Novel Phosphinite−Ruthenium(II) Complexes Covalently Bound on Silica: Synthesis, Characterization, and Catalytic Behavior versus Oxidation Reactions of Alcohols into Aldehydes

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The novel tridentate phosphinite−Ru complex **5** has been prepared, characterized, and bound on silica via the spacer arm **16**. The efficiency of this heterogenized catalyst for the oxidation of alcohols into aldehydes with *N*-methylmorpholine oxide has been examined, in comparison to the efficiency of the corresponding heterogenized monodentate phosphinite−Ru complex (without **7** and with the spacer arm **11**) and the corresponding homogeneous catalysts **3** and **5**, respectively. The heterogenized monodentate catalysts were 2 and 3 times more active than the soluble phosphinite−Ru complex, while the heterogenized tridentate catalyst showed almost the same activity. All catalysts are endowed with good to excellent selectivities. The heterogenized monodentate catalysts could not be efficiently recycled; on the other hand, the heterogenized tridentate catalyst **16** worked for four cycles. However, the major problem was a significant metal leaching, after the first cycle.

Introduction

Numerous efforts have been devoted to the development of new supported catalysts combining the advantages of conventional homogeneous and heterogeneous catalysts.[1] Application to the field of transition-metal catalysis was particularly addressed,[2] since in this case recovery and reuse of the catalyst could bring valuable economical and environmental advantages. Functionalized cross-linked polystyrene[3] and silica[4] were the most currently used supports, on which organic ligands could be immobilized either by covalent linkage or by hydrogen-bonding interaction.[5] The grafting of transition-metal complexes on such solid supports has been well illustrated with rhodium[2c] and, to a lesser extent, ruthenium complexes,[5a] useful in various reduction processes such as hydrogenation and hydrogen transfer reactions. The supported catalysts were stable and reusable without significant loss of activity or selectivity.[3] The situation is totally different considering oxidation processes,[6] most probably because the available homogeneous catalysts[7] are not so numerous, but also (and mainly) because the oxidation catalysts based on transition-metal complexes are usually less stable and more sensitive toward the reaction conditions.[8] Accordingly, most of the examples of heterogenizing homogeneous oxidation catalysts concern Sharpless- and Jacobsen-type catalysts used for olefin dihydroxylation[9] and epoxidation.[10] On the other hand, oxidation of alcohols into aldehydes (ketones) catalyzed by supported ruthenium complexes appears to be scarcely studied at the present time.[11−13]

In this paper, we describe our attempts to construct heterogeneous ruthenium catalysts which would operate as if they were in solution. In preliminary experiments,[14a] we have already selected phosphinite derivatives as metal ligands because they appear to be more stable

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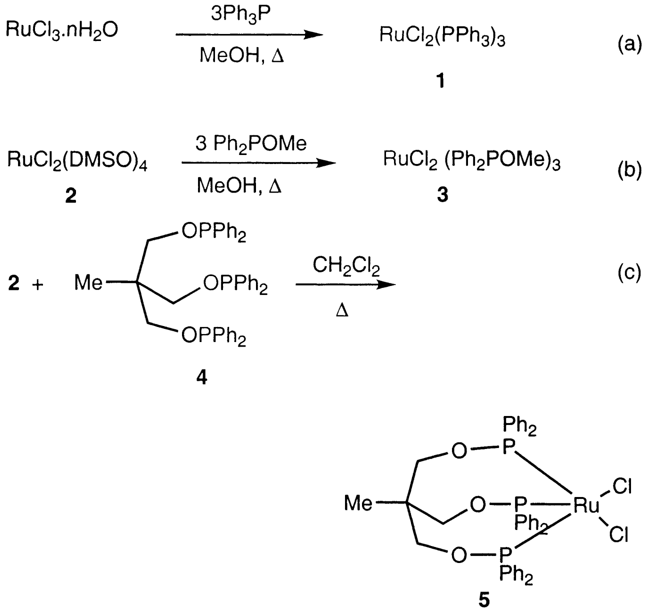
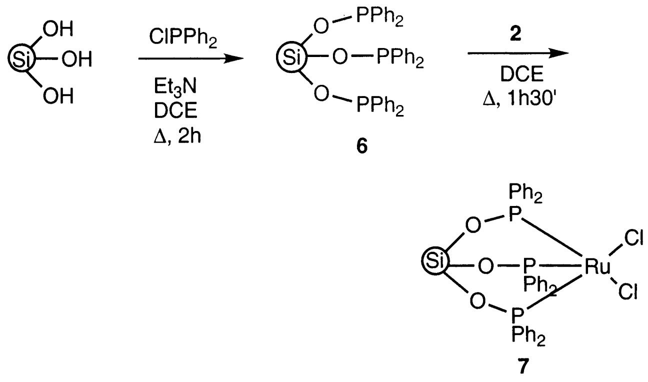
Scheme 1. Preparation of Homogeneous Catalysts



Scheme 2. Preparation of Heterogenized Catalyst 7



toward self-oxidation than the traditional phosphine ligands. The selected support was silica, a material chemically stable to oxidation, which can be easily derivatized by standard reactions.[15] Thus, a novel tripodal phosphinite–Ru complex has been prepared and bound on silica via a spacer arm. The efficiency of this material as catalyst for the oxidation of alcohols into aldehydes has been examined, comparatively to the corresponding homogeneous catalyst. The possibility of recycling the heterogenized catalyst and, more particularly, the extent of Ru leaching under reaction conditions were also considered.

Results and Discussion

Synthesis and Characterization of Homogeneous Catalysts (Reference Systems). Dichlorotris(triphenylphosphine)ruthenium(II) (**1**) (Scheme 1a) is a commercially available catalyst, very popular for alcohol oxidation with *N*-methylmorpholine oxide (NMMO);[16] this will constitute our reference system. As previously stated,[14] we used phosphinite complexes, which are more convenient for our purposes. Thus, starting with dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (**2**) as a practical source of Ru(II),[17] we prepared dichlorotris(methoxydiphenylphosphine)ruthenium(II) (**3**)[14a] by reaction with methoxydiphenylphosphine in refluxing methanol (Scheme 1b). Similarly, the corresponding tridentate complex **5** was obtained from **2** and 1,1,1-tris(((diphenylphosphino)oxy)methyl)ethane (**4**) (Scheme 1c) by reaction of the triol precursor with chlorodiphenylphosphine in the presence of triethylamine in dichloromethane. Compound **5** was purified by chromatography on Sephadex gel and well identified by mass spectrometry, which displayed the typical isotopic pattern of Ru centered at *m*/*e* 808.8 (M − Cl). X-ray diffraction analysis[14b] of a monocrystal (obtained by slow evaporation from a chloroform solution) showed a dimeric structure in the solid state, very similar to that of compound **3**.[14a] On the other hand, ^{31}P NMR spectroscopy revealed two broad signals at 142.8 and 153.7 ppm, assigned respectively to equatorial and apical phosphorus in the monomeric complex **5**. The dimer of **5**, which presents a local symmetry of order 3 around the axis linking the two Ru atoms, should give only one signal in ^{31}P NMR; thus, in chloroform solution, a significant part of the complex exists as the monomeric form.

Synthesis and Characterization of Heterogenized Catalysts. Three systems of increasing complexities were considered: (i) catalyst **7** (Scheme 2) with diphenylphosphine ligands directly bound on the OH groups of the silica surface, (ii) catalyst **11** (Scheme 3) with a monopodal phosphinite ligand bound on the inorganic support via a flexible spacer arm, and (iii) catalyst **16** (Scheme 4) with a tripodal phosphinite ligand bound via the same spacer as above. Complex **3** (Scheme 1b) can be considered as the soluble model of heterogeneous catalysts **7** and **11**, while complex **5** (Scheme 1c) mimics the catalytic site of the heterogenized catalyst **16**.

We used a silica support displaying about 2.5 mmol/g of hydroxyl functions. Reaction with chlorodiphenylphosphine and triethylamine in refluxing dichloroethane (DCE) gave the phosphinite-derivatized silica species **6**, which was directly transformed into Ru(II) complex **7** (Scheme 2) by treatment with dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (**2**) as described in the case of homogeneous catalysts. After a 2 day extraction with CH_2Cl_2 and ether, the modified silica was characterized by thermogravimetry: we found 0.44 mmol/g of grafted ligand (i.e. theoretically 0.15 mmol/g of Ru complex), corresponding to about 18% of surface derivatization. Fixed ruthenium has been experimentally assayed by atomic absorption spectrometry as follows: the catalyst was successively treated with perchloric acid (10% in water) and sodium hydroxide (5% in water) in order to recover all the ruthenium species in solution; after filtration of silica, the solution was concentrated to a standard volume and analyzed by atomic absorption (the apparatus being previously calibrated with reference solutions of ruthenium chloride). We found 0.08 mmol/g of Ru; this value corresponds to a P/Ru ratio of

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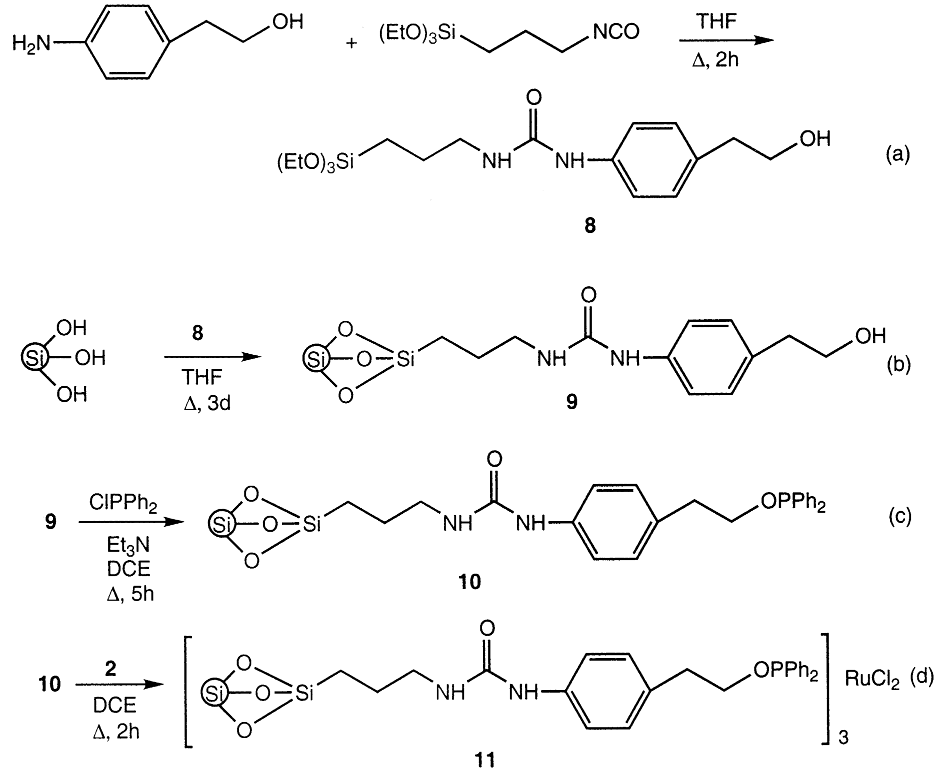
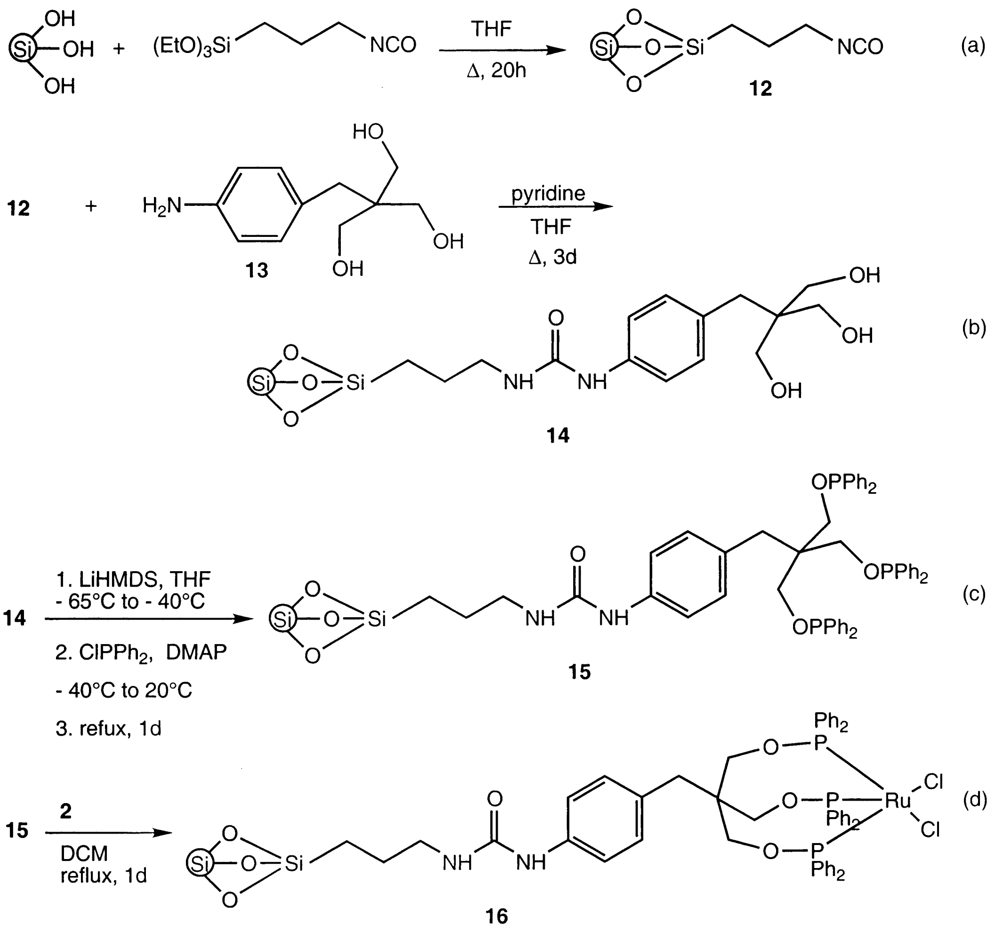
Scheme 3. Preparation of Heterogenized Monodentate Catalyst 11



Scheme 4. Preparation of Heterogenized Tridentate Catalyst 16



5.5 (the theoretical P/Ru value was 3 for structure **7**; Table 1, entry 2).

The spacer arm **8** required for the construction of catalyst **11** was prepared by reacting (*p*-amino)phen-

Table 1. Characterization of Derivatized Supports

entry	support	support no.	amt of grafted ligand, mmol/g	% surface derivat	amt of fixed Ru, mmol/g	P/Ru
1	Si−OH (native support)	-	2.50			
2	Si−OPPh$_2$Ru	**7**	0.44	18	0.08	5.5
3	Si−spacer−OH	**9**	0.50	60		
4	Si−spacer−OPPh$_2$Ru	**11**	0.40	48	0.16	2.5
5	Si−spacer−(CH$_2$OH)$_3$	**14**	0.45	54		
6	Si-spacer−(CH$_2$OPPh$_2$)$_3$Ru	**16**	0.33	40	0.62	1.6
7	PS−PPh$_2$Ru[11]	**17**	n.d.	n.d.	0.80	n.d.

ethyl alcohol with 3-isocyanato-1-(triethoxysilyl)propane in tetrahydrofuran (THF) at reflux (Scheme 3a). The complete chemoselectivity of this reaction was proved by the NMR and IR analysis of the product. Compound **8** was immediately adsorbed on silica in suspension in THF at 20 °C (3 h) and then grafted by heating the mixture for 3 days. After several washings (see the Experimental Section), the derivatized silica **9** (Scheme 3b) was characterized by thermogravimetry: we determined the presence of 11% of organic materials, i.e. 0.5 mmol/g of grafted silanols. Thus, assuming that each molecule **8** occupies three silanol functions of the native silica, we could consider that about half of the available Si−OH groups has reacted (maximum value 1/3 of 2.5 mmol/g = 0.83 mmol/g). The modified silica **9** was further treated with chlorodiphenylphosphine and triethylamine in refluxing DCE (Scheme 3c) to furnish silica **10**, immediately transformed into Ru catalyst **11**, as described for **7** (Scheme 3d). Thermogravimetry and elemental analysis gave very concordant results: silica **11** contains 0.4 mmol/g of ligand, corresponding to 48% of surface derivatization. The measurement of fixed ruthenium by atomic absorption, as previously described, confirmed the presence of 0.16 mmol Ru/g, corresponding to a P/Ru atomic ratio of 2.5 (theoretical value 3 for catalyst **11**; Table 1, entry 4). The characteristics of **11** are in good agreement with those of its precursor **9** (Table 1, entry 3); thus, the chemical yields of the reactions performed on the solid support (Scheme 3, steps c and d) are nearly quantitative.

The preparation of catalyst **16** made use of the triol **13** as precursor of the tripodal ligand. The synthesis of this molecule has been fully described elsewhere.[18] The solvents which solubilize **13** (H_2O, CH_3OH, pyridine, ...) are not compatible with the stability of 3-isocyanato-1-(triethoxysilyl)propane. Therefore, this last reagent was first grafted on silica in refluxing THF (Scheme 4a), and the resulting material **12** (1.2 mmol/g of isocyanate reactive termini, most probably contaminated with unreactive carbamate termini resulting from EtOH addition) was coupled to **13** in a mixture of THF and pyridine (Scheme 4b). After 3 days of heating, the modified silica **14** was washed, dried, and analyzed as before. From thermogravimetry and elemental analysis, we found 0.45 mmol/g of fixed ligand, i.e. 54% of surface derivatization, considering that three silanol functions are used to immobilize one molecule of ligand (Table 1, entry 5). The next step, i.e. reaction of triol **14** with chlorodiphenylphosphine (Scheme 4c), appeared somewhat arduous. In the presence of triethylamine (as before), diazabicyclooctane (DABCO), diazabicycloundecene (DBU), or (dimethylamino)pyridine (DMAP), the yields of substitution were less than 20% (thermogravimetric analysis). Therefore, we first deprotonated the triol **14** by treatment with lithium hexamethyldisilazanate (LiHMDS) in THF at −70 °C and then added chlorodiphenylphosphine at −40 °C, in the presence of DMAP. The mixture was further heated for 1 day to achieve the nucleophilic substitution. The resulting silica **15** (Scheme 4c) was washed and directly reacted with $RuCl_2(DMSO)_4$ (**2**) in refluxing DCM to furnish the complex **16** (Scheme 4d). Thermogravimetric analysis, confirmed by the elemental analysis, gave 0.33 mmol/g of grafted catalyst (about 80% yield from **14**) corresponding to 40% of surface derivatization (Table 1, entry 6). The amount of ruthenium, measured by atomic absorption, was 0.62 mmol/g. Accordingly, the P/Ru atomic ratio was 1.6, instead of 3 (theoretical value); thus, an excess of ruthenium is fixed on the modified silica **16**, which could not be removed by extraction (Soxhlet) with DCM.

Catalytic Properties of Homogeneous Catalysts. The activity and selectivity of the new catalysts **3** and **5** (Scheme 1) have been evaluated comparatively to catalyst **1** (commercially available) in classical oxidation reactions of alcohols with *N*-methylmorpholine oxide (NMMO).[14,16] Benzyl alcohol, 1-octanol, *trans*-2-hexen-1-ol, *cis*-2-hexen-1-ol, 2-octanol, and 1-phenylethanol, respectively, dissolved in DCM (100 μL/5 mL) were treated at room temperature with NMMO (2 equiv) in the presence of the tested catalyst (2 mol %). The crude reaction mixtures were quantitatively analyzed by gas chromatography (GC) or high-performance liquid chromatography (HPLC). The conversions (percentages of transformed alcohol) and selectivities to aldehydes (percentages of aldehyde with respect to alcohol converted), after 6 h of reaction for catalysts **3** and **5** (phosphinite ligands) and 1.5 h of reaction for catalyst **1** (Ph_3P ligand), are given in Table 2. The only side product observed, in very few cases, was the corresponding carboxylic acid.

The selectivities of the three catalysts are high and quite similar, though the selectivity of the Ru−phosphinite complexes appears slightly better (see entry 2, oxidation of 1-octanol). On the other hand, the Ru−phosphine catalyst **1** is significantly more active (short reaction time and high conversion) than the corresponding Ru−phosphinite catalyst **3**, but some activity is restored in the case of catalyst **5** built from the tripodal phosphinite ligand. The catalytic performances of **5** were considered as good enough to envisage its heterogenization. Moreover, a great advantage of **5** over **1** was its stability in an air atmosphere, allowing easy manipulations for further catalyst recovery. A solution of **5** in $CDCl_3$ was stable for several hours, while complex **1** transformed into triphenylphosphine oxide within 90 min (^{31}P NMR analysis).

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Table 2. Catalytic Performances of Various Homogeneous Catalysts in Alcohol Oxidation (Alcohol Conversion, Selectivity to Aldehyde) at 20 °C with NMMO as Oxidant (2 mol % Ru)

		cat. **3**[a]		cat. **5**[a]		cat. **1**[b]	
entry	alcohol	conversn, %	select, %	conversn, %	select, %	conversn, %	select, %
1	benzyl alcohol	32	94	73	91	94	93
2	1-octanol	22	100	58	90	97	82
3	2-hexen-1-ol (trans)	13	100	50	100	90	100
4	2-hexen-1-ol (cis)	30	100	87	100	100	100
5	2-octanol	23		66		100	
6	1-phenylethanol	24		82		76	

[a] After 6 h of reaction. [b] After 1.5 h of reaction.

Scheme 5. Preparation of Heterogeneous Reference Catalyst 17

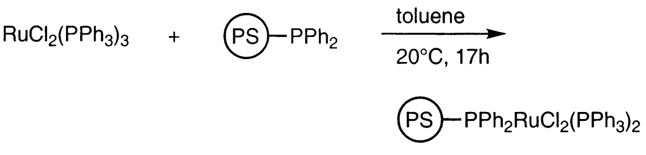

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Table 3. Catalytic Performances of Various Heterogenized Catalysts in the Oxidation of 1-Octanol with NMMO as Oxidant ($T = 20$ °C; $t = 6$ h; 2 mol % Ru)[a]

	cat. **7**			cat. **11**			cat. **16**			cat. **17**		
run	X, %	S, %	A	X, %	S, %	A	X, %	S, %	A	X, %	S, %	A
1	48	100	27	75	85	34	46	85	14	48	87	21
2	0		0	5	100	4	22	100	16	26	100	14
3				0		0	40	100	32	27	100	17
4							20	100	16	14	100	9
5							0		0	15	100	10
6										0		0

[a] The definitions of X, S, and A are as follows. X = conversion: GC analysis (percentage of transformed 1-octanol). S = selectivity toward octanal: GC analysis (percentage of octanal versus transformed 1-octanol). A = activity expressed as mmol of alcohol transformed per mmol of Ru effectively present in the catalyst (see Table 4).

Table 4. Ru Leaching from the Supports during the Recycling Assays[a]

	cat. **7**		cat. **11**		cat. **16**		cat. **17**	
cycle	[Ru], mmol/g	%	[Ru], mmol/g	%	[Ru], mmol/g	%	[Ru], mmol/g	%
0	0.077	100	0.158	100	0.618	100	0.800	100
1	0.053	69	0.076	48	0.353	57	0.119	15
2	0.008	10	<0.005		0.021	3	0.048	6
3			<0.005		0.006	1	0.027	3
4					<0.005		0.008	1
5					<0.005		0.008	1
6							<0.005	

[a] [Ru] was measured by atomic absorption analysis of the solutions, after filtration of the catalyst; values are expressed per g of catalyst and as the percentage of released Ru from the native catalyst.

Catalytic Properties of Heterogenized Catalysts. The performances of heterogenized catalysts **7** (Scheme 2), **11** (Scheme 3), and **16** (Scheme 4) (Table 1) have been evaluated comparatively to the reference catalyst **17**, formed by ligand exchange between $RuCl_2(PPh_3)_3$ (**1**) and polystyrene-supported triphenylphosphine (Scheme 5) according to a recent literature procedure.[11] In all cases, the reaction considered was the oxidation of 1-octanol with NMMO under the standard conditions previously described.

The first use of the heterogenized catalysts **7**, **11**, and **16** (Table 3, first run) gave conversion ratios different from those of the corresponding homogeneous catalysts **3** and **5** (Table 2, entry 2); monodentate catalysts **7** and **11** were more active than their soluble model **3** (48% and 75% of conversion versus 22%), and the use of a spacer arm to anchor the ligand brought a significant advantage. The tridentate catalyst **16** was slightly less active than its soluble model **5** (46% of conversion versus 58%), while the reference system **1** (phosphine ligands instead of phosphinite ones) became sluggish when immobilized on PS: 48% of conversion after 6 h (**17**) versus 97% after 1.5 h (**1**). These observations could result from two antagonistic effects: (i) catalyst heterogenization favors the monomeric form of the ruthenium complex, which should be more active than the dimeric one;[14,19] (ii) catalyst immobilization reduces mobility and accessibility of the partners and, hence, the reactivity of the system.

The heterogenized catalysts **11** and **16** were found to be stable under an air atmosphere, as the corresponding soluble complexes. After prolonged storage (3−6 months) at room temperature, our silica-bound catalysts showed the same features (activity and selectivity) as the freshly prepared catalysts in the standard oxidation reaction of 1-octanol (run 1, Table 3).

Recycling of Heterogenized Catalysts. After their first use, all the catalysts were filtered off from the solutions and engaged again in successive oxidation reactions of 1-octanol under the standard conditions.

Catalyst **7** was totally deactivated after the first utilization (Table 3, run 2); thus, Ru complexes with phosphinite ligands directly bound to silanol groups of the silica support, entities susceptible to be formed during the synthesis of catalysts **11** and **16**, could not be responsible for the activity of these catalysts, after the first run. Catalysts **11**, **16**, and **17** are still operational in the second use, with a total selectivity (Table 3, run 2). However, the monodentate catalyst **11** induced a very low conversion ratio, comparatively to the tridentate catalyst **16** and the reference **17**; this catalyst became totally inactive in the third use (Table 3, run 3). On the other hand, the tridentate catalyst **16** and the reference **17** worked until the fifth and sixth uses, respectively (Table 3, runs 4−6).

During the recycling assays, leaching of ruthenium from the supports occurred; this has been measured by atomic absorption analysis of the solutions, after removal of the catalysts upon filtration (Table 4). Taking into account the loss of metal, a "normalized catalytic

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Table 5. Effects of the Catalyst Preincubation (17 h at 20 °C) in Solvent, Neat, and Containing One of the Reaction Partners[a]

cat.		DCM	1-octanol	octanal	octanoic acid	NMMO	NMM
7	*X*, %	44	31	23	25	<5	11
	S, %	100	100	100	100	n.d.	100
	Ru loss, %	15	13	19	19	98	51
16	*X*, %	66	41	45	58	22	55
	S, %	89	87	87	90	100	84
	Ru loss, %	2	1	4	6	61	18
17	*X*, %	35	33	38	41	23	38
	S, %	100	92	93	88	100	93
	Ru loss, %	<1	1	<1	<1	15	5

[a] For definitions of *X* and *S*, see Table 3.

activity" could be calculated after each cycle: i.e., the ratio of 1-octanol transformed per mmol of Ru actually present in the catalyst. We are aware that such an activity is difficult to interpret, since a lot of weakly bound ruthenium is lost in the first run. However, the values collected in Table 3 (column A for each catalyst) showed that Ru leaching is well responsible for the deactivation of the tridentate catalyst (**16**): after extensive loss of about 60% of metal in the first cycle, the catalyst works with almost constant activity (and 100% selectivity) during three further cycles. On the other hand, the loss of about 50% of the metal after the first cycle could not be the only reason for the dramatic deactivation of the corresponding monodentate catalyst (**11**). Only small quantities of Ru were lost from the polymer-bound catalyst (**17**), most probably because the catalytic sites are mainly buried into the material bulk; leaching from the more active surface catalytic sites caused an important deactivation.

We have no explanation for the sudden break in activity of catalysts **7** (cycle 2), **11** (cycle 3), **16** (cycle 5), and **17** (cycle 6), although significant quantities of Ru are still present on the supports (about 20%, 50%, 40%, and 75%, respectively; see Table 4).

Stability of Heterogenized Catalysts. Since the synthesis procedure of all silica-bound catalysts involved a final washing with DCM, this solvent could not be solely responsible for the important Ru leaching during the first catalytic cycle. We therefore investigated the individual effects of each component of the oxidation mixture on this process. Fresh catalysts **7**, **16**, and **17** were incubated into DCM solutions containing respectively 1-octanol, octanal, octanoic acid, *N*-methylmorpholine *N*-oxide (NMMO), and *N*-methylmorpholine (NMM) (2 mol % Ru). After 17 h at 20 °C, soluble ruthenium was assayed by atomic absorption analysis (Table 5). The pretreated catalysts were then recovered by filtration and used in the standard oxidation procedure of 1-octanol (see conversions and selectivities in Table 5).

An important metal leaching occurred in the presence of NMMO and NMM, to a lesser extent. The catalytic features (activity and selectivity) of catalysts **7**, **16**, and **17** after preincubation were similar to those of the corresponding fresh catalysts, except after pretreatment with NMMO; in this case, the situation was similar to the second use of catalysts described above (see Table 3, run 2). Accordingly, the deactivation of our heterogenized catalysts is mainly due to an important loss of weakly bound ruthenium under the influence of competitive ligands such as NMMO (or NMM). After this first step, the further slow deactivation could result from a very gradual metal leaching, progressive poisoning, and modification of the catalytic sites, mechanical degradation of the silica particles, or other undefined factors.

Conclusion

We have succeeded in the preparation of novel silica-bound ruthenium catalysts based on phosphinite ligands. In particular, the tridentate complex **16** was designed to be stable under air and oxidative conditions and, hence, to be reusable. This catalyst (**16**) has been compared to the corresponding silica-bound monodentate catalysts **11**, constructed with the same spacer arm, and **7**, devoid of spacer arm. With respect to the related soluble catalysts **3** and **5**, the heterogenized monodentate catalysts **7** and **11** were 2 and 3 times more active, while the tridentate complex **16** showed almost the same activity. All catalysts were endowed with good to excellent selectivities.

The recycling experiments were somewhat disappointing: the monodentate catalysts **7** and **11** could not be reused and the tridentate catalyst **16** refused to work again after four cycles. We identified the metal leaching due to the presence of NMMO/NMM as being the main factor of catalyst deactivation. We thus tried to replace this oxidant with oxygen (of air), hydrogen peroxide, or *tert*-butyl hydroperoxide, but without success: no catalytic effect on the oxidation of 1-octanol could be observed in the presence of our silica-bound Ru complexes. Also, the TEMPO/O_2 system,[20] recently described, did not work under our experimental conditions.

The challenging search for recoverable oxidation catalysts based on Ru complexes has been studied by other groups, leading to similary mitigated achievements. Ram et al.[12] reported the grafting of an Ru−Schiff base complex on cross-linked polystyrene and the use of the resulting catalyst for the oxidation of benzyl alcohol with molecular oxygen. The problem of metal leaching (35%) after the first cycle was mentioned by the authors; the catalyst was found to be stable for four cycles. Leadbeater[11] prepared the resin-bound Ru−triphenylphosphine catalyst **17** for transfer hydrogenation and hydrocarbon oxidation reactions. This material catalyzed the oxidation of cyclohexanol with *tert*-butyl hydroperoxide in yield comparable to that of the soluble catalyst **1**. The supported catalyst could be reused, but the number of cycles was not reported by the authors. In our hands, catalyst **17** was working for five cycles in the NMMO oxidation of 1-octanol. Heterogenization of a Ru−2-(phenylazo)pyridine complex on silica was described by Reedijk et al.[13] This catalyst was found to be active for stilbene epoxidation and alcohol oxidation, but with a very low selectivity. Recycling experiments performed on the catalytic oxidation of *n*-butanol with $NaBrO_3$ revealed the loss of 30% of the initial Ru after the first cycle; the catalyst kept its activity over four cycles. Accordingly, our silica-bound catalyst **16**, containing an original Ru−triphosphinite complex, ranges among the best catalysts which could be actually

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obtained by heterogenizing a homogeneous Ru complex active for alcohol oxidation. However, better results were obtained by Ley et al. when immobilizing perruthenate ions (RuO_4^-) on an ion exchange resin (Amberlyst A-26)[21] or on a mesoporous silicate (MCM-41) derivatized with ammonium groups.[22]

Experimental Section

Materials. Reagents (quality 99+%) and solvents (analytical grade) were purchased from Acros, Aldrich, or Fluka and used without purification. The reactions were performed under an argon atmosphere, in flame-dried glassware. Dichloromethane and -ethane (DCM and DCE) were distilled over CaH_2; tetrahydrofuran (THF) was distilled over Na.

Silica used for the preparation of catalysts was obtained from Aldrich (reference number 40,360-1; specific area 300 m^2/g; 2.5 mmol of silanol/g; 100 Å; 70−230 mesh). The material has been washed with methanol (Soxhlet; 3 days) and ether (Soxhlet; 2 days) and then dried under vacuum (70 °C; 5×10^{-3} mbar).

Reference catalyst **17** (dichlorotris(triphenylphosphine)-ruthenium(II) (**1**) immobilized on polystyrene (PS)) has been prepared according to ref 11; its ruthenium content was determined by TG analysis under air, from the difference of weight losses at 850 °C between $PS-PPh_2$ (94.4%) and $PS-PPh_2RuCl_2(PPh_3)_2$ (84.4%), by assuming that the final residue corresponds to RuO_2 (0.8 mmol of Ru/g of catalyst).

Methods. Melting points (uncorrected) were determined with an electrothermal apparatus. Elemental analyses were carried out at University College London (Christopher Ingold Laboratory). ^1H (200 or 300 MHz) and ^{13}C (50 or 75 MHz) NMR spectra were recorded on Varian Gemini spectrometers with $CDCl_3$ as the solvent and $SiMe_4$ as internal reference. Chemical shifts are reported as δ values downfield from TMS; coupling constants J are given in hertz. ^{31}P NMR spectra were recorded on a Bruker WM250 spectrometer at 250 MHz with H_3PO_4 as external reference. IR spectra were taken with a Bio-Rad FTS 135 apparatus. Mass spectra were obtained with a Finnigan MAT TSQ-70 spectrometer in the FAB mode (Ion Tech, 8 keV).

TGA measurements were carried out with a microbalance from Mettler Toledo (TGA/SDTA 851^e) under air flux (100 mL/min), between 25 and 850 °C, at a heating rate of 10 °C/min.

Atomic absorption analyses were performed on a Perkin-Elmer 5000 instrument using an air/acetylene flame. The samples were prepared as follows: an aliquot of the catalyst was incubated overnight in 30% aqueous $HClO_4$ (2 mL) and then filtered and reincubated for 10 min in 10% aqueous NaOH (2 mL). Silica was filtered and washed with water (HPLC grade, 3 × 2 mL). The filtrates were collected and diluted to 50 mL with water.

Gel permeation chromatography was performed on a homemade glass column packed with a cyclodextrin gel (LH 20 Sephadex), swollen, and eluted with methanol.

GC analyses (oxidation solutions of 1-octanol, 2-octanol, and *cis*- and *trans*-2-hexen-1-ol) were carried out on a GC 8000 TOP Interscience gas chromatograph equipped with a flame ionization detector and a fused silica capillary column (Optima 5 from Macherey-Nagel; 30 m × 25 mm). Temperature programming was as follows: 60 °C for 3 min and then an increase of 5 °C/min up to 110 °C and 20 °C/min up to 250 °C. HPLC analyses (oxidation solutions of benzyl alcohol and 1-phenylethanol) were performed on a Beckman instrument (System Gold; Model 128 Solvent Module and Model 168 Detector) equipped with an Alltima C18 column (5 mm; 250 mm × 4.6 mm) from Alltech. We used $H_2O-MeOH$ (60:40) as eluent (1 mL/min) and UV detection at 240 nm. Calibration was carried out with standard solutions.

Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (2). A solution of $RuCl_3{\cdot}nH_2O$ (5.32 g; about 0.02 mol) in DMSO (25 mL) was refluxed for 5 min. The dark red solution was concentrated under vacuum, until precipitation occurred. After addition of acetone (20 mL) and filtration, a yellow powder was recovered which was washed with acetone (3 × 10 mL) and ether (1 × 10 mL). After several days, a second fraction of yellow crystals was formed in the mother liquor and washed as above. Total yield: 8.69 g (85%). Mp: 198−200 °C (lit. 193 °C dec). Anal. Found (calcd) for $C_8H_{24}Cl_2O_4RuS_4$: C, 19.92 (19.83); H, 4.90 (4.99). IR (KBr, cm^{-1}): 3019, 2917 (C−H), 1119−1096 (br, st O−S−Ru), 921 (st S−O−Ru). ^1H NMR ($CDCl_3$, δ): 3.53, 3.51, 3.44, and 3.32 (Me of DMSO, S−Ru linked), 2.74 (Me of DMSO, O−Ru linked), 2.63 (Me of free DMSO); ratio S−Ru:O−Ru 4:1. ^{13}C NMR ($CDCl_3$, δ): 47.6, 46.6, 44.4, and 44.2 (Me of DMSO, S−Ru linked), 38.8 (Me of DMSO, O−Ru linked). MS (*m*/*e* (%)): 485.3 (2, M + 1), 449 (15), 407 (6), 371 (35, M − Cl − DMSO), 329 (50, M − 2DMSO), 309 (100).

1-((Diphenylphosphino)oxy)-2,2-bis(((diphenylphosphino)oxy)methyl)propane (4). Chlorodiphenylphosphine (0.70 g, 3.0 mmol, 3 equiv) was added dropwise to a suspension of 1,1,1-tris(hydroxymethyl)ethane (0.13 g, 1.0 mmol, 1 equiv) and triethylamine (0.4 mL, 2.8 mmol, 3 equiv) in CH_2Cl_2 (5 mL). The mixture was refluxed for 2 h under an argon atmosphere and then filtered. Concentration of the filtrate under vacuum gave crude **4** as a yellow oil (sensitive toward air oxidation) that was not further purified but directly engaged in the synthesis of complex **5**. Yield: 0.74 g (100%). ^1H NMR ($CDCl_3$, δ): 7.5−7.2 (m, 30 H, Ar), 3.77 (d, 6 H, $^3J_{HP}$ = 6.5, $O-CH_2$), 1.0 (s, 3 H, CH_3-C). ^{13}C NMR ($CDCl_3$, δ): 128.2 (d, $^2J_{CP}$ = 7, C-*o*, PPh_2), 129.1 (s, C-*p*, PPh_2), 130.2 (d, $^3J_{CP}$ = 22, C-*m*, PPh_2), 140.0 (d, $^1J_{CP}$ = 18, C-*i*, PPh_2), 71,6 (d, $^2J_{CP}$ = 19, CH_2O), 43.5 (s, Me−*C*), 17.1 (d, $^3J_{CP}$ = 7, CH_3-C). MS (*m*/*e* (%)): 672.3 (4, M − 1; $C_{41}H_{39}O_3P_3$), 595.2 (12), 471.1 (28), 200.9 (100, $OPPh_2$).

Dichloro[1-((diphenylphosphino)oxy)-2,2-bis(((diphenylphosphino)oxy)methyl)propane]ruthenium(II) (5). To a refluxing solution of **2** (2.30 g, 5 mmol, 1 equiv) in CH_2Cl_2 (15 mL) was added a solution of **4** (3.96 g, 5 mmol, 1 equiv) in CH_2Cl_2 (10 mL). The yellow solution became dark red. After 30 min of reflux, the solvent was evaporated under vacuum. The solid residue (6.2 g) was washed with water and purified by exclusion chromatography on Sephadex gel. Yield: 64%. Mp: 183.2−184.6 °C (recrystallization from $CHCl_3$; orange solid). IR (KBr, cm^{-1}): 3055, 2927, 1435, 1070, 1019. ^{31}P NMR ($CDCl_3$, δ): 153.7 (br s), 142.8 (br s). MS (*m*/*e* (%)): isotopic massif centered at 808.8 (96, M − Cl; $C_{41}H_{39}Cl_2O_3P_3Ru$), 200.9 (100, $OPPh_2$). X-ray data: λ = 0.710 69 Å; monoclinic; a = 21.985 Å; b = 25.644 Å; c = 23.103 Å; α = 90°; β = 114.54°; γ = 90°.

***N*-(3-(Triethoxysilyl)propyl)-*N*′-(4-(hydroxyethyl)-phenyl)urea (8).** A solution of 4-aminophenethyl alcohol (0.14 g, 1 mmol, 1 equiv) in THF (5 mL) was added dropwise to a solution of 3-isocyanato-1-(triethoxysilyl)propane (0.29 mL, 1.1 mmol, 1.1 equiv) in THF (5 mL). The mixture was stirred for 3 h at 20 °C and then for 2 h at reflux. Solvent evaporation led the product to crystallize as brown needles. Crude **8** was directly used for the preparation of the silica-grafted material **9**. Yield: 100% (crude). IR (KBr, cm^{-1}): 3471, 2976, 1650. ^1H NMR ($CDCl_3$, δ): 7.30 (d, 2 H, $^3J_{HH}$ = 8, Ar), 7.24 (d, 2 H, $^3J_{HH}$ = 8, Ar), 6.54 (s, 1 H, N*H*−Ar), 5.12 (t, 1 H, $^3J_{HH}$ = 6, N*H*−CH_2), 3.90 (q, 6 H, $^3J_{HH}$ = 5, OCH_2), 3.38 (t, 1 H, $^3J_{HH}$ = 7, OH), 3.32 (td, 2 H, CH_2-OH), 2.90 (t, 2 H, $^3J_{HH}$ = 6, CH_2-Ar), 1.8−1.7 (m, 4 H, CH_2CH_2NH), 1.30 (t, 9 H, $^3J_{HH}$ = 7, CH_3), 0.79−0.70 (m, 2 H, Si−CH_2). ^{13}C NMR ($CDCl_3$, δ): 156.3 (*C*=O), 137.3 and 133.6 (C_{Ar}), 129.6 and 121.1 (CH_{Ar}), 63.5 (CH_2-OH), 58.4 (CH_2O-Si), 42.7 (CH_2-NH), 38.5 (CH_2-Ar), 18.2

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(CH_3−CH_2O), 7.7 (CH_2−Si). MS (*m/e* (%)): 385.2 (20, M + 1; $C_{18}H_{32}N_2O_5$), 339.1 (100, M − EtOH).

Silica Grafted with Dichlorotris(diphenylphosphine)ruthenium(II) (7). Chlorodiphenylphosphine (0.49 g, 2.2 mmol, 1 equiv) was added dropwise to a suspension of silica (1.03 g, 2.5 mmol, 1.1 equiv of silanol groups) in CH_2Cl_2 (10 mL) containing triethylamine (0.3 mL, 2.2 mmol, 1 equiv). The mixture was refluxed for 2 h. The grafted silica **6** was filtered off, washed twice with CH_2Cl_2 (2 × 5 mL), and placed again in fresh CH_2Cl_2 (10 mL). After addition of the Ru complex **2** (0.51 g, 1.0 mmol, 0.45 equiv), the mixture was refluxed for 90 min. The yellowish silica-grafted catalyst **7** recovered by filtration was washed with CH_2Cl_2 in a Soxhlet apparatus for 2 days and then with ether, in the same manner. Yield of grafting: 0.435 mmol of derivatized silanols/g. TGA (air): loss of water 2.1%; loss of organic materials 8.6%. Thus, 1 g of silica **7** contains 0.086 g (0.145 mmol) of $C_{36}H_{30}Cl_2P_3Ru$. Atomic absorption: 0.077 mmol of Ru/g.

Silica Grafted with *N*-Propyl-*N′*-(4-(2-hydroxyethyl)phenyl)urea (9). A solution of triethoxysilane **8** (0.49 g, 1.3 mmol, 1 equiv) in THF (30 mL) was added dropwise to a suspension of silica (0.63 g, 1.6 mmol of silanol groups, 1.2 equiv) in THF (30 mL). The mixture was stirred for 3 h at 20 °C and then refluxed for 3 days. The grafted silica **9**, recovered by filtration as a white powder, was washed in a Soxhlet apparatus, successively with methanol (2 days), THF (2 days), CH_2Cl_2 (2 days), and ether (2 days), and then dried under vacuum (5×10^{-3} mbar) at 70 °C for 4 h. Yield of grafting: 0.5 mmol of derivatized silanols/g. TGA (air): loss of water 2%; loss of organic materials 11%. Thus, 1 g of silica **9** contains 0.11 g (0.50 mmol) of $C_{12}H_{17}N_2O_2$. Anal. Found (calcd) for $(SiO_2)_nC_{12}H_{17}N_2O_2\cdot 2H_2O$: C, 7.18 (7.28); H, 1.18 (1.07).

Silica Grafted with Dichlorotris[*N*-propyl-*N′*-(4-(((diphenylphosphino)oxy)ethyl)phenyl)urea]ruthenium(II) (11). Chlorodiphenylphosphine (0.27 g, 1.2 mmol, 5 equiv) was added dropwise to a suspension of grafted silica **9** (0.52 g, 0.24 mmol, 1 equiv of alcohol functions) in CH_2Cl_2 (10 mL) containing triethylamine (0.14 mL, 1.0 mmol, 4 equiv). The mixture was refluxed for 5 h. The grafted silica (**10**) was filtered off, washed twice with CH_2Cl_2 (2 × 5 mL), and then poured again into CH_2Cl_2 (10 mL). The mixture was refluxed, and a solution of Ru complex **2** (0.14 g, 0.28 mmol, 1.4 equiv) in CH_2Cl_2 (5 mL) was added in one fraction. After 2 h, the silica-grafted catalyst **11** was filtered off and washed in a Soxhlet apparatus, successively with CH_2Cl_2 (2 days) and ether (2 days). Yield: 80% (=ratio of alcohol conversion) of a pale yellow powder. TGA (air): loss of water 1.6%; loss of organic materials 16.8%. Thus, 1 g of silica **11** contains 0.168 g (0.13 mmol) of $C_{72}H_{78}N_6O_6P_3RuCl_2$: i.e., 0.39 mmol/g of grafted ligand. Anal. Found (calcd) for $(SiO_2)_nC_{72}H_{78}N_6O_6P_3RuCl_2\cdot 10H_2O$: C, 10.68 (10.64); H, 1.42 (1.22); P, 1.14 (1.14). Atomic absorption: 0.158 mmol of Ru/g.

Silica Grafted with Propyl Isocyanate (12). 3-(Triethoxysilyl)propyl isocyanate (4 g, 16 mmol, 2.1 equiv) was added dropwise to a suspension of dried silica (3 g, 7.5 mmol, 1 equiv of silanol functions) in THF (150 mL). The mixture was stirred for 3 h at 20 °C and then refluxed for 20 h. The grafted silica **12** was filtered off, washed with THF (2 × 50 mL), and directly used for the coupling of **13**. Yield (white powder) of functionalization: 1.2 mmol of isocyanate/g. TGA (air): loss of water 1.2%; loss of organic materials 10.5%. Thus, 1 g of silica **12** contains 0.105 g (1.2 mmol) of C_4H_6NO.

Silica Grafted with *N*-Propyl-*N′*-[4-(2,2-bis(hydroxymethyl)propan-1-ol)phenyl]urea (14). A solution of 3-(4-aminophenyl)-2,2-bis(hydroxymethyl)propan-1-ol (**13**;[18] 0.27 g, 1.28 mmol, 1 equiv) in pyridine (3 mL) was added to a suspension of grafted silica **12** (2 g, 2.4 mmol of NCO, 1.9 equiv) in THF (50 mL). The mixture was refluxed for 2 days. The grafted silica **14** was filtered off as a yellow powder and washed in a Soxhlet apparatus with CH_2Cl_2 (1 day). Yield of functionalization: 0.45 mmol of tripodal ligand/g. TGA (air): loss of water 1.6%; loss of organic materials 13.4%. Thus, 1 g of silica **14** contains 0.134 g (0.45 mmol) of $C_{15}H_{23}N_2O_4$. Anal. Found (calcd) for $(SiO_2)_nC_{15}H_{23}N_2O_4\cdot 3H_2O$: C, 6.38 (6.55); H, 1.13 (1.06).

Silica Grafted with [*N*-Propyl-*N′*-(4-(2,2,2-(((diphenylphosphino)oxy)methyl)ethyl)phenyl)urea]ruthenium(II) (16). Lithium hexamethyldisilazide (0.24 g, 1.42 mmol, 6 equiv) and (dimethylamino)pyridine (0.26 mL, 2.09 mmol, 9.1 equiv) were added to a stirred suspension of grafted silica **14** (0.51 g, 0.23 mmol of triol, 1 equiv) in THF (20 mL) at −65 °C. After 30 min, the temperature was raised to −40 °C, and chlorodiphenylphosphine (0.61 g, 2.75 mmol, 12.0 equiv) was added dropwise. The temperature was slowly raised to 20 °C. The mixture was then refluxed for 20 h. The grafted silica **15** was filtered off from the hot solution, rinsed successively with acetone (2 × 5 mL) and CH_2Cl_2 (2 × 5 mL), and then poured into fresh CH_2Cl_2 (20 mL) and refluxed. After 5 min, the Ru complex **2** (0.22 g, 0.45 mmol, 2 equiv) was added and the mixture was further refluxed for 24 h. After filtration, the recovered silica-grafted catalyst **16**, as a yellow powder, was rinsed with acetone and washed in a Soxhlet apparatus with CH_2Cl_2 (1 day). Yield: 82% (ratio of alcohol conversion). TGA (air): loss of water 1.7%; loss of organic materials 28.1%. Thus, 1 g of silica **16** contains 0.281 g (0.33 mmol) of $C_{51}H_{50}Cl_2N_2O_4P_3Ru$. Anal. Found (calcd) for $(SiO_2)_nC_{51}H_{50}Cl_2N_3O_4P_3Ru\cdot H_2O$: C, 8.79 (9.68); H, 1.18 (0.99); N, 0.52 (0.44). Atomic absorption: 0.618 mmol Ru/g.

Catalytic Oxidation of Alcohols: General Procedure. The Ru catalyst (2 mol %, 0.02 equiv of Ru) was introduced into a solution of alcohol (1 mmol, 1 equiv) and *N*-methylmorpholine *N*-oxide (2 mmol, 2 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred at 20 °C, in an air atmosphere, for 6 h. Under these experimental conditions, Ru-catalyzed slow degradation of the solvent was not an embarrassing side reaction. The evolution of the reaction was monitored (30 min; 1 h 30 min; 3 h; 6 h) by GC with tetradecane as internal standard (for the oxidation of 1-octanol, 2-octanol, cis and trans 2-hexen-1-ols) or by HPLC (for the oxidation of benzyl alcohol and 1-phenylethanol). Heterogenized Ru catalysts were separated by filtration and reused under the same conditions. The filtrates were analyzed by atomic absorption to determine the amount of released Ru (Table 4).

Evaluation of the Catalyst Stability: General Procedure. A suspension of heterogenized catalyst (±2 mol %, 0.02 equiv of Ru) in CH_2Cl_2 (5 mL) containing one of the partners of the oxidation reaction mixture (1 mmol, 1 equiv) was stirred overnight at room temperature into a closed flask. After filtration, the catalyst was reused in the standard oxidation procedure. The filtrate was analyzed by atomic absorption spectrometry (assay of released Ru; Table 5).

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