

Recycling of Rhodium-Based Hydrosilylation Catalysts; A Fluorous Approach

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Received February 12, 2001

The concept of fluorous biphasic separation has been applied in the recycling of rhodium-based catalysts for the hydrosilylation of 1-alkenes and fluorinated 1-alkenes by following two approaches. Hydrosilylation of 1-hexene using various silanes and fluorous versions of Wilkinson's catalyst $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{R}_f)_3\}_3]$ (**1**; $\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$) or $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}(\text{R}_f)_2)_3\}_3]$ (**2**; $\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$) in fluorous biphasic solvent systems afforded the corresponding *n*-hexylsilanes in high yield. The catalyst activities were similar to those obtained using conventional $[\text{RhCl}(\text{PPh}_3)_3]$. The fluorous phase containing the catalyst was recycled at least twice without noticeable loss of activity, despite the fact that 12 and 1.7% of $[\text{Rh}]$ was lost for **1** and **2**, respectively, in the first cycle. The fluorous hydride intermediate $[\text{Rh}(\text{H})(\text{Cl})(\text{SiCl}_3)\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{R}_f)_3\}_2]$ (**3**; $\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$) was identified by NMR spectroscopy. In a reverse approach, the original Wilkinson's catalyst was used for the hydrosilylation of 1*H*,1*H*,2*H*-perfluoro-1-alkenes in benzene or toluene as solvent. Fluorous extraction of the products enabled recycling of the nonfluorous catalyst.

Introduction

Hydrosilylation of 1-alkenes is an important synthetic route to higher alkylsilanes, which in turn are important precursors for silicon-based polymers, lubricants, and water-repellent coatings.¹ Often relatively expensive precious-metal catalysts are needed,² of which tris-(triphenylphosphine)rhodium chloride is probably the best known.^{3,4} Recently, fluorous biphasic catalyst separation⁵ was employed for the mild recycling of rhodium trialkylphosphine catalysts in the hydrogenation of 1-alkenes⁶ and hydrosilylation of ketones and enones.⁷ A disadvantage of these systems is the lower activity compared to Wilkinson's catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$. Nota-

bly, the use of *p*-silyl-substituted fluorous triarylphosphines, developed in our laboratory,⁸ resulted in similar activities compared to $[\text{RhCl}(\text{PPh}_3)_3]$.⁹ This study, furthermore, showed that it is not leaching of the catalyst (0.1%) that is the main issue here but rather the leaching of the free fluorous ligand (3.0%) and possibly the fluorous solvent.

We now present the application of fluorous biphasic separation for the recycling of hydrosilylation catalysts following two approaches (Scheme 1). For the hydrosilylation of 1-hexene, fluorous derivatives of Wilkinson's complex, $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{R}_f)_3\}_3]$ (**1**; $\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$), and the newly prepared $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}(\text{R}_f)_2)_3\}_3]$ (**2**; $\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$), have been used. Here, the alkylsilane product is isolated from the organic phase (Scheme 1, path A). In the alternative, second approach, fluorous 1-alkenes are hydrosilylated using the nonfluorous $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst. In this case the products have been isolated from the organic phase by fluorous extraction.¹⁰ The latter approach we like to refer to as *reversed* fluorous biphasic catalyst separation (Scheme 1, path B), which involves recycling of the catalytically active organic layer.

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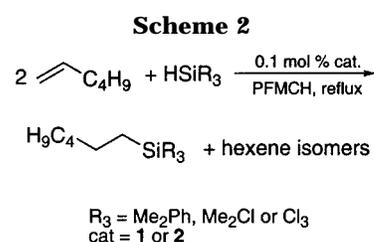
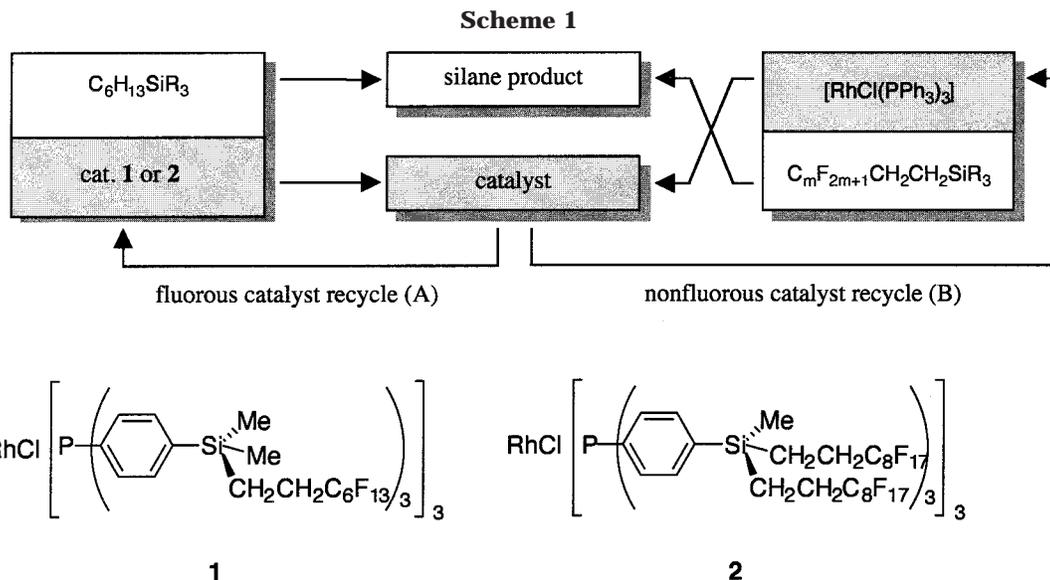
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Results and Discussion

Hydrosilylation of 1-Hexene using Fluorous Rhodium Catalysts. Fluorous catalysts **1** and **2** were prepared by evaporating all volatiles from a solution containing $[\text{Rh}(\text{cod})\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) and 6 equiv of free fluororous phosphine, $\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2(\text{R}_f))_3$ ($\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$) and $\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}(\text{R}_f))_3$ ($\text{R}_f = \text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$), respectively.⁸ In this way, the fluororous derivatives of Wilkinson's complex could be obtained in high yield without contamination by excess free phosphine or other rhodium species and controlled Rh:P ratio.

The hydrosilylation of 1-hexene using various silanes was performed at reflux temperature under monophasic conditions (Scheme 2). $\text{c-C}_6\text{F}_{11}\text{CF}_3$ (PFMCH) was used as the fluororous phase, while the organic phase contained the substrates (1:4 volume ratio). A 2:1 ratio of 1-hexene to silane was used to prevent the formation of substantial amounts of less fluororous $[\text{Rh}(\text{H})(\text{Cl})(\text{SiR}_3)\{\text{P}(\text{Ar}_f)_3\}_2]$ ($\text{Ar}_f = \text{C}_6\text{H}_4\text{-4-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$, $\text{C}_6\text{H}_4\text{-4-SiMe}(\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2$) at the end of the reaction.

The results of the hydrosilylation reactions are shown in Table 1, along with the reaction times needed to achieve full conversion. As was reported for nonfluorous Wilkinson's complex,¹¹ in all cases selective anti-Markovnikov addition and some isomerization of the excess of 1-hexene (ca. 13% by ^1H NMR) took place.

The activities of both **1** and **2** are comparable to those of Wilkinson's complex (Table 1). Longer reaction times were needed in the case of chlorosilanes, which previously was also reported to be the case for the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalyzed reaction^{4c} and has been attributed to

Table 1. Fluorous Phase Hydrosilylation of 1-Hexene^a

catalyst precursor	product ^b	t ^c
$\text{RhCl}(\text{PPh}_3)_3^d$	$\text{C}_6\text{H}_{13}\text{SiMe}_2\text{Ph}$	15 min
1	$\text{C}_6\text{H}_{13}\text{SiMe}_2\text{Ph}$	15 min
2	$\text{C}_6\text{H}_{13}\text{SiMe}_2\text{Ph}$	15 min
1	$\text{C}_6\text{H}_{13}\text{SiMe}_2\text{Cl}$	15 h
1	$\text{C}_6\text{H}_{13}\text{SiCl}_3$	15 h

^a Conditions: catalyst:silane:1-hexene = 1:1000:2000; reflux; solvent (unless otherwise indicated) PFMCH; $[\text{Rh}] = 2 \text{ mM}$. ^b Ca. 13% of the excess of 1-hexene was isomerized. ^c Reaction time needed for full conversion of the silane (>99%). ^d With benzene as solvent.

the higher stability of the intermediate $[\text{Rh}(\text{H})(\text{Cl})(\text{SiR}_3)(\text{PPh}_3)_2]$. It should be noted that although the fluororous solvent gave a single phase with the substrates upon heating to the reaction temperature, the solubility of the highly fluororous complex **2** in the fluororous-organic reaction medium was low. Consequently, **2** was at least partly emulsified in the reaction mixture. Remarkably, this heterogeneous system showed activity similar to that of **1**.

Catalyst recycling was performed by phase separation at ambient temperature. Although the organic substrates were fully miscible with the fluororous solvent at room temperature or slightly above (depending on the silane used), a biphasic system was obtained after the reaction was completed, which is due to the lower miscibility of the organic products with the fluororous phase. Full conversion of silane was achieved in all cases without observable drop in activity (Table 2). As noted before,⁹ the activity of the catalyst in subsequent cycles can, apart from catalyst leaching, be influenced by leaching of free fluororous ligand and fluororous solvent as well. Therefore, these three types of leaching are considered.

For HSiMe_2Ph and **1** a yellow to orange organic layer was obtained, suggesting that some leaching of the catalyst took place. This was confirmed by the results of ICP-AAS analysis of the organic layer (Table 2). Remarkably, the activity of **1** increased upon recycling, despite the substantial leaching of the catalyst (12% as measured by the amount of rhodium in the organic layer). The effect of catalyst leaching on the activity is

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Table 2. Catalyst Recycling in the Hydrosilylation of 1-Hexene^a

catalyst precursor	product	no. of cycles (t, min ^b)	leaching, % ^c	
			Rh	P
1	C ₆ H ₁₃ SiMe ₂ Ph	3 (15) ^d	12 (41)	19 (58)
2	C ₆ H ₁₃ SiMe ₂ Ph	3 (15)	1.7 (5.7)	2.2 (6.6)

^a For conditions see Table 1. ^b Reaction time needed for full conversion of silane in each cycle. ^c Determined by ICP-AAS analysis of the organic phase after phase separation at ambient temperature, relative to the initial amount of catalyst used. The values in parentheses represent the absolute amount (by weight in ppm) in the organic phase. ^d The reaction time decreased to 5 min after the first cycle (full conversion of silane).

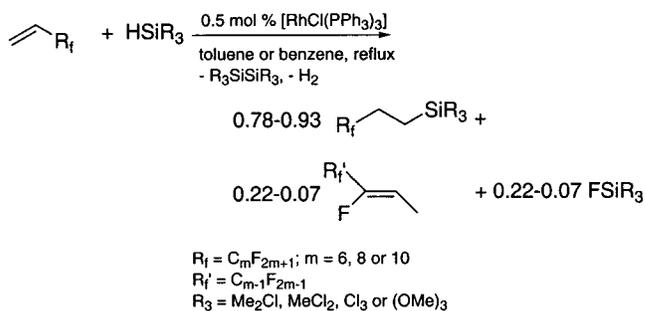
most probably overcompensated by the combined effects of increase in catalyst concentration⁹ as a result of solvent leaching (ca. 20% per cycle) and loss of free phosphine.¹² Since it is clear from the extent of rhodium leaching that a more fluororous catalyst is needed, we did not study catalyst **1** any further and decided to focus attention on **2**.

No change in catalytic activity was observed when **2** was recycled, although leaching of fluororous solvent still took place. As judged from the ICP-AAS data, leaching of the catalyst and the free ligand has been significantly reduced in comparison with **1** (Table 2), which results in a more constant P:Rh ratio upon recycling and hence a more constant catalytic activity. Also, the fact that **2** is not completely dissolved under the reaction conditions could be partially responsible for this phenomenon. Although catalyst leaching and catalytic activity indicate that recycling of the intact catalyst system is indeed possible, it may be clear that in a viable semicontinuous process the fluororous solvent would have to be recovered as well.

According to the Chalk–Harrod mechanism for hydrosilylation,^{11a} a rhodium hydride, [Rh(H)(Cl)(SiR₃)(PAr₃)₂] (Ar = aryl), is formed as a crucial intermediate. When **1** was reacted with HSiCl₃, [Rh(H)(Cl)(SiCl₃){P(Ar₃)₂}] (**3**; Ar₃ = C₆H₄-4-SiMe₂CH₂CH₂C₆F₁₃) and 1 equiv of free P(Ar₃)₃ were formed (³¹P and ¹H NMR). Attempts to isolate **3** in pure form were unsuccessful, as a result of the high solubility of **3** and the free phosphine in different organic (CH₂Cl₂, pentane) and fluororous solvents. Compound **3** showed a doublet in the ³¹P NMR spectrum for the two equivalent P atoms (δ 39.1, ¹J_{RhP} = 111 Hz) and a doublet of triplets in the ¹H NMR spectrum for the hydride (δ -14.2, ¹J_{RhH} = 19.6 Hz; ²J_{PH} = 13.6 Hz). These values correspond closely to those reported for nonfluororous [Rh(H)(Cl)(SiCl₃)(PPh₃)₂],^{4c} indicating a similar trigonal-bipyramidal structure for **3**.

The formation of **3** from **1** and HSiCl₃ suggests similar mechanisms for hydrosilylations employing [RhCl(PPh₃)₃] and fluororous catalysts **1** or **2**. One of the crucial steps in this mechanism involves dissociation of one of the phosphine ligands from the complex. This step might explain the leaching of the free ligand, which may ultimately also lead to increased catalyst leaching because of the lower fluororous character of the resulting rhodium species. Because the phosphines employed have generally lower partition coefficients than their corresponding transition-metal complexes, phosphine leaching is difficult to prevent. One way to circumvent

(12) A lower P:Rh ratio is known to lead to an increase of catalytic activity for [RhCl(PPh₃)₃]. See, e.g., ref 2a.

Scheme 3

this problem is to use catalysts based on chelating fluororous bisphosphines, which we are currently investigating.¹³

Hydrosilylation of 1H,1H,2H-Perfluoro-1-alkenes using [RhCl(PPh₃)₃]. To enable catalyst recycling in the synthesis of fluororous alkylsilanes, a *reversed* approach compared to the approach described above was used. The hydrosilylation reactions of 1H,1H,2H-perfluoro-1-alkenes were performed using 2 equiv of non-fluororous hydrosilane per equivalent of alkene in benzene or toluene as solvent (Scheme 3). When the fluororous olefin was fully converted, the reaction mixture was extracted with FC-72 (mixture of perfluorohexanes). The higher boiling silanes (R_f = C₈F₁₇, C₁₀F₂₁) were purified by removing volatiles (FC-72, traces of toluene,¹⁴ and (Z)-R_f'CF=CHCH₃, R_f' = C₇F₁₅, C₉F₁₉) in vacuo. For the lower boiling silanes (R_f = C₆F₁₃), volatiles (FC-72 and traces of benzene¹⁴) were first removed by atmospheric distillation followed by in vacuo removal of the side product ((Z)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-2-octene). In all cases, FC-72 was recovered by distillation and reused in the next cycle, thus reducing the costs related to the total amount of fluororous solvent needed.

In Table 3 the present results are compared with those reported using H₂PtCl₆ as catalyst.¹⁵ The higher selectivity of the rhodium catalyst for the formation of the anti-Markovnikov product¹⁶ results in higher isolated yields (entries 1–5). Furthermore, the small differences between isolated yield and selectivities for the rhodium system are clearly related to the partition coefficient (*P*) of the different silane products.

In the case of trimethoxysilane the selectivity for the anti-Markovnikov addition product was lower (entry 6) and a moderate yield was obtained which is comparable to the yield obtained in the two-step reaction involving platinum-catalyzed hydrosilylation of C₆F₁₃CH=CH₂ using HSiCl₃, followed by reaction with sodium methoxide.¹⁷ It should also be noted that four instead of three fluororous extractions were needed, which is related to

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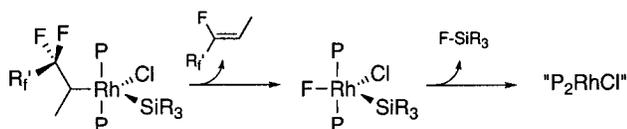
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Table 3. Rhodium-^a and Platinum-Catalyzed Hydrosilylation of C_mF_{2m+1}CH=CH₂ (m = 6, 8, 10)

entry	product	selectivity [RhCl(PPh ₃) ₃] ^b	P ^c	isolated yield (%)	
				[RhCl(PPh ₃) ₃]	H ₂ PtCl ₆
1	C ₆ F ₁₃ CH ₂ CH ₂ SiMe ₂ Cl	90	1.9 ^d	79	50–63 ^e
2	C ₈ F ₁₇ CH ₂ CH ₂ SiMe ₂ Cl	92	4.8 ^f	85	60–79 ^g
3	C ₁₀ F ₂₁ CH ₂ CH ₂ SiMe ₂ Cl	88	18 ^f	85	64 ^h
4	C ₆ F ₁₃ CH ₂ CH ₂ SiMeCl ₂	92	2.8	86	85 ⁱ
5	C ₆ F ₁₃ CH ₂ CH ₂ SiCl ₃	93	4.8	88	79 ⁱ
6	C ₆ F ₁₃ CH ₂ CH ₂ Si(OMe) ₃	78	1.1 ^f	56 ^j	55 ^k

^a Conditions: catalyst:alkene:silane = 1:200:400; reflux for 15 h; phase separation at 0 °C. ^b Selectivity toward the anti-Markovnikov product, determined by ¹H NMR. ^c Partition coefficient for the silane product ($P = C_{\text{fluorous layer}}/C_{\text{organic layer}}$) in a toluene/FC-72 biphasic system determined by ICP-AAS unless noted otherwise. ^d Equal values were found by both ICP-AAS and gravimetric methods. ^e From ref 14a. ^f Determined by gravimetric methods. ^g From ref 9 and 14a. ^h Unpublished result from our laboratory following a procedure from ref 9. A yield of 76% was reported for a coupling of C₁₀F₂₁I with CH₂=CH–SiMe₂Cl.^{1e} ⁱ From ref 14c. ^j Yield after four instead of three fluoruous extractions. ^k Yield based on hydrosilylation of C₆F₁₃CHCH₂ with HSiCl₃ (79%), followed by reaction with 3 equiv of NaOMe (70%, from ref 16).

Scheme 4

R_f = C_{m-1}F_{2m-1}; m = 6, 8 or 10
 R₃ = Me₂Cl, MeCl₂, Cl₃ or (OMe)₃
 P = PPh₃

the lower partition coefficient of the fluoruous trimethoxysilane compared to the chlorosilanes.

In contrast to the reported hydrosilylation of CF₃CH=CH₂ catalyzed by [RhCl(PPh₃)₃],^{16a} which gave significant amounts of CF₃CH₂CH₃, hydrosilylation of the longer chain olefins C_mF_{2m+1}CH=CH₂ (m = 6, 8, 10) did not produce alkanes as byproduct but the fluoruous compounds (*Z*)-C_{m-1}F_{2m-1}CF=CHCH₃¹⁸ and an equivalent amount of the corresponding fluorosilane (Scheme 3).¹⁹ These lower boiling fluoruous 2-alkenes were easily removed in vacuo after extraction and phase separation. Their formation as side products in catalytic hydrosilylation has been attributed to thermal decomposition of the Markovnikov addition product, although the pure Markovnikov addition product was found to be stable up to 100 °C.²⁰ A metal-mediated F abstraction from the 2,1-insertion product involving reductive elimination of F–SiR₃ has been suggested as well²⁰ (Scheme 4). When H₂PtCl₆ is used as catalyst, larger amounts of fluoruous 2-alkenes are formed, resulting in a lower selectivity.^{8,9,15}

The excess of starting silane HSiR₃ (R₃ = Me₂Cl, MeCl₂, Cl₃, (OMe)₃) could not be recovered from the organic layer. Disilane formation, which is known to be catalyzed by Wilkinson's complex,²¹ is probably taking place. For C₆F₁₃CH=CH₂ and HSiMe₂Cl, this was

(18) The ¹H and ¹³C{¹H} NMR spectra of C_mF_{2m-1}CF=CHCH₃ (m = 6, 8, 10) were similar. No attempts were made to purify these compounds. The *Z* configuration of the olefin was confirmed by the characteristic value of the ³J_{FH} (33.2 Hz) coupling constant. See: Silverstein, R. M.; Clayton Bassler, G.; Mottill, T. C. In *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 222.

(19) The expected doublet for F–SiR₃ (R₃ = Me₂Cl, MeCl₂) in the ¹H NMR spectrum overlapped with the resonances of the product and could therefore not be integrated separately. However, both (*Z*)-C_{m-1}F_{2m-1}CF=CHCH₃ and F–SiMe₂Ph (d, δ = 0.50, ³J_{FH} = 7.3 Hz) were observed in a 1:1 ratio by ¹H NMR in the crude reaction mixture resulting from C₆F₁₃CH=CH₂ and HSiMe₂Ph.

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Table 4. Recycling of [RhCl(PPh₃)₃] in the Hydrosilylation of C_mF_{2m+1}CH=CH₂ (m = 6, 8)

m	product	cycle	selectivity ^a	isolated yield (%)
6	C ₆ F ₁₃ CH ₂ CH ₂ SiMe ₂ Cl	1	90	79
		2	89	75
		3	90	78
8	C ₈ F ₁₇ CH ₂ CH ₂ SiMe ₂ Cl	1	92	85
		2	91	85

^a Selectivity toward the anti-Markovnikov product, determined by ¹H NMR.

confirmed by ¹H NMR analysis of the organic layer after extraction of the product. A singlet characteristic for ClMe₂SiSiMe₂Cl (δ 0.47) was observed. In the case of repeated recycling, this (slow) disilane formation can be suppressed by immediate recycling and readdition of substrates as soon as the olefin conversion reaches 100%.

An important advantage of the use of [RhCl(PPh₃)₃] over H₂PtCl₆ as catalyst is the homogeneous nature of the reaction mixture. This allows the recycling of the intact rhodium catalyst by mild fluoruous biphasic extraction of the catalyst-containing organic phase. For the reaction of C_mF_{2m+1}CH=CH₂ (m = 6, 8) with HSiMe₂Cl, both the conversion and selectivity remained unchanged upon recycling (Table 4). Furthermore, no leaching (i.e., <1 ppm by ICP-AAS) of rhodium and phosphorus into the fluoruous layer was detected for the hydrosilylation of C₆F₁₃CH=CH₂ with HSiMe₂Cl. This was also obvious from the colorless fluoruous silane residue which was obtained after each cycle.

Conclusions

In conclusion, the two fluoruous approaches to the concept of biphasic catalyst recycling, i.e., *normal* and *reversed* fluoruous biphasic catalyst separation, have been successfully applied to the recycling of rhodium-based catalysts for the hydrosilylation of 1-alkenes as well as fluorinated 1-alkenes by employing fluoruous and non-fluoruous rhodium catalysts, respectively. Because of the mild character of these separation techniques, recycling and reuse of both fluoruous and nonfluoruous rhodium catalysts could be performed without observable changes in activity and selectivity.

Experimental Section

General Considerations. All experiments were performed under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl

and distilled before use. Deuterated solvents were obtained from Isotec Inc. PFMCH (Lancaster) and all other chemicals (Lancaster, Acros) were degassed and stored under a dinitrogen atmosphere. $\text{P}[\text{C}_6\text{H}_4\text{-4-SiMe}(\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2]_3$ ⁵ and **1**⁹ were synthesized as reported previously. ICP-AAS and elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. ³¹P NMR spectra were externally referenced against 85% H_3PO_4 (δ 0.00 ppm). NMR spectra of **2** were measured using a capillary filled with C_6D_6 as lock.

Rh[P{C₆H₄-4-(SiMe₂CH₂CH₂C₈F₁₃)₂}]₃Cl (1**).** $\text{P}[\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{13}]_3$ (1.33 g, 0.90 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (73.9 mg, 0.15 mmol) were dissolved in benzene. All volatiles were evaporated in vacuo, upon which the color of the oil turned from orange to red. The red oil was heated in vacuo for 2 h, which yielded 1.34 g (98%) of **1**. Spectral data were similar to those reported before.^{9b,c}

Rh[P{C₆H₄-4-(SiMe(CH₂CH₂C₈F₁₇)₂}]₃Cl (2**).** The procedure was similar to that mentioned above for **1**. $\text{P}[\text{C}_6\text{H}_4\text{-4-SiMe}(\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2]_3$ (1.48 g, 0.48 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (39.6 mg, 0.080 mmol) gave 1.48 g (99%) of a red oil. Anal. Calcd for $\text{C}_{243}\text{H}_{99}\text{ClF}_{306}\text{P}_3\text{RhSi}_9$: C, 31.21; H, 1.46; P, 0.99; Rh, 1.10. Found: C, 31.11; H, 1.49; P, 0.99; Rh, 1.04. ¹H NMR (200 MHz, PFMCH): δ 0.23 (br, 27 H), 0.98 (br, 36 H), 1.98 (br, 36 H), 7.51 (br, 36 H). ³¹P NMR (81.0 MHz, PFMCH): δ 32.6 (dd, ¹*J*_{RhP} = 141.5 Hz; ²*J*_{PP} = 37.5 Hz), 49.4 (dt, ¹*J*_{RhP} = 189.6 Hz; ²*J*_{PP} = 37.5 Hz).

Reaction of 1 with HSiCl₃. To a solution of **1** (260 mg, 57 μmol) containing 1 equiv of free phosphine in benzene (20 mL) was added HSiCl_3 (0.50 mL, 4.95 mmol). The yellow solution was stirred at room temperature for 10 min and then evaporated to dryness, yielding a yellow oil, which was analyzed to be a 1:1 mixture of **3** and free phosphine by NMR. ¹H NMR (200 MHz, C_6D_6): δ -14.2 (dt, ¹*J*_{RhH} = 19.6 Hz; ²*J*_{PH} = 13.6 Hz, 1H), -0.01 (s, 36 H), 0.80 (m, 18 H), 1.82 (m, 18 H), 7.19–7.38 (m, 36 H). ³¹P NMR (81.0 MHz, C_6D_6): δ -5.0 (s, 1P), 39.1 (d, ¹*J*_{RhP} = 111 Hz, 2P).

Fluorous Phase Hydrosilylation of 1-Hexene. In a typical experiment, 37 μmol of catalyst was dissolved in 4.0 mL of PFMCH. For $[\text{RhCl}(\text{PPh}_3)_3]$, benzene (4.0 mL) was used as solvent. To this solution, silane (37 mmol) and 1-hexene (9.4 mL, 74 mmol) were added. The reaction mixture was heated to reflux. In the case of HSiMe_2Ph samples were taken and analyzed by GC and ¹H NMR. The two phases were separated at room temperature, and new substrates were

added to the fluorous phase. Leaching data were obtained from ICP-AAS analysis of the upper phase from the first cycle.

Hydrosilylation of Fluorous Olefins and Reversed Fluorous Extraction. To 10 mL of a benzene ($m = 6$) or toluene ($m = 8, 10$) solution containing 0.5 mol % $[\text{RhCl}(\text{PPh}_3)_3]$ were added 1 equiv of $\text{C}_m\text{F}_{2m+1}\text{CHCH}_2$ and 2 equiv of HSiR_3 ($\text{R}_3 = \text{Me}_2\text{Cl}, \text{MeCl}_2, \text{Cl}_3, (\text{OMe})_3$) were added. This mixture was refluxed for 15 h and subsequently cooled to room temperature. The selectivity of the reaction was calculated from the integral ratios of the $\text{C}_m\text{F}_{2m+1}\text{CH}_2\text{CH}_2\text{SiR}_3$ and $\text{C}_{m-1}\text{F}_{2m-1}\text{CF}=\text{CHCH}_3$ signals in the ¹H NMR spectrum of this crude reaction mixture. Three extractions with FC-72 (20 mL) were performed at 0 °C. The fluorous phases were collected, and solvents were removed by atmospheric distillation ($m = 6$) or in vacuo ($m = 8, 10$). All remaining volatiles were evaporated in vacuo. The purity was checked with ¹H NMR, and the yield was determined.

(Z)-C_{m-1}F_{2m-1}CF=CHCH₃ ($m = 6, 8, 10$).¹⁸ ¹H NMR (200 MHz, CDCl_3): δ 1.78 (m, 3H), 5.63 (dq, ³*J*_{FH} = 33.2 Hz, ³*J*_{HH} = 7.0 Hz). ¹³C NMR (200 MHz, CDCl_3): δ 8.74 (s), 111.2 (m), 106–126 (m), 146.5 (dt, ¹*J*_{CF} = 257 Hz, ²*J*_{CF} = 29 Hz).

In a typical recycling experiment, new substrates ($\text{C}_m\text{F}_{2m+1}\text{CH}=\text{CH}_2$ ($m = 6, 8$) and HSiMe_2Cl) were added to the organic layer and the procedure was repeated. Leaching of the catalyst after the first cycle was determined by taking a sample (500 μL) of the colorless fluorous layer of the first extraction, immediately after the reaction was completed.

Determination of Partition Coefficients of the Fluorous Silanes. To a known amount of silane were added equal volumes of toluene and FC-72. The mixture was stirred for 30 min and equilibrated at 0 °C for another 30 min. Subsequently, equal volume samples were taken and [Si] was determined from both layers by ICP-AAS. Alternatively, all solvent was evaporated at room temperature and the weight of the liquid residue was determined.

Acknowledgment. This work was supported by ATOFINA Vlissingen BV and the Dutch Ministry of Economic Affairs/SENTER. Dr. B. Richter is gratefully acknowledged for the synthesis of **2** and Mr. H. Kleijn for supplying data on the platinum-catalyzed hydrosilylation of $\text{C}_{10}\text{F}_{21}\text{CHCH}_2$.

OM010115R