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HYDRIDO-COMPLEXES OF RUTHENIUM WITH CARBORANE LIGANDS. (U)
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⁶ Hydrido-Complexes of Ruthenium with Carborane Ligands

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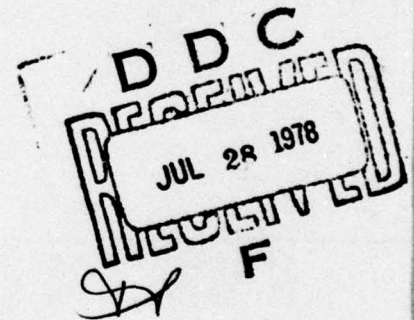
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Hydrido-Complexes of Ruthenium with Carborane Ligands

by

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ABSTRACT

The synthesis and characterization of the complexes $2,2-(PPh_3)_2-2,2-H_2-2,1,7-RuC_2B_9H_{11}$ and $3,3-(PPh_3)_2-3,3-H_2-3,1,2-RuC_2B_9H_{11}$ via the oxidative addition of 7,9- and 7,8- $C_2H_9H_{12}^-$, respectively, to $(PPh_3)_3RuHCl$ is 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 $3,3-(PPh_3)_2-3-H-7-C_5H_5N-3,1,2-RuC_2B_9H_{10}$ was also prepared and characterized.

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The versatile homogeneous catalysts based on the rhodium and ruthenium metals include $(PPh_3)_3RhCl$ and $(PPh_3)_3RuHCl$ 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 $C_2B_9H_{12}^-$ 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 tris(triphenylphosphine)ruthenium hydrido-chloride complex, $(PPh_3)_3RuHCl$. Oxidative addition of $NHMe_3^+$ salts of the carborane anions⁷ 7,9- and 7,8- $C_2B_9H_{12}^-$ to $(PPh_3)_3RuHCl \cdot \phi CH_3^8$ in boiling ethanol gave 2,2- $(PPh_3)_2$ -2,2-H₂-2,1,7- $RuC_2B_9H_{11}$ (I) and 3,3- $(PPh_3)_2$ -3,3-H₂-3,1,2- $RuC_2B_9H_{11}$ (II), respectively, in high yields.

Spectral Data

The ir spectra of I and II, shown in Table I, contain bands characteris-

Table I

ic 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.

(3)

The 100 MHz ^1H nmr of I (tetrahydrofuran, THF) showed a 1:2:1 triplet centered at 16.9 τ (Table II) as expected for hydride ligands on a ruthenium

Table II

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

The ^{31}P nmr of I (36.4 MHz, ^1H -decoupled) in THF consisted of a singlet at -34.5 ppm from 85% H_3PO_4 .⁹

80.5 MHz ^{11}B nmr of I in CH_2Cl_2 solution (^1H -decoupled) as shown in Table III is consistent with a closo-metallo-carborane of the 2,1,7- structure³ and the ^{11}B spectrum of II is also reminiscent of analogous 3,1,2-rhoda- and similar metallocarboranes.³

Table III

Elemental analyses (Table IV) also support the characterization of these compounds as dihydrido-bis(triphenylphosphine)-Ru(IV) complexes. If the dicarbollide moiety is regarded as a three electron-pair donor analogous to cyclopentadienide anion, C_5H_5^- , we can formally describe the ruthenium centers to be d^4 and assign them a coordination number of seven.

Table IV

(4)

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 have 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.

Figure 1

The 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 to 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° in vacuum, an intense blue color developed with concurrent elimination of hydrogen gas; one mole of H₂ being lost upon complete reaction. The resulting dark blue complex III showed no metal-hydride bands in the ir and the absence of high-field hydride resonances in the ¹H nmr. Its ¹¹B nmr spectrum in THF consisted of resonances typical of closo-metallocarboranes and its ³¹P nmr 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 $\rightleftharpoons$ H₂ + (PPh₃)₂-RuC₂B₉H₁₁ 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° in 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 $(PPh_3)_2RuC_2B_9H_{11}$ compared to the 2,1,7-isomer may account for this behavior.

Reactions of I

Although complex I in the 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° in the solid state and at room temperature in toluene or dichloromethane solution. A yellow complex, IV, was obtained that analyzed for $2,2-(PPh_3)_2-2-H-2-Cl-2,1,7-RuC_2B_9H_{11}$. 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° in the solid state and slowly at room temperature in CH_2Cl_2 solution. A yellow complex, V, was obtained that analyzed for $2,2-(PPh_3)_2-2-CO-2,1,7-RuC_2B_9H_{11}$. A single, sharp ν_{CO} was observed in its ir spectrum at 1957 cm^{-1} . V is a formally six-coordinate, 18-electron d^6 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 in both the solid state and in solution and methylene chloride solutions survived brief exposure to air. Slightly more vigorous conditions were necessary to synthesize derivatives analogous to those of complex I.

In toluene solution, II reacted with dry HCl gas to give an orange-red complex, VI, that analyzed for $3,3-(PPh_3)_2-3-H-3-Cl-3,1,2-RuC_2B_9H_{11}$. Its ir 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 $100-110^\circ$ in the solid state and slowly at room temperature in CH_2Cl_2 solution to give a yellow complex VII which analyzed for $3,3-(PPh_3)_2-3-CO-3,1,2-RuC_2B_9H_{11}$. A very strong, sharp ν_{CO} band was observed in its ir at 1960 cm^{-1} .

Preparation of $3,3-(PPh_3)_2-2-H-7-(C_5H_5N)-3,1,2-RuC_2B_9H_{10}$

Since a low-oxidation state for a transition metal complex is one of the generally accepted prerequisites for catalytic activity,¹¹ a formal Ru(II) complex based on the dicarbollide-pyridine adduct, $9-C_5H_5N-7,8-C_2B_9H_{10}^\ominus$ was synthesized.¹² Addition of freshly prepared $Na^+C_5H_5N-C_2B_9H_{10}^-$ in THF solution to a suspension of $(PPh_3)_3RuHCl \cdot \phi CH_3$ in THF and stirring for 16 hrs 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} at 2540 cm^{-1} which is characteristic of an uncharged species. Its ^{11}B nmr consisted of resonances (Table III) that were grossly similar to that for $9-C_5H_5N-7,8-C_2B_9H_{11}$.¹² Its 1H nmr exhibited signals for pyridine protons at 1.55τ , phenyl protons at 2.74τ , and two equal hydride doublets at 19.6τ and 21.0τ ($J_{P-H} = 31 \pm \text{Hz}$),

(7)

respectively. This suggested the presence of two slightly differing ^{31}P environments. The asymmetry introduced into the dicarbollide ligand by the pyridine adduct with associated steric and (or) electronic effects may be the cause of this non-equivalence. Complex VIII was thus postulated to be 3,3-(PPh_3)₂-3-H-7- $\text{C}_5\text{H}_5\text{N}$ -3,1,2- $\text{RuC}_2\text{B}_9\text{H}_{10}$. Its proposed structure is shown in Figure 2.

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 d^6 -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-(PPh_3)₂-3-H-7- $\text{C}_5\text{H}_5\text{N}$ -3,1,2- $\text{RuC}_2\text{B}_9\text{H}_{10}$, 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 conc. 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 D. C. Young, et al.¹² $(PPh_3)_3RuHCl \cdot \phi Me$ was synthesized in accordance with an Inorganic Synthesis procedure.⁸

Physical Measurements

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

Preparation of 2,2-(PPh₃)₂-2,2-H₂-2,1,7-RuC₂B₉H₁₁, 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-Me₃NHC₂B₉H₁₂ and 5.00 g (4.52 mmol) of (PPh₃)₃RuHCl·φMe. While maintaining a N₂ atmosphere, 125 ml of degassed absolute ethanol was added. The purple suspension was gently refluxed for about 1 hr or until the purple crystals had all changed to grayish-blue. After cooling, 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 in high-vacuum. The yield of I was 3.30 gm (87% based on Ru). I may be recrystallized from toluene-ethanol in an inert atmosphere.

Preparation of 3,3-(PPh₃)₂-3,3-H₂-3,1,2-RuC₂B₉H₁₁, II

II was prepared using the 7,8-Me₃NHC₂B₉H₁₂ 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-(PPh₃)₂-2,1,7-RuC₂B₉H₁₁, 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° and placed around the sample. A non-condensable gas was evolved along with the development of an intense blue coloration in the residue. After 0.5 hr, 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-(PPh₃)₂-2-H-2-Cl-2,1,7-RuC₂B₉H₁₁, 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 ml of degassed toluene was added and dry HCl gas was bubbled into the suspension for 2 hrs.

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-(PPh₃)₂-2-CO-2,1,7-RuC₂B₉H₁₁, V

A sample of I (300 mg, 0.395 mmol) and 30 ml 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 hrs. 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-(PPh₃)₂-3-H-3-Cl-3,1,2-RuC₂B₉H₁₁, 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-(PPh₃)₂-3-CO-3,1,2-RuC₂B₉H₁₁, 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-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀, VIII

One gram (1 mmol) of (PPh₃)₃RuHCl·φCH₃ and 20 ml THF was placed in a 250 ml 3-necked flask equipped with a magnetic stirring bar, and an addition funnel with a medium-porosity frit. One hundred forty mg (3 mmol) of a NaH/oil suspension was placed in the addition funnel and 232 mg (1.1 mmol) of 9-C₅H₅N-7,8-C₂B₉H₁₁ in 20 ml of THF was added to the NaH. After 1 hr 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 in 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).

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References

1. (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1711 (1966); (b) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, ibid., 31 (1968).
2. E.g., see (a) J. Kwiatak in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., M. Dekker, N.Y., 1971, pp. 13-51; (b) B. R. James, "Homogeneous Hydrogenation," Wiley, N.Y., 1973; (c) R. Cramer, Ann. N.Y. Sci., 172, 507 (1971); (d) A. J. Chalk, Ann. N.Y. Acad. Sci., 172, 533 (1971).
3. T. E. Paxson and M. F. Hawthorne, J. Amer. Chem. Soc., 96, 4674 (1974).
4. T. E. Paxson and M. F. Hawthorne, to be submitted to J. Amer. Chem. Soc.
5. E. H. S. Wong and M. F. Hawthorne, J. Chem. Soc. Chem. Commun., 257, 1976.
6. C. W. Jung and M. F. Hawthorne, J. Chem. Soc. Chem. Commun., 499, 1976.
7. (a) For a review on metallocarborane nomenclature, see: R. M. Adams, Pure Appl. Chem., 30, 683 (1972); D. D. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, J. Amer. Chem. Soc., 96, 3085 (1974); (b) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, J. Amer. Chem. Soc., 90, 862 (1968).
8. R. A. Schunn and E. R. Wonchoba, Inorganic Synthesis, 13, 131 (1972).
9. We thank Dr. T. Onak of the California State University, Los Angeles, for ^{31}P nmr.
10. Due to solvent disorder, refinement has not yet given satisfactory convergence. We have renewed our attempts to obtain alternate crystal forms and a low-temperature data set.
11. J. P. Collman, Acc. Chem. Res., 1, 136 (1968).
12. D. C. Young, D. V. Howe, and M. F. Hawthorne, J. Amer. Chem. Soc., 91, 859 (1969).
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.

Table I

Infrared Data for Ruthenium Carborane Complexes

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

^a Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad

^b Spectrum from Nujol mull of sample except for peaks labelled c.

^c Spectrum from KBr pellet of sample.

Table II

Proton nmr Data for Ruthenium Carborane Complexes in Tetrahydrofuran

<u>No.</u>	<u>Compound</u>	<u>Chemical Shift^a</u>	<u>Assignment</u>
I	2,2-(PPh ₃) ₂ ⁻	2.74	Phenyl protons
	2,2-H ₂ -2,1,7-RuC ₂ B ₉ H ₁₁	16.9	Metal hydride triplet J _{p-H} = 29 Hz
II	3,3-(PPh ₃) ₂ ⁻	2.73	Phenyl protons
	3,3-H ₂ -3,1,2-RuC ₂ B ₉ H ₁₁	16.3	Metal hydride triplet J _{p-H} = 28 Hz
III	2,2-(PPh ₃) ₂ ⁻	2.75	Phenyl protons
	2,1,7-RuC ₂ B ₉ H ₁₁		
VIII	3,3-(PPh ₃) ₂ ⁻	1.55	Pyridine protons
	3-H-7-C ₅ H ₅ N-	2.74	Phenyl protons
	3,1,2-RuC ₂ B ₉ H ₁₀	19.6	Metal hydride doublet J _{p-H} = 31 Hz
		21.0	Metal hydride doublet J _{p-H} = 31 Hz

^aAll chemical shifts are in τ.

Table III

80.5-MHz ^{11}B nmr Data for Ruthenium Carborane Complexes

<u>No.</u>	<u>Compound</u>	<u>Solvent</u>	<u>Shifts^a</u>
I	2,2-(PPh ₃) ₂ -2,2-H ₂ - 2,1,7-RuC ₂ B ₉ H ₁₁	CH ₂ Cl ₂	-1.2(1), 7.6(3), 13.1(4), 18.3(1)
II	3,3-(PPh ₃) ₂ -3,3-H ₂ - 3,1,2-RuC ₂ B ₉ H ₁₁	CH ₂ Cl ₂	-13.9(2), -4.6(5), 5.4(2)
III	2,2-(PPh ₃) ₂ - 2,1,7-RuC ₂ B ₉ H ₁₁	THF	-3.0(1), 0.0(1), 5.2(2), 10.9(2), 22.1(3)
VIII	3,3-(PPh ₃) ₂ -3-H- 7-C ₅ H ₅ N-3,1,2- RuC ₂ B ₉ H ₁₀	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 BF₃·OEt₂. The relative areas are in parentheses.

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Table IV
Analytical Data for Ruthenium Carborane Complexes

No.	Compound	Calc'd					Found					Analysis, %		
		C	H	P	B	Other	C	H	P	B	Other			
I	2,2-(PPh ₃) ₂ -2,2-H ₂ - 2,1,7-RuC ₂ B ₉ H ₁₁	60.08	5.66	8.15	12.81	13.30 (Rh)	60.00	5.70	8.26	12.77	12.60 (Rh)			
II	3,3-(PPh ₃) ₂ -3,3-H ₂ - 3,1,2-RuC ₂ B ₉ H ₁₁	60.08	5.66	8.15	12.81	—	60.15	5.85	7.85	12.51	—			
III	2,2-(PPh ₃) ₂ -2,1,7- RuC ₂ B ₉ H ₁₁	60.23	5.41	8.18	12.84	—	59.93	5.69	7.91	12.36	—			
IV	2,2-(PPh ₃) ₂ -2-H-2-Cl- 2,1,7-RuC ₂ B ₉ H ₁₁	57.47	5.29	7.80	—	4.46 (Cl)	57.82	5.58	7.93	—	4.26 (Cl)			
V	2,2-(PPh ₃) ₂ -2-CO- 2,1,7-RuC ₂ B ₉ H ₁₁ ·THF	60.2	5.6	7.22	—	—	60.24	5.63	7.06	—	—			
VI	3,3-(PPh ₃) ₂ -3-H-3-Cl- 3,1,2-RuC ₂ B ₉ H ₁₁	57.47	5.29	7.80	12.25	4.46 (Cl)	57.18	5.08	7.43	11.94	4.85 (Cl)			
VII	3,3-(PPh ₃) ₂ -3-CO- 3,1,2-RuC ₂ B ₉ H ₁₁	59.62	5.22	7.88	12.38	—	59.98	5.34	7.98	12.59	—			
VIII	3,3-(PPh ₃) ₂ -3-H-7- C ₅ H ₅ N-3,1,2-RuC ₂ B ₉ H ₁₀	60.20	5.60	7.22	—	—	60.24	5.63	7.06	—	—			

Figure 1. An ORTEP drawing (ref. 5) of $2,2-(PPh_3)_2-2,2-H_2-2,1,7-RuC_2B_9H_{11}$, 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).

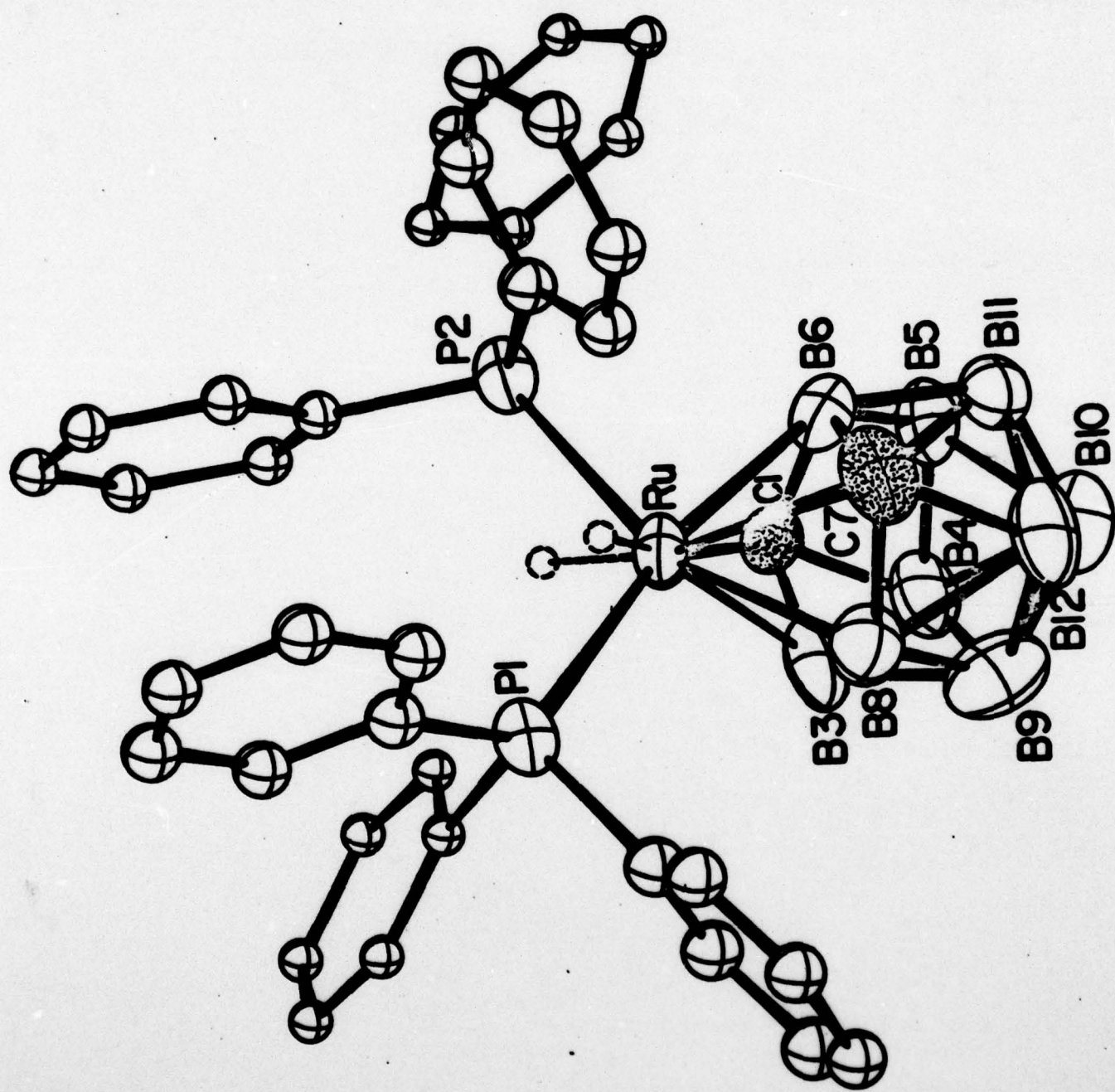
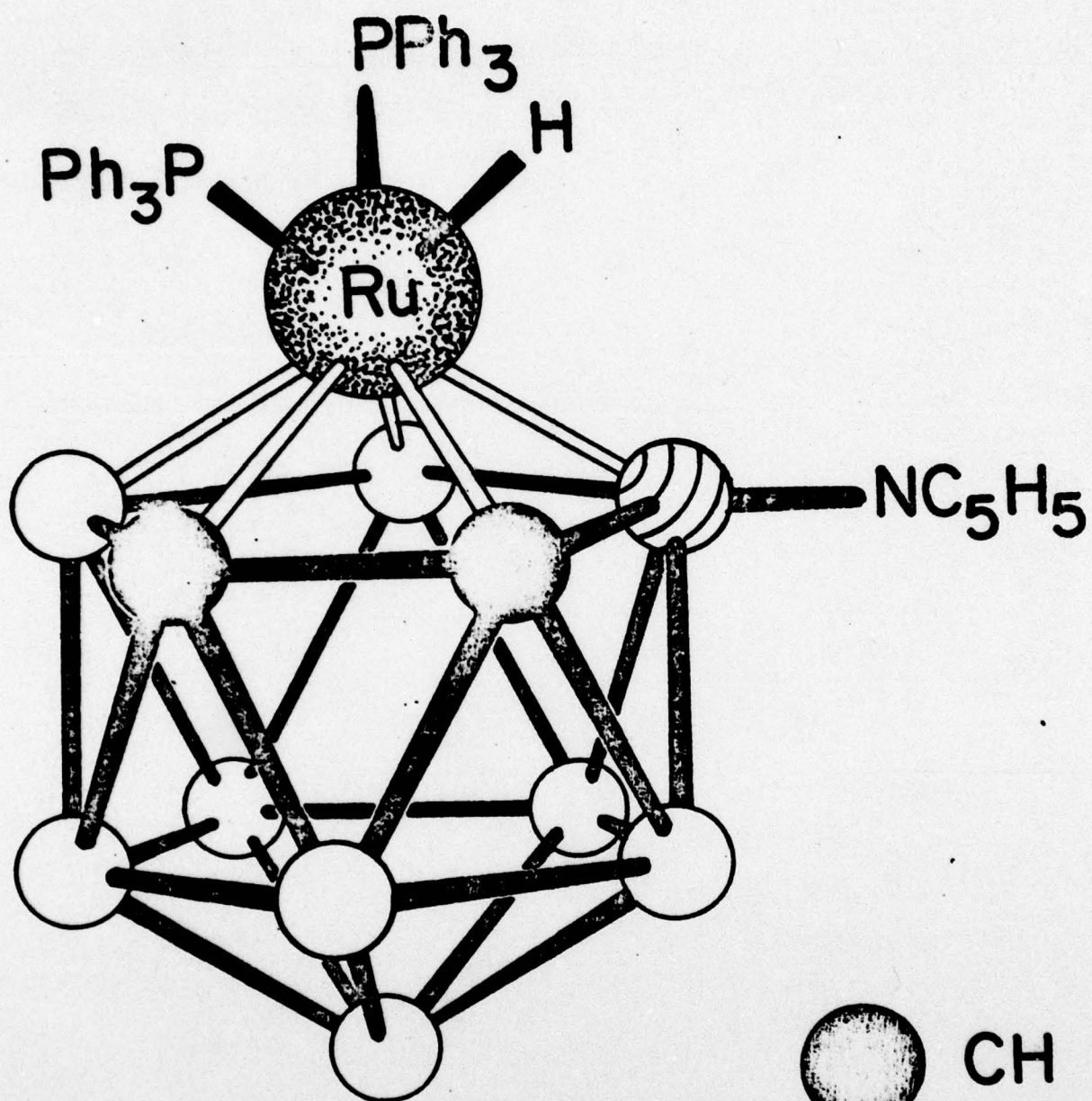


Figure 4. Proposed structure of $3,3-(PPh_3)_2-3-H-7-C_5H_5N-3,1,2-RuC_2B_9H_{10}$

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis and characterization of the complexes 2,2-(PPh₃)₂-2,2-H₂-2,1,7-RuC₂B₉H₁₁ and 3,3-(PPh₃)₂-3,3-H₂-3,1,2-RuC₂B₉H₁₁ via the oxidative addition of 7,9- and 7,8-C₂H₉H₁₂⁻, respectively, to (PPh₃)₃RuHCl is 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 H₂ with in vacuo to give a five-coordinate d⁶, 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-(PPh₃)₂-3-H-7-C₅H₅N-3,1,2-RuC₂B₉H₁₀ was also prepared and characterized.

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