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Articles

Preparation, Characterization, and Performance of the Supported Hydrogen-Bonded Ruthenium Catalyst [(sulphos)Ru(NCMe)$_3$](OSO$_2$CF$_3$)/SiO$_2$. Comparisons with Analogous Homogeneous and Aqueous-Biphase Catalytic Systems in the Hydrogenation of Benzylideneacetone and Benzonitrile

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The Ru(II) complex [(sulphos)Ru(NCMe)$_3$](OSO$_2$CF$_3$) (**1**) has been immobilized on partially dehydroxylated high-surface-area silica via hydrogen-bonding interactions between the silanol groups of the support and the SO$_3^-$ groups from both the sulphos ligand and the triflate counteranion (sulphos = $^-$O$_3$S(C$_6$H$_4$)CH$_2$C(CH$_2$PPh$_2$)$_3$). Compound **1** has been authenticated in the solid state by a single-crystal X-ray analysis and in solution by NMR spectroscopy, while its silica-grafted form [(sulphos)Ru(NCMe)$_3$](OSO$_2$CF$_3$)/SiO$_2$ (**1**/SiO$_2$) has been characterized by DRIFT and CP MAS ^{31}P NMR studies. The supported hydrogen-bonded (SHB) complex **1**/SiO$_2$ is an effective and selective catalyst for the hydrogenation of benzylideneacetone to benzylacetone and of benzonitrile to benzylidenebenzylamine in *n*-octane. No appreciable ruthenium leaching into the hydrocarbon phase was observed in either case. Analogous hydrogenation reactions catalyzed by either the aqueous-biphase catalyst **1** in water/*n*-octane or the homogeneous analogue [(triphos)Ru(NCMe)$_3$](OSO$_2$CF$_3$)$_2$ in THF have been carried out (triphos = MeC(CH$_2$PPh$_2$)$_3$). The silica-supported catalyst is slightly less active but much more selective and recyclable than the soluble congeners. In an attempt to rationalize the selectivity exhibited by the SHB catalyst, various model studies have been performed in different phase variation systems. Incorporation of the results obtained led to the conclusion that, in contrast to fluid solution reactions, no heterolytic splitting of H$_2$ at ruthenium occurs in the heterogeneous phase.

Introduction

The development of efficient methods for the separation of homogeneous catalysts from substrates and products is being intensely pursued in both industry and academia.[1] A relatively widespread paradigm involves the immobilization of a molecular catalyst on solid supports, among which silica plays a major role for its resistance to elevated temperatures and most solvents

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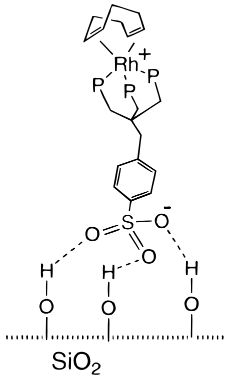
as well as its ease of functionalization.[2,3] Covalent grafting to silica is commonly achieved by either coordination of organometallic fragments to donor ligands already bound to the support (e.g. phosphines and amines) or reaction of the isolated silanols on the silica surface with various reactive groups contained in the molecular structure of the tethered metal complexes ($-Si(OR)_3$, NR_2, $-OH$).[3] Covalent anchoring of homogeneous catalysts to the inner walls of mesoporous silica has also been reported.[4]

In a recent work, we have introduced an alternative, facile, and clean method of preparing silica-tethered polyphosphine metal catalysts, denoted supported hydrogen-bonded (SHB) catalysts, for use in both solid−gas and solid−liquid reactions in hydrocarbon solvents.[5] The procedure involves a hydrogen-bonding interaction between the silanol groups of the support and a sulfonate group far away from the phosphorus donor atoms of the ligands. In this way, all the metal centers are potential reagents dispersed on a very high interfacial area. One of these SHB catalysts, namely (sulphos)Rh(cod)/SiO_2, was successfully employed in the heterogeneous hydrogenation and hydroformylation of alkenes (sulphos = $^{-}O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$; cod = cycloocta-1,5-diene):



(sulphos)Rh(cod)/SiO_2

In either case, no appreciable rhodium leaching was observed, while an effective catalyst recycling was simply accomplished by standard filtration procedures. Moreover, in all the cases investigated there was no evidence whatsoever of the formation of contiguous Rh−Rh sites, indicating that the catalytically active sites were isolated rhodium complexes, as in the homogeneous phase.

Encouraged by the results obtained with the immobilization of the zwitterionic complex (sulphos)Rh(cod), we decided to explore the possibility of extending the SHB methodology to cationic metal complexes, of which very few heterogenized examples, obtained via the ion-pairing technique, are known.[6] To this purpose, we synthesized the Ru(II) complex $[(sulphos)Ru(NCMe)_3](OSO_2CF_3)$ (**1**). In this paper is described the immobilization of **1** on silica and is reported a preliminary study of the potential of the resulting SHB catalyst $[(sulphos)Ru(NCMe)_3](OSO_2CF_3)/SiO_2$ (**1**/SiO_2) in the heterogeneous hydrogenation of α,β-unsaturated ketones and organic nitriles. The performances of both the aqueous-biphase catalyst **1** and the homogeneous catalyst $[(triphos)Ru(NCMe)_3](OSO_2CF_3)_2$ (triphos-**1**) were scrutinized in the same hydrogenation reactions under experimental conditions comparable with those of the SHB catalyst (triphos = $MeC(CH_2PPh_2)_3$). This comparative study has shown that the rates of the reactions with the SHB catalyst are slower than those with the homogeneous and biphasic congeners; the heterogeneous reactions show a much higher chemoselectivity, however.

Experimental Section

General Information. All reactions and manipulations were routinely performed under a nitrogen or argon atmosphere by using standard Schlenk techniques. CH_2Cl_2 (Fluka, $H_2O \leq 0.005\%$) was further distilled from CaH_2. Deuterated solvents for NMR measurements (Merck, Aldrich) were dried over molecular sieves. All the other reagents and chemicals were reagent grade and were used as received by commercial suppliers. The ruthenium complexes $Na[\{(sulphos)Ru\}_2(\mu\text{-}Cl)_3]$,[7] $[(triphos)Ru(NCMe)_3](OSO_2CF_3)_2$ (triphos-**1**),[8] and (triphos)Ru(H)(BH_4)[9] were prepared as previously described. All the isolated metal complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Elemental analyses (C, H, N) were performed using a Carlo Erba Model 1106 elemental analyzer. Atomic absorption analyses for the metal complexes were performed with a Perkin-Elmer 5000 instrument. Batch reactions under a controlled pressure of gas were performed with a stainless steel Parr 4565 reactor (100 mL) equipped with a Parr 4842 temperature and pressure controller. GC analyses of the solutions were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column. The Davison 62 (Grace) silica employed in this work is a high-surface-area ($S_{BET} = 357$ m^2/g), hydrophilic mesoporous material, with a narrow pore size distribution ($\phi = 13.8$ nm). The pore volume is 1.23 cm^3/g, as determined by adsorption of nitrogen at −196 °C. The support was ground, washed with 1 M HNO_3 and then with distilled water to neutrality, and dried overnight in an oven at 100 °C.

Synthesis of $[(sulphos)Ru(NCMe)_3](OSO_2CF_3)$ (1). To a suspension of the dimer $Na[\{(sulphos)Ru\}_2(\mu\text{-}Cl)_3]$ (2.9 g, 1.5 mmol) in MeCN (100 mL) was added 1.67 g (6.5 mmol) of $Ag(OSO_2CF_3)$. After this mixture was refluxed for 5 h under nitrogen, the pale yellow suspension was cooled to room temperature and the AgCl precipitate was removed by filtration. The resulting solution was concentrated to ca. half volume in vacuo. Addition of toluene (25 mL) caused the precipitation of **1** as colorless crystals, which were washed with toluene and ethyl ether and then dried under a stream of nitrogen. Yield: 70%. Anal. Calcd (found) for $C_{54}H_{51}F_3N_3O_6P_3RuS_2$: C, 56.25 (55.84); H, 4.46 (4.53); N, 3.64 (3.62); Ru, 8.76 (8.29). IR (cm^{-1}): 2318 (w, CN str, MeCN), 2286 (w, CH_3 def + CC str, MeCN). ^1H NMR (MeCN-d_3, 20 °C): δ 7.93 (d, 2H, $J(HH) = 8$ Hz, $m\text{-}C_6H_4$), 7.61 (d, 2H, $J(HH) = 8$ Hz, $o\text{-}C_6H_4$), 7.5−7.1 (m, 30H,

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Ph), 3.31 (m, 2H, C*H*$_2$C$_6$H$_4$), 2.69 (m, 6H, CH$_2$P), 2.22 (s, 9H, MeCN). ^{31}P{^{1}H} NMR (MeCN-*d*$_3$, 20 °C): δ 26.8 (s).

Well-shaped crystals of **1**·2MeCN·H$_2$O, suitable for an X-ray analysis, were obtained by slow crystallization from MeCN/toluene solutions of **1** under nitrogen at room temperature. Anal. Calcd (found) for $C_{58}H_{59}F_3N_5O_7P_3RuS_2$: C, 55.59 (55.11); H, 4.75 (4.67); N, 5.59 (5.41).

Synthesis of [(sulphos)Ru(NCMe)$_3$]BPh$_4$ (1BPh$_4$). To a solution of **1** (150 mg, 0.13 mmol) in 30 mL of MeCN was added solid NaBPh$_4$ (220 mg, 0.65 mmol) at room temperature. Addition of ethanol (50 mL) followed by concentration of the solution under a steady stream of nitrogen gave white crystals of **1**BPh$_4$, which was collected by filtration and washed with ethanol and *n*-pentane. Yield: 90%. Anal. Calcd (found) for $C_{77}H_{71}BN_3O_3P_3RuS$: C, 69.89 (69.41); H, 5.41 (5.38); N, 3.18 (3.22). IR (cm^{-1}): 2312 (w, CN str, MeCN), 2280 (w, CH$_3$ def + CC str, MeCN), 1580 and 613 (m, BPh$_4$). ^{1}H NMR (MeCN-*d*$_3$, 20 °C): δ 7.94 (d, 2H, *J*(HH) = 8 Hz, *m*-C$_6$H$_4$), 7.62 (d, 2H, *J*(HH) = 8 Hz, *o*-C$_6$H$_4$), 7.5−6.8 (m, 50H, Ph), 3.31 (m, 2H, C*H*$_2$C$_6$H$_4$), 2.72 (m, 6H, CH$_2$P), 2.23 (s, 9H, MeCN). ^{31}P{^{1}H} NMR (MeCN-*d*$_3$, 20 °C): δ 27.2 (s).

Synthesis of (sulphos)Ru(CO)$_2$(OSO$_2$CF$_3$) (2). A solution of **1** (23 mg, 0.02 mmol) in 70 mL of CH$_2$Cl$_2$ was introduced by suction into a Parr reactor previously evacuated by a vacuum pump. After pressurization with 3 bar of CO, the autoclave was stirred (500 rpm) for 2 h at room temperature. After the reactor was depressurized and vented under a nitrogen stream, the contents were transferred into a Schlenk-type flask. Evaporating the solvent under vacuum gave a yellow solid, which was filtered off and washed with *n*-pentane. Yield: 86%. Anal. Calcd (found) for $C_{50}H_{42}F_3O_8P_3RuS$: C, 55.30 (54.89); H, 3.90 (3.78). IR (cm^{-1}): 2088 and 2050 (s, CO). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 7.98 (d, 2H, *J*(HH) = 8 Hz, *m*-C$_6$H$_4$), 7.64 (d, 2H, *J*(HH) = 8 Hz, *o*-C$_6$H$_4$), 7.6−6.8 (m, 30H, PPh), 3.65 (m, 2H, C*H*$_2$C$_6$H$_4$), 3.5−2.8 (m, 6H, CH$_2$P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): AM$_2$ pattern, δ(P$_A$) 30.1 (t, *J*(PP) = 32.5 Hz), δ(P$_M$) −2.3 (d).

Synthesis of [(sulphos)Ru(CO)$_2$(NCMe)]BPh$_4$ (3). Compound **3** was obtained in 60% yield from **1**BPh$_4$ and CO as described above for **2**. Anal. Calcd (found) for $C_{75}H_{65}BNO_5P_3RuS$: C, 69.44 (69.11); H, 5.05 (4.86); N, 1.08 (0.92). IR (cm^{-1}): 2308 (w, CN str, MeCN), 2280 (w, CH$_3$ def + CC str, MeCN), 2092 and 2050 (s, CO), 1578 and 612 (m, BPh$_4$). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 7.98 (d, 2H, *J*(HH) = 8 Hz, *m*-C$_6$H$_4$), 7.68 (d, 2H, *J*(HH) = 8 Hz, *o*-C$_6$H$_4$), 7.6−6.7 (m, 50H, Ph), 3.61 (m, 2H, C*H*$_2$C$_6$H$_4$), 3.3−2.9 (m, 6H, CH$_2$P), 2.23 (s, 3H, MeCN). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): AM$_2$ pattern, δ(P$_A$) 30.1 (t, *J*(PP) = 31.7 Hz), δ(P$_M$) −2.4 (d).

Sequential Reactions of 1 with H$_2$ and CO. A solution of **1** (23 mg, 0.02 mmol) in CH$_2$Cl$_2$ (70 mL) was introduced by suction into a Parr reactor previously evacuated by a vacuum pump. After pressurization with 30 bar of H$_2$ at room temperature, the autoclave was heated to 100 °C with stirring (500 rpm). After 2 h, the reactor was cooled to −40 °C and depressurized. The gas phase was analyzed by GC, showing the presence of NH$_3$. GC and GC/MS analysis of the cold liquid phase showed the formation of NEt$_3$. The contents were warmed to room temperature and then gently swept with a flow of Ar to remove the dissolved H$_2$. The reactor was pressurized with CO to 3 bar at room temperature. After 2 h, the reactor was depressurized and the contents were transferred into a Schlenk-type flask. The volatiles were evaporated in vacuo, and the resulting crude solid product was characterized as **2** by NMR spectroscopy.

Sequential Reactions of triphos-1 with H$_2$ and CO in CH$_2$Cl$_2$. (A) High-Pressure NMR Experiment (HPNMR). A 10 mm sapphire HPNMR tube was charged with a solution of triphos-**1** (50 mg, 0.04 mmol) in CD$_2$Cl$_2$ (2 mL) under nitrogen. After ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded, the tube was pressurized with 30 bar of H$_2$ at room temperature. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The NMR analysis showed the complete disappearance of the starting complex already after 30 min at 80 °C, with formation of a new species that we assign as the unstable bis(ammonia) complex [(triphos)Ru(NH$_3$)$_2$(OSO$_2$CF$_3$)](OSO$_2$CF$_3$) (triphos-**4**, ^{31}P{^{1}H} NMR δ(P$_A$) 41.7 (t, *J*(PP) = 37.1 Hz), δ(P$_M$) 27.5 (d)). Formation of amines of the type NR$_2$Et (R = H, Et; triplets and doublets at δ(H) 1.2 and 3.1, *J*(HH) = 7.3 Hz) was found to occur during the transformation of triphos-**1** into triphos-**4** by ^{1}H NMR spectroscopy. When all of triphos-**1** had disappeared, NEt$_3$ was the only amine present in solution. The tube was then removed from the probe of the spectrometer and depressurized. After the solution inside the tube was swept with a flow of Ar to remove the dissolved H$_2$, the tube was pressurized with 3 bar of CO. NMR spectra, acquired every 20 min for 2 h, showed the gradual conversion of triphos-**4** into the known [(triphos)Ru(CO)$_2$(OSO$_2$CF$_3$)](OSO$_2$CF$_3$) (triphos-**2**).[8]

(B) Preparative Experiments. All our attempts to isolate triphos-**4** by scaling up the NMR experiment in a Parr autoclave were unsuccessful. In all cases, extensive decomposition to give several sulphos-Ru products occurred. In contrast, triphos-**2** was isolated in the solid state by following the procedure employed for the HPNMR experiment.

Reaction of [(triphos)RuH$_3$]$^-$ with HBF$_4$·OEt$_2$ in the Presence of MeCN. A sample of the ruthenate complex [(triphos)RuH^3]$^-$ was generated in a screw-cap 5 mm NMR tube from (triphos)Ru(H)(BH$_4$) (10 mg, 0.013 mmol) and KOBu^t (5 mg, 0.04 mmol) in THF-*d*$_8$ (1 mL).[10] After the selective formation of the ruthenate complex was confirmed by NMR spectroscopy, MeCN (200 μL) was syringed into the tube. A rapid check of the reaction mixture by ^{31}P{^{1}H} NMR spectroscopy showed that the ruthenate complex had not reacted with MeCN at room temperature. At this point, a 3-fold excess of HBF$_4$·OEt$_2$ was syringed into the tube, which was then immediately introduced into the spectrometer. In a ^{31}P{^{1}H} NMR spectrum immediately acquired, only the tris(acetonitrile) complex triphos-**1** was detected, while a ^{1}H NMR spectrum showed the presence of free H$_2$ and no formation of hydrogenation products of MeCN.

Heterogenization of 1. The silica-grafted complex **1**/SiO$_2$ was prepared by the solvent impregnation method previously described.[5] To this purpose, the silica was pretreated as follows: in air at 500 °C for 3 h; under vacuum (10^{-5} Torr) overnight at the same temperature; rehydration with deionized water by stirring for 3 h followed by drying at room temperature; in air at 300 °C for 3 h; under vacuum (10^{-5} Torr) overnight at the same temperature. In a typical experiment, the ruthenium precursor **1** (ca. 100 mg) was stirred in anhydrous CH$_2$Cl$_2$ at room temperature under Ar. The resulting suspension was added to pretreated silica (ca. 500 mg) in 10 mL of anhydrous CH$_2$Cl$_2$. Stirring was maintained for 6 h at room temperature. The separation of the grafted material was performed with a Pyrex Büchner filtering funnel under Ar. Once separated as yellowish powders, the solid products were washed several times with 10 mL portions of CH$_2$Cl$_2$. The grafted complex was maintained under vacuum (10^{-3} Torr) overnight at room temperature and, afterward, stored under Ar prior to use. With this procedure, catalysts with metal loadings up to 1.6 wt % were obtained in a reproducible way. The Ru contents were determined by inductively coupled plasma atomic emission (ICP-AES) with a Jobin Yvon (Series JY24) instrument at a sensitivity level of 500 ppb. Each sample (20−50 mg) was treated in a microwave-heated digestion bomb (Milestone, MLS-200) with concentrated HNO$_3$ (1.5 mL), 98% H$_2$SO$_4$ (2 mL), 37% HCl (0.5 mL), and a pellet (0.5 g) of a digestion aid reagent (0.1% Se in K$_2$SO$_4$). After the silica particles were filtered off, the solutions were analyzed. The addition of selenium was necessary to get an effective digestion

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of the phosphine ligand, which was hardly achievable by usual acid dissolution procedures. The same digestion method was employed to determine the Ru contents in the metal products recovered after catalysis as well as the organic solutions.

IR Spectroscopy. In situ diffuse reflectance infrared (DRIFT) spectra were recorded on a Digilab FTS-40 instrument fitted with a Harrick DRA-2CI diffuse reflectance accessory equipped with a Harrick HVC catalytic chamber with ZnSe windows, which allows one to acquire spectra of the sample in granular form under controlled temperature and pressure conditions. The DRIFT cell was connected to a flow system suited to flow purified gases or to evacuate the cell at 10^{-3} Torr. A trap containing molecular sieves was installed between the Ar cylinder and the flow system to reduce the water content. The model organometallic complexes or **1**/SiO_2 (20 mg) were transferred into the cell sample holder using a drybox. After the cell was purged with an Ar flow at room temperature for 10 min, an infrared spectrum was recorded. All spectra were recorded against a KBr standard at 4 cm^{-1} resolution with accumulation of 300 scans for each spectrum using a TGS detector. The spectra were converted into Kubelka−Munk units and plotted against wavenumbers.

The IR spectra of the sulphos and triphos complexes were routinely recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates.

In Situ DRIFT Studies of the Reactions of 1/SiO_2 with CO or H_2. The solid−gas reactions of **1**/SiO_2 with either CO or H_2 have been monitored by using a DRIFT cell. The grafted ruthenium product was heated under a stream of gas (6 mL min^{-1}) at a heating rate of 3 °C min^{-1}. All spectra were recorded against a KBr standard at 4 cm^{-1} resolution with accumulation of 150 scans during the thermal treatments and 300 scans when not specified otherwise. The volatile products were detected downstream in the carrier gas by means of an on-line quadrupole mass spectrometer (Leda-Mass Satellite, 0−200 amu), interfaced to the DRIFT cell with a stainless steel line. Details of the apparatus are described elsewhere.[11] The choice of the mass channels to be monitored was made on the basis of the standard mass spectra, available in the literature. To obtain specific information about the solid−gas reaction with H_2, the following mass channels (*m*/*z*, mass fragment, compound) were chosen: 45, $CH_3CH_2NH_2^+$, $CH_3CH_2NH_2$; 41, $CH_2{=}C{=}N^+$, CH_3CN; 29, HCO^+, H_2CO; 28, CO^+ and N_2^+, CO and N_2; 14, N^+, N-containing; 12, C^+, C-containing.

NMR Spectroscopy. Liquid-phase ^1H (200.13 MHz) and $^{31}P\{^1H\}$ (81.01 MHz) NMR spectra were obtained on a Bruker ACP 200 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H) or 85% H_3PO_4 (^{31}P). High-pressure NMR (HPNMR) experiments were carried out on the Bruker ACP 200 instrument. The high-pressure 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Firenze, Italy).[12] *Note*: *Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.*

Solid-state ^{31}P NMR spectra were recorded at room temperature on a Bruker AMX 300 WB spectrometer equipped with a 4 mm BB-CP MAS probe at a working frequency of 121.50 MHz. The spectra were recorded using the cross-polarization pulse sequence[13] under magic angle spinning at a spinning rate of 10 kHz at room temperature. The 90° pulse was 3.9 μs, and the contact pulse was 1 ms. In the case of unsupported **1**, the spectra were collected after 800 scans using a recycle delay of 60 s, while the spectrum of the supported complex **1**/SiO_2 was acquired with 16 000 scans and a relaxation delay of 4 s. The line broadening was set to be 10 Hz for **1** and 50 Hz for **1**/SiO_2. H_3PO_4 (85%) was used as the external standard. The samples were transferred in the rotor in a dry glovebox under N_2.

Table 1. Hydrogenation of Benzylideneacetone in the Heterogeneous Phase Recycling the Catalyst 1/SiO_2[a,b]

cycle	substrate (%)	**A** (%)	**B** (%)	**C** (%)	**E** (%)	**F** (%)	selectivity in **B** (%)
1	89.4	0.4	9.3	0.9			88
2	88.3	0.4	10.2	1.1			87
3	90.1	0.4	8.4	1.1			85

[a] Reaction conditions: **1**/SiO_2, 28 mg (4.3×10^{-3} mmol of Ru); substrate, 2.15 mmol; *n*-octane, 30 mL; H_2, 30 bar; temperature, 130 °C; time, 1 h; stirring rate, 1500 rpm. Products: *trans*-4-phenyl-3-buten-2-ol (**A**), benzylacetone (**B**), 4-phenylbutan-2-ol (**C**), phenylbutenes (**E**), 1-phenylbutane (**F**). [b] The amount of ruthenium in the liquid phase recovered after each cycle was below the detection limit of the ICP-AES instrument (500 ppb).

Heterogeneous Hydrogenation Reactions with 1/SiO_2. A 100 mL Parr autoclave was charged with **1**/SiO_2 (28 mg, 4.3 $\times$ 10^{-3} mmol Ru), the unsaturated substrate (2.15 mmol), *n*-octane (30 mL), and H_2 (30 bar). The ensemble was heated to the appropriate temperature and then stirred (1500 rpm) for the desired time, after which the vessel was cooled to ambient temperature and depressurized. The liquid contents were analyzed by GC and GC/MS. Above 1500 rpm, the rates were independent of the agitation speed at all the temperatures studied, thus indicating the absence of mass transfer resistance. The stability of the immobilized catalyst against leaching from the support was tested as follows. (i) After a catalytic run, the grafted Ru product was separated by filtration from the liquid phase under nitrogen, washed with *n*-octane and CH_2Cl_2, and then reused for a second, identical run. After the liquid phase was analyzed by GC, the solvent was removed under vacuum and the residue was analyzed by both $^{31}P\{^1H\}$ NMR spectroscopy and ICP-AES. No trace of phosphorus was seen by NMR spectroscopy in all cases, while the amounts of ruthenium detected by ICP-AES were <1 ppm. A similar loss of ruthenium was generally determined in the tethered termination products. (ii) To refrain from filtering the solid catalyst after each catalytic run, several reactions were carried out in a 100 mL Parr reactor fitted with a dip pipe with a sintered (2 μm) metal piece at its dipping end. Upon termination of the reaction, the reaction solution was forced out through the sintered dip pipe by applying a nitrogen pressure of ca. 3 bar at the gas inlet valve of the reactor, thus retaining the catalyst in the reactor. After a sample of the filtrate was analyzed by GC, most of the solvent was distilled out and the residue was analyzed by ICP-AES. A fresh *n*-octane solution of the substrate to be hydrogenated was then loaded through a thin Teflon pipe connected to the reactor. The reactor was then pressurized with hydrogen, heated to the appropriate temperature, and then stirred for the desired time. Tables1 and 2 report recycling data for the two substrates hydrogenated in this work, showing that no appreciable Ru leaching occurred.

In a separate experiment, finely crushed **1** was used also as catalyst precursor in the place of the supported species **1**/SiO_2. No hydrogenation of the substrate was observed under comparable reaction conditions.

Study of the Termination Metal Products after Heterogeneous Hydrogenation Reactions with 1/SiO_2. A Parr reactor containing **1**/SiO_2 (150 mg, 2.3 $\times$ 10^{-2} mmol Ru), *n*-octane (30 mL), and either benzylideneacetone or benzonitrile (1 mmol) was pressurized with 30 bar of H_2. The mixture was heated to 130 (benzylideneacetone) or 100 °C (benzonitrile) with stirring for 2 h. After this time, the reactor was cooled to

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Table 2. Hydrogenation of Benzonitrile in the Heterogeneous Phase Recycling the Catalyst $1/SiO_2$[a,b]

cycle	substrate (%)	**A** (%)	**B** (%)	**C** (%)	**D** (%)	**E** (%)	selectivity in **B** (%)
1	76.5		23.2	0.3			99
2	74.4		25.2	0.4			98
3	77.7		22.3				100

[a] Reaction conditions: **1**/SiO_2, 28 mg (4.3×10^{-3} mmol of Ru); substrate, 2.15 mmol; *n*-octane, 30 mL; H_2, 30 bar; temperature, 100 °C; time, 1 h; stirring rate, 1500 rpm. Products: benzylamine (**A**), benzylidenebenzylamine (**B**), dibenzylamine (**C**), benzaldehyde (**D**), benzyl alcohol (**E**). [b] The amount of ruthenium in the liquid-phase recovered after each cycle was below the detection limit of the ICP-AES instrument (500 ppb).

room temperature and degassed. The grafted Ru product was separated by filtration from the liquid phase under argon, washed with *n*-octane, and dried under a stream of dry argon. The solid product was then stirred for 30 min in a Schlenk tube containing 2 mL of MeOH-d_4. Alternatively, the solid product was treated with a 2:1 mixture of MeOH-d_4 and MeCN-d_3. By this procedure, all the anchored ruthenium complex was extracted from silica and the resulting solutions were analyzed by NMR spectroscopy. The results of these esperiments are presented in a forthcoming section.

Homogeneous Hydrogenation Reactions with Triphos-1. As a general procedure, a 100 mL Parr autoclave was charged with triphos-**1** (5.5 mg, 4.3×10^{-3} mmol), the unsaturated substrate (2.15 mmol), THF (30 mL), and H_2 (30 bar). The ensemble was heated to the appropriate temperature and then stirred (750 rpm) for the desired time, after which the vessel was cooled to ambient temperature and the liquid contents analyzed by GC and GC/MS.

Some experiments with triphos-**1** were carried out in CH_2Cl_2, keeping constant all the other experimental parameters.

Aqueous-Biphase Hydrogenation Reactions with 1. A 100 mL Parr autoclave was charged with **1** (5.5 mg, 4.3×10^{-3} mmol), the unsaturated substrate (2.15 mmol), *n*-octane (15 mL), water (15 mL), and H_2 (30 bar). The ensemble was heated to the appropriate temperature and then stirred (1500 rpm) for the desired time, after which the vessel was cooled to ambient temperature. As a general procedure, THF was added to the final catalytic mixtures until a unique phase was observed, which was analyzed to obtain the total distribution of products. Above 1500 rpm, the rates were independent of the agitation speed at all the temperatures studied, thus indicating the absence of mass transfer resistance.

X-ray Data Collection and Structure Determination of $1{\cdot}2MeCN{\cdot}H_2O$. A crystal sealed in a glass capillary with its mother liquor was mounted on a Enraf-Nonius CAD4 diffractometer, and data were collected at room temperature. A set of 25 carefully centered reflections having $6.5 \le \theta \le 8.5°$ was used to determine the lattice constants. The intensities of three standard reflections were measured every 2 h for orientation and intensity control. This procedure revealed no decay of intensity. The data were corrected for Lorentz−polarization effects. Atomic scattering factors with anomalous dispersion correction were taken from refs 14 and 15. An empirical absorption correction was applied via ψ scan with transmission factors in the range 0.94−0.99. The computational work was performed with a DIGITAL DEC 5000/200 workstation using the program SHELX-93.[16] Crystallographic details are reported in Table 3. The structure was solved by direct methods using the SIR92 program,[17] and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and finally with anisotropic thermal parameters for all the atoms but the hydrogens. Phenyl rings were treated as rigid bodies with D_{6h} symmetry, and hydrogen atoms were introduced in calculated positions.

Table 3. Summary of Crystallographic Data for $1{\cdot}2MeCN{\cdot}H_2O$

formula	$C_{58}H_{59}F_3N_5O_7P_3RuS_2$
mw	1253.24
cryst size, mm	$0.87 \times 0.37 \times 0.25$
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.154(8)
b, Å	15.008(3)
c, Å	29.868(6)
β, deg	90.840(5)
V, Å^3	5896(3)
Z	4
ρ_{calcd}, g cm^{-3}	1.411
abs coeff, mm^{-1}	0.470
F(000)	2552
radiation	Mo, 0.71069 Å
θ range, deg	1.36−24.97
index ranges	$-15 \le h \le 15, 0 \le k \le 17, 0 \le l \le 35$
rflns collected	10 540
indep rflns	10 325 ($R_{int} = 0.0188$)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	10 325/0/598
goodness of fit on F^2	1.037
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0683, wR2 = 0.1755
R indices (all data)	R1 = 0.1347, wR2 = 0.2152
largest diff peak and hole, e Å^{-3}	1.576 and −1.237

Results and Discussion

Synthesis and Characterization of $[(sulphos)Ru(NCMe)_3](OSO_2CF_3)$ (1). Complex **1** was prepared by treatment of the known dimer $Na[\{(sulphos)Ru\}_2(\mu\text{-}Cl)_3]$ with silver triflate in MeCN solution (Scheme 1).[7] The compound is isolated as almost colorless, air-stable crystals that exhibit good solubility in polar solvents such as MeOH and MeCN. The complex is fairly soluble in neat water only at high temperature, while it is poorly soluble in CH_2Cl_2 at room temperature. The $^{31}P\{^1H\}$ NMR spectrum in MeCN-d_3 consists of a temperature-invariant singlet at 26.8 ppm down to −45 °C, as expected for three magnetically equivalent phosphorus nuclei. A singlet at the same chemical shift features also the ^{31}P NMR spectrum of the triphos derivative $[(triphos)Ru(NCMe)_3](OSO_2CF_3)_2$ (triphos-**1**),[8] thus confirming that the introduction of the polar sulfonate group away from the phosphorus atoms does not affect their donor properties.[5,18]

An X-ray analysis on a single crystal of **1**·2MeCN·H_2O has been carried out. A ZORTEP drawing of the complex cation $[(sulphos)Ru(NCMe)_3]^+$ is reported in Figure 1 with the atomic labeling scheme, while selected bond lengths and angles are given in Table 4.

The structure consists of complex cations and triflate anions in a 1:1 ratio with interspersed MeCN and water

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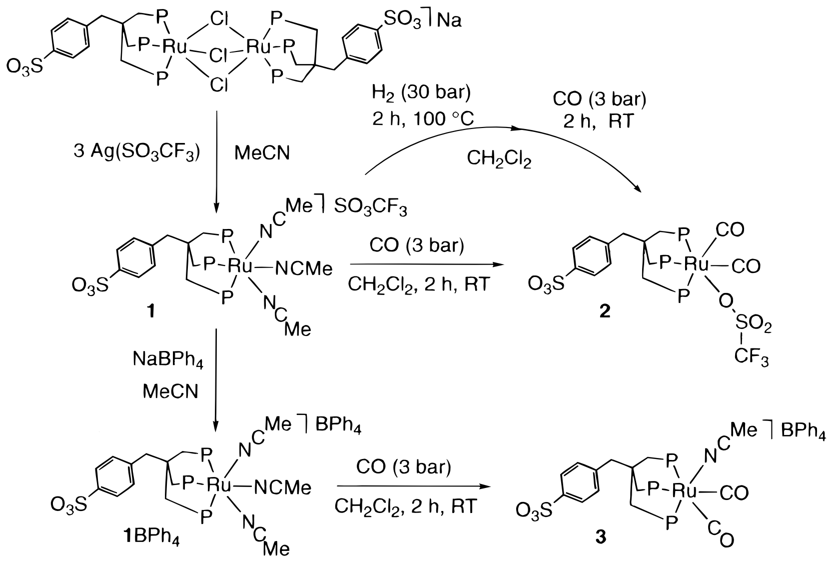
Scheme 1



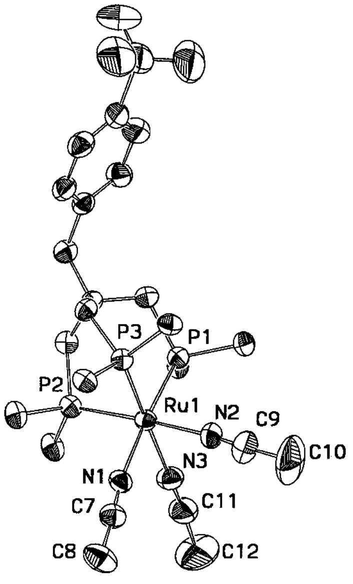


Figure 1. ZORTEP drawing of the complex cation in **1**·2MeCN·H_2O. All the hydrogen atoms and phenyl substituents at the phosphorus atoms of sulphos are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 1·2MeCN·H₂O

	Distances		
Ru(1)−N(1)	2.089(6)	Ru(1)−P(3)	2.3022(17)
Ru(1)−N(2)	2.093(6)	Ru(1)−P(1)	2.3166(17)
Ru(1)−N(3)	2.115(6)	Ru(1)−P(2)	2.3167(19)
	Angles		
N(1)−Ru(1)−N(2)	82.1(2)	N(3)−Ru(1)−P(1)	92.33(17)
N(1)−Ru(1)−N(3)	83.4(2)	P(3)−Ru(1)−P(1)	89.01(6)
N(2)−Ru(1)−N(3)	83.5(2)	N(1)−Ru(1)−P(2)	93.65(15)
N(1)−Ru(1)−P(3)	95.14(16)	N(2)−Ru(1)−P(2)	175.55(17)
N(2)−Ru(1)−P(3)	93.59(17)	N(3)−Ru(1)−P(2)	97.41(17)
N(3)−Ru(1)−P(3)	176.95(17)	P(3)−Ru(1)−P(2)	85.36(6)
N(1)−Ru(1)−P(1)	175.42(16)	P(1)−Ru(1)−P(2)	88.63(6)
N(2)−Ru(1)−P(1)	95.69(17)		

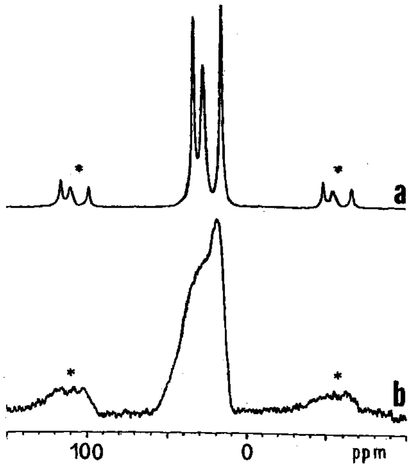


Figure 2. CP MAS ^{31}P NMR spectra: (a) **1**; (b) **1**/SiO_2. Spinning sidebands are denoted by asterisks.

molecules. The metal center is surrounded by three phosphorus atoms from a facial sulphos ligand and by three nitrogen atoms from acetonitrile ligands. The slight distortion from the idealized octahedral geometry is a well-known consequence of the geometrical constraints imposed by the tripodal ligand, which subtends three P−Ru−P angles with an average value of 87.66(6)°. The three Ru−P distances (2.089(6), 2.093(6), and 2.115(6) Å) reflect a small degree of geometrical distortion in the solid state which, on the other hand, is visible also in the CP MAS ^{31}P NMR spectrum shown in Figure 2a. The three phosphorus resonances at δ 33.6, 26.1, and 15.8, with a δ_{av} value of 25.2, are not too far from the solution shift, given the sensitivity of the ^{31}P shifts to solvent and temperature.[5]

Synthesis and Characterization of the Tethered Complex 1/SiO₂. It is well-known that two main kinds of either adsorption sites or functional groups are present on the silica surface: silanols (≡Si−OH) and siloxane groups (≡Si−O−Si≡).[19] Silanols have been classified into three types: (i) isolated silanols (or free silanols), where the surface silicon atom has three bonds to the bulk structure and a fourth bond to a single OH group; (ii) vicinal silanols (or bridged silanols), where single OH groups are attached to different silicon atoms which are close to each other enough to interact via

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hydrogen bonding; (iii) geminal silanols, which consist of two hydroxyl groups on the same silicon atoms. While the existence of geminal silanols is still a matter of debate, vicinal and isolated silanols have been experimentally identified by NMR and IR spectroscopy.[20]

The thermal treatment of the silica surface leads generally to both loss of physisorbed water (dehydration) and condensation of the hydroxyl groups to form siloxane bonds (dehydroxylation). Heating nonporous silica at 100 °C for a prolonged time removes all the physisorbed water.[21] This does not occur for mesoporous silica, even upon thermal treatment at 200 °C.[22] The dehydroxylation process implies first vicinal silanols (temperature range 200−400 °C) and then isolated silanols (above 400 °C). Overall, the dehydroxylation leads to a decrease in the concentration of the surface hydroxyl groups.

The silica employed in this work is a mesoporous material, and therefore, a thermal treatment at 300 °C was chosen. To have a clean surface before the last activation at 300 °C, the support was exposed to a dehydration/dehydroxylation and rehydration/rehydroxylation cycle.

The heterogenization of **1** was carried out by the solvent impregnation method using anhydrous dichloromethane for its aprotic nature. Alcohols cannot be used, as they compete with the Ru complexes for interaction with the silica surface.[5] The grafting procedure was complete and reproducible up to 1.6 wt % Ru loading.

Once grafted to silica, the Ru complex was not extracted back into CH_2Cl_2 solutions, even after repeated washings with this solvent. In contrast, stirring **1**/SiO_2 in MeOH or EtOH for 3 h at room temperature resulted in the complete delivery of the complex **1** into solution (^{31}P NMR experiments in MeOH-d_4).

Figure 3a shows the DRIFT spectrum in the ν(OH) region of silica after the pretreatment at 300 °C. The sharp band at 3741 cm^{-1} is due to the free silanols, and the broad band centered at 3690 cm^{-1} is characteristic of vicinal silanols. Adsorption of **1** clearly resulted in the almost complete disappearance of the high-frequency band, while the other ν(OH) band was significantly reduced (Figure 3b). The new broad absorption band centered at ca. 3400 cm^{-1} in the spectrum of the anchored complex can be assigned to the silanols in hydrogen interactions with the sulfonate groups from both complex cations and triflate anions.[5,23] Just these latter contribute substantially to consume the free silanols via hydrogen-bonding interactions. It can be concluded, therefore, that **1** does form a clean monolayer on the silica surface in which the molecules of the grafted complex are separated from each other, as occurs in solution. A similar molecularly dispersed state was previously observed for the neutral complex (sulphos)Rh(cod) chemisorbed on silica.[5]

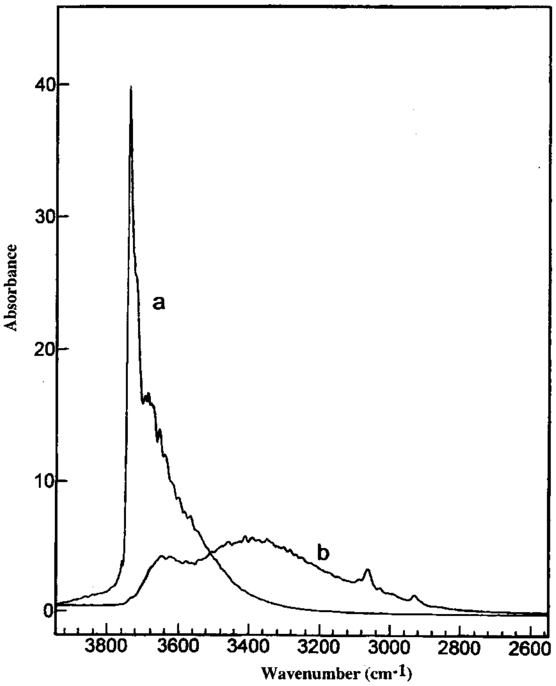

Figure 3. DRIFT spectra in the ν(OH) region under an argon flow at room temperature: (a) activated silica before complex impregnation; (b) **1**/SiO_2.

The CP MAS ^{31}P NMR spectrum of the grafted complex **1**/SiO_2 is shown in Figure 2b and consists of a broad signal with a peak and a shoulder at 22 and 36 ppm, respectively. The asymmetric profile of the resonance indicates that different types of phosphorus atoms may be present. Despite the greater shift dispersion due to small conformational differences as compared to the unsupported sample,[5,24] the solid-state NMR spectra of **1**/SiO_2 and **1** are substantially similar and thus consistent with the immobilization of the complex on the silica through a functional group away from the metal coordination sphere.

In conclusion, a structure can be proposed for **1**/SiO_2 in which both the complex cations and the triflate anions are tethered to silica by hydrogen-bond interactions involving the oxygens from the $-SO_3$ groups and the OH groups from the terminal silanols on the silica surface. Obviously, the sketch reported below for **1**/SiO_2 is only a schematic representation of the reality, as there will be cations and anions H-bonded to silica via two or even one Si−OH units:

Hydrogenation of Benzylideneacetone and of Benzonitrile in Different Phase-Variation Systems. The catalytic performance of the supported Ru complex under liquid−solid conditions was tested in the hydrogenation of an α,*β*-unsaturared ketone and of an organic nitrile. For comparative purposes, the activities of the aqueous-biphase catalyst **1** and of the homogeneous catalyst triphos-**1** have been studied under similar experimental conditions.

Benzylideneacetone. *trans*-4-Phenyl-3-buten-2-one, commonly known as benzylideneacetone, is an α,*β*-

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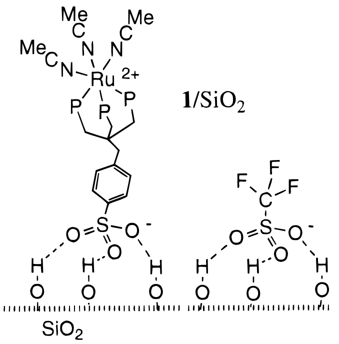


1/SiO$_2$

unsaturated ketone that may undergo the selective hydrogenation of the keto group, the double bond, or both, depending on the metal catalyst (Scheme 2).[25] Accordingly, *trans*-4-phenyl-3-buten-2-ol (**A**), benzylacetone (**B**), or 4-phenylbutan-2-ol (**C**) may be produced. The dehydration of the unsaturated alcohol **A** may also be catalyzed to give butadienylbenzene (**D**), whose subsequent hydrogenation may yield either partially (**E**) or fully (**F**) reduced species.

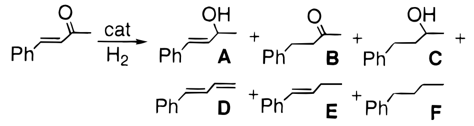
The hydrogenation of benzylideneacetone has been studied in different phase-variation systems using as catalyst precursors the heterogeneous complex **1**/SiO$_2$, the water-soluble complex **1**, and the organic-solvent-soluble triphos-**1** under the following experimental conditions: 30 bar of H$_2$, 130 °C, substrate-to-catalyst ratio 500 (Table 5). These relatively harsh experimental conditions were purposefully chosen to test the thermal stability of the anchored catalyst.

In the presence of **1**/SiO$_2$ suspended in *n*-octane, benzylideneacetone was selectively converted to benzylacetone. After 3 h, the conversion was 27% and the selectivity was close to 100% (entry 1). The conversion increased to ca. 61% for 12 h reaction without significantly affecting the selectivity (96%, entry 2).

In aqueous-biphase conditions (water/*n*-octane, 1:1 v:v) **1** was much more active than the grafted catalyst (100% conversion after 3 h, entry 3). The selectivity, however, was much lower, as the saturated alcohol **C** was produced in ca. 55% yield. The regioselectivity in the double-bond hydrogenation was significantly improved (87%) by decreasing the reaction temperature to 80 °C. However, both the unsaturated alcohol **A** (1.5%) and the saturated alcohol **C** (10%) were obtained (entry 4). Other experimental conditions were attempted, but in no case was the selectivity higher than that provided by the grafted complex.

The most active catalyst system was the homogeneous one (entry 5). Even after 1.5 h, all the substrate disappeared, yielding as the major product the saturated alcohol **C**. Appreciable amounts of the dehydration/hydrogenation products **E** (2%) and **F** (6%) were obtained, however. A systematic variation of the experimental parameters was carried out. Again, the selectivity was invariably lower than that of the heterogeneous reaction. Independent reactions of **A** with triphos-**1** in THF gave the dehydration product **D** and, in the presence of 30 bar of H$_2$, **E** and **F**.

Scheme 2



The chemoselective hydrogenation of α,β-unsaturated ketones is a rather difficult task for traditional heterogeneous catalysts, which generally are much more efficient for the reduction of α,β-unsaturated aldehydes.[26] To the best of our knowledge, no metal complex grafted to mesoporous silica has ever been reported to selectively catalyze the hydrogenation of an α,β-unsaturated ketone. However, the hydrogenation of 3-nonen-2-one to 2-nonanone has recently been achieved with a chromium complex bound to sol−gel siloxane polymers.[27] The catalytic activity of these Cr systems is much lower than that of **1**/SiO$_2$.

Benzonitrile. Like benzylideneacetone, the metal-catalyzed hydrogenation of benzonitrile can give various products due to the presence of a triple bond, and therefore of two stages of H$_2$ addition, as well as the intrinsic reactivity of the nitrile with nucleophiles. The imine PhCH=NH is the first hydrogenation product which is then reduced to benzylamine. This in turn can bring about a nucleophilic attack on the starting nitrile to form an enamide that, by sequential hydrogenation and NH$_3$ elimination, produces a secondary imine.[9,28]

Scheme 3 illustrates the products obtained with the catalysts employed in this work: benzylamine (**A**), benzylidenebenzylamine (**B**) and dibenzylamine (**C**). The hydrolysis product of benzonitrile, benzaldehyde (**D**), and its hydrogenated product benzyl alcohol (**E**) were also produced in some cases. The results of the catalytic reactions in different phase-variation systems under comparable experimental conditions (30 bar of H$_2$, 100 °C, substrate-to-catalyst ratio 500) are reported in Table 6.

In the presence of **1**/SiO$_2$ suspended in *n*-octane, benzonitrile was chemoselectively transformed into **B** (35% conversion and 99% selectivity after 1.5 h) (run 1). Increasing the reaction time to 12 h increased the overall conversion to 95% without significantly affecting the chemoselectivity (92%, run 2). Notably, the reductive transformation of an organic nitrile into a secondary imine has never been reported to occur in a heterogeneous fashion. The results obtained in this work are thus quite interesting, as they outline a new and clean route to the preparation of secondary bis(aryl)imines, which are important organic synthons.

In aqueous-biphase conditions using **1** as catalyst precursor, the overall conversion after 1.5 h was similar to that in the heterogeneous phase but the chemoselectivity was indeed much lower, as four products were formed. The hydrolysis/hydrogenation products **D** (12%) and **E** (5%) were invariably produced, due to the presence of water in the reaction medium (run 3). This

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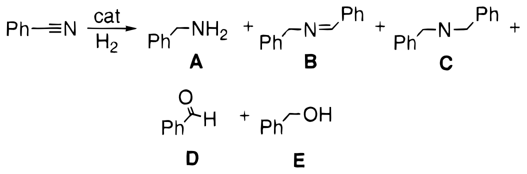
Table 5. Hydrogenation of Benzylideneacetone in Different Phase-Variation Systems[a]

entry	catalyst	phase syst	substrate (%)	**A** (%)	**B** (%)	**C** (%)	**E** (%)	**F** (%)	*T* (°C)	*t* (h)	selectivity in **B** (%)
1	**1**/SiO_2	heterogeneous[b]	73.4		25.8	0.8			130	3	97
2	**1**/SiO_2	heterogeneous[b]	38.6		59.4	2.4			130	12	96
3	**1**	biphasic[c]			44.7	55.3			130	3	45
4	**1**	biphasic[c]	13.5	1.5	75.0	10.0			80	3	87
5	triphos-**1**	homogeneous[d]			0.7	91.5	1.8	6.0	130	1.5	1

[a] Products: *trans*-4-phenyl-3-buten-2-ol (**A**), benzylacetone (**B**), 4-phenylbutan-2-ol (**C**), phenylbutenes (**E**), 1-phenylbutane (**F**). [b] Reaction conditions: **1**/SiO_2, 28 mg (4.3×10^{-3} mmol of Ru); substrate, 2.15 mmol; *n*-octane, 30 mL), H_2, 30 bar; stirring rate, 1500 rpm. [c] Reaction conditions: **1**, 5.5 mg (4.3×10^{-3} mmol); substrate, 2.15 mmol; *n*-octane, 30 mL; water, 15 mL; H_2, 30 bar; stirring rate, 1500 rpm. [d] Reaction conditions: triphos-**1**, 5.5 mg (4.3×10^{-3} mmol); substrate, 2.15 mmol; THF, 30 mL; H_2, 30 bar; stirring rate, 750 rpm.

Scheme 3



unavoidable drawback makes the aqueous-biphase technique useless for the hydrogenation of organic nitriles.

Finally, the homogeneous catalyst triphos-**1** converted all benzonitrile only after 1.5 h, yielding the primary amine **A** (34%) and the secondary imine **B** (65%) as major products (run 4). Only decreasing the reaction temperature to 70 °C allowed triphos-**1** to catalyze the conversion of benzonitrile with the same selectivity of the hetereogeneous reaction. Under these conditions, the overall conversion (98% in 1.5 h, run 5) was higher than that observed in the heterogeneous reaction (run 1).

From a perusal of all of these data, one may reasonably conclude that the chemoselectivity of the hydrogenation of benzylideneacetone follows the order heterogeneous catalyst > aqueous-biphase catalyst > homogeneous catalyst, while the catalytic efficiency decreases in the order homogeneous catalyst > aqueous-biphase catalyst > heterogeneous catalyst. For benzonitrile hydrogenation, the heterogeneous and homogeneous catalysts give comparable chemoselectivities by appropriate choice of the reaction parameters. If, however, one considers that **1**/SiO_2 is the easiest catalyst to recycle by simple filtration and that the Ru leaching into the hydrocarbon phase after each catalytic run is practically negligible, then it is reasonable to conclude that the immobilization of the homogeneous catalyst has indeed generated an improved catalytic system, particularly in terms of “green chemistry”.

The reduced contact time of the reactants with the anchored catalyst may account for the lower activity of the latter as compared to that of the homogeneous and biphasic systems. This kinetic effect might also control the different selectivity observed at equal reaction times; one cannot exclude, however, that a different reaction mechanism may be operative in the heterogeneous phase. On the basis of the results of the following model studies, this latter hypothesis is probable, in fact.

Model Reactions. In an attempt to gain insight into the chemical reactivity of the grafted ruthenium product toward H_2 as well as its catalytic performance, a number of independent reactions involving either **1**/SiO_2 or isolated compounds with sulphos or triphos have been carried out.

A. Liquid−Liquid Reactions. Complex **1** is insoluble in *n*-octane, and therefore, no evidence could be obtained for its reactivity toward H_2 in the solvent employed in the heterogeneous reactions. Much is known, however, on the hydrogenation of triphos-**1** in THF.[10,29] In this slightly basic solvent, for $p(H_2) > 5$ bar, the acetonitrile ligands are transformed into a mixture of $NHEt_2$, NEt_3, and NH_3 through the amine redistribution sequence summarized in eq 1.[30]

$$\begin{gathered} RCN \xrightarrow{H_2} RCH{=}NH \xrightarrow{H_2} RCH_2NH_2 \xrightarrow{RCN} (R)NH_2 \\ (R){=}NH \xrightarrow{H_2} RCH_2NHCH \\ RCH_2NHC \xrightarrow{-NH_3} RCH_2N{=}CHR \xrightarrow{H_2} \\ (RCH_2)_2NH \xrightarrow{RCN} \xrightarrow{H_2} \xrightarrow{-NH_3} \xrightarrow{H_2} (RCH_2)_3N \end{gathered} \tag{1}$$

Various monohydrido complexes such as $[(triphos)Ru(H)(NCMe)_2]BPh_4$, $[(triphos)Ru(H)(NH_3)_2]BPh_4$, and $[(triphos)Ru(H)(NH_3)(NH_2Et)]BPh_4$ are formed at different stages of the hydrogenation reaction. Below 5 bar of H_2, no hydrogenation of MeCN occurs and all the ruthenium is recovered as $[(triphos)Ru(H)(NCMe)_2]BPh_4$. The formation of monohydrido Ru(II) species upon hydrogenation of the Ru(II) tris(acetonitrile) complex triphos-**1** takes place via heterolytic splitting of H_2 promoted by the THF solvent.[10,29] Consistently, we have now found that the hydrogenation of triphos-**1** in the neutral solvent CH_2Cl_2 does not produce any monohydrido species even under 30 bar of H_2, although the MeCN ligands are analogously converted to NH_3 and NEt_3. A sequence of high-pressure NMR (HPNMR) spectra recorded in a sapphire tube during a hydrogenation of triphos-**1** in CH_2Cl_2 at a constant temperature of 60 °C is shown in Figure 4.

As is apparent from a perusal of the $^{31}P\{^1H\}$ NMR traces a−d, the starting complex (singlet at 27.1 ppm) slowly converted into a fluxional species distinguished by a broad band centered at ca. 31 ppm. No resonance attributable to hydride ligands was seen in the ^1H NMR spectra recorded after each $^{31}P\{^1H\}$ NMR spectrum. The broad hump at 31 ppm resolved into a canonical AM_2 pattern at room temperature (trace e), which was identified as that of the bis(ammonia) complex $[(triphos)Ru(NH_3)_2(OSO_2CF_3)](OSO_2CF_3)$ (triphos-**4**). The same ^{31}P NMR pattern was indeed observed upon treatment of triphos-**1** with NH_3 in CH_2Cl_2. The complex triphos-**4** is too unstable to be isolated in the solid state. Its

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Table 6. Hydrogenation of Benzonitrile in Different Phase-Variation Systems[a]

entry	catalyst	phase syst	substrate (%)	**A** (%)	**B** (%)	**C** (%)	**D** (%)	**E** (%)	*T* (°C)	*t* (h)	selectivity in **B** (%)
1	**1**/SiO_2	heterogeneous[b]	65.4		34.2	0.4			100	1.5	99
2	**1**/SiO_2	heterogeneous[b]	5.0	2.8	87.5	4.7			100	12	92
3	**1**	biphasic[c]	74.6		8.0	0.5	11.6	5.3	100	1.5	32
4	triphos-**1**	homogeneous[d]	0.5	33.9	64.7	0.9			100	1.5	65
5	triphos-**1**	homogeneous[d]	1.8		98.2				70	1.5	100

[a] Products: benzylamine (**A**), benzylidenebenzylamine (**B**), dibenzylamine (**C**), benzaldehyde (**D**), benzyl alcohol (**E**). [b] Reaction conditions: **1**/SiO_2, 28 mg (4.3×10^{-3} mmol Ru); substrate, 2.15 mmol; *n*-octane, 30 mL; H_2, 30 bar; stirring rate, 1500 rpm. [c] Reaction conditions: **1**, 5.5 mg (4.3×10^{-3} mmol); substrate, 2.15 mmol; *n*-octane, 30 mL; water, 15 mL; H_2, 30 bar; stirring rate, 1500 rpm. [d] Reaction conditions: triphos-**1**, 5.5 mg (4.3×10^{-3} mmol); substrate, 2.15 mmol; THF, 30 mL; H_2, 30 bar; stirring rate, 750 rpm.

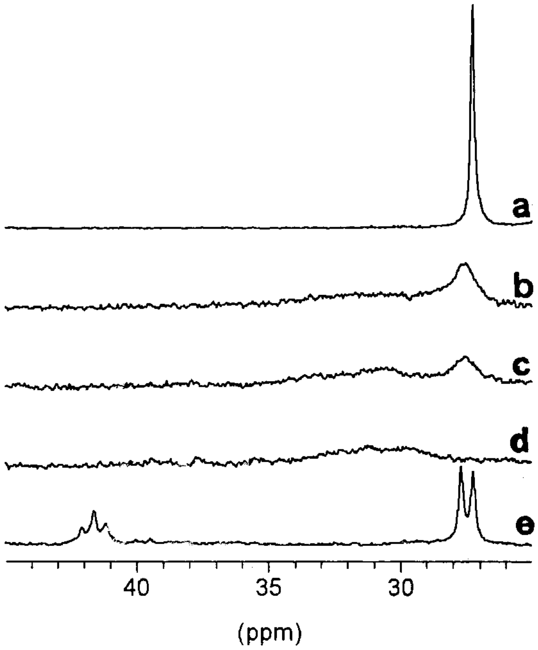

Figure 4. $^{31}P\{^1H\}$ HPNMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of the reaction of triphos-**1** with H_2 (30 bar): (a) at room temperature; (b) at 60 °C for 10 min; (c) at 60 °C for 1 h; (d) at 60 °C for 2 h; (e) after the tube was cooled to room temperature.

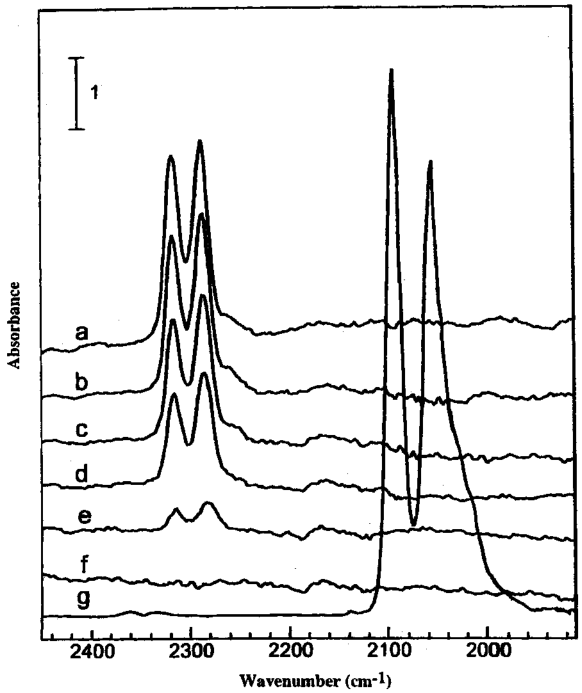

Figure 5. DRIFT spectra acquired during a solid–gas reaction between **1**/SiO_2 and H_2 (6 mL min^{-1}): (a) room temperature; (b) 67 °C; (c) 89 °C; (d) 100 °C; (e) 111 °C; (f) 122 °C. Trace g reports the spectrum obtained after the hydrogenated sample was cooled to room temperature and H_2 was replaced by CO.

carbonylation in either a HPNMR tube or an autoclave, however, gave the known dicarbonyl derivative $[(triphos)Ru(CO)_2(OSO_2CF_3)](OSO_2CF_3)$ (triphos-**2**).[8] The sulphos analogue $(sulphos)Ru(CO)_2(OSO_2CF_3)$ (**2**) was similarly prepared by sequential treatment of **1** with H_2 and CO, as shown in Scheme 1. Complex **2** was unambiguously characterized by a variety of analytical techniques detailed in the Experimental Section. It is important to stress here that the two carbonyl ligands in **2** give rise to two solid-state bands centered at 2088 and 2050 cm^{-1}. Quite identical IR bands (2092 and 2050 cm^{-1}) are displayed by the cationic dicarbonyl complex $[(sulphos)Ru(CO)_2(NCMe)]BPh_4$ (**3**), obtained by carbonylation of $[(sulphos)Ru(NCMe)_3]BPh_4$ (**1**BPh_4) (Scheme 1). This IR evidence indicates that the stretching frequency of the CO ligands in complexes containing the moiety "$(sulphos)Ru(CO)_2$" is only slightly affected by the nature of the third coligand. Indeed, very similar IR bands (2085 and 2045 cm^{-1}) are also displayed by the dicarbonyl derivative triphos-**2**.[8]

B. Solid–Gas Reactions. The reactions between **1**/SiO_2 and H_2 have been monitored by variable-temperature DRIFT spectroscopy in a cell coupled to a quadrupole mass spectrometer.

Figure 5 illustrates the changes observed in the *ν*(CN) region during a solid–gas reaction between **1**/SiO_2 and H_2 (6 mL min^{-1}). The bands at 2318 and 2289 cm^{-1}, due to the coordinated MeCN ligands, decreased in intensity with the temperature (traces a–e) until they disappeared at ca. 120 °C (trace f). At this point, the sample was cooled to room temperature and H_2 was replaced by CO. As a result, two strong carbonyl bands grew up at 2095 and 2056 cm^{-1} (trace g) to give a spectrum closely resembling that of the dicarbonyl complex **3** in the *ν*(CO) region. Any other complex containing the "$(sulphos)Ru(CO)_2$" unit would display the same *ν*(CO) bands, however.

In the course of the variable-temperature experiment, the volatile products were detected downstream by the on-line quadrupole mass spectrometer. The evolution of MeCN took place already at 90 °C with a peak centered at 110 °C (Figure 6). At this low H_2 pressure, the reduction of MeCN to ethylamine occurred to a minor extent only at higher temperature, as shown by a peak with *m*/*z* 45 centered at 150 °C.

In conclusion, below 150 °C, the tethered ruthenium complex **1**/SiO_2 undergoes exclusively the thermal elimination of the MeCN ligands, which are presumably replaced by either H_2 molecules or hydride ligands

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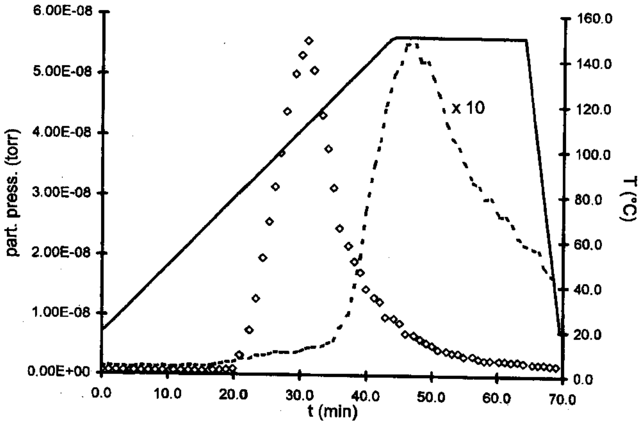


Figure 6. Volatile products detected downstream by the on-line quadrupole mass spectrometer during a variable-temperature solid–gas reaction between **1**/SiO_2 and H_2 (6 mL min^{-1}): (◊) acetonitrile, *m*/*z* 41; (- - -) ethylamine, *m*/*z* 45.

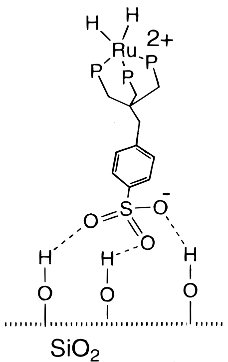
(unfortunately, neither M–$(H)_2$ nor M–(H_2) moieties can be detected by DRIFT spectroscopy). Subsequent displacement of H_2 by carbon monoxide would give the $Ru(CO)_2$ moiety responsible for the bands at 2095 and 2056 cm^{-1}.

The thermal stability of carbonylated **1**/SiO_2 was studied under a flow of Ar. The CO ligands were completely removed at ca. 150 °C, but a a reexposure of the sample to a CO atmosphere regenerated the dicarbonyl species with bands at 2095 and 2056 cm^{-1} even at room temperature.

Mechanistic Considerations. The model reactions described above show that the reactivity toward H_2 of discrete molecules of $[(sulphos)Ru(NCMe)_3]^+$ tethered to the silica surface is quite similar to that of the molecular complexes **1** and triphos-**1** in solution, with the condition that the solvent is not a base. In our opinion, this finding provides a key to rationalize the different selectivities of the hydrogenation of benzylideneacetone in the phase systems investigated.

In either THF or H_2O/*n*-octane, the catalyst precursor **1** has been found to react with H_2 to form monohydrido species via heterolytic splitting of H_2 prior to the hydrogenation of the MeCN ligands.[10,29] The catalytic cycle for any hydrogenation reaction catalyzed by **1** or triphos-**1** in basic solvents thus involves the participation of the four-coordinate monohydrido fragments (sulphos)RuH and $[(triphos)RuH]^+$, respectively.

Under the heterogeneous conditions with **1**/SiO_2, the reaction medium is virtually neutral, and therefore, the heterolytic splitting of H_2 at ruthenium would not occur. Either Ru(IV) dihydride (**I**) or Ru(II) η^2-dihydrogen (**II**) species might form on the silica surface and ultimately interact with the substrate to be reduced. Accordingly, the different chemoselectivity observed for the heterogeneous hydrogenation of benzylideneacetone as compared to the homogeneous and biphasic reactions may simply be due to the action of a different catalyst.



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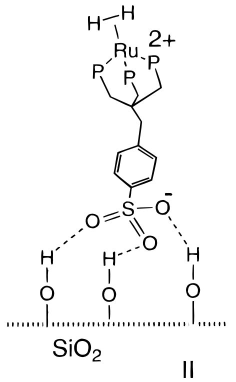

II

Indirect but sound experimental evidence supporting the hypothesis of different catalysts operating under either homogeneous/biphasic or heterogeneous conditions has been provided by the hydrogenation of benzylideneacetone catalyzed by triphos-**1** in CH_2Cl_2, where no heterolytic cleavage of H_2 takes place. Indeed, under the experimental conditions of run 5 of Table 5, except for the use of CH_2Cl_2 in the place of THF, a 24% conversion of benzylideneacetone was observed to give benzylacetone (22%) and 4-phenylbutan-2-ol (2%) with a selectivity in the former product of 92%, which is quite comparable to that found in the heterogeneous phase (run 1, Table 5). Increasing the reaction time up to 3 h increased the substrate conversion (40%) without changing the chemoselectivity.

In an attempt to prove experimentally that, unlike the case for the homogeneous system, no heterolytic cleavage of H_2 occurs on the tethered catalyst **1**/SiO_2, the termination metal products after heterogeneous catalysis were studied by NMR spectroscopy. Extraction of the sulphos–Ru products was carried out as previously reported.[5] However, when either neat MeOH-d_4 or a 1:2 mixture of MeOH and CD_2Cl_2 was employed as the complex scavenger, no useful information on the nature of the termination product was obtained due to extensive decomposition of the extracted Ru complex. With a 2:1 mixture of MeOH-d_4/MeCN-d_3 was obtained a much simpler spectrum containing only the signals, in ca. 1:1 ratio, due to the tris(acetonitrile) complex **1** and to a complex that is assigned the formula $[(sulphos)Ru(NH_3)(NCMe)_2](OSO_2CF_3)$ (**5**: $^{31}P\{^1H\}$ NMR, AM_2 pattern, $\delta(P_M)$ 30.4 (d, $J(PP) = 41.1$ Hz), $\delta(P_A)$ 23.3 (t)) by comparison with the spectrum of $[(triphos)Ru(NH_3)(NCMe)_2](BPh_4)_2$.[29] Blank experiments in the absence of substrate gave identical results, indicating that the Ru termination product tethered to the silica surface derives exclusively from the hydrogenation of the catalyst precursor. Therefore, the formation of **1** and **5** upon extraction with MeOH/MeCN suggests that the ruthenium atom in the tethered termination product is coordinated by ligands which can easily be displaced by MeCN: either intact H_2 or pairs of hydride ligands undergoing facile reductive coupling are excellent candidates. Indeed, were a monohydride Ru species to be formed in the heterogeneous phase as in the homogeneous phase, the treatment of the product extracted with MeOH/MeCN would give the complex $(sulphos)Ru(H)(NCMe)_2$, which is not observed in fact.[10,31]

As a final model study, we have tried to mimic the reaction of MeCN with $(sulphos)Ru(H)_x$ moieties ($x = 2, 4$). To this end, the trihydride complex $[(triphos)RuH_3]^-$ was generated in THF-d_8 as previously reported.[10] To

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(31) This hydride bis(acetonitrile) complex was prepared by treating a solution of **1** in MeCN with a 4-fold excess of $LiHBEt_3$. ^1H NMR (MeCN-d_3, 20 °C): δ −5.45 (dt, $J(HP) = 104.9$, 8.9 Hz, Ru–H). $^{31}P\{^1H\}$ NMR (MeCN-d_3, 20 °C): AM_2 pattern, $\delta(P_M)$ 47.1 (d, $J(PP) = 19.9$ Hz), $\delta(P_A)$ 5.1 (t).

the solution of the ruthenate complex was first added MeCN via syringe, causing no chemical change, and then HBF_4. Immediately after the addition of the acid, H_2 evolution was detected by ^1H NMR spectroscopy, while ^{31}P NMR spectroscopy showed the exclusive formation of the tris(acetonitrile) complex triphos-**1**. No hydrogenation of MeCN was observed by GC/MS. Since it has been reported that $[(triphos)RuH_3]^-$ reacts with protic acids to form the unstable tetrahydrido complex $(triphos)RuH_4$,[10] one may reasonably conclude that, in the absence of H_2, MeCN is able to scavenge all the hydride (or dihydrogen) ligands from ruthenium without being reduced.

In conclusion, the results obtained from the model studies show that the hydrogenation of **1**/SiO_2 under either solid–gas or solid–liquid conditions does not involve a heterolytic splitting of H_2. This finding is in contrast with the behavior of **1** and triphos-**1** in fluid solution systems and reasonably accounts for the different chemoselectivities of benzylideneacetone reduction.[10,29]

Concluding Remarks

We have reported the first synthesis and characterization of a supported hydrogen-bonded (SHB) catalyst containing a cationic organometallic complex. As compared to neutral SHB catalysts,[5] the cationic one has been found to be more robust toward metal leaching in solid–liquid reactions, due to the simultaneous contribution of both hydrogen-bonding and ion-pairing interactions to the overall anchoring mode. No appreciable metal leaching was actually observed for the solid–liquid hydrogenation of either an α,β-unsaturated ketone or an organic nitrile catalyzed by the Ru(II) SHB catalyst described in this work. Both of these hydrogenation reactions have no precedent for heterogenized metal complexes and, most importantly, have been found to be more selective than those carried out in either homogeneous or aqueous-biphasic systems with structurally related Ru(II) catalysts.

Despite the drawback of the need for an aprotic solvent, SHB catalysis may constitute a valid alternative to other heterogeneous processes involving the heterogenization of molecular complexes. Indeed, the ease of preparation and separation from products, the excellent selectivity, and the negligible metal leaching make SHB catalysts attractive for the production of fine chemicals, especially when noble metals are used.

Last but not least, the facile and quantitative extraction of the SHB metal catalysts with alcohols allows one to study the metal products of single-site heterogeneous reactions by applying standard spectroscopic techniques in solution.

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Supporting Information Available: Tables of final coordinates with equivalent isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and atomic coordinates of the hydrogen atoms for $\mathbf{1}\cdot 2MeCN\cdot H_2O$, along with a fully labeled ZORTEP plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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