

Solventless Silane Alcoholysis Catalyzed by Recoverable Dirhodium(II) Perfluorocarboxylates

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Abstract: We have developed a novel reaction protocol for the highly efficient and sustainable catalysis of the silane alcoholysis reaction. The catalysts of choice are dirhodium(II) perfluorocarboxylates bearing long perfluoroalkyl chains, which are easily prepared in one step from commercial precursors. Under optimized reaction conditions, these catalysts exhibit up to about 50 times higher activity and 100 times higher productivity than analogous dirhodium(II) complexes described in the prior art. Furthermore, the reaction can be run in a completely solventless fashion. Finally, heterogenization of these catalysts has been accom-

plished through a novel strategy based on fluororous chemistry. Indeed, perfluorinated catalysts of this kind are easily adsorbed on silica which has been previously functionalized at its surface with perfluoroalkyl chains. Use of such supported catalysts (bonded fluororous phase catalysts) allows an easy and almost complete catalyst separation and recycling with improved catalytic performance.

Keywords: catalysis; fluororous chemistry; green chemistry; rhodium; silanes

Introduction

The recent history of chemistry has witnessed the development of a myriad of homogeneous transition metal catalysts for the most diverse reactions.^[1] Often enough, such catalysts exhibit very positive features in terms of activity and selectivity under mild conditions, but in most cases their technological application is hampered by the need for their efficient recovery and recycling. In fact, incomplete catalyst recovery and recycling results in losses of (precious) metal, losses of (expensive) ligands, and pollution of the reaction products. Consequently, it is not surprising that quite a number of strategies have been developed over the last three decades to overcome this problem,^[2] and that this kind of research has enjoyed a further increase of interest over the last few years, particularly due to the growing concern for the cleanness and efficiency of chemical processes which generally goes under the name of "green chemistry".^[3]

Recently, we have started a project aimed at the development of recoverable catalysts for silane alcoholysis, Eq. (1).^[4] This reaction is a practical alternative to the classical silylation protocol which is routinely employed in organic synthesis for the protection of hydroxy groups.^[5] The reaction is usually accomplished utilising a chlorosilane to introduce the silyl group, Eq. (2). However, this invariably requires the presence of a base in order to neutralize the hydrochloric acid formed as by-product, which implies the production of

one equivalent of salt per equivalent of product. On the contrary, with silane alcoholysis H_2 is the only by-product. Quite remarkably, the field of application of the silane alcoholysis reaction has been recently extended to the preparation and functionalization of silicones.^[6]



A catalyst is needed in order for silane alcoholysis to proceed at a synthetically useful rate.^[7] Over the years, quite a number of catalysts have been proposed in the literature, ranging from heterogeneous metal catalysts^[8] to organic compounds^[9] and transition metal complexes.^[10] The latter, most notably those of ruthenium, rhodium, iridium, manganese and platinum appear to be currently the most productive and versatile catalysts. However, they usually tolerate only a limited range of reaction solvents, i.e., non-polar, non-coordinating solvents such as benzene or dichloromethane, which are of concern for the environment and health. Furthermore, in most cases they require strictly anhydrous reaction conditions and the exclusion of atmospheric oxygen. Finally, they present the problem of the separation of the catalyst from the reaction products and of its recycling. In this contribution, we describe in full length our results on the discovery of a solventless protocol for efficient

silane alcoholysis using dirhodium(II) perfluorocarboxylate catalysts, as well as on the development of novel strategies for complete catalyst recovery and recycling.

Results and Discussion

The application of a dirhodium(II) perfluorocarboxylate as catalyst for silane alcoholysis was originally reported by Doyle et al.,^[10i] who utilized 1 mol % dirhodium(II) perfluorobutyrate in dichloromethane at room temperature. This rhodium catalyst does not apparently require the strict exclusion of water and oxygen, and its selectivity for the alcoholysis reaction product is very good even with unsaturated alcohols, which easily undergo metal-catalyzed hydrogenation along with silane alcoholysis. However, the amount of catalyst which has to be employed is intolerably high for commercial applications. Therefore, it is mandatory to increase the productivity of this catalytic system, for example, by efficiently recovering and recycling the catalyst. In a previous publication,^[4a] we have introduced dirhodium(II) perfluorocarboxylates bearing long perfluoroalkyl chains (i.e., from 7 to 13 carbon atoms long, Figure 1) as catalysts for this reaction. Such highly fluorinated dirhodium(II) complexes can be easily prepared in one step from common commercial precursors and are air-stable, easy to handle solid compounds which are preferentially soluble in fluorinated solvents.^[4,11] Consequently, we have employed them as silane alcoholysis catalysts in a dichloromethane/Fluorinert® FC-77 fluorinated biphasic system,^[12] which ensures the easy recovery and recycling of the catalyst. However, their catalytic activity in the fluorinated biphasic system was found to be lower than in the related homogeneous system, which was attributed to mass-transport limitations between the two liquid phases.^[4a]

In the search for a more efficient way to run the reaction while maintaining the possibility of an easy recovery and recycling of the catalyst, we have been looking for a reaction medium in which the reaction could be run in a monophasic fashion at room temperature, and from which the catalyst could still be easily separated by liquid-liquid extraction with a fluorinated

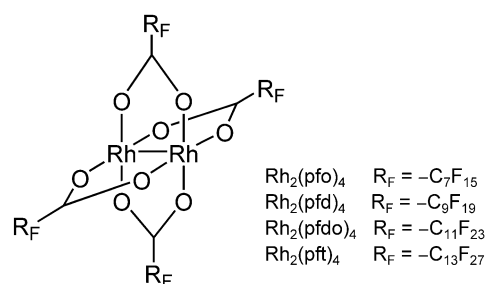


Figure 1.

solvent at the end of the reaction. This preliminary investigation was performed using the triethylsilane alcoholysis with 1-octanol as a model reaction. Relevant results are reported in Table 1.

In the absence of other solutes, the investigated catalysts are only soluble in organic solvents able to coordinate to the free apical positions of the complex, most notably in solvents containing oxygen donor atoms such as ethers. These solvents, however, deactivate the catalyst, since they block its active site (Table 1, Entry 2). On the other hand, the solubility of the catalyst in non-coordinating solvents such as dichloromethane is promoted by the presence of a primary alcohol substrate such as 1-octanol. In fact, the alcohol is able to interact with the free apical positions of the catalyst as well. The resulting complex adduct is less fluorinated, hence more prone to be solubilized by a conventional organic solvent.

The catalyst could be easily and quantitatively recovered from the dichloromethane solution by extraction with a fluorinated solvent such as Fluorinert® FC-77. However, the observed catalytic activity was only slightly higher than in the biphasic system and still significantly lower than that of the benchmark literature catalyst dirhodium(II) perfluorobutyrate under comparable reaction conditions (compare Entries 1, 3 and 4 in Table 1). We attribute the lower catalytic activity of our catalysts under these conditions to some degree of aggregation of the fluorinated catalyst molecules in the organic phase. Aggregation of dirhodium(II) perfluorocarboxylates due to intermolecular interaction between the oxygen atoms of a carboxylate group on one

Table 1. Triethylsilane alcoholysis with 1-octanol catalyzed by $\text{Rh}_2(\text{pft})_4$ using different solvent systems.

Entry	Catalyst	Solvent	Yield ^[a] [%]	TON	TOF [h ⁻¹]
1 ^[b]	$\text{Rh}_2(\text{pft})_4$	Dichloromethane/FC-77	68	68	11
2	$\text{Rh}_2(\text{pft})_4$	THF	23	23	4
3	$\text{Rh}_2(\text{pft})_4$	Dichloromethane	74	74	12
4	$\text{Rh}_2(\text{pfb})_4$ ^[c]	Dichloromethane	96(3 h)	96	32

Reaction conditions: 1 mmol of each reagent, 0.01 mmol (1 mol %) catalyst, 5 mL solvent, room temperature.

^[a] GC yield after 6 h.

^[b] Data from Ref.^[4a]

^[c] Dirhodium(II) perfluorobutyrate catalyst: literature data from Ref.^[10i]

complex molecule with the free apical position of another complex molecule has been described in the solid state^[13] and there is indirect evidence suggesting its presence also in solution.^[14] Such an aggregation could be further promoted by the presence of long perfluoro-alkyl chains tending to segregate from the organic medium, thereby leading to clustering of catalyst molecules and consequently decreased catalytic efficiency.

In view of the high solubilizing power of alcohols such as 1-octanol, we finally resolved to try the reaction without any organic solvent. Indeed, coordination of alcohol molecules to the free apical positions of the catalyst renders it soluble in the neat alcohol as well as in a 1:1 mixture of 1-octanol and triethylsilane. Actually, the solubility of the complex in such a mixture is so good that it is extracted from a fluoruous phase by treatment with it, the extent of extraction depending on the catalyst and fluoruous solvent employed: for example, $\text{Rh}_2(\text{pfd})_4$ is completely extracted from a Fluorinert® FC-77 solution, whereas $\text{Rh}_2(\text{pft})_4$ migrates only partially. The results reported in Table 2 show that the activity of the highly fluoruous catalysts in the solventless system actually equals that of the benchmark literature catalyst in methylene chloride as reported by Doyle.^[10] However, the productivity of the catalyst can be significantly increased, as apparent from the reported turnover numbers, and no hazardous organic solvent is needed for the reaction. No significant difference in reactivity is observed for catalysts with differently long fluoruous chains (Entries 1–4), in accordance with the idea that changing the chain length does not influence the reactivity of the active site. Secondary alcohols such as 2-octanol react much more slowly (Entry 6), as was the case with Doyle's catalyst.^[10] However, by allowing

properly long reaction times good yields can be reached also with this substrate, in contrast to the previously described fluoruous biphasic system,^[4a] in which mass-transport limitations virtually stopped the reaction of secondary alcohols at about 20% yield. Nevertheless, the significant difference in reaction rate between primary and secondary alcohols can be exploited in competitive silane alcoholysis experiments performed in a deficit of silane, leading to preferential silylation of the primary alcohol function (Entry 7).

After reaction completion, the catalyst finds itself dissolved in the reaction product, which is a much worse ligand for the rhodium complex than the alcohol substrate. As a consequence, the catalyst does not precipitate out of the solution, but it readily migrates into a separated fluoruous phase as soon as the product phase comes in contact with it. The fluoruous phase containing the catalyst can be subsequently contacted with a second batch of liquid reagents mixture, which extracts it back, thereby starting the reaction again. Thus, under these reaction conditions, dirhodium(II) perfluorocarboxylates represent a further example of "smart" homogeneous catalysts, which readily and spontaneously separate from the product phase at the end of the reaction.^[15] Unfortunately, the recovery of the rhodium catalysts using this strategy is not complete. This is partly due to incomplete extraction of the catalyst from the product phase and partly to the long reaction time needed for the reaction to reach completion, which causes partial catalyst decomposition. Best results obtained with $\text{Rh}_2(\text{pfd})_4$ and Fluorinert® FC-77 as the extractant account for 60% catalyst recovery after the first cycle. Nevertheless, it is important to remark that the recovered catalyst retains the initial catalytic activity (Entry 5, Table 2).

Table 2. Triethylsilane alcoholysis catalyzed by dirhodium(II) perfluorocarboxylates under solventless conditions at room temperature.

Entry	Catalyst	Mol % catalyst	Alcohol	Yield ^[a] [%]	TON	TOF [h ⁻¹]
1	$\text{Rh}_2(\text{pfo})_4$	0.1	1-octanol	73	730	30
2	$\text{Rh}_2(\text{pfd})_4$	0.1	1-octanol	75	750	31
3	$\text{Rh}_2(\text{pfdo})_4$	0.1	1-octanol	60	600	25
4	$\text{Rh}_2(\text{pft})_4$	0.1	1-octanol	69	690	29
5 ^[b]	$\text{Rh}_2(\text{pfd})_4$	0.060	1-octanol	52	870	36
6	$\text{Rh}_2(\text{pfd})_4$	0.1	2-octanol	24 ^[c]	240	10
7 ^[d]	$\text{Rh}_2(\text{pfd})_4$	0.1	1-octanol	71	710	30
			2-octanol	14	140	6
8	$\text{Rh}_2(\text{pfb})_4$ ^[e]	1	1-octanol	96(3 h)	96	32
9	$\text{Rh}_2(\text{pfb})_4$ ^[e]	1	2-octanol	94(14 h)	94	7

Reaction conditions: see the Experimental Section.

^[a] GC yield after 24 h.

^[b] Recycle of Entry 2.

^[c] Yield is 66% after 5 days.

^[d] Competitive reaction experiment.

^[e] Dirhodium(II) perfluorobutyrate catalyst: literature data from Ref.^[10]

In order to overcome the problems associated with partial catalyst decomposition, we tried to reduce the reaction time by running the reaction at a slightly higher temperature (50 °C). We were delighted to observe that the catalytic activity increased considerably at this temperature, reaching values one order of magnitude higher than at room temperature (Table 3). High yields could be reached in reasonable time with only 0.01% catalyst, i.e., 100 times less than in the original paper by Doyle.^[10] However, the extent of catalyst decomposition apparently increased together with the reaction rate, so that the amount of catalyst that could be recovered by extraction after reaction completion was even lower than at room temperature.

The problem of recycling could be solved by developing a novel form of supported fluororous catalyst using an approach that we have named “bonded fluororous phase catalysis” (BFPC, Figure 2).^[4b] In this approach, a fluororous film is built on a solid support by covalently binding perfluoroalkyl chains on its surface. Such materials are not entirely new: they have been used for a long time as stationary phases for liquid chromatography (bonded phase chromatography) and have recently enjoyed a considerable revival of interest due to their application in the extraction of fluororous-tagged molecules from complex mixtures.^[16] Indeed, such supports can, in principle, also extract fluororous catalysts from their solution in an organic solvent, thereupon forming a novel kind of supported catalyst. We have preliminarily reported on the viability of this strategy in a very recent communication.^[4b]

Related approaches using silica functionalization with non-fluororous chains were previously proposed by Neumann and Cohen,^[17] and Williams et al.^[18] Very recently, Pozzi et al. tried to apply the same BFPC strategy for supporting fluororous chiral Co(salen) catalysts for the hydrolytic kinetic resolution of terminal epoxides.^[19] However, the supported catalyst turned out to be completely inactive. Contemporarily to the publication of our preliminary results on this methodology, another example of application of the same strategy was published by Bannwarth.^[20] Finally, very recent work carried out independently by Jessop and Tsang must be mentioned, in which fluororous silica supports act as a reservoir of catalytically active species which are

reversibly released from the support by applying CO₂ pressure.^[21] In our case and in the case of Bannwarth, however, the catalyst remains on the solid support for the whole duration of the experiment, i.e., it is truly “heterogenized” on the support.

We have prepared our silica support by derivatization of silica gel following a procedure originally reported by Curran.^[22] Functionalization of the silica surface with 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane results in a material with high affinity for fluororous compounds. Such derivatized silica can be conveniently loaded with dirhodium(II) perfluorocarboxylate complexes [either Rh₂(pfo)₄ or Rh₂(pft)₄] by contacting it with a solution of the complex of choice (see the Experimental Section); adsorption of the complex on the fluororous layer covering the silica surface takes place in good yields and the resulting product can be easily isolated by simple filtration.^[4b] In this way, BFP catalysts with metal complex loadings of 22 µmol/g fluororous silica for Rh₂(pfo)₄ and of 12 µmol/g fluororous silica for Rh₂(pft)₄ could be prepared.

Preliminary experiments performed at room temperature pointed out that the BFP catalyst derived from Rh₂(pfo)₄ was highly active under solventless conditions (Table 4, entries 1 and 2), reaching activities up to five

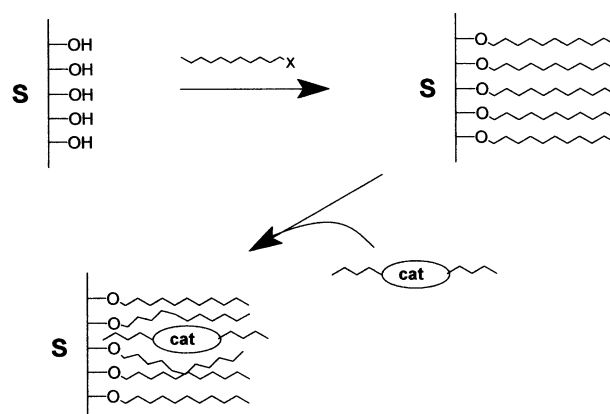


Figure 2. The “bonded fluororous phase catalysis” (BFPC) approach. The surface of a solid support **S** is derivatized with molecules bearing long fluororous chains; in this way, a surface layer is created in which a fluororous catalyst can be embedded.

Table 3. Triethylsilane alcoholysis catalyzed by dirhodium(II) perfluorocarboxylates under solventless conditions at 50 °C.

Entry	Catalyst	Mol % catalyst	Alcohol	Yield ^[a] [%]	TON	TOF [h ⁻¹]
1	Rh ₂ (pfd) ₄	0.1	1-octanol	100	1000	42
2	Rh ₂ (pfd) ₄	0.01	1-octanol	97	9700	404
3	Rh ₂ (pfo) ₄	0.01	1-octanol	98	9800	408
4	Rh ₂ (pfdo) ₄	0.01	1-octanol	100	10000	417
5	Rh ₂ (pft) ₄	0.01	1-octanol	98	9800	408

Reaction conditions: see the Experimental Section.

^[a] GC yield after 24 h.

times higher than those observed with the unsupported analogues. Furthermore, the catalysts could be separated by simple filtration with < 3% rhodium leaching and could be recycled.^[4b] In contrast, the BFP catalyst based on $\text{Rh}_2(\text{pft})_4$ was found to be much less active (Entry 3). We speculate that such lower activity may be due to the lower degree of dispersion of the latter complex on the fluorosilica surface, i.e., to the presence of aggregates of catalyst molecules.

We then moved to the evaluation of the performance of the supported catalysts at 50 °C. Table 4 shows the relevant results. It can be appreciated that also in this case the activities spring up dramatically for both supported catalysts and are fully comparable with the values for the unsupported complexes, at least in the case of BFP- $\text{Rh}_2(\text{pfo})_4$. Furthermore, the supported catalysts remain separable by simple filtration and are recyclable. Complete recycling in the small laboratory-scale experiments performed up to now is somewhat difficult due to the small amount of solid catalyst involved, which makes it difficult to collect the whole of the catalyst batch employed in one run. Nevertheless, we have been able to show that the recovered BFP catalysts maintain their catalytic activity at least for one recycling (Table 4, Entry 5). Even higher catalytic activities (50 times higher than the originally reported homogeneous catalysts) can be reached by further increasing the temperature to 80 °C, while the catalyst still remains perfectly recyclable (Table 4, Entries 11 and 12). A preparative experiment performed with 1 mL (1 equivalent) of each reagent using the reaction conditions of Entry 11 yields after 16 hours reaction time and catalyst separation by simple filtration the silyl ether product in

almost quantitative yield; the purity of the product was assessed to be >95% by gas chromatography, NMR spectroscopy and elemental analysis.

Primary alcohols such as 1-octanol and benzyl alcohol react more rapidly than secondary alcohols such as 2-octanol also under BFP catalysis (Table 4, Entry 7). Consequently, competitive silane alcoholysis experiments can be performed in this case as well, leading to preferential silylation of the primary alcohol function (Entry 8). However, cyclic secondary alcohols such as cyclohexanol are also quite efficiently silylated (Entry 10).

Finally, a preliminary evaluation of the effect of the nature of the silane on the reactivity of BFP catalysts has been performed (Table 5). It is interesting to note that the nature of the organic substituents on the silane may have an influence both on the overall activity of the catalytic system as well as on its selectivity towards primary alcohols in competitive experiments. Indeed, phenyldimethylsilane displays a much lower selectivity than triethylsilane while reacting at a comparable rate, whereas *t*-butyldimethylsilane is much more selective but also quite less reactive. The differences in reactivity observed with the BFP catalyst are much more pronounced than those observed with the homogeneous literature catalyst;^[10i] we are currently looking for a suitable explanation of this phenomenon.

Conclusion

In conclusion, we have developed a novel reaction protocol for silane alcoholysis catalyzed by dirhodi-

Table 4. Solventless triethylsilane alcoholysis using BFPC at different reaction temperatures.

Entry	Catalyst	Mol % catalyst	Alcohol	T [°C]	Yield ^[a] [%]	TON	TOF [h ⁻¹]
1 ^[b]	BFP- $\text{Rh}_2(\text{pfo})_4$	0.1	1-octanol	RT	100	1000	42
2 ^[b]	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	1-octanol	RT	39	3900	162
3	BFP- $\text{Rh}_2(\text{pft})_4$	0.01	1-octanol	RT	4	400	17
4	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	1-octanol	50	93	9300	388
5 ^[c]	BFP- $\text{Rh}_2(\text{pfo})_4$	0.0060	1-octanol	50	63	10500	438
6	BFP- $\text{Rh}_2(\text{pft})_4$	0.01	1-octanol	50	55	5500	229
7	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	2-octanol	50	18	1800	75
8 ^[d]	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	1-octanol	50	65	6500	271
			2-octanol		15	1500	63
9	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	benzyl alcohol	50	83	8300	346
10	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	cyclohexanol	50	77	7700	321
11	BFP- $\text{Rh}_2(\text{pfo})_4$	0.01	1-octanol	80	95 ^[e]	9500	1580
12 ^[f]	BFP- $\text{Rh}_2(\text{pfo})_4$	0.0081	1-octanol	80	92 ^[e]	11360	1890

Reaction conditions: see the Experimental Section.

^[a] GC yield after 24 h.

^[b] Data from Ref.^[4b]

^[c] Recycle of Entry 4.

^[d] Competitive reaction experiment.

^[e] Yield after 6 h.

^[f] Recycle of Entry 11.

Table 5. Competitive solventless silane alcoholysis using 0.01 mol % BFP-Rh₂(pfo)₄ catalyst at 50 °C.

Entry	Silane	Alcohol	Yield ^[a] [%]	Relative reactivity
1	Et ₃ SiH	1-octanol	65	4.3
		2-octanol	15	
2	Me ₂ PhSiH	1-octanol	48	1.3
		2-octanol	38	
3	<i>t</i> -BuMe ₂ SiH	1-octanol	11	11
		2-octanol	1	

Reaction conditions: 1 equivalent of each reagent, catalyst, 24 h.

^[a] GC yield after 24 h.

um(II) perfluorocarboxylates which, in comparison with the one originally described in the literature, allows us to reach up to 50 times higher catalytic activity and 100 times higher catalytic productivity. The new reaction protocol uses down to 100 times less catalyst than the original one and runs in a completely solventless fashion. Furthermore, heterogenization of these catalysts has been accomplished by adsorbing them on silica which has been previously functionalized at its surface with perfluoroalkyl chains. Use of such supported catalysts (bonded fluororous phase catalysts) allows an easy and almost complete catalyst separation and recycling with improved catalytic performance. We are currently pursuing the application of these novel supported catalysts to other alcohol substrates of synthetic interest as well as to other technologically relevant reactions which are known to be catalyzed by dirhodium(II) perfluorocarboxylates.^[23]

Experimental Section

Solvents (Carlo Erba), fluorinated solvents and reagents (ABCR) and common reagents (Aldrich) were used as received unless otherwise stated. The preparation of dirhodium(II) perfluorocarboxylates has been previously reported.^[4a,11]

Preparation of Fluororous Silica

The fluororous silica was prepared starting from high purity silica gel 60 (Fluka) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylchlorosilane following a procedure fully analogous to that reported by Curran.^[22] The degree of silica functionalization, determined gravimetrically and by elemental analysis, was found to be 0.81 mmol/g.

Preparation of BFP Catalysts

BFP-Rh₂(pfo)₄: Rh₂(pfo)₄ (25 mg) was suspended in 5 mL toluene. Fluororous silica (0.5 g) was then added and the resulting mixture was briefly heated at reflux with efficient stirring, upon which the metal complex quantitatively dissolved. The mixture was allowed to cool to room temperature while stirring was continued, after which the green solid was

filtered off, thoroughly washed with toluene and dried under vacuum to constant weight. The mother liquor and the solution from the washings were collected and the solvent was removed at reduced pressure. The residue was dissolved in 6 mL hot aqua regia and the resulting solution was diluted to 100 mL with water. The Rh content in the solution was quantitatively estimated by ICP-AAS, and from this result the Rh content in the BFP catalyst was determined by difference. The yield in supported complex turned out to be 22 μmol/g fluororous silica (86% in respect to the initial amount of complex).

BFP-Rh₂(pft)₄: Rh₂(pft)₄ (25 mg) was dissolved in 2 mL THF. Fluororous silica (0.5 g) was then added and the resulting mixture was stirred at room temperature for 4 hours, after which the supported catalyst was filtered off, thoroughly washed with THF and dried under vacuum to constant weight. The Rh content in the resulting BFP catalyst was determined as described above for BFP-Rh₂(pfo)₄. The yield in supported complex turned out to be 12 μmol/g fluororous silica (78% in respect to the initial amount of complex).

Catalytic Tests

Reactions in organic solvents: Catalytic tests were run in a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was charged with the required quantity of catalyst, evacuated and filled with argon. The anhydrous organic solvent (5 mL) was then added under argon, followed by 162 μL (1 mmol) 1-octanol and 173 μL (1.05 mmol) triethylsilane. The resulting solution was vigorously stirred at room temperature. Samples of 0.5 mL were taken after 6 h reaction time and analyzed by GC following the previously established procedure.^[4a]

Solventless reactions with homogeneous catalysts: In a typical procedure, a Schlenk tube equipped with a magnetic stirring bar was charged with the required quantity of catalyst, evacuated and filled with argon. 1-Octanol (1 mL) and triethylsilane (1.1 mL, 1.08 equivalents) were then added, and the resulting solution was vigorously stirred at room temperature or at 50 °C (thermostatted oil bath) for 24 hours. Samples of 0.1 mL were withdrawn after this period, diluted with 1 mL dichloromethane and analyzed by GC following the previously established procedure.^[4a] Catalyst recycling was performed by adding 1 mL fluororous solvent to the reaction mixture, stirring for a few minutes to allow partition to come to equilibrium, removing the product phase and adding fresh reagents before resuming the stirring. The amount of rhodium remaining in the product phase was determined by ICP-AAS

on an aliquot of the product phase (0.5 mL), which was treated with 6 mL hot aqua regia and diluted to 100 mL with water before the measurement.

Solventless reactions with BFP catalysts: In a typical procedure, a Schlenk tube equipped with a magnetic stirring bar was charged with the required quantity of catalyst, evacuated and filled with argon. 1-Octanol (1 mL) and triethylsilane (1.1 mL, 1.08 equivalents) were then added, and the resulting suspension was vigorously stirred at the required reaction temperature (thermostatted oil bath) for 24 hours. Samples of 0.1 mL were withdrawn after this period, diluted with 1 mL dichloromethane and analyzed by GC following the previously established procedure.^[4a] Catalyst recycling was performed by filtering off the catalyst under air, washing it with a little dichloromethane and drying under vacuum before starting the new run. Rhodium leaching was determined by ICP-AAS on an aliquot of the filtrate (0.5 mL), which was treated with 6 mL hot aqua regia and diluted to 100 mL with water before the measurement.

Competitive reaction experiments: A Schlenk tube equipped with a magnetic stirring bar was charged with the required quantity of catalyst, evacuated and filled with argon. 1-Octanol (1 mL), 2-octanol (1 mL, 1 equivalent) and silane (1 equivalent) were then added, and the resulting mixture was vigorously stirred at the required reaction temperature (thermostatted oil bath) for 24 hours. Samples of 0.1 mL were withdrawn after this period, diluted with 1 mL dichloromethane and analyzed by GC following the previously established procedure.^[4a]

Preparative silane alcoholysis with BFP-Rh₂(pfo)₄ catalyst: A Schlenk tube equipped with a magnetic stirring bar was charged with 27.6 mg BFP-Rh₂(pfo)₄ (0.6 μmol catalyst, 0.01 mol %), evacuated and filled with argon. 1-octanol (1 mL, 6.35 mmol) and 1 mL (6.35 mmol, 1 equivalent) triethylsilane were then added. The resulting suspension was placed in a thermostatted oil bath preheated at 80 °C and vigorously stirred for 16 hours. The solid catalyst was filtered off affording the triethylsilyl ether product; yield: 1.5 g (97%). The product was analyzed without further purification by GC, NMR spectroscopy and elemental analysis, and found to be >95% pure. Anal. calcd. for C₁₄H₃₂OSi: C 68.73, H 13.35; found: C 68.78, H 13.19.

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