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Transfer Hydrogenation Reactions Catalyzed by Free or Silica-Immobilized $[RuCl_2(ampy)\{RN(CH_2PPh_2)_2\}]$ Complexes

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The complexes *cis*-$[RuCl_2(ampy)\{R^1N(CH_2PPh_2)_2\}]$ [ampy = (2-aminomethyl)pyridine, R^1 = C_6H_5 or $(CH_3CH_2O)_3Si(CH_2)_3$] showed very high catalytic activity in the homogeneous transfer hydrogenation of acetophenone (TOF > 300000 h^{-1}) with the use of 2-propanol as the hydrogen donor and in the presence of sodium isopropoxide. The ligand $(CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$ (ATM) was prepared in high yield by reacting (3-aminopropyl)triethoxysilane, paraformaldehyde, and diphenylphosphane in toluene heated at 80 °C. The $-N(CH_2PPh_2)_2$ function was attached to the surface of three different kinds of silica by means of two alternative methods. Thus, MA-Si-150 and mesoporous MA-Si-MCM-41 were prepared by the reaction of the inorganic matrix with ATM, whereas MA-Si-60 was synthesized by reaction of the commercially available 3-aminopropyl-functionalized silica gel with HCHO and $PHPh_2$ in refluxing toluene. The $-(CH_2)_3N(CH_2PPh_2)_2$ functionalized inorganic materials were used to anchor the $RuCl_2(ampy)$ moiety; thus, three different silica-immobilized versions of the *cis*-$[RuCl_2(ampy)(ATM)]$ complex were obtained. The silica-anchored complexes were tested in the transfer hydrogenation of acetophenone, which was found to be fast and quantitative; the effect of the nature of the silica support on the activity of the catalyst was almost negligible. It was possible to reuse the catalytic system for a second cycle without a decrease in the activity, but the efficiency of the catalyst considerably diminished in successive reuses.

Introduction

The catalytic transfer hydrogenation of ketones has recently emerged as a useful and convenient method to prepare secondary alcohols, including chiral compounds.[1] Several transition-metal complexes have been found to catalyze the reduction of ketones by using 2-propanol as a hydrogen donor or the system formic acid/triethylamine. In particular, significant results were obtained, mainly by Noyori and co-workers, using ruthenium(II) complexes with monotosylated diamines[2] or amino alcohols.[3] These catalysts, as well as those based on rhodium and iridium with the same type of ligands, have been largely investigated in recent years by several research groups.[4] Many efforts have been made to design highly efficient catalysts but, for large-scale applications, increasing activity and productivity of the catalytic reactions is still a target of primary importance as is the ability to separate, recover, and recycle the catalyst.

Recently, we reported the synthesis of a series of phosphanyl–Ru^{II} complexes bearing the (2-aminomethyl)pyridine (ampy)[5–8] ligand or the related 6-(4′-methylphenyl)-2-pyridylmethylamine ligand,[9,10] and examined their ability to catalyze the reduction of ketones. Among complexes with the ampy ligand, exceptionally high catalytic activity was observed for complexes also bearing diphosphane ligands (Figure 1) with the *cis* isomer showing higher efficiency. TOF values up to 4×10^5 h^{-1} and *ee* values up to 94% with the use of chiral diphosphane ligands were obtained.[7] The analogous species with two triphenylphosphane ligands was less active;[7] however, they seemed to be suitable precursors for the anchoring of the $RuCl_2(ampy)$ moiety to a solid support. The grafting of a complex active in the homogeneous phase to an inert solid support is find-

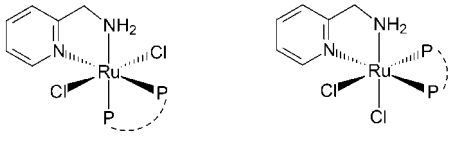

Figure 1. Ru^{II}–ampy complexes efficient in transfer hydrogenation.

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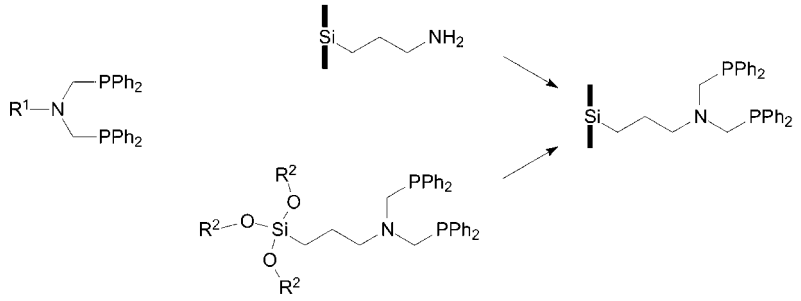


Scheme 1.

ing fast growing interest because the use of immobilized catalysts can provide a significant improvement to overcome the problems of separation and recycling of the catalyst. Silica is the most common support for the heterogenization of molecular catalysts[11] owing to its high stability, inertness, and low cost, all of which render this matrix attractive for medium-scale synthesis and industrial applications. However, the use of catalysts immobilized on inorganic supports for the transfer hydrogenation of ketones is still rare.

With the very active *cis*-[$RuCl_2$(ampy)(dppp)][7] [dppp = 1,3-bis(diphenylphosphanyl)propane] complex in mind, we turned our attention to the $R^1N(CH_2PPh_2)_2$ ligand (Scheme 1), which is topologically analogous to dppp, easily prepared, and used to anchor the $RuCl_2$(ampy) moiety to a solid support. A suitable choice for the R^1 group, as in the case of $(OR^2)_3Si(CH_2)_3$–, allows the diphosphane to be conveniently grafted onto a silica support. Alternatively, the $–N(CH_2PPh_2)_2$ function linked to the inorganic matrix can be obtained by reacting a suitable amino-functionalized silica with H_2CO and PPh_2H (Scheme 1).

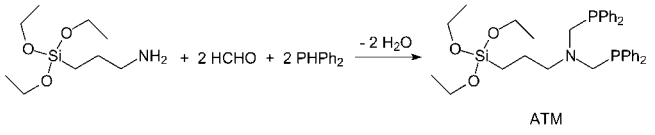
Similar Ru^{II}-functionalized silicas, where the metal is surrounded by a $Cl_2N_2P_2$ donor set, were prepared by Kumar and Ghosh starting from supports with ethylenediamino arms.[12] Such catalytic systems were successfully applied to the hydrogenation of carbonyl compounds. Furthermore, Reek, van Leeuwen, and co-workers used silica-immobilized Ru^{II} complexes for the asymmetric reduction of acetophenone where the metal was anchored to the inert support by chelation to an aminoalcohol moiety.[13] Finally, Tu and co-workers investigated the asymmetric transfer hydrogenation of different prochiral ketones by using Ru^{II} complexes immobilized on amorphous or mesoporous silicas functionalized through chiral diamine arms.[14]

In this paper, we present the preparation and characterization of the Ru^{II} complexes [$RuCl_2$(ampy){$R^1N(CH_2PPh_2)_2$}] [R^1 = C_6H_5 or $(CH_2)_3Si(OCH_2CH_3)_3$] as well as of three different $–N(CH_2PPh_2)_2$ functionalized silicas along with the corresponding Ru^{II} derivatives containing the $RuCl_2$(ampy) moiety. Furthermore, the catalytic application of both free and immobilized complexes to the transfer hydrogenation of acetophenone by using 2-propanol as the hydrogen source is reported and discussed.

Results and Discussion

Synthesis and Characterization of the Diphosphanes and Diphosphanyl-Functionalized Silicas

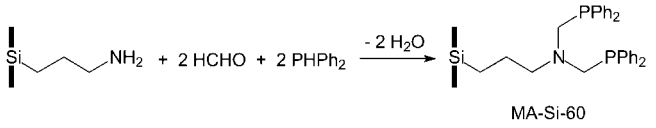
Following a known synthetic method,[15] the diphosphane (3-{bis[(diphenylphosphanyl)methyl]amino}propyl)-triethoxysilane (ATM) was obtained as a colorless oil by reacting (3-aminopropyl)triethoxysilane with paraformaldehyde and diphenylphosphane in a 1:2.5:2 molar ratio in toluene heated at 80 °C [Equation (1)]. Unreacted paraformaldehyde was easily eliminated by filtration after dissolving the crude product in ethyl ether. The product, which was isolated in high yield, showed a single resonance at δ = –28.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a clean ^1H NMR spectrum, which confirmed its very high purity.



(1)

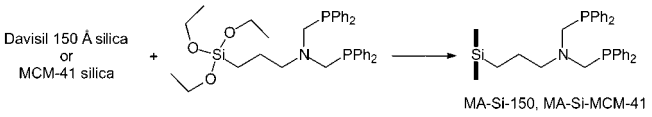
As the morphology of the inorganic support (surface area and porosity) as well as the distance between the catalytic sites could influence the activity of the anchored transition-metal complex,[11] we prepared three different silica-immobilized versions of the ATM ligand. The first one was synthesized according to Equation (2) by starting from the commercially available 3-aminopropyl-functionalized silica gel (mean pore size: 60 Å, surface area: 550 $m^2 g^{-1}$, loading: 1 $mmol g^{-1}$), which was heated at reflux in toluene for 48 h together with HCHO and $PHPh_2$. The product, 3-{bis-[(diphenylphosphanyl)methyl]amino}propyl-functionalized silica gel (MA-Si-60) was obtained as a white cream powder, which was characterized by elemental analysis (C, H, N, P), TGA measurements, and CP-MAS ^{31}P NMR spectroscopy. The latter confirmed the presence of the anchored diphosphane function (broad singlet at δ = –25.3 ppm). Two minor broad signals centered at δ = 20.3 and 30.8 ppm, within the range for the P=O resonances, and a shoulder on the high-field signal were indicative of the formation of small amounts of products resulting from the oxidation of the ligand.[16] Furthermore, from the elemental analysis of ni-

trogen and phosphorus, it was possible to determine 0.86 and 0.70 mmol g^{-1} loading, respectively. The relative P/N molar ratio (1.6) is lower than that expected (2.0) for total conversion of the $–NH_2$ functions to $–N(CH_2PPh_2)_2$. This finding could be reasonably explained in terms of a material still showing about 20% of the amine function unchanged. The possibility of formation of $HNCH_2PPh_2$ functions on the inorganic surface seems to be excluded by the NMR spectroscopic data, though the presence of both $–NHCH_2PPh_2$ and $–N(CH_2PPh_2)_2$ groups cannot be excluded as the resonances of the P nuclei could be superimposed. It should be noted that no appreciable variation in the loading was observed when the reaction time was increased, whereas a lower value (0.49 mmol g^{-1}, based on P analysis) was determined when the reaction was stopped after 24 h. Two further preparations of MA-Si-60 confirmed the good reproducibility of the synthesis.



(2)

Two other 3-{bis[(diphenylphosphanyl)methyl]amino}-propyl-functionalized silicas, namely, MA-Si-150 and MA-Si-MCM-41, were conveniently prepared starting from Davisil silica with a 150 Å mean pore size and a surface area of 300 $m^2 g^{-1}$ and MCM-41 mesoporous silica with a surface area of 1000 $m^2 g^{-1}$, respectively. Both were obtained by combining ATM and the appropriate matrix in toluene heated at 80 °C according to Equation (3). As per MA-Si-60, the two products were characterized by elemental analysis. The calculated loading, based on phosphorus, was 0.46 mmol g^{-1} for MA-Si-150 and 0.59 mmol g^{-1} for MA-Si-MCM-41. As observed for MA-Si-60, the syntheses of MA-Si-150 and MA-Si-MCM-41 showed very good reproducibility. Compounds MA-Si-60, MA-Si-150, and MA-Si-MCM-41 were also characterized by TGA measurements, which were run under an atmosphere of argon in the temperature range 20–800 °C. From 20 to ca. 250 °C, all samples showed about 5% weight loss due to water release, whereas the progressive weight decrease above 250 °C was attributed to organic material release only. Thus, in the range 250–800 °C, MA-Si-60, MA-Si-150, and MA-Si-MCM-41 lost 24, 15, and 20% of their weight, respectively. These data, combined with the relative amounts of $–(CH_2)_3NH_2$ and $–(CH_2)_3N(CH_2PPh_2)_2$ groups, present in each material, calculated from the P/N molar ratio, allowed MA-Si-60, MA-Si-150, and MA-Si-MCM-41 to be obtained following the loading 0.64, 0.39, and 0.50 mmol g^{-1}, respectively. Such values are lower than those obtained from the elemental analysis of phosphorus.



(3)

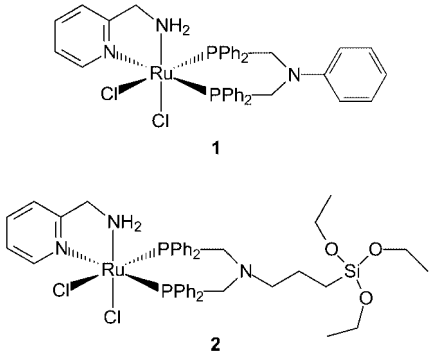


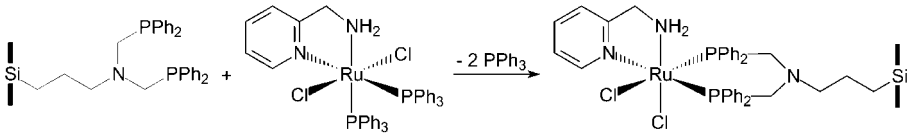
Figure 2. Ru^{II}–ampy complexes with the ligands $PhN(CH_2PPh_2)_2$ and ATM.

Synthesis of the Ruthenium(II)–ampy Complexes

The synthesis of the six-coordinate *cis*-$[RuCl_2(ampy)\{R^1N(CH_2PPh_2)_2\}]$ [$R^1 = C_6H_5$ **1**, $R^1 = (CH_2)_3Si(OCH_2CH_3)_3$ **2**] (Figure 2) complexes was carried out as described previously for analogous compounds starting from $[RuCl_2(PPh_3)_3]$, ampy, and the diphosphane in a 1:1:1 molar ratio.[7] The complexes precipitated spontaneously as sand yellow microcrystals from hot solutions of toluene and were almost insoluble in common solvents. However, acceptable quality $^{31}P\{^1H\}$ NMR spectra were recorded from saturated CD_2Cl_2 solutions. The spectra of **1** and **2** appeared as AB spin systems with a coupling constant of about 45 Hz; the doublets of **1** were centered at δ = 39.7 and 43.2 ppm and those of **2** at δ = 37.8 and 45.9 ppm. As the NMR spectroscopic parameters agree with those found for the *cis*-$[RuCl_2(ampy)(dppp)]$[7] complex, we propose for complexes **1** and **2** the same stereochemistry to that shown by *cis*-$[RuCl_2(ampy)(dppp)]$, with P-*trans*-Cl and P-*trans*-N(pyridine) arrangements. As a matter of fact, this represents the common stable geometry shown by several complexes bearing ampy and different diphosphane ligands with C_3 and C_4 backbones.[7]

Synthesis and Characterization of Silica-Immobilized Ruthenium(II) Complexes

As depicted in Equation (4), by reacting the appropriate functionalized silica and the *trans,cis*-$[RuCl_2(PPh_3)_2(ampy)]$ complex in boiling 2-propanol, three different Ru^{II}-based immobilized catalysts, namely, Ru-MA-Si-60, Ru-MA-Si-150, and Ru-MA-Si-MCM-41, were prepared. The catalysts were thoroughly washing with dichloromethane to eliminate all traces of physisorbed metal–organic species from the inert support. All materials appeared as yellow to yellow–orange microcrystalline solids, which were characterized by

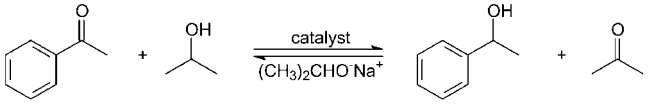


(4)

elemental analysis (C, H, N, Ru) and TGA measurements in the range 20–800 °C to assess the metal loading. The yield of the reaction (based on ruthenium), was generally high (88, 91, and 84% for Ru-MA-Si-60, Ru-MA-Si-150, and Ru-MA-Si-MCM-41, respectively). The calculated loading values were 0.35, 0.29, and 0.33 mmol g^{-1} of complex, in the respective order. To address the reaction to the formation of the *cis* dichloro isomer immobilized on silica, the reagents were heated at reflux and allowed to react for 2 h. In the case of Ru-MA-Si-60, a ^{31}P CP/MAS NMR spectroscopic investigation was undertaken. The spectrum showed, in addition to signals due to uncoordinated diphosphane and the corresponding oxide, two signals at δ = 47 and 53 ppm. The rather large line width may be the reason for the lack of observable coupling between the two inequivalent P nuclei. The NMR measurements are in agreement with the presence of a unique Ru^{II} species immobilized on the inert support.

Transfer Hydrogenation of Acetophenone in the Homogeneous Phase

The metal-catalyzed transfer hydrogenation of ketones was accomplished by using 2-propanol as the hydrogen donor heated at reflux [Equation (5)]. It is well-documented that the presence of a strong base as a cocatalyst enhances the rate of the reaction.[17] Accordingly, all catalytic tests were run in the presence of sodium 2-propoxide generated by dissolution of metallic sodium into the alcohol.



(5)

As complexes **1** and **2** showed only partial solubility in 2-propanol, even when heated at reflux and in catalytic conditions, we turned our attention to in situ prepared catalytic systems. Thus, the catalytic reactions were carried out with the use of a 0.1 M solution of acetophenone in 2-propanol in the presence of 0.05 mol-% of the *cis,cis*-[$RuCl_2(PPh_3)_2$(ampy)] complex, 0.06 mol-% of the appropriate $R^1N(CH_2PPh_2)_2$ ligand, and 2 mol-% of $(CH_3)_2CHO^-Na^+$ (substrate/Ru/base = 2000:1:40) under reflux conditions. ^{31}P NMR spectroscopic monitoring of a dilute $CDCl_3$ solution containing *trans,cis*-[$RuCl_2(PPh_3)_2$(ampy)] and the ligand ATM in a 1:1 molar ratio showed that on increasing the temperature the PPh_3 ligands are completely replaced by the diphosphane ligand and that after prolonged heating the only Ru-containing species detectable in solution was complex **2**. Analogous results were obtained by monitoring the *trans,cis*-[$RuCl_2(PPh_3)_2$(ampy)]/[$C_6H_5N(CH_2PPh_2)_2$] system, for which the exclusive formation of **1** was observed. These findings confirm that the in situ prepared catalytic systems effectively correspond to isolated complexes **1** and **2**, which are obtained in almost insoluble form in refluxing toluene.

A comparison of the catalytic efficiency of the complexes bearing $R^1N(CH_2PPh_2)_2$ ligands with that of isostructural *cis*-[$RuCl_2$(ampy)(dppp)] shows that the modification of the diphosphane by substitution of the central carbon atom of the P–C–C–C–P skeleton with a N–R^1 moiety has only a little influence on the activity of the relative ruthenium complex. As a matter of fact, by using complexes **1** and **2**, the catalytic reduction of acetophenone was completed (98%) within 1 min (Table 1, Entries 1 and 2), and the corresponding very high TOF values (>300000 h^{-1} at 50% conversion) were of the same magnitude to that found for *cis*-[$RuCl_2$(ampy)(dppp)] (220000 h^{-1}).[7]

Transfer Hydrogenation of Acetophenone in the Heterogeneous Phase

All three silica-immobilized ruthenium complexes were examined as catalysts in the transfer hydrogenation of acetophenone. Standard reactions were carried out by using 500:1 and 20:1 acetophenone/Ru and $(CH_3)_2CHO^-Na^+$/Ru molar ratios, respectively, at the reflux temperature of 2-propanol (82 °C). The results are collected in Table 1. Although, as expected, the immobilized complexes were much less active than their counterparts in the homogeneous phase, a quantitative conversion of the substrate into 1-phenylethanol was observed within 90 min (Table 1, Entries 3–5), and the results showed that the nature of the inorganic support played an almost negligible role on the performance of the catalyst. An analogous behavior was observed for ruthenium complexes anchored on mesoporous MCM-41 and MCM-48 and amorphous silicas.[12] The concentration of the strong base is crucial for the activity of the supported complex. In fact, a decrease in the $(CH_3)_2CHO^-Na^+$/Ru molar ratio from 20:1 to 5:1 resulted in a 94% conversion achieved in 8 h by using Ru-MA-Si-MCM-41 (Table 1, Entry 6). It should be stressed that the stability of the functionalized silicas Ru-MA-Si-60, Ru-MA-Si-150, and Ru-MA-Si-MCM-41, as well as that of the precursor 3-aminopropyl-functionalized silica gel, towards $(CH_3)_2CHO^-Na^+$ was analyzed. All samples, after treatment with a 20-fold excess of base for 2 h at 100 °C showed a 15–20% reduction in the linked organic moiety (based on nitrogen analysis). These results are in agreement with the metal

Table 1. Catalytic transfer hydrogenation of acetophenone with the use of silica-supported complexes at 82 °C.

Entry[a]	Catalyst	S/C[b]	B/C[c]	Yield[d] [%]	Time [min]
1	*cis*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)]/$PhN(CH_2PPh_2)_2$[e]	2000	40	98	1[f]
2	*cis*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)]/ATM[e]	2000	40	98	1[g]
3	Ru-MA-Si-60	500	20	97	90
4	Ru-MA-Si-150	500	20	99	90
5	Ru-MA-Si-MCM-41	500	20	99	90
6	Ru-MA-Si-MCM-41	500	5	94	480
7	Ru-MA-Si-150	500	20	99	90
7(1)	–	–	–	99	240
7(2)	–	–	–	12	1440
8	Ru-MA-Si-150	100	20	99	60
8(1)	–	–	–	98	60
8(2)	–	–	–	98	720
8(3)	–	–	–	82	1440
9	Ru-MA-Si-MCM-41[h]	500	20	6	720

[a] The values reported in parenthesis for Entries 7 and 8 indicate the successive reuses of the catalyst. [b] Substrate/catalyst(Ru) molar ratio. [c] Base/catalyst molar ratio. [d] The yield of 1-phenylethanol was determined by GC. [e] Reaction run in the homogeneous phase, Ru/ligand, 1:1.2 molar ratio. [f] TOF = 320000 h^{-1} (turnover frequency = mol of acetophenone converted to 1-phenylethanol per mole of catalyst per hour at 50% conversion). [g] TOF = 340000 h^{-1}. [h] At 40 °C.

leaching measured after the first use of the catalyst (see below).

Recycling tests were run on all three silica-immobilized ruthenium complexes with the use of both the 500:1 and the 100:1 substrate/ruthenium molar ratios. As almost identical results were observed with the three different silica supports, only those obtained with the representative Ru-MA-Si-150 catalyst are presented in Table 1. By using a high substrate/ruthenium molar ratio, such as 500:1, the activity of the recycled catalyst in the second run resulted reduced [Table 1, Entries 7 and 7(1)], although complete conversion of acetophenone into 1-phenylethanol was achieved. In the next reuse, only low amounts of product were obtained, which indicates that there is a breakdown in the catalytic system [Table 1, Entry 7(2)]. The measurements were repeated by using a lower substrate/ruthenium molar ratio (100:1). As can be seen in Table 1 [Entries 8–8(3)], the efficiency of the catalyst was apparently retained in the first reuse, but then it drastically decreased; however, in the third run the substrate underwent complete transformation into 1-phenylethanol. It should be stressed that in each successive catalytic trial, the recovered catalyst was mixed not only with acetophenone and solvent, but also with a 20-fold excess of $(CH_3)_2CHO^-Na^+$ with respect to the amount of ruthenium effectively present. It is important to note that the efficiency of the catalyst did not appreciably fade from the first to the second use. This finding should be compared with the observed breakdown in the activity of complexes **1** and **2**, as well as of all similar derivatives,[7] when reused as homogeneous catalysts.

As decomposition processes should be reduced by working at low temperature, the catalytic potential of Ru-MA-Si-MCM-41 was verified at 40 °C. In this case, the reaction proceeded at an extremely low rate as only 6% conversion was observed after 12 h (Table 1, Entry 9). ICP MS measurements carried out on both Ru-MA-Si-150 and Ru-MA-Si-MCM-41 systems treated at 100 °C for 2 h in the presence of a strong excess of $(CH_3)_2CHO^-Na^+$ (20:1 with respect to the metal) indicated that for both samples about 15% of the ruthenium present in the immobilized catalyst was released into the solution. Not surprisingly, analogous results concerning the metal leaching were obtained by measuring the ruthenium amount in solution after the first catalytic trial. By contrast, an almost negligible metal leaching (<2%) was measured in the successive reuse of the catalyst. Thus, as the activity of the immobilized complex remained unchanged from the first to the second use, one can conclude that the ruthenium released into the solution is present in a catalytically inactive form. It should be noted that ^{31}P NMR spectroscopic measurements run on the recovered solutions did not give any useful information about the decomposition pattern of the catalyst. The neat decline of the efficiency of the catalyst in the successive reuses can be ascribed to a decomposition of the structure of the supported metal complex.

Conclusions

We have shown that the *cis*-[$RuCl_2$(ampy)-{$R^1N(CH_2PPh_2)_2$}] complexes are highly efficient homogeneous catalysts in the transfer hydrogenation of acetophenone with 2-propanol and that they may have great potential for a broad application in the reduction of carbonyl compounds. We have also demonstrated that the anchoring of the $RuCl_2$(ampy) moiety to a silica support can be easily accomplished when the surface of the inorganic matrix is prior functionalized with $-N(CH_2PPh_2)_2$ arms. Such a modification of the support was done by two alternative pathways, which allowed the syntheses of three different mesoporous or amorphous silicas and of the relative immobilized ruthenium(II) complexes. These systems have shown to be catalytically active in the transfer hydrogenation of acetophenone, which is rapidly and quantitatively transformed into 1-phenylethanol. Recovery and recycling of the inorganic material still resulted in good catalytic perform-

ance but only for the first reuse as decomposition of the catalyst limited successive reuses.

Experimental Section

General: All reagents were purchased from Aldrich and used without further purification. Commercial reagent grade solvents were dried according to standard methods and freshly distilled under an atmosphere of argon before use. All syntheses and manipulations were carried out under an atmosphere of argon by using either standard Schlenk or glove box techniques. The diphosphane $PhN(CH_2PPh_2)_2$[15b] and the complexes $[RuCl_2(PPh_3)_3]$,[18] *trans*,*cis*-$[RuCl_2(PPh_3)_2(ampy)]$,[7] and *cis*,*cis*-$[RuCl_2(PPh_3)_2(ampy)]$[7] were synthesized according to literature procedures. The solution of $(CH_3)_2CHO^-Na^+$ in 2-propanol used in the catalytic trials was prepared by dissolving 46 mg of freshly cut Na into 20 mL of solvent and kept under an atmosphere of argon in the dark. The ^1H and ^{31}P NMR spectra in solution (at 200.13 and 81.02 MHz, respectively) were recorded with a Bruker AC 200 F QNP spectrometer. The ^1H chemical shifts were referenced to $SiMe_4$, whereas positive ^{31}P NMR chemical shifts are reported downfield from 85% H_3PO_4 as an external standard. The NMR characterization of solid samples was performed with a Bruker AC 200 spectrometer equipped for solid state analysis. Samples were spun at 7000 Hz in 7 mm diameter zirconia rotors with Kel-F caps. ^{31}P SPE MAS NMR spectra were obtained at 80.90 MHz by using a single pulse experiment and high-power proton decoupling, with 120 s relaxing delay. ^{31}P NMR chemical shifts were externally calibrated with respect to solid triphenylphosphane at $\delta = -7.2$ ppm and were referenced to 85% H_3PO_4. The GC analyses of the catalytic mixtures were run with a Fisons GC 8000 Series gas chromatograph equipped with a Supelco PTA-5 column [30 m long, 0.53 mm i.d., coated with a 3.0 μm poly(5% diphenyl-95% dimethylsiloxane) film] Injector temperature was kept at 250 °C and the column temperature was programmed from 50 °C to 170 °C with a gradient of 8 °C min^{-1}. The elemental analyses (C, H, N) were carried out at the Microanalytical Laboratory of the Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, with a Carlo Erba 1106 elemental analyzer. Phosphorus and ruthenium quantitative determination were carried out at the Dipartimento di Scienze e Tecnologie Chimiche and the Dipartimento di Scienze Agrarie e Ambientali, Università di Udine by using a Varian Vista MPX axial Inductively Coupled Plasma-Optical Emission spectrometer (for the determination of P) and a Spectro Analytical Instruments Spectromass 2000 Type MSDIA10B Inductively Coupled Plasma Mass spectrometer (for the determination of Ru). Samples (20 mg) were digested on a microwave apparatus MILESTONE Mega 1200 by use of 1 mL of 65% HNO_3, 0.4 mL of 30% H_2O_2 and 0.1 mL of 40% HF with a mineralization program at 650 W for 20 min in Teflon vessels. Thermogravimetric analyses were performed by using a TA Instrument (Waters) TGA Q500 apparatus. Weight loss was measured in the range 20–800 °C with a heating rate of 10 °C min^{-1}, under an argon atmosphere.

(3-{Bis[(diphenylphosphanyl)methyl]amino}propyl)triethoxysilane (ATM): A mixture of (3-aminopropyl)triethoxysilane (0.89 g, 4.0 mmol), paraformaldehyde (0.30 g, 10 mmol) and diphenylphosphane (1.49 g, 8.0 mmol) was stirred in toluene (20 mL) and heated at 80 °C for 1 h with complete dissolution of solid paraformaldehyde. The solvent was removed under vacuum. The resulting oil was treated with ethyl ether (20 mL), the mixture was filtered, and the product was recovered from the solution as a colorless oil by elimination of the solvent under vacuum. Yield: 2.18 g (88%). ^1H NMR (200 MHz, $CDCl_3$, 295 K): δ = 7.1–7.5 (m, 20 H, *phenyl*), 3.73 (q, $J_{H,H}$ = 7.0 Hz, 6 H, CH_2CH_3), 3.55 (d, $J_{P,H}$ = 3.3 Hz, 4 H, NCH_2P), 2.82 (m, 2 H, CH_2CH_2N), 1.48 (m, 2 H, $CH_2CH_2CH_2$), 1.16 (t, $J_{H,H}$ = 7.0 Hz, 9 H, CH_3), 0.46 (m, 2 H, CH_2Si) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 295 K): δ = 138.2 (d, $J_{C,P}$ = 12.8 Hz, C^i), 133.0 (d, $J_{C,P}$ = 18.3 Hz, C^o), 128.3 (C^p), 128.2 (d, $J_{C,P}$ = 8.5 Hz, C^m), 59.2 (t, $J_{C,P}$ = 9.2 Hz, CH_2CH_2N), 58.6 (dd, $J_{C,P}$ = 5.5, 9.1 Hz, NCH_2P), 58.2 (CH_2CH_3), 19.7 ($CH_2CH_2CH_2$), 18.3 (CH_2CH_3), 7.6 (CH_2Si) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 295 K): δ = –28.0 ppm.

***cis*-[$RuCl_2$(ampy){$PhN(CH_2PPh_2)_2$}] (1):** $[RuCl_2(PPh_3)_3]$ (384 mg, 0.40 mmol) and 2-(aminomethyl)pyridine (45 mg, 0.42 mmol) were mixed in toluene (15 mL), and the slurry was heated at reflux for 2 h. The ligand $PhN(CH_2PPh_2)_2$ (196 mg, 0.40 mmol) was then added, and the mixture was heated at reflux for another 20 h. Upon cooling, a sand yellow powder precipitated, which was isolated by filtration, washed with ethyl ether, and dried under reduced pressure. Yield: 225 mg (73%). $C_{38}H_{37}Cl_2N_3P_2Ru$ (769.66): calcd. C 59.30, H 4.85, N 5.46; found C 59.23, H 4.66, N 5.31. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2): δ = 39.7 (d, $J_{P,P}$ = 44.7 Hz), 43.2 (d, $J_{P,P}$ = 44.7 Hz) ppm.

***cis*-[$RuCl_2$(ampy)(ATM)] (2):** As for **1**, but with the use of the ATM ligand instead of $PhN(CH_2PPh_2)_2$. Sand yellow solid. Yield: 246 mg (68%). $C_{41}H_{53}Cl_2N_3O_3P_2RuSi$ (897.90): calcd. C 54.84, H 5.95, N 4.68; found C 54.01, H 5.92, N 4.59. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2): δ = 37.8 (d, $J_{P,P'}$ = 46.2 Hz), 45.9 (d, $J_{P,P'}$ = 46.2 Hz) ppm.

Preparation of 3-{Bis[(diphenylphosphanyl)methyl]amino}propyl-Functionalized Silica Gels

MA-Si-60 from Silica with 60 Å Mean Pore Size: A mixture of 3-aminopropyl-functionalized silica gel (60 Å mean pore size) (1.00 g, 1.0 mmol of amine), paraformaldehyde (90 mg, 3.0 mmol), and diphenylphosphane (465 mg, 2.5 mmol) was stirred in toluene (20 mL) and heated at reflux for 48 h. A cream white product was recovered by filtration, washed with ethyl ether, and dried under vacuum. Yield: 1.15 g. Composition found: C 19.90, H 2.30, N 1.21, P 4.32. TGA analysis (20–800 °C, under argon): Δw = 24% (water loss excluded).

MA-Si-150 from Silica with 150 Å Mean Pore Size: A mixture of Davisil silica gel (150 Å mean pore size) (510 mg), which was activated by heating at 150 °C under vacuum for 15 h, and ATM (302 mg) was stirred in toluene (10 mL) and heated at 110 °C for 20 h. The pale yellow mixture was cooled, filtered, washed with toluene, dichloromethane, ethanol, and ethyl ether, and finally dried under reduced pressure to obtain a cream white solid. Yield: 782 mg. Composition found: C 13.01, H 1.56, N 0.77, P 2.83. TGA analysis (20–800 °C, under argon): Δw = 14% (water loss excluded).

MA-Si-MCM-41 from MCM-41 Mesoporous Silica: A mixture of MCM-41 mesoporous silica gel (440 mg) which was activated by treatment at 150 °C under vacuum for 2 h, and ATM (310 mg) was stirred in toluene (10 mL) and heated at 110 °C for 18 h. After cooling, the mixture was filtered, and the white solid was washed with toluene, dichloromethane, ethanol, and ethyl ether. The white product was then dried under reduced pressure. Yield: 714 mg. Composition found: C 19.87, H 2.21, N 0.96, P 3.64. TGA analysis (20–800 °C, under argon): Δw = 20% (water loss excluded).

Synthesis of Silica-Supported Ru^{II} Complexes

Ru^{II} Complex Supported on MA-Si-60 Silica (Ru-MA-Si-60): A suspension of silica MA-Si-60 (100 mg) and *trans*,*cis*-$[RuCl_2(PPh_3)_2(ampy)]$ (32 mg) was heated at reflux in 2-propanol (5 mL) for 2 h.

After cooling, the mixture was filtered, and the solid was carefully washed with 2-propanol, dichloromethane (until the discarded solvent resulted colorless), and ethyl ether to give a yellow powder, which was dried under reduced pressure. Yield: 102 mg. Composition found: C 21.29, H 2.47, N 1.55, Ru 3.48. TGA analysis (20–800 °C, under argon): Δw = 20% (water loss excluded).

Ru^{II} Complex Supported on MA-Si-150 Silica (Ru-MA-Si-150): Ru-MA-Si-150 was prepared as indicated above for Ru-MA-Si-60 from silica MA-Si-150 (100 mg) and *trans*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)] (26 mg). The isolated product is a yellow powder. Yield: 92 mg. Composition found: C 15.38, H 1.70, N 1.10, Ru 3.22. TGA analysis (20–800 °C, under argon): Δw = 16% (water loss excluded).

Ru^{II} Complex Supported on MA-Si-MCM-41 Silica (Ru-MA-Si-MCM-41): Ru-MA-Si-MCM-41 was prepared as indicated above for Ru-MA-Si-60 from functionalized mesoporous silica MA-Si-MCM-41 (100 mg) and *trans*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)] (32 mg). The product is a yellow–orange microcrystalline powder. Yield: 99 mg. Composition found: C 20.95, H 2.18, N 1.34, Ru 3.41. TGA analysis (20–800 °C, under argon): Δw = 20% (water loss excluded).

Studies on the Stability of the Functionalized Silicas Towards Sodium Isopropoxide: A 25-mL Schlenk was charged with silica (3-aminopropyl-functionalized silica gel, MA-Si-60, MA-Si-150, or MA-Si-MCM-41) (15 mg), 2-propanol (10 mL), and the suitable amount of a 0.1 M solution of $(CH_3)_2CHO^-Na^+$ in 2-propanol to obtain a 1:20 molar ratio between the organic function linked to silica and base. The mixture was warmed under an atmosphere of argon, at 100 °C for 2 h. After cooling, the solid was filtered off, washed with 2-propanol and dichloromethane, dried, and analyzed (C, H, N).

Catalytic Transfer Hydrogenation of Acetophenone in Homogeneous Phase: Two solutions containing (a) acetophenone and (b) *cis*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)]/ATM were prepared as follows: (a) a 50-mL Schlenk was charged with acetophenone (240 μL, 2 mmol) and 2-propanol (19 mL), and the vessel was put into an oil bath at 100 °C; (b) a 10-mL Schlenk was charged with *cis*,*cis*-[$RuCl_2(PPh_3)_2$(ampy)] (4.0 mg, 5 μmol), ATM (6.8 mg, 10 μmol), 2-propanol (3 mL), and $(CH_3)_2CHO^-Na^+$ (0.1 M in 2-propanol, 2 mL). The mixture was then gently warmed until complete dissolution of the complex was achieved. Finally, 1 mL of solution (b) was added to solution (a) kept at reflux, with immediate starting of the catalytic reaction. For the GC analysis of the reaction mixture, 0.2 mL of the solution was extracted by means of a syringe, cooled, mixed with ethyl ether (2 mL), and the resulting suspension was passed through a microcolumn filled with silica gel to eliminate any inorganic material.

General Procedure for the Transfer Hydrogenation of Acetophenone with Silica-Supported Catalysts: Under an argon atmosphere, a 25-mL Schlenk was charged with the silica-anchored ruthenium(II) complex (10^{-3} mmol of metal). Then, 2-propanol (10 mL) and $(CH_3)_2CHONa$ (0.1 M in 2-propanol, 0.2 mL) were added and the mixture was heated at reflux. Finally, by addition of acetophenone (0.5 mmol) the catalytic reaction started. Samples for the GC analysis were prepared as indicated above.

General Procedure for Recycling of Silica-Supported Catalysts: The mixture recovered after the first catalytic trial was centrifuged, and the solution was discarded. The solid was washed with dichloromethane and 2-propanol and vacuum dried. It was then weighed and transferred into a 25-mL Schlenk, which was charged under an atmosphere of argon, with 2-propanol and $(CH_3)_2CHO^-Na^+$ (0.1 M in 2-propanol). The mixture was warmed to reflux, and the catalytic reaction was started by the addition of acetophenone. Amounts of solvent, base, and substrate were based on the weight of the recovered catalyst to maintain a constant substrate/metal/base ratio. Analogous procedures were adopted for successive reuses of the catalysts.

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