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Transfer Hydrogenation of Ketones Catalysed by New Half-Sandwich Ruthenium(II) Complexes Bearing the Sulfonated Phosphane (*meta*-Sulfonatophenyl)diphenylphosphane Potassium Salt (TPPMS)

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Dedicated to Professor Victor Riera on the occasion of his 70th birthday

Keywords: Water-soluble catalysts / Sulfonated phosphanes / Arene complexes / Ruthenium(II) / Hydrogen transfer

New half-sandwich ruthenium(II) complexes [$RuCl_2$(η^6-arene)(TPPMS)] [η^6-arene = *p*-cymene (**1a**), benzene (**1b**)] and [RuCl(η^6-arene)$(TPPMS)_2$][Cl] [η^6-arene = *p*-cymene (**2a**), benzene (**2b**)] containing the water-soluble (*meta*-sulfonatophenyl)diphenylphosphane potassium salt (TPPMS) have been synthesised. The X-ray analysis for complex **1a** revealed that, in the solid state, complex anions are held together in the crystal lattice by weak electrostatic interactions with potassium cations leading to a linear chain structure. The extent of the association in solution depends on the solvent and the determination of the size of the particles in THF can be accomplished using Multiangle Light Scattering (MALS). The new complexes proved to be excellent catalysts for transfer hydrogenation of ketones and the hydrophilic properties of the TPPMS ligand allow the catalyst recovery. The hydride derivative [RuClH(η^6-*p*-cymene)(TPPMS)] (**4**) has also been shown to be an efficient catalyst for these processes. Moreover, when **1a** was used as catalyst, complex **4** was observed as the main product after the catalysis, supporting the implication of hydride species in transfer hydrogenation catalysis.

Introduction

Over the last decades, aqueous organometallic chemistry has become a priority research area. This interest has arisen from the advantages of replacing organic solvents with water and from the attention directed to the aqueous-biphasic technology in catalysis which allows the separation of the products from the catalyst and subsequent catalyst recovery and recycling.[1]

One of the most common approaches to obtain water-soluble organometallic compounds is the use of ligands with hydrophilic properties. The phosphane ligands containing sulfonated groups are among the most widely used ligands for this purpose.

In particular, complexes containing the sodium or potassium salt of (*meta*-sulfonatophenyl)diphenylphosphane (TPPMS) have been used as catalysts in a number of processes.[2] Thus, palladium complexes with TPPMS act as catalysts in cross coupling reactions[3] and cationic iridium(I) complexes show a moderate catalytic activity in hydrogenation reactions.[4] Ruthenium complexes containing the TPPMS ligand[5] have been widely used in two phase and aqueous hydrogenation reactions.[6] Thus the preformed complexes [RuClH(CO)$(TPPMS)_3$],[7] [$Ru(CO)_3$-$(TPPMS)_2$],[8] [$RuH_2(CO)(TPPMS)_3$][8] and [RuH(CO)-(NCMe)$(TPPMS)_3$][9] have shown catalytic activity for the hydrogenation of olefins. Furthermore, ruthenium complexes with *N*-donor ligands [$RuHCl(L)_2(TPPMS)_2$] (L = 1,2,3,4-tetrahydroquinoline, aniline) catalyse the hydrogenation of quinoline and benzothiophene[10] and the complexes [$RuCl_3(TPPMS)_2(NO)$][11] and [$RuCl_2(TPPMS)_2]_2$[12] show catalytic activity in the hydrogenation of carbon dioxide and hydrogencarbonate.

Aqueous transfer hydrogenation has been less developed and, in spite of the recent studies in aqueous transfer hydrogenation,[13] the only ruthenium-TPPMS complex reported as a catalyst for these reactions[14] has been [$RuCl_2$-$(TPPMS)_2$].[15] In addition, to the best of our knowledge, the only isolated half-sandwich ruthenium(II) complexes

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bearing the TPPMS ligand[16] are the complexes [RuCl(η^5-C_5H_5)(TPPMS)$_2$][17] and [RuCl(η^5-C_5H_5)(TPPMS)$_2$]-[$SnCl_3$][18] and no catalytic studies have been carried out.

Due to the lack of half-sandwich ruthenium(II) complexes containing the water-soluble ligand TPPMS and our interest in the catalytic activity of new half-sandwich ruthenium(II) complexes[19] and their reactivity in coupling-coupling reactions,[20] we have considered the synthesis of η^6-arene complexes and in this paper we report the synthesis and catalytic activity of new water-soluble half-sandwich ruthenium(II) complexes with the ligand TPPMS on the transfer hydrogenation of ketones.

Results and Discussion

Synthesis of Half-Sandwich Ruthenium(II) Complexes Containing the TPPMS Ligand

a) Synthesis of [$RuCl_2$(η^6-arene)(TPPMS)] [η^6-arene = p-cymene (1a), benzene (1b)]

The reaction of two equiv. of the potassium salt of (*meta*-sulfonatophenyl)diphenylphosphane (TPPMS) with the dinuclear complex [RuCl(μ-Cl)(η^6-arene)]$_2$ (η^6-arene = *p*-cymene, benzene) in methanol at room temperature gives the complexes [$RuCl_2$(η^6-arene)(TPPMS)] [η^6-arene = *p*-cymene (**1a**), benzene (**1b**)] which can be isolated as air-stable orange solids in yields of 95% (**1a**) and 68%[21] (**1b**) (Scheme 1).

Complexes **1a** and **b** are soluble in water and in common organic solvents such as alcohols, acetone, chloroform, dichloromethane, acetonitrile and dimethylsulfoxide but insoluble in diethyl ether and hexane. The complexes have an ionic character due to the potassium sulfonate group of the TPPMS ligand as shown in the conductivity measurements (see Exp. Sect.).

Spectroscopic data (IR as well as ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR) support the proposed formulation (see Exp. Sect. for details). In particular, the following must be noted: i) The IR spectra (KBr) show the characteristic strong $\nu(SO_3)$ absorption for the TPPMS ligand at 1200 (**1a**) and 1198 (**1b**) cm^{-1}; ii) a singlet resonance can be observed at 26.1 (**1a**) and 29.6 (**1b**) ppm in the ^{31}P{^{1}H} NMR spectra; iii) the ^{1}H NMR spectra show a high field doublet at 8.37 ($^3J_{H,P}$ = 10.2 Hz) (**1a**) and 8.28 ($^3J_{H,P}$ = 11.1 Hz) (**1b**) corresponding to the hydrogen atom in an *ortho* position with respect to the phosphorus atom and to the sulfonato group (H_o).

Slow diffusion of diethyl ether into a solution of **1a** in methanol resulted in crystals suitable for X-ray diffraction studies. In this ruthenium derivative, the asymmetric unit consists of two anionic complexes which are held together in the crystal lattice by electrostatic interactions with potassium cations. An ORTEP type representation is shown in Figure 1. Selected bonding data are collected in the caption.

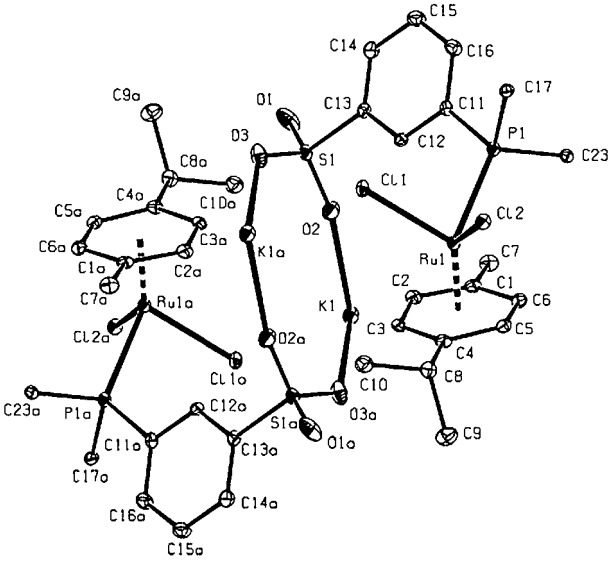
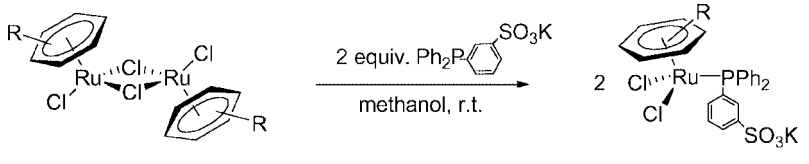


Figure 1. Molecular structure and atom labelling scheme for complex **1a**. Nonhydrogen atoms are represented by their 20% probability ellipsoids. Hydrogen atoms and phenyl rings (Ph_2P) have been omitted for clarity. Selected bond lengths [Å]: Ru(1)–C* 1.7061(3), Ru(1)–P(1) 2.3656(11), Ru(1)–Cl(1) 2.4046(10), Ru(1)–Cl(2) 2.4227(10), O(2)–K(1) 2.573(4). Selected bond angles [°]: C*–Ru(1)–P(1) 132.38 (3), C*–Ru(1)–Cl(1) 125.49(3), C*–Ru(1)–Cl(2) 123.46(3), Cl(1)–Ru(1)–P(1) 84.64(4), Cl(2)–Ru(1)–P(1) 88.54(4), Cl(1)–Ru(1)–Cl(2) 88.81 (4). C* means the centroid of C(1), C(2), C(3), C(4), C(5) and C(6) atoms.

The ruthenium atom, which exhibits a pseudo-octahedral three-legged piano stool geometry, is bonded to the phosphorus atom of the TPPMS ligand, to two chlorine atoms and η^6- to the *p*-cymene ring. An important feature of this crystal structure is that the complex in the solid state consists of linear chains (Figure 2) generated by the crystal periodicity along the *a* axis. These chains are generated by



Scheme 1.

electrostatic interactions between the anionic complexes and the potassium atoms. Thus, three ruthenium complexes surround each potassium atom leading to a pentacoordinate environment provided by two chlorine atoms of one anionic moiety, a chlorine and an oxygen from a second and an oxygen atom from a third unit (Figure 3).

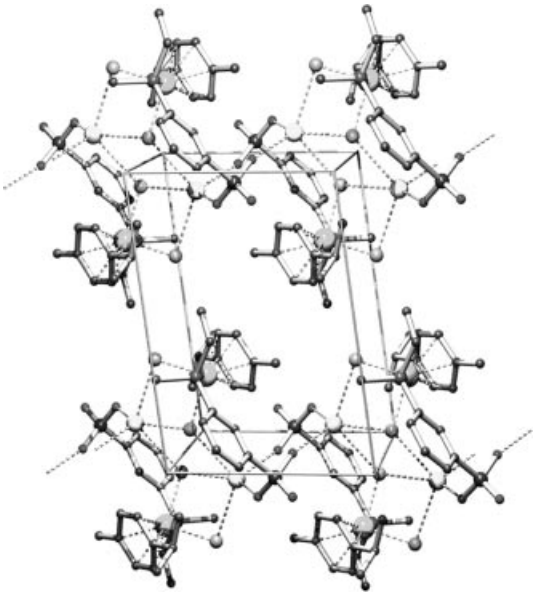


Figure 2. Layer structure for complex **1a**. Hydrogen atoms and phenyl rings have been omitted for clarity.

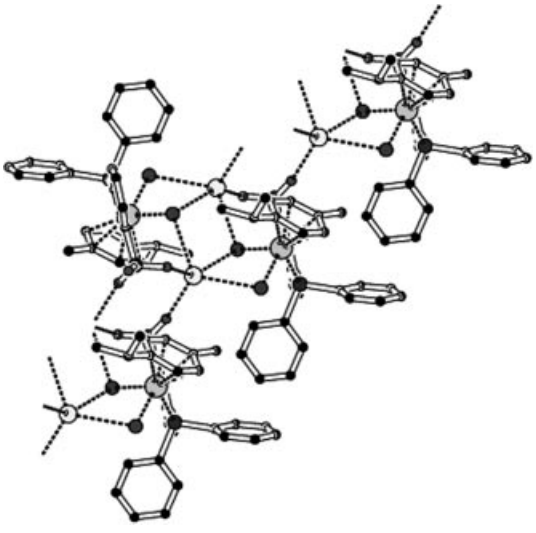


Figure 3. Potassium environment in the chain structure of **1a**. Hydrogen atoms have been omitted for clarity.

In addition, this complex shows different NMR spectroscopic behaviour depending on the solvent. In polar solvents such as CD_3OD or D_2O the NMR spectra show sharp signals while in CD_2Cl_2, $CDCl_3$ or $[D_8]$THF very broad signals may be observed. This prompted us to explore whether the chains are retained in solution leading to aggregates, the size of which being dependent on the solvent. In order to find the particle size in solution, the radius of gyration of the complex in THF solution has been measured using a detector of multiangle light scattering (MALS) coupled to size exclusion chromatographic equipment. The MALS spectrophotometer measures the excess Rayleigh ratio of the light scattered by the solute molecules in solution at different scattering angles. Thus, it enables the determination of the molecular dimensions, in terms of the radius of gyration, from the angular dependence of the scattered light (see Exp. Sect.). The mean square of the radius of gyration, $<s^2>$, is a very convenient quantity for expressing the molecular dimensions because it can be directly obtained from light scattering data and its definition is applicable to macromolecules of any shape.

When MALS is used as a second detector in size exclusion chromatography (SEC), together with a concentration dependent detector such as a differential refractive index interferometer (RI), the radius of gyration for each individual slice across the whole chromatogram of the sample can be determined. Thus, the SEC-MALS technique allows the analysis of the distribution of the radius of gyration with elution volume.[22]

The chromatograms obtained from different injections are reproducible and there were no adsorption problems in the columns. Figure 4 depicts the signal of the differential refractive index detector (RI) (which is sensitive to the sample concentration) and the light scattering signals, determined with the MALS spectrophotometer, at different values of the scattering angle θ. The dependence of the intensity of the signal on the angle is evident and the scattering is therefore anisotropic. Thus the size of the molecules, i.e. the radius of gyration, can be determined for each slice of the chromatogram.[22] These values of the radii of gyration for the different slices are shown in Figure 5. The signal of the light scattering detector at 90° is superimposed. As can be seen in this figure, if we do not take into account the values determined for the head and tail of the chromatogram, the precision of which is lower, the monodispersity of the radius of gyration values is impressive. Both the appearance of the chromatogram, a very neat and defined peak, and the uniformity of the radius of gyration obtained through the slices of the chromatogram support the stability of the aggregates in THF. This stability is enough to bear the high pressures used in the chromatography. The average value for the root mean squared radius of gyration calculated for the sample is $<s^2>^{1/2} = 25 \pm 5$ nm. A water-soluble organometallic polymer which retains the polymeric structure in solution has been recently reported.[23]

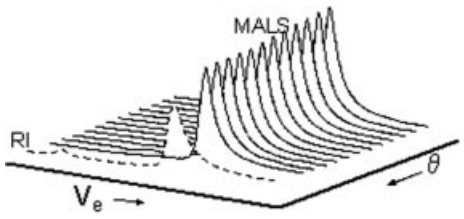


Figure 4. Refractive index, RI, signal (dashed line) and light scattering signals (solid lines) at different scattering angles, vs. elution volume.

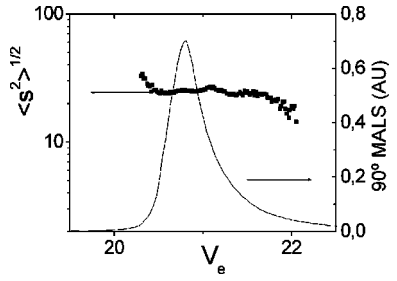


Figure 5. Root mean squared radius of gyration, $<s^2>^{1/2}$, in nm and 90° light scattering signal vs. elution volume.

b) Synthesis of [RuCl(η⁶-arene)(TPPMS)₂][Cl] [η⁶-arene = p-cymene (2a), benzene (2b)]

Addition of an aqueous solution of TPPMS to a solution of [RuCl(μ-Cl)(η⁶-arene)]$_2$ (η⁶-arene = *p*-cymene, benzene) in toluene affords, after five minutes at room temperature, the disubstituted complexes [RuCl(η⁶-arene)(TPPMS)$_2$][Cl] [η⁶-arene = *p*-cymene (**2a**), benzene (**2b**)] isolated from the aqueous phase as yellow solids in yields of 94% (**2a**) and 90% (**2b**) (Scheme 2).

Complexes **2a** and **b** are soluble in water, alcohols and dichloromethane but insoluble in diethyl ether. Elemental analyses agree with the proposed stoichiometry for each.[24] Conductivity measurements for these complexes were not very useful since the observed values are strongly dependent on the solvent (112–166 $\Omega^{-1}cm^2mol^{-1}$ in water, 66–80 $\Omega^{-1}cm^2mol^{-1}$ in acetone). The reason can be found in ionic associations between the ions which are important for these types of electrolytes and which increase when the dielectric constant of the solvent decreases.[25]

The most remarkable features of complexes **2a** and **2b** are: i) the ν(SO$_3$) absorption for the TPPMS ligand at 1197 cm^{-1} (**2a**) and 1198 cm^{-1} (**2b**) in the IR spectra (KBr); ii) the $^{31}P\{^1H\}$ NMR spectra show a singlet signal at δ = 22.5 (**2a**) and 22.8 ppm (**2b**) and iii) the high field signal at 8.39 (**2a**) and 8.24 ppm (**2b**) corresponding to the two H$_o$ hydrogen atoms of the TPPMS ligand which appears as a broad unresolved signal for these complexes.

Metathesis of the halide with KPF_6 in complex **2a** allows the synthesis of [RuCl(η⁶-*p*-cymene)(TPPMS)$_2$][PF$_6$] (**2a′**) which shows almost the same spectroscopic data as the former complex **2a**, except for the signals due to the PF_6^- group in the IR and in the $^{31}P\{^1H\}$ NMR spectra.

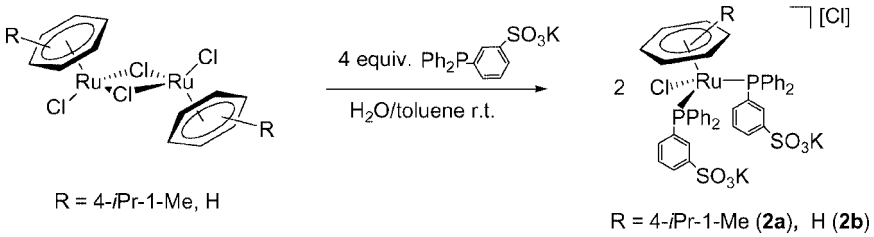
It is worth noting that **1a** and **b** as well as **2a** and **b** have been synthesised under very mild conditions in comparison with the recently reported analogous complexes with the tris(*meta*-sulfonatophenyl)phosphane trisodium salt (TPPTS) ligand, namely [RuCl$_2$(η⁶-*p*-cymene)(TPPTS)][26] and [RuCl(η⁶-benzene)(TPPTS)$_2$][Cl][27] which require reflux temperatures (methanol and water, respectively).

Reactivity of the Complex [RuCl$_2$(η⁶-*p*-cymene)(TPPMS)] (1a)

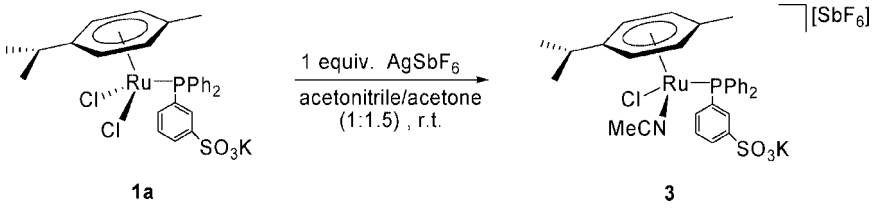
a) Synthesis of the Complex [RuCl(η⁶-p-cymene)(NCMe)-(TPPMS)][SbF₆] (3)

Treatment of complex **1a** with an appropriate chloride abstractor easily generates the non-isolated unsaturated species [RuCl(η⁶-*p*-cymene)(TPPMS)]$^+$ which can be identified by means of its reactivity. Thus, the reaction of complex **1a** with $AgSbF_6$ in the presence of acetonitrile gives rise to the adduct [RuCl(η⁶-*p*-cymene)(NCMe)-(TPPMS)][SbF$_6$] (**3**) in a moderate yield (58%) (Scheme 3).

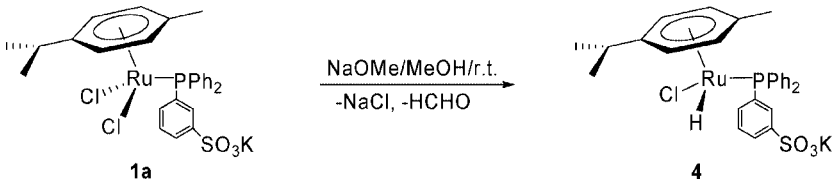
Complex **3** can be isolated as an air-stable yellow solid which is soluble in water, methanol, acetonitrile and acetone but insoluble in diethyl ether and hexane. It has been analytically and spectroscopically characterised. The spectroscopic data agree with the proposed stoichiometry (see the Exp. Sect. for details). Thus, the IR spectrum shows a strong band at 1199 cm^{-1} for the sulfonato group and one at 660 cm^{-1} for the SbF_6^- anion. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at δ = 35.1 ppm. The expected signals for the methyl group of the acetonitrile ligand appear at δ = 2.12 ppm in the ^1H NMR spectrum and at δ = 3.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum.



Scheme 2.



Scheme 3.



Scheme 4.

b) Synthesis of [RuClH(η⁶-p-cymene)(TPPMS)] (4)

One of the most efficient synthetic methods for transition metal hydrides is that using sodium alkoxides bearing β hydrogen atoms as hydrogen transfer agents.[28] Thus, the reaction of [$RuCl_2$(η⁶-*p*-cymene)(TPPMS)] (**1a**) with NaOMe in methanol yields the hydride derivative [RuClH(η⁶-*p*-cymene)(TPPMS)] (**4**) which can be isolated as a yellow solid in 63% yield after work-up (Scheme 4).

IR and NMR spectroscopic data of **4** are in accordance with the proposed formulation (see Exp. Sect. for details). Significantly, i) the IR spectrum of **4** shows the ν(RuH) absorption at 1954 cm^{-1} and the ν(SO_3) absorption at 1196 cm^{-1}; ii) the $^{31}P\{^1H\}$ spectrum displays a singlet resonances at δ = 55.0 ppm and iii) the ^1H NMR spectrum shows a high-field doublet resonance (δ = –7.45 ppm, $^2J_{H,P}$ = 53.0 Hz) due to the hydride ligand. This value is in agreement with that reported by Bennett for the analogous complex [RuClH(C_6Me_6)(PPh_3)].[29]

Catalytic Transfer Hydrogenation of Ketones

In recent years, transition metal catalysed transfer hydrogenation reactions between alcohols and ketones have become an efficient and clean alternative to the hydrogenation of carbonyl groups as illustrated by useful applications recently reported.[30] Also, ruthenium(II) complexes have been widely applied as efficient catalysts in these processes.[31] However, as in most of the homogeneous processes, the main problem stems from the difficulty in separating the products from the catalysts and in the recycling of expensive noble metals. The use of catalysts with hydrophilic properties can be a clean alternative for these processes since a simple extraction with water easily enables catalyst recovery.

This prompted us to explore the catalytic activity of the water-soluble complexes **1a** and **b** and **2a** and **b** in the reaction of transfer hydrogenation. The transfer hydrogenation of cyclohexanone by propan-2-ol was used as a model reaction. For comparative purposes, the activity of the derivative [RuCl(η⁵-C_9H_7)($TPPMS)_2$] is also reported.[32] Thus, in a typical experiment, KOH was added to an *i*PrOH solution of the ruthenium catalyst precursor (0.2 mol-%) and the ketone at 82 °C and the reaction was monitored by gas chromatography. In order to optimise the reaction, the following parameters were investigated: i) concentration: the best results were obtained with concentrated solutions (0.5 or 1 M). This result allows the reduction of the volume of *i*PrOH used in the catalysis in contrast with the conditions reported for other catalysts, where the best conditions are 0.1 or 0.2 M.[31] ii) base: KOH was the preferred option. Again, in our system, the amount of base could be drastically reduced (1.2 mol-%) compared with the usual conditions reported for this reaction (2–4 mol-%); iii) temperature: the activity of the catalyst decreases with temperature and almost no reactivity was observed at room temperature.

On the basis of our results, we conclude that the best conditions for the catalysis with these systems are as follow: 0.5 M cyclohexanone, 0.2 mol-% catalyst and 1.2 mol-% KOH in a total volume of 10 mL of *i*PrOH

Table 1 shows the results obtained with the different complexes in the reduction of cyclohexanone under the optimised reaction conditions. Although all the complexes studied have been shown to be active catalysts for the reduction of cyclohexanone to cyclohexanol, the arene complexes **1a** and **b**, and **2a** and **b** are much more efficient than the indenyl complex [RuCl(η⁵-C_9H_7)($TPPMS)_2$].

Table 1. Transfer hydrogenation of cyclohexanone.[a]

Complex	*t* (min)	Conv. (%)	*TOF* (h^{-1})
[$RuCl_2$(η⁶-*p*-cymene)(TPPMS)] (**1a**)	15	> 99	1994
[$RuCl_2$(η⁶-benzene)(TPPMS)] (**1b**)	10	> 99	2982
[RuCl(η⁶-*p*-cymene)($TPPMS)_2$][Cl] (**2a**)	45	> 99	663
[RuCl(η⁶-benzene)($TPPMS)_2$][Cl] (**2b**)	30	> 99	1000
[RuCl(η⁵-C_9H_7)($TPPMS)_2$]	270	63	70

[a] 0.2 mol-% catalyst, 0.5 M cyclohexanone, 10 mL *i*PrOH and 0.06 mmol KOH.

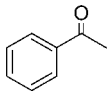
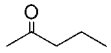
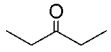
Complexes **1a** and **b** are very efficient catalysts leading to quantitative conversions in very short times. Therefore, the activity of complex **1a** as catalyst in the reduction of a variety of ketones to the corresponding alcohols was explored. Table 2 summarises the results obtained.

For all ketones, quantitative conversions were obtained. The observed TOF decrease appreciably when open-chain ketones with bulkier substituents were used (entries 5 and 7 vs. 4 and 6) indicating that steric requirements are important. Finally, aliphatic ketones are easier to reduce than aromatic ketones as shown for phenyl methyl ketone (entry 3).

Unfortunately, the activity of the catalyst decreases drastically when using water as a solvent or in biphasic conditions. The possibility of chloride dissociation in aqueous solutions, which would explain this behaviour, can be ruled out since the NMR spectra of complexes **1a** and **1b** were recorded in both D_2O and CD_3OD and no significance differences were detected. In addition, the conductivity measurements do not indicate chloride dissociation.

Although the diminished catalytic activity of **1a** in the presence of water prevents further studies on transfer hy-

Table 2. Transfer hydrogenation of ketones[a] by the complex [$RuCl_2$(η⁶-*p*-cymene)(TPPMS)] (**1a**).

Entry	Ketone	*t* [min]	Conv. [%]	*TOF* [h^{-1}]
1		15	> 99	1994
2		75	99	394
3		285	97	102
4		70	> 99	425
5		120	98	245
6		90	98	328
7		210	> 99	142

[a] 0.2 mol-% catalyst, 0.5 M ketone, 10 mL of *i*PrOH and 0.06 mmol of KOH.

drogenation with these complexes, the hydrophilic character of the complexes allows catalyst recovery. Thus, once the catalytic process has finished, the solvents can be evaporated under vacuum and diethyl ether and water added. The catalyst can be then easily recovered by extracting the mixture with water while the alcohol remains in the organic phase. Evaporation of the water under vacuum leads to a brown solid which can be reused for a further catalytic cycle. Figure 6 shows the results for three consecutive catalytic cycles.

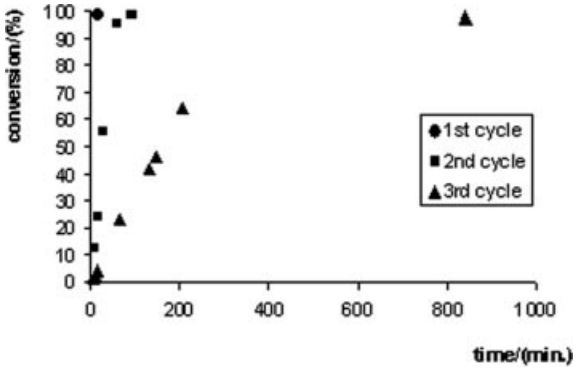


Figure 6. Transfer hydrogenation of cyclohexanone in three consecutive catalytic cycles.

The $^{31}P\{^1H\}$ and ^1H NMR spectra of the sample recovered after the catalysis show the presence of the hydride complex **4**, along with some other species. This observation agrees with the proposed hydride active species as a catalysts in the transfer hydrogenations reactions.[33] We have also tested the isolated hydride **4** as a catalyst. The reaction was complete within 40 minutes when a 1:1 ratio of KOH to catalyst was added. When the reaction was carried out without base, the catalytic activity decreased with time showing that a minimum amount of base is required, probably to promote the hydrogen transfer and/or the regeneration of the catalyst during the catalytic cycle.

Conclusions

In summary, we have reported the mild synthetic conditions of new water-soluble half-sandwich ruthenium(II) complexes and a preliminary study of their reactivity. The structure of complex **1a** has been determined X-ray diffraction studies showing a linear chain structure which is retained in nonpolar solvents. The radius of gyration calculated for the sample in a THF solution of $<s^2>^{1/2}$ = 25 ± 5 nm supports this assertion.

The derivatives **1a** and **b** as well as **2a**, **2b** and **4** allow fast transfer hydrogenation of ketones at low catalyst and base loading with TOF values of up to 3000 h^{-1}. Furthermore, the catalyst can be recycled due to the hydrophilic properties of the TPPMS ligand. The implication of hydride species in transfer hydrogenation catalysis can be assessed by the presence of the hydride derivative [RuClH(η⁶-*p*-cymene)(TPPMS)] (**4**) in the reaction mixture after the catalytic reactions.

Experimental Section

General Procedures: All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [RuCl(μ-Cl)(η⁶-*p*-cymene)]$_2$,[34] [RuCl(μ-Cl)(η⁶-benzene)]$_2$[34] and (*meta*-sulfonatophenyl)diphenylphosphane potassium salt (TPPMS)[35] were prepared by previously reported methods. Infrared spectra were recorded on a Perkin–Elmer FTIR Paragon 1000 spectrometer. The conductivities were measured at room temperature in ca. 5×10^{-4} mol dm^{-3} solutions with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyser. NMR spectra were recorded on Bruker AC300 and 300DPX instruments at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all the compounds. Coupling constants *J* are given in Hertz. Abbreviations used: br, broad signal; d, doublet; dd, double doublet; m, multiplet; sept, septuplet; s, singlet. Gas chromatographic measurements were made on Hewlett–Packard HP6890 instrument using a Supelco Beta-Dex 120 (30 m, 0.25 mm) column. The instability of complex **4** prevented us from obtaining any satisfactory analyses.

Synthesis of [$RuCl_2$(η⁶-*p*-cymene)(TPPMS)] (1a): To a solution of the dimer [RuCl(μ-Cl)(η⁶-*p*-cymene)]$_2$ (100 mg, 0.16 mmol) in methanol (15 mL) was added the (*m*-sulfonatophenyl)diphenylphosphane potassium salt (TPPMS) (103 mg, 0.32 mmol) and the reaction mixture was stirred for 30 min at room temperature. The solvents were removed under vacuum and the residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum to afford

complex **1a** as an orange solid. Yield: 201 mg (95%). IR (KBr): $\tilde{\nu}$ (SO_3) = 1200 cm^{-1}. Conductivity (water): 159 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.37 (d, $^3J_{H,P}$ = 10.2 Hz, 1 H, H_o), 7.78 (m, 5 H, TPPMS), 7.40 (m, 8 H, TPPMS), 5.33 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH of *p*-cymene), 5.20 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH of *p*-cymene), 2.63 [sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*(CH_3)$_2$], 1.87 (s, 3 H, CH_3), 1.06 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 20 °C): δ = 143.3–126.0 (TPPMS), 108.5 (d, $^2J_{C,P}$ = 2.4 Hz, C of *p*-cymene), 95.4 (s, C of *p*-cymene), 87.7 (d, $^2J_{C,P}$ = 3.8 Hz, CH of *p*-cymene), 85.8 (d, $^2J_{C,P}$ = 4.9 Hz, CH of *p*-cymene), 28.8 [s, *C*H(CH_3)$_2$], 19.4 [s, CH(*C*H$_3$)$_2$], 15.2 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 25 °C): δ = 26.1 (s) ppm. $C_{28}H_{28}Cl_2KO_3PRuS$ (686.60): calcd. C 48.98, H 4.11; found C 48.90, H 4.13.

Synthesis of [$RuCl_2$(η⁶-benzene)(TPPMS)] (1b): To a solution of TPPMS (160 mg, 0.40 mmol) in methanol (100 mL) was added the dimer [RuCl(μ-Cl)(η⁶-benzene)]$_2$ (100 mg, 0.20 mmol) and the reaction mixture was stirred for 2 h at room temperature. The solution was then filtered through kieselguhr and concentrated under vacuum to a volume of approx. 1 mL. Addition of diethyl ether afforded an orange precipitate. The solvents were decanted and the solid residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum to afford complex **1b** as an orange solid. Yield: 170 mg (68%). Conductivity (water): 160 Ω^{-1} cm^2mol^{-1}. IR (KBr): $\tilde{\nu}$ (SO_3) = 1198 cm^{-1}. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.28 (d, $^3J_{H,P}$ = 11.1 Hz, 1 H, H_o), 7.90 (br. s, 1 H, TPPMS), 7.72–7.65 (m, 4 H, TPPMS), 7.50–7.30 (m, 8 H, TPPMS), 5.52 (s, 6 H, CH of C_6H_6) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 20 °C): δ = 137.3–126.7 (m, TPPMS), 90.6 (d, $^2J_{C,P}$ = 3.7 Hz, CH of C_6H_6) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 20 °C): δ = 29.6 (s) ppm.

Syntheses of [RuCl(η⁶-arene)(TPPMS)$_2$][Cl]·2H_2O (2a) and (2b): A solution of TPPMS (206 mg, 0.64 mmol) in water (20 mL) was added dropwise to a solution of the respective dimer [RuCl(μ-Cl)(η⁶-*p*-cymene)]$_2$ (100 mg, 0.16 mmol) or [RuCl(μ-Cl)(η⁶-benzene)]$_2$ (80 mg, 0.16 mmol) in toluene (5 mL) and the reaction mixture was stirred for 5 min at room temperature. Then the aqueous layer was separated, filtered through kieselguhr and the solvent was removed under vacuum. The residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum to afford the complexes **2a** or **2b** as yellow solids. **2a**: Yield: 330 mg (94%). IR (KBr): $\tilde{\nu}$ (SO_3) = 1197 cm^{-1}. Conductivity (water): 176 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.39 (br. s, 2 H, H_o), 7.87 (d, $J_{H,H}$ = 7.7 Hz, 2 H,TPPMS), 7.49–7.17 (m, 24 H, TPPMS), 5.76 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH of *p*-cymene), 5.51 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH of *p*-cymene), 2.87 [sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 1.21 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.00 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 20 °C): δ = 144.5–125.5 (TPPMS), 109.4 (s, C of *p*-cymene), 99.8 (s, C of *p*-cymene), 97.0 (s, CH of *p*-cymene), 88.7 (d, $J_{C,P}$ = 4.5 Hz, CH of *p*-cymene), 30.4 [s, *C*H(CH_3)$_2$], 20.0 [s, CH(*C*H$_3$)$_2$], 13.6 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 20 °C): δ = 22.5 (s) ppm. $C_{46}H_{46}Cl_2K_2O_8P_2RuS_2$ (1067.08): calcd. C 50.09, H, 4.20; found C 49.03, H 4.20. **2b**: Yield: 340 mg (90%). IR (KBr): $\tilde{\nu}$ (SO_3) = 1198 cm^{-1}. Conductivity (water): 200 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.24 (br. s, 1 H, TPPMS), 7.91 (br. s, 1 H, TPPMS), 7.16 (m, 26 H, TPPMS), 5.67 (s, 6 H, CH of C_6H_6) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 20 °C): δ = 143.9–128.4 (TPPMS), 96.6 (s, CH of C_6H_6) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 20 °C): δ = 22.8 (s) ppm. $C_{42}H_{38}Cl_2K_2O_8P_2RuS_2$ (1010.97): calcd. C 48.18, H 3.66; found C 48.20, H 3.03.

Synthesis of [RuCl(η⁶-*p*-cymene)(NCMe)(TPPMS)][SbF_6] (3): To a solution of [$RuCl_2$(η⁶-*p*-cymene)(TPPMS)] (**1a**) (100 mg, 0.15 mmol) in a mixture acetonitrile (20 mL) and acetone (50 mL) was added $AgSbF_6$ (50 mg, 0.15 mmol) and the reaction mixture was stirred for 14 h at room temperature in the absence of light. The solution was then filtered through kieselguhr and concentrated under vacuum to a volume of approx. 1 mL. Addition of diethyl ether afforded a yellow precipitate. The solvents were decanted and the solid residue was washed with diethyl ether (2 × 10 mL) and dried under reduced pressure to afford complex **3**. Yield: 80 mg (58%). IR (KBr): $\tilde{\nu}$ (SO_3) = 1199, $\tilde{\nu}$ (SbF_6) = 660 cm^{-1}. Conductivity (acetonitrile): 92 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.19 (d, $^3J_{H,P}$ = 12.2 Hz, 1 H, H_o), 7.95 (m, 1 H, TPPMS), 7.62–7.46 (m, 12 H, TPPMS), 6.05 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH of *p*-cymene), 5.56 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH of *p*-cymene), 5.53 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH of *p*-cymene), 5.21 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, CH of *p*-cymene), 2.72 [sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*(CH_3)$_2$], 2.12 (m, 3 H, NCC*H*$_3$), 1.87 (s, 3 H, CH_3), 1.23 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.19 [d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 135.3–128.4 (TPPMS and N*C*CH_3), 114.6 (s, C of *p*-cymene), 103.1 (s, C of *p*-cymene), 93.7 (s, CH of *p*-cymene), 89.0 (s, CH of *p*-cymene), 88.7 (s, CH of *p*-cymene), 31.3 [s, CH(*C*H$_3$)$_2$], 22.8 [s, CH(*C*H$_3$)$_2$], 21.0 [s, *C*H(CH_3)$_2$], 18.0 (s, CH_3), 3.4 (s, NC*C*H$_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 20 °C): δ = 35.1 (s) ppm. $C_{30}H_{31}ClF_6KNO_3PRuSSb$ (927.98): calcd. C 38.83, H 3.37, N 1.51; found C 38.39, H 3.63, N 1.36. MS (FAB+): *m*/*z* = 614 [M^+–K–NCMe], 576 [M^+–Cl –K–$NCCH_3$], 271 [M^++2–NCMe –TPPMS].

Synthesis of [RuClH(η⁶-*p*-cymene)(TPPMS)] (4): A solution of complex **1a** (100 mg, 0.15 mmol) in methanol (5 mL) was added dropwise to a solution of NaOMe (4 mg, 0.17 mmol) in methanol (5 mL) and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed and the solid residue was extracted with dichloromethane and the resultant solution filtered through kieselguhr and concentrated under vacuum to a volume of approx. 1 mL. Addition of diethyl ether afforded a yellow precipitate. The solvents were decanted and the solid residue was washed with diethyl ether (4 × 10 mL) and dried under reduced pressure to afford complex **4**. Yield: 45 mg (46%). IR (KBr): $\tilde{\nu}$ (Ru–H) = 1954, $\tilde{\nu}$ (SO_3) = 1199 cm^{-1}. Conductivity (methanol): 87 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.34–7.36 (m, 14 H, TPPMS), 5.68 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH of *p*-cymene), 5.20 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH of *p*-cymene), 4.97 (dd, $^3J_{H,H}$ = 6.4 and 5.6 Hz, 1 H, CH of *p*-cymene), 4.25 (d, $^3J_{H,H}$ = 5.6 Hz, 1 H, CH of *p*-cymene), 2.16 [m, 1 H, C*H*(CH_3)$_2$], 1.99 (s, 3 H, CH_3), 1.12 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.06 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$], –7.45 (d, $^2J_{H,P}$ = 53.0 Hz, 1 H, Ru–H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 20 °C): δ = 144.0–125.2 (m, TPPMS), 104.6 (s, 2 × C of *p*-cymene), 91.4 (s, CH of *p*-cymene), 91.3 (s, CH of *p*-cymene), 79.3 (s, CH of *p*-cymene), 79.2 (s, CH of *p*-cymene), 30.5 [s, *C*H(CH_3)$_2$], 22.6 [s, CH(*C*H$_3$)$_2$], 21.3 [s, CH(*C*H$_3$)$_2$], 17.0 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD, 20 °C): δ = 55.0 (s) ppm.

Synthesis of [RuCl(η⁶-*p*-cymene)(TPPMS)$_2$][PF_6]·2H_2O (2a′): To a solution of complex **2a** (50 mg, 0.05 mmol) in methanol (5 mL) was added KPF_6 (11 mg, 0.06 mmol). The mixture was stirred for 30 min at room temperature and was then evaporated to dryness. The residue was extracted with dichloromethane and concentrated under vacuum to a volume of approx. 1 mL. Addition of diethyl ether afforded a yellow precipitate. The solvents were decanted and the solid residue was washed with diethyl ether (2 × 10 mL) and

dried under vacuum to afford complex **2a′**. IR (KBr): $\tilde{\nu}$ (PF_6^-) = 844 cm^{-1}.

Transfer Hydrogenation of Ketones – General Procedure: The samples were typically prepared as follows: the ketone (5 mmol), ruthenium catalyst precursor (0.01 mmol, 0.2 mol-% of Ru) and propan-2-ol (9.25 mL) were introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min in an inert atmosphere. KOH was then added (0.75 mL of a 0.08 M solution in propan-2-ol, 1.2 mol-%) and the reaction monitored by gas chromatography. The corresponding alcohol and acetone were the only products detected in all cases. The identity of the alcohols was assessed by comparison with commercially available (Aldrich Chemical Co. or Acros Organics) pure samples.

X-ray Crystal Structure Determination of Complex 1a: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in methanol. The most relevant crystal and refinement data are collected in Table 3. A light-orange prismatic single crystal was mounted on a glass fibre and transferred to a Bruker SMART 6 K CCD area-detector three-circle diffractometer (Cu-K_α radiation, λ = 1.5418 Å).[36] X-ray data were collected at 100(2) K with a combination of three runs at different φ and 2θ angles. The data were collected using 0.3° wide ω scans with a crystal-to-detector distance of 4.0 cm. The substantial redundancy in data allowed empirical absorption corrections (SADABS)[37] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission = 0.602305). A total number of 8520 reflections were collected, with 4401 independent reflections (R_{int} = 0.0316). The raw intensity data frames were integrated with the SAINT program[38] which also applied corrections for Lorentz and polarisation effects.

Table 3. Crystal data and structure refinement for **1a**.

	1a
Chemical formula	$C_{28}H_{28}Cl_2KO_3PRuS$
*F*w	686.60
T [K]	100(2)
Wavelength [Å]	1.5418
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.1813(2)
b [Å]	12.1763(2)
c [Å]	12.5166(2)
α [°]	94.1940(10)
β [°]	96.1750(10)
γ [°]	94.8240(10)
V [Å^3]	1381.46(4)
Z	2
$\rho_{calcd.}$ [g cm^{-3}]	1.651
μ [mm^{-1}]	9.219
F(000)	696
Crystal size [mm]	0.12 × 0.09 × 0.104
θ range [°]	3.56 to 66.73
Index ranges	$-9 \le h \le 10$; $-14 \le k \le 13$; $-13 \le l \le 14$
No. of reflections collected	8520
No. of unique reflections	4401 [R_{int} = 0.0316]
Completeness to $\theta_{max.}$	90.1%
No. of parameters/restraints	337/0
Goodness-of-fit on F^2	1.034
R_1[a] [$I > 2\sigma(I)$]; wR_2[a] [$I > 2\sigma(I)$]	0.0400; 0.1011
R_1(all data); wR_2(all data)	0.0497; 0.1078
Largest diff peak and hole [e Å^{-3}]	1.295 and –0.510

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-290177 (for **1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The software package WINGX was used for space group determination, structure solution and refinement.[39] The space group determination was based on a check of the Laue symmetry and systematic absences and ascertained from the structure solution. The structure was solved by Patterson interpretation and phase expansion using DIRDIF,[40] completed with difference Fourier syntheses and refined with full-matrix least-squares using SHELXL-97.[41] Weighted *R* factors (R_w) and all goodness of fit *S* are based on F^2. Conventional *R* factors (*R*) are based on *F*. All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were geometrically located and their coordinates were refined as riding on their parent atoms. The function minimised was $[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0921P)^2 + 0.0000P]$ with $\sigma^2(F_o^2)$ from counting statistics and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[42] Geometrical calculations were made with PARST.[43] Plots were made with PLATON.[44]

Radius of Gyration Measurements: Size exclusion chromatography (SEC) measurements were carried out using a Waters Associates instrument coupled with an Optilab interferometric differential refractive index detector (RI) and a multiangle light scattering (MALS) DAWN DSP-F laser photometer detector both from the Wyatt Technology Corp. The photometer was calibrated with spectrometric grade toluene (Scharlau) and the normalisation of its detectors in THF was performed with low molecular weight standard samples of polystyrene. The same polystyrene standard was used to determine the interdetector volume. Two columns PLgel mixed B (Polymer Laboratories) in series completed the setup and THF freshly distilled from sodium and benzophenone, filtered through a 0.2 μm Fluoropore membrane (Millipore) and degassed, was used as eluent. The flow rate was 1.0 mL min^{-1} and the temperature 25 °C.

The basic light-scattering equation at the small concentrations used in the size exclusion chromatography is[45] given by Equation (1).

$$\frac{K_c}{\Delta R_\theta} = \frac{1}{M}\left(1 + \frac{16\pi^2}{3\lambda^2} < s^2 > \sin^2\left(\frac{\theta}{2}\right) + \cdots\right) \quad (1)$$

where R_θ is the excess Rayleigh ratio of the light scattered by the solute molecules in a solution, *c* is the concentration of the solution, λ is the wavelength of the incident light in the medium, θ is the scattering angle, $<s^2>$ the mean squared radius of gyration and *K* is an optical constant.

The parentheses of Equation (1) contain the terms of the particle form factor which takes into account the interferences among light scattered at different angles for large molecules. At $\theta = 0$ the interferences vanish and the following expression can be written (Equation 2).

$$\frac{\Delta R_{\theta=0}}{\Delta R_\theta} = 1 + \frac{16\pi^2}{3\lambda^2} < s^2 > \sin^2\left(\frac{\theta}{2}\right) + \cdots \quad (2)$$

Thus the angular dependence of the scattered light enables the measurement of radius of gyration provided that the size of the par-

ticles is large enough compare with the wavelength and that the normalisation constants for the different detectors have been determined.[22,45]

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