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Transition metal catalysis in fluorous media: application of a new immobilization principle to rhodium-catalyzed hydrogenation of alkenes

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Abstract

Biphase systems were generated by combining toluene solutions of alkenes (2-cyclohexen-1-one, 1-dodecene, cyclododecene, 4-bromostyrene) and $CF_3C_6F_{11}$ solutions of the pre-catalyst $ClRh[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ ((**1**); 1.1–0.8 mol%) and placed under 1 atm of H_2. The perfluoroalkyl segments in (**1**) confer high affinities for fluorocarbons. After 8–26 h at 45°C, the $CF_3C_6F_{11}$ phases were separated, and extracted with an equal volume of toluene. GLC analyses of the toluene solutions showed 98–87% yields of the hydrogenation products cyclohexanone, dodecane, cyclododecane, and 4-bromoethylbenzene (turnover numbers 120–87). The $CF_3C_6F_{11}$ phases were charged with new toluene solutions of 2-cyclohexen-1-one or 1-dodecene, and similarly treated with H_2. There was no significant loss of catalyst activity over three cycles. A preparative reaction gave cyclohexanone in 89% yield. Some C=C isomerization could be detected during the course of 1-dodecene hydrogenation, and (**1**) gave a dihydride complex in the absence of alkene. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Among the many frontiers of homogeneous catalysis, two of the most active involve (1) non-traditional reaction media, and (2) new catalyst immobilization or recovery strategies to facilitate reuse [1]. Accordingly, a new design principle, ‘fluorous biphase catalysis’, has been discovered in our laboratories [2]. The term fluorous is utilized as an analog to aqueous for highly fluorinated alkane, ether, or tertiary amine solvents. These are distinguished by their non-polar character, and often give bilayers with organic solvents. Many systems become miscible at higher temperatures.

As detailed previously, fluorous catalysts are obtained by appending fluoroalkyl groups or ‘pony tails’ such as $(CH_2)_y(CF_2)_xCF_3$ [2,3]. When sufficient numbers of fluorinated carbons are present, exceptional affinities for fluorous media are possible. This allows facile catalyst/product separation. The $(CH_2)_y$ spacers serve to insulate the catalyst from the electron withdrawing fluorines [2(c)]. Mechanistic studies with

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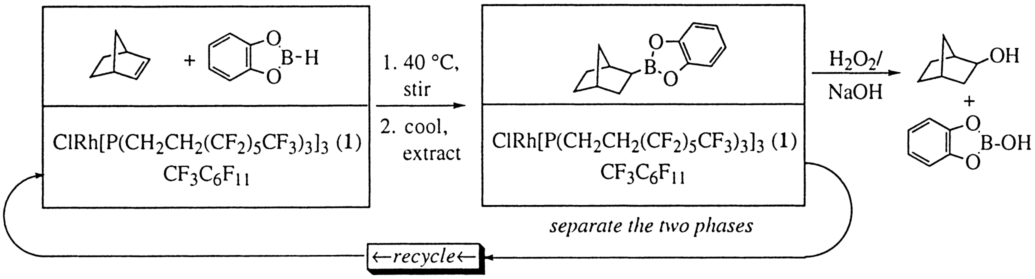


Scheme 1. Fluorous biphase rhodium-catalyzed hydroboration.

coordinatively unsaturated iridium(I) complexes show that the relative rates of various types of oxidative additions change in fluorous media [4]. Thus, new types of selectivities are also likely.

We recently reported the preparation of an aliphatic fluorous phosphine analog of Wilkinson's catalyst, $ClRh[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ (**1**) [5]. This compound is soluble in $CF_3C_6F_{11}$ and $CF_3C_6H_5$ but insoluble in virtually all common organic solvents. We have furthermore shown that (**1**) is an active and long-lived catalyst for the hydroboration of alkenes. As summarized pictorially in Scheme 1, $CF_3C_6F_{11}$ solutions of (**1**) are combined with catecholborane and an alkene, either with or without an organic solvent. The organoborane is extracted into THF, separating product from catalyst. The organoborane can then be oxidized to the desired alcohol – a step that would irreversible degrade nearly all catalysts – and the $CF_3C_6F_{11}$ solution of (**1**) reused.

We were naturally curious whether (**1**) could duplicate other reactions of Wilkinson's catalyst. Accordingly, we undertook a survey. In this paper, we report that (**1**) catalyzes the hydrogenation of alkenes, and is easily separated from the reduced products. Hydrosilylations and other transformations will be described in future reports.

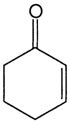
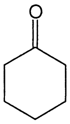
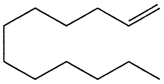
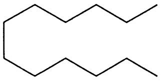
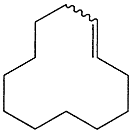
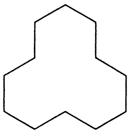
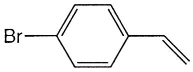
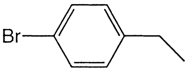
2. Results

2.1. Reaction scope

We sought to examine a range of simple representative alkenes. For reasons evident below, the conjugated enone 2-cyclohexen-1-one was evaluated first. As summarized in Fig. 1, a Schlenk tube was charged with a toluene solution of 2-cyclohexen-1-one (0.124 mmol in 1.0 ml) and a $CF_3C_6F_{11}$ solution of (**1**) (1.05 mol% in 1.0 ml). The biphase system was vigorously stirred under a balloon pressure of H_2 at 45°C. The lower fluorous phase decolorized. GLC analyses showed the clean conversion to cyclohexanone over the course of 8 h. No significant quantities of C=O hydrogenation by-products formed, as verified by GLC comparisons with authentic samples of 2-cyclohexen-1-ol or cyclohexanol.

The sample was cooled, and the upper toluene phase was removed by syringe. The $CF_3C_6F_{11}$ phase was extracted with toluene (1.0 ml). Control experiments (below) showed that this simple workup removes essentially all reduction products from the $CF_3C_6F_{11}$. An internal standard was added to the combined toluene layers, which were analyzed by GLC. As tabulated in Fig. 1, cyclohexanone was present in 98% yield, corresponding to a turnover number (TON) of 94. In a separate preparative reaction (0.55 mol% (**1**), 18 h), cyclohexanone was isolated in 89% yield, and was >98% pure by ^{1}H NMR and GLC.

A similar reaction was conducted with 1-dodecene and 0.90 mol% of (**1**). GLC analysis showed that hydrogenation was complete after 16 h. As summarized in Fig. 1, dodecane formed in 88% yield, corresponding to a TON value of 98. A disubstituted alkene, cyclododecene (*cis*/*trans* 32:68), was investigated next (0.78 mol% (**1**)). Reaction was complete after 26 h, and GLC showed cyclododecane in 94% yield (TON 120). Finally, the hydrogenation of 4-bromostyrene (1.00 mol% (**1**)) was complete after 26 h. GLC showed 4-bromoethylbenzene in 87% yield (TON 87). In each case, product identities were verified by GLC/MS.

Entry	Educt	Product	**1** (mol%)	Time (h)	Yield (%)[a]	TON
1			1.05 (0.55)	8 (18)	98 (89)[b]	94 (160)[b]
2			0.90	16	88	98
3			0.78	26	94	120
4			1.00	26	87	87

[a]Determined by Gas Chromatography. [b]For product isolated from a preparative reaction.

Fig. 1. Fluorous biphase alkene hydrogenations catalyzed by (**1**) ($CF_3C_6F_{11}$/toluene, 45°C, 1 atm).

2.2. *Monitoring data*

GLC analysis of the hydrogenation of 1-dodecene revealed two significant features. First, as illustrated in Fig. 2, there was an induction period of ca. 8 h. In contrast, 2-cyclohexen-1-one did not give an induction period. Second, a significant portion of the 1-dodecene isomerized to *cis* and *trans* 2- and 3-dodecene. These were hydrogenated at slower rates. With certain substrates, such phenomena lead to undesired side-reactions and compromise catalyst utility.

To ensure that workups removed all products from the fluorous phase, selected $CF_3C_6F_{11}$/toluene partition coefficients were carefully measured as described in Section 4. These are summarized in Table 1. Interestingly, even linear hydrocarbons exhibit a marked preference for the toluene phase (3.4–2.5:96.6–97.5). The more polar, oxygen-containing cyclohexane derivatives appear to have even greater toluene affinities.

Table 1
Partition coefficients (24°C)

Analyte	$CF_3C_6F_{11}$/toluene
Dodecane	3.4:96.6
1-dodecene	2.5:97.5
2-cyclohexen-1-one	1.7:98.3
Cyclohexanone	2.2:97.8
Cyclohexanol	1.6:98.4

A reaction of (**1**) and H_2 (1 atm) in $CF_3C_6F_{11}$ was conducted in an NMR tube in the absence of an alkene. Over the course of 12 h, the orange-yellow solution became greenish yellow. As shown in Scheme 2, NMR spectra showed complete conversion to a new compound, which was assigned as the dihydride complex $ClRh(H)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ (**2**). In particular, (**2**) exhibited two ^{31}P signals in a 2:1 area ratio (22.8 and 3.9 ppm). The former was a doublet of doublets due to coupling to rhodium and the unique phosphorus atom (J_{PRh}=108 Hz, J_{PP}=24 Hz). The latter was a doublet of triplets due to coupling to rhodium and two equivalent phosphorus atoms (J_{PRh}=90 Hz, J_{PP}=24 Hz). The ^1H NMR spectrum showed two hydride signals (δ −10.7, br d, J_{HP}=163 Hz; −18.4, br s). Accordingly, (**2**) must have meridional phosphine and *cis* hydride ligands as shown in Scheme 2. Under similar conditions, H_2 and $ClRh(PPh_3)_3$ react to give the analogous dihydride complex $ClRh(H)_2(PPh_3)_3$ [6].

2.3. *Catalyst recovery and reuse*

We sought to demonstrate that the catalyst (**1**) could be recycled. Accordingly, the reaction of

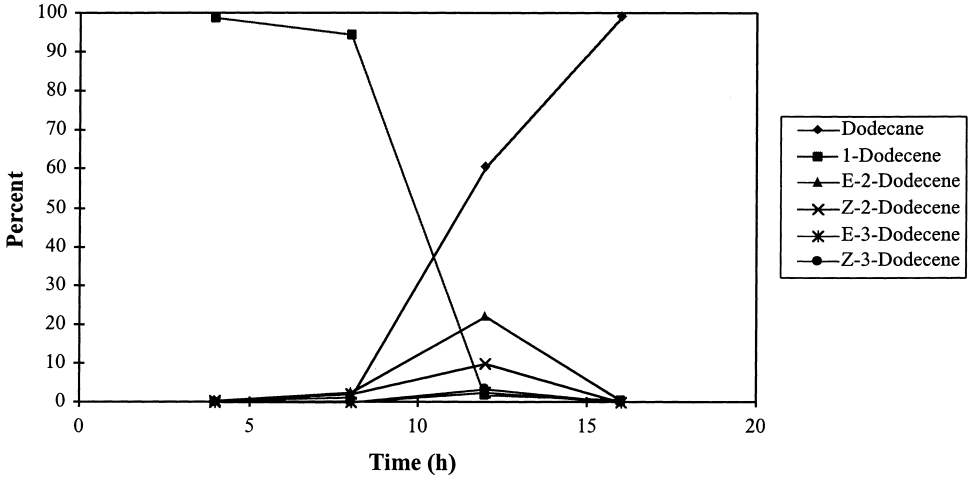
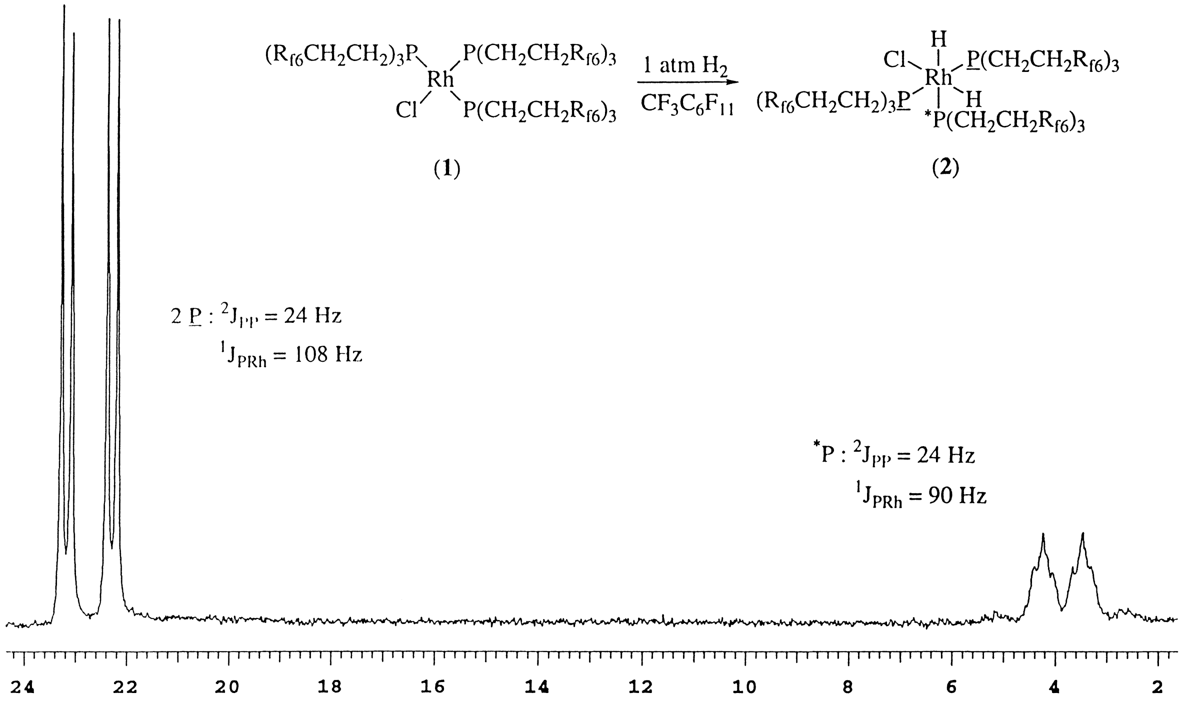
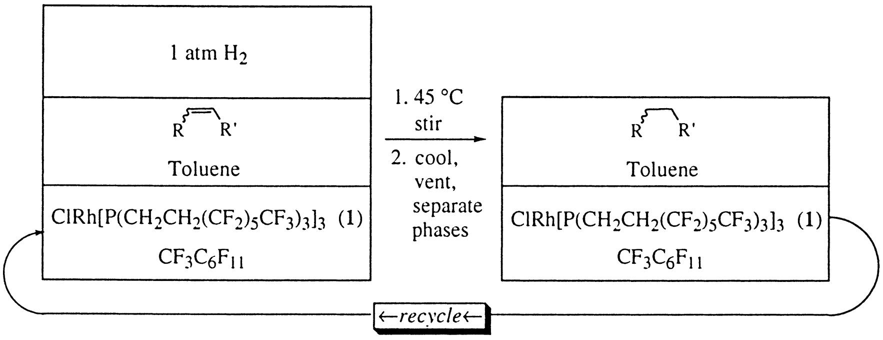


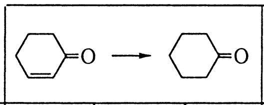
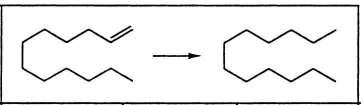
Fig. 2. Course of the hydrogenation of 1-dodecene under the conditions of Scheme 3 and Fig. 1.



Scheme 2. Oxidative addition of hydrogen.

2-cyclohexen-1-one (0.124 mmol), H_2, and (**1**) (1.05 mol%) was conducted as described above (8 h). The phases were separated, and the $CF_3C_6F_{11}$ was washed once with toluene. Tridecane was added to the toluene extracts. GLC analysis indicated a 96% yield of cyclohexanone (TON 91). As illustrated in Scheme 3, the $CF_3C_6F_{11}$ mother solution was recharged with 2-cyclohexen-1-one and toluene.



						
cycle	mmol[a]	yield	TON	mmol[b]	yield	TON
1	0.119	96%	91	0.121	92%	92
2	0.115	93%	89	0.122	93%	93
3	0.114	92%	88	0.141	108%[c]	108

[a] 0.124 mmol substrate/cycle; 1.05 mol% 1 initial charge
[b] 0.130 mmol substrate/cycle; 1.00 mol% 1 initial charge
[c] see text

Scheme 3. Fluorous biphase rhodium-catalyzed alkene hydrogenation.

An identical sequence gave a 93% yield of cyclohexanone (TON 89). A third cycle gave a 92% yield of cyclohexanone (TON 88), for a combined TON value of 268.

Analogous recycling was possible with the other alkenes, but was less successful. For example, 1-dodecene (0.131 mmol), H_2, and (**1**) (1.0 mol%) were combined as described above (16 h). Workup and GLC analysis indicated a 92% yield of dodecane (TON 92). The $CF_3C_6F_{11}$ mother solution was recharged with 1-dodecene, toluene, and H_2. Hydrogenation was complete in 8 h, reflecting the absence of an induction period after the first cycle. GLC indicated a 93% yield of dodecane (TON 93). During the course of the third cycle, a black solid precipitated on the walls of the tube. GLC indicated a 108% yield of dodecane (TON 108), possibly due to incomplete extraction from the previous cycle.

When further cycles were attempted, hydrogenation rates greatly decreased. When hydrogenations were conducted at higher temperatures or pressures, black solids formed in earlier cycles. After a sufficient number of cycles, black solids also formed in 2-cyclohexen-1-one reductions. When recycled catalyst solutions were transferred to new tubes, hydrogenations proceeded normally.

3. Discussion

Countless transition metal-based hydrogenation catalysts have been developed [7]. From a reactivity standpoint, (**1**) is not comparable with the best homogeneous catalysts. However, from a recycling standpoint, (**1**) offers fundamentally new solubility attributes and extraction possibilities. As a wider variety of fluorous ligands become available, more active and long-lived catalysts are certain to be developed. In this context, it is well known that alkyl phosphines give much less effective $ClRhL_3$ catalysts than aryl phosphines [8]. Thus, the deactivation observed with 1-dodecene is not unprecedented. Also, although Wilkinson's catalyst is often advertised as free from complicating isomerization or label scrambling processes, increasing numbers of such reactions are being detected [9].

The mechanism of hydrogenation with (**1**) is also an issue. It is quite probable that 2-cyclohexen-1-one reacts by a different pathway that the other alkenes, as reflected by the absence of an induction period. In general, α,β-unsaturated ketones are more nucleophilic than simple alkenes towards transition metal electrophiles, and would be expected to bind to catalysts more rapidly [10]. We were concerned that the induction periods might reflect the generation of small amounts of a heterogeneous catalyst. However, insoluble residues are only detected at later stages, and other homogeneous rhodium(I) catalysts also exhibit induction periods [8]. The chemoselectivity of the 2-cyclohexen-1-one reduction (C=C>C=O) has precedent with other rhodium(I) catalysts and α,β-unsaturated aldehydes [11].

In summary, we have demonstrated the applicability of fluorous biphase catalysis to one of the most fundamental laboratory scale and commodity chemical transformations, hydrogenation. Our data complement a growing literature on transition metal hydrogenation catalysts that are similarly immobilized in water [11]. Future reports will detail other transformations that can be catalyzed by (**1**), and syntheses of new types of phosphine ligands and rhodium(I) catalysts [12].

4. Experimental

4.1. General

IR and NMR spectra were recorded on Mattson Polaris and Varian 300 MHz FT spectrometers. GLC analyses were conducted on a Hewlett Packard 5890 chromatograph equipped with a flame ionization detector and Supelcowax 10 capillary column (30 m×0.2 mm, 0.2 μm thickness). GLC/MS analyses were conducted on a Hewlett Packard 5971A instrument equipped with 5890 chromatograph and a DB-5 capillary column (30 m×0.25 mm). All glassware was oven dried (80°C, ≥12 h) and either assembled hot and cooled during a three cycle evacuation/dry nitrogen backfill, or taken directly into a glove box. Reactions were set up under inert atmospheres using standard techniques, and heated with silicone oil baths (continuously stirred, ±1°C).

Solvent and reactant data: $CF_3C_6F_{11}$ (Oakwood) and toluene were distilled under N_2 from P_2O_5 and Na/benzophenone, respectively, and stored under N_2; 1-dodecene and cyclododecene (Aldrich) were dried over CaH_2 and fractionally distilled at reduced pressure; 2-cyclohexen-1-one (Aldrich) was dried over $MgSO_4$ and fractionally distilled at reduced pressure; 4-bromostyrene (Aldrich) was dried over CaH_2 and vacuum transferred; $ClRh[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ (**1**) was prepared as described earlier [5]. Authentic samples were obtained as follows: cyclohexanone, EM Science; cyclohexanol, MCB, 2-cyclohexen-1-ol, dodecane and 4-bromoethylbenzene, Aldrich; cyclododecane, TCI.

4.2. Cyclohexanone

(**A**) A Schlenk tube was charged with a solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 1.05 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), and 2-cyclohexen-1-one (0.012 ml, 0.124 mmol, 95 equiv/Rh), flushed with H_2 (5 min), fitted with an H_2-filled balloon, and immersed in a 45°C bath. The lower pale yellow fluorous layer became colorless, and the sample was vigorously stirred. Every 4 h, the bath was removed and the layers allowed to separate (15 min). An aliquot (10 μl) from the toluene layer was analyzed by GLC. The sample was returned to the oil bath and again stirred. After 8 h, the toluene layer was removed via syringe, and the fluorous layer extracted with toluene (1 ml). The combined extracts were added to a solution of tridecane in hexanes (2.0 ml, 0.0403 M). GLC showed only cyclohexanone (98%, TON=93.8).

(**B**) A Schlenk tube was charged with a solution of (**1**) in $CF_3C_6F_{11}$ (2.20 ml, 0.0026 M, 0.0057 mmol, 0.55 mol%), toluene (2.0 ml), and 2-cyclohexen-1-one (0.100 ml, 1.03 mmol, 181 equiv/Rh), and treated with H_2, heated, and stirred as in procedure (**A**). After 18 h, the toluene layer was similarly separated, and the fluorous layer extracted with toluene (2 ml). The toluene was carefully removed from the combined extracts by rotary evaporation and a brief exposure to high vacuum. This gave spectroscopically pure cyclohexanone as a colorless oil (0.0895 g, 0.912 mmol, 89%, TON=160). IR (cm^{-1}, C_6D_6) 1716 s. ^1H NMR (δ, C_6D_6) 2.05 (t, J=7 Hz, 4H), 1.43–1.35 (m, 4H), 1.28–1.23 (m, 2H). ^{13}C NMR (ppm, C_6D_6) 208.9, 41.8, 26.9, 25.0 [13].

4.3. *Dodecane*

A solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 0.90 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), 1-dodecene (0.032 ml, 0.144 mmol, 111 equiv/Rh) and H_2 were combined as in procedure (**A**) for cyclohexanone. An analogous reaction (16 h), series of GLC assays (Fig. 2), and workup gave dodecane (88%, TON=97.7).

4.4. *Cyclododecane*

A solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 0.78 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), cyclododecene (68:32 E/Z; 0.032 ml, 0.166 mmol, 128 equiv/Rh), and H_2 were combined as in procedure (**A**) for cyclohexanone. An analogous reaction (26 h), series of GLC assays, and workup gave cyclododecane (94%, TON=120).

4.5. *4-Bromoethylbenzene*

A solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 1.0 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), 4-bromostyrene (0.017 ml, 0.130 mmol, 100 equiv/Rh), and H_2 were combined as in procedure (**A**) for cyclohexanone. An analogous reaction (26 h), series of GLC assays, and workup gave 4-bromoethylbenzene (87%, TON=86.6).

4.6. *Catalyst recycling (Scheme 3)*

(**A**) A solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 1.05 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), 2-cyclohexen-1-one (0.012 ml, 0.124 mmol, 95 equiv/Rh), and H_2 were combined as in procedure (**A**) above. An analogous reaction (8 h), workup, and GLC assay gave cyclohexanone (96%, TON=91). The $CF_3C_6F_{11}$ layer was recharged with 2-cyclohexen-1-one (0.012 ml, 0.124 mmol, 95 equiv/Rh) and toluene (1.0 ml). An identical reaction (H_2, 8 h), workup, and GLC assay gave cyclohexanone (93%, TON=89). The $CF_3C_6F_{11}$ layer was recharged with 2-cyclohexen-1-one (0.012 ml, 0.124 mmol, 95 equiv/Rh) and toluene (1.0 ml). An identical reaction (H_2, 8 h), workup, and GLC assay gave cyclohexanone (92%, TON=88).

(**B**) A solution of (**1**) in $CF_3C_6F_{11}$ (0.500 ml, 0.0026 M, 0.00130 mmol, 1.0 mol%), $CF_3C_6F_{11}$ (0.5 ml), toluene (1.0 ml), 1-dodecene (0.029 ml, 0.131 mmol, 101 equiv/Rh) and H_2 were combined as in the preceding experiment. An analogous reaction (16 h), workup, and GLC assay gave dodecane (92%, TON=92). The $CF_3C_6F_{11}$ layer was recharged with 1-dodecene (0.029 ml, 0.131 mmol, 101 equiv/Rh) and toluene (1.0 ml). An analogous reaction (H_2, 8 h; no induction), workup, and GLC assay gave dodecane (93%, TON=93). The $CF_3C_6F_{11}$ layer was recharged with 1-dodecene (0.029 ml, 0.131 mmol, 101 equiv/Rh) and toluene (1.0 ml). An identical reaction (H_2, 8 h), workup, and GLC assay gave dodecane (108%, TON=108). During this cycle, a black solid precipitated.

4.7. *$ClRh(H)_2[P(CH_2CH_2(CF_2)_5CF_3)_3]_3$ (2)*

A J-Young valve capped NMR tube was charged with a solution of (**1**) (0.0349 g, 0.0104 mmol) in $CF_3C_6F_{11}$ (0.7 ml) and attached to a vacuum line. The orange solution was degassed (3x), and H_2 (1 atm) was added. After 12 h, NMR spectra of the light greenish-yellow solution showed complete conversion to (**2**). ^1H NMR (δ, $CF_3C_6F_{11}$, external $CDCl_3$ lock) -18.4 (br s, 1H), -10.7 (br d, 1H, J_{PH}=163 Hz). $^{31}P\{^1H\}$ NMR (ppm, $CF_3C_6F_{11}$, unlocked, external H_3PO_4) 3.9 (dt, J_{PRh}=90 Hz, J_{PP}=24 Hz, 1P), 22.8 (dd, J_{PRh}=108 Hz, J_{PP}=24 Hz, 2P); ^{31}P NMR 3.9 (apparent dd, J_{PRh}=85 Hz, J_{PH}=160 Hz, 1P), 22.8 (apparent d, J_{PRh}=119 Hz, 2P).

4.8. *Partition coefficients*

The following procedure is representative. A 1 dram vial was charged with dodecane (0.0300 g), $CF_3C_6F_{11}$ (2.0 ml), and toluene (2.0 ml), capped with a mininert valve, vigorously shaken (2 min), and immersed (cap-level) in a 40°C bath. After 12 h, the sample was allowed to cool to ambient temperature (24°C). After 1 h, 0.400 ml aliquots of each layer were added to stock solutions of tridecane in hexane (2.0 ml, 0.0403 M). GLC analysis showed 3.45×10^{-2} mmol of dodecane in the toluene aliquot and 1.21×10^{-3} mmol of dodecane in the $CF_3C_6F_{11}$ aliquot, for a partition coefficient of 28.51 (96.6:3.4). The total mass of dodecane calculated from these data

(0.0304 g following 2.0/0.400 volume correction) was in close agreement with that originally added.

Acknowledgements

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