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Recycling of Rhodium-Based Hydrosilylation Catalysts; A Fluorous Approach

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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 $[RhCl\{P(C_6H_4\text{-}4\text{-}SiMe_2R_f)_3\}_3]$ (**1**; $R_f = CH_2CH_2C_6F_{13}$) or $[RhCl\{P(C_6H_4\text{-}4\text{-}SiMe(R_f)_2)_3\}_3]$ (**2**; $R_f = CH_2CH_2C_8F_{17}$) in fluorous biphasic solvent systems afforded the corresponding *n*-hexylsilanes in high yield. The catalyst activities were similar to those obtained using conventional $[RhCl(PPh_3)_3]$. 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 [Rh] was lost for **1** and **2**, respectively, in the first cycle. The fluorous hydride intermediate $[Rh(H)(Cl)(SiCl_3)\{P(C_6H_4\text{-}4\text{-}SiMe_2R_f)_3\}_2]$ (**3**; $R_f = CH_2CH_2C_6F_{13}$) was identified by NMR spectroscopy. In a reverse approach, the original Wilkinson's catalyst was used for the hydrosilylation of $1H,1H,2H$-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 separation[5] was employed for the mild recycling of rhodium trialkylphosphine catalysts in the hydrogenation of 1-alkenes[6] and hydrosilylation of ketones and enones.[7] A disadvantage of these systems is the lower activity compared to Wilkinson's catalyst, $[RhCl(PPh_3)_3]$. Notably, the use of *p*-silyl-substituted fluorous triarylphosphines, developed in our laboratory,[8] resulted in similar activities compared to $[RhCl(PPh_3)_3]$.[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, $[RhCl\{P(C_6H_4\text{-}4\text{-}SiMe_2R_f)_3\}_3]$ (**1**; $R_f = CH_2CH_2C_6F_{13}$), and the newly prepared $[RhCl\{P(C_6H_4\text{-}4\text{-}SiMe(R_f)_2)_3\}_3]$ (**2**; $R_f = CH_2CH_2C_8F_{17}$), 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 $[RhCl(PPh_3)_3]$ 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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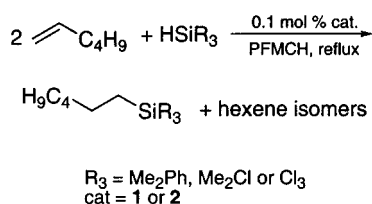
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Scheme 1

fluorous catalyst recycle (A)   nonfluorous catalyst recycle (B)

1   **2**

Scheme 2
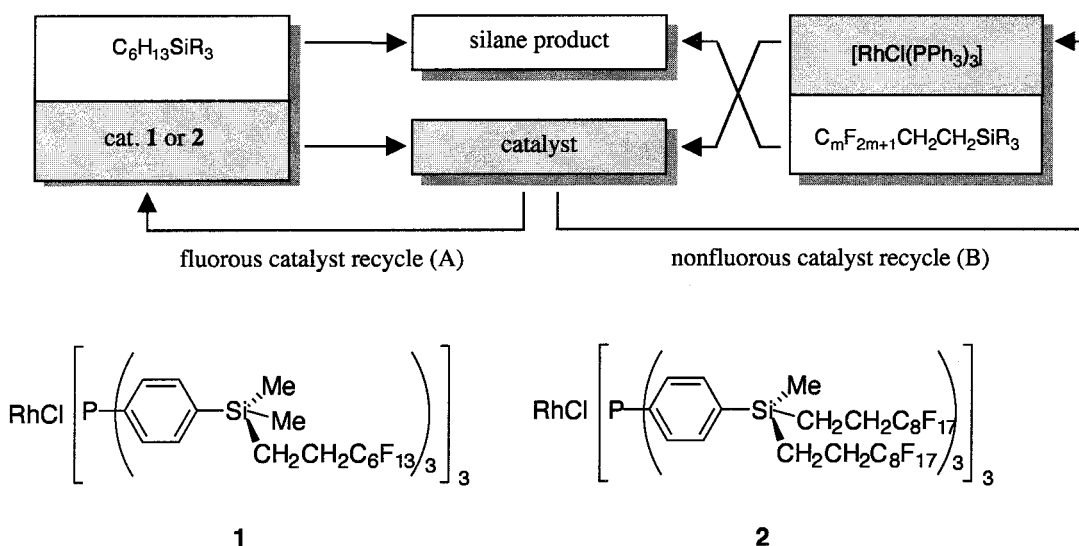
$R_3 = Me_2Ph, Me_2Cl$ or Cl_3
cat = **1** or **2**

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 $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) and 6 equiv of free fluorous phosphine, $P(C_6H_4\text{-}4\text{-}SiMe_2(R_f))_3$ ($R_f = CH_2CH_2C_6F_{13}$) and $P(C_6H_4\text{-}4\text{-}SiMe(R_f)_2)_3$ ($R_f = CH_2CH_2C_8F_{17}$), respectively.[8] In this way, the fluorous 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). c-$C_6F_{11}CF_3$ (PFMCH) was used as the fluorous 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 fluorous $[Rh(H)(Cl)(SiR_3)-\{P(Ar_f)_3\}_2]$ ($Ar_f = C_6H_4\text{-}4\text{-}SiMe_2CH_2CH_2C_6F_{13}$, $C_6H_4\text{-}4\text{-}SiMe(CH_2CH_2C_8F_{17})_2$) 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 ^{1}H 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 [RhCl-(PPh_3)_3]-catalyzed reaction[4c] and has been attributed to

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Table 1. Fluorous Phase Hydrosilylation of 1-Hexene[a]

catalyst precursor	product[b]	t[c]
RhCl(PPh_3)_3[d]	$C_6H_{13}SiMe_2Ph$	15 min
1	$C_6H_{13}SiMe_2Ph$	15 min
2	$C_6H_{13}SiMe_2Ph$	15 min
1	$C_6H_{13}SiMe_2Cl$	15 h
1	$C_6H_{13}SiCl_3$	15 h

[a] Conditions: catalyst:silane:1-hexene = 1:1000:2000; reflux; solvent (unless otherwise indicated) PFMCH; [Rh] = 2 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 $[Rh(H)(Cl)(SiR_3)-(PPh_3)_2]$. It should be noted that although the fluorous solvent gave a single phase with the substrates upon heating to the reaction temperature, the solubility of the highly fluorous complex **2** in the fluorous–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 fluorous 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 fluorous 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 fluorous ligand and fluorous 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

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	$C_6H_{13}SiMe_2Ph$	3 (15)[d]	12 (41)	19 (58)
2	$C_6H_{13}SiMe_2Ph$	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 concentration[9] 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 fluorous catalysts 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 fluorous 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 fluorous solvent would have to be recovered as well.

According to the Chalk−Harrod mechanism for hydrosilylation,[11a] a rhodium hydride, $[Rh(H)(Cl)(SiR_3)(PAr_3)_2]$ (Ar = aryl), is formed as a crucial intermediate. When **1** was reacted with $HSiCl_3$, $[Rh(H)(Cl)(SiCl_3)\{P(Ar_f)_3\}_2]$ (**3**; $Ar_f = C_6H_4-4-SiMe_2CH_2CH_2C_6F_{13}$) and 1 equiv of free $P(Ar_f)_3$ were formed (^{31}P 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 (CH_2Cl_2, pentane) and fluorous solvents. Compound **3** showed a doublet in the ^{31}P 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 nonfluorous $[Rh(H)(Cl)(SiCl_3)(PPh_3)_2]$,[4c] indicating a similar trigonal-bipyramidal structure for **3**.

The formation of **3** from **1** and $HSiCl_3$ suggests similar mechanisms for hydrosilylations employing $[RhCl(PPh_3)_3]$ and fluorous 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 fluorous 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

Scheme 3

$R_f = C_mF_{2m+1}$; m = 6, 8 or 10
$R_f' = C_{m-1}F_{2m-1}$
$R_3 = Me_2Cl, MeCl_2, Cl_3$ or $(OMe)_3$
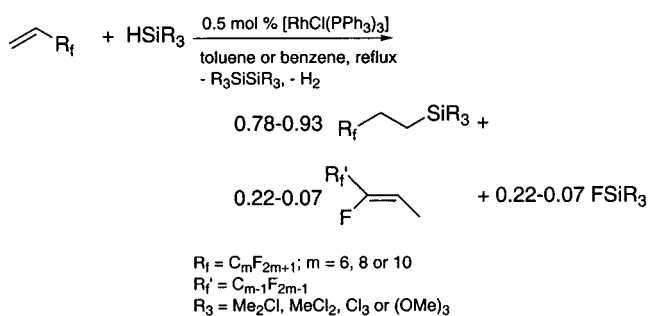
this problem is to use catalysts based on chelating fluorous bisphosphines, which we are currently investigating.[13]

Hydrosilylation of 1H,1H,2H-Perfluoro-1-alkenes using $[RhCl(PPh_3)_3]$. To enable catalyst recycling in the synthesis of fluorous 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 nonfluorous hydrosilane per equivalent of alkene in benzene or toluene as solvent (Scheme 3). When the fluorous olefin was fully converted, the reaction mixture was extracted with FC-72 (mixture of perfluorohexanes). The higher boiling silanes ($R_f = C_8F_{17}$, $C_{10}F_{21}$) were purified by removing volatiles (FC-72, traces of toluene,[14] and (Z)-$R_f'CF=CHCH_3$, $R_f' = C_7F_{15}$, C_9F_{19}) in vacuo. For the lower boiling silanes ($R_f = C_6F_{13}$), volatiles (FC-72 and traces of benzene[14]) 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 fluorous solvent needed.

In Table 3 the present results are compared with those reported using H_2PtCl_6 as catalyst.[15] The higher selectivity of the rhodium catalyst for the formation of the anti-Markovnikov product[16] 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 $C_6F_{13}CH=CH_2$ using $HSiCl_3$, followed by reaction with sodium methoxide.[17] It should also be noted that four instead of three fluorous extractions were needed, which is related to

(12) A lower P:Rh ratio is known to lead to an increase of catalytic activity for $[RhCl(PPh_3)_3]$. See, e.g., ref 2a.

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Table 3. Rhodium-[a] and Platinum-Catalyzed Hydrosilylation of $C_mF_{2m+1}CH=CH_2$ (m = 6, 8, 10)

				isolated yield (%)	
entry	product	selectivity $[RhCl(PPh_3)_3]^b$	P^c	$[RhCl(PPh_3)_3]$	H_2PtCl_6
1	$C_6F_{13}CH_2CH_2SiMe_2Cl$	90	1.9[d]	79	50–63[e]
2	$C_8F_{17}CH_2CH_2SiMe_2Cl$	92	4.8[f]	85	60–79[g]
3	$C_{10}F_{21}CH_2CH_2SiMe_2Cl$	88	18[f]	85	64[h]
4	$C_6F_{13}CH_2CH_2SiMeCl_2$	92	2.8	86	85[i]
5	$C_6F_{13}CH_2CH_2SiCl_3$	93	4.8	88	79[i]
6	$C_6F_{13}CH_2CH_2Si(OMe)_3$	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 ^{1}H NMR. [c] Partition coefficient for the silane product ($P = c_{fluorous\ layer}/c_{organic\ layer}$) 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 $C_{10}F_{21}I$ with $CH_2=CH-SiMe_2Cl$.[1e] [i] From ref 14c. [j] Yield after four instead of three fluorous extractions. [k] Yield based on hydrosilylation of $C_6F_{13}CHCH_2$ with $HSiCl_3$ (79%), followed by reaction with 3 equiv of NaOMe (70%, from ref 16).

Scheme 4
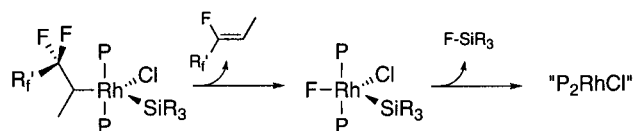
$R_f' = C_{m-1}F_{2m-1}$; m = 6, 8 or 10
R_3 = Me$_2$Cl, MeCl$_2$, Cl$_3$ or (OMe)$_3$
P = PPh$_3$

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

In contrast to the reported hydrosilylation of $CF_3CH=CH_2$ catalyzed by $[RhCl(PPh_3)_3]$,[16a] which gave significant amounts of $CF_3CH_2CH_3$, hydrosilylation of the longer chain olefins $C_mF_{2m+1}CH=CH_2$ (m = 6, 8, 10) did not produce alkanes as byproduct but the fluorous compounds $(Z)-C_{m-1}F_{2m-1}CF=CHCH_3$[18] and an equivalent amount of the corresponding fluorosilane (Scheme 3).[19] These lower boiling fluorous 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 $F-SiR_3$ has been suggested as well[20] (Scheme 4). When H_2PtCl_6 is used as catalyst, larger amounts of fluorous 2-alkenes are formed, resulting in a lower selectivity.[8,9,15]

The excess of starting silane $HSiR_3$ (R_3 = Me$_2$Cl, MeCl$_2$, Cl$_3$, (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 $C_6F_{13}CH=CH_2$ and $HSiMe_2Cl$, this was

(18) The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of $C_mF_{2m-1}CF=CHCH_3$ (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 $F-SiR_3$ (R_3 = Me$_2$Cl, MeCl$_2$) in the ^{1}H NMR spectrum overlapped with the resonances of the product and could therefore not be integrated separately. However, both (Z)-$C_{m-1}F_{2m-1}CF=CHCH_3$ and $F-SiMe_2Ph$ (d, δ = 0.50, $^3J_{FH}$ = 7.3 Hz) were observed in a 1:1 ratio by ^{1}H NMR in the crude reaction mixture resulting from $C_6F_{13}CH=CH_2$ and $HSiMe_2Ph$.

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Table 4. Recycling of $[RhCl(PPh_3)_3]$ in the Hydrosilylation of $C_mF_{2m+1}CH=CH_2$ (m = 6, 8)'

m	product	cycle	selectivity[a]	isolated yield (%)
6	$C_6F_{13}CH_2CH_2SiMe_2Cl$	1	90	79
		2	89	75
		3	90	78
8	$C_8F_{17}CH_2CH_2SiMe_2Cl$	1	92	85
		2	91	85

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

confirmed by ^{1}H NMR analysis of the organic layer after extraction of the product. A singlet characteristic for $ClMe_2SiSiMe_2Cl$ (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 $[RhCl(PPh_3)_3]$ over H_2PtCl_6 as catalyst is the homogeneous nature of the reaction mixture. This allows the recycling of the intact rhodium catalyst by mild fluorous biphasic extraction of the catalyst-containing organic phase. For the reaction of $C_mF_{2m+1}CH=CH_2$ (m = 6, 8) with $HSiMe_2Cl$, 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 fluorous layer was detected for the hydrosilylation of $C_6F_{13}CH=CH_2$ with $HSiMe_2Cl$. This was also obvious from the colorless fluorous silane residue which was obtained after each cycle.

Conclusions

In conclusion, the two fluorous approaches to the concept of biphasic catalyst recycling, i.e., *normal* and *reversed* fluorous 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 fluorous and nonfluorous rhodium catalysts, respectively. Because of the mild character of these separation techniques, recyling and reuse of both fluorous and nonfluorous 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. $P[C_6H_4\text{-}4\text{-}SiMe(CH_2CH_2C_8F_{17})_2]_3$[8] 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. ^{31}P 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-(SiMe₂CH₂CH₂C₆F₁₃)₃}]₃Cl (1). $P[C_6H_4\text{-}4\text{-}SiMe_2CH_2CH_2C_6F_{13}]_3$ (1.33 g, 0.90 mmol) and $[Rh(cod)Cl]_2$ (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)₃}]₃Cl (2). The procedure was similar to that mentioned above for **1**. $P[C_6H_4\text{-}4\text{-}SiMe(CH_2CH_2C_8F_{17})_2]_3$ (1.48 g, 0.48 mmol) and $[Rh(cod)Cl]_2$ (39.6 mg, 0.080 mmol) gave 1.48 g (99%) of a red oil. Anal. Calcd for $C_{243}H_{99}ClF_{306}P_3RhSi_9$: 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). ^{31}P NMR (81.0 MHz, PFMCH): δ 32.6 (dd, $^1J_{RhP} = 141.5$ Hz; $^2J_{PP} = 37.5$ Hz), 49.4 (dt, $^1J_{RhP} = 189.6$ Hz; $^2J_{PP} = 37.5$ 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, $^1J_{RhH} = 19.6$ Hz; $^2J_{PH} = 13.6$ Hz, 1H), −0.01 (s, 36 H), 0.80 (m, 18 H), 1.82 (m, 18 H), 7.19−7.38 (m, 36 H). ^{31}P NMR (81.0 MHz, C_6D_6): δ −5.0 (s, 1P), 39.1 (d, $^1J_{RhP} = 111$ 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 $[RhCl(PPh_3)_3]$, 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 % $[RhCl(PPh_3)_3]$ were added 1 equiv of $C_mF_{2m+1}CHCH_2$ and 2 equiv of $HSiR_3$ ($R_3 = Me_2Cl, MeCl_2, Cl_3, (OMe)_3$) 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 $C_mF_{2m+1}CH_2CH_2SiR_3$ and $C_{m-1}F_{2m-1}CF{=}CHCH_3$ 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)-Cₘ₋₁F₂ₘ₋₁CF=CHCH₃ (m = 6, 8, 10).[18] ^1H NMR (200 MHz, CDCl₃): δ 1.78 (m, 3H), 5.63 (dq, $^3J_{FH} = 33.2$ Hz, $^3J_{HH} = 7.0$ Hz). ^{13}C NMR (200 MHz, CDCl₃): δ 8.74 (s), 111.2 (m), 106−126 (m), 146.5 (dt, $^1J_{CF} = 257$ Hz, $^2J_{CF} = 29$ Hz).

In a typical recycling experiment, new substrates ($C_mF_{2m+1}CH{=}CH_2$ ($m = 6, 8$) 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.