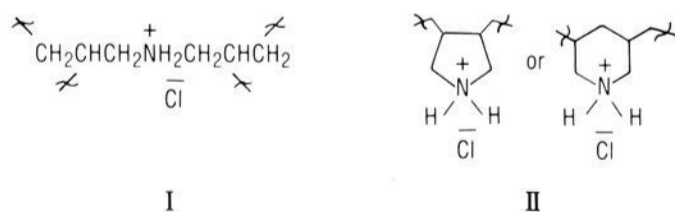


**Figure 2.** Electron micrograph of a stained (uranyl acetate) thin section of **3** (bar represents 2000 Å).

Redispersal of **3** (0.5 mg) was readily achieved by simple vortex mixing in distilled water (2.0 mL) at 60 °C. Passage of this dispersion through a Sephadex G-50 column afforded an 84% recovery of the polymer in the void volume of the column (nitrogen analysis).<sup>7</sup> Electron microscopic examination (negative staining) confirmed the presence of closed spheres having diameters ranging between ca. 200 and 2000 Å (Figure 1A). Incubation of the dispersion with an aqueous solution containing (<sup>14</sup>C)sucrose for 100 h at room temperature, followed by gel filtration (Sephadex G-50), resulted in negligible entrapment of the marker.<sup>5</sup> The inability of these ghosts to retain low molecular weight species is presumed to be due to the absence of a continuous lipid layer.

Examination of an *unstained* dispersion by scanning transmission electron microscopy (STEM) at low magnification revealed a size distribution similar to that found by negative staining (Figure 1B).<sup>8,9</sup> A plot of the measured mass for a representative sample of ghosts (46 particles having diameters ranging from 100 to 520 Å) as a function of particle radius gave a best fit to a hollow sphere model with a membrane thickness of 14 Å (assuming a density for the bulk polymer of 0.92).<sup>10</sup> Virtually none of the data fell within a solid sphere model. Some of the membranes of the larger ghosts appeared to be torn (Figure 1C). Analysis of such vesicles (600–2300 Å diameter) indicated an apparent quantization in membrane thickness; i.e., the thinnest layers observed were 14 Å; most other thicknesses measured were ca. 28, 42, or 56 Å. We presume that the larger thicknesses observed are due to vesicle aggregation.

In principle, every surfactant bilayer containing **1** should be capable of generating two concentric polymeric spheres. Electron micrographs of stained thin sections of **3** (ca. 900 Å) not only confirm their hollow nature but also reveal regions where two distinct membranes can be identified (Figure 2). Whether or not portions of these membranes have joined together during the polymerization remains to be established. Polymerization of **1** in the highly condensed vesicular state is expected to result in substantial cross-linking and the formation of a porous network,<sup>11,12</sup> i.e., the generation of type I monomer units. The observed



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(10) Ultracentrifugation (100 000 rpm, 30 min) of an aqueous dispersion of **3** in pure water indicated a very slow rate of flotation. Taking 1.00 g/cm<sup>3</sup> as an upper limit for the density of the bulk polymer, and 0.85 g/cm<sup>3</sup> (density of polypropylamine) as an estimate for the lower limit, the density of **3** is estimated to be ca. 0.92 g/cm<sup>3</sup>; within a density range 0.75–1.00 g/cm<sup>3</sup> the calculated membrane thickness varied by less than 25%.

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retention of the spherical state of **3** in water provides very strong indirect evidence for the existence of such cross-linking. The extent to which competing cyclopolymerization occurs (yielding 5- or 6-membered rings II in each of the monolayers), however, is less certain.

Experiments now in progress are aimed at defining and controlling the porosity of **3**, further characterizing its membrane structure, and extending this methodology to the synthesis of related polymer colloids. The results of these studies will be reported in due course.

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**Registry No.** Diallylammonium dihexadecylphosphate (homopolymer), 91550-89-9; sodium dihexadecylphosphate, 60285-46-3.

### Metal-Promoted Insertion of an Activated Alkene into a B–H Bond of an Exopolyhedral *nido*-Rhodacarborane: Rhodium-Catalyzed Hydroboration

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In conjunction with our mechanistic studies of the catalytic hydrogenation of alkenes using *exo-nido*-[(PPh<sub>3</sub>)<sub>2</sub>Rh][7,8-μ-(CH<sub>2</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (I),<sup>1-3</sup> we have observed the metal-promoted insertion of an activated alkene into a terminal B–H bond of the carborane ligand of I. We report here the synthesis<sup>4</sup> and X-ray crystallographic structure determination<sup>5</sup> of the product of this reaction, *exo-nido*-[(PPh<sub>3</sub>)<sub>2</sub>Rh][7,8-μ-(CH<sub>2</sub>)<sub>3</sub>-10-[(CH<sub>2</sub>)<sub>2</sub>C(O)-O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (II), and propose a mechanism for its formation from I.

The molecular structure of II (Figure 1) consists of a rhodium(I) bis(triphenylphosphine) moiety attached to a *nido* C<sub>2</sub>B<sub>9</sub> icosahedral fragment through a pair of three-center, two-electron Rh–H–B bonds. The unique BH at vertex 10 in I has been transformed into B(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>(1-C<sub>4</sub>H<sub>9</sub>) in II by formal hydroboration of the acrylate ester.

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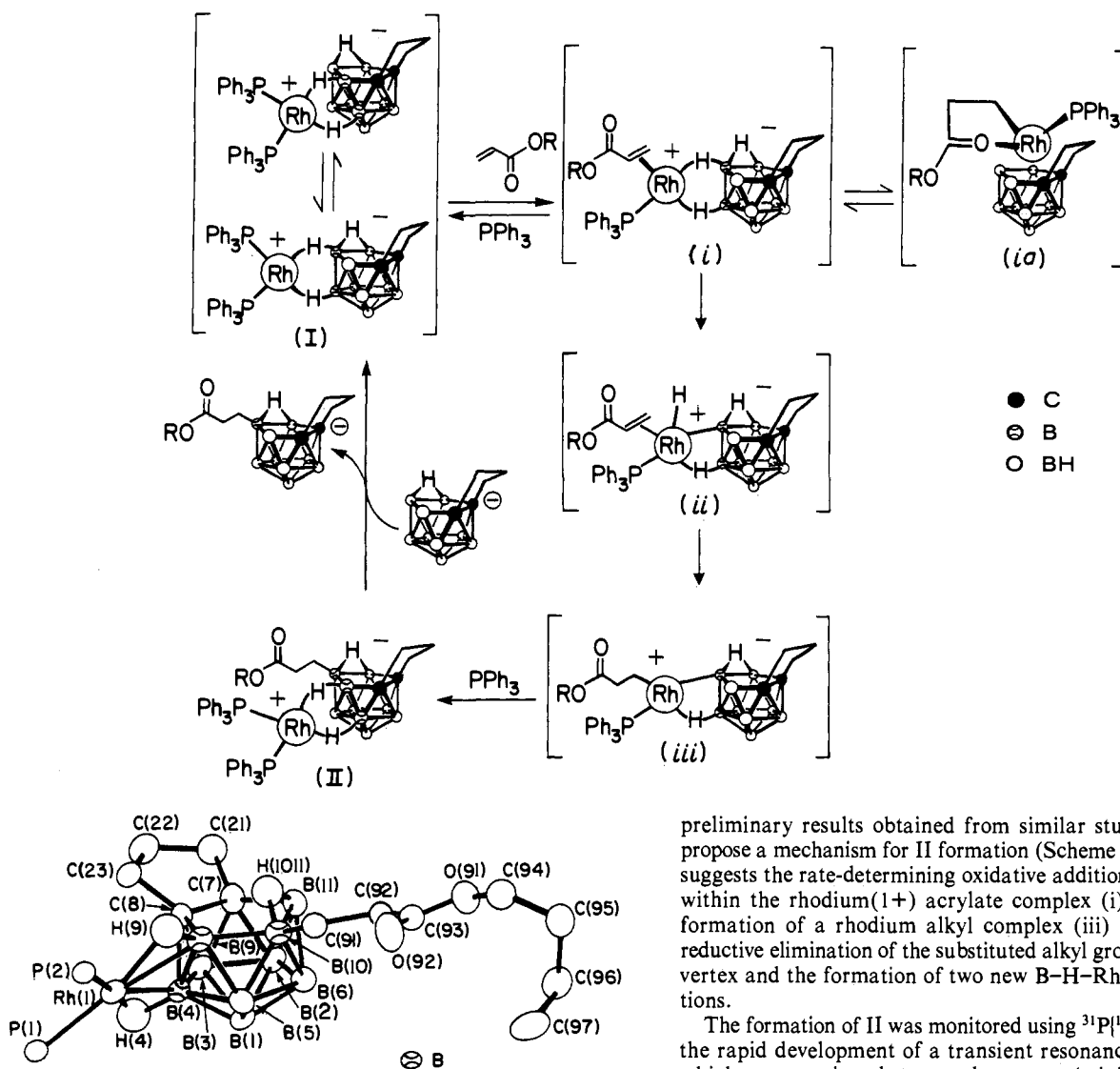
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(4) A 10 mL of THF solution containing 0.50 g (0.57 mmol) of I, 4.0 mL (28 mmol) of 1-butyl acrylate, and a trace of hydroquinone was stirred at 40 °C for 5 days in a sealed Pyrex tube. Concentration of the solution in vacuo and addition of heptane produced dark red crystals of II in 69% yield. Anal. Calcd for C<sub>48</sub>H<sub>58</sub>B<sub>9</sub>P<sub>2</sub>O<sub>2</sub>Ph: C, 62.04; H, 6.29; B, 10.47; Rh, 11.08; P, 6.67. Found: C, 62.22; H, 6.58; B, 10.14; Rh, 10.66; P, 6.73. Results from spectroscopic analysis were consistent with the observed structure and with previously reported structures.<sup>1,2</sup>

(5) Crystal data for II: A red, thin, irregularly shaped parallelepiped crystal suitable for X-ray analysis was grown from pentane/CH<sub>2</sub>Cl<sub>2</sub> by vapor diffusion under N<sub>2</sub>. Triclinic, *P1*; *a* = 12.404 (3) Å, *b* = 13.826 (4) Å, *c* = 14.941 (4) Å, α = 95.58 (2)°, β = 101.92(2)°, γ = 109.35(2)°; *V* = 2327 (4) Å<sup>3</sup>; *Z* = 2; *d*<sub>calcd</sub> = 1.326 g/cm<sup>3</sup>; μ(Mo Kα) = 4.68 cm<sup>-1</sup>. An automated diffractometer (Syntex P1) was used to gather 6220 reflections with *I* > 3(*I*), corrected for absorption, with the crystal at 133 K. The structure was solved by using standard Patterson, Fourier, and least-squares techniques and refined to residuals of *R* = 0.053 and *R*<sub>w</sub> = 0.064 with a "goodness-of-fit" index of 1.66. *R* = Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|; *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>]/Σ(w|*F*<sub>o</sub>|<sup>2</sup>)]<sup>1/2</sup> where *w* = [1/Σ|*F*<sub>o</sub>|<sup>2</sup>]; "goodness-of-fit" = [Σ[w(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>]/(N<sub>obsd</sub> - N<sub>parameters</sub>)]<sup>1/2</sup>.

Scheme I. Proposed Mechanism of II Formation, from One of the Several Possible Isomers of I



**Figure 1.** Molecular structure of II, with nonbridging hydrogen atoms and phenyl groups omitted for clarity and thermal ellipsoids drawn at 50% probability level. Rh-P(1) = 2.225 (1), Rh-P(2) = 2.215 (1), Rh-B(4) = 2.355 (6), Rh-B(9) = 2.388 (6), B(10)-C(91) = 1.574 (8) Å; P(1)-Rh-P(2) = 95.83 (5)°, B(9)-H(9)-Rh = 97.7 (4)°, B(4)-H(4)-Rh = 99.5 (3)°.

The rhodium center of I was necessary to effect alkene insertion: results from control experiments excluded mechanisms invoking nucleophilic attack upon the acrylate ester (Michael addition) by the carborane dianion  $[7,8-\mu-(\text{CH}_2)_3-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^{2-}$  and/or the anion  $[7,8-\mu-(\text{CH}_2)_3-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$  separately and in mixtures of the two ions.

In an unprecedented application of facile carborane ligand exchange,<sup>6,7</sup> we have observed the insertion of 1-butyl acrylate into the B(10)-H bond of the carborane salt  $\text{Cs}^+[7,8-\mu-(\text{CH}_2)_3-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$  if a catalytic amount of I is present, giving  $\text{Cs}^+[7,8-\mu-(\text{CH}_2)_3-10-[(\text{CH}_2)_3\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3]-7,8-\text{C}_2\text{B}_9\text{H}_9]^-$ .

On the basis of extensive studies which demonstrated deuterium exchange between deuterium-labeled olefins and the B-H vertices of *closo*-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> (III)<sup>3,8</sup> as well as the

preliminary results obtained from similar studies<sup>9</sup> using I, we propose a mechanism for II formation (Scheme I). This proposal suggests the rate-determining oxidative addition of a B-H vertex within the rhodium(1+) acrylate complex (i) followed by the formation of a rhodium alkyl complex (iii) then, finally, the reductive elimination of the substituted alkyl group with the boron vertex and the formation of two new B-H-Rh bonding interactions.

The formation of II was monitored using <sup>31</sup>P{<sup>1</sup>H} FT-NMR and the rapid development of a transient resonance<sup>10</sup> was observed which was assigned to a *closo*-mono(triphenylphosphine)-rhodacarborane chelated alkyl complex<sup>3,8</sup> (structure ia).

The acrylate insertion reaction is not observed using the three isomers of *closo*-[(PPh<sub>3</sub>)<sub>2</sub>HRhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>],<sup>8</sup> although the reaction is observed for the disubstituted [(PPh<sub>3</sub>)<sub>2</sub>RhC(R)C(R')B<sub>9</sub>H<sub>10</sub>] species<sup>1,2</sup> (R, R' = 1',2'-μ-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, IV; CH<sub>3</sub>, CH<sub>3</sub>, V; CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, VI; and C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>, VII). While species IV is observed to be *closo* in the solid state and species V is observed to be *exo-nido* in the solid state, FT-NMR<sup>3</sup> indicates that appreciable concentrations of their *exo-nido* tautomers exist in solution; species VI and VII are exclusively *exo-nido* tautomers both in the solid state and in solution. These results point to the conclusion that only those systems that normally exhibit high equilibrium concentrations of *exo-nido* tautomers will undergo the hydroboration reaction with 1-butyl acrylate at an appreciable rate.

The inability of I to insert simple alkenes (e.g., 1-hexene) into a B-H vertex can be contrasted to the reactivity established for small reactive boranes,<sup>11</sup> thiaboranes,<sup>12</sup> diboranes and related

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(9) Autocatalyzed BH/D<sub>2</sub> exchange studies of I in THF at 0 °C proved that the most reactive vertex for autocatalyzed BH/D<sub>2</sub> exchange is atom B(10). Preliminary <sup>2</sup>H FT-NMR studies using 1-d<sub>8</sub> show CH/D exchange with the alkene 3-methyl-3-phenyl-1-butene.<sup>3</sup>

(10) The formation of a doublet centered at 32.75 ppm (*J*<sub>Rh-P</sub> = 139 Hz) was accompanied by the simultaneous formation of free PPh<sub>3</sub> having the same integrated intensity. (See ref 3 and 8 for a discussion of the chelate complexes.)

(6) Addition of  $\text{Cs}^+[7,8-\mu-(\text{CH}_2)_3-7,8-\text{C}_2\text{B}_9\text{H}_{10}]^-$  to a THF solution of I with excess 1-butyl acrylate (anion:catalyst = 10:1)<sup>4</sup> gives the substituted anion (turnover = 0.3 day<sup>-1</sup>) which can be recovered in 40% yield by removing the solvents in vacuo, washing with benzene, and recrystallization from THF/benzene.

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borane derivatives,<sup>13</sup> where hydroboration is relatively facile. More recently, transition-metal catalyst precursors have been utilized<sup>14,15</sup> to activate alkenes and alkynes toward hydroboration of boranes for the production of small carboranes.

Detailed investigations are continuing in an effort to more fully define the scope of reaction reported herein with respect to other rhodacarboranes and alkenes.

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**Supplemental Material Available:** FT-NMR and IR data,  $x$ ,  $y$ ,  $z$ , and  $B$  values, atomic distances and angles, and X-ray data for II (32 pages). Ordering information is given on any current masthead page.

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## Ortho-Alkylation of Acetanilides Using Alkyl Halides and Palladium Acetate

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Palladium-mediated catalysis which is useful in carbon-carbon bond formation usually involves  $Pd^0$  to  $Pd^{II}$  recycle.<sup>1</sup> The halogenation of azobenzene with palladium chloride represents an intriguing catalytic reaction that does not involve a palladium recycle.<sup>2</sup> A  $Pd^{II}$  to  $Pd^{IV}$  transformation has been postulated for this reaction. We wish to describe a new catalytic carbon-carbon bond-forming reaction that does not involve recycle of palladium and may involve a  $Pd^{IV}$  intermediate.

Our studies began with the observation of a direct one-pot synthesis of exclusively *o*-methylacetanilides using stoichiometric amounts of palladium acetate and methyl iodide (Table I). This reaction produced high yields of exclusively ortho-methylated products and can be used to synthesize a variety of highly functionalized acetanilides. By varying the solvent system, either mono- or di-ortho-substituted products were obtained. For example, the reaction of acetanilide with 2 equiv of palladium acetate and excess methyl iodide produced a quantitative yield of 2,6-dimethylacetanilide.<sup>3</sup> If the reaction of acetanilide with 1 equiv of palladium acetate was quenched with acetonitrile before methyl iodide

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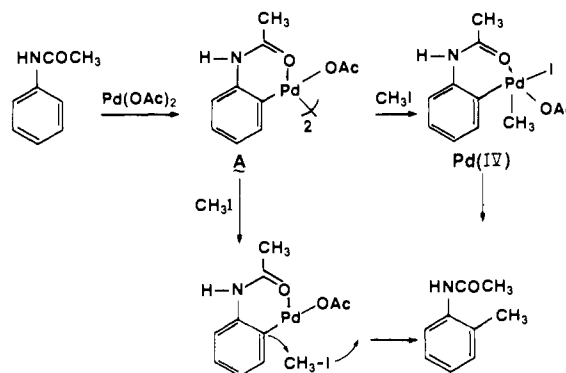
(3) Sample Preparation of 2,6-dimethylacetanilide: To a solution of acetanilide (0.8 g, 5.9 mmol), palladium acetate (4 g, 18 mmol), and 7.0 g of acetic acid was added methyl iodide (4.5 g, 31.7 mmol). The reaction was capped with a septum and heated to 100 °C with stirring for 18 h. The  $PdI_2$  precipitate was removed by filtration and the filtrate was concentrated by means of a rotary evaporator. Recrystallization of the crude product from toluene resulted in an 81.1% isolated yield of 2,6-dimethylacetanilide.

**Table I.** Ortho-Alkylation of Acetanilides with  $Pd(OAc)_2$  and Alkyl Iodides<sup>a</sup>

Substrate	Method	Product <sup>f</sup>	Isolated <sup>g</sup> yield, %	glpc. yield, %
	A <sup>b</sup>		81	100
	A		81.4	
	A		86.4	
	B <sup>c</sup>		81.1	100
	B		79.7	
	C <sup>d</sup>		71.7	93.7
	A		71.3	100
	D <sup>e</sup>		76.2	

<sup>a</sup> All reactions were run in HOAc except for method C. <sup>b</sup> Method A: 1.5 equiv of  $Pd(OAc)_2$ , 3 h; 10-15 equiv of MeI, 27 equiv of  $CH_3CN$ , 8 h, 60 °C. <sup>c</sup> Method B: 1.5 equiv of  $Pd(OAc)_2$  per ortho-positioned hydrogen, 15 equiv of  $CH_3I$ , 100 °C. <sup>d</sup> 3 equiv of  $Pd(OCOCF_3)_2$  in  $CF_3CO_2H$ , 80 °C, 3 h; 10 equiv of  $CH_3I$ , 2 h, 70 °C. <sup>e</sup> 10 equiv of allyl iodide, 0 °C, 4 h. <sup>f</sup> Products identical in all respects with material prepared by alternate procedures. <sup>g</sup> Isolated yields were purified by recrystallization.

### Scheme I



was added to the reaction, then quantitative yields of *o*-methylacetanilide were produced. This *o*-alkylation reaction, which is summarized in Table I, represents a new direct method of ortho-alkylating highly functionalized acetanilides under mild conditions. Holton has previously demonstrated the synthesis of aryl ketones by acylation of preformed ortho-palladated benzylamines.<sup>4</sup>

Other electrophiles such as ethyl iodide and allyl iodide reacted with acetanilide and palladium acetate to produce ortho-alkylated products (Table I). At 25 °C the reaction of allyl iodide with ortho-palladated acetanilide<sup>6</sup> produced *o*-allylacetanilide in a 76% yield (Table I),<sup>5b</sup> addition of triethylamine to this reaction, at 100 °C for 8 h, converted *o*-allylacetanilide to *N*-acetyl-2-methylindole in a 23% yield (eq 1).<sup>5</sup>

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