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Single and double metallic layer-containing ruthenium dendrimers. Synthesis and catalytic properties

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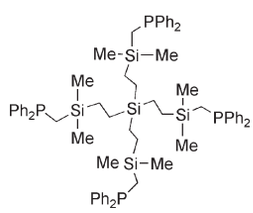
The reaction of a series of phosphanyl-terminated carbosilane dendrimers displaying only one phosphorus ligand per arm with $[RuCl_2(p\text{-cymene})]_2$ resulted in the grafting of RuCl(*p*-cymene) moieties on the periphery of the dendrimer. In these species, the chloride ligand is easily displaced by the organic bases pyridine, 4-cyanopyridine and 4,4′-bipyridine to afford new cationic metallodendrimers. NMR studies have confirmed the chirality of the ruthenium centre. The species containing 4,4′-bipyridine reacts through the uncoordinated pyridyl nitrogen with a new equivalent of $[RuCl_2(p\text{-cymene})]_2$ or $[RhCl(CO)_2]_2$ to lead to homo- or hetero-bimetallic layer-containing dendrimeric systems. The ruthenodendrimers were tested as catalysts in the transfer hydrogenation of cyclohexanone by propan-2-ol and their activity compared with that of some analogous mononuclear ruthenium(II) complexes.

Introduction

The preparation of organometallic dendrimers constitutes one of the most exciting frontiers of current chemical research because these compounds may have the potential for a range of applications in different areas of science and technology owing to their precisely defined nanoscale, often globular, molecular structure.[1]

Although examples containing metals as dendrimer cores, branching centres, or building block connectors have been published, the majority of the compounds include organometallic fragments as terminal groups. In many cases, such species are synthesized by reacting $-PR_2$[2] or $-NR_2$[3] functionalized dendrimers on the surface with metal complexes containing labile ligands. Processes based on direct complexation of alkyne-terminated dendrimers have also been described.[4] Following these synthetic procedures, metallodendrimers of almost all the transition metals are known.[5] In the last five years we have reported the synthesis of carbosilane dendrimers decorated on the surface by Au,[6] Pd,[7] Pt,[7] Rh,[8] and Ir[8] fragments. Some of these compounds have proved to be catalytically active in processes such as the hydrovinylation of styrene[6] or the hydrogenation of 1-hexene.[7] Furthermore, gold dendrimers were found to be excellent precursors for the synthesis of mixed transition metal clusters grafted on the periphery of the dendrimer.[9] Here, we report the formation of new neutral and cationic ruthenium carbosilane dendrimers and their activity in the catalytic transfer hydrogenation process. In addition, we discuss a new synthetic method for the preparation of double metallic layer dendritic systems, which may contribute to homogeneous catalysis in the near future.



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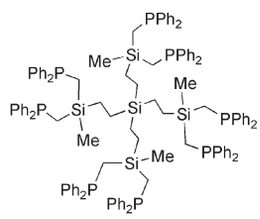

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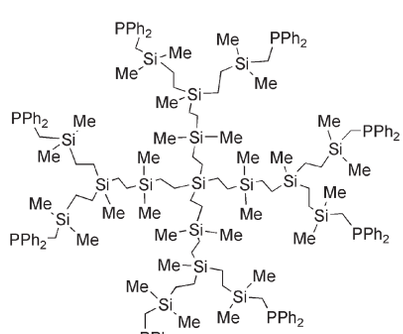

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Chart 1

Results and discussion

Neutral ruthenium dendrimers

The alkyldiphenylphosphino terminated carbosilane dendrimers studied here are shown in Chart 1. Their synthesis and characterization have been reported elsewhere.[6] It should be noted that the presence of $-CH_2-CH_2-SiMe_2-$ spacers in **3** reduces the surface congestion and increases the solubility in common organic solvents.

The ruthenium-containing dendrimers $\mathbf{1[Ru]_4}$ and $\mathbf{3[Ru]_8}$ were obtained by the reaction between **1** or **3** with $[RuCl_2(p\text{-cymene})]_2$ in dichloromethane at room temperature [eqn. (1)]. The metallation was complete within minutes as shown by ^{31}P NMR spectroscopy. Thus, the complete complexation of the PPh_2 end groups was confirmed by the absence of unreacted phosphine units along with the emergence of a new signal showing the expected deshielding effect. The identity of the dendrimers was further confirmed by elemental analysis as well as ^1H, ^{13}C and ^{29}Si NMR spectroscopy. The $^{29}Si\{^1H\}$NMR spectrum showed two or four silicon environments expected for $\mathbf{1[Ru]_4}$ or $\mathbf{3[Ru]_8}$, respectively. In both cases external silicon is coupled with the phosphorus nucleus (^2J (SiP) = 14.8 Hz for $\mathbf{1[Ru]_4}$ and 15.1 Hz for $\mathbf{3[Ru]_8}$). The ^1H spectrum showed the resonances for the methyl, methylene, and ethylene protons, as well as the presence of the *p*-cymene ligand. The molecular peaks in the ES mass spectrum at *m*/*z* 2361.4 ($[M - Cl]^+$) (calcd. 2359.1) and 1162.06 ($[M - 2Cl]^{2+}$) (calcd. 1161.8) for $\mathbf{1[Ru]_4}$ and 1761.6 ($[M - 3Cl]^{3+}$) (calcd. 1761.4) and 1314.2 ($[M - 4Cl]^{4+}$) (calcd. 1312.2) for $\mathbf{3[Ru]_8}$ confirms the identity of the ruthenodendrimers. The metallation of dendrimer **2** was not so straightforward. When **2** was allowed to react with $[RuCl_2(p\text{-cymene})]_2$ in a 2 : 1 P : Ru molar ratio, the ^{31}P NMR spectroscopy showed two broad signals at δ 20 and −24 which were resolved in two others at low temperature. This is consistent with a mixture of compounds resulting from the aleatory distribution of the ruthenium fragments on the surface of the dendrimer. Note that, statistically, species going from $\mathbf{2[Ru]_0}$ to $\mathbf{2[Ru]_8}$ can be formed.

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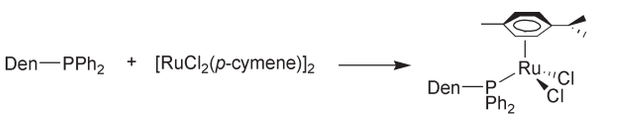
Moreover, some of these species may show positional isomers due to different possibilities of grafting the ruthenium fragments onto the phosphino-terminated branches. Interestingly, the remaining free phosphine ligands of each component of the mixture reacted with ClAu(tht) allowing the grafting of ClAu units on the periphery of the dendrimer. Thus, we obtained a mixture of metallodendrimers with a 1 : 1 P : metal (ruthenium + gold) ratio for all of them. It is remarkable that in the MALDI-TOF experiments, all P–Ru bonds were cleaved and only the gold-containing fragments peaks $[\mathbf{2} + m(\mathrm{AuCl}) - \mathrm{Cl}]^+$ were detected, those at 2566,93 ($m = 3$) and 2799,92 ($m = 4$) being the most intense. Obviously, the number of ruthenium fragments in each of the species in the initial mixture can be inferred from the number of AuCl units, given that the total number of AuCl and [$RuCl_2$(*p*-cymene)] moieties should be eight.



1 **1[Ru]$_4$**

3 **3[Ru]$_8$**

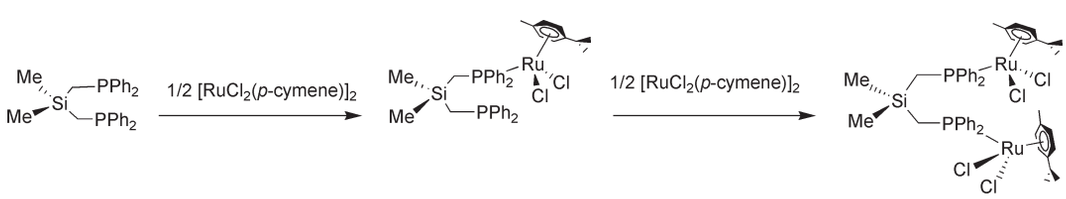
[Ru]= $RuCl_2$(*p*-cymene) (1)

It is worth noting that the addition of a new amount of the dinuclear Ru compound to the solution of **2** to achieve the P : Ru molar ratio 1 : 1 gave a complicated ^{31}P NMR spectrum, in which signals at 20.1, 21.3 and 7.4 ppm were the most intense. Despite the different strategies employed, we were unable to obtain the expected **2[Ru]$_8$** dendrimer and this result suggests that because of the steric congestion on the surface of **2**, not all the branches are able to coordinate the ruthenium fragment. This behavior is in clear contrast with that found for the model compound $Me_2Si(CH_2PPh_2)_2$, which reacted with [$RuCl_2$(*p*-cymene)]$_2$ in a 2 : 1 P : Ru molar ratio to afford a mixture of three compounds, (the starting dimethylsilane, the mono- and the dimetallated ruthenium). However, the addition of a new equivalent of the ruthenium complex gave pure $Me_2Si(CH_2PPh_2RuCl_2$(*p*-cymene))$_2$ according to the ^{31}P NMR spectrum (δ 21.4) [eqn. (2)]. Obviously, in this case the small volume of the methyl ligands helps the branches to span to avoid steric impediments.

Cationic ruthenium dendrimers and synthesis of double metallic layer dendritic systems

We anticipated that the abstraction of one chloride atom from the ruthenium centre grafted to the dendrimer would give the possibility of generating a vacant binding site which could be occupied by a bifunctional ligand, such as 4,4′-bipyridine. Thus, for example, in this case, the uncoordinated pyridyl nitrogen could serve as the coordination site for a second metal fragment, consequently generating double metal layer dendrimeric systems. To this end, the **2[Ru]$_4^{4+}$** was thought to be an appropriate precursor. Therefore, in order to establish the best reaction conditions for its synthesis we first examined the formation of the model compound $[Me_2Si(CH_2PPh_2)_2\{RuCl($*p*-cymene)$\}]PF_6$. This was successfully prepared by stirring $Me_2Si(CH_2PPh_2)_2$ with a solution of $[RuCl(NCMe)_2$(*p*-cymene)$]PF_6$. The reaction was completed in ten days and the product was unambiguously characterized by spectroscopy. Using the same method, **2** let us isolate the cationic dendrimer **2[Ru]$_4^{4+}$** [eqn. (3)]. The complete reaction, however, took 27 days. Interestingly, both the ^{1}H and ^{13}C NMR spectra showed two groups of signals for the *p*-cymene group and the ^{31}P NMR spectrum showed two very close peaks of similar intensity at δ 30.6 and 31.0. Both groups of signals appear to be attributable to the presence of two isomers resulting from the high steric crowding on the periphery of the dendrimer. When a DMSO solution of **2[Ru]$_4^{4+}$** was heated the two peaks in the ^{31}P NMR spectrum did not collapse in the range of temperatures studied. Despite these results, the slowness of the reaction made us discontinue the initial strategy: we decided to perform our studies on the less congested dendrimer **1[Ru]$_4$**, which has only one phosphorus ligand for each branch and is more easily accessed. Thus, the reaction of **1[Ru]$_4$** with pyridine in methanol gave, after the addition of $(NH_4)PF_6$, the cationic dendrimer **1[Ru(py)]$_4^{4+}$** in 24 h. The species containing the organic bases 4,4′-bipyridine, **1[Ru(bipy)]$_4^{4+}$**, and 4-cyanopyridine, **1[Ru(CNpy)]$_4^{4+}$**, were obtained similarly [eqn. (4)]. The ^{1}H and the ^{13}C NMR spectra of all these cationic species feature interesting points. For example, the methyl groups of the *p*-cymene in **1[Ru(py)]$_4^{4+}$** appear split at δ 1.09 and 0.96, and this fact confirms that the substitution of the chloride ligand for the pyridine breaks the symmetry plane passing through the ruthenium and makes the metal centre chiral. In addition, the high congestion on the ruthenium precludes the free rotation of both the *p*-cymene and the pyridine ligands. Moreover, the lack of free rotation induces the protons of the methylene group (–CH_2P) to become diastereotopic. For **1[Ru(py)]$_4^{4+}$** they have been assigned to the signals at δ 2.23 and 1.78 by 2D-COSY and NOESY experiments and this was corroborated by comparison with a HSQC ^{1}H–^{13}C experiment carried out on the analogous **1[Ru(bipy)]$_4^{4+}$**. The latter species displays one bipyridine ligand with two non-equivalent rings: the protons belonging to the ring bonded to the ruthenium were named H_α, and H_β and those of the second and non-coordinate ring, $H_{\alpha'}$ and $H_{\beta'}$. Unexpectedly, the alpha protons of both rings resonated simultaneously at δ 8.74 in CD_2Cl_2 while the ^{13}C NMR spectrum showed the expected two signals for the alpha carbon atoms at δ 156.8 and 151.1 (and, obviously, two more for each one of the rest of the carbon atoms). 2D-COSY and HSQC ^{1}H–^{13}C experiments revealed that the identical shift for the alpha protons of the bipyridine rings was simply a coincidence. The proton integration ratio confirmed the structure proposed in all cases. The ν(CN) band in the IR spectrum may be used also as a useful diagnostic tool for the chloride displacement by L. Thus, the bonding of L to the ruthenium centre shifts the absorption to higher frequencies (about 15 cm^{-1}).

In order to graft a bifunctional N, P ligand through the N donor atom to the dendrimer and thus, consequently, to have a new phosphorus atom for the coordination of other new metal fragments, we reacted the ligand $pyPPh_2$ with the dendrimer **1[Ru]$_4$**. After several hours of stirring, the ^{31}P NMR spectrum of the solution evidenced a mixture of two products, as a result of the coordination of the N, P ligand through both functions. This fact was further confirmed by ^{1}H and ^{13}C NMR spectroscopy. To correct our strategy, we designed the reaction of the same dendrimer **1[Ru]$_4$** with the gold complex $(py)PPh_2AuCl$. Now, the strong coordination of the gold to the phosphorus makes the nitrogen atom the only coordination site facing the dendrimer. Indeed, although the reaction proceeded slowly, ^{31}P NMR spectroscopy revealed that the gold complex displaces the chloride ligand in **1[Ru]$_4$** and is grafted into the surface of the dendrimer [eqn. (5)]. After twenty days of stirring, $(NH_4)PF_6$ was added to the solution and a solid was separated. The ^{31}P NMR spectrum showed two products: the expected bimetallic dendrimer **1[RuAu]$_4^{4+}$** and unreacted starting dendrimer **1[Ru]$_4$**. The proton integration indicated that the mixture



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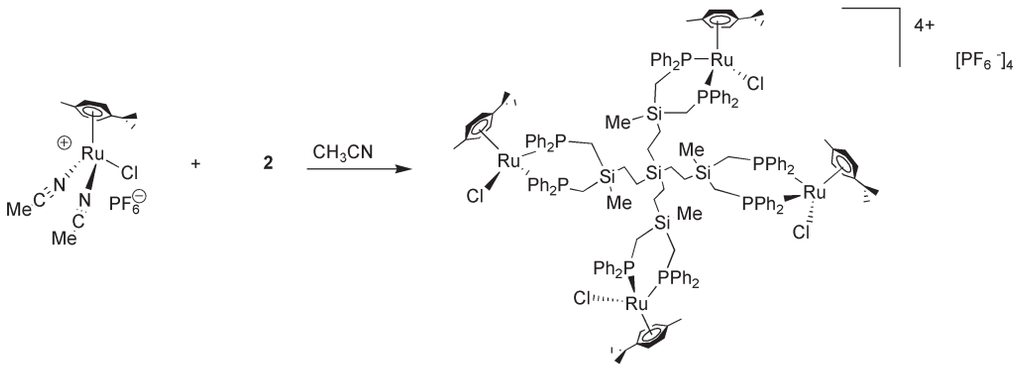

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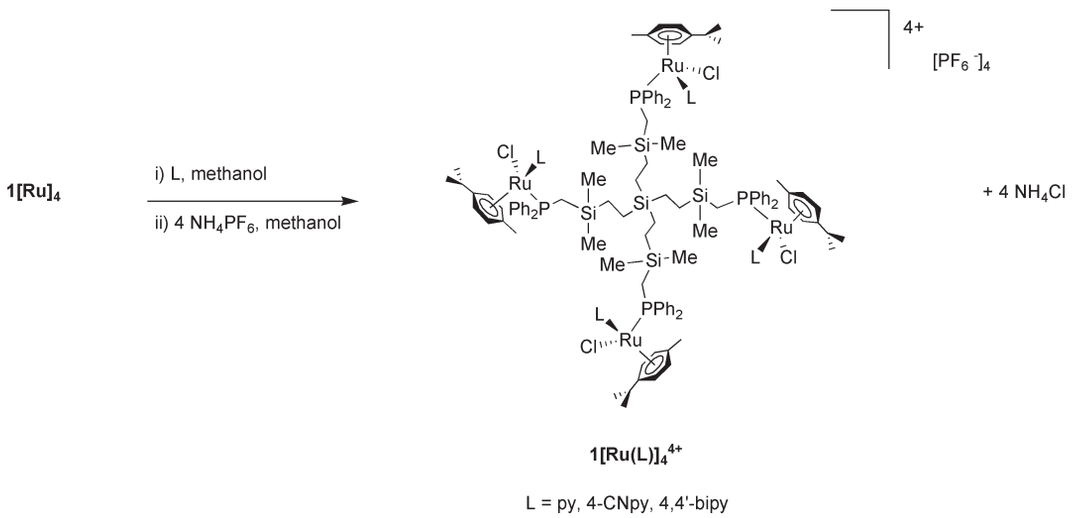


(4)

contained 70% of the gold-dendrimer. **1[RuAu]$_4^{4+}$** was not isolated. In the ^{1}H NMR spectrum, the H_α of the pyridine ring appeared at δ 8.77, very close to that found, for example, in **1[Ru(py)]$_4^{4+}$**(δ 8.65). The carbosilane dendrimer exhibited the expected ^{13}C and ^{29}Si NMR spectral features. On the other hand, note that the coordination of the gold complex to the dendrimer induces only a slight upfield shift of about 0.4 ppm of the phosphorus signal of the $AuPPh_2$ unit, as expected. These observations are clearly consistent with the formation of the bimetallic Ru/Au dendrimer, but unfortunately, neither the slowness nor the yield of the process made it attractive. Thus, we sought to enter this area by paying attention to the coordinative ability of the cationic dendrimer **1[Ru(bipy)]$_4^{4+}$** towards some metal fragments. We first studied the reaction of **1[Ru(bipy)]$_4^{4+}$** with ClAu(tht) in CH_2Cl_2. The process was carried out at room temperature but no reaction was observed after several hours. This was not surprising due to the fact that gold has little tendency to coordinate to nitrogen donor atoms. Then, we tested the reaction of **1[Ru(bipy)]$_4^{4+}$** with $[RuCl_2(p\text{-cymene})]_2$ in acetone-d_6 in an attempt to attach a new $RuCl_2$(*p*-cymene) unit to the second pyridine ring of the 4,4′-bipyridine [eqn. (6)]. After 2 h the ^{31}P NMR spectrum showed the phosphorus signal slightly shifted downfield in relation to the starting ruthenium dendrimer. In addition, the ^{1}H NMR spectrum showed the presence of two different cymene groups with a 1 : 1 ratio. Moreover, the signal corresponding to the $H_{\alpha'}$ at δ 8.92 was displaced at δ 9.31 ppm after the reaction, confirming the incorporation of the ruthenium fragment into the molecule. The IR spectrum of the new species revealed the shift of the ν(CN) frequency of the reagent from 1595 cm^{-1} to 1609 cm^{-1}. Workup of the solution allowed us to obtain a yellow powder in moderate yields. All these facts show that the dendrimer **1[Ru(bipy)Ru]$_4^{4+}$**, displaying a double layer of ruthenium atoms, has been really obtained. Unfortunately, **1[Ru(bipy)Ru]$_4^{4+}$** is not very stable in solution and it decomposes rapidly, so we were unable to take the ^{13}C NMR spectrum.

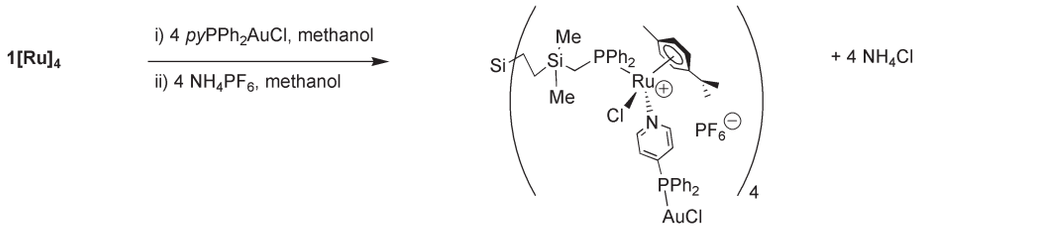
The reaction of **1[Ru(bipy)]$_4^{4+}$** with $[RhCl(CO)_2]_2$ proceeded similarly [eqn. (6)]. It was monitored by IR spectroscopy in the ν(CO) region showing the IR bands of the $RhCl(CO)_2$ unit to shift to higher frequencies (about 2088 and 2010 cm^{-1}) in comparison with the starting $[RhCl(CO)_2]_2$. Besides, the ν(CN) band for **1[Ru(bipy)]$_4^{4+}$** at 1595 cm^{-1} was shifted to 1609 cm^{-1}, overlapping with the frequency due to the other CN group bonded to the ruthenium. The ^{1}H NMR spectrum was also informative in that the two H_α's appeared slightly shifted in relation to the starting ruthenium dendrimer. The methyl, methylene, and ethylene protons as well as the *p*-cymene resonances are also present with the correct proton integration. Like dendrimer **1[Ru(bipy)Ru]$_4^{4+}$**, the stability of **1[Ru(bipy)Rh]$_4^{4+}$** in solution was rather reduced and the attempts to register the ^{13}C NMR spectrum resulted in the decomposition of the product. Probably the very high steric congestion derived from the volume of the metal fragments makes the stabilization of the final product difficult.

However, despite the instability of these species, the methodology reported here opens up a route for the synthesis of multilayer metal dendrimers.

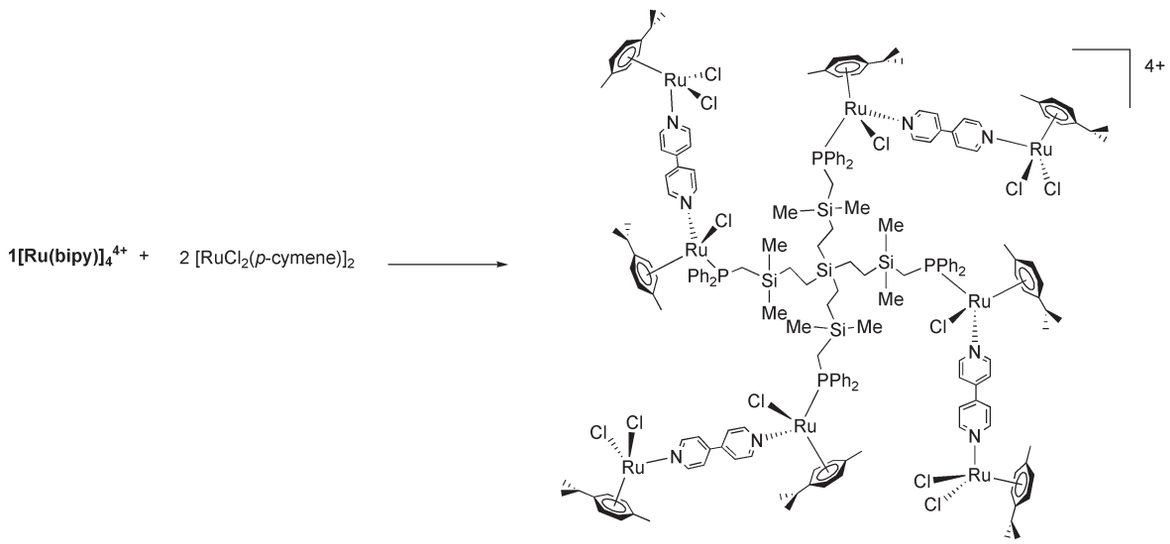
Catalytic transfer hydrogenation of cyclohexanone

In recent years, the attachment of molecular precursors of homogeneous catalysts to soluble dendrimer supports has received considerable attention because of the potential advantages regarding the fixation and recovery or recycling of catalyst.[1d,1g,10] The dendrimers have a well-defined structure with the possibility of attaching a known large number of active sites on the periphery while basically, retaining the properties of the simple molecular counterpart.

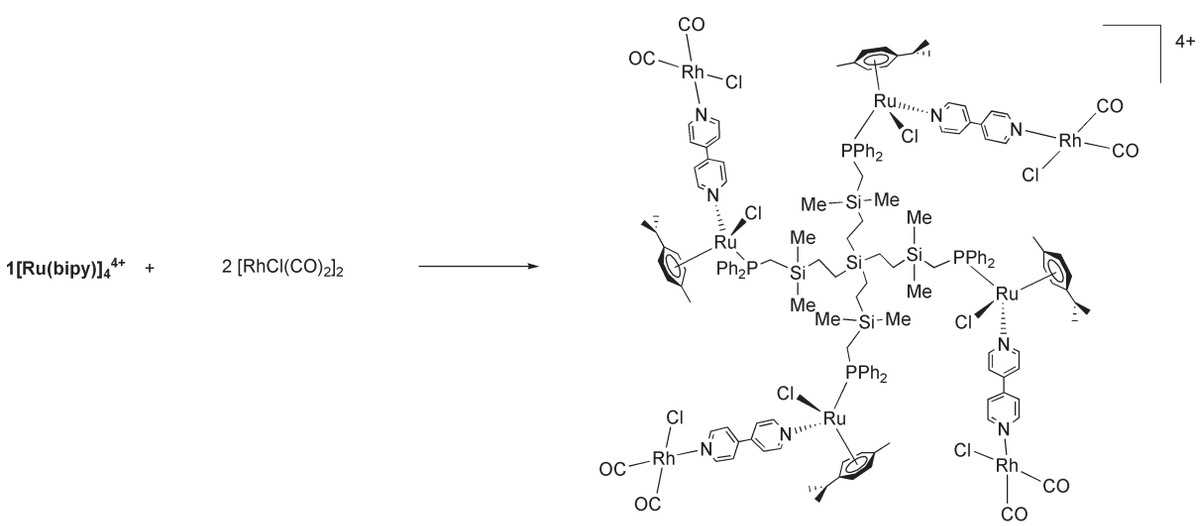
Therefore, dendrimers loaded mainly with Ni, Pd, Ru and Rh complexes have been tested as supports for homogeneous catalysts in a wide number of reactions. Generally, the results show a slightly lower range of activities than those obtained with



1[RuAu]$_4^{4+}$ (5)



1[Ru(bipy)Ru]$_4^{4+}$



1[Ru(bipy)Rh]$_4^{4+}$ (6)

conventional homogeneous catalysts, probably due to their reduced accessibility.

The catalytic hydrogenation of organic substrates is one of the most widely studied processes. An alternative method, which avoids the use of gaseous hydrogen and allows the use of standard reflux techniques, consists of hydrogen transfer reactions. The hydrogen is supplied by a donor molecule (usually alcohols, formic acid), which itself undergoes dehydrogenation during the course of the reaction. These catalytic systems are relatively stable, easy to handle and environmentally friendly.[11]

For example, ruthenium complexes of the type $[RuCl_2(PPh_3)_3]$ have been used as homogeneous catalysts for reduction of both aliphatic and aromatic ketones by propan-2-ol[12] and (η^6-arene)–ruthenium(II) complexes have proved efficient homogeneous catalysts for the reduction of ketones and imines. Noyori and Hashiguchi have successfully developed the asymmetric version of the reaction with chiral bidentate ligands,[13] where different reaction mechanisms are proposed to operate.[14] Furthermore, bidentate chiral ligands have been attached to Fréchet's polyether dendritic wedges giving excellent enantiomeric excesses but limited TOF values (<100 h^{-1}) in the model reaction with acetophenone.[15] On the other hand, Deng *et al.*[16] reported the synthesis of a nitrogen functionalized dendrimer and its application to the asymmetric transfer hydrogenation.

A previous paper[8] has described our test of a rhodium dendritic system in the hydrogenation of olefins. Here, we compare the

Table 1 Transfer hydrogenation of cyclohexanone using mononuclear Ru(II) catalytic systems[a]

Entry	Catalyst[b]	*T*/°C	Base/cat/substrate[c]	Time/min	Conversion (%)[d]
1	A	r.t.	24/1/100	1440	3.9
2	A	r.t.	4/1/100	1440	4.8
3	A	r.t.	24[e]/1/100	1440	7
4	A	82	24/1/100	30	93
5	A	82	24/1/100	60	100
6	A	82	12/1/100	30	87
7	A	82	12/1/100	60	95
8	A	82	6/1/100	30	84
19	A	82	6/1/100	60	100
10	A	82	6/1/1000	30	61.8
11	A	82	6/1/1000	60	98
12	B	r.t.	6/1/100	1440	6.6
13	B	82	6/1/100	15	96
14	B	82	6/1/1000	30	81
15	B	82	6/1/1000	60	>99

[a] Results from duplicated experiments. [b] A: $[RuCl_2(p\text{-cymene})(PPh_3)]$; B: $[RuCl_2(p\text{-cymene})(PMePh_2)]$. [c] Ratio *t*-BuOK/cat/cyclohexanone. [d] Conversions determined by GC. [e] Base: NaOH.

activity of the analogous (η^6-arene)–ruthenium(II) dendritic species with ruthenium(II) mononuclear complexes in the reduction of cyclohexanone by the hydrogen transfer reaction [eqn. (7)].

We performed preliminary catalytic studies on the transfer hydrogenation of cyclohexanone by propan-2-ol for screening optimal conditions using the mononuclear complexes $[RuCl_2(p\text{-cymene})(PPh_3)]$ and $[RuCl_2(p\text{-cymene})(PMePh_2)]$ as catalysts. As shown in Table 1 experiments at room temperature were carried out with different substrate/catalyst/base ratios, using *t*-BuOK as base. Very low activities were found for both catalysts (entries 1–3 and 12), and the use of NaOH instead of *t*-BuOK as base did not improve significantly the activity of the system. When the reactions were carried out in refluxing propan-2-ol, the activity increased and total conversion was found after 30 min with a substrate/catalyst ratio of 100/1 and no dependence on substrate/base ratio being observed (entries 4, 6, 8 and 13). For better measurements of activities the substrate/catalyst ratio was increased to 1000/1 and total conversion was achieved after 1 h reaction (entries 11 and 15). Therefore we established the standard conditions for the reaction, 82 °C temperature and a cyclohexanone/catalyst/*t*-BuOK ratio of 1000/1/6. For good reproducibility of the catalytic results the *t*-BuOK solution must be freshly prepared.

Under the same conditions, the catalytic activity of **1[Ru]$_4$**, **1[Ru(py)]$_4^{4+}$** and **3[Ru]$_8$** metallodendrimers and related mononuclear complexes $[RuCl_2(p\text{-cymene})(PPh_3)]$ $[RuCl_2(p\text{-cymene})(PMePh_2)]$ and $[RuCl(p\text{-cymene})(PMePh_2)(py)]PF_6$ in the transfer hydrogenation of cyclohexanone by propan-2-ol has been investigated and the results are displayed in Table 2.

Mononuclear species can be observed to show better activities than analogous complexes reported in the literature containing only PPh_3 ligand[12a] or arene and phosphine ligand[13c] when similar reaction conditions are used. The neutral complex containing $PMePh_2$ ligand is more active than that containing PPh_3 (entries 1 and 2). Analogously the neutral complex is also more active than the corresponding cationic complex with pyridine ligand $[RuCl(p\text{-cymene})(PMePh_2)(py)]PF_6$ (entries 2 and 3) but in the same order of magnitude. The system seems to be slightly more active when the electron density of the metal centre increases.

On the other hand, dendrimeric systems show lower activities than that found for related mononuclear complexes. Table 2 shows that among first generation dendrimers, the neutral species **1[Ru]$_4$** is more active than the cationic analogue **1[Ru(py)]$_4$**

Table 2 Transfer hydrogenation of cyclohexanone using Ru(II) catalytic systems[a]

Entry	Catalyst	Yield (%)[b]	TOF_{50}/h^{-1}[c]
1	$[RuCl_2(p\text{-cymene})(PPh_3)]$	61	1135
2	$[RuCl_2(p\text{-cymene})(PMePh_2)]$	81	1250
3	$[RuClpy(p\text{-cymene})(PMePh_2)]PF_6$	56	1110
4	$1[Ru]_4$	34	680
5	$1[Ru(py)]_4$	26	450
6	$3[Ru]_8$	19	270

[a] Conditions: reactions were carried out at 82 °C using *t*-BuOK/catalyst/cyclohexanone ratio: 6/1/1000. [b] Yield of cyclohexanol determined after 30 min reaction. GC determined. [c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion.

(entries 4 and 5), following the same trend found for the mononuclear species. Moreover, in standard conditions the cationic species raises only 62% conversion, showing probable decomposition of the catalyst. The third generation dendrimer **3[Ru]$_8$** is less active than the first generation one (entries 4, 5 and 6). Nevertheless our ruthenodendrimers show higher activities than those reported in the literature for other dendrimeric systems.[16]

Fig. 1 shows conversion of cyclohexanone *versus* time. Variation of TOF values with time points to the existence of an induction period necessary for the formation of an active species as represented tentatively in Scheme 1. The cationic and the third generation dendrimers showed deactivation or clear decomposition giving limited conversions.

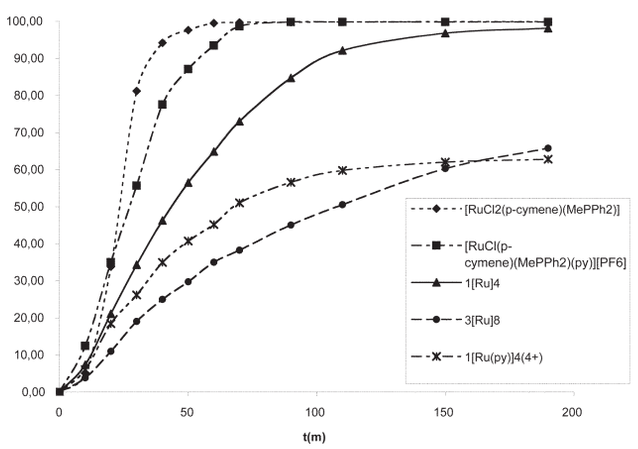
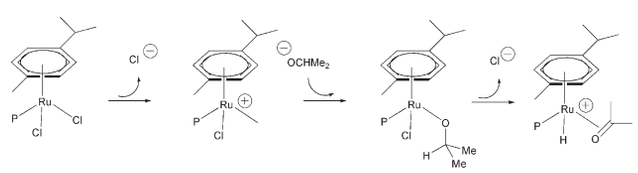


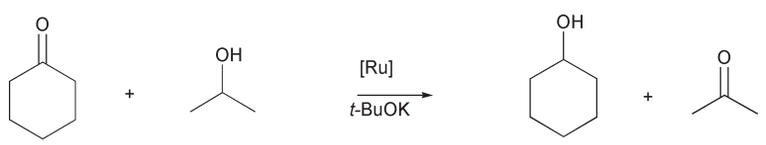
Fig. 1 Mol% of hydrogenation of cyclohexanone *vs.* time using monomer and metallodendrimer Ru(II) compounds as precursors.



Scheme 1

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (thf and Et_2O), $CaCl_2$ and storage over molecular sieves (acetone) or dried with $CaCl_2$ and distilled from CaH_2 (CH_2Cl_2) under N_2 prior to use. Elemental analyses (C, H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC). ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ and $^{31}P\{^1H\}$ NMR



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spectra were recorded at 25 °C on Bruker 250, Bruker 500 and Mercury 400 spectrometers. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^1H, ^{13}C and ^{29}Si, 85% H_3PO_4 for ^{31}P) and coupling constants are given in Hz. Infrared spectra were recorded with FT-IR 520 Nicolet or Impact 400 Nicolet spectrometers in the 4000–400 cm^{-1} range as KBr pellets. MS (ES) spectra were recorded on a Fisons VG Quatro spectrometer. MALDI-TOF spectra were recorded on a Voyager DE-RP (Perspective Biosystems) time-of-flight (TOF) spectrometer using as a matrix SA (salicylic acid). The GC analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m, HP Ultra-2 ((5% phenyl)-methylpolysiloxane) with a FID detector.

The starting materials $[RuCl_2(p\text{-cymene})]_2$,[17] 4-pyridyldiphenylphosphine,[18] ClAu(tht),[19] $[RhCl(CO)_2]_2$,[20] $[RuCl_2(p\text{-cymene})(PPh_3)]$,[21] $[RuCl_2(p\text{-cymene})(PMePh_2)]$,[22] and phosphine-terminated dendrimers **1**, **2** and **3** were prepared following published procedures.[7,9] Other reagents were purchased from commercial suppliers.

Syntheses

$Si^0(C^1H_2C^2H_2Si^1(CH_3)_2CH_2PPh_2RuCl_2(p\text{-cymene}))_4$ (1[Ru]$_4$). To a solution of dendrimer **1** (180 mg, 0.15 mmol) in 20 ml of CH_2Cl_2 was added $[RuCl_2(p\text{-cymene})]_2$ (188 mg, 0.30 mmol) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated to dryness, the residue was washed with diethyl ether and dried under vacuum. The complex was obtained as a red solid (360 mg, 98%). (Found: C, 54.32; H, 6.12. $C_{108}H_{144}Cl_8P_4Ru_4Si_5$ requires C, 54.17; H, 6.06%; *M* 2394.6); $\delta_H(CDCl_3)$: 7.95 (m, 16H, C_6H_5), 7.47 (m, 24H, C_6H_5), 5.19 (d, 8H, $^3J(HH) = 6$ Hz, C_6H_4), 4.99 (d, 8H, $^3J(HH) = 6$ Hz, C_6H_4), 2.50 (sep, 4H, $^3J(HH) = 7.0$ Hz, $CH(CH_3)_2$), 1.93 (d, 8H, $^2J(HP) = 14.5$ Hz, CH_2P), 1.81 (s, 12H, CH_3), 0.74 (d, 24H, $^3J(HH) = 7.0$ Hz, $CH(CH_3)_2$), −0.3–(−0.55) (m, 40H, CH_2Si, CH_3Si); $\delta_C(CDCl_3)$: 134.8 (d, $^1J(CP) = 43.3$, *ipso*-C_6H_5), 132.7 (d, $^2J(CP) = 8.7$ Hz, *o*-C_6H_5), 130.8 (s, *p*-C_6H_5), 128.4 (d, $^3J(CP) = 9.6$ Hz, *m*-C_6H_5), 107.8 (s, *C*–$CH(CH_3)_2$), 92.5 (s, *C*–CH_3), 91.0 (d, $^2J(CP) = 4$ Hz, C_6H_4), 85.3 (d, $^2J(CP) = 6$ Hz, C_6H_4), 30.1 (s, $CH(CH_3)_2$), 21.3 (s, $CH(CH_3)_2$), 17.4 (s, CH_3), 10.7 (m, CH_2P), 8.6 (s, $C^2H_2Si^1$), 2.2 (s, $C^1H_2Si^0$), −2.2 (s, CH_3Si^1); $\delta_{Si}(CDCl_3)$: 8.9 (s, Si^0), 3.6 (d, $^2J(SiP) = 14.8$ Hz, Si^1); $\delta_P(CDCl_3)$: 22.7 (s, PPh_2). MS (ES^+): $m/z = 2361.4$ $[M - Cl]^+$, 1162.1 $[M - 2Cl]^{2+}$, 762.6 $[M - 3Cl]^{3+}$.

$Si^0(C^1H_2C^2H_2Si^1(C^1H_3)_2C^3H_2C^4H_2Si^2(C^2H_3)(C^5H_2C^6H_2Si^3(C^3H_3)_2CH_2PPh_2RuCl_2(p\text{-cymene}))_2)_4$ (3[Ru]$_8$). Experimental conditions and workup were identical to those of the preparation of **1[Ru]$_4$**. (183 mg, 88%). (Found: C, 54.10; H, 6.48. $C_{244}H_{356}Cl_{16}P_8Ru_8Si_{17}$ requires C, 54.37; H, 6.66%; *M* 5390.6); $\delta_H(CDCl_3)$: 7.99 (m, 32H, C_6H_5), 7.47 (m, 48H, C_6H_5), 5.20 (m, 16H, C_6H_4), 5.00 (m, 16H, C_6H_4), 2.50 (sep, 8H, $^3J(HH) = 7.0$ Hz, $CH(CH_3)_2$), 1.95 (d, 16H, $^2J(HP) = 14.0$ Hz, CH_2P), 1.82 (s, 24H, CH_3), 0.73 (d, 48H, $^3J(HH) = 7.0$ Hz, $CH(CH_3)_2$), 0.28–(−0.53) (m, 148H, CH_2Si, CH_3Si); $\delta_C(CDCl_3)$: 134.9 (d, $^1J(CP) = 43.0$, *ipso*-C_6H_5), 132.8 (d, $^2J(CP) = 8.5$ Hz, *o*-C_6H_5), 130.8 (s, *p*-C_6H_5), 128.4 (d, $^3J(CP) = 9.1$ Hz, *m*-C_6H_5), 107.8 (s, *C*–$CH(CH_3)_2$), 92.5 (s, *C*–CH_3), 91.1 (s, C_6H_4), 85.3 (d, $^2J(CP) = 5.5$ Hz, C_6H_4), 30.1 (s, $CH(CH_3)_2$), 21.3 (s, $CH(CH_3)_2$), 17.4 (s, CH_3), 14.3 (d, $^1J(CP) = 14.3$ Hz, CH_2P), 8.9 (s, $C^6H_2Si^3$), 7.0, 6.6, 4.7, 4.2, 2.7 (s, CH_2Si), −2.1 (s, CH_3Si^3), −4.2 (s, CH_3Si^1), −6.6 (s, CH_3Si^2); $\delta_{Si}(CDCl_3)$: 7.9 (s, Si^2), 5.7 (s, Si^1), 3.7 (d, $^2J(SiP) = 15.1$ Hz, Si^3); $\delta_P(CDCl_3)$: 22.7 (s, PPh_2). MS (ES^+): $m/z = 1761.6$ $[M - 3Cl]^{3+}$, 1314.2 $[M - 4Cl]^{4+}$, 1162.4 $[M - 4Cl - 2RuCl_2(p\text{-cymene})]^{4+}$, 1008.3 $[M - 4Cl - 4RuCl_2(p\text{-cymene})]^{4+}$.

$(CH_3)_2Si(CH_2PPh_2RuCl_2(p\text{-cymene}))_2$. Experimental conditions and workup were identical to those of the preparation of **1[Ru]$_4$**. (444 mg, 93%). (Found: C, 53.80; H, 5.49. $C_{48}H_{58}Cl_4P_2Ru_2Si$ requires C, 53.93; H, 5.47%; *M* 1069.0); $\delta_H(CDCl_3)$: 7.83(m, 8H, C_6H_5), 7.42 (m, 12H, C_6H_5), 5.11 (d, 4H, $^3J(HH) = 6.2$ Hz, C_6H_4), 4.93 (d, 4H, $^3J(HH) = 6.2$ Hz, C_6H_4), 2.43 (sep, 2H, $^3J(HH) = 6.9$ Hz, $CH(CH_3)_2$), 1.74 (s, 6H, CH_3), 1.71 (d, 4H, $^2J(HP) = 13.7$ Hz, CH_2P), 0.74 (d, 12H, $^3J(HH) = 6.9$ Hz, $CH(CH_3)_2$), −1.04 (s, 6H, CH_3Si); $\delta_C(CDCl_3)$: 134.8 (d, $^1J(CP) = 43.3$, *ipso*-C_6H_5), 132.9 (d, $^2J(CP) = 8.9$ Hz, *o*-C_6H_5), 130.6 (s, *p*-C_6H_5), 128.4 (d, $^3J(CP) = 9.7$ Hz, *m*-C_6H_5), 108.0 (s, *C*–$CH(CH_3)_2$), 92.9 (s, *C*–CH_3), 90.7 (d, $^2J(CP) = 4.3$ Hz, C_6H_4), 85.2 (d, $^2J(CP) = 6.2$ Hz, C_6H_4), 30.1 (s, $CH(CH_3)_2$), 21.4 (s, $CH(CH_3)_2$), 17.3 (s, CH_3), 11.8 (d, $^1J(CP) = 22.4$ Hz, CH_2P), 0.19 (s, CH_3Si); $\delta_{Si}(CDCl_3)$: 1.96 (t, $^2J(SiP) = 13.5$ Hz, Si); $\delta_P(CDCl_3)$: 21.4 (s, PPh_2). MS (ES^+): $m/z = 1035.7$ $[M - Cl]^+$, 499.2 $[M - 2Cl]^{2+}$.

$Si^0(C^1H_2C^2H_2Si^1\{(CH_3)(CH_2PPh_2RuCl_2(p\text{-cymene}))_2\})_4$ (2-[Ru]$_8$). Experimental conditions and workup were identical to those of the preparation of **1[Ru]$_4$** using 190 mg (0.10 mmol) of dendrimer 2 and 244 mg (0.40 mmol) of $[RuCl_2(p\text{-cymene})]_2$. $\delta_P(CD_2Cl_2, 298K)$: 21.3 (s), 20.1 (s_{br}), 7.4 (s).

$Si^0(C^1H_2C^2H_2Si^1\{(CH_3)(CH_2PPh_2)(CH_2PPh_2RuCl_2(p\text{-cymene}))\})_4$. Experimental conditions and workup were identical to those of the preparation of **1[Ru]$_4$** using 190 mg (0.10 mmol) of dendrimer **2** and 122 mg (0.20 mmol) of $[RuCl_2(p\text{-cymene})]_2$. $\delta_{Si}(CD_2Cl_2)$: 9.4 (s, Si^0), 4.0 (m, Si^1); $\delta_P(CD_2Cl_2, 298K)$: 21.3 (m, PPh_2Ru), −23.3 (m, PPh_2); $\delta_P(CD_2Cl_2, 220K)$: 21.7, 21.3 (s, PPh_2Ru), −24.6, −24.9 (s, PPh_2).

$Si^0(C^1H_2C^2H_2Si^1\{(CH_3)(CH_2PPh_2AuCl)(CH_2PPh_2RuCl_2(p\text{-cymene}))\})_4$. Experimental conditions and workup were identical to those of the preparation of **1[Ru]$_4$** using 190 mg (0.10 mmol) of dendrimer **2**, 122 mg (0.20 mmol) of $[RuCl_2(p\text{-cymene})]_2$ and 128 mg (0.40 mmol) of ClAu(tht). MS (MALDI-TOF): 2335.1 $[M - 6RuCl_2(p\text{-cymene}) - Cl]^+$, 2566.9 $[M - 5RuCl_2(p\text{-cymene}) - Cl]^+$, 2799.9 $[M - 4RuCl_2(p\text{-cymene}) - Cl]^+$, 3032.4 $[M - 3RuCl_2(p\text{-cymene}) - Cl]^+$, 3264.2 $[M - 2RuCl_2(p\text{-cymene}) - Cl]^+$; $\delta_{Si}(CD_2Cl_2)$: 8.8 (s, Si^0), 2.0 (m, Si^1); $\delta_P(CD_2Cl_2)$: 21.8–20.1 (m, PPh_2Ru, PPh_2Au).

$[Si^0(C^1H_2C^2H_2Si^1(CH_3)(CH_2PPh_2)_2RuCl(p\text{-cymene}))_4][PF_6]_4$ (2[Ru]$_4^{4+}$). To a solution of $[RuCl_2(p\text{-cymene})]_2$ (74 mg, 0.12 mmol) in 20 ml of acetonitrile was added $(NH_4)PF_6$ (42 mg, 0.24 mmol). The mixture was stirred overnight and the NH_4Cl formed was removed by filtration through Celite. To this solution was added another of **2** (115 mg, 0.06 mmol) in 10 ml of thf and the mixture was stirred for 27 days. The solvent was evaporated to dryness and the product was recrystallised with CH_3CN/diethyl ether. A yellow solid was obtained (132 mg, 73%). (Found: C, 53.01; H, 4.98. $C_{156}H_{180}Cl_4F_{24}P_{12}Ru_4Si_5$ requires C, 52.50; H, 5.08%; *M* 3569.3); $\delta_H(acetone\text{-}d_6)$: 7.7–7.1 (m, 80H, C_6H_5), 6.02 (m, 8H, C_6H_4), 5.41 (d_{br}, 4H, C_6H_4), 5.32 (d_{br}, 4H, C_6H_4), 2.61 (m, 2H, $CH(CH_3)_2$), 2.34 (m, 10H, $CH(CH_3)_2$, CH_2P), 1.56–1.42 (m, 8H, CH_2P), 1.19 (m, 12H, CH_3), 1.01 (d, 12H, $^3J(HH) = 6.8$ Hz, $CH(CH_3)_2$), 0.83 (d, 12H, $^3J(HH) = 6.8$ Hz, $CH(CH_3)_2$), 0.26–(−0.39) (m, 28H, CH_2Si, CH_3Si); $\delta_C(acetone\text{-}d_6)$: 133.5–128.8 (m, C_6H_5), 96.4 (s_{br}, C_6H_4), 91.8 (s_{br}, C_6H_4), 30.9 (s, $CH(CH_3)_2$), 20.9, 20.8 (s, $CH(CH_3)_2$), 15.0 (s, CH_3), 10.5 (m, CH_2P), 8.4 (s, $C^2H_2Si^1$), 2.8 (s, $C^1H_2Si^0$), 1.9 (s, CH_3Si), −1.2 (s, CH_3Si); $\delta_{Si}(acetone\text{-}d_6)$: 2.0 ($s_{br}$, Si^1); $\delta_P(acetone\text{-}d_6)$: 31.0, 30.6 (s, PPh_2), −144.2 (sep, PF_6^-). MS (ES^+): $m/z = 1639.6$ $[M - 2PF_6]^{2+}$, 1045.8 $[M - 3PF_6]^{3+}$, 747.4 $[M - 4PF_6]^{4+}$.

$[(CH_3)_2Si(CH_2PPh_2)_2RuCl(p\text{-cymene})][PF_6]$. Experimental conditions and workup were identical to those for the preparation of **2[Ru]$_4^{4+}$**. (445 mg, 89%). (Found: C, 52.81; H, 5.31. $C_{38}H_{44}ClF_6P_3RuSi$ requires C, 52.32; H, 5.08%; *M* 872.3); $\delta_H(CDCl_3)$: 7.66–7.34 (m, 20H, C_6H_5), 5.66 (d, 2H, $^3J(HH) = 6$ Hz, C_6H_4), 5.25 (d, 2H, $^3J(HH) = 6$ Hz, C_6H_4), 2.34 (m, 3H, $CH(CH_3)_2$, CH_2P), 1.43 (m, 2H, CH_2P), 1.31 (s, 3H, CH_3), 0.98 (d, 6H, $^3J(HH) = 7.0$ Hz, $CH(CH_3)_2$), 0.01 (s, 3H, CH_3Si), −0.37 (s, 3H, CH_3Si); $\delta_C(CDCl_3)$: 138.7 (d, $^1J(CP) = 24.4$, *ipso*-C_6H_5), 133.3 (pt, $^2J(CP) = 5$ Hz, *o*-C_6H_5), 132.2 (s, *p*-C_6H_5), 131.3 (pt, $^2J(CP) = 4.4$ Hz, *o′*-C_6H_5), 131.0 (s, *p′*-C_6H_5), 129.3 (pt, $^3J(CP) = 5$ Hz, *m*-C_6H_5), 128.9 (pt, $^3J(CP) = 5$ Hz, *m′*-C_6H_5), 126.6 (s, *C*–$CH(CH_3)_2$), 101.4 (s, *C*–CH_3), 94.9, 92.9 (s, C_6H_4), 30.7 (s, $CH(CH_3)_2$), 21.6 (s, $CH(CH_3)_2$), 16.5 (s,

CH_3), 10.8 (pt, ^1J(CP) = 11.6 Hz, CH_2P), 1.42 (s_{br}, CH_3Si), 1.11 (s_{br}, CH_3Si); δ_P($CDCl_3$): 29.3 (s, PPh_2), −144.3 (sep, PF_6^-). MS (ES^+): m/z = 727.6 $[M - PF_6]^{2+}$.

[$Si^0(C^1H_2C^2H_2Si^1(CH_3)_2CH_2PPh_2RuCl(4,4'$-bipy)($p$-cymene))$_4$][$PF_6$]$_4$ (1[Ru(bipy)]$_4^{4+}$). A solution of 1**[Ru]**$_4$ (215 mg, 0.09 mmol) in 10 ml of methanol was added to a solution of 4,4′-bipyridine (280 mg, 1.76 mmol) in 10 ml of methanol, dropwise and with vigorous stirring. The mixture was stirred for 24 h. Then, a solution of NH_4PF_6 (63 mg, 0.36 mmol) in 5 ml of methanol was added and stirred for 2 h. The orange solid was filtered off, washed several times with diethyl ether and dried under vacuum. (195 mg, 63%). δ_H(CD_2Cl_2): 8.74 (m, 16H, bipy(*Hα*, *Hα′*)), 7.91 (m, 8H, *o*-C_6H_5), 7.71 (m, 8H, *m*-C_6H_5), 7.66 (m, 4H, *p*-C_6H_5), 7.51 (m, 8H, bipy(*Hβ′*)), 7.46 (d, 8H, ^3J(HH) = 6.8 Hz, bipy(*Hβ*)), 7.39 (m, 8H, *o′*-C_6H_5), 7.20 (m, 4H, *p′*-C_6H_5), 7.08 (m, 8H, *m′*-C_6H_5), 5.36 (d, 4H, ^3J(HH) = 6 Hz, C_6H_4(*A′*)), 5.28 (d, 4H, ^3J(HH) = 6 Hz, C_6H_4(*A*)), 5.25 (d, 4H, ^3J(HH) = 6 Hz, C_6H_4(*B′*)), 5.18 (d, 4H, ^3J(HH) = 6 Hz, C_6H_4 (*B*)), 2.34 (d, 4H, ^2J(HP) = 15 Hz, CH_aH_bP), 2.30 (sep, 4H, ^3J(HH) = 7 Hz, $CH(CH_3)_2$), 1.76 (s, 12H, CH_3), 1.73 (m, 4H, CH_aH_bP), 1.10 (d, 12H, ^3J(HH) = 7 Hz, $CH(CH_3)_2$), 0.99 (d, 12H, ^3J(HH) = 7 Hz, $CH(CH_3)_2$), −0.17 (m, CH_2Si), −0.24 (m, CH_2Si), −0.40 (s, CH_3Si), −0.60 (s, CH_3Si) (40H); δ_C(CD_2Cl_2): 156.8 (s, bipy(*Cα*)), 151.1 (s, bipy(*Cα′*)), 148.2 (s, bipy(*Cγ*)), 143.1 (s, bipy(*Cγ′*)), 132.7–132.5 (m, *o*-, *o′*-C_6H_5), 132.0, 130.9 (s, *p*-, *p′*-C_6H_5), 129.6 (m, *m*-C_6H_5), 128.6 (m, *m′*-C_6H_5), 123.3 (s, bipy(*Cβ*)), 121.4 (s, bipy(*Cβ′*)), 110.4 (s, *C*–$CH(CH_3)_2$), 100.4 (s, *C*–CH_3), 91.7 (s, C_6H_4 (*B*)), 90.4 (s, C_6H_4 (*A′*)), 89.1 (s, C_6H_4 (*B′*)), 88.0 (C_6H_4 (*A*)), 30.7 (s, *CH*$(CH_3)_2$), 22.1, 21.8 (s, $CH(CH_3)_2$), 17.6 (s, CH_3), 12.45 (d, ^1J(CP) = 25.4 Hz, CH_2P), 8.8 (s, $C^1H_2Si^1$), 2.3 (s, $C^1H_2Si^0$), −2.1, −2.5 (s, CH_3Si^1); δ_{Si}(CD_2Cl_2): 9.2 (s, Si^0), 4.5 (m, Si^1); δ_P(CD_2Cl_2): 25.2 (s, PPh_2), −144.2 (sep, PF_6^-). MS (ES^+): m/z = 1583.2 $[M - 2PF_6]^{2+}$, 1505.8 $[M - 2PF_6$-bipy$]^{2+}$, 1426.8 $[M - 2PF_6$-2bipy$]^{2+}$, 1008.6 $[M - 3PF_6]^{2+}$, 956.6 $[M - 3PF_6$-bipy$]^{3+}$, 904.1 $[M - 3PF_6$-2bipy$]^{3+}$. IR: ν_{max}/cm^{-1} (CN) 1613, 1595 (KBr).

[$Si^0(C^1H_2C^2H_2Si^1(CH_3)_2CH_2PPh_2RuCl(p$-cymene)(py))$_4$][$PF_6$]$_4$ (1[Ru(py)]$_4^{4+}$). Experimental conditions and workup were identical to those for the preparation of **1[Ru(bipy)]**$_4^{4+}$ (55 mg, 76%). δ_H(CD_2Cl_2): 8.65 (m, 8H, py(*Hα*)), 7.90–7.11 (m, 52H, C_6H_5, py(*Hβ*), py(*Hγ*)), 5.33–5.19 (m, 16H, C_6H_4), 2.23 (m, 8H, *CH*$(CH_3)_2$, CH_aH_bP), 1.78 (m, 4H, CH_aH_bP), 1.72 (s, 12H, CH_3), 1.09 (d, 12H, ^3J(HH) = 6.8 Hz, $CH(CH_3)_2$), 0.96 (d, 12H, ^3J(HH) = 6.8 Hz, $CH(CH_3)_2$), −0.1–(−0.58) (m, 40H, CH_2Si, CH_3Si); δ_C(CD_2Cl_2): 156.2 (s, py(*Cα*)), 139.0 (s, py(*Cγ*)), 132.8–132.4 (m, *o*-, *o′*-C_6H_5), 131.9, 131.1 (s, *p*-, *p′*-C_6H_5), 129.5 (d, ^3J(CP) = 9.6 Hz, *m*-C_6H_5), 128.6 (d, ^3J(CP) = 9.6 Hz, *m′*-C_6H_5), 125.9 (s, py (*Cβ*)), 110.7 (s, *C*–$CH(CH_3)_2$), 100.1 (s, *C*–CH_3), 92.0, 90.2, 88.5, 87.8 (m, C_6H_4), 30.7 (s, *CH*$(CH_3)_2$), 22.0, 21.8 (s, $CH(CH_3)_2$), 17.5 (s, CH_3), 12.1 (m, CH_2P), 8.8 (s, $C^2H_2Si^1$), 2.3 (s, $C^1H_2Si^0$), −2.2, −2.5 (s, CH_3Si^1); δ_{Si}(CD_2Cl_2): 9.2 (s, Si^0), 4.4 (d, ^2J(SiP) = 14.2 Hz, Si^1); δ_P(CD_2Cl_2): 25.2 (s, PPh_2), −144.2 (sep, PF_6^-). MS (ES^+): 1429.7 $[M - 2PF_6]^{2+}$, 906.0 $[M - 3PF_6]^{3+}$. IR: ν_{max}/cm^{-1} (CN) 1603 (KBr).

[$Si^0(C^1H_2C^2H_2Si^1(CH_3)_2CH_2PPh_2RuCl(4$-CNpy)($p$-cymene))$_4$][$PF_6$]$_4$ (1[Ru(CNpy)]$_4^{4+}$). Experimental conditions and workup were identical to those for the preparation of **1[Ru(bipy)]**$_4^{4+}$. (76 mg, 71%). δ_H(CD_2Cl_2): 8.76 (m, 8H, CNpy(*Hα*)), 7.70–7.14 (m, 48H, C_6H_5, CNpy(*Hβ*)), 5.39–5.24 (m, 16H, C_6H_4), 2.22 (m, 8H, *CH*$(CH_3)_2$, CH_aH_bP), 1.82 (m, 4H, CH_aH_bP), 1.75 (s, 12H, CH_3), 1.08 (d, 12H, ^3J(HH) = 6.8 Hz, $CH(CH_3)_2$), 0.98 (d, 12H, ^3J(HH) = 6.8 Hz, $CH(CH_3)_2$), −0.16 (m, CH_2Si), −0.38 (s, CH_3Si), −0.57 (s, CH_3Si) (40H); δ_C(CD_2Cl_2): 157.0 (s, CNpy(*Cα*)), 132.8 (m, *o*-, *o′*-C_6H_5), 132.2, 131.4 (s, *p*-, *p′*-C_6H_5), 129.8 (m, *m*-C_6H_5), 129.0 (m, *m′*-C_6H_5), 123.3 (s, CNpy(*Cβ*)), 121.1 (s, CNpy(*Cγ*)), 110.8 (s, *C*–$CH(CH_3)_2$), 100.6 (s, *C*–CH_3), 92.2, 90.5, 89.0, 88.5 (m, C_6H_4), 30.9 (s, *CH*$(CH_3)_2$), 22.3, 21.9 (s, $CH(CH_3)_2$), 17.8 (s, CH_3), 12.4 (m, CH_2P), 9.0 (m, $C^2H_2Si^1$), 2.5 (m, $C^1H_2Si^0$), −1.9, −2.3 (s, CH_3Si^1); δ_{Si}(CD_2Cl_2): 3.4 (d, ^2J(SiP) = 14 Hz, Si^1); δ_P(CD_2Cl_2): 25.3 (s, PPh_2), −144.2 (sep, PF_6^-). MS (ES^+): 937 $[M - 3PF_6]^{3+}$, 667.0 $[M - 4PF_6]^{4+}$. IR: ν_{max}/cm^{-1} (CN) 1647, 1616 (KBr).

[$Si^0(C^1H_2C^2H_2Si^1(CH_3)_2CH_2PPh_2RuCl(p$-cymene)(py$PPh_2$-AuCl))$_4$][$PF_6$]$_4$ (1[RuAu]$_4^{4+}$). Experimental conditions and workup were identical to those for the preparation of **1[Ru(bipy)]**$_4^{4+}$. (46 mg, 53%). δ_H(CD_2Cl_2): 8.77 (s_{br}, 8H, py(*Hα*)), 7.98–7.05 (m, 88H, C_6H_5, py(*Hβ*)), 5.47–4.99 (m, 16H, C_6H_4), 2.44 (m, 8H, *CH*$(CH_3)_2$, CH_2P), 1.91 (m, 4H, CH_2P), 1.75 (s, 12H, CH_3), 1.16 (m, 12H, $CH(CH_3)_2$), 1.03 (m, 12H, $CH(CH_3)_2$), 0.1–(−0.58) (m, 40H, CH_2Si, CH_3Si); δ_C(CD_2Cl_2): 156.3 (s, py(*Cα*)), 134.7–128.1 (m, C_6H_5), 125.0 (s, py(*Cβ*)), 90.9, 89.3, 86.2, 85.2 (m, C_6H_4), 30.6 (s, *CH*$(CH_3)_2$), 21.8, 20.9 (s, $CH(CH_3)_2$), 17.4 (s, CH_3), 15.0 (m, CH_2P), 8.6 ($C^2H_2Si^1$), 2.2 ($C^1H_2Si^0$), −2.6 (CH_3Si^1); δ_{Si}(CD_2Cl_2): 9.2 (s, Si^0), 4.6 (d, ^2J(SiP) = 14.7 Hz, Si^1); δ_P(CD_2Cl_2): 32.1 (s, PPh_2Au), 25.5 (s, PPh_2Ru), −144.4 (sep, PF_6^-). IR: ν_{max}/cm^{-1} (CN) 1628, 1603 (KBr).

[RuCl(p-cymene)($PMePh_2$)(py)][PF_6]. Experimental conditions and workup were identical to those for the preparation of **1[Ru(bipy)]**$_4^{4+}$. (97 mg, 94%). δ_H($CDCl_3$): 8.76 (m, 2H, py(*Hα*)), 7.48–7.20 (m, 13H, C_6H_5, py(*Hβ*), py(*Hγ*)), 5.76 (dd, 1H, ^3J(HH) = 6 Hz, J = 1.2 Hz, C_6H_4(*A′*)), 5.65 (d, 1H, ^3J(HH) = 6 Hz, C_6H_4(*A*)), 5.61 (d, 1H, ^3J(HH) = 6 Hz, C_6H_4(*B′*)), 5.44 (d, 1H, ^3J(HH) = 6 Hz, C_6H_4(*B*)), 2.30 (sep, 1H, ^3J(HH) = 6.9 Hz, *CH*$(CH_3)_2$), 2.17 (d, 3H, ^2J(HP) = 9.9 Hz, CH_3P), 1.72 (s, 3H, CH_3), 1.11 (d, 3H, ^3J(HH) = 6.9 Hz, $CH(CH_3)_2$), 1.00 (d, 3H, ^3J(HH) = 6.9 Hz, $CH(CH_3)_2$); δ_C($CDCl_3$): 155.8 (s, py(*Cα*)), 138.7 (s, py(*Cγ*)), 132.1 (pt, ^2J(CP) = 9.3 Hz, *o*-C_6H_5), 131.4, 131.0 (s, *p*-, *p′*-C_6H_5), 129.2 (d, ^3J(CP) = 10.1 Hz, *m*-C_6H_5), 128.8 (d, ^3J(CP) = 10.8 Hz, *m′*-C_6H_5), 126.1 (s, py(*Cβ*)), 112.2 (d, ^2J(CP) = 4.7 Hz, *C*–$CH(CH_3)_2$), 103.6 (s, *C*–CH_3), 91.4, 90.1, 88.5, 85.9 (s, C_6H_4), 30.9 (s, *CH*$(CH_3)_2$), 22.3, 22.2 (s, $CH(CH_3)_2$), 18.0 (s, CH_3), 14.0 (d, ^1J(CP) = 34.7 Hz, CH_3P); δ_P($CDCl_3$): 16.8 (s, PPh_2), −144.2 (sep, PF_6^-). MS (ES^+): 550.8 $[M - PF_6]^+$. IR: ν_{max}/cm^{-1} (CN) 1602 (KBr).

Syntheses of 1[Ru(bipy)Rh]$_4^{4+}$ and 1[Ru(bipy)Ru]$_4^{4+}$. The dendrimer **1[Ru(bipy)]**$_4^{4+}$ (12 mg, 3.5 μmol) was solved in 2 ml of acetone-d_6 and 2 mg (7 μmol) of $[RhCl(CO)_2]_2$ or 4 mg (7 μmol) of $[RuCl_2(p$-cymene$)]_2$ was added. The reactions were monitored by NMR.

1[Ru(bipy)]$_4^{4+}$. δ_H(acetone-d_6): 8.92 (d, 8H, ^3J(HH) = 5.9 Hz, bipy(*Hα*)), 8.76 (m, 8H, bipy(*Hα′*)), 8.15–7.13 (m, 56H, C_6H_5, bipy(*Hβ*), bipy(*Hβ′*)), 5.75 (d, ^3J(HH) = 6 Hz), 5.61 (d, ^3J(HH) = 6 Hz), 5.47 (d, ^3J(HH) = 6 Hz), 5.34 (d, ^3J(HH) = 6 Hz) (16H, C_6H_4), 2.41 (m, 8H, *CH*$(CH_3)_2$, CH_aH_bP), 1.83 (s, 12H, CH_3), 1.14 (d, ^3J(HH) = 6.8 Hz), 1.02 (d, ^3J(HH) = 6.8 Hz) (24H, $CH(CH_3)_2$), 0.1–(−0.52) (m, 40H, CH_2Si, CH_3Si); δ_P(acetone-d_6): 25.2 (s, PPh_2Ru), −144.1 (sep, PF_6). IR: ν_{max}/cm^{-1} (CN) 1613, 1595 (KBr).

1[Ru(bipy)Rh]$_4^{4+}$. δ_H(acetone-d_6): 8.97 (d, 8H, ^3J(HH) = 5 Hz, bipy(*Hα*)), 8.85 (m, 8H, bipy(*Hα′*)), 8.14–7.13 (m, 56H, C_6H_5, bipy(*Hβ*), bipy(*Hβ′*)), 5.75 (d, ^3J(HH) = 6 Hz), 5.61 (d, ^3J(HH) = 6 Hz), 5.47 (d, ^3J(HH) = 6 Hz), 5.34 (d, ^3J(HH) = 6 Hz) (16H, C_6H_4), 2.41 (m, 8H, *CH*$(CH_3)_2$, CH_aH_bP), 1.83 (s, 12H, CH_3), 1.14 (d, ^3J(HH) = 6.8 Hz), 1.02 (d, ^3J(HH) = 6.8 Hz) (24H, $CH(CH_3)_2$), 0.1–(−0.52) (m, 40H, CH_2Si, CH_3Si); δ_P(acetone-d_6): 25.4 (s, PPh_2Ru), −144.1 (sept, PF_6). IR: ν_{max}/cm^{-1} (C≡O) 2088, 2010, (CN) 1609 (KBr).

1[Ru(bipy)Ru]$_4^{4+}$. δ_H(acetone-d_6): 8.84 (m, 8H, bipy(*Hα*)), 9.31 (m, 8H, bipy(*Hα′*)), 8.15–7.13 (m, 56H, C_6H_5, bipy(*Hβ*), bipy(*Hβ′*)), 5.7–5.4 (m, 32H, C_6H_4), 3.05 (m, 4H, *CH*$(CH_3)_2$), 2.41 (m, 8H, *CH*$(CH_3)_2$, CH_aH_bP), 2.13 (s, 12H, CH_3), 1.80 (s, 12H, CH_3), 1.37 (m, 24H, $CH(CH_3)_2$), 1.14 (m), 1.02 (m) (24H, $CH(CH_3)_2$),

0.1–(−0.52) (m, 40H, CH_2Si, CH_3Si); δ_P(acetone-d_6): 25.5, 25.4 (s, PPh_2Ru), −144.1 (sep, PF_6). IR: ν_{max}/cm^{-1} (CN) 1609 (KBr).

General procedure for catalysed hydrogen transfer

The precursor complex (6×10^{-3} mmol) was dissolved in 3 ml of a freshly prepared solution 0.012M of *t*-BuOK in propan-2-ol at room temperature. The resulting solution was stirred for 30 min. Then 10 ml of a 0.6M solution of cyclohexanone in propan-2-ol was added. The solution was stirred at room temperature or at 82 °C for the required time. Before evaluation by GC of the cyclohexanol amount, the mixture was diluted with ethyl acetate and the solution passed through a short column (silica gel).

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