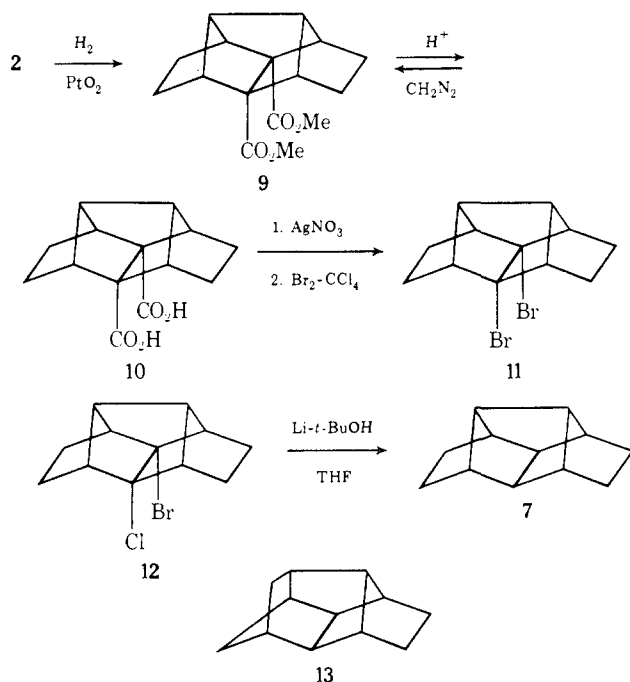


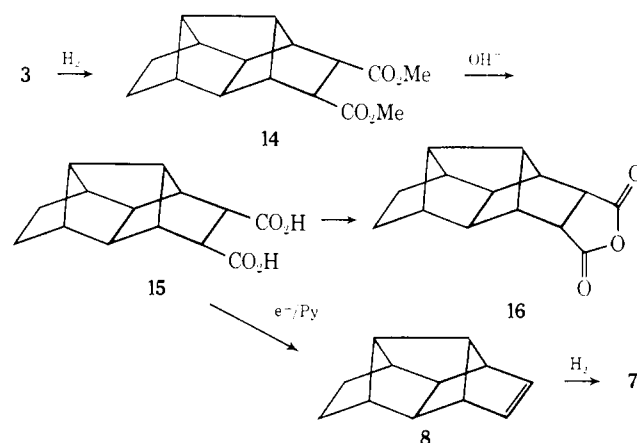
ether. The diacid **10** was subjected to a double Hunsdieker reaction by refluxing its silver salt in bromine-carbon tetrachloride solution. A 50% yield of the dibromide **11** contaminated by about 10% of bromochloro product **12** was obtained. Pure **11** was obtained by preparative glpc: mp 170–171°; nmr (CCl<sub>4</sub>)  $\delta$  2.5 (m, 4), 2.2–1.4 (m, 10); partial ir (KBr) 3.4, 7.8, 8.3, 10.4, 12.7, 12.9, 14.0, and 14.4  $\mu$ . The dibromide reaction mixture was dehalogenated by lithium-*tert*-butyl alcohol in refluxing tetrahydrofuran to give **7**, which was isolated in 37% yield as an oil by preparative glpc: ir (neat) 3.42, 3.52, 6.85 w, 6.95 w, 7.75, 7.79, 8.35 w, 8.79 w, and 14.0 w  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\delta$  2.15 (s, 6), 1.48 (s, 10). The simplicity of the nmr was striking; the spectrum taken at 220 MHz was essentially the same. In contrast, the twisted decahydromethenocyclopenta[*a*]pentalene isomer **13** has a very complex



nmr in the region  $\delta$  0.8–2.5;<sup>9,10</sup> the ir of **13** was very similar to that of **7**.<sup>10</sup>

Isomer **3** was utilized for the synthesis of monoolefin **8**. Hydrogenation over platinum oxide gave a saturated diester **14** which was hydrolyzed in 10% potassium hydroxide to give diacid **15** (~70% yield overall). The diacid was converted by trifluoroacetic anhydride to the anhydride **16** for characterization: mp 171–173°; nmr (CDCl<sub>3</sub>)  $\delta$  3.35 (m, 2), 2.7 (m, 3), 2.25 (br, s, 3), 1.8 (br, s, 2), 1.55 (s, 4); partial ir (KBr) 3.39, 3.48, 5.38, and 5.6  $\mu$ . Electrolytic decarboxylation<sup>11</sup> of the diacid **15** in 10% aqueous pyridine and a small amount of triethylamine using platinum gauze electrodes gave crude olefin **8** in about 50% yield, which was purified by preparative glpc or by column chromatography on alumina: nmr (CDCl<sub>3</sub>)  $\delta$  5.8 (t, 2,  $J$  = 2 Hz), 2.78 (m, 2), 2.45 (m, 3), 1.7 (m, 1), 1.4–1.6 (m,

6); partial ir (neat) 3.28, 3.40, 3.50, 6.30, 7.82, 13.83, 14.15, and 15.10  $\mu$ . Hydrogenation of **8** over platinum oxide gave the same saturated hydrocarbon **7** obtained above.



A particularly challenging synthetic application of the reactions and products described here is as starting points for a dodecahedrane synthesis. For example, **2** possesses functionality which can be potentially exploited to strategically add the additional six carbon atoms required for construction of a C<sub>20</sub> framework which subsequently can be converted to dodecahedrane by rational synthetic steps. We have found in preliminary experiments with this objective in mind that the central carbon-carbon bond of **2** can be reductively cleaved<sup>12</sup> using sodium in toluene containing trimethylsilyl chloride whereas zinc in acetic acid failed. Evidence was obtained for three isomers (endo-exo, endo-endo, and exo-exo); the exo-endo isomer could be assigned by nmr, while a tentative assignment was made for the other isomers. We anticipate that kinetically controlled, base-catalyzed isomerization of exo-carboxyl to endo-carboxyl should occur owing to steric hindrance of the endo-hydrogen, and our first results were encouraging. Various five-membered ring annulations of the double bonds also have been considered.

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## Preparation of Hydridometalloboranes and Their Use as Homogeneous Catalysts

Sir:

In recent years the discovery and utility of homogeneous hydrogenation,<sup>1</sup> isomerization,<sup>2</sup> hydrosilylation,<sup>3</sup> and hydrogen-deuterium exchange<sup>4</sup> catalysts

(1) *E.g.*, see (a) J. Kwiatek in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, pp 13–51. (b) B. R. James, "Homogeneous Hydrogenation," Wiley, New York, N. Y., 1973.

(2) *E.g.*, see (a) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966), and references therein; (b) R. Cramer, *Ann. N. Y. Acad. Sci.*, **172**, 507 (1971); (c) B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Well, *J. Chem. Soc. A*, 37 (1968).

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have expanded in scope to become one of the largest areas of endeavor in inorganic chemistry. To date, however, no reports of catalytic systems utilizing the very stable<sup>5</sup> family of metallocarboranes have appeared. We now wish to report the preparation of two novel hydridometallocarboranes and the application of these complexes to homogeneous catalysis.

When a methanolic solution of the tris(triphenylphosphine)rhodium(I) cation<sup>6</sup> was allowed to react at 60° with a methanolic solution of either (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> (Ia) or (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>[7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> (IIa)<sup>7</sup> high yields (>80%) of yellow crystalline products I and II, respectively, were obtained. Compounds I and II could also be obtained by treatment of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>RhCl<sup>9</sup> with a methanolic solution of AgBF<sub>4</sub> and subsequent reaction with Ia or IIa (yields >85%) or by direct reaction of Ia or IIa with [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>RhCl in alcoholic solutions (yields >90%).

The ir spectra of I and II contained absorptions characteristic of triphenylphosphine and the carborane moiety, and two additional bands (2080 and 2120 cm<sup>-1</sup> (I), 2070 and 2110 cm<sup>-1</sup> (II), Nujol mull) assigned to ν(RhH). Elemental analyses, <sup>1</sup>H, <sup>11</sup>B, and <sup>31</sup>P nmr data confirmed the formulation as 3,3-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>-3-H-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (I) and 2,2-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>-2-H-2,1,7-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (II).

The 100-MHz <sup>1</sup>H nmr of I in CD<sub>2</sub>Cl<sub>2</sub> displayed a complex series of resonances centered at τ 2.73 (30)<sup>10</sup> assigned to the phenyl protons and a broad resonance centered at τ 7.76 (2) assigned to the carboranyl protons. The hydride resonance was observed at τ 18.4 as a triplet of doublets. Upon <sup>31</sup>P decoupling, this pattern collapsed to a doublet (*J*<sub>P-H</sub> = 29 ± 2 Hz, *J*<sub>Rh-H</sub> = 17 ± 2 Hz). The phenyl resonances of II were centered at τ 2.75 (30), and the carboranyl resonance was located at τ 8.74 (2). The high field triplet of doublets was centered at τ 21.1 and <sup>31</sup>P decoupling collapsed these signals to a doublet (*J*<sub>P-H</sub> = 25 ± 2 Hz, *J*<sub>Rh-H</sub> = 14 ± 2 Hz). The high field pattern of II is depicted in Figure 1.

The 101-MHz, proton-decoupled, <sup>31</sup>P spectrum of I in CH<sub>2</sub>Cl<sub>2</sub> displayed a doublet (*J*<sub>Rh-P</sub> = 128 ± 20 Hz) centered at -40.8 ppm,<sup>11</sup> while the spectrum of II contained the doublet (*J*<sub>Rh-P</sub> = 144 ± 20 Hz) centered at -41.5 ppm. Although the 80.5-MHz <sup>11</sup>B nmr spectra (in CH<sub>2</sub>Cl<sub>2</sub>) of the complexes were broad and unresolved, the proton decoupled spectra were more revealing. The spectrum of I contained resonances at +0.4 (1),<sup>12</sup> +1.2 (1), +8.7 (4), and +20.7 (3) ppm, while II displayed resonances at +1.2 (1), +7.5 (2), +12.5 (3), +15.9 (1), and +19.5 (2) ppm. The <sup>11</sup>B spectra of

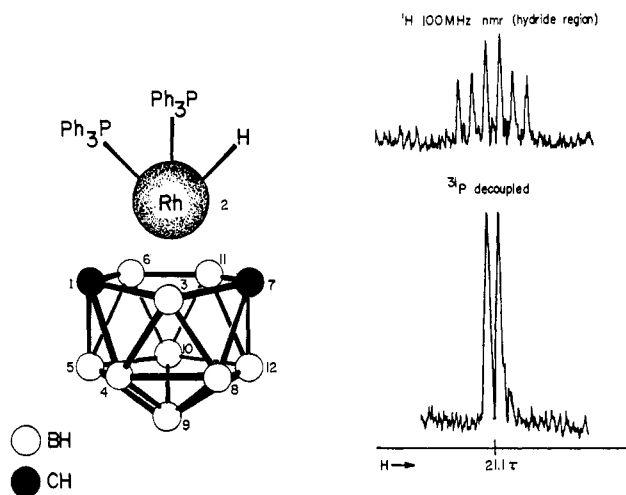


Figure 1. The proposed structure of 2,2-bis(triphenylphosphine)-2-hydridoundecahydro-1,7-dicarbido-2-rhoda-closo-dodecaborane (II) and the 100-MHz <sup>1</sup>H nmr spectrum of the hydride region.

both I and II were very similar to the <sup>11</sup>B spectra of 3-(η-C<sub>5</sub>H<sub>5</sub>)-3,1,2-CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> and 2-(η-C<sub>5</sub>H<sub>5</sub>)-2,1,7-CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>, respectively.<sup>13</sup>

We formulate the complexes as formal d<sup>6</sup> Rh(III) hydrides with triphenylphosphine ligands occupying two coordination sites. Consistent with d<sup>6</sup> metallocarboranes,<sup>3b,14</sup> we suggest that the C<sub>2</sub>B<sub>9</sub>H<sub>11</sub><sup>2-</sup> (dicarbollide) ligand is symmetrically bonded to the rhodium atom which completes the carborane icosahedron. The proposed stereochemistry of II is depicted in Figure 1.

Both I and II are indefinitely air and water stable in the solid state, and solutions (CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, THF) are stable under an inert atmosphere but slowly decompose over a period of days when exposed to the air.

Benzene solutions (~20°, under N<sub>2</sub>) of I or II (10<sup>-3</sup> M) rapidly catalyzed the isomerization of 1-hexene (0.5 M). Within 24 hr the reaction mixture contained 1-hexene and *cis*-2-hexene (total 17%),<sup>15</sup> *trans*-2-hexene (56%), *cis*-3-hexene (3%), and *trans*-3-hexene (24%). The complex was recovered unaltered as determined by its ir spectrum. The addition of excess triphenylphosphine (1.0 M) greatly inhibited the isomerization.

Under a hydrogen atmosphere (1 atm), solutions of I or II (10<sup>-3</sup> M) in benzene (35°) catalyzed the hydrogenation of 1-hexene (0.1 M). Concurrent isomerization was observed, but, at the end of 52 hr, essentially all of the hexenes were converted to *n*-hexane.<sup>17</sup> Again, I and II were recovered unaltered. The intriguing mechanistic role played by these rhodium complexes in hydrogenation and isomerization is currently under investigation.<sup>18</sup>

We have found that I and II catalyze the deuterium

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(9) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(10) All proton chemical shifts reported are with respect to TMS; the number in parentheses refers to the relative area.

(11) Chemical shifts of <sup>31</sup>P nmr spectra reported are from 85% H<sub>3</sub>PO<sub>4</sub>.

(12) All <sup>11</sup>B chemical shifts reported are from BF<sub>3</sub>·OEt<sub>2</sub>. The number in parentheses is the relative area associated with the resonance.

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(14) R. M. Wing, *J. Amer. Chem. Soc.*, **90**, 4828 (1968).

(15) *cis*-2-hexene and 1-hexene had coincident retention times on the glc column used; all other components were sufficiently resolved to determine the relative areas, the number in parentheses. The calculated thermodynamic distributions<sup>16</sup> are 1-hexene (1%), *cis*-2-hexene (20%), *trans*-2-hexene (47%), and 3-hexenes (32%).

(16) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

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(18) C. W. Jung, T. E. Paxson, and M. F. Hawthorne, to be submitted for publication.

exchange of terminal {BH} groups in boranes, carboranes, and metalloboranes,<sup>19</sup> as well as the hydrosilylation of ketones.<sup>20</sup> In THF solution (55°, 10<sup>-2</sup> M I or II), 1.6 mmol of acetophenone was quantitatively hydrosilylated (2.0 mmol of diphenylsilane used) in ~17 hr as determined by <sup>1</sup>H nmr spectroscopy of the hydrosilylated product.

We have successfully expanded this chemistry to include the iridium congeners and are presently exploring the catalytic capabilities of these complexes. Several rhodium complexes from aryl- and alkyl-substituted [C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> anions have been synthesized and have also proved to be hydrogenation catalysts. Intriguing reactions of ruthenium complexes with carborane anions have also been discovered, and the characterization and catalytic properties of the products are currently under investigation in these laboratories.

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(20) R. A. Grey and M. F. Hawthorne, unpublished data.

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### Transition Metal Catalyzed Exchange of Deuterium Gas with Terminal Boron-Hydrogen Bonds in Carboranes, Metallocarboranes, and Other Boron Compounds

Sir:

Deuterated boron hydrides may be prepared by synthesis from B<sub>2</sub>D<sub>6</sub><sup>1-3</sup> or by deuterium exchange on a boron hydride employing B<sub>2</sub>D<sub>6</sub>,<sup>2,3</sup> D<sub>2</sub>O,<sup>1,4</sup> DCl catalyzed by AlCl<sub>3</sub>,<sup>5</sup> or DCl catalyzed by dioxane<sup>5</sup> as the deuterium sources. Deuterated carboranes and metallocarboranes have only been prepared from deuterated decaboranes.<sup>6,7</sup> We wish to report that a number of group VIII hydrogenation catalysts will effect the exchange of deuterium gas with terminal B-H bonds in a wide variety of boron compounds, including carboranes, metallocarboranes, and boron hydrides.

We recently reported the first example of oxidative addition of a B-H bond to a transition metal.<sup>7</sup> The

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reaction was an "ortho" metallation in an L<sub>3</sub>IrCl complex where L was the carboranylphosphine 1-(PMe<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (I), a reaction analogous to well-known ortho metallations in arylphosphine complexes.<sup>8</sup>

In the presence of catalytic amounts of (PPh<sub>3</sub>)<sub>3</sub>-RuHCl, an effective catalyst for the specific ortho deuteration of triphenylphosphine,<sup>9</sup> I has been found to exchange hydrogen atoms for deuterium gas at boron atoms but not at carbon atoms. A mechanism involving exchange only *via* an "ortho" metallated, complexed carboranylphosphine could introduce a maximum of four deuterium atoms into I. However, mass spectral analysis of the product revealed species with more than four deuterium atoms per molecule, ruling out intramolecular exchange on the carboranylphosphine as the sole mechanism of deuterium incorporation. Subsequent experiments have revealed that a wide variety of noncomplexing boron compounds undergo similar catalytic exchange.

In a typical procedure, 1 mmol of the substrate and 0.05 mmol of the catalyst were stirred under N<sub>2</sub> in 20 ml of toluene at temperatures from 65 to 100° while deuterium gas was bubbled through the solution at a rate of about 3 ml/min. Table I lists the results for a

Table I. Preliminary Results of Selected Catalytic Deuterations

Substrate	Catalyst	Conditions <sup>a</sup> (days)	Av no. of D in product <sup>b</sup>
1,2-C <sub>2</sub> B <sub>10</sub> H <sub>12</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl	3	8
	III	1 (65°)	10
1,7-C <sub>2</sub> B <sub>10</sub> H <sub>12</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl	3	8
1,12-C <sub>2</sub> B <sub>10</sub> H <sub>12</sub>	III	1	10
1,6-C <sub>2</sub> B <sub>8</sub> H <sub>10</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl	1	8
3-( $\eta$ -C <sub>3</sub> H <sub>5</sub> )-3,1,2-CoC <sub>2</sub> B <sub>9</sub> H <sub>11</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl	3	5
	III	1	6
1-( $\eta$ -C <sub>3</sub> H <sub>5</sub> )-1,2,4-CoC <sub>2</sub> B <sub>9</sub> H <sub>10</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl	1 (80°)	6
B <sub>10</sub> H <sub>14</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl <sup>c</sup>	3	3
	III <sup>c</sup>	1	6
(Me <sub>3</sub> NH) <sub>2</sub> [B <sub>10</sub> H <sub>10</sub> ] <sup>2-</sup>	(PPh <sub>3</sub> ) <sub>3</sub> (CH <sub>3</sub> CN)RuHCl	3 (80° in CH <sub>3</sub> CN)	2
Me <sub>3</sub> NBH <sub>3</sub>	(PPh <sub>3</sub> ) <sub>3</sub> RuHCl <sup>c</sup>	1	3

<sup>a</sup> Except where noted, reactions were at 100° with 1 mmol of substrate + 0.05 mmol of catalyst in 20 ml of toluene with D<sub>2</sub> bubbling at ~3 ml/min. <sup>b</sup> Estimated from ir, <sup>11</sup>B nmr, and mass spectra. <sup>c</sup> Reaction with catalyst was noted.

number of substrates with two of the more effective catalysts found. The preliminary results of a comparison of different catalysts with 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> as the constant substrate are presented in Table II.

Examples of both homogeneous and heterogeneous active catalysts have been found, although the homogeneous catalysts are much more effective and selective. The most active catalysts are two metallocarboranes discovered in these laboratories,<sup>10</sup> 3,3-(PPh<sub>3</sub>)<sub>2</sub>-3-H-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (II) and 2,2-(PPh<sub>3</sub>)<sub>2</sub>-2-H-2,1,7-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (III), solutions of which have also been found to catalyze homogeneous hydrogenation, hydrosilylation, and alkene isomerization.<sup>10</sup> Compounds II and III effect

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