex II. Complex II was found to be slightly more stable than I both in the solid state and in solution, and methylene chloride solutions survived brief exposure to air. Slightly more vigorous conditions were necessary to
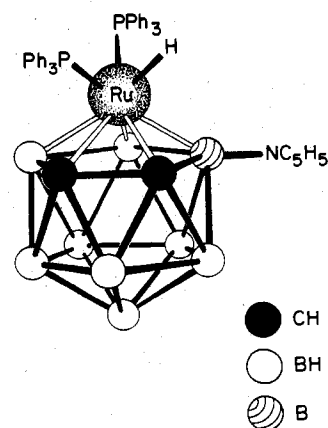
Figure 2. Proposed structure of 3,3-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀.

synthesize derivatives analogous to those of complex I.

In toluene solution, II reacted with dry HCl gas to give orange-red complex VI that analyzed for 3,3-(PPh₃)₂-3-H-3-Cl-3,1,2-RuC₂B₉H₁₁. Its IR spectrum also exhibited a weak ν_{Ru-H} at 2160 cm⁻¹ and a weak and broad ν_{Ru-Cl} at 330 cm⁻¹.

II reacted with CO at 100–110 °C in the solid state and slowly at room temperature in CH₂Cl₂ solution to give a yellow complex VII which analyzed for 3,3-(PPh₃)₂-3-CO-3,1,2-RuC₂B₉H₁₁. A very strong, sharp ν_{CO} band was observed in its IR spectrum at 1960 cm⁻¹.

Preparation of 3,3-(PPh₃)₂-3-H-7-(C₅H₅N)-3,1,2-RuC₂B₉H₁₀. Since a low oxidation state for a transition-metal complex is one of the generally accepted prerequisities for catalytic activity,[11] a formal Ru(II) complex based on the pyridine-substituted dicarbollide 9-C₅H₅N-7,8-C₂B₉H₁₀⁻ was synthesized.[12] Addition of freshly prepared Na⁺C₅H₅N-C₂B₉H₁₀⁻ in THF solution to a suspension of (PPh₃)₃RuHCl·PhCH₃ in THF and stirring for 16 h at room temperature yielded a red-brown crystalline complex VIII. This compound has a ν_{Ru-H} band at 2100 cm⁻¹ (weak, doublet), and a ν_{B-H} band at 2540 cm⁻¹ which is characteristic of an uncharged species. Its ¹¹B NMR consisted of resonances (Table III) that were grossly similar to that for 9-C₅H₅N-7,8-C₂B₉H₁₁.[12] Its ¹H NMR exhibited signals for pyridine protons at τ 1.55, phenyl protons at τ 2.74, and two equal hydride doublets at τ 19.6 and 21.0 (J_{P-H} = 31 Hz), respectively. This suggested the presence of two slightly differing ³¹P environments. The asymmetry introduced into the dicarbollide ligand by the pyridine substituent with associated steric and (or) electronic effects may be the cause of this nonequivalence. Complex VIII was thus postulated to be 3,3-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀. Its proposed structure is shown in Figure 2.

Conclusion

The synthesis and characterization of two novel ruthenium–carborane complexes as well as some of their derivatives have been presented. These dihydrido complexes have been shown to have formally seven-coordinate Ru(IV) centers. That these sterically crowded compounds should readily undergo reactions to give lower coordination numbers was dramatically illustrated by the isolation of a reductive elimination product for the 2,1,7 isomer and by the facile reactions of both isomers with neutral donor ligands like carbon monoxide to give air-stable six-coordinate d⁶ derivatives.

Preliminary results have shown both dihydrido complexes to be active isomerization and hydrogenation catalysts for some olefins whereas the corresponding monohydrido complex 3,3-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀ was devoid of catalytic activity.[13] This may well stem from the inability of the latter to generate vacant coordination sites while the

dihydrido complexes can readily become unsaturated via reductive elimination of its hydride ligands. These and other interesting ruthenium–carborane complexes are currently under further investigation.

Experimental Section

Materials. Reagent grade absolute ethanol and reagent grade methylene chloride were used without further purification. Tetrahydrofuran (THF) was freed of peroxide and water by distillation from sodium benzophenone and stored under N_2. Toluene was dried over calcium hydride and distilled under N_2. Hydrogen chloride gas from Liquid Carbonic Co. was dried by scrubbing with concentrated H_2SO_4. Carbon monoxide was also obtained from Liquid Carbonic Co. *All* reactions were carried out in Schlenk glassware using purified nitrogen (BTS catalyst, followed by KOH and silica gel). Solvents were all degassed before use by repeated applications of a vacuum followed with nitrogen saturations.

The $C_2B_9H_{12}^-$ salts were prepared following literature methods.[7] The ligand adduct $C_2B_9H_{11} \cdot C_5H_5N$ was prepared as described by Young et al.[12] $(PPh_3)_3RuHCl \cdot PhMe$ was synthesized in accordance with the procedure given in ref 8.

Physical Measurements. Infrared spectra were recorded using the Perkin-Elmer 421 double-grating spectrophotometer and the Beckman IR5A instrument. The 60-MHz proton NMR were recorded with the Varian A60-D while the 100-MHz spectra were from the Varian HA-100 NMR instrument. The 80.5-MHz ^{11}B NMR spectra were obtained on the instrument constructed by Professor F. A. L. Anet of this department.

Preparation of 2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$ (I). In a 250-mL Schlenk flask, equipped with a magnetic stir bar and reflux condenser, were placed 1.00 g (5.16 mmol) of 7,9-Me$_3$NHC$_2$B$_9$H$_{12}$ and 5.00 g (4.52 mmol) of (PPh$_3$)$_3$RuHCl·PhMe. While maintaining a N_2 atmosphere, 125 mL of degassed absolute ethanol was added. The purple suspension was gently refluxed for about 1 h or until the purple crystals had all changed to grayish blue. After cooling of the mixture, the product was separated by filtration using Schlenk techniques and washed with degassed ethanol followed by diethyl ether. The light blue crystals were then dried under high vacuum. The yield of I was 3.30 g (87% based on Ru). I may be recrystallized from toluene–ethanol in an inert atmosphere.

Preparation of 3,3-(PPh$_3$)$_2$-3,3-H$_2$-3,1,2-RuC$_2$B$_9$H$_{11}$ (II). II was prepared using the 7,8-Me$_3$NHC$_2$B$_9$H$_{12}$ salt in similar fashion as for the preparation of I. II was obtained as white crystals in 80% yield.

Thermolysis of I, Preparation of 2,2-(PPh$_3$)$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$ (III). An amount of 550 mg (0.72 mmol) of the complex was placed in a pyrolysis tube attached to a vacuum-line and Toepler pump. An oil bath was heated to 140–160 °C and placed around the sample. A noncondensable gas was evolved along with the development of an intense blue coloration in the residue. After 0.5 h, the gas evolution was complete and the volume collected corresponded to 0.66 mmol or 91% of the theoretical yield. The identity of this gas was confirmed to be hydrogen by mass spectral evidence. Exposure of the dark blue residue to hydrogen gas regenerated the starting material as demonstrated by identical spectral data. The dehydrogenation–hydrogenation cycle can be repeated at least three times without extensive decomposition of the starting complex.

Preparation of 2,2-(PPh$_3$)$_2$-2-H-2-Cl-2,1,7-RuC$_2$B$_9$H$_{11}$ (IV). A sample of I (300 mg, 0.395 mmol) was placed in a Schlenk tube equipped with a magnetic stirring bar and a gas-dispersion tube. Thirty milliliters of degassed toluene was added and dry HCl gas was bubbled into the suspension for 2 h. The orange-yellow suspension was filtered through Celite and layered with ethanol. Standing overnight gave yellow crystals of IV (40% yield).

Preparation of 2,2-(PPh$_3$)$_2$-2-CO-2,1,7-RuC$_2$B$_9$H$_{11}$ (V). A sample of I (300 mg, 0.395 mmol) and 30 mL of methylene chloride were placed in a Schlenk flask equipped with a magnetic stir bar and a

reflux condenser. Carbon monoxide was passed over the rapidly stirred suspension for 24 h. The yellow suspension was filtered through Celite and diluted with an equal volume of ethanol. Slow concentration on the rotary evaporator gave yellow crystals of V (45% yield).

Preparation of 3,3-(PPh$_3$)$_2$-3-H-3-Cl-3,1,2-RuC$_2$B$_9$H$_{11}$ (VI). VI was prepared from II using the same method for the synthesis of IV. It was obtained as red-orange crystals in 40% yield.

Preparation of 3,3-(PPh$_3$)$_2$-3-CO-3,1,2-RuC$_2$B$_9$H$_{11}$ (VII). VII was prepared from II using the same method for the preparation of V. It was obtained as yellow crystals in 45% yield.

Preparation of 3,3-(PPh$_3$)$_2$-3-H-7-C$_5$H$_5$N-3,1,2-RuC$_2$B$_9$H$_{10}$ (VIII). One gram (1 mmol) of (PPh$_3$)$_3$RuHCl·PhCH$_3$ and 20 mL of THF was placed in a 250-mL three-necked flask equipped with a magnetic stirring bar and an addition funnel with a medium-porosity frit. One hundred forty milligrams (3 mmol) of a NaH/oil suspension was placed in the addition funnel and 232 mg (1.1 mmol) of 9-C$_5$H$_5$N-7,8-C$_2$B$_9$H$_{11}$ in 20 mL of THF was added to the NaH. After 1 h had passed or when effervescence had ceased, the red solution was slowly added to the ruthenium complex with vigorous stirring. After overnight stirring, the red suspension was filtered, and the filtrate was evaporated to dryness under vacuum and redissolved in 5 mL of THF. Addition of 10 mL of ethanol gave red crystals of VIII. The yield was 550 mg (67% based on Ru).

Registry No. I, 60172-16-9; II, 60172-21-6; III, 60172-18-1; IV, 67350-80-5; V, 60172-19-2; VI, 67328-91-0; VII, 56465-05-5; VIII, 67375-46-6; (PPh$_3$)$_3$RuHCl, 19631-00-6; 7,9-Me$_3$NHC$_2$B$_9$H$_{12}$, 39430-48-3; 7,8-Me$_3$NHC$_2$B$_9$H$_{12}$, 57409-10-6; 9-C$_5$H$_5$N-7,8-C$_2$B$_9$H$_{11}$, 12403-60-0.

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(9) We thank Dr. T. Onak of the California State University, Los Angeles, for ^{31}P NMR spectra.

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(13) It was found that both I and II catalyze the hydrogenation of activated olefins such as ethyl acrylate and the isomerization of the terminal olefins 1-hexene and 1-octene. They can both be recovered without change from reaction mixtures. We thank Dr. N. Zlotin for the catalytic screening work.