

# Transition Metal Catalysis in Fluorous Media: Practical Application of a New Immobilization Principle to Rhodium-Catalyzed Hydroborations of Alkenes and Alkynes

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Received August 17, 1998

**Abstract:** Addition of a yellow-orange toluene solution of  $[\text{Rh}(\text{Cl})(\text{COD})]_2$  to a colorless  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution of  $\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3$  ( $\text{R}_{\text{f6}} = (\text{CF}_2)_5\text{CF}_3$ ) gives a colorless toluene solution of COD and an orange  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution of  $\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (**1**). Evaporation of  $\text{CF}_3\text{C}_6\text{F}_{11}$  gives analytically pure **1** (94%), which is insoluble in most organic solvents and stable to 300 °C. Alkenes, catecholborane, and  $\text{CF}_3\text{C}_6\text{F}_{11}$  solutions of **1** (950:950:1 mol ratio for norbornene) are stirred for 1–24 h at 40 °C (heterogeneous conditions). The resulting alkylboranes are extracted with benzene (2×; turnover number (TON) 854 (90%) for norbornene), toluene, or THF, and the catalyst solution is reused (TON 2409 for three cycles). Subsequent reactions with  $\text{H}_2\text{O}_2/\text{NaOH}$  give alcohols, which are isolated in 92–77% yields (11 examples). Longer reaction times afford TON values higher than 10 000 (<0.1 mol % **1**). Analogous reactions of alkynes yield alkenylboranes (89–88%). Pinacolborane additions are also catalyzed. A higher homologue of **1**,  $\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f8}})_3]_3$  (**2**), and the nonfluorinated analogue  $\text{ClRh}[\text{P}((\text{CH}_2)_7\text{CH}_3)_3]_3$  are similarly prepared. Solubilities and reactivities are compared. Atomic absorption analyses shows rhodium losses of 0.4% (**1**) and 0.2% (**2**) per cycle, corresponding to 4.5–2.2 ppm rhodium/mol of addition product. These data demonstrate the viability and practicality of an exciting new approach to catalyst immobilization.

The design of new or improved chemical transformations invariably turns to catalysis. Two especially active frontiers are (1) nontraditional reaction media and (2) new catalyst immobilization or recovery strategies to facilitate reuse.<sup>2</sup> Toward these ends, a conceptually new protocol, “fluorous biphasic catalysis”, has been developed in our laboratories.<sup>3–7</sup> The term “fluorous” is used analogously to “aqueous” for highly fluori-

nated alkane, ether, and tertiary amine solvents. A variety of such solvents are commercially available and commonly give bilayers with organic solvents. As such, fluorous media represent a greatly underutilized “orthogonal phase” for synthesis and separations.<sup>8</sup> Furthermore, many solvent combinations become miscible at elevated temperatures. This allows chemistry to be effected under homogeneous one-phase or heterogeneous two-phase conditions.

How can catalysts be engineered to have high affinities for fluorous media? Our approach has been to append fluoroalkyl groups or “pony tails” such as  $(\text{CH}_2)_y(\text{CF}_2)_x\text{CF}_3$ .<sup>3a</sup> These serve, when of sufficient length and quantity, a “like dissolves like” function. Similar strategies are used to design dyes capable of sticking to Teflon.<sup>9</sup> The  $(\text{CH}_2)_y$  spacers provide tuning elements that can be adjusted to insulate the active site from the electron-withdrawing fluorines (higher  $y$  values) or to enhance Lewis acidity (lower  $y$  values).<sup>3c</sup> The viability of this protocol was first demonstrated<sup>3</sup> with a commodity chemical transformation, alkene hydroformylation, using a catalyst that was generated in situ from a rhodium precursor and the fluorous phosphine  $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ .<sup>10</sup> The latter features six perfluorinated carbons per pony tail and is henceforth abbreviated

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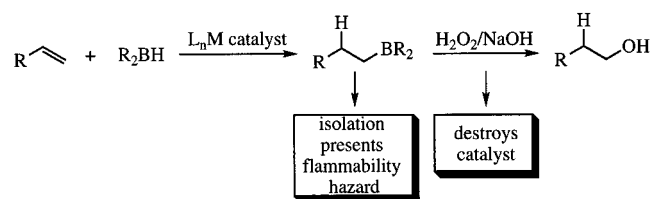
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**Scheme 1.** Complicating Issues in Transition-Metal-Catalyzed Hydroboration



$\text{P}(\text{CH}_2\text{CH}_2\text{R}_f)_3$ . The product aldehyde was isolated from the organic phase, and the rhodium was recovered in essentially quantitative yield from the fluorous phase.<sup>3</sup>

We sought to develop applications of this protocol in laboratory-scale catalytic reactions that see use in fine chemical synthesis. Our attention was drawn to hydroborations of alkenes, which often require elevated temperatures. A variety of transition metal and lanthanide catalyst precursors that allow milder conditions have recently been discovered.<sup>12,13</sup> Representative examples include  $\text{CIRhL}_3$ ,  $[\text{M}(\text{COD})(\text{L})(\text{L}')^+]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ),  $\text{PdCl}_2\text{L}_2$ ,  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , and  $\text{SmI}_3$ . However, as diagrammed in Scheme 1, these are destroyed by the customary oxidations of alkylborane intermediates to alcohol end products ( $\text{H}_2\text{O}_2/\text{NaOH}$ ). An alternative would be to separate the alkylboranes prior to oxidation. However, they are commonly flammable and inconvenient to handle. Fluorous catalysts that could be recovered by phase separations would have obvious advantages.

Wilkinson's catalyst,  $\text{CIRh}(\text{PPh}_3)_3$ , is particularly active for alkene hydroboration, as well as many related transformations. Hence, we set out to prepare and evaluate fluorous analogues. As detailed below, fluorous trialkylphosphines give easily recovered hydroboration catalysts that are effective at 25–40 °C and loadings of 0.009–0.26 mol %, and they give turnover numbers (TON) higher than 10 000. A portion of this work has been communicated.<sup>4</sup> Applications of these complexes in catalytic hydrogenations<sup>5</sup> and hydrosilylations,<sup>14</sup> and syntheses of related rhodium diphosphine compounds,<sup>15</sup> are described elsewhere.

## Results

**1. Rhodium Complexes.** Efforts were first directed at catalyst synthesis and characterization. As shown in Scheme 2, a yellow-orange toluene solution of  $[\text{Rh}(\text{Cl})(\text{COD})]_2$  and a colorless  $\text{CF}_3\text{C}_6\text{F}_{11}$  (perfluorinated methylcyclohexane)<sup>16</sup> solution of the fluorous phosphine  $\text{P}(\text{CH}_2\text{CH}_2\text{R}_f)_3$ <sup>10</sup> were stirred at room temperature. A 1:6 mol ratio was employed, appropriate for the

target complex  $\text{CIRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_f)_3]_3$  (**1**). The upper toluene phase became colorless, and the  $\text{CF}_3\text{C}_6\text{F}_{11}$  phase became orange. The latter was separated and taken to dryness to give **1** in 94% yield as an analytically pure orange powder. The COD remained in the toluene. This simple workup dramatically illustrates the utility of fluorous biphasic conditions for stoichiometric syntheses.

As rendered in Scheme 2, **1** is evocative of a “Teflon greaseball”. A DSC trace showed a melting point at 90 °C but no significant decomposition or phase transitions below 300 °C. To our surprise, single crystals could be obtained from  $\text{CF}_3\text{C}_6\text{F}_{11}$ /hexane (layering or vapor diffusion). However, they were soft and diffracted poorly. Crystal structures of related iridium and rhodium diphosphine complexes have been solved and exhibit packing motifs with parallel  $(\text{CF}_2)_x$  segments and anti CCCC conformations.<sup>15,17</sup> The NMR and IR properties of **1** (Experimental Section) were unexceptional, but very dilute solutions appeared yellow as opposed to orange.<sup>18</sup>

For comparison experiments, we sought analogues of **1** in which (a) the  $(\text{CF}_2)_x$  segment was lengthened and (b) all fluorines were replaced by hydrogens. Accordingly,  $[\text{Rh}(\text{Cl})(\text{COD})]_2$  and the phosphine  $\text{P}(\text{CH}_2\text{CH}_2\text{R}_f)_3$ ,<sup>10</sup> which features eight perfluorinated carbons per pony tail, were reacted under the conditions used for **1**. Workup gave the higher homologue  $\text{CIRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_f)_3]_3$  (**2**; Scheme 2) as an analytically pure orange powder in 91% yield. Next,  $[\text{Rh}(\text{Cl})(\text{NBD})]_2$  and commercially available tri(*n*-octyl)phosphine,  $\text{P}((\text{CH}_2)_7\text{CH}_3)_3$ , were reacted in THF. Workup gave the target complex  $\text{CIRh}[\text{P}((\text{CH}_2)_7\text{CH}_3)_3]_3$  (**3**) in 87% yield as a red oil. The NMR purity was >96%, but correct microanalyses could not be obtained. Surprisingly, we could not locate a previous report of this compound in the literature.

The solubility properties of  $\text{CIRh}(\text{PPh}_3)_3$  and the new complexes **1–3** are compared in Chart 1. As expected, the fluorinated complexes **1** and **2** are very soluble in  $\text{CF}_3\text{C}_6\text{F}_{11}$ , whereas **3** and  $\text{CIRh}(\text{PPh}_3)_3$  are insoluble. Complex **1** is also soluble in  $\text{CF}_3\text{C}_6\text{H}_5$  (trifluoromethyl benzene), which often dissolves both fluorous and nonfluorous compounds.<sup>8a</sup> Complex **1** very faintly colors THF and acetone but is otherwise insoluble in organic solvents. In contrast, **3** is soluble in all common organic solvents. Thus, the interchange of  $(\text{CF}_2)_x$  and  $(\text{CH}_2)_x$  chains in trialkylphosphine complexes can give striking solubility differences. Unlike **1**, **2** is insoluble in  $\text{CF}_3\text{C}_6\text{H}_5$ , THF, and acetone. The corresponding free phosphines also show a decrease in absolute solubilities as the  $(\text{CF}_2)_x$  segments are lengthened.<sup>10</sup>

The data in Chart 1 are qualitative. We sought quantitative data on *relative* solubilities, or partition coefficients. These have a direct bearing on catalyst recovery. Accordingly, **1** and **2** (0.0600–0.0805 g) were added to  $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene mixtures (1:1 v/v).<sup>19</sup> After 24 h at 27 °C, aliquots were withdrawn from each phase. Atomic absorption analyses as described in the Experimental Section gave partition coefficients of 696:1 (99.86:0.14) and 811:1 (99.88:0.12). Hence, the catalyst with the longer  $(\text{CF}_2)_x$  segments shows the greater fluorous phase affinity.

(16) We commonly utilize  $\text{CF}_3\text{C}_6\text{F}_{11}$  in exploratory and mechanistic studies. Other perfluoroalkane solvents should serve equally well but are often sold as mixtures of isomers or by boiling point range. This could compromise the reproducibility and interpretation of rate constants, partition coefficients, and related measurements.

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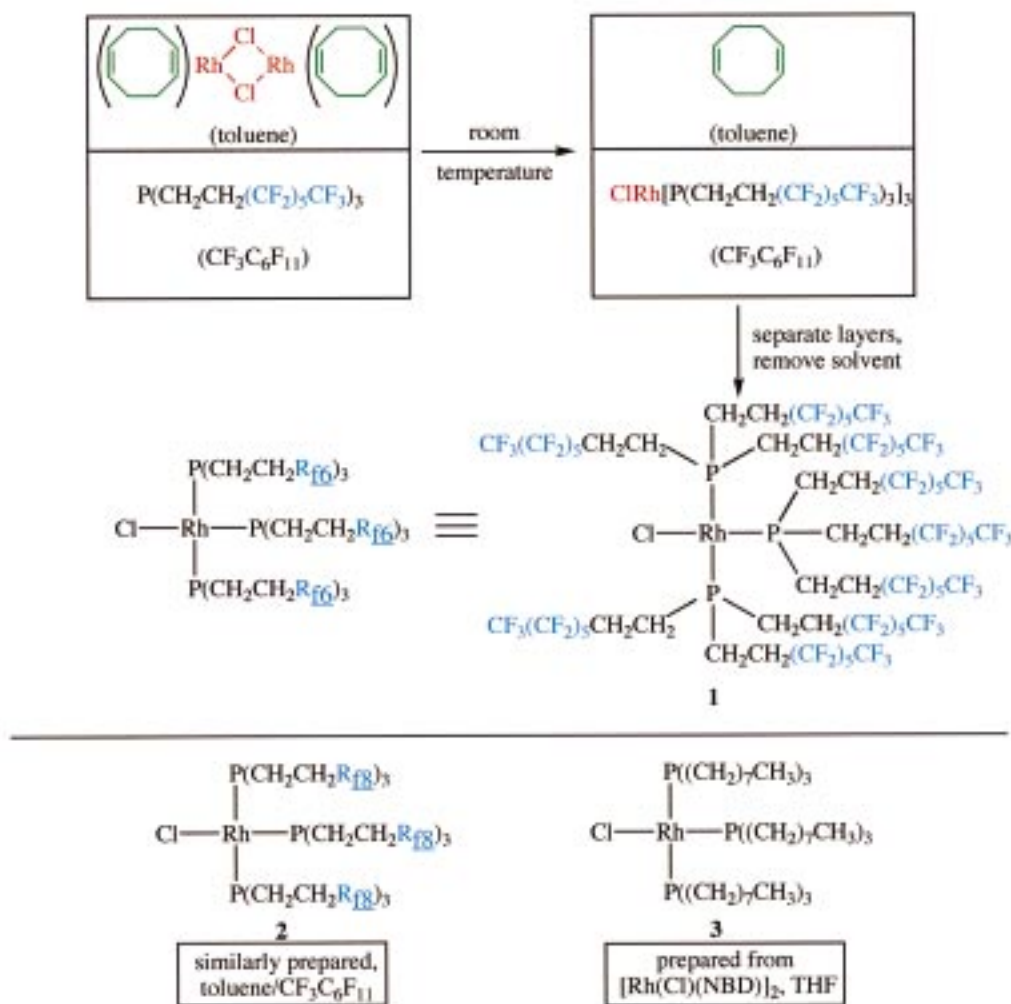
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## Scheme 2. Syntheses of Fluorous and Non-Fluorous Catalysts 1–3

Chart 1. Solubilities of Rhodium Complexes<sup>a</sup>

solvent	$\text{ClRh}(\text{PPh}_3)_3$	$\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{f6})_3]_3$ (1)	$\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{f8})_3]_3$ (2)	$\text{ClRh}[\text{P}(\text{CH}_2)_7\text{CH}_3]_3$ (3)
$\text{CF}_3\text{C}_6\text{F}_{11}$	insol	sol	sol	insol
$\text{CF}_3\text{C}_6\text{H}_5$	v sl sol	sol	insol	sol
pentane	insol	insol	insol	sl sol
hexane	sl sol	insol	insol	sol
benzene	sol	insol	insol	sol
toluene	sol	insol	insol	sol
ether	sol	insol	insol	sol
acetone	sl sol	v sl sol	insol	sol
$\text{CHCl}_3$	sol	insol	insol	sol
$\text{CH}_2\text{Cl}_2$	sol	insol	insol	sol
THF	sol	v sl sol	insol	sol

<sup>a</sup> insol, insoluble; sol, soluble; sl sol, slightly soluble; v sl sol, very slightly soluble.

**2. Catalytic Hydroboration and Catalyst Recycling.** Mixtures of alkenes and freshly distilled catecholborane (**4**)<sup>20</sup> were treated with **1**.<sup>21</sup> In all cases, the color of **1** (orange to yellow)

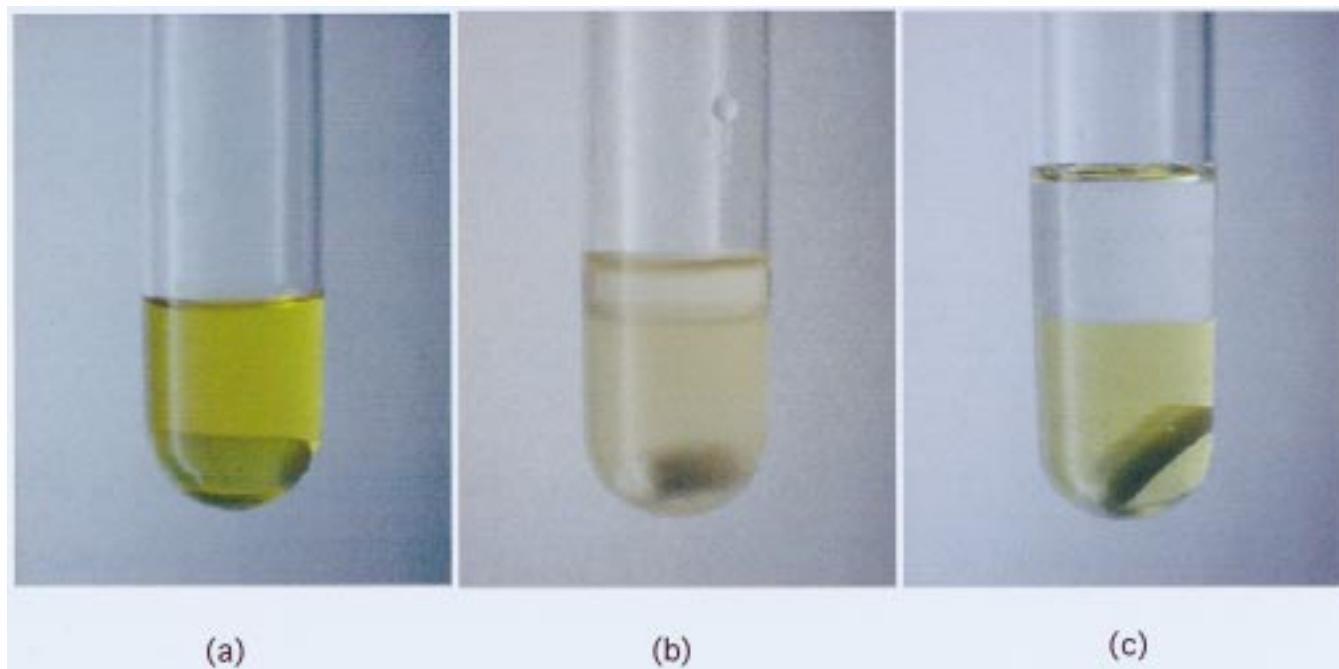
(19) It should be emphasized that liquid biphasic systems can contain both components in each phase. One familiar example is ether/water. After the ether layer is separated, drying agents are required to render it anhydrous. With toluene/ $\text{CF}_3\text{C}_6\text{F}_{11}$  at 25 °C, we measure ratios of 98.4:1.6 (molar), 94.2:5.8 (mass), and 97.1:2.9 (volume) in the upper organic layer, and 3.8:96.2, 1.0:99.0, and 2.0:98.0 in the lower fluorous layer (Supporting Information). Since these ratios depend on solutes and temperature, we approximate our biphasic systems as immiscible components that retain their original volumes in all calculations.

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(21) Sequences in which **1** and **4** were combined in the absence of alkenes were avoided. <sup>1</sup>H NMR experiments showed the formation of rhodium hydride complexes of limited thermal stability.

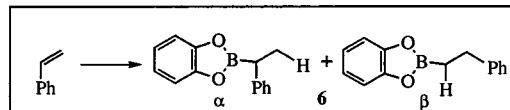
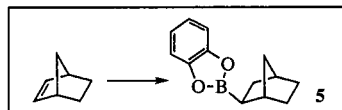
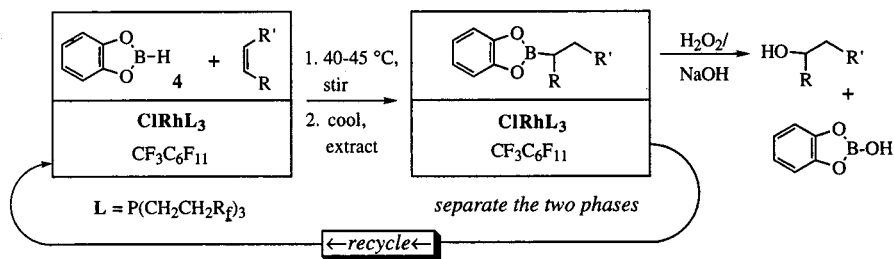
rapidly discharged. Many exploratory runs using the solvent combinations  $\text{CF}_3\text{C}_6\text{F}_{11}$ /THF or  $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene and biphasic conditions (20–45 °C) were successful. The higher temperatures necessary to achieve single phases were not required. The original colors returned when reactions were complete. However, it was soon found that reactions were more rapidly and economically effected *without* a nonfluorous solvent, per the sequence of photographs in Figure 1.

Thus, as shown in Scheme 3 (experiment A), a stock solution of **1** in  $\text{CF}_3\text{C}_6\text{F}_{11}$  (0.500 mL, 0.00179 M,  $8.95 \times 10^{-4}$  mmol or 0.10 mol %) was added to a 1:1 mixture of norbornene and **4** (0.849 mmol or 950 equiv/Rh).<sup>21</sup> Not all of the reactants dissolved, as indicated by beads or a layer atop the  $\text{CF}_3\text{C}_6\text{F}_{11}$ .



**Figure 1.** Representative fluororous rhodium-catalyzed hydroboration: (a) **1** in  $\text{CF}_3\text{C}_6\text{F}_{11}$ ; (b) after additions of styrene and catecholborane (**4**); (c) after completion of reaction and addition of THF.

**Scheme 3.** Fluorous Rhodium-Catalyzed Hydroboration



**A.** 40 °C,  $\text{C1Rh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (1: 0.10 mol%, 1 h)

cycle	mmol educt	mmol <b>5</b>	yield	TON
1	0.849	0.765	90%	854
2	0.849	0.702	83%	785
3	0.849	0.688	81%	770

**B.** 40 °C,  $\text{C1Rh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (1: 0.11 mol%, 3 h)

cycle	mmol educt	mmol <b>5</b>	yield	TON
1	0.792	0.698	88%	780
2	0.813	0.683	84%	763
3	0.765	0.685	90%	765
4	0.664	0.584	88%	653

**C.** 45 °C,  $\text{C1Rh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (2: 0.12 mol%, 3 h)

cycle	mmol educt	mmol <b>5</b>	yield	TON
1	0.978	0.844	86%	747
2	0.764	0.646	85%	572
3	0.765	0.652	85%	577
4	0.818	0.659	81%	583

**D.** 40 °C,  $\text{C1Rh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (1: 0.19 mol%, 5 h)

cycle	mmol educt	mmol <b>6</b>	yield	TON
1	0.551	0.506	92%	473
2	0.560	0.556	99%	520
3	0.654	0.583	89%	545
4	0.557	0.429	77%	401
5	0.616	0.505	82%	472

**E.** 45 °C,  $\text{C1Rh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{\text{f6}})_3]_3$  (2: 0.20 mol%, 5 h)

cycle	mmol educt	mmol <b>6</b>	yield	TON
1	0.566	0.464	82%	411
2	0.634	0.509	80%	450
3	0.672	0.532	79%	471
4	0.568	0.438	77%	388
5	0.600	0.462	77%	409

**Chart 2.** Alcohols Synthesized under the Conditions of Scheme 3<sup>a</sup>

Educt	Product(s)	Isolated Yield (%)	<b>1</b> , mol%	TON
		80	0.19	413
		90 (93)	0.04 (0.009)	2487 (10370) <sup>b</sup>
		82	0.14	604
		77	0.10	778 <sup>b</sup>
		89	0.16	552
		82	0.26	305
		86	0.16	522
		89	0.20	441
	 55:45 	90	0.05	1906
	 39:61 	82	0.13	651
	 65:35 	92	0.21	442

<sup>a</sup> 40 °C, 0.5–16 h. <sup>b</sup> These data are from 23–24-h reactions.

The sample was kept for 1 h at 40 °C, cooled to room temperature, and extracted twice with C<sub>6</sub>D<sub>6</sub> (0.5 mL). A weighed amount of Ph<sub>3</sub>SiCH<sub>3</sub> was added to the extract, and NMR analysis showed 0.765 mmol of the organoborane **5** (90%, TON 854). The CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> mother solution was added to a second sample of norbornene and **4** (950 equiv). An identical reaction and workup gave a C<sub>6</sub>D<sub>6</sub> solution containing 0.702 mmol of **5** (83%, TON 785). A third cycle gave similar data, for a combined TON value of 2409, as summarized in Scheme 3.

Similar sequences were conducted with catalysts **1** and **2** (Scheme 3, experiments B and C; 1.00:1.05 norbornene/**4**). It was independently shown that **2** was not quite as reactive as **1** (TON 129 vs 102; 1 h, 40 °C, 0.11 mol %). Thus, experiment C was conducted at 45 instead of 40 °C. Over four cycles, combined TON values of 2961 and 2479 were achieved. As with experiment A, yields for each cycle fluctuated somewhat (90–84% and 86–81%). Furthermore, experiment B did not give appreciably better yields than A, despite longer cycle times (3 vs 1 h). NMR spectra showed that some alkene remained. Catalyst **1** routinely gave 90–100% conversions in similar alkene hydrogenation cycles, as detailed elsewhere.<sup>5</sup> However, rhodium-catalyzed hydroborations are, as discussed below, mechanistically more complex and possibly subject to inhibition by non-fluorous side products that are removed by extraction.

Similar reactions were conducted with styrene, **1**, and **2** (Scheme 3, experiments D and E). The yield of organoborane **6**, which formed as a mixture of  $\alpha/\beta$  (branched/linear) regioisomers, was assayed by NMR. The cycle times were lengthened (5 h), but yields still fluctuated, and the average remained less

than 90%. A small amount of gelatinous and possibly polymeric material was noted. Over five cycles, combined TON values of 2411 and 2129 were achieved. Although the yields in experiments A–E generally appear to drift downward, the rhodium loss per cycle is minuscule, as described below. An experiment analogous to D was conducted at room temperature (8-h cycles), and data are summarized in footnote 8b of our communication.<sup>4</sup>

Control experiments relating to Scheme 3 were conducted. First, no reactions of norbornene (40 °C, 2 h) or styrene (room temperature, 14 h) and **4** were detected in the absence of **1**. Uncatalyzed reactions of alkenes and **4** commonly require 100 °C.<sup>22</sup> Second, the reaction with norbornene was repeated (0.701 mmol, 0.16 mol % **1**), but the two C<sub>6</sub>D<sub>6</sub> extracts were analyzed separately. The first contained 0.610 mmol of **5** (87%), and the second 0.028 mmol (4%). Thus, yields should not be significantly increased by a third extraction. Finally, the CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub>/toluene partition coefficient of 1-dodecene was carefully determined by GLC.<sup>5,8b</sup> The result, 2.5:97.5 (24 °C), illustrates the limited affinity of the types of alkenes used in this study for fluoruous media. However, it also shows that alkenes are, to some extent, fluorocarbon soluble.

**3. Isolation of Alcohols.** We next sought to transform alkenes to alcohols. Thus, norbornene and **4** (1:1.1) and a CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> solution of **1** (0.04 mol %) were combined as described above. The sample was kept at 40 °C for 5 h, cooled, and extracted with THF. An oxidative workup (H<sub>2</sub>O<sub>2</sub>/NaOH) gave *exo*-norborneol as a spectroscopically pure white solid in 90% yield (TON 2487), as shown in Chart 2.

Analogous reactions were conducted with a variety of educts, as summarized in Chart 2. These include monosubstituted, all patterns of disubstituted, and trisubstituted alkenes. Some THF was added to dissolve the only solid substrate, *trans*-stilbene. With the exception of the least reactive alkene, cyclopentene, reaction times ranged from 1 to 16 h, and no special efforts were made to optimize catalyst loadings (0.04–0.26 mol %) or isolated yields (92–77%). All product identities were verified by at least two criteria (<sup>1</sup>H/<sup>13</sup>C NMR or <sup>1</sup>H NMR/GLC).

For several alkenes, more than one alcohol regioisomer or diastereomer is possible. However, only styrene, *p*-methoxystyrene, and *p*-chlorostyrene gave mixtures. These are also the only alkenes for which selectivities differ from those of uncatalyzed reactions (in which primary alcohols constitute >90% of the product). Interestingly, the regiochemistry of rhodium-catalyzed hydroborations of styrenes can vary, and catalyst purity has been shown to be a critical factor.<sup>12c,d</sup> The ratios in Chart 2 have been reproduced many times with different batches of both **1** and **4**.

Finally, the feasibility of lower catalyst loadings and commensurably higher TON values was tested. Thus, the reaction of norbornene, **4**, and **1** was repeated, but with a 11150:13520:1 mol ratio (0.009 mol % **1**). As would be expected, the reaction time had to be lengthened (23 h). However, workup gave *exo*-norborneol in 93% yield, corresponding to a TON of 10 370!

**4. Isolation of Organoboron Products.** We sought to extend the reactions in Scheme 3 and Chart 2. In particular, alkenylboranes are much more robust and easier to isolate than alkylboranes and are versatile substrates for a variety of metal-catalyzed coupling reactions.<sup>23</sup> As shown by the first two examples in Chart 3, **1** catalyzed the addition of **4** to alkynes. Reactions were more rapid than those in Chart 2 (0.5 h, 40 °C). Spectroscopically pure alkenylboranes were isolated in 89–88%

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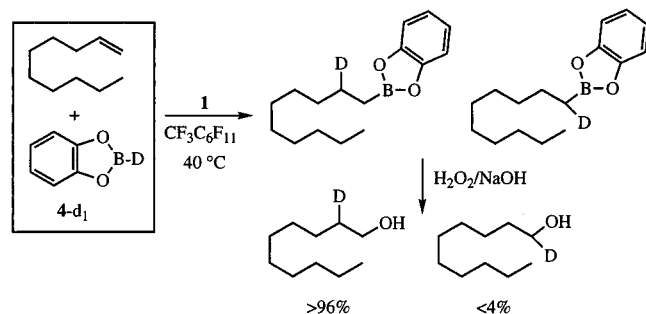
Chart 3. Organoborane Compounds Isolated<sup>a</sup>

Educt	Product(s)	Yield (%)	1, mol%	TON
		89	0.19	473
		88	0.19	474
		90 <sup>b</sup>	0.13	709
		87	0.078	1112
		89	0.29	310

32:49:19

<sup>a</sup> 40 °C, 0.5–16 h. <sup>b</sup> 95:5 mixture of isomers (see refs 25 and 39).

Scheme 4. Deuterium Labeling Experiments



yields, as assayed by integration vs a weighed amount of an NMR standard. The catalyst was recovered from the reaction with phenylacetylene and reused (88% and TON 474 for second cycle).

During the course of this study, Pereira and Srebnik reported the zirconium- and rhodium-catalyzed addition of pinacolborane (**7**) to alkenes and alkynes.<sup>12g,24</sup> Importantly, the resulting organoboranes are stable to air, moisture, and chromatography.<sup>25</sup> As shown by the last three examples in Chart 3, **1** also efficiently catalyzed the addition of **7** to alkenes and alkynes. The product mixture obtained with styrene is similar to that produced by  $\text{CIRh}(\text{PPh}_3)_3$ .<sup>12g</sup>

We sought to probe for hidden scrambling processes by deuterium labeling. As shown in Scheme 4, *B*-deuteriopinacolborane (**4-d**<sub>1</sub>), excess 1-decene, and a  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution of **1** were combined at 40 °C. After 24 h, the  $\text{C}_6\text{D}_6$  extract was analyzed by <sup>2</sup>H NMR before and after the removal of excess 1-decene. The alkylborane showed an intense signal for a C<sub>2</sub> label (1.54 ppm). The analogous natural abundance adduct was isolated as a white solid in 82% yield (TON 424) from the reaction in Chart 2 and characterized by <sup>1</sup>H NMR. The labeled sample was oxidized to 1-decanol, and <sup>1</sup>H and <sup>2</sup>H NMR spectra were recorded. At all stages, only C<sub>2</sub> deuterium was observed. As little as 4% of a C<sub>1</sub>-labeled alcohol (3.68 ppm) would have been detected. Hence, the addition of **4** to 1-decene occurs without significant scrambling. Interestingly,  $\text{CIRh}(\text{PPh}_3)_3$ -

catalyzed reactions give deuterium at both C<sub>2</sub> and C<sub>1</sub> (85:15).<sup>7c</sup> This has been interpreted in the context of a reversible addition of a rhodium deuteride intermediate to a coordinated alkene.

**5. Catalyst Activity, Mechanism, and Leaching.** Although **1** has obvious advantages over  $\text{CIRh}(\text{PPh}_3)_3$  from the standpoint of catalyst recovery, there is the attendant question of relative reactivity. As is obvious from Chart 1, few solvents dissolve both species. However, with effort, 0.00086 M solutions of  $\text{CIRh}(\text{PPh}_3)_3$  in  $\text{CF}_3\text{C}_6\text{H}_5$  could be obtained. Equimolar  $\text{CF}_3\text{C}_6\text{H}_5$  solutions of **1** and the tri(*n*-octyl)phosphine complex **3** were also prepared. These were combined with norbornene and **4** (0.61–0.63 mmol) in NMR tubes. After 15 min at room temperature, the sample with  $\text{CIRh}(\text{PPh}_3)_3$  had completely reacted. The sample with **1** showed no reaction after 5 h. That with **3** showed 4% conversion after 3 h and 10% conversion after 22 h. This establishes the reactivity order  $\text{CIRh}(\text{PPh}_3)_3 > \mathbf{3} > \mathbf{1}$  (and **1** > **2** from data above). Hence, arylphosphine ligands give more reactive catalysts than alkylphosphines, and the fluorine substituents in **1** further retard reactivity.

The mechanism of rhodium-catalyzed hydroboration has been studied in detail. It has been shown that  $\text{CIRh}(\text{PPh}_3)_3$  and **4** react in the absence of alkenes to give complex mixtures of rhodium hydrides and redistribution products, many of which may independently participate in or inhibit catalysis.<sup>12d,26</sup> This may account for some of the yield trends in Scheme 3. There is also the possibility of a change of mechanism in fluorous media. One probe is provided by the regiochemistry of addition to styrene, which is, as noted above, very sensitive to catalyst purity and, presumably, mechanism. However, **1** (in  $\text{CF}_3\text{C}_6\text{F}_{11}$ ) and **3** (in  $\text{C}_6\text{D}_6$ ) gave similar mixtures of isomers (styrene,  $\alpha/\beta$  55:45 vs 54:46; *p*-methoxystyrene, 39:61 vs 30:70). In general, rhodium alkylphosphine catalysts do not give high regioselectivities,<sup>12d,26</sup> whereas under rigorously anaerobic conditions  $\text{CIRh}(\text{PPh}_3)_3$  gives exclusively the branched  $\alpha$  isomer.<sup>12c</sup>

Catalyst leaching was probed by atomic absorption analysis. Norbornene, **4**, and **1** (0.0302 g, 0.112 mol %) were reacted in  $\text{CF}_3\text{C}_6\text{F}_{11}$  (2.5 mL) as described above. Then  $\text{CF}_3\text{C}_6\text{F}_{11}$  (7.5 mL) and toluene (10 mL) were added with shaking. After 15 min, a large toluene aliquot (8.0 mL) was removed by syringe. More toluene was added (8.0 mL), and the extraction was repeated (8.0 mL). Both aliquots gave identical rhodium analyses (0.20 ppm), and an aliquot of the  $\text{CF}_3\text{C}_6\text{F}_{11}$  phase (8.0 mL) gave, as expected, a much higher rhodium analysis (46.9 ppm). These values correspond to 0.4% leaching over two extractions. After adjustment for the solvent volumes not analyzed,<sup>19</sup> the rhodium mass recovery is 91%. An identical experiment with **2** gave 0.2% leaching and a mass recovery of 96%. If all of the norbornene is consumed, this corresponds to a loss of 4.5 ppm rhodium/mol of product for **1**, and 2.2 ppm for **2**.

There was no loss of activity when recovered catalyst solutions were transferred to fresh vials. No evidence for the formation of heterogeneous rhodium-containing substances was ever observed. In contrast, **1** is not indefinitely stable to hydrogenation conditions,<sup>5</sup> and a black solid usually deposits after three cycles. Activity then drops precipitously. Solid **1** (0.2 mol %) was added to a  $\text{C}_6\text{D}_6$  solution of norbornene and **4** and remained undissolved. After 2 and 24 h at 40 °C, reaction was 17% and 62% complete, respectively. Thus, **1** appears to serve as a heterogeneous catalyst at a solid/solution interface. However, it is also possible that, within the limits set by the leaching experiments, very small quantities of a soluble active catalyst are generated. The issue of whether the dominant

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catalytic pathway in Scheme 3 involves the fluororous phase or the interface is also complex and will be addressed with mechanistically less complicated transformations in the future.

## Discussion

The above data demonstrate the viability and practicality of a new approach to catalyst immobilization in the context of an important laboratory-scale reaction that is extensively utilized in fine chemical synthesis. To our knowledge, **1** and **2** represent the first recoverable hydroboration catalysts—a type of attribute that is increasingly important from environmental standpoints. Both **1** and **2** (and the constituent phosphines)<sup>10</sup> are readily prepared and exhibit impressive thermal stability. However, it should be emphasized they are by no means optimized. Many further refinements can be envisioned.

First, it should be possible to further enhance partition coefficients and catalyst recovery by using phosphines with longer or branched  $R_f$  segments. In this context, it should be kept in mind that **1** and **2** are catalyst precursors. Rhodium loss during product extraction will depend more upon the partition characteristics of the catalyst rest state, or a catalyst–product complex. Furthermore, phosphines commonly dissociate from rhodium during catalysis.<sup>19</sup> Thus, most intermediates will be “less fluororous” than **1** and **2**, and increased equilibrium concentrations in the nonfluorous phase are probable. Partition coefficients for  $P(CH_2CH_2R_f)_3$  and  $P(CH_2CH_2R_f)_3$  are 98.8:1.2 and >99.7:<0.3, respectively (toluene/ $CF_3C_6F_{11}$ , 27 °C).<sup>10</sup>

Second, our data and those of prior investigators<sup>12d</sup> show that rhodium trialkylphosphine complexes are less active hydroboration catalysts than rhodium triarylphosphine complexes. Accordingly, syntheses of fluororous triarylphosphines are under intense investigation in our laboratory<sup>27</sup> and others.<sup>28</sup> However, we chose not to measure turnover rates as a function of cycle in Scheme 3. As noted above, compositions of rhodium hydroboration catalysts have been shown to change.<sup>12d,e,26</sup> Also, Figure 1 shows a slight color change between panels a (virgin catalyst) and c (after reaction and extraction of nonfluorous species), as well as a dramatic bleaching in panel b (where a different rest state is probable). Hence, we plan to assay the activities of recovered **1** and **2** in connection with mechanistically less complex addition reactions. The critically important result from this study is the very low level of rhodium loss.

Some related reactions deserve note. First, the fluororous hydroformylation catalyst reported earlier exhibits, in the absence of alkene, a  $HRh(CO)[P(CH_2CH_2R_f)_3]_3$  rest state.<sup>3</sup> It shows better long-term stability than the analogous  $PPh_3$  catalyst and lower leaching levels than **1** and **2** (1.18 vs 4.5 and 2.2 ppm rhodium/product). However, we made no attempt to optimize our values, which should be even lower under the high TON conditions for norbornene in Chart 2. Second, there is increasing precedent for carbon–fluorine bond oxidative additions involving coordinatively unsaturated metal fragments.<sup>29</sup> Fortunately, we see no evidence for such deactivation pathways, including extensive studies with related 16-valence-electron iridium complexes.<sup>15</sup> The iridium complexes also exhibit unique

selectivities for oxidative additions in  $CF_3C_6F_{11}$ . However, Charts 2 and 3 show only normal hydroboration selectivity patterns.

The successful application of **1** and **2** in catalytic hydrogenations and hydrosilylations<sup>5,14</sup> augers well for future extensions of this chemistry. For example, it is highly probable that other boron–X bond additions, such as the diborylation of alkenes,<sup>30</sup> can be effected under the conditions of Scheme 3. More speculatively, it might be possible to eliminate waste products altogether by designing a recoverable boron compound that could be recycled to a boron hydride. Chiral, nonracemic fluororous phosphines should allow enantioselective syntheses. Finally, there are tantalizing possibilities for liquid-phase combinatorial syntheses involving a sequence of fluororous catalysts.<sup>8a</sup>

In conclusion, this paper has rigorously documented (1) the facile synthesis and fundamental physical properties of the new fluororous rhodium catalysts **1** and **2**, (2) the exceptional affinities of **1** and **2** for fluororous media, and (3) numerous preparative catalytic hydroboration reactions from which alcohol or organoboron products have been isolated in high yields from organic phases, very high levels of catalysts recovered from fluororous phases, and TON values optimized to higher than 10 000/cycle. Similar studies involving other new fluororous catalysts and reagents will be reported soon.

## Experimental Section

**General Data.** Reactions were conducted under  $N_2$  atmospheres. Instrumentation and solvent and reagent purifications were similar to those described earlier<sup>5,15</sup> and are fully documented in the Supporting Information.

**$ClRh[P(CH_2CH_2R_f)_3]_3$  (**1**).** A flask was charged with  $P(CH_2CH_2R_f)_3$  (0.643 g, 0.600 mmol)<sup>10</sup> and  $CF_3C_6F_{11}$  (1 mL), and a solution of  $[Rh(Cl)(COD)]_2$  (0.049 g, 0.0994 mmol) in toluene (1 mL) was added. The biphasic mixture was stirred overnight. The phases were separated and the  $CF_3C_6F_{11}$  removed by oil pump vacuum to give **1** as a bright orange solid (0.620 g, 0.186 mmol, 94%), mp 89.8 °C ( $T_e$ , DSC;<sup>31</sup> no other phase transitions between 23 °C and the onset of thermal decomposition, >304 °C). Anal. Calcd for  $C_{72}H_{36}ClF_{117}P_3Rh$ : C, 25.77; H, 1.08. Found: C, 25.85; H, 1.09. IR ( $cm^{-1}$ , KBr): 1247 m, 1145 m, 949 w.  $^1H$  NMR ( $\delta$ ,  $CF_3C_6F_{11}$ , external  $C_6D_6$  lock): 2.20 (br, 6H), 1.90 (br, 6H).  $^{31}P\{^1H\}$  NMR (ppm,  $CF_3C_6F_{11}$ , external  $C_6D_6$  lock): 12.9 (dd,  $J_{PRh} = 136$  Hz,  $J_{PP} = 39$  Hz), 29.3 (dt,  $J_{PRh} = 186$  Hz,  $J_{PP} = 39$  Hz).

**$ClRh[P(CH_2CH_2R_f)_3]_3$  (**2**).** Compounds  $P(CH_2CH_2R_f)_3$  (1.860 g, 1.356 mmol),<sup>10</sup>  $CF_3C_6F_{11}$  (3 mL),  $[Rh(Cl)(COD)]_2$  (0.110 g, 0.226 mmol), and toluene (2 mL) were combined in a procedure analogous to that for **1**. An identical workup gave **2** as a bright orange solid (1.749 g, 0.411 mmol, 91%), mp 103.7 °C ( $T_e$ , DSC;<sup>31</sup> no other phase transitions between 23 °C and the onset of thermal decomposition, >270 °C). Anal. Calcd for  $C_{90}H_{36}ClF_{153}P_3Rh$ : C, 25.40; H, 0.85. Found: C, 25.43; H, 0.93. IR ( $cm^{-1}$ , KBr): 1244 m, 1203 m, 1148 m, 967 w.  $^1H$  NMR ( $\delta$ ,  $CF_3C_6F_{11}$ , external  $CDCl_3$  lock): 1.95 (br, 2H), 2.20 (br, 4H), 2.45 (br, 6H).  $^{31}P\{^1H\}$  NMR (ppm,  $CF_3C_6F_{11}$ ): 14.5 (dd,  $J_{PRh} = 134$  Hz,  $J_{PP} = 40$  Hz), 28.5 (dt,  $J_{PRh} = 183$  Hz,  $J_{PP} = 40$  Hz).

**$ClRh[P((CH_2)_7CH_3)_3]_3$  (**3**).** A flask was charged with  $[Rh(Cl)(NBD)]_2$  (0.080 g, 0.173 mmol) and THF (5 mL), and  $P((CH_2)_7CH_3)_3$  (0.464 mL, 0.386 g, 1.041 mmol) was added with stirring. The yellow solution turned red. After 2 h, the volatiles were removed by oil pump vacuum to give crude **3** as a red oil (0.380 g, 0.304 mmol, 87%, >96% purity by  $^{31}P$  NMR). Anal. Calcd for  $C_{72}H_{155}ClP_3Rh$ : C, 69.17; H, 12.33. Found: C, 68.25; H, 12.16.<sup>32</sup>  $^1H$  NMR ( $\delta$ ,  $C_6D_6$ ): 2.18–2.04 (br, 2H), 1.90–1.69 (br, 2H) 1.60–1.22 (m, 10H), 1.02–0.88 (m, 3H).  $^{31}P\{^1H\}$

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NMR (ppm,  $C_6D_6$ ): 29.1 (dt,  $J_{Prh} = 185$  Hz,  $J_{pp} = 41$  Hz), 13.4 (dd,  $J_{Prh} = 134$  Hz,  $J_{pp} = 41$  Hz).  $^{13}C\{^1H\}$  NMR (ppm,  $C_7D_8$ ): 32.8, 32.8, 32.7 (br overlapping C1/C6); 30.8, 30.6, 30.5, 30.3, 30.3 (br overlapping C4/C5); 27.2, 27.1, 26.9, 26.4, 26.2 (br overlapping C2/C3); 23.6 (s, C7); 14.8, 14.8 (2s, C8, ca. 2:1).<sup>33</sup>

**Hydroborations. General Aspects.** (1) Catecholborane (**4**, Aldrich) was vacuum transferred (oil pump) and stored at  $-30$  °C under  $N_2$  for no more than 72 h. (2) Reactions were conducted under rigorously anaerobic conditions with magnetic stirring, such that **1** and **4** were not combined in the absence of an alkene.<sup>21</sup> (3) Silicone oil baths (continuously stirred,  $\pm 1$  °C) were used for temperature control. (4) All  $CF_3C_6F_{11}$ /solvent mixtures were allowed to settle for 5 min before phase separation. Otherwise, small amounts of  $CF_3C_6F_{11}$  sometimes later separated from the nonfluorous phase.

**Sequential Reactions (Scheme 3).** The following are representative and others are given in the Supporting Information.

**Series B.** A flask was charged with norbornene (0.0746 g, 0.792 mmol, 885 equiv/Rh), **4** (0.100 g, 0.834 mmol), and a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $1.79 \times 10^{-3}$  M;  $8.95 \times 10^{-4}$  mmol, 0.11 mol %). The mixture was kept in a 40 °C bath (3 h), cooled to room temperature, and extracted with  $C_6D_6$  ( $2 \times 0.5$  mL). Then  $Ph_3SiCH_3$  (0.0481 g, 0.175 mmol) was added to the  $C_6D_6$ , and the yield of the adduct **5** was assayed by  $^1H$  NMR (see Scheme 3).<sup>34</sup> The  $CF_3C_6F_{11}$  solution was subjected to three similar charge/workup cycles.

**Series D.** A flask was charged with a  $CF_3C_6F_{11}$  solution of **1** (0.600 mL,  $1.79 \times 10^{-3}$  M;  $1.07 \times 10^{-3}$  mmol; 0.19 mol %), styrene (0.0574 g, 0.551 mmol, 515 equiv/Rh), and **4** (0.068 g, 0.567 mmol). The mixture was stirred (5 h) and extracted with  $C_6D_6$  ( $2 \times 0.5$  mL). Then  $Ph_3SiCH_3$  was added (0.0837 g, 0.305 mmol), and the yields of the regioisomeric adducts **6** ( $\alpha$  or branched/ $\beta$  or linear = 57:43) were assayed by  $^1H$  NMR (see Scheme 3).<sup>35</sup> The  $CF_3C_6F_{11}$  solution was subjected to four similar charge/workup cycles ( $\alpha/\beta$  58:42, 61:39, 61:39, 60:40).

**Alcohol Syntheses (Chart 2).** The following are representative, and others are given in the Supporting Information.

**A. Reaction of Norbornene.**<sup>36</sup> A flask was charged with norbornene (0.2458 g, 2.61 mmol, 2762 equiv/Rh), **4** (0.342 g, 2.85 mmol), and a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $1.89 \times 10^{-3}$  M;  $9.45 \times 10^{-4}$  mmol, 0.04 mol %). The mixture was kept in a 40 °C bath (5 h), cooled to room temperature, and extracted with THF ( $2 \times 5$  mL). Solvent was removed by oil pump vacuum at 0 °C to give a white solid. Then ethanol/THF (10 mL, 1:1 v/v) and NaOH (5 mL, 2 M in  $H_2O$ ) were added. The mixture was placed in an ice bath, and 30%  $H_2O_2$  (1.0 mL, 8.8 mmol) was added dropwise with stirring. After 0.5 h, the ice bath was removed. After 6 h, the mixture was extracted with ether ( $3 \times 15$  mL). The extract was washed with NaOH (10 mL, 0.5 M in  $H_2O$ ),  $H_2O$  (25 mL), and brine (15 mL) and dried over  $MgSO_4$ . Solvent was removed by rotary evaporation to give *exo*-norborneol as a white solid (0.2633 g, 2.35 mmol, 90%, TON 2487). The  $^1H$  and  $^{13}C$  NMR spectra (Supporting Information) matched those in the Sadler reference series. The former spectrum was recorded with weighed amounts of sample and  $Ph_3SiCH_3$  standard, and integration established a product purity of >98%.

**B. Reaction of Styrene.**<sup>37</sup> A flask was charged with a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $4.47 \times 10^{-3}$  M;  $2.24 \times 10^{-3}$  mmol, 0.05 mol %), styrene (0.495 g, 4.75 mmol, 2121 equiv/Rh), and **4** (0.507 mL, 0.570 g, 4.75 mmol). The mixture was kept in a 40 °C bath (10 h), cooled to room temperature, and extracted with THF ( $3 \times 3$  mL). The extract was treated with NaOH (10 mL, 2 M in  $H_2O$ ) and 30%  $H_2O_2$

(0.75 mL, 6.7 mmol) as described in the reaction of norbornene. An identical workup gave phenylethanol as a clear, colorless oil (0.522 g, 4.27 mmol, 90%, TON 1906). The  $^1H$  and  $^{13}C$  NMR spectra (Supporting Information) matched those in the Sadler reference series and indicated a 55:45 mixture of  $\alpha/\beta$  regioisomers.

**Organoborane Syntheses (Chart 3).** The following are representative, and others are given in the Supporting Information.

**A. Phenylacetylene and **4**.**<sup>38a</sup> A flask was charged with a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $1.79 \times 10^{-3}$  M;  $8.95 \times 10^{-4}$  mmol, 0.19 mol %), phenylacetylene (0.053 mL, 0.049 g, 0.48 mmol, 536 equiv/Rh), and **4** (0.065 mL, 0.073 g, 0.61 mmol). The mixture was kept in a 40 °C bath (0.5 h), cooled to room temperature, and extracted with THF ( $2 \times 0.5$  mL). Solvent was removed by oil pump vacuum to give the phenylacetylene/**4** adduct as a white solid (0.100 g, 0.450 mmol, 94%, TON 503).<sup>38</sup> The  $CF_3C_6F_{11}$  solution of **1** was subjected to an identical charge/workup cycle (0.422 mmol adduct, 88%; TON = 474).

**B. Phenylacetylene and Pinacolborane (**7**).**<sup>39a</sup> A flask was charged with **7** (0.179 g, 1.400 mmol), phenylacetylene (0.143 g, 1.400 mmol, 786 equiv/Rh), and a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $3.56 \times 10^{-3}$  M;  $1.78 \times 10^{-3}$  mmol, 0.13 mol %). The yellow solution turned colorless. The mixture was kept in a 40 °C bath (12 h), cooled to room temperature, and extracted with toluene ( $3 \times 0.5$  mL). Solvent was removed by water aspirator vacuum. The yellow oil was flash chromatographed on silica gel (98:2 v/v hexanes/ether) to give the phenylacetylene/**7** adduct as a lightly colored mixture of isomers (95:5 trans/minor; 0.291 g, 1.26 mmol, 90%, TON 709) that was pure by  $^1H$  and  $^{13}C$  NMR.<sup>39b,c</sup>

**Deuterium Labeling (Scheme 4).** A flask was charged with a  $CF_3C_6F_{11}$  solution of **1** (0.500 mL,  $3.56 \times 10^{-3}$  M;  $1.78 \times 10^{-3}$  mmol, 0.35 mol % vs **4**-d<sub>1</sub>), freshly distilled 1-decene (0.719 g, 5.13 mmol; 10 equiv vs **4**-d<sub>1</sub>), and *B*-deuteriocatecholborane (**4**-d<sub>1</sub>; <sup>12</sup>C 0.062 g, 0.513 mmol; Supporting Information). The mixture was kept in a 40 °C bath (24 h), cooled to room temperature, and extracted with  $C_6D_6$  ( $2 \times 0.5$  mL). A  $^2H$  NMR spectrum showed the natural abundance  $^2H$  signals of excess 1-decene and a much stronger signal at 1.54 ppm (vs  $C_6D_6$  at 7.15 ppm; ca. 40% more intense than the total 1-decene  $^2H$  integral). The 1-decene was removed by vacuum transfer, and a  $^2H$  NMR spectrum of the residue showed only a signal at 1.55 ppm. A signal with 4% of this area would have been detected. The sample was oxidized (NaOH/ $H_2O_2$  as in Chart 2) to 1-decanol, and the  $^1H$  NMR spectrum ( $\delta$  ( $CDCl_3$ ) 3.68 (d, 2H,  $CH_2OH$ ), 1.60–1.55 (m, 1H), 1.40–1.20 (m, 14 H), 0.87 (t, 3H)) was compared to that of authentic 1-decanol. The  $^2H$  NMR spectrum showed only one signal, coincident with the 1.55 ppm  $CH_2CH_2OH$  signal of 1-decanol.

**Relative Catalyst Reactivities.** Run A: An NMR tube was charged with  $ClRh(PPh_3)_3$  (0.300 mL,  $8.6 \times 10^{-4}$  M in  $CF_3C_6H_5$ ;  $2.58 \times 10^{-4}$  mmol, 0.04 mol %), norbornene (0.057 g, 0.61 mmol, 2352 equiv/Rh), and **4** (0.065 mL, 0.073 g, 0.61 mmol).  $^1H$  NMR spectra (external  $C_6D_6$  lock/reference) showed complete conversion to **5** after 15 min.<sup>34a</sup> Run B: An NMR tube was charged with **3** (0.500 mL,  $8.6 \times 10^{-4}$  M in  $CF_3C_6H_5$ ;  $4.3 \times 10^{-4}$  mmol, 0.07 mol %), norbornene (0.058 g, 0.62 mmol, 1432 equiv/Rh), and **4** (0.067 mL, 0.075 g, 0.63 mmol). After 3 and 22.5 h, NMR spectra showed 4% and 10% conversion to

(38) (a) For the analogous uncatalyzed reaction, which gives a 91:9 mixture of isomers, see ref 22. No data were given for the minor isomer, but it was assigned as a regioisomer. A second set of very minor  $^{13}C$  NMR signals was also detected in some samples of our phenylacetylene/**4** adduct. (b) NMR ( $C_6D_6$ ):  $^1H$  ( $\delta$ ) 7.73 (d,  $J = 19$  Hz, 1H), 7.26–7.21 (m, 2H), 7.05–6.99 (m, 5H), 6.80–6.77 (m, 2H), 6.37 (d,  $J = 19$  Hz, 1H);  $^{13}C$  (ppm) 152.3, 137.3, 132.4, 129.7, 128.9, 127.7, 122.9, 122.8, 112.6, 112.4. The  $^1H$  NMR spectrum was recorded with weighed amounts of sample and  $Ph_3SiCH_3$  standard, and integration ( $\delta$  7.73 vs 0.69) confirmed the product yield and purity (>98%). The  $^1H$  NMR data closely matched those previously reported.<sup>22</sup>

(39) (a) For the analogous uncatalyzed reaction (96:4 mixture of isomers), see ref 25. (b) Our NMR data for the major (trans) isomer closely match those previously reported.<sup>25</sup> No data were given for the minor isomer, but it was assigned as a stereoisomer (in contrast to the minor isomer from phenylacetylene and **4**<sup>38a</sup>). (c) NMR ( $CDCl_3$ ):  $^1H$  ( $\delta$ ) 7.38–6.94 (arH, 12H), *trans* at 6.06 (d,  $J = 18$  Hz, 1H) and 1.30 (s, 12H), minor (partial) at 1.22 (s, 12H);  $^{13}C\{^1H\}$  (ppm) *trans* at 149.4, 128.8, 128.7, 128.4, 128.0, 126.9, 116.2 (br), 83.1, 24.6, minor at 137.7, 137.3, 130.7, 128.0, 127.0, 125.1, 116.2 (br), 83.5, 21.0.

(33) The resonances were assigned as in footnote 39 of ref 15.

(34) (a) NMR ( $C_6D_6$ ):  $^1H$  ( $\delta$ ) 7.05–6.95 (m, 2H), 6.85–6.70 (m, 2H), 2.43 (s, 1H), 2.09 (br s, 1H), 1.80–1.75 (m, 1H), 1.43–1.26 (m, 4H), 1.22–1.01 (m, 4H);  $^{13}C$  (ppm) 148.9, 122.7, 112.5, 39.3, 38.5, 37.0, 32.7, 32.4, 29.4. (b) The  $\delta$  2.43 resonance of **5** was integrated vs the  $\delta$  0.69 resonance of  $Ph_3SiCH_3$ .

(35) The  $\delta$  1.42 and 1.36 resonances of **6** <sub>$\alpha$</sub>  (d,  $J = 8$  Hz, 3H) and **6** <sub>$\beta$</sub>  (t,  $J = 7$  Hz, 2H) were integrated vs the  $\delta$  0.69 resonance of  $Ph_3SiCH_3$ .

(36) For the analogous uncatalyzed reaction, see ref 22 and the following: Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Academic Press: New York, 1988; p 194.

(37) For the analogous uncatalyzed reaction, see refs 20 and 22.



5, respectively. Run C: An NMR tube was charged with **1** (0.300 mL,  $8.6 \times 10^{-4}$  M in  $\text{CF}_3\text{C}_6\text{H}_5$ ;  $2.58 \times 10^{-4}$  mmol, 0.04 mol %), norbornene (0.059 g, 0.63 mmol, 2437 equiv/Rh), and **4** (0.067 mL, 0.075 g, 0.63 mmol). After 0.25 and 5 h, NMR spectra showed no reaction.

**Partition Coefficients.** A 2-dram vial was charged with **1** (0.0600 g = 0.00184 g of rhodium),  $\text{CF}_3\text{C}_6\text{F}_{11}$  (5.00 mL; shaken to dissolve **1**), and toluene (5.00 mL). The vial was vigorously shaken (2 min) and equilibrated (27 °C, 24 h) in an inert atmosphere glovebox. An aliquot (3.0 mL) was removed from each layer by syringe. Analysis by ICP-AES indicated 0.27 ppm or 0.0000012 g of rhodium (toluene), and 188 ppm or 0.001680 g of rhodium ( $\text{CF}_3\text{C}_6\text{F}_{11}$ ).<sup>19</sup> An analogous experiment with **2** (0.0805 or 0.00195 g of rhodium) gave 0.27 ppm or 0.0000012 g of rhodium (toluene), and 219 ppm or 0.00196 g of rhodium ( $\text{CF}_3\text{C}_6\text{F}_{11}$ ).

**Rhodium Leaching.** A 6-dram vial was charged with **1** (0.0302 g = 0.000926 g of rhodium,  $9.00 \times 10^{-3}$  mmol, 0.112 mol %),  $\text{CF}_3\text{C}_6\text{F}_{11}$  (2.5 mL; shaken to dissolve **1**), norbornene (0.7602 g, 8.07 mmol), **4** (1.013 g, 8.45 mmol), and a stir bar. The vial was sealed and moved from an inert atmosphere glovebox to a 45 °C bath. The sample was stirred (3 h) and returned to a glovebox, and  $\text{CF}_3\text{C}_6\text{F}_{11}$  (7.50 mL) and

toluene (10.00 mL) were added. The vial was vigorously shaken (5 min). After 15 min (27 °C), a toluene aliquot (8.0 mL) was removed by syringe. Fresh toluene (8.0 mL) was added, and the vial was vigorously shaken. After 15 min, a second toluene aliquot and a  $\text{CF}_3\text{C}_6\text{F}_{11}$  aliquot (8.0 mL each) were removed. Analysis by ICP-AES as described earlier<sup>3c</sup> indicated 0.20, 0.20, and 46.9 ppm (0.0000017, 0.0000014, and 0.000838 g; 91% mass balance) of rhodium. An analogous experiment with **2** (0.0383 g = 0.000926 g of rhodium,  $9.00 \times 10^{-3}$  mmol, 0.111 mol %), norbornene (0.7605 g, 8.08 mmol), and **4** (1.026 g, 8.56 mmol) gave 0.10, 0.10, and 49.8 ppm (0.0000009, 0.0000007, and 0.000890 g; 96% mass balance) of rhodium.

**Acknowledgment.** We thank the NSF (CHE-9401572) for support of this research.

**Supporting Information Available:** Additional experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA982955B