Synthesis of a Ruthenium Complex Bound to a Polyimide Matrix: Investigating the Catalytic Properties in a Hydrosilylation Reaction

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3,6-Bis(dimethylamino)acridine(hexamethylbenzene)dichlororuthenium(II) was used as a tricyclic heteroatomic monomer to prepare polyimides from the corresponding dianhyrides by solution condensation. The ruthenium complex monomer was synthesized starting from $[RuCl_2(HMB)]_2$ and 3-6-*bis*(dimethylamino)acridine. The polymers had inherent viscosities of 1.77 to 2.11 and were soluble in most polar solvents. The glass transition temperatures were in the range of 204 to 298 °C and the 10% weight loss in the range of 506-626 °C, depending upon the structure of the dianhyride monomer. The catalytic activity of the polyimides tested in a hydrosilylation reaction of acetophenone was up to 90%. Leaching of ruthenium into the reaction mixture, found to be in the range of 60-75 ppm, was an indication of reduced catalyst bleeding.

Key Words: Heterogeneous catalysis, Ruthenium, Polyimide, Hydrosilylation.

Introduction

As a consequence of the importance of the synthesis of synthetically relevant substances, catalytic reactions using transition metal complexes are still of considerable interest. The transition metals most commonly employed in hydrosilylation reactions are Pd, Pt, Rh, Ir, Ni and Cu. In terms of the transition metal complexes used for catalysis, 2 major groups should be mentioned. The first comprises transition metal ions complexed by neutral ligands in which the metal is coordinated with a heteroatom, e.g., bipyridyls, ethylenediamine, and diphosphines. For the synthesis of organosilicon compounds, the use of the catalytic hydrosilylation reaction of unsaturated compounds such as alkenes, ketones and imines is the most versatile method. The use of organosilicon substances is important not only in terms of being a powerful tool in

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synthesis, but also the hydrosilylation reaction is used in many ways in the industrial manufacture of silicon polymers[1].

Since the first report on catalyzed hydrosilylation in 1947 by Sommer et al.,[2] many efforts have been directed towards the development of optimized catalytic systems. Platinum catalysts and other transition metal containing catalysts, including metal groups 8, 9, and 10 are very active in the hydrosilylation of alkenes[3−5]. Catalysts are often used. However, a problem associated with platinum is its limited stability in the reaction media, and the formation of platinum colloids that have no catalytic effect takes place. The catalysts $[Ru_3(CO)_{12}]$ and $[Fe_3(CO)_{12}]$ [6−7] are used in the hydrosilylation of several alkenes. Rhodium(I) and palladium(II) catalysts were tested for the hydrosilylation of styrene [8−9]. However, many of the known platinum(0) catalysts suffer from deactivation [10]. Murai has reported the dihydrocarbonyl *tris*(tripenylphosphine) ruthenium catalyzed anti-Markovnikov addition of the *ortho* C-H bonds of acetophenones across the C=C double bonds of vinyl silanes to yield *ortho* alkyl substituted acetophenones [11].

We reported the first examples of a polyimide supported catalytic system in which 3,6-bis(dimethylamino)acridine(*p*-cymene)dichloro ruthenium(II) for catalytic application in the furan formation reaction of (Z)-3-methylpent-2-en-4-yn-1-ol [12].

We report here the hydrosilylation reaction of acetophenone catalyzed by Ru(II) complex supported with thermally and chemically stable polyimides. These reactions provide an almost quantitative yield of the silylated products. It is claimed that this reaction system is technically attractive, since it does not require high pressure or temperature. It is chemically attractive because many aspects of the reaction may be probed systematically, varying the complexing agents of the catalyst.

Experimental

Infrared spectra were recorded as KBr pellets in the range 4000-400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. ^{1}H-NMR spectra (300 MHz) and ^{13}C-NMR spectra (75.5 MHz) were obtained on a Bruker AM 300 WB FT spectrometer with δ referenced to the solvent CDCl$_3$. Elemental analyses were conducted on a Carlo Erba Elemental Analyzer, model 1106. Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively.

GPC analyses were performed at 30 °C using N-methylpyrrolidone (NMP) as eluant at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses of 200-1,200,000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer samples.

All chemicals were purchased from Aldrich and used after purification. NMP was distilled over CaH$_2$ under reduced pressure and stored over 4 Å molecular sieves. Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPDA), 4,4′-oxydiphthalic anhydride (ODPA) sublimed at 250 °C under reduced pressure, 2,2′-*bis*[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), and hexafluorodianhyride (6FDA) were used after crystallization from the appropriate solvents. All the dianhydrides were dried under vacuum at 120 °C prior to use.

Inherent viscosities ($\eta_{inh} = \ln\eta_r/c$ at a polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent.
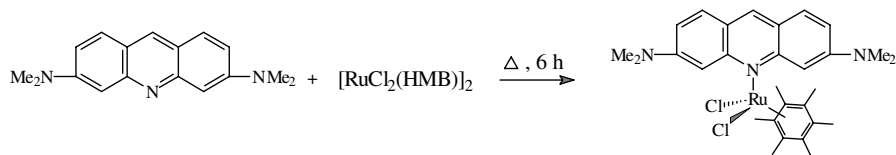
Scheme 1. Synthesis of 3,6-bis(dimethylamino) acridine(hexamethylbenzene) dichlororuthenium(II), RuAO.

Synthesis of 3,6-bis(dimethylamino) acridine(hexamethylbenzene) dichlororuthenium(II), RuAO,

The general conditions for the preparation of the 3,6-*bis*(dimethylamino) acridine (*hexamethylbenzene*)-dichlororuthenium(II), as shown in Scheme 1, were as follows. 3,6-*Bis*(dimethylamino)acridine (1.061 g, 4 mmol), the required [RuCl$_2$(*HMB*)]$_2$ (1.336 g, 4 mmol) and toluene (40 mL) were heated under reflux for 6 h. Upon cooling to room temperature, orange crystals were deposited. They were filtered, washed with Et$_2$O (3 x 15 mL) and recrystallized in CH$_2$Cl$_2$/Et$_2$O; Yield, 1.01 g (88%). C$_{29}$H$_{37}$N$_3$Cl$_2$Ru (599.58): C, 58.09; H, 6.22; N, 7.01; found: C, 58.04; H, 6.21; N, 7.00. ^{1}H-NMR in CDCl$_3$ [δ (ppm), J (Hz), multiplicity, integration, assignment]: 8.21 [s, 1H, (CH$_3$)$_2$NC$_6$H$_3$C*H*NC$_6$H$_3$N(CH$_3$)$_2$], 7.23 [m, 6H, (CH$_3$)$_2$NC$_6$*H*$_3$CHNC$_6$*H*$_3$N(CH$_3$)$_2$], 3.09 [s, 12H, (C*H*$_3$)$_2$NC$_6$H$_3$CHNC$_6$H$_3$N(C*H*$_3$)$_2$], 2.09 [s, 18H, C$_6$(C*H*$_3$)$_6$].

^{13}C{^{1}H}-NMR in CDCl$_3$, δ (ppm) [assignment]: 154.2, 143.4, 142.5, 130.4, 116.8, 114.5, 107.3 [(CH$_3$)$_2$NC$_6$H$_3$*C*HN*C*$_6$H$_3$N(CH$_3$)$_2$], 90.7 [*C*$_6$(CH$_3$)$_6$], 40.5 [(*C*H$_3$)$_2$NC$_6$H$_3$CHNC$_6$H$_3$N(*C*H$_3$)$_2$], 15.6 [C$_6$(*C*H$_3$)$_6$].

Catalytic reactions

The cyclization experiments were carried out in a 10 mL Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was evacuated and flushed with argon before the reaction mixture was introduced. Acetophenenone (10 mmol) and an appropriate amount of the catalyst (a catalyst loading of 0.6% w/w) were mixed and the mixture was stirred in an oil bath at 80 °C. The progress of the reaction was monitored by gas chromatography (GC). After purification the product was characterized by ^{1}H- and ^{13}C-NMR spectra. The analyses were performed quantitatively on a capillary GC equipped with a thermal conductivity detector and a 6-foot column of 10% = V-101 on chromosorp W-HP, 100-120 mesh.

Synthesis of polyimides

A typical polyimide (p-RuAO1 to p-RuAO5, Scheme 2) synthesis was performed as follows: RuAO (2.48 g, 4.15 mmol) was dissolved in NMP (15 mL) in a 50 mL Schlenck tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. PMDA (0.90 g, 4.15 mmol) was added to the amine solution, followed by stirring overnight to give a viscous solution. The mixture was heated to 70 °C, xylene (5 mL) was added, and the mixture was refluxed for 3 h. Following the removal of xylene by distillation, the reaction mixture was cooled to room temperature and the product was precipitated by the

addition of a large excess of methanol. A yellow product was isolated and dried at 100 °C under vacuum and then at 200-250 °C under nitrogen for 2 h.
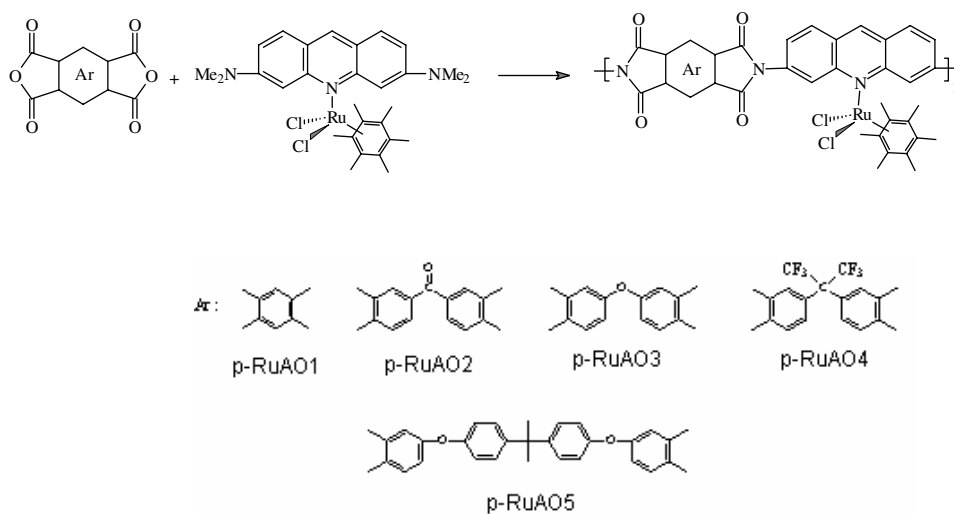
Scheme 2. Polyimide synthesis.

Results and Discussion

The immobilization of catalysts is nowadays an intensively investigated area of research for various reasons. There is an increasing demand for supported versions of modern highly selective and active catalysts.
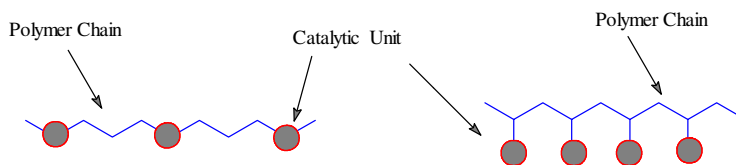
First, contamination of products with metal ions and/or ligands needs to be low, particularly in cases relevant to pharmaceutical chemistry. Second, modern catalysts significantly add to the total costs of a product; therefore regeneration or reuse is highly desirable. Third, supported catalysts offer access to high-throughput techniques and continuous flow reactors. Key issues associated with the supported catalysts are (i) preservation of high activities, and reaction rates observed with homogeneous catalysts, (ii) ease of catalyst separation, (iii) multiple catalyst recycling, (iv) metal and contaminant free products. To date, immobilization has been simply accomplished by attaching phosphine or diaminomethane based ligands to a suitable support such as silica and poly(styrene-*co*-divinylbenzene); in addition, pyridine containing polyamides and N,P-ligand derivatized zeolites have been used [13−17].

For the immobilization of 3,6-bis(dimethylamino)acridine (hexamethylbenzene) dichlororuthenium(II), an approach for the immobilization of ruthenium based catalysis into the backbone of chemically and thermally stable polyimide was chosen [18−30].

RuAO was formed by the reaction of $[RuCl_2(HMB)]_2$ and acridine orange in toluene (Scheme 1). This monomer was subject to reaction with dianhyrides to yield the desired polyimides coded as p-RuAO1 to P-RuAO5 (Scheme 2).

FT-IR spectra of the monomers and polyimides were recorded separately in the mid IR (4000-400 cm^{-1}) to ascertain the imide ring formation presented in Figure 1. In the 1720-1770 cm^{-1} region all polymers exhibited imide carbonyl peaks due to C=O asymmetric stretching and C=O symmetric stretching. The peak at 720 cm^{-1} is attributed to the C=O bending, and a C-N peak showed up at 1390 cm^{-1}, but no amide carbonyl peak was observed at 1650 cm^{-1}, suggesting complete imidization. Elemental analysis and FT-IR spectroscopic data of the monomer RuAO and the polymer p-RuAO1 to p-RuAO5 are given in Table 1.
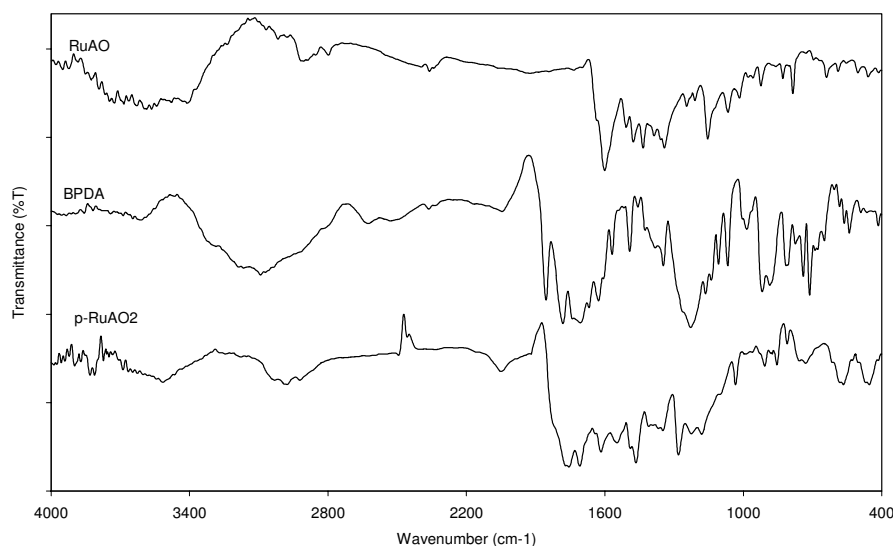

Figure 1. FTIR spectra of monomers RuAO, BPDA and the polyimide (p-RuAO2).

Table 1. Elemental analysis and spectroscopic data of the monomer and polyimides.

	Formula		Elemental Analysis			IR (cm^{-1})			
			C	H	N	Asym C=O Stretch.	Sym C=O Stretch.	C-N-C Stretch.	C-N bending
RuAO	$C_{29}H_{37}N_3Cl_2Ru$	Calcd	58.09	6.22	7.01	-	-	-	-
	599,58	Found	58.04	6.21	7.00				
p-RuAO 1	$(C_{35}H_{27}N_3O_4\ Cl_2Ru)_n$	Calcd	57.94	3.75	5.79	1771	1722	1388	732
	$(725,55)_n$	Found	57.85	3.81	5.67				
p-RuAO 2	$(C_{42}H_{31}N_3O_5\ Cl_2Ru)_n$	Calcd	60.81	3.77	5.06	1770	1716	1390	731
	$(829,65)_n$	Found	61.02	3.71	5.14				
p-RuAO 3	$(C_{41}H_{31}N_3O_5\ Cl_2Ru)_n$	Calcd	60.22	3.82	5.14	1768	1720	1395	727
	$(817,64)_n$	Found	61.02	3.89	5.07				
p-RuAO 4	$(C_{44}H_{31}N_3O_4\ Cl_2RuF_6)_n$	Calcd	60.35	3.57	4.79	1765	1720	1394	725
	$(875,68)_n$	Found	60.42	3.62	4.86				
p-RuAO 5	$(C_{56}H_{45}N_3O_6\ Cl_2Ru)_n$	Calcd	65.43	4.41	4.09	1771	1725	1399	721
	$(1027,90)_n$	Found	66.87	4.45	4.16				

The thermal properties of the polymers were evaluated by DTA (Figure 2) and TGA (Figure 3), and the data are compiled in Table 2. The p-RuAO1 had a relatively high thermal decomposition temperature because of its rigid structure. The T_g derived from the DSC curve was taken as the midpoint of the change in the slope of the base line. The transition (T_g) appearing above 200 °C is attributed to the rigid structural morphology and the relaxation of the imide segment.
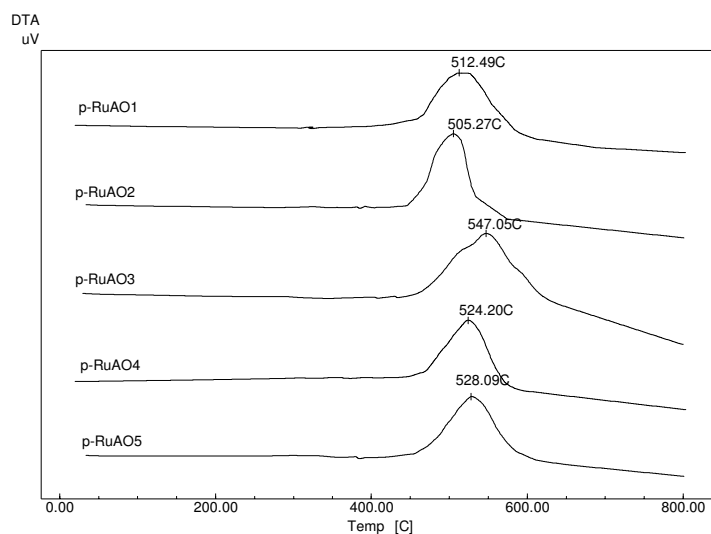
Figure 2. DTA Thermograms of the polyimides (p-RuAO1 to p-RuAO5).

Table 2. Thermal properties of polyimides.

Polymer	p-RuAO1	p-RuAO2	p-RuAO3	p-RuAO4	p-RuAO5
TGA Analyisis					
On set	571	514	469	398	395
End set	698	659	634	571	610
% 10^a	626	588	532	506	514
Char^b	33.4	23.6	20.0	17.3	18.5
IDT^c	503	491	452	419	415
DTA Analyisis^d					
TDP^e	512	505	547	524	528
On set	458	445	450	463	454
End set	589	557	622	578	588
Heat (kJ/g)	19.35	14.9	18.86	14.43	12.45
DSC Analyisis					
On set	282	228	200	219	224
End set	304	236	207	223	234
Transition (mW)	-4.50	-3.22	-1.85	-0.98	-1.95
Tg (°C)^f	298	232	204	221	228

a. Temperature of 10% weight loss was assessed by TGA at a heating rate of 10 °C/min. in N_2.
b. Assessed by TGA at 800 °C in N_2 atmosphere.
c. IDT (initial decomposition temperature) is the temperature at which an initial loss of mass was observed.
d. DTA thermograms of polyimides with a heating rate of 10 °C/min in a air atmosphere.
e. TDP (thermal decomposition peak)
f. Determined by DSC in N_2 atmosphere.

The transitions (T_m) ranged between 505 to 547 °C are the crystalline melting points of the organic segments. As shown in Figure 2, the 10% weight loss temperatures (T_{10}) for polymers were between 506

and 626 °C. T_{10} therefore depends on the oxidative degradation of the organic segment, such that the formation of star-shaped morphology may reduce the chain mobility of the PMDA segment, so that the thermal degradation of the material shifts to higher temperatures. All polymers showed good solubility in NMP and partial solubility in DMSO at room temperature (Table 3). The GPC data of all polyimides are outlined in Table 4.

Table 3. Basic properties of polyimides.

Polymer	p-RuAO1	p-RuAO2	p-RuAO3	p-RuAO4	p-RuAO5
Anhydride	PMDA	BPDA	ODPA	6FDA	BPPDA
Yield (%)	79	84	74	71	72
d $(g/cm^3)^a$	1,44	1,58	1,32	1,23	1,30
η $(dL/g)^b$	1,87	2,11	1,80	1,72	1,77
Solubility^c					
NMP	+	+	+	+	+
DMF	±	±	±	±	+
DMAc	±	+	+	+	+
Ether	-	-	-	-	-
THF	-	±	-	-	±
Hexane	-	-	-	-	-
DMSO	±	±	±	-	±

a. Determined by suspension method at 30 °C.
b. Measured at a concentration of 0.5 g/dL in NMP at 30 °C using an Ubbelohde viscometer.
c. (Solubility tested at 2% solid concentration; + soluble at room temperature (25 °C); ± soluble upon heating; - insoluble at room temperature)
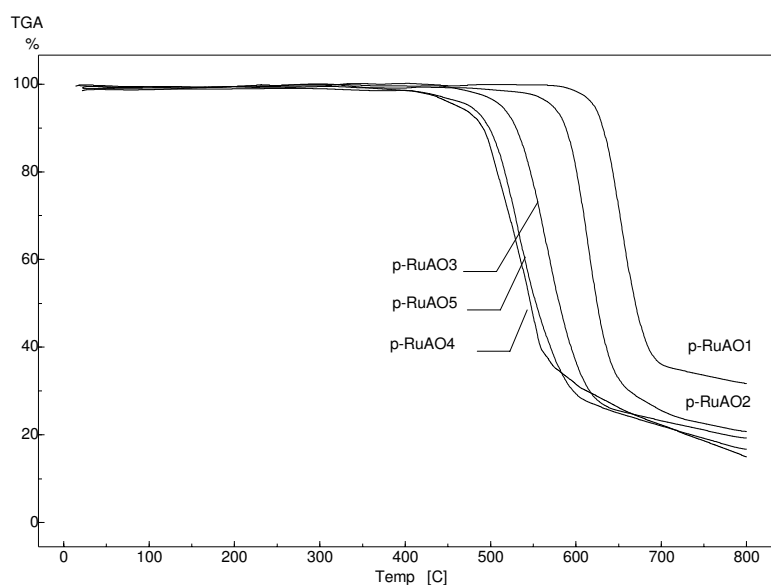

Figure 3. TGA thermograms of the polyimides (p-RuAO1 to p-RuAO5).

Table 4. Properties of polyimides obtained by the one-step method.

Polyimide	p-RuAO1	p-RuAO2	p-RuAO3	p-RuAO4	p-RuAO5
Diahyride	PMDA	BPDA	ODPA	6FDA	IPPDA
$[\eta]$ (dL/g)	1.87	2.11	1.80	1.72	1.77
M_n x 10^{-5}	3.82	4.56	3.89	3.01	3.45
M_w x 10^{-5}	9.36	8.48	7.62	9.19	9.97
P.D.I.	2.45	1.86	1.96	3.05	2.89

To retrieve information about the catalytic behavior of 3,6-bis(dimethylamino) acridine(hexamethyl-benzene)dichlororuthenium(II), RuAO, in comparison with the polymer supported case, the reaction of hydrosilylation of acetophenone was used. The results are summarized in Table 5. Interestingly, p-RuAO-1 and p-RuAO-4 displayed an even enhanced reactivity in the hydrosilylation process of acetophenone. Thus, TON_{max} in the range 430-1220 were obtained using 2 mmol of catalyst. This may be explained by the heterogeneous nature of the catalysts, effectively reducing bimetallic decomposition reactions.

Table 5. The hydrosilylation of acetophenone with various aycridine base polyimide catalysts.
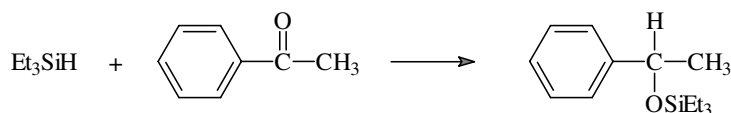
Catalyst	Time (h)	Conversion (%)^{a,b,c}	Turnover (/h)
RuAO	6	92	256
p-RuAO1	20	87	73
p-RuAO 2	20	85	71
p-RuAO 3	20	81	68
p-RuAO 4	20	86	72
p-RuAO 5	20	82	68

Reaction condition: 1 mmol acetophenone, 2 mmol % Ru catalyst, 100 °C.
Average of 4th run
Yields were determined by gas chromatography.

Determination of leaching in heterogeneous reactions was carried out with the reaction mixture. Briefly, the reaction mixture was transferred to a Teflon tube. After removal of the solvent 1 mL HNO_3 (aq) and 3 mL HCl (aq) were added to the mixture, and the mixture was exposed to microwave conditions (450 W pulsed, t = 40 min). The ruthenium content was determined by ICP. Leaching of ruthenium into the reaction mixture was found to be in the range 60-75 ppm.

Conclusion

The N-heteocyclic Ru(II) complex 3,6-bis(dimethylamino)acridine(hexamethyl benzene) dichlororuthenium(II) was used to prepare metal supported catalysts that were used for the hydrosilylation of acetophenone. The supported version of Ru(II) complex showed at least similar, and in some cases even enhanced reactivity

for the substrates, and allowed the synthesis of the target compounds with a comparably low ruthenium content.

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