

Monophasic and biphasic hydrosilylations of enones and ketones using a fluororous rhodium catalyst that is easily recycled under fluororous–organic liquid–liquid biphasic conditions

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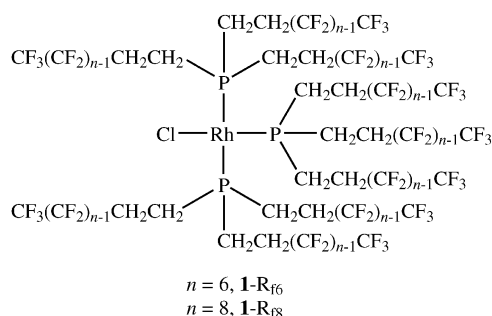
Additions of PhMe_2SiH to 2-cyclohexen-1-one, 2-cyclopenten-1-one, 4,4-dimethyl-2-cyclohexen-1-one, and cyclohexanone (**11**) are catalyzed by the rhodium complexes $\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_{n-1}\text{CF}_3)_3]_3$ (**1**; $n = 6, 8$), which have very high affinities for fluororous liquid phases. Reactions of the enones are conducted with 0.80 mol% **1** at 60 °C under biphasic conditions in $\text{CF}_3\text{C}_6\text{F}_{11}$ –toluene or monophasic conditions in $\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes. The reactions are faster under the latter conditions and the catalyst and products are efficiently separated at lower temperatures under biphasic conditions. Distillations of the non-fluororous phases give mixtures of 1,4- and 1,2-hydrosilylation products (>99 – 92 : <1 – 8) in 93–88% yields. The catalyst-containing $\text{CF}_3\text{C}_6\text{F}_{11}$ phases are recycled two times with similar results. Reactions of **11** are studied under analogous conditions (0.2 mol% **1**) at 28 and 40 °C and give cyclohexyl dimethylphenylsilyl ether. Rate profiles show induction periods for the first cycle, indicating an irreversible transformation of **1**, but not for subsequent cycles. Only minor decreases in activity are observed over four cycles, consistent with little catalyst leaching or decomposition. When catalyst loadings are decreased to 0.02 mol%, TON of 4400 can be obtained.

Introduction

Fluororous catalysts contain varying numbers of “pony tails” of the formula $(\text{CH}_2)_m(\text{CF}_2)_{n-1}\text{CF}_3$ or $(\text{CH}_2)_m\text{R}_{fn}$.¹ These labels or “phase tags” allow catalyst recovery by a number of protocols, most commonly involving a fluororous liquid or solid phase.² The first report, by Horváth and Rabai, featured rhodium catalysts with fluororous phosphine ligands.³ These showed excellent activity for the hydroformylation of alkenes. Due to the large number of pony tails or high “fluororous content”, they were easily separated from the products under fluororous–organic liquid–liquid biphasic conditions. Cartoons that illustrate such procedures are presented in the Results section. Since this time, fluororous catalysts have been developed for a number of metal-catalyzed reactions.⁴

We have had a long-standing interest in fluororous rhodium catalysts or precatalysts of the formula $\text{ClRh}[\text{P}(\text{CH}_2\text{CH}_2\text{R}_{fn})_3]_3$, with $n = 6$ (**1-R₆**) or 8 (**1-R₈**).⁵ These can be regarded as aliphatic analogs of Wilkinson’s catalyst. They are easily synthesized from $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ and the corresponding fluororous phosphines,⁵ and exhibit high fluororous phase affinities. In the case of **1-R₆**, the partition coefficient between $\text{CF}_3\text{C}_6\text{F}_{11}$ [perfluoro(methylcyclohexane)] and toluene is 99.86:0.14 (696:1) at 27 °C. That for **1-R₈** is at least 99.88:0.12 (811:1). As detailed in two previous full papers, **1-R₆** and **1-R₈** afford effective and easily recycled catalysts for the hydroboration and hydrogenation of alkenes.^{5,6} However, it should be emphasized that what is actually being recycled is the catalyst rest state—a species that is usually distinct from the precatalyst.

As communicated earlier, **1-R₆** and **1-R₈** also afford excellent catalysts for the hydrosilylation of carbonyl compounds,⁷ a reaction of considerable importance in fine chemical synthesis.⁸ The catalysts were efficiently recycled under fluororous–organic liquid–liquid biphasic conditions. Since that time, alternative protocols have been developed that



are not dependent upon fluororous solvents.^{2,9–12} Hence, the original results have taken on added significance as a benchmark for newer studies. This has prompted us to present and document the full details of this work in this full paper, together with new, unreported experiments. Additional observations are collected elsewhere.¹³ Other fluororous rhodium hydrosilylation catalysts have since been described,¹⁴ and these complementary studies are treated in the discussion section.

Results

1. Hydrosilylations under biphasic conditions

As summarized in Fig. 1, mixtures of 2-cyclohexen-1-one (**3**; 1.30 mmol), PhMe_2SiH (1.1 equiv.), and toluene (1.0 ml) were treated with $\text{CF}_3\text{C}_6\text{F}_{11}$ solutions of **1-R₆** or **1-R₈** (1.00 ml; 0.80 mol%). The samples were heated to 60 °C. Toluene and $\text{CF}_3\text{C}_6\text{F}_{11}$ are miscible in all proportions only above 88.6 °C,¹⁵ so it was not surprising that the phases did not mix.¹⁶ Nonetheless, hydrosilylation went to completion over the course of

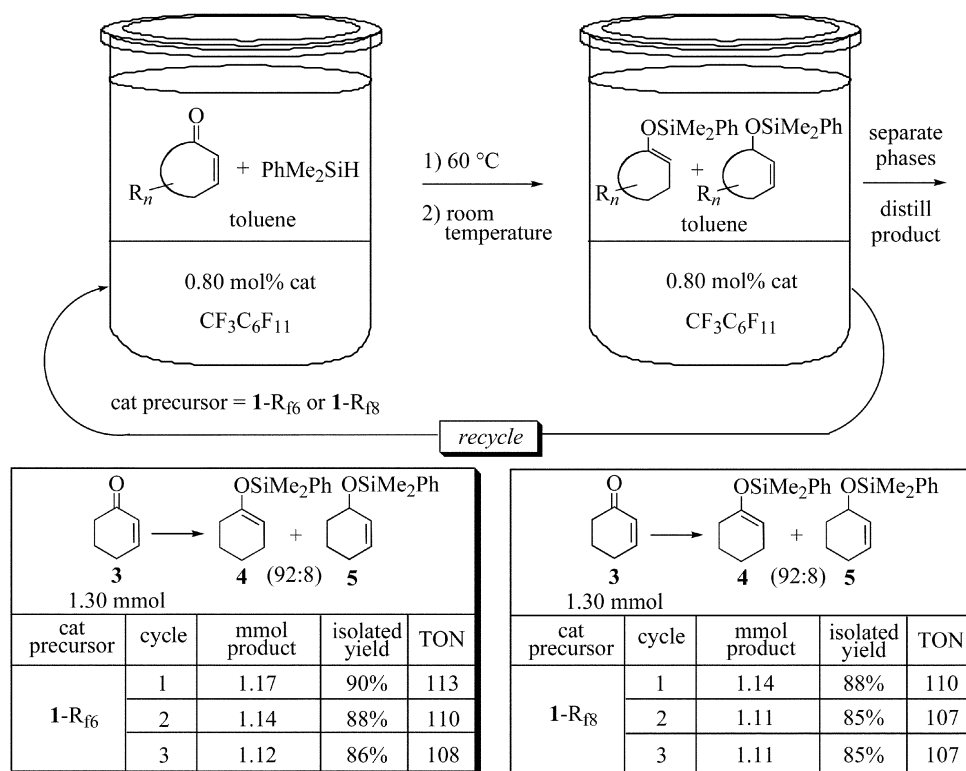


Fig. 1 Hydrosilylation of 2-cyclohexen-1-one (**3**) under biphasic conditions (CF₃C₆F₁₁–toluene, 60 °C).

10 h, as assayed by GC. The samples were cooled to room temperature and the upper toluene layers carefully separated by syringe. The remaining CF₃C₆F₁₁ layers, which contain the catalyst rest states, were extracted with toluene (1.0 ml).

Distillations of the toluene phases gave 92 : 8 mixtures of the isomeric 1,4-hydrosilylation product **4** and 1,2-hydrosilylation product **5** as clear liquids in 90–88% yields, as summarized in Fig. 1. This corresponds to TON values of 113–100. Product **4** was characterized by NMR and the data were in good agreement with those reported earlier.¹⁷ Isomer **5** exhibited a SiOC^{HR}₂ ¹H NMR signal at *ca.* δ 3.90, very close to the HOCHR₂ signal of the corresponding allylic alcohol, and CH=CH signals at δ 5.55–5.68 ppm (CDCl₃).¹⁸ The CF₃C₆F₁₁ catalyst solutions were recharged with **3**, PhMe₂SiH, and toluene. A second cycle gave **4** and **5** in 88–85% yields (TON 110–107) and a third cycle gave similar results (Fig. 1).

As summarized in Fig. 2, analogous three-cycle sequences were conducted with 2-cyclopenten-1-one (**6**) and 1-R_{f6} or 1-R_{f8}. Both the 1,4-hydrosilylation product **7** and a minor species believed to be the 1,2-hydrosilylation product **8** formed.^{18c} However, as with **3**, the former greatly dominated. Distillations gave 98 : 2 mixtures in 93–90% yields (TON 116–113). The NMR properties of **7** were in good agreement with those reported earlier.¹⁷ A comparable series of experiments with 4,4-dimethyl-2-cyclohexen-1-one (**9**) gave only the known 1,4-addition product **10**,^{17,19} and essentially identical yields.

2. Partition coefficients

In order to better analyze the preceding reactions, quantitative data on reactant and product fluorophilicities were sought. Thus, CF₃C₆F₁₁–toluene partition coefficients were determined

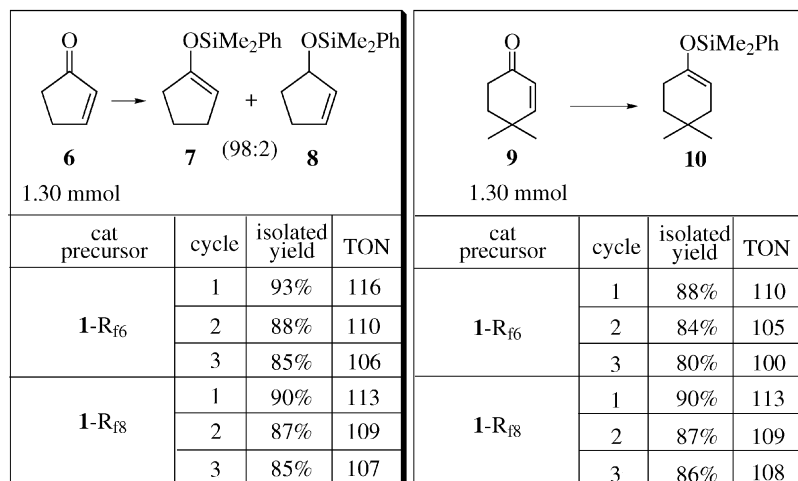
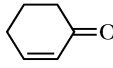
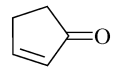
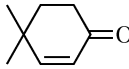
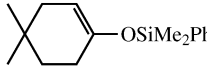
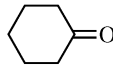
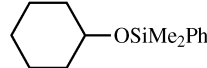


Fig. 2 Hydrosilylation of additional enones under the conditions of Fig. 1.

Table 1 Partition coefficients of selected educts and products

Compound	Partition coefficient (CF ₃ C ₆ F ₁₁ –toluene, 24 °C)
PhMe ₂ SiH	3.6:96.4
3 	1.7:98.3
6 	1.9:98.1
9 	1.7:98.3
10 	0.6:99.5
11 	2.2:97.8
12 	0.8:99.2

for PhMe₂SiH, the enones **3**, **6**, **9**, cyclohexanone (**11**), and representative silyl ethers under standard conditions at 24 °C.²⁰ Data are summarized in Table 1. The silyl ethers showed very low fluororous phase affinities (<1: >99) and thus should be efficiently isolated under the conditions of Fig. 1. The carbonyl compounds showed marginally higher fluororous phase affinities

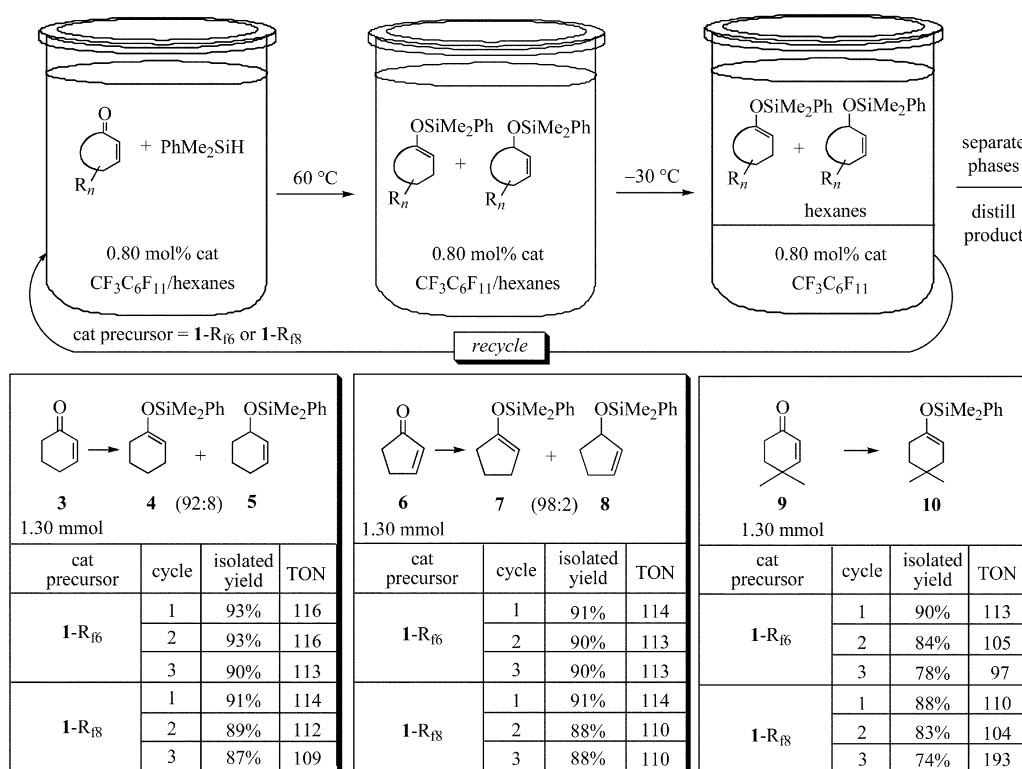
(1.7–2.2:98.3–97.8), as did PhMe₂SiH (3.6:96.4). All of these values are in the expected ranges based upon measurements of other monofunctional organic compounds.²⁰

The low fluororous phase affinities of the carbonyl compounds and PhMe₂SiH mean that under the conditions of Fig. 1, the educts and catalyst reside predominantly in different liquid phases. With monophasic conditions, much faster reactions would normally be expected. Accordingly, we sought to replace toluene with non-fluororous solvents that would become miscible with CF₃C₆F₁₁ at lower temperatures.

3. Hydrosilylations under monophasic conditions

Hexane and ether are among the few solvents miscible with CF₃C₆F₁₁ at room temperature, consistent with their low polarities and small volumes.^{15b} However, two phases are obtained at 0 °C or below, providing a means for catalyst/product separation. Thus, the hydrosilylations of **3**, **6** and **9** were repeated with **1-R₁₆** and **1-R₁₈** in CF₃C₆F₁₁–hexanes. As summarized in Fig. 3, reactions occurred smoothly under monophasic conditions at 60 °C. GC analyses showed product formation to be complete on time scales of 1–2 h as opposed to 4–10 h for Figs. 1 and 2. The CF₃C₆F₁₁ and hexanes phases were separated at –30 °C, the temperature of a conveniently located freezer. The hydrosilylation products were isolated in yields comparable to those in Figs. 1 and 2, and the catalysts could be used for a minimum of three cycles.

For the purposes of assaying rates and catalyst recovery (below), a substrate that can give only one type of addition product was desired. Thus, as summarized in Fig. 4, cyclohexanone (**11**; 1.30 mmol) and PhMe₂SiH (1.1 equiv.) were reacted in the presence of tridecane as an internal standard. As more fully analyzed elsewhere, higher catalyst loadings can be used to mask poor catalyst recoverabilities.^{2,21} Hence, the amount of **1-R₁₆** was reduced to 0.20 mol%. Two solvent systems, CF₃C₆F₁₁–hexanes and CF₃C₆F₁₁–ether, were screened under monophasic conditions at 28 °C. After 8 h, the phases were separated as in Fig. 3. GC analyses indicated 96–97% yields of

**Fig. 3** Hydrosilylation of enones under monophasic conditions (CF₃C₆F₁₁–hexanes, 60 °C).

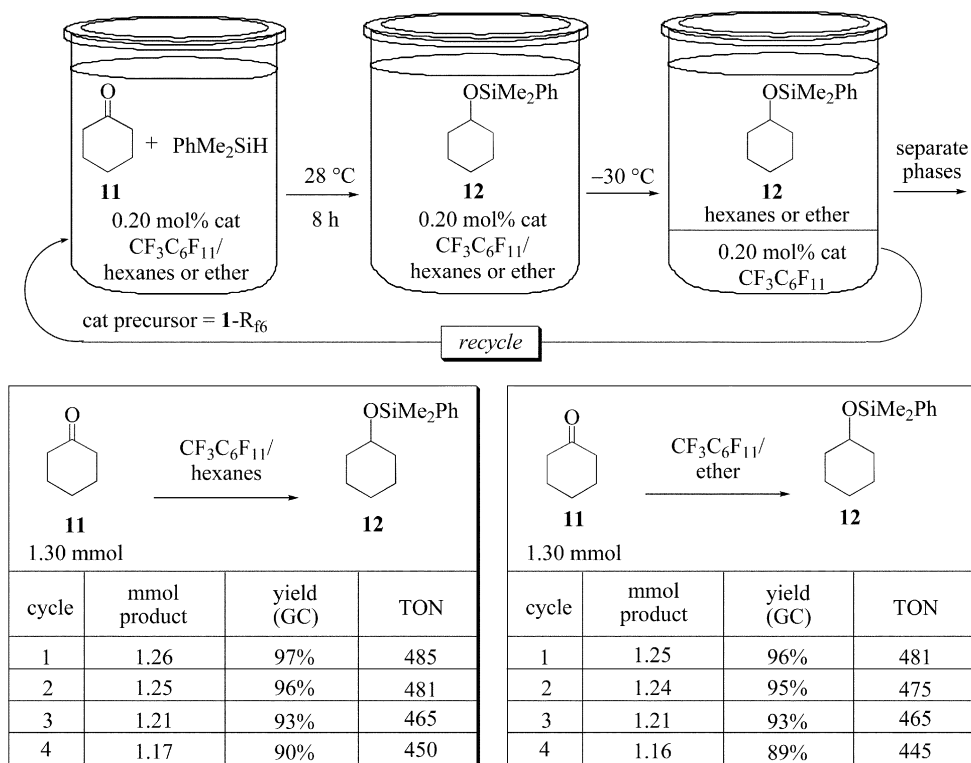


Fig. 4 Hydrosilylation of cyclohexanone (**11**) under monophasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes or $\text{CF}_3\text{C}_6\text{F}_{11}$ –ether, 28 °C).

cyclohexyl dimethylphenylsilyl ether (**12**),²² corresponding to TON values of 485–481. A total of four cycles could be conducted, with similar results for both solvent systems and only modest decreases in yields (Fig. 4).

A preparative reaction was conducted in $\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes with 13.0 mmol of **11**. The catalyst loading was reduced still further to 0.02 mol%. After 72 h, distillation gave **12** in 88% yield, corresponding to a TON value of 4400. However, the reaction times for **11** under these monophasic conditions were considered longer than optimum, especially for rate studies. Hence, temperatures were increased to 40 °C for the experiments in the following section.

4. Rates of hydrosilylation

As analyzed elsewhere, rates constitute one of the best criteria for catalyst recovery.^{2,21} Thus, the reaction sequence conducted in $\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes in Fig. 4 was repeated at 40 °C. Aliquots were removed every 0.5 h for GC analyses. Yields of **12** reached maximum values after 3 h. The reaction profiles for four cycles are illustrated in Fig. 5.

Importantly, the first cycle exhibited an induction period (10–15 min), indicating some irreversible transformation needed to convert **1-R_{f6}** to the active catalyst. However, subsequent cycles showed no induction periods, indicating that the active catalyst—not just a catalyst precursor²³—is recycled. The rate of formation of **12** or consumption of **11** slowed somewhat in the third cycle and more noticeably in the fourth cycle. The implications are analyzed in the discussion section.

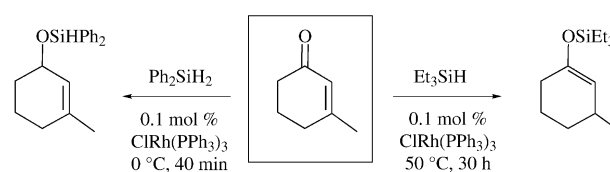
For comparison, an analogous set of experiments were conducted under biphasic conditions in $\text{CF}_3\text{C}_6\text{F}_{11}$ –toluene, as summarized in Fig. 6. As noted for Fig. 3 vs. Figs. 1 and 2 above, the hydrosilylations became slower. However, the product yields were similar. In this experiment, the tridecane internal standard can partition between two phases. Fortunately, the $\text{CF}_3\text{C}_6\text{F}_{11}$ –toluene partition coefficient (2.4 : 97.6)^{15b} is similar to those of **11** and **12** (Table 1), so the small errors approximately cancel. The first cycle again showed a brief

induction period and there was a similar drop in activity in the third and fourth cycles.

Discussion

Figs. 1–5 demonstrate that **1-R_{f6}** and **1-R_{f8}** are highly effective catalyst precursors for hydrosilylations of enones and ketones. Naturally, a variety of other rhodium(i) hydrosilylation catalysts are known. In the most relevant earlier work, Ojima and Kogure reported that $\text{ClRh}(\text{PPh}_3)_3$ (Wilkinson's catalyst) effects hydrosilylations of enones as summarized in Scheme 1.²⁴ In general, monohydrosilanes afforded 1,4-additions to give silyl enol ethers, whereas dihydrosilanes afforded 1,2-additions to give silyl ethers of allylic alcohols. Chan obtained comparable results with the more active catalyst $\text{HRh}(\text{PPh}_3)_4$.¹⁷

The monohydrosilane that we used with **1-R_{f6}** and **1-R_{f8}**, PhMe_2SiH , gives similar regioselectivity. Scouting reactions with the dihydrosilane Ph_2SiH_2 were also conducted. With 2-cyclohexen-1-one (**3**), GC analyses indicated complete conversion to a 1,2-addition product analogous to **5**. Multiple cycles could be conducted. However, technical difficulties were encountered with initial preparative syntheses and the isolation of the corresponding allylic alcohol, and this chemistry was not further pursued. Nonetheless, it is significant that the fluororous catalysts **1-R_{f6}** and **1-R_{f8}** give the same regioselectivities as $\text{ClRh}(\text{PPh}_3)_3$ in Scheme 1. The fluororous medium and phosphine ligands apparently have no effect.



Scheme 1 Typical regioselectivities for rhodium(i)-catalyzed enone hydrosilylations.

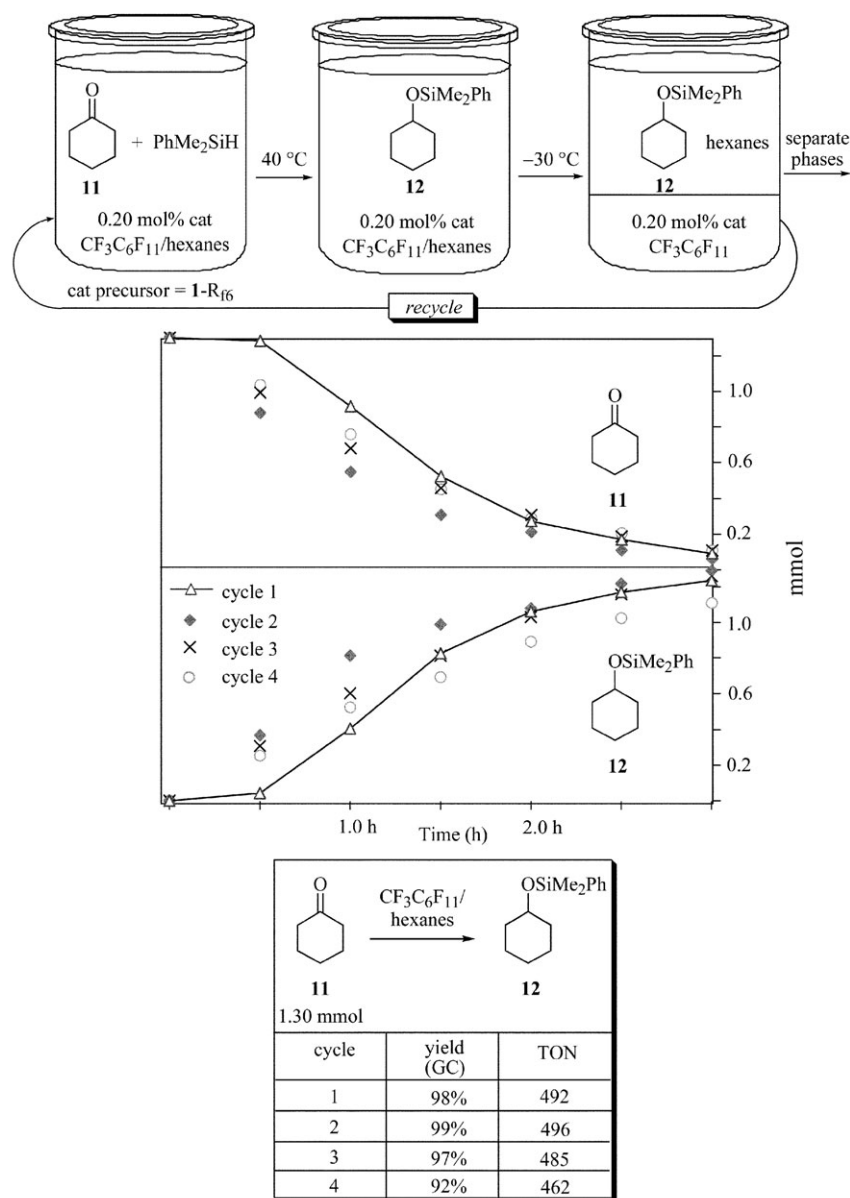
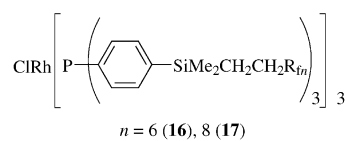
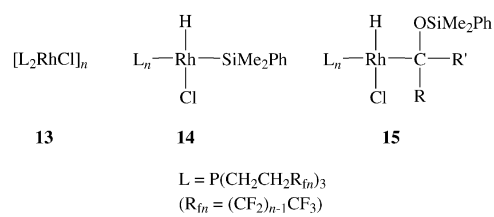


Fig. 5 Rate profile for the hydrosilylation of cyclohexanone (**11**) under monophasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes, 40 °C).

Thus, the major advantage of **1-R_{f6}** and **1-R_{f8}** over $\text{ClRh}(\text{PPh}_3)_3$ is their recyclability. Over the course of three (Figs. 1–3) or four (Figs. 4–6) cycles, product yields are essentially constant. However, as analyzed elsewhere,^{2,21} yields are normally misleading measures of catalyst recovery. Rates are much more accurate indicators and the profiles in Figs. 5 and 6 establish very high levels of recovery. The modest declines in activities reflect the aggregate losses due to catalyst deactivation and leaching.

Although leaching was not specifically assayed in this study, measurements have been carried out for similar hydrosilylations using other fluoros recycling protocols, showing that rhodium losses are minor.¹² For catalytic hydroborations conducted under comparable conditions, only four rhodium atoms from **1-R_{f6}** (or two from **1-R_{f8}**) are leached for every 1 000 000 product molecules.⁵ However, some leaching of the fluoros phosphines occurs.¹² We suggest this is connected to the induction period that generates the active catalyst. Also, it is quite probable that only two phosphine ligands remain bound during the catalytic cycle. Based upon currently accepted mechanisms,^{8,17} possibilities for the other ligands of the catalyst rest state include hydride, silyl, α -silyloxyalkyl, alkoxide and ketone moieties. A rest state can also depend upon

which of two reactants are in excess; representative possibilities include species of the types **13**–**15**.



Following our communication,⁷ the fluoros rhodium(I) complexes **16** and **17** were employed as catalyst precursors for the hydrosilylation of alkenes.¹⁴ These contain fluoros triarylphosphine ligands and are therefore closer analogs of Wilkinson's catalyst. They are also likely effective catalyst

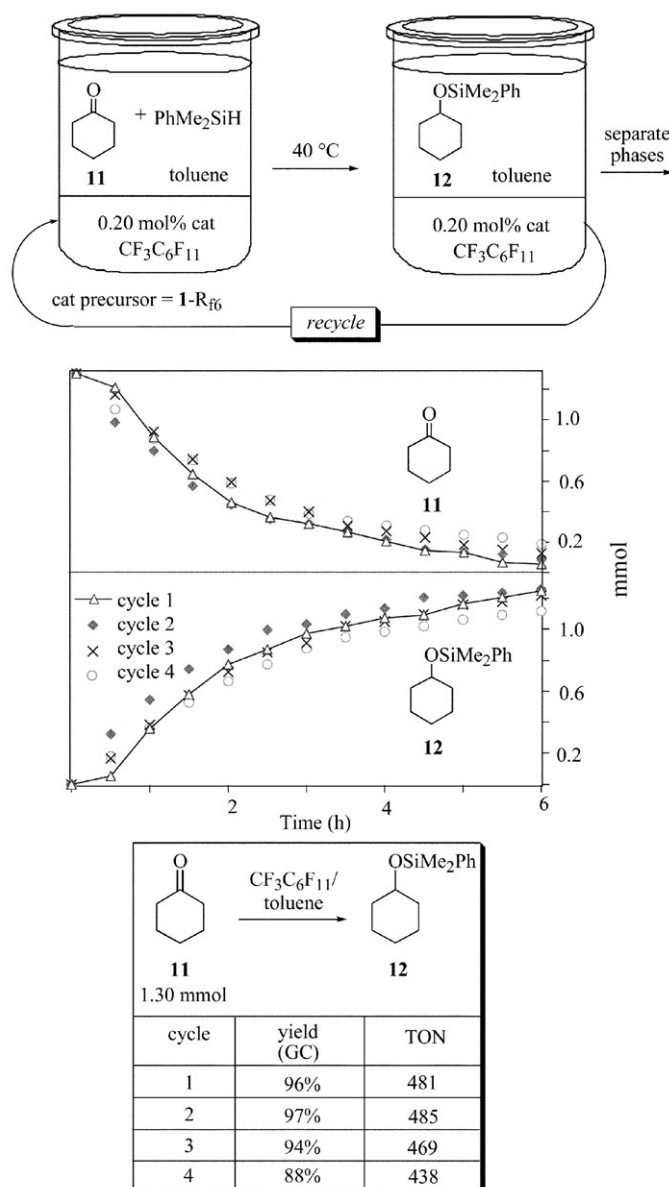


Fig. 6 Rate profile for the hydrosilylation of cyclohexanone (**11**) under biphasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ -toluene, 40 °C).

precursors for hydrosilylations of carbonyl compounds. Many other strategies have been applied to the immobilization and/or recovery of rhodium(i) hydrosilylation catalysts,²⁵ all of which have various merits or advantages.

No catalyst recovery method is without drawbacks. The liquid/liquid biphasic product/catalyst separations in Figs. 1–6 require fluoruous solvents, which are expensive. However, this is less of an issue with laboratory scale or fine chemical synthesis than with commodity chemical synthesis. Also, it should be possible to carry out the preceding reactions with FC-72, a mixture of perfluorinated hexanes that is the cheapest fluoruous solvent available. For this study, the isomerically homogeneous solvent $\text{CF}_3\text{C}_6\text{F}_{11}$ was selected in the interest of maximizing reproducibility. It should also be noted that small equilibrium amounts of fluoruous solvents remain in organic solvents under biphasic conditions (and *vice versa*).^{15b} Thus, there is some leaching of fluoruous solvents into the organic phases under the conditions of Figs. 1–6.

There are active ongoing efforts to address these issues,^{9–11} and the next paper in this series will feature alternative protocols that allow the catalysts in Figs. 1–6 to be recovered without recourse to fluoruous solvents.¹² In the interim, this work provides another convincing demonstration of the con-

venience, efficiency, and generality with which appropriately designed fluoruous catalysts can be recovered *via* liquid/liquid biphasic methods. It furthermore extends the repertoire of fluoruous reactions to an important laboratory scale transformation, the hydrosilylation of carbonyl compounds.

Experimental

General

Reactions were conducted under inert atmospheres. Hexanes, ether and toluene were distilled from Na/benzophenone and then freeze-pump-thaw degassed (3×); $\text{CF}_3\text{C}_6\text{F}_{11}$ (ABCR) was distilled from CaH_2 and analogously degassed. 2-Cyclohexen-1-one (**3**; Aldrich, 99%), 2-cyclopenten-1-one (**6**; Fluka, ≥ 99%), 4,4-dimethyl-2-cyclohexen-1-one (**9**; Fluka, 96%), cyclohexanone (**11**; Fluka, ≥ 99%), PhMe_2SiH (Aldrich, 99%) and tridecane (Aldrich, ≥ 99%) were freeze-pump-thaw degassed (3×). Complexes **1-R₆** and **1-R₈** were prepared as described earlier.⁵ NMR spectra were recorded on 300 or 400 MHz instruments at ambient probe temperature and referenced to residual internal CHCl_3 (^1H , δ 7.27) or CDCl_3 (^{13}C , δ

77.2). Gas chromatography was conducted on a ThermoQuest Trace GC 2000 instrument.

Hydrosilylations under biphasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –toluene, 60 °C; Figs. 1 and 2)²⁶

4 and 5. In a glove box, a 4 dram vial was charged with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **3** (0.126 ml, 1.30 mmol) and toluene (1.0 ml). The vial was heated in a sand bath (60 °C) with stirring, and analyzed by GC every 2 h. After 10 h, the upper toluene layer was removed by syringe. The lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was extracted with toluene (1.0 ml). The toluene layers were combined and the solvent was removed by rotary evaporation. The cloudy residue was distilled (40–45 °C/0.075 mm Hg, Kugelrohr) to give **4/5** as a clear oily liquid (0.271 g, 1.14 mmol, 88%, TON = 110). The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with **3** (0.126 ml, 1.30 mmol), toluene (1.0 ml) and PhMe_2SiH (0.219 ml, 1.43 mmol). An identical reaction and workup gave **4/5** (0.264 g, 1.11 mmol, 85%, TON = 107; identical third cycle: 0.264 g, 1.11 mmol, 85%, TON = 107).

7 and 8. An analogous reaction sequence was conducted starting with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **6** (0.110 ml, 1.30 mmol) and toluene (1.0 ml). This gave, after distillation (35–40 °C/0.075 mm Hg, Kugelrohr), **7/8** as a clear oily liquid (0.256 g, 1.17 mmol, 90%, TON = 113).²⁷ Data for subsequent cycles: see Fig. 2.

10. An analogous reaction sequence was conducted starting with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **9** (0.171 ml, 1.30 mmol) and toluene (1.0 ml). This gave, after distillation (45–50 °C/0.075 mm Hg, Kugelrohr), **10** as clear oily liquid (0.305 g, 1.17 mmol, 90%, TON = 113).²⁷ Data for subsequent cycles: see Fig. 2.

Product characterization

NMR samples were prepared under conditions slightly different from Figs. 1 and 2.

4 and 5. In a glove box, a 4 dram vial was charged with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **3** (0.126 ml, 1.30 mmol) and hexanes (1.0 ml). The vial was heated in a sand bath with stirring (60 °C). After 1 h, GC analysis showed conversion to be complete. The sample was cooled to –30 °C. After 4 h, the upper hexane layer was removed *via* syringe. The lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was similarly extracted with cold hexanes (1.0 ml). Solvent was removed from the combined hexane solutions by rotary evaporation. The slightly brown liquid was distilled (40–45 °C/0.075 mm Hg, Kugelrohr) to give **4/5** as a colorless liquid (0.272 g, 1.14 mmol, 88%, TON = 113).^{18c} NMR (δ , CDCl_3)¹⁷ for **4**: ¹H, 7.66–7.63 (m, 2H), 7.34–7.40 (m, 3H), 4.91–4.88 (m, 1H), 2.05–1.97 (m, 4H), 1.68–1.64 (m, 2H), 1.55–1.49 (m, 2H), 0.48 (s, 6H); ¹³C 150.39, 138.23, 133.39, 129.67, 127.97, 104.83, 30.00, 23.93, 23.27, 22.43, –0.85; for **5**, ¹H, 3.90 (m), 5.55–5.68 (m).

7 and 8. An analogous reaction was conducted with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **6** (0.110 ml, 1.30 mmol) and hexanes (1.0 ml). A similar workup and distillation (35–40 °C/0.075 mm Hg, Kugelrohr) gave **7/8** as a colorless liquid (0.258 g, 1.18 mmol, 91%, TON = 114).^{18c,27} NMR (δ , CDCl_3)¹⁷ for **7**: ¹H, 7.67–7.64 (m, 2H), 7.45–7.42 (m, 3H), 4.63–

4.61 (m, 1H), 2.31–2.33 (m, 4H), 1.91–1.81 (q, J = 7.0 Hz, 2H), 0.51 (s, 6H); ¹³C 154.99, 137.67, 133.55, 129.92, 128.03, 103.01, 33.64, 28.89, 21.47, –1.07.

10. An analogous reaction was conducted with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **9** (0.171 ml, 1.30 mmol) and hexanes (1.0 ml). After 2 h, a similar workup and distillation (45–50 °C/0.075 mm Hg, Kugelrohr) gave **10** as a colorless liquid (0.304 g, 1.17 mmol, 90%, TON = 113).²⁷ NMR (δ , CDCl_3)^{17,19} for **10**: ¹H, 7.63–7.60 (m, 2H), 7.42–7.36 (m, 3H), 4.78–4.75 (m, 1H), 2.01–1.96 (m, 2H), 1.77–1.75 (m, 2H), 1.37–1.35 (t, 2H), 0.88 (s, 6H), 0.44 (s, 6H); ¹³C 149.38, 138.19, 133.56, 129.78, 127.97, 103.86, 38.01, 36.04, 28.74, 28.09, 27.69, –0.81.

Hydrosilylations under monophasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes, 60 °C; Fig. 3)²⁶

4 and 5. In a glove box, a 4 dram vial was charged with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **3** (0.126 ml, 1.300 mmol) and hexanes (1.0 ml). The vial was heated in a sand bath with stirring (60 °C, 1 h). A workup analogous to that for the reaction under biphasic conditions gave **4/5** (0.288 g, 1.21 mmol, 93%, TON = 116). The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with **3** (0.126 ml, 1.300 mmol), hexanes (1.0 ml) and PhMe_2SiH (0.219 ml, 1.43 mmol). An identical reaction and workup gave **4/5** (0.288 g, 1.21 mmol, 93%, TON = 116; identical third cycle: 0.278 g, 1.17 mmol, 90%, TON = 113).

7 and 8. An analogous reaction sequence was conducted starting with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **6** (0.110 ml, 1.30 mmol), and hexanes (1.0 ml). This gave **7/8** (0.258 g, 1.18 mmol, 91%, TON = 114).²⁷ Data for subsequent cycles: see Fig. 3.

10. An analogous reaction sequence was conducted starting with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0104 M, 0.80 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **9** (0.171 ml, 1.30 mmol), and hexanes (1.0 ml). This gave **10** (0.304 g, 1.17 mmol, 90%, TON = 113).²⁷ Data for subsequent cycles: see Fig. 3.

Hydrosilylations under monophasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes or –ether, 28 °C; Fig. 4)

In hexanes. In a glove box, a 4 dram vial was charged with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0026 M, 0.20 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), tridecane (0.100 ml, 0.410 mmol) and hexanes (2.0 ml). The solution was stirred vigorously at glove box ambient temperature (28 °C). An aliquot (0.001 ml) was removed every 0.5 h for GC analysis until the reaction was complete. After 8 h, **12** was present in 97% yield (1.26 mmol). The solution was cooled to –30 °C. After 4 h, the upper hexanes layer was removed by syringe. The lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was similarly extracted with cold hexanes (1.0 ml). The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), tridecane (0.100 ml, 0.410 mmol) and hexanes (2.0 ml). The preceding sequence was repeated. After 8 h, **12** was present in 96% yield (1.25 mmol). Data for additional cycles: see Fig. 4.

In ether. An analogous sequence was conducted starting with a solution of **1-R₁₈** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0026 M, 0.20 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), tridecane (0.100 ml, 0.410 mmol) and ether (2.0 ml). After 8 h, **12** was present in 96% yield (1.25 mmol). The solution was cooled to –30 °C. After 4 h, the upper ether layer

was removed by syringe. The lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was similarly extracted with cold ether (1.0 ml). The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), tridecane (0.100 ml, 0.410 mmol) and ether (2.0 ml). Additional data: see Fig. 4.

Reduced catalyst loading. In a glove box, a Schlenk flask was charged with a solution of **1-R₆** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0026 M, 0.02 mol%), PhMe_2SiH (2.2 ml, 14.4 mmol), **11** (1.35 ml, 13.0 mmol) and hexanes (5.0 ml). The solution was stirred vigorously at glove box ambient temperature (28 °C). After 72 h, solvents, unreacted **11**, and PhMe_2SiH were removed by vacuum. The residue was distilled (Kugelrohr) to give **12** as a clear oil (2.68 g, 11.4 mmol, 88%, TON = 4400). NMR (δ , CDCl_3)²² for **12**: ¹H, 7.62–7.59 (m, 2H), 7.41–7.27 (m, 3H), 3.63–3.59 (m, 1H), 1.79–1.69 (m, 2H), 1.51–1.50 (m, 2H), 1.35–1.15 (m, 6H), 0.410 (s, 6H); ¹³C 133.68, 129.60, 127.94, 71.59, 36.10, 25.72, 24.58, –0.75.

Hydrosilylation rate profiles

Monophasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –hexanes, 40 °C; Fig. 5). A 10 ml vial was charged with a solution of **1-R₆** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0026 M, 0.20 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), hexanes (2.0 ml) and tridecane (0.100 ml, 0.410 mmol). The vial was heated in a sand bath with stirring (40 °C). An aliquot (0.001 ml) was removed every 0.5 h for GC analysis (data in Fig. 5). When conversion was complete, the sample was cooled to –30 °C. After 4 h, the upper hexanes layer was removed by syringe. The lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was similarly extracted with cold hexanes (1.0 ml). The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with PhMe_2SiH (0.219 ml, 1.430 mmol), **11** (0.135 ml, 1.30 mmol), hexanes (2.0 ml) and tridecane (0.100 ml, 0.410 mmol). The vial was heated in a sand bath (40 °C) and similarly monitored by GC. Data, including analogous additional cycles, are given in Fig. 5.

Biphasic conditions ($\text{CF}_3\text{C}_6\text{F}_{11}$ –toluene, 40 °C; Fig. 6). A 10 ml vial was charged with a solution of **1-R₆** in $\text{CF}_3\text{C}_6\text{F}_{11}$ (1.00 ml, 0.0026 M, 0.20 mol%), PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), toluene (1.0 ml) and tridecane (0.100 ml, 0.410 mmol). The vial was heated in a sand bath with stirring (40 °C). An aliquot (0.001 ml) was removed every 0.5 h for GC analysis (data: Fig. 6). When conversion was complete, the sample was cooled to ambient temperature and the upper toluene layer removed by syringe. Toluene (1.0 ml) was added to the lower $\text{CF}_3\text{C}_6\text{F}_{11}$ layer. The sample was shaken and the toluene was removed by syringe. The $\text{CF}_3\text{C}_6\text{F}_{11}$ layer was recharged with PhMe_2SiH (0.219 ml, 1.43 mmol), **11** (0.135 ml, 1.30 mmol), toluene (2.0 ml) and tridecane (0.100 ml, 0.410 mmol). The vial was heated in a sand bath (40 °C) and similarly monitored by GC. Data, including analogous additional cycles, are given in Fig. 6.

Partition coefficients

The following are representative.

A. A 1 dram vial was charged with PhMe_2SiH (0.0505 g), $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.000 ml) and toluene (2.000 ml), capped with a mininert valve, vigorously shaken (2 min) and immersed (to 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 decane in hexanes (2.0 ml, 0.0394 M). GC analysis (average of 3 injections) showed 7.127×10^{-2} mmol of PhMe_2SiH in the toluene aliquot and 2.647×10^{-3} mmol in the $\text{CF}_3\text{C}_6\text{F}_{11}$ aliquot (96.4:3.6). The total mass of PhMe_2SiH calculated

from these data (0.0503 g following a 2.000/0.400 volume correction) was in close agreement with that originally added.

B. A 1 dram vial was charged with **10** (0.1002 g), $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.000 ml) and toluene (2.000 ml), capped with a mininert valve, vigorously shaken (2 min) and immersed (to 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 decane in hexane (2.0 ml, 0.0394 M). GC analysis showed 7.77×10^{-2} mmol of **10** in the toluene aliquot and 4.543×10^{-4} mmol in the $\text{CF}_3\text{C}_6\text{F}_{11}$ aliquot (99.4:0.6). The total mass of **10** calculated from these data (0.1018 g following a 2.000/0.400 volume correction) was in close agreement with that originally added.

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References

- General reference: *Handbook of Fluorous Chemistry*, eds. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley-VCH, Weinheim, 2004.
- J. A. Gladysz and R. C. da Costa, in *Handbook of Fluorous Chemistry*, eds. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley-VCH, Weinheim, 2004, pp. 24–40.
- (a) I. T. Horváth and J. Rábai, *Science*, 1994, **266**, 72; (b) I. T. Horváth, G. Kiss, R. A. Cook, J. E. Bond, P. A. Stevens, J. Rábai and E. J. Mozeleski, *J. Am. Chem. Soc.*, 1998, **120**, 3133; (c) I. T. Horváth, in *Handbook of Fluorous Chemistry*, eds. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley-VCH, Weinheim, 2004, pp. 5–10.
- (a) R. C. da Costa and J. A. Gladysz, in *Transition Metals for Organic Synthesis*, eds. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2004, pp. 527–543; (b) See also ch. 10.8–10.14 in ref. 1.
- J. J. Juliette, D. Rutherford, I. T. Horváth and J. A. Gladysz, *J. Am. Chem. Soc.*, 1999, **121**, 2696.
- D. Rutherford, J. J. Juliette, C. Rocaboy, I. T. Horváth and J. A. Gladysz, *Catal. Today*, 1998, 42.
- L. V. Dinh and J. A. Gladysz, *Tetrahedron Lett.*, 1999, **40**, 8995.
- Reviews covering rhodium-catalyzed hydrosilylations of carbonyl compounds: (a) H. Brunner, in *Transition Metals for Organic Synthesis*, eds. M. Beller and C. Bolm, Wiley-VCH, Weinheim and New York, 1998, vol. 2, ch. 1.4.2; (b) I. Ojima, Z. Li and J. Zhu, in *The Chemistry of Fluorous Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, vol. 2, ch. 29.
- (a) M. Wende, R. Meier and J. A. Gladysz, *J. Am. Chem. Soc.*, 2001, **123**, 11490; (b) M. Wende and J. A. Gladysz, *J. Am. Chem. Soc.*, 2003, **125**, 5861.
- (a) K. Ishihara, S. Kondo and H. Yamamoto, *Synlett.*, 2001, 1371; (b) K. Ishihara, A. Hasegawa and H. Yamamoto, *Synlett.*, 2002, 1299; (c) J. Otera, *Acc. Chem. Res.*, 2004, **37**, 288; (d) G. Maayan, R. H. Fish and R. Neumann, *Org. Lett.*, 2003, **5**, 3547.
- (a) C. C. Tzschucke, C. Markert, H. Glatz and W. Bannwarth, *Angew. Chem., Int. Ed.*, 2002, **41**, 4500; (b) C. C. Tzschucke, C. Markert, H. Glatz and W. Bannwarth, *Angew. Chem.*, 2002, **114**, 4678; (c) A. Biffis, M. Zecca and M. Basato, *Green Chem.*, 2003, **5**, 170.
- L. V. Dinh and J. A. Gladysz, *J. Am. Chem. Soc.*, submitted.
- L. V. Dinh, *Ph.D. Thesis*, University of Utah, Salt Lake City, Utah, 2004.
- (a) E. de Wolf, E. A. Speets, B. J. Deelman and G. van Koten, *Organometallics*, 2001, **20**, 3686; (b) J. van den Broeke, F. Winter, B.-J. Deelman and G. van Koten, *Org. Lett.*, 2002, **4**, 3851; (c) E. de Wolf, E. Riccomagno, J. J. M. de Pater, B.-J. Deelman and G. van Koten, *J. Combinat. Chem.*, 2004, **6**, 363.
- (a) J. H. Hildebrand and D. R. Cochran, *J. Am. Chem. Soc.*, 1949, **71**, 22; (b) J. A. Gladysz and C. Emnet, in *Handbook of Fluorous Chemistry*, eds. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley-VCH, Weinheim, 2004, pp. 11–23.

- 16 Furthermore, solutes often raise the temperatures at which mixing occurs.
- 17 T. H. Chan and G. Z. Zheng, *Organometallics*, 1995, **14**, 70.
- 18 (a) For another reaction that yields a **4/5** mixture (both isomers were isolated), see: M. Koreeda and S. Koo, *Tetrahedron Lett.*, 1990, **31**, 831; (b) The properties of **5** also compare well with those of a related silyl ether: M. D. Cavanaugh, B. T. Gregg and A. R. Cutler, *Organometallics*, 1996, **15**, 2764; (c) The **4/5** and **7/8** ratios were determined by integrating the olefinic proton of **4** or **7** versus the SiOCHR₂ proton of **5** or **8**; (d) For the trimethylsilyl analog of **8**, see: R. Noyori, S. Murata and M. Suzuki, *Tetrahedron*, 1981, **37**, 3899.
- 19 J. M. Blackwell, D. J. Morrison and W. M. Piers, *Tetrahedron*, 2002, **58**, 8247.
- 20 J. A. Gladysz, C. Emnet and J. Rábai, in *Handbook of Fluorous Chemistry*, eds. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley-VCH, Weinheim, 2004, pp. 56–100.
- 21 J. A. Gladysz, *Pure Appl. Chem.*, 2001, **73**, 1319.
- 22 I. Ojima, R. J. Donovan and N. Clos, *Organometallics*, 1991, **10**, 2606.
- 23 C. Rocaboy and J. A. Gladysz, *New J. Chem.*, 2003, **27**, 39.
- 24 I. Ojima and T. Kogure, *Organometallics*, 1982, **1**, 1390.
- 25 (a) I. Ojima, in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley, New York, 1989, vol. **1**, part 2, pp. 1491–1492; (b) Z. Lu, E. Lindner and H. A. Mayer, *Chem. Rev.*, 2002, **102**, 3543; (c) D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, **102**, 3640.
- 26 Experiments with **1-R₁₈** were conducted analogously.
- 27 Additional details are given in ref. 13.