

Cationic Carboxylato Complexes of Dirhodium(II) with Oxo Thioethers: Catalysts for Silane Alcoholysis under Homogeneous and Liquid-Liquid Biphasic Conditions

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Abstract: A set of cationic dirhodium(II) complexes with oxo thioethers was prepared and employed as catalysts for the silane alcoholysis reaction. The complexes were found to be highly active under homogeneous conditions, both in the absence and in the presence of a solvent, including coordinating solvents such as *N,N*-dimethylformamide; the catalysts could be conveniently employed in concentrations as low as 0.01 mol %, and a maximum TON of 30000 was recorded after 24 h. The same catalysts were also employed under liquid-liquid biphasic conditions

with an ionic liquid as the catalyst-containing phase: comparable catalytic activity was observed under these conditions, and the catalyst-containing phase could be recovered and recycled. A chiral cationic dirhodium(II) complex was also prepared in the frame of this work; kinetic resolution of a racemic alcohol was attempted with this catalyst, unfortunately without success.

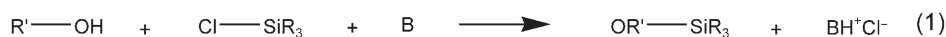
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Introduction

Silylation undoubtedly plays a major role among the routinely employed methodologies for the protection of hydroxy groups in organic synthesis.^[1] The reaction is usually accomplished utilising a chlorosilane to introduce the silyl group [Eq. (1)]. However, this invariably requires the presence of a base in order to neutralise the hydrochloric acid formed as by-product, which implies the production of one equivalent of salt per equivalent of product. Use of disilazanes together with a suitable catalyst in place of chlorosilanes is in principle much more atom economical, ammonia being the only by-product [Eq. (2)], but the usefulness of this synthetic strategy has been thus far dem-

onstrated only in the case of hexamethyldisilazane (HMDS).^[2] A more general and even more atom economical silylation protocol is represented by silane alcoholysis [Eq. (3)], where H₂ is the only by-product. Remarkably, the field of application of this reaction has been recently extended far beyond protection/deprotection strategies to embrace asymmetric synthesis,^[3] as well as the preparation and functionalisation of silicones.^[4]

A catalyst is needed in order for silane alcoholysis to proceed at a synthetically useful rate.^[5] Over the years, quite a number of catalysts have been proposed in the literature, ranging from heterogeneous metal catalysts^[6] to organic compounds^[7] and transition metal complexes.^[8] The latter appear to be currently

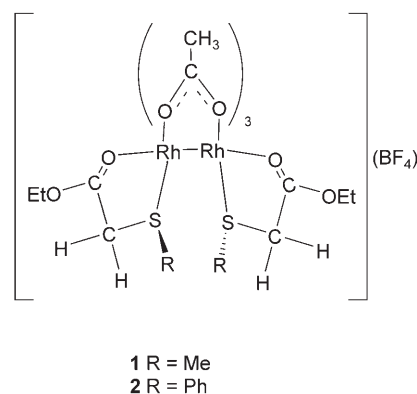


the most productive and versatile catalysts. However, most of these catalysts are quite unreactive with electron-rich trialkylhydrosilanes, which incidentally yield the most commonly employed protecting silyl ether groups.^[1] Furthermore, in many cases such catalysts require strictly anhydrous reaction 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.

We have previously shown that these disadvantages can be overcome using dirhodium(II) perfluorocarboxylate catalysts.^[9] We have built on previous results by Doyle et al., who demonstrated that dirhodium(II) perfluorobutyrate is a robust catalyst which can be used without special precautions at room temperature in dichloromethane solution.^[8n] We have developed novel reaction protocols using longer chain dirhodium(II) perfluorocarboxylates, which display higher catalyst productivities and are easily removed from the reaction mixture upon extraction into a perfluorinated phase or heterogenised by adsorption onto a perfluorinated fluorous support. Both these strategies allow to quantitatively recover and recycle the catalyst; furthermore, with the heterogenised catalyst it is possible to run the reaction in a completely solventless fashion.

Recently, we have started a related research program aimed at the preparation of different kinds of *cationic* dirhodium(II) complexes and at the evaluation of their catalytic performance in technologically relevant reactions involving silanes (silane alcoholysis, hydrosilylations, silylformylations).^[10] Our motivation is that despite the recognised fundamental importance of the electrophilicity of *neutral* dirhodium(II) complexes in determining their activity and selectivity in catalytic reactions of this kind,^[11] no study on the catalytic efficiency of related *cationic* complexes has been apparently carried out. The investigated complexes are all derived from simple dirhodium(II) acetate upon partial or complete substitution of the acetate ligands with neutral ligands such as 1,8-naphthyridine^[10a] or oxothioether molecules.^[10b] The latter ligands give rise to complexes with a rather unusual bidentate O-S coordination of the oxo thioether, highlighted in the general structure reported in Scheme 1; preliminary tests indicate that complex **1** is indeed a promising catalyst of the silylformylation of 1-hexyne with dimethylphenylsilane.^[10b]

In this contribution we report on the catalytic activity of cationic dirhodium(II) complexes with oxothioether ligands in the silane alcoholysis reaction, under homogeneous (both with and without solvent) as well as liquid-liquid biphasic conditions involving an ionic liquid as the catalyst-containing phase. The latter approach potentially allows the easy separation and reuse of the liquid phase containing the catalyst. This issue will be discussed as well. Finally, preliminary



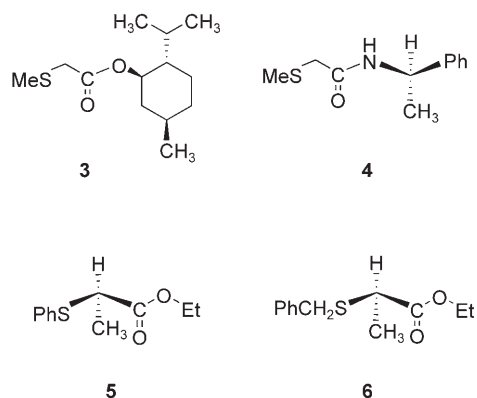
Scheme 1. Structure of the cationic dirhodium(II) complexes with oxothioether ligands.

ry results on our attempts to develop chiral variants of cationic dirhodium(II) catalysts with oxothioether ligands will be reported.

Results and Discussion

We started our work by selecting a suitable set of cationic dirhodium(II) catalysts. Besides the metal complexes which we disclosed in our previous communication on the subject,^[10b] that is, complexes **1** and **2**, we were interested in developing chiral complexes of the same kind in order to test their enantioselectivity in the silane alcoholysis reaction; indeed, such reaction is potentially useful for the kinetic resolution of alcohols; it is worth noting that diastereoselective variants of this reaction have been recently disclosed, which employ a chiral silane^[3a] or a chiral alcohol + chiral catalyst.^[3b] We started by trying to link a chiral functional group to the carboxy group of the oxothioester ligands: in particular, we envisaged the substitution of the methyl group by a (–)-menthyl one or the formation of an amide with the chiral amine (+)-1-methylbenzylamine (Scheme 2, compounds **3** and **4**) however, although it was as expected very easy to prepare the chiral ligands and the corresponding neutral adducts **7** and **8** with dirhodium(II) acetate, the synthesis of the cationic complexes proved difficult, owing to the apparent instability of the resulting complexes and/or to ligand decomposition (hydrolysis of the ester/amide function under reaction conditions). In fact, using our standard protocols for the removal of the acetate ligands with HBF₄ or Meerwein's salt OEt₃⁺BF₄[–],^[10b] complex mixtures of products were invariably obtained. Apparently, steric crowding on the carboxylate function negatively affects the stability of the resulting complex.

Better results were obtained by introducing a chiral centre on the carbon atom α to the sulfur. Enantiomerically pure ligands possessing a chiral centre in



Scheme 2. Chiral ligands 3–6.

that position (**5** and **6**) were easily prepared from enantiomerically pure (*S*)-lactate following literature procedures,^[12] and readily gave the corresponding neutral adducts **9** and **10** with dirhodium(II) acetate, albeit in much lower yields than in the case of unbranched ligands. The related cationic dirhodium(II) complexes were still characterised by limited stability, although the complexes appeared more stable than their analogues with the chiral information on the carboxy function. The cationic complex with ligand **5** was isolated only in impure form; however, we were able to purify and characterise complex **11**, derived from ligand **6**.

The far-infrared spectrum of complex **11** presents an intense band at 281 cm^{-1} , corresponding to the Rh–carboxylic oxygen stretching, in the range of similar compounds present in the literature,^[13] and a medium band at 180 cm^{-1} , corresponding to $\nu(\text{Rh}–\text{Rh})$.^[14] The last signal was absent in the parent neutral dirhodium complex, since in that case the vibration is IR silent because of the centrosymmetric structure of the compound. As expected, in the ^1H NMR spectrum two distinct set of signals for the bridging acetato ligands are present with a 2/1 intensity ratio. Furthermore in the ^{13}C NMR spectrum the carboxylic carbon of the thioether ligand is shifted well downfield from the value observed in the neutral axial adduct, as the consequence of the oxygen coordination.

Crystals of **11** suitable for X-ray structure determination were grown upon slow evaporation of a solution of the complex in acetone:*n*-hexane (1:1). In the crystals, two independent but very similar cations $[\text{Rh}_2(\text{OAc})_3[(R)\text{-PhCH}_2\text{SCH}(\text{CH}_3)\text{C}(\text{O})\text{OEt}]_2]^+$ (labelled A and B) and anions BF_4^- were found. Cations A and B have slightly different conformations but the same configuration of all chiral centers. An ORTEP view of the cation (B) is shown in Figure 1, together with the atomic labelling scheme. A selection of the most important bond distances and angles for A and B is listed in Table 1.

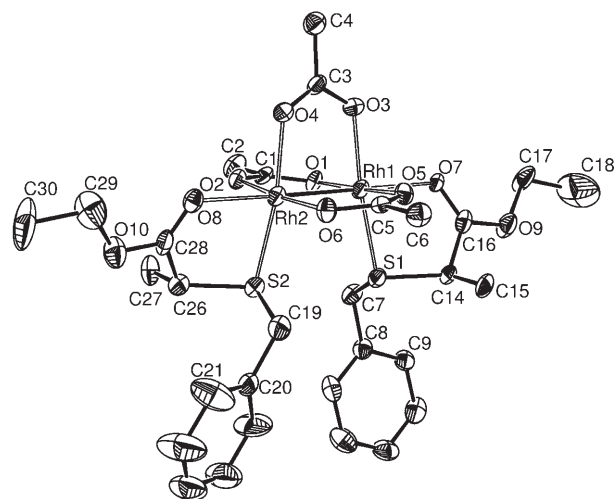


Figure 1. ORTEP view of one of the two independent cationic complexes of **11** (cation B). Ellipsoids are drawn at 30 % probability level.

Table 1. Selected bond distances [Å] and angles [deg] of complex (**11**).

	Cation A	Cation B
Rh1–Rh2	2.438(1)	2.435(1)
Rh1–O7	2.284(7)	2.311(6)
Rh2–O8	2.316(6)	2.323(6)
Rh1–S1	2.274(3)	2.260(2)
Rh2–S2	2.267(3)	2.286(3)
O7–C16	1.208(14)	1.207(11)
O8–C28	1.207(12)	1.217(12)
C14–S1	1.816(12)	1.815(9)
C26–S2	1.856(11)	1.848(11)
C16–C14	1.532(18)	1.510(14)
C26–C28	1.454(15)	1.486(16)
S1–Rh1–O7	81.32(20)	80.92(16)
S2–Rh2–O8	81.44(17)	80.33(20)

The cationic complex has an approximate C_2 symmetry and the coordination of each Rh atom is octahedral with three acetate ligands and two chiral (*R*)- $\text{PhCH}_2\text{SCH}(\text{CH}_3)\text{C}(\text{O})\text{OEt}$ ligands respectively bridging and chelating the two Rh atoms. The Rh–O bond distances involving the acetate ligands range from 2.024(6) to 2.048(6) Å and the Rh–Rh ones of 2.438(1) and 2.435(1) Å fall within the expected range for dirhodium(II) complexes. The two chiral ligands chelate through the sulfur and the carbonyl oxygen atoms, forming five membered rings. The S–Rh–O bite angles span from 80.92(16) to 81.44(17)°. The chelation rings adopt an envelope conformation. The absolute configuration of chiral C14, C26, S1, S2 atoms is *R,R,S,S*.

The cationic dirhodium(II) complexes **1**, **2** and **11** were subsequently employed as catalysts in the silane alcoholysis reaction. In order to gain a first insight

Table 2. Solventless triethylsilane alcoholysis catalysed by cationic dirhodium(II) complexes with oxothioethers.^[a]

Entry	Catalyst [mol %]	Alcohol	Yield [%]
1	Rh ₂ (OAc) ₄ (0.1)	benzyl alcohol	10
2	1 (0.1)	benzyl alcohol	100
3	1 (0.1)	1-octanol ^[b]	100
4	2 (0.1)	benzyl alcohol	100
5	11 (0.1)	benzyl alcohol	100
6	11 (0.1)	1-octanol ^[b]	96
7	11 (0.1)	1-phenylethanol	100
8	11 (0.01)	benzyl alcohol	93
9	11 (0.01)	1-phenylethanol	61
10	11 (0.01)	2-octanol	> 99

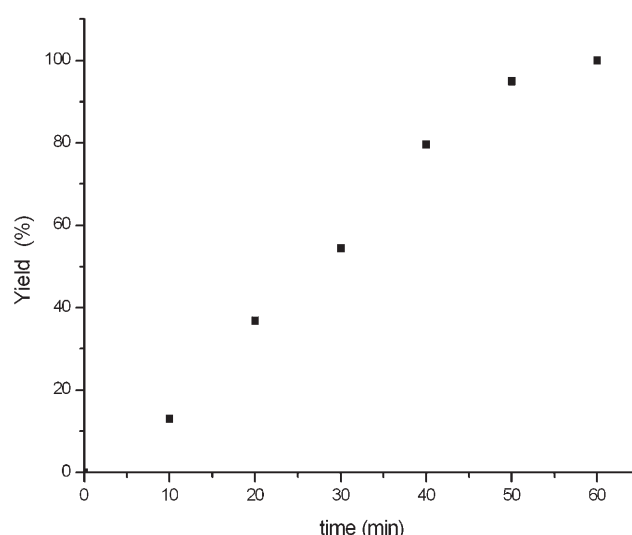
^[a] Reaction conditions: see the Experimental Section.^[b] Catalyst only partially soluble.

into the reactivity of the complexes, we chose the reaction between benzyl alcohol and triethylsilane as a suitable test reaction. We initially employed reaction conditions which already proved useful in our previous work with dirhodium(II) perfluorocarboxylates, running the reaction in a solventless fashion, with 0.1 mol % catalyst, at 50 °C for 24 h. As it is apparent from Table 2, entries 2, 4 and 5, all catalysts provided essentially quantitative yields of the silyl ether. In contrast, simple dirhodium(II) acetate gave only 10 % reaction yield under the same reaction conditions (entry 1). Thus, it was proved that the presence of a positive charge on our catalysts greatly enhanced their reactivity in this reaction.

We then moved to test other alcohols in the same reaction, such as 1-octanol and 1-phenylethanol. Although the yields with these substrates were almost quantitative as well, we observed that, in the case of hydrophobic alcohols such as 1-octanol as the reactant, the cationic catalysts were only partially soluble in the mixture of the reagents. This observation could appear as a limitation of our synthetic protocol, but on the other hand it made it apparent that the soluble fraction of the catalyst was already sufficient to drive the reaction to completion in the given reaction time. We further corroborated this hypothesis by determining the conversion profiles of the various reactions. In Figure 2, the conversion profile of the reaction with 1-phenylethanol and catalyst **11** is reported. It is apparent that even with this comparatively less reactive alcohol the reaction reaches completion in just one hour.

Consequently, we carried out some additional test reactions with complex **11** using only 0.01 mol % catalyst; as reported in Table 2, entries 8–10 the yields were still very good.

Having established the high reactivity of our catalysts in the silane alcoholysis reaction, we set out to devise means for overcoming their shortcomings. The first important limitation to be tackled was the poor

**Figure 2.** Conversion profile of the reaction with 1-phenylethanol and catalyst **11** (Table 2, entry 7)

catalyst solubility in reaction mixtures containing a hydrophobic alcohol. An obvious way to cope with this problem is to add a conventional organic solvent to the reaction mixture, and we selected 1,2-dichloroethane (DCE) as a suitable candidate. Addition of DCE had no significant effect on catalyst reactivity; yields fully comparable or even slightly superior to the tests run without solvent were reached under otherwise identical reaction conditions (Table 3). Using only 0.001 mol % catalyst, a remarkable maximum TON of 30000 was reached in 24 h with benzyl alcohol (Table 3, entry 10). This represents the highest TON ever reported for the silane alcoholysis reaction, significantly higher than that with our heterogenised dirhodium(II) perfluorocarboxylate system (maximum TON with benzyl alcohol 8300).^[9c] The corresponding average TOF also ranks among the highest ever measured, significantly better results having to the best of our knowledge been obtained only with Crabtree's catalyst [IrH₂(Solv)₂(PPh₃)₂][SbF₆]^[8o] (see, for example, Table 5 in ref.^[8d,l]). Interestingly, preliminary results obtained in polar, coordinating aprotic solvents such as DMF indicate that the catalysts are highly active under these conditions as well (Table 3, entry 17). Use of a polar, coordinating solvent is known to cause a decrease in the reactivity of most transition metal catalysts for silane alcoholysis, with very few exceptions;^[6a,8a,b] in particular, partial catalyst deactivation in even slightly coordinating solvents, evidently due to solvent competition with the reagents for coordination to the free apical positions of the complex, was observed using dirhodium(II) perfluorocarboxylate catalysts.^[9c] This finding is important in connection to the possible application of these catalysts to the protection of hydroxy groups in hydrophilic polyols such

Table 3. Triethylsilane alcoholysis in DCE catalysed by cationic dirhodium(II) complexes with oxothioethers.^[a]

Entry	Catalyst [mol %]	Alcohol	Yield [%]
1	1 (0.1)	benzyl alcohol	99
2	1 (0.01)	benzyl alcohol	75
3	1 (0.1)	1-octanol	99
4	1 (0.01)	1-octanol	95
5	1 (0.01)	2-octanol	80
6	1 (0.01)	cyclohexanol	91
7	1 (0.01)	1-phenylethanol	26
8	2 (0.1)	benzyl alcohol	100
9	2 (0.01)	benzyl alcohol	100
10	2 (0.001)	benzyl alcohol	30
11	2 (0.01)	1-octanol	99
12	2 (0.01)	2-octanol	85
13	2 (0.01)	cyclohexanol	96
14	2 (0.01)	1-phenylethanol	33
15	11 (0.1)	benzyl alcohol	96
16	11 (0.01)	benzyl alcohol	90
17 ^[b]	11 (0.1)	benzyl alcohol	100
18	11 (0.1)	1-octanol	99
19	11 (0.01)	1-octanol	93
20	11 (0.01)	2-octanol	62
21	11 (0.01)	cyclohexanol	95
22	11 (0.01)	1-phenylethanol	64
23	11 (0.01)	<i>t</i> -butyl alcohol	8

^[a] Reaction conditions: see the Experimental Section.^[b] DMF as solvent.

as carbohydrates, which are not soluble in apolar organic solvents.^[6a,8a]

No substantial difference in catalytic efficiency was observed between the various catalysts; catalyst (**1**) was only slightly less active than the other two, which exhibited fully comparable efficiency. The catalysts were found to be active with primary as well as with secondary alcohols. Secondary alcohols often gave slightly lower yields, but the observed differences in reactivity were anyway far less marked than with dirhodium(II) perfluorocarboxylate catalysts.^[8n,9] Poor reactivity was instead observed with tertiary alcohols like *tert*-butyl alcohol (Table 3, entry 23). We also performed a preliminary evaluation of the enantiomeric discrimination of **11** in the kinetic resolution of racemic 1-phenylethanol. Thus, the alcohol was reacted with 0.5 equivalents of triethylsilane under the homogeneous conditions reported in Table 3. Unfortunately, no enantioselection was observed in the reaction.

We also wanted to check the possibility of catalyst recovery and recycling, and envisaged to do so by switching from homogeneous to liquid-liquid biphasic conditions, using a second liquid phase in which only the catalyst was soluble. Given the cationic nature of our catalysts, ionic liquids offered themselves as a very natural choice.^[15] We initially employed commercial ionic liquid media from Fluka (>97% purity) such as *n*-butylmethylimidazolium tetrafluoroborate

(BMIM BF₄) and *n*-methyloctylimidazolium tetrafluoroborate (MOIM BF₄). All catalysts proved to be very well soluble in these media, whereas reagents and products built up a second organic phase when contacted with the ionic liquid. However, the reaction outcome observed with different alcohols and catalysts under these conditions was not very satisfactory. Only 20–30% yields were reached with 0.1 mol% catalyst at 50°C after 24 h. Furthermore, extensive decomposition of the catalyst was observed in the course of the reaction, with formation of rhodium colloids which then partly migrated into the reagent and product phase. Consequently, high contents of leached rhodium, usually amounting to one third to one half of the total rhodium present, were measured in the reagents and product phase.

We reasoned that the lower reactivity of the catalysts in the liquid-liquid biphasic system could be caused by the chosen ionic liquids. For example, it is well-known that impurities present in commercial imidazolium ionic liquids (water, halide anions, free 1-alkylimidazole species) may heavily affect the performance of catalysts dissolved therein.^[16] Indeed, by switching to higher purity ionic liquids containing the more stable hexafluorophosphate anion (BMIM PF₆) much better catalyst performances in the reaction between benzyl alcohol and triethylsilane could be achieved in 24 h at 50°C with only 0.01 mol% of catalyst **11**. The obtained reaction yield was, however, found to be significantly dependent on the source of the employed ionic liquid: best results were obtained with a home-made sample kindly made available to us by the group of Prof. Valeria Conte, University of Roma “Tor Vergata” (93% yield), whereas commercial high purity samples from Fluka and Solvent Innovation (>98.5% and 99% purity, respectively) gave significantly lower yields (57 and 73%, respectively) under identical reaction conditions.

Using commercial BMIM PF₆ from Solvent Innovation, we carried out a screening of different alcohols and silanes in order to assess the applicability of the liquid-liquid biphasic system. As can be seen from Table 4, entries 1–8, most primary and secondary alcohols and silanes could be converted using 0.01 mol% catalyst of **11**, with catalytic efficiencies in many instances fully comparable to those observed in the homogeneous system (Table 3), in spite of the fact that the employed ionic liquid was not the optimal one. Only the reactivity of 2-octanol was found to be unexpectedly low in comparison to other tested secondary alcohols, although a somewhat lower reactivity was observed with this alcohol also using the homogeneous system. Considering the silane screening, Me₂PhSiH (Table 4, entry 7) displayed a reactivity similar to Et₃SiH, while sterically encumbered silanes such as *t*-BuMe₂SiH (Table 4, entry 8) gave unsatisfactory yields; these results are in accordance with those

Table 4. Silane alcoholysis in ionic liquids catalysed by cationic complex **11**.^[a]

Entry	Alcohol	Silane	Yield [%]
1	benzyl alcohol	Et ₃ SiH	73
2	2-phenylethanol	Et ₃ SiH	99
3	1-phenylethanol	Et ₃ SiH	45
4	1-octanol	Et ₃ SiH	50
5	2-octanol	Et ₃ SiH	14
6	cyclohexanol	Et ₃ SiH	99
7	benzyl alcohol	Me ₂ PhSiH	65
8	benzyl alcohol	<i>t</i> -BuMe ₂ SiH	17
9 ^[b]	benzyl alcohol	Et ₃ SiH	57
10 ^[c]	benzyl alcohol	Et ₃ SiH	20

^[a] Reaction conditions: see the Experimental Section.

^[b] Recycle of entry 1.

^[c] Recycle of entry 9.

obtained with dirhodium(II) perfluorocarboxylate catalysts.^[9c]

We also preliminarily evaluated the ease of recovery and recycling of the catalyst. After the first catalytic run under the conditions of Table 4, entry 1, the ionic liquid phase containing the catalyst was successfully separated by simple decantation and extraction with diethyl ether. ICP-AAS analysis of the Rh content in the organic phase demonstrated that 90 % of rhodium was recovered in this case. The catalyst-containing phase was recycled twice (Table 4, entries 9 and 10) but a significant decrease in the reaction yield, most notable after the second recycle, was apparent. This is most probably the consequence of partial catalyst decomposition, as qualitatively confirmed by the progressive darkening of the catalyst-containing phase. Thus, although the use of commercial BMIM PF₆ enables an efficient recovery of the precious metal from the reaction mixture, it does not allow us at this stage to perform repeated recycles of the same catalyst batch. On the other hand, we are confident that besides the efficiency of the catalytic system also the effectiveness of the recovery/recycling procedure can be further improved to a significant extent through optimisation of the employed high-purity ionic liquid.

Conclusions

In conclusion, we have demonstrated that cationic dirhodium(II) complexes with oxothioether ligands are highly efficient catalysts for silane alcoholysis. In comparison with dirhodium(II) perfluorocarboxylates, the catalysts exhibit higher reactivity, in particular with secondary alcohols. Furthermore, the catalysts appear to work well under solventless conditions, in the presence of organic solvents (including polar, coordinating ones), and also under liquid-liquid biphasic conditions. These findings clearly point out that placing a

positive charge on dirhodium(II) complexes can be considered as a viable strategy for rendering them efficient electrophilic catalysts in respect to more conventional ligand substitution with electron-withdrawing groups. The peculiar nature of the employed thioether ligands, that are expected to act as hemilabile ligands with the carbonyl group being displaced by the silane in solution, may also positively contribute to the catalytic efficiency of these catalysts. Use of these catalysts under liquid-liquid biphasic conditions allows a convenient separation of the catalyst from the products; on the other hand, partial catalyst decomposition under the employed reaction conditions prevents at present its efficient recycling. We are currently aiming at developing more robust cationic dirhodium(II) complexes and optimised reaction conditions in order to overcome this limitation.

Experimental Section

Synthesis of the Neutral Complex {Rh₂(OAc)₄[(*R*)-PhCH₂SCH(CH₃)C(O)OEt]₂} (**10**)

Rh₂(OAc)₄ (360 mg, 0.82 mmol) was suspended in toluene (25 mL). (*R*)-PhCH₂SCH(CH₃)C(O)OEt (**6**) (380 mg, 16.8 mmol) was then added, and the reaction mixture was stirred for 3 h at room temperature, evaporated to a small volume under reduced pressure, and treated with diethyl ether to afford the product as a purple solid, which was filtered and dried under vacuum. Yield: 25 %. Anal. calcd. for C₃₂H₄₄O₁₂Rh₂S₂ (M=890.6): C 43.55, H 4.98, S 7.20; found: C 43.69, H 5.27, S 7.14 %; ¹H NMR (CDCl₃): δ=1.25 (t, 3H, CH₃CH₂), 1.64 (d, 3H, CH₃CH), 1.88 (s, 6H, CH₃COO⁻), 3.94 (q, 1H, CH), 4.04 (q, 2H, CH₃CH₂), 4.32 (AB system, 2H, CH₂Ph), 7.25–7.55 (m, 5H, Ph); ¹³C NMR (CDCl₃): δ=14.0 (CH₃CH₂), 15.5 (CH₃CH), 23.8 (CH₃COO⁻), 36.2 (CH₂Ph), 42.7 (CH), 61.2 (CH₃CH₂), 127.2–130.5 (Ph), 171.9 [C(O)OEt], 191.4 (CH₃COO⁻); FT-IR (KBr): ν=3056–2882, 1734, 1589, 1435, 1235, 381, 351, 329 cm⁻¹.

Synthesis of the Cationic Complex {Rh₂(OAc)₃[(*R*)-PhCH₂SCH(Me)C(O)OEt]₂}BF₄ (**11**)

{Rh₂(OAc)₄[(*R*)-PhCH₂SCH(Me)C(O)OEt]₂} (**10**) (210 mg, 0.23 mmol) was dissolved in dichloromethane (25 mL) and 42 μL of a 54 % w/w solution of HBF₄ in diethyl ether (0.3 mmol) were added to the resulting solution. The reaction mixture was stirred for 3 h, during which time the color changed from purple to green; evaporation to a small volume under reduced pressure and treatment with diethyl ether afforded a green compound, which was filtered off and dried under vacuum. Yield: 84 %. Anal. calcd. for C₃₀H₄₁BF₄O₁₀Rh₂S₂ (M=918.4): C 39.24, H 4.50, S 6.98; found: C 39.67, H 4.88, S 6.48 %; ¹H NMR (CDCl₃): δ=1.42 (t, 6H, CH₃CH₂), 1.54 (d, 6H, CH₃CH), 1.96 (s, 6H, CH₃COO⁻), 2.47 (s, 3H, CH₃COO⁻), 3.80 (AB system, 4H, CH₂Ph), 4.04 (q, 2H, CH), 4.64 (q, 4H, CH₃CH₂), 7.35–7.55 (m, 10H, Ph); ¹³C NMR (CDCl₃): δ=14.0 (CH₃CH₂), 17.5 (CH₃CH), 22.6 and 24.5 (CH₃COO⁻), 38.6 (CH₂Ph), 51.2

(CH), 66.2 (CH₃CH₂), 129.1–131.2 (Ph), 181.5 [C(O)OEt], 188.3 and 193.3 (CH₃COO[−]); FT-IR (KBr): ν =3061–2850, 1657, 1570, 1447, 1254, 1082, 1003, 376, 359, 322, 281, 173 cm^{−1}.

Solventless Catalytic Tests; General Procedure

The reaction was run in a Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the rhodium catalyst (0.01 mmol, 0.1 mol %), evacuated and filled with argon. The alcohol (10 mmol) was then added and the resulting solution was heated with stirring to 50 °C in a thermostated water bath. After addition of triethylsilane (15 mmol, 1.5 equivs.) the solution was further stirred at 50 °C for 24 h. After this period, the yield was determined spectroscopically or by gas chromatography. In the case of benzyl alcohol and 1-phenylethanol, yields were determined by NMR analysis of a drop of the reaction mixture dissolved in CDCl₃. In the case of the other alcohols, 0.1 mL samples of reaction mixture were instead withdrawn, diluted with 1 mL dichloromethane and analysed by gas chromatography (on a Shimadzu GC-8 A instrument equipped with a 25 m OV-1701 capillary column: 100 °C isotherm for 60 s followed by heating at 16 °C min^{−1} to 200 °C). The GC system was previously calibrated by determining the retention times and the response factors of the alcohol reagents and of the silylated products. Experiments with 0.01 mol % catalyst were run as described above with 0.002 mol catalyst, 20 mmol alcohol and 30 mmol triethylsilane.

Catalytic Tests in Homogeneous Solution; General Procedure

The reaction was run in a Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the required amount of rhodium catalyst (0.01 mmol, 0.1 mol %), evacuated and filled with argon. The solvent (1,2-dichloroethane or dimethylformamide, 6.5 mL for experiments with 0.1 mol % of catalyst, 0.7 mL with 0.01 mol % catalyst, 0.5 mL with 0.001 mol % of catalyst) and the alcohol (10 mmol) were added and the resulting solution was heated with stirring to 50 °C in a thermostated water bath. After addition of triethylsilane (15 mmol, 1.5 equivs.) the mixture was further stirred at 50 °C for 24 h. After this period, the residue was analysed by NMR (for benzyl alcohol, 1-phenylethanol and *tert*-butyl alcohol) or by GC (for the 1-octanol, 2-octanol and cyclohexanol) to determine the yield, as described above. Experiments with 0.01 mol % catalyst were run as described above with 0.002 mol catalyst, 1.6 mL solvent, 20 mmol alcohol and 30 mmol triethylsilane. Experiments with 0.001 mol % catalyst were run as described above with 0.0001 mol catalyst (0.1 mL of a 1 M solution in the solvent of choice), 0.5 mL solvent, 10 mmol alcohol and 15 mmol triethylsilane.

Catalytic Tests in Liquid-Liquid Biphasic Systems; General Procedure

The reaction was run in a Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the rhodium catalyst (0.001 mmol, 0.01 mol %), evacuated and filled with argon. The ionic liquid (0.7 mL) and the alcohol

(10 mmol) were added and the resulting mixture was heated with stirring to 50 °C in a thermostated water bath. After addition of triethylsilane (15 mmol, 1.5 equivs.) the mixture was further stirred at 50 °C for 24 h. After this period, the organic phase was separated and the ionic liquid phase was extracted with diethyl ether (3 × 5 mL). The organic phases were combined and the solvent was removed under reduced pressure. The residue was analysed for the determination of the yield as described above. The extent of rhodium leaching was determined by digestion in 6 mL hot aqua regia of an 0.5 mL aliquot of the organic phase in the reaction mixture. The resulting solution was diluted to 100 mL with water and its rhodium content was determined by ICP-AAS.

Kinetic Resolution of Alcohols

The reaction was run in a Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the rhodium catalyst (**11**) (7 mg, 0.008 mmol), evacuated and filled with argon. 1-Phenylethanol (0.9 mL, 8 mmol, 1 equiv.) and triethylsilane (0.6 mL, 4 mmol, 0.5 equivs.) were then added and the resulting solution was stirred at room temperature. 10 μ L samples of the reaction mixture were withdrawn at regular intervals, diluted with 0.6 mL CDCl₃ and analysed by NMR, until the conversion of the silane was complete. The enantiomeric excess was determined by ¹H NMR in CDCl₃ solution after addition of 0.2 equivs. of the chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethylene]-(-)-camphorato]praseodymium(III).

Supporting Information Available

Synthetic procedures for the preparation of ligands and complexes, summary of X-ray crystallographic data for the structure determination of [Rh₂(OAc)₃((*R*)-PhCH₂SCH(Me)C(O)OEt)₂]BF₄.

X-ray crystallographic files are available in CIF format (CCDC 653126). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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