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Journal of Organometallic Chemistry 692 (2007) 851–858
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Rhodium or ruthenium units peripherally coordinated to carbosilane dendrimers functionalized with P-stereogenic monophosphines

Lara-Isabel Rodríguez, Oriol Rossell *, Miquel Seco, Guillermo Muller

Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain

Received 19 September 2006; received in revised form 16 October 2006; accepted 17 October 2006
Available online 24 October 2006

Abstract

Carbosilane dendrimers containing P-stereogenic monophosphines as terminal groups, *Dend*-$\{CH_2PPhR\}_n$ (R = 2-biphenylyl or 9-phenanthryl), were reacted with $[RhCl(COD)]_2$ or $[RuCl_2(p\text{-cymene})]_2$ to afford the corresponding chiral metalladendrimers *Dend*-$\{CH_2PPhR(RhCl(COD))\}_n$ or Dend-$\{CH_2PPhR(RuCl_2(p\text{-cymene}))\}_n$, respectively. Attempts to obtain the first generation Ru-dendrimer for R = 2-biphenylyl proved unsuccessful, probably due to the steric hindrance of R. Complete characterization of these species was achieved by multinuclear NMR spectra, including 2D experiments, mass spectrometry, and optical rotation determinations. The catalytic properties of the rhodium dendrimers were tested in the hydrogenation of dimethylitaconate and those of the ruthenium derivatives in the asymmetric hydrogen transfer of acetophenone. The following model chiral compounds, $(CH_3)_3Si\{CH_2PPhR(RhCl(COD))\}$ and $(CH_3)_3Si\{CH_2PPhR(RuCl_2(p\text{-cymene}))\}$, were prepared in order to detect potential dendritic effects. All compounds were active in the catalytic conditions tested, but low or null e.e. were found.

Keywords: Dendrimers; Chirality; Rhodium; Ruthenium; Catalysis

1. Introduction

The preparation and characterization of dendrimers containing transition metal fragments has received considerable attention in recent years because they have proved to have the potential to combine the advantage of homogeneous and heterogeneous catalysts in one system [1]. Although a number of dendritic catalysts have been described, so far, relatively few reports on catalytic asymmetric synthesis are available. This is because chiral ligands are expensive or difficult to obtain. Some examples include the amino alcohol-zinc alkyl compounds attached to phosphine-functionalized poly(propyleneimine) (PPI) [2], the Ti-TADDOL systems [3], the chiral Salen systems [4], the "pyrphos"-functionalized PPI dendrimers [5], the species resulting by grafting chiral ferrocenyl diphosphines ("Josiphos") into the periphery of a dendrimer [6], and the third generation chiral phosphorus-containing dendrimer used in Pd-catalyzed asymmetric allylic alkylation [7]. In addition, a dendrimer displaying a Ru-BINAP chiral core is also known [8]. Very recently, we undertook a program consisting of the preparation of the first dendritic systems peripherally functionalized with *P*-stereogenic monophosphines, (*S*)-MePPh(2-biphenylyl) and (*S*)-MePPh(9-phenanthryl), with the aim to assess their potential catalytic properties, after grafting into the periphery selected transition metal fragments. It is well known that the introduction of chirality within dendritic architectures enables these systems to be used in enantioselective catalysis. Thus, our first report in this area described the use of allylpalladium-containing carbosilane dendrimers as catalysts in the asymmetric hydrovinylation of styrene [9]. The excellent results obtained in terms of selectivity and enantiomeric excess of 3-phenyl-1-butene prompted us to extend this study to new chiral metalladendrimers. In the present study, we wish to report the synthesis and characterization of two metalladendrimer families, resulting from the grafting of

* Corresponding author.
E-mail address: oriol.rossell@qi.ub.es (O. Rossell).

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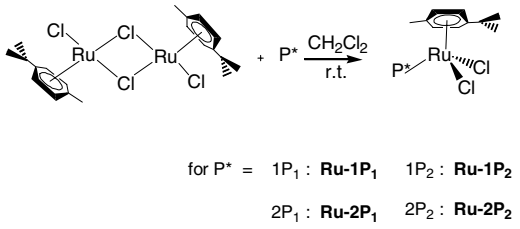
doi:10.1016/j.jorganchem.2006.10.035

rhodium, RhCl(COD), or ruthenium, $RuCl_2$(*p*-cymene) fragments onto the surface of chiral phosphine-functionalized carbosilane dendrimers. The efficiency of the rhodium complexes for the asymmetric hydrogenation of dimethylitaconate and the ruthenium species for the asymmetric transfer hydrogenation of acetophenone is also described. Mononuclear metal models were prepared in order to detect dendritic effects.



Scheme 1.

2. Results and discussion

2.1. Synthesis and characterization of ruthenium dendrimers

The starting carbosilane dendrimers peripherally functionalized with (*S*)-MePPh(2-biphenylyl) or (*S*)-MePPh(9-phenanthryl) are represented in Chart 1.

These compounds, as well as the model compounds **1P**$_1$ and **1P**$_2$, were obtained as described earlier [9]. The ruthenium dendrimers were obtained following the protocol shown in Scheme 1. The process was monitored by ^{31}P NMR spectroscopy which evidenced a new signal for the new species, showing the expected deshielding effect. Complete metallation was deduced from the absence of ^{31}P NMR resonances due to unreacted phosphine units. In fact, the process is identical to that described in the synthesis of ruthenium dendrimers with alkyldiphenylphosphino terminated carbosilane dendrimers [10].

The metalladendrimers were isolated as red solids in high yields. Attempts to obtain **Ru-3P**$_1$ were unsuccessful, given that only a partial functionalization of the dendrimer branches was achieved, probably due to the steric hindrance of the biphenylyl moiety. The failure of this synthesis was evidenced by its ^{31}P NMR spectrum, which contained very broad bands. In fact, the singlet observed for **Ru-2P**$_1$ was also relatively broad. The new species are soluble in moderately polar organic solvents (CH_2Cl_2, $CHCl_3$, acetone, thf) and were characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy as well as electrospray mass spectroscopy. The ^{1}H NMR spectra for both groups of compounds, **Ru-nP**$_1$ or **Ru-nP**$_2$, were similar, showing, in all cases, the ring protons of the *p*-cymene groups to be different, as a consequence of the presence of the chiral phosphine. For the same reason, the protons of the CH_2P, $Si(CH_3)_2$ and the $(CH_3)_2CH$ groups became diastereotopic. As expected, the protons of the $(CH_3)CH$ and CH_3 units of the *p*-cymene ligand gave only one signal, which appeared as a septet by the coupling with the six protons of the methyl groups, and, as a singlet, respectively. The most interesting feature in the ^{13}C NMR spectra is the confirmation of the diastereotopic character of the carbon methyl atoms of the isopropyl group and those of the $(CH_3)_2$Si units. Complete assignation of ^{1}H and ^{13}C signals was obtained from NOESY ^{1}H–^{1}H and HSQC ^{1}H–^{13}C experiments. For example, the HSQC ^{1}H–^{13}C spectra showed the correlation between the CH_3 carbons of the isopropyl group with the corresponding protons. In the ^{29}Si NMR spectra, the internal silicon centres of the dendrimers were observed, as well as the expected doublet (J(Si–P) = 7.4 Hz) for the external silicon atoms. ES mass spectra gave in all cases peaks at $[M-Cl]^+$, along with other fragments, confirming the nature of the compounds.

2.2. Synthesis and characterization of rhodium dendrimers

The rhododendrimers **Rh-nP**$_1$ and **Rh-nP**$_2$ were cleanly obtained by reacting [RhCl (COD)]$_2$ with the corresponding dendrimer in CH_2Cl_2 at room temperature. Recrystallization in CH_2Cl_2/diethylether gave the targeted compounds as yellow solids in good yields. They are soluble in most common organic solvents and were characterized by elemental analyses, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and ES mass spectrometry (see Scheme 2).

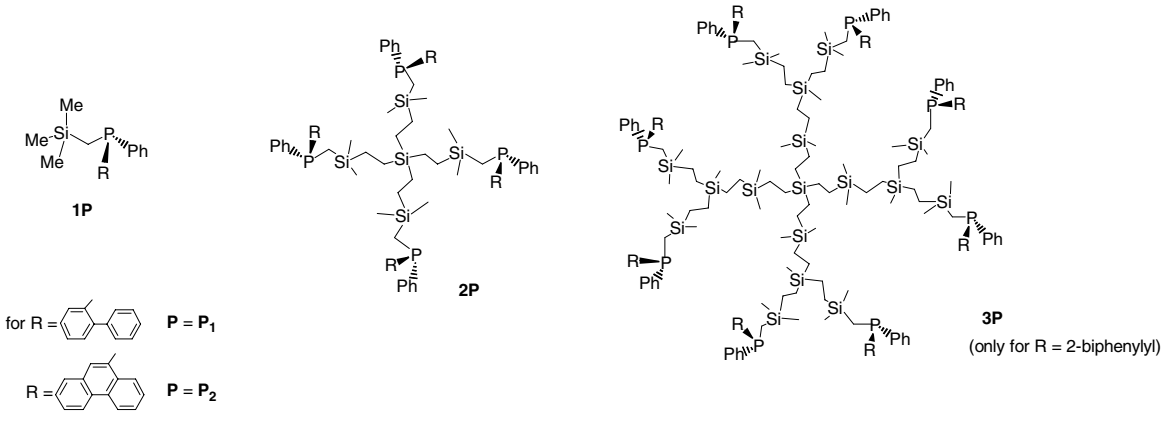
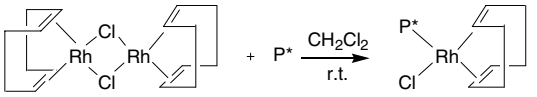


Chart 1.



for P* = 1P1 : **Rh-1P1** 1P2 : **Rh-1P2**
2P1 : **Rh-2P1** 2P2 : **Rh-2P2**
3P1 : **Rh-3P1**

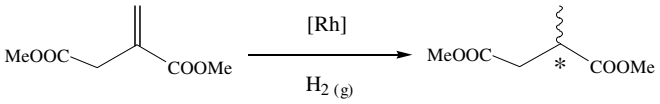
Scheme 2.

In all cases, the unique phosphorous signal appeared as a doublet (J(P–Rh) was about 150 Hz). HSQC ^{1}H–^{13}C experiments allowed us the full assignation of the signals in both groups of dendrimers. The coordination of the Rh(COD)Cl moiety to the chiral phosphine induced all the protons and carbons of the COD to be different. Thus, although the CH protons *trans* to the phosphine resonated at the same δ, the *cis* CH protons appeared, at higher field, as two singlets. Analogously, the protons of the CH_2 units of the COD appeared as four superimposed multiplets that could be assigned by a ^{1}H–^{13}C HSQC experiment (Fig. 1). The different nature of the carbon atoms of the CH_2 units was also corroborated in the ^{13}C NMR spectra. On the other hand, both the ^{1}H and the ^{13}C NMR spectra revealed the diastereoscopic character of the protons and carbon atoms of the CH_3Si and CH_2P groups, due to the chiral character of the phosphines. In particular, for example, the CH_2P protons for **Rh-1P$_1$** and **Rh-2P$_1$** appeared as two pseudotriplets (J(HH) = J(HP)) while for **Rh-3P$_1$** the same protons appeared as two multiplets. ES mass spectrometry showed $[M-Cl]^+$ peaks for the models **Rh-1P$_1$** and **Rh-1P$_2$** and $[M-Rh(COD)Cl-Cl]^+$ and other fragmentations for the metalladendrimers, confirming the nature of the products.

2.3. Catalytic reactions: hydrogenation of dimethylitaconate

One of the most known methods for the asymmetric hydrogenation of dimethylitaconate under mild conditions uses rhodium or ruthenium complexes generated in situ via the addition of a metal complex precursor and a monodentate or bidentate chiral phosphine ligand [11,12], Eq. (1).

In general, rhodium complexes have afforded better results in terms of efficiencies and enantiomeric excesses than the ruthenium compounds. This can be attributed to the extraordinary capacity of ruthenium(II) to generate a large number of coordination environments, with or without chiral ligand, as well as polynuclear-type complexes



Eq. 1. Hydrogenation of dimethylitaconate.

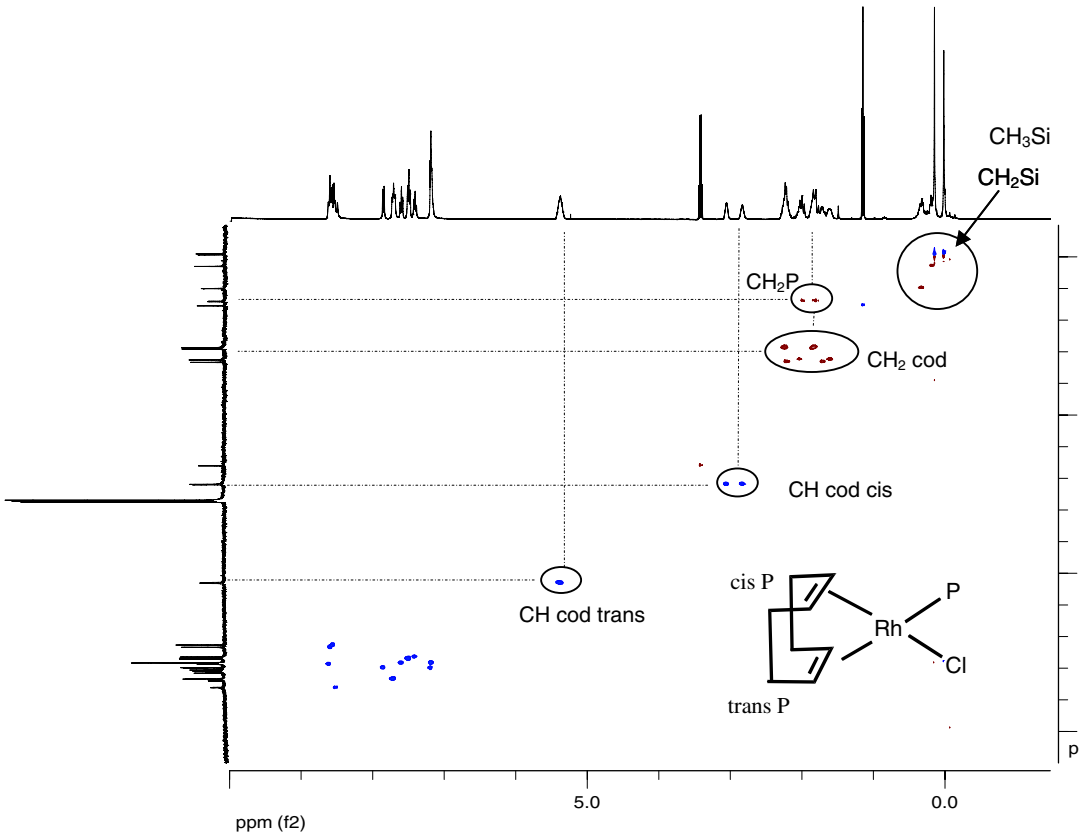


Fig. 1. ^{1}H–^{13}C HSQC spectrum of compound **Rh-2P$_2$**.

[13]. With these precedents, we tested the catalytic capability of the rhododendrimers for the asymmetric hydrogenation of dimethyl itaconate. Our interest was to establish the relationship between the size/generation of the dendrimer and its catalytic properties. As the standard reaction conditions we chose a substrate:catalyst (catalytic site) ratio of 500:1, 10 bar hydrogen pressure, and a reaction temperature of 20 °C. The conversion was monitored by GC. We found that the precursors were active and that compounds belonging to the $\mathbf{P}_2$-family were the most active, although the enantiomeric excess proved to be zero in all cases. As can be seen from Table 1, the activity decreases regularly upon going from the model compound **Rh-1P**$_1$ to the first generation dendrimer, **Rh-3P**$_1$. The reduction in activity observed may be due to the reduced accessibility of the metal centres in **Rh-3P**$_1$. The effect of increasing approach of peripheral groups in dendrimers at higher generations has been demonstrated in a large number of cases [14]. This effect is also observed for the $\mathbf{P}_2$-containing family of compounds, for which the **Rh-1P**$_2$ model was the most active (Table 2).

In order to improve the enantioselectivity of the process, we decided to apply the strategy by Reetz et al. [15,16] in combinatorial asymmetric transition-metal-catalyzed reactions, consisting in the formation of a rhodium species containing simultaneously two different chiral monodentate phosphines, L^a and L^b. This hetero-combination, RhL^aL^b, was shown to be more active, in terms of enantioselectivity in the Rh-catalyzed olefin hydrogenation, than its related homo-combinations, RhL^aL^a or RhL^bL^b. Thus, trying to take advantage of the anchored chiral phosphine that avoids the formation of the homo-combinations, we added, in this case, non-chiral PPh_3 to our two dendritic systems, in order to evaluate the results of the hydrogenation of the dimethylitaconate. The most notorious effect observed was the sharp decrease of the activity of the rhododendrimers, as expected, but, unfortunately, the enantiomeric excess was not improved, remaining null. At this point, it is clear that much more work is needed to understand the catalytic properties of the dendritic systems reported in this paper.

Table 1
Hydrogenation of dimethylitaconate using catalytic precursors **Rh-nP**$_1$ ($n = 1,2,3$)

Run	Catalytic precursor	t (h)	Conversion (%)	TOF (h^{-1})	e.e. (%)
1	**Rh-1P**$_1$	1	61.2	306	~0
2		2	98.1	245	~0
3[a]		2	16.8	42	~0
4	**Rh-2P**$_1$	2	94.4	236	~0
5[a]		2	11.2	28	~0
6	**Rh-3P**$_1$	2	68.6	171	~0

Conditions: ratio [Rh]/substrate 1/500; $T = 20$ °C; 10 bar H_2; 20 ml thf.
[a] Ratio [Rh]/substrate/PPh_3 1/500/1.

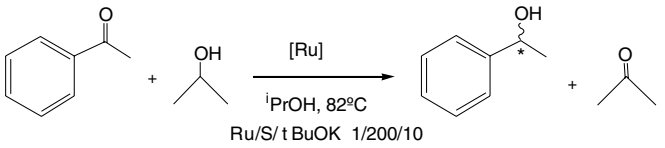
Table 2
Hydrogenation of dimethylitaconate using catalytic precursors **Rh-nP**$_2$ ($n = 1,2$)

Run	Catalytic precursor	t (h)	Conversion (%)	TOF (h^{-1})	e.e. (%)
1	**Rh-1P**$_2$	1	85.5	428	~0
2[a]		1	13.5	68	~0
3	**Rh-2P**$_2$	1	64.0	320	~0
4[a]		1	7.4	37	~0

Conditions: ratio [Rh]/substrate 1/500; $T = 20$ °C; 10 bar H_2; 20 ml thf.
[a] Ratio [Rh]/substrate/PPh_3 1/500/1.

2.4. Catalytic transfer hydrogenation of acetophenone

The catalytic hydrogenation of organic substrates by hydrogen transfer reactions avoids the use of gaseous hydrogen and allows the use of standard reflux techniques. A drawback is the often low catalytic activity and productivity. The hydrogen is usually supplied by 2-propanol or formic acid and the process is catalyzed by transition metals, ruthenium being one of the most widely used so far [17]. For this purpose, several ruthenodendrimers have been also employed [18]. In this paper, we describe the catalytic behaviour of our derivatives in the asymmetric transfer hydrogenation of acetophenone (Eq. (2)), by using 6×10^{-3} M solutions of the ruthenium compounds and a Ru/acetophenone/tBuOK ratio of 1/200/10. The reaction solution was stirred at 82 °C.



Eq. 2. Catalytic transfer hydrogenation of acetophenone.

The time course curves of the hydrogenation acetophenone for both families of compounds are represented in Fig. 2. It can be seen that the species containing 2-biphenylyl ($\mathbf{P}_1$) are more active than those having 9-phenanthryl ($\mathbf{P}_2$), in clear contrast with the results observed in the hydrogenation of dimethylitaconate. In addition, it is particularly noteworthy that some positive dendritic effects were observed. Thus, the zeroth generation dendrimers were more active than the model compounds for both series of products, although the enantiomeric excesses were low (about 15%) and difficult to reproduce. After 22 h of refluxing, the conversion of acetophenone was not total and the catalysts appeared deactivated, as can be deduced from the green color of the solution and the precipitation of a solid.

3. Conclusion

In summary, two series of novel chiral rhodium and ruthenium dendrimers have been prepared and characterized and their catalytic properties in the hydrogenation of dimethylitaconate and acetophenone, respectively, have

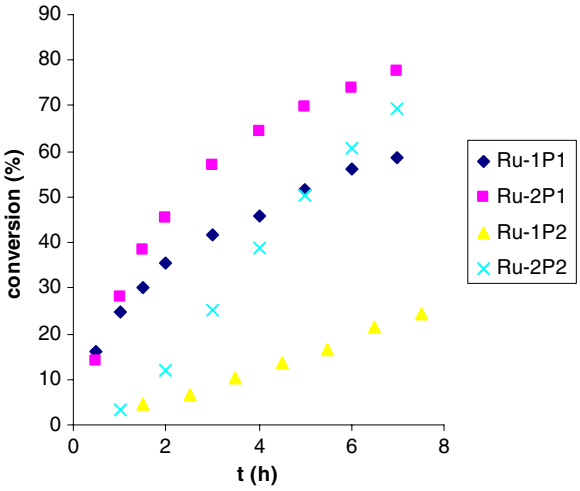


Fig. 2. Conversion of hydrogenation of acetophenone vs. time using Ru (II) compounds as precursors.

been investigated. In both studies, the dendritic systems were active, although their behaviour in terms of activity and enantiomeric excesses were not satisfactory.

4. Experimental

4.1. Reagents and general techniques

All manipulations were performed under purified nitrogen using standard schlenk techniques. All solvents were distilled from appropriate drying agents. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ were obtained on Varian Gemini 200, Bruker DRX 250 and Varian Mercury 400 spectrometers. 2D NMR spectra (NOESY ^{1}H–^{1}H and HSQC ^{1}H–^{13}C) were recorded on a Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^{1}H, ^{13}C and ^{29}Si and 85% H_3PO_4 for ^{31}P) and coupling constants are given in Hz. MS (ES) spectra were recorded with a Fisions VGQuattro spectrometer. Enantiomeric excesses and conversions were determined by GC on a Hewlett-Packard 5890 Series II gas chromatograph (30-m Chiraldex DM column) with a FID detector. Elemental analysis (C,H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC). $[RuCl_2(p\text{-cymene})]_2$, $[RhCl(COD)]_2$ as well as the starting chiral carbosilane compounds were prepared as previously described [9]. Other reagents were used as received from commercial suppliers.

4.2. Synthesis and characterization data

4.2.1. Synthesis of *Rh-P*$_1$

The model compound **1P**$_1$ (0.200 g, 0.574 mmol) was dissolved in 10 ml of CH_2Cl_2 and the rhodium dimer $[RhCl(COD)]_2$ (0.141 g, 0.287 mmol) was added. After stirring for 20 min, the solvent was removed and the resulting pasty solid was recrystallized from CH_2Cl_2/diethyl ether. The product **Rh-1P**$_1$ was obtained as a yellow solid. Yield: 0.304 g (89%). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 24.9 (d, $^{1}J_{PRh} = 147.3$ Hz). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.32–7.15 (m, Ar, 14H), 5.45 (s(br), CH_{trans}, 2H), 3.17 (m, CH_{cis}, 1H), 2.84 (m, CH_{cis}, 1H), 2.45–1.81 (m, CH_2, 8H), 1.49 (pt, $J \approx 13$ Hz, CH_2P, 1H), 0.67 (pt, $J \approx 14$ Hz, CH_2P, 1H), 0.02 (s, CH_3Si, 9H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 145.7–126.4 (m, Ar), 102.9 (m, CH_{trans}), 71.3 (d, $^{1}J_{CRh} = 14.2$ Hz, CH_{cis}), 69.9 (d, $^{1}J_{CRh} = 14.0$ Hz, CH_{cis}), 33.4 (d, $^{1}J_{CRh} = 3.0$ Hz, CH_2), 32.7 (d, $^{1}J_{CRh} = 2.5$ Hz, CH_2), 29.2 (s(br), CH_2), 28.7 (d, $^{1}J_{CRh} = 1.3$ Hz, CH_2), 14.0 (d, $^{1}J_{CP} = 14.6$ Hz, CH_2P), 1.65 (d, $^{3}J_{CP} = 3.0$ Hz, CH_3Si). EA: Calcd for $C_{30}H_{37}ClPRhSi$: C, 60.56; H, 6.27. Found: C, 60.42; H, 6.41%. MS (ES(+), *m*/*z*): 559.1 (559.6 calcd) $[M-Cl]^+$, 451.1 (451.4 calcd) $[M-Cl-COD]^+$.

4.2.2. Synthesis of *Rh-2P*$_1$

This complex was obtained in the same way as **Rh-1P**$_1$. Starting from **2P**$_1$ (0.160 g, 0.108 mmol) and the rhodium dimer $[RhCl(COD)]_2$ (0.107 g, 0.217 mmol), a pale yellow solid was obtained. Yield: 0.256 g (96%). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 25.8 (d, $^{1}J_{PRh} = 147.0$ Hz). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.26–7.12 (m, Ar, 56H), 5.43 (s(br), CH_{trans}, 8H), 3.18 (s(br), CH_{cis}, 4H), 2.82 (s(br), CH_{cis}, 4H), 2.47–1.77 (m, CH_2, 32H), 1.50 (pt, $J = 13.6$ Hz, CH_2P, 4H), 0.77 (pt, $J = 15.0$ Hz, CH_2P, 4H), 0.25 to (−0,19) (m, CH_2Si, 16H), 0.14 (s, CH_3Si, 12H), −0.02 (s, CH_3Si, 12H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 145.8 −126.5 (m, Ar), 102.9 (m, CH_{trans}), 71.5 (d, $^{1}J_{CRh} = 13.9$ Hz, CH_{cis}), 70.1 (d, $^{1}J_{CRh} = 14.1$ Hz, CH_{cis}), 33.6 (s, CH_2), 32.7 (s, CH_2), 29.5 (s, CH_2), 28.8 (s, CH_2), 12.7 (d, $^{1}J_{CP} = 13.8$ Hz, CH_2P), 10.2 (d, $^{3}J_{CP} = 3.6$ Hz, CH_2Si_0), 3.2 (s, CH_2Si_1), −0.4 (s, CH_3Si), −0.8 (s, CH_3Si). $^{29}Si\{^{1}H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), δ (ppm): 8.98 (s, Si_0), 3.34 (s, Si_1). EA: Anal. Calc. for $C_{124}H_{152}Cl_4P_4Rh_4Si_5$: C, 60.53; H, 6.23. Found: C, 60.68; H, 6.34%. MS (ES(+), *m*/*z*): 2177.8 (2178.2 calcd) $[M-RhCODCl-Cl]^+$, 2087.6 (2088.0 calcd) $[M-RhCODCl-COD-Cl+H_2O]^+$.

4.2.3. Synthesis of *Rh-3P*$_1$

This complex was obtained using the same procedure as for **Rh-1P**$_1$. Starting from **3P**$_1$ (0.060 g, 0.017 mmol) and the rhodium dimer $[RhCl(COD)]_2$ (0.033 g, 0.068 mmol), a yellow solid was obtained. Yield: 0.085 g (91%). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 26.9 (d, $^{1}J_{PRh} = 146.9$ Hz). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.27–7.10 (m, Ar, 112H), 5.43 (s(br), CH_{trans}, 16H), 3.16 (s(br), CH_{cis}, 8H), 2.81 (s(br), CH_{cis}, 8H), 2.40–1.76 (m, CH_2, 64H), 1.45 (m, CH_2P, 8H), 0.74 (m, CH_2P, 8H), 0.50 to (−0,19) (m, $CH_2Si + CH_3Si$, 148H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 145.6 −126.4 (m, Ar), 102.9 (m, CH_{trans}), 71.3 (d, $^{1}J_{CRh} = 14.9$ Hz, CH_{cis}), 69.9 (d, $^{1}J_{CRh} = 13.6$ Hz, CH_{cis}), 33.5 (s, CH_2), 32.6 (s, CH_2), 29.3 (s, CH_2), 28.7 (s, CH_2),

12.2 (m, CH_2P), 10.9–2.5 (m, CH_2Si), −0.6 (s, CH_3Si_3), −0.8 (s, CH_3Si_3), −4.1 (s, CH_3Si_1), −6.3 (s, CH_3Si_2). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), δ (ppm): 7.90 (s, Si_2), 5.71 (s, Si_1), 3.32 (s, Si_3) EA Anal. Calc. for $C_{276}H_{372}Cl_8P_8Rh_8$ Si_{17}: C, 60.03; H, 6.79. Found: C, 60.18; H, 6.88%.

4.2.4. Synthesis of *Rh-1P₂*

This procedure was analogous to that used for **Rh-1P$_1$**. Starting from **1P$_2$** (0.147 g, 0.394 mmol) and the rhodium dimer $[RhCl(COD)]_2$ (0.097 g, 0.197 mmol), a yellow solid was obtained using hexane instead of diethyl ether to precipitate the product. Yield: 0.228 g (93%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 19.7 (d, $^1J_{PRh} =$ 147.7 Hz). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.73–7.30 (m, Ar, 14H), 5.52 (m, CH_{trans}, 2H), 3.13 (m, CH_{cis}, 1H), 2.98 (m, CH_{cis}, 1H), 2.45–1.73 (m, $CH_2 + CH_2P$, 10H), 0.16 (s, CH_3Si, 9H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 137.5–122.9 (m, Ar), 103.5 (m, CH_{trans}), 72.1 (pt, $^1J_{CRh} = 14.0$ Hz, CH_{cis}), 33.5 (d, $^1J_{CRh} = 2.9$ Hz, CH_2), 33.4 (d, $^1J_{CRh} = 2.7$ Hz, CH_2), 29.3 (d, $^1J_{CRh} = 1.0$ Hz, CH_2), 29.0 (d, $^1J_{CRh} =$ 1.2 Hz, CH_2), 15.8 (d, $^1J_{CP} = 13.7$ Hz, CH_2P), 1.9 (d, $^3J_{CP} = 2.8$ Hz, CH_3Si). EA: Anal. Calc. for $C_{32}H_{37}$-ClPRhSi: C, 62.09; H, 6.02. Found: C, 62.20; H, 6.19. MS (ES(+), *m*/*z*): 583.1 (583.6 calcd) $[M-Cl]^+$.

4.2.5. Synthesis of *Rh-2P₂*

This complex was obtained using the same procedure as for **Rh-1P$_2$**. Starting from **2P$_2$** (0.110 g, 0.070 mmol) and the rhodium dimer $[RhCl(COD)]_2$ (0.069 g, 0.140 mmol), a yellow solid was obtained. Yield: 0.170 g (95%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 17.8 (d, $^1J_{PRh} = 147.1$ Hz). ^1H NMR ^1H (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.66–7.40 (m, Ar, 56H), 5.44 (s(br), CH_{trans}, 8H), 3.12 (s(br), CH_{cis}, 4H), 2.90 (s(br), CH_{cis}, 4H), 2.40–1.60 (m, $CH_2 + CH_2P$, 40H), 0.40–0.19 (m, CH_2Si, 16H), 0.21 (s, CH_3Si, 12H), 0.08 (s, CH_3Si, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 136.3–122.8 (m, Ar), 103.2 (m, CH_{trans}), 72.1 (d(br), $^1J_{CRh} = 13.6$ Hz, CH_{cis}), 33.5 (s, CH_2), 32.7 (s, CH_2), 29.3 (s, CH_2), 28.9 (s, CH_2), 14.3 (d, $^1J_{CP} = 12.9$ Hz, CH_2P), 10.2 (d, $^3J_{CP} = 3.1$ Hz, CH_2Si_0), 3.2 (s, CH_2Si_1), −0.5 (d, $^3J_{CP} = 2.7$ Hz, CH_3Si), −0.8 (d, $^3J_{CP} = 1.5$ Hz, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), δ (ppm): 9.50 (s, Si_0), 3.98 (s, Si_1). EA: Calcd for $C_{132}H_{152}Cl_4P_4Rh_4$ Si_5: C, 62.02; H, 5.99. Found: C, 62.14; H, 6.08%. MS (ES(+), *m*/*z*): 2026.9 (2027.8 calcd) $[M-(RhCODCl)_2-Cl]^+$.

4.2.6. Synthesis of *Ru-1P₁*

The model compound **1P$_1$** (0.150 g, 0.430 mmol) was dissolved in 10 ml of CH_2Cl_2 and the ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ (0.132 g, 0.215 mmol) was added. After stirring for 20 min, the solvent was removed and the resulting solid was washed with diethyl ether. The product **Ru-1P$_1$** was obtained as a red solid. Yield: 0.253 g (90%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 22.4 (s). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.56–6.88 (m, Ar, 14H), 5.36–5.29 (m, H–C_6H_4, 3H), 4.59 (d, $^3J_{HH} = 5.8$ Hz, H–C_6H_4, 1H), 2.51 (sep, $^3J_{HH} = 6.9$ Hz, C*H*–$(CH_3)_2$, 1H), 2.17 (pt, $J = 14.3$ Hz, CH_2P, 1H), 2.00 (s, C*H*$_3$–C_6H_4, 3H), 1.17 (m, CH_2P, 1H), 1.01 (d, $^3J_{HH} = 7.0$ Hz, CH–(C*H*$_3$)$_2$, 3H), 0.63 (d, $^3J_{HH} = 6.9$ Hz, CH–(C*H*$_3$)$_2$, 3H), −0.15 (s, CH_3Si, 9H). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 298 K), δ (ppm): 146.1–126.3 (m, Ar), 107.7 (s, *C*–$CH(CH_3)_2$), 101.3 (s, *C*–CH_3), 93.4 (d, $J_{CP} =$ 6.0 Hz, C_6H_4), 87.2 (d, $J_{CP} = 7.5$ Hz, C_6H_4), 86.8 (d, $J_{CP} = 3.4$ Hz, C_6H_4), 85.4 (d, $J_{CP} = 4.2$ Hz, C_6H_4), 29.7 (s, *C*H$(CH_3)_2$), 22.9 (s, CH(*C*H$_3$)$_2$), 20.0 (s, CH(*C*H$_3$)$_2$), 17.2 (s, CH_3), 12.1 (d, $^1J_{CP} = 18.4$ Hz, CH_2P), 1.7 (d, $^3J_{CP} = 2.5$ Hz, CH_3Si). EA: Anal. Calc. for $C_{32}H_{39}Cl_2$-PRuSi: C, 58.71; H, 6.00. Found: C, 58.35; H, 6.32%. MS (ES(+), *m*/*z*): 619.1 (619.2 calcd) $[M-Cl]^+$.

4.2.7. Synthesis of *Ru-2P₁*

Experimental conditions were identical to those of the preparation of **Ru-1P$_1$** using 0.150 g of dendrimer **2P$_1$** (0.102 mmol) and 0.125 g of the ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ (0.204 mmol). A deep red compound was obtained. Yield: 0.271 g (98%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 21.0 (s (br)). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.63–6.68 (m, Ar, 56H), 5.27 (pt, $^3J_{HH} = 5.6$ Hz, H–C_6H_4, 8H), 5.21 (d, $^3J_{HH} = 6.0$ Hz, H–C_6H_4, 4H), 4.80 (d (br), $^3J_{HH} \approx 5$ Hz, H–C_6H_4, 4H), 2.22 (s (br), C*H*-$(CH_3)_2$, 4H), 2.00 (pt, $J = 14.0$ Hz, CH_2P, 4H), 1.92 (s, C*H*$_3$–C_6H_4, 12H), 1.34 (m, CH_2P, 4H), 0.96 (d, $^3J_{HH} = 7.2$ Hz, CH–(C*H*$_3$)$_2$, 12H), 0.71 (d, $^3J_{HH} = 6.8$ Hz, CH–(C*H*$_3$)$_2$, 12H), 0.14 to (−0.16) (m, CH_2Si, 16H), −0.04 (s, CH_3Si, 12H), −0.25 (s, CH_3Si, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 146.3–126.5 (m, Ar), 107.2 (s, *C*–$CH(CH_3)_2$), 96.7 (s (br), *C*–CH_3), 91.1 (s (br), C_6H_4), 87.3–86.7 (m, C_6H_4), 29.8 (s, *C*H$(CH_3)_2$), 23.4 (s, CH(*C*H$_3$)$_2$), 20.8 (s, CH(*C*H$_3$)$_2$), 17.7 (s, CH_3), 13.7 (s (br), CH_2P), 9.8 (s, CH_2Si_0), 3.1 (s, CH_2Si_1), −0.4 (s, CH_3Si), −1.3 (s, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), δ (ppm): 3.77 (s, Si_1). EA: Anal. Calc. for $C_{132}H_{160}Cl_8P_4Ru_4$ Si_5: C, 58.74; H 5.97. Found: C, 58.80; H, 6.09%. MS (ES(+), *m*/*z*): 2666.7 (2663.5 calcd) $[M-Cl]^+$, 2359.7 (2357.3 calcd) $[M-RuCl_2(p\text{-cymene})-Cl]^+$, 2048.2 (2051.1 calcd) $[M-2(RuCl_2(p\text{-cymene}))-Cl]^+$, 1313.3 (1314.0 calcd) $[M-2Cl]^{2+}$, 1160.9 (1160.9 calcd) $[M-RuCl_2(p\text{-cymene})-2Cl]^{2+}$.

4.2.8. Synthesis of *Ru-1P₂*

Experimental conditions and workup were identical to those of the preparation of **Ru-1P$_1$** using 0.130 g of compound **1P$_2$** (0.349 mmol) and 0.107 g of the ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ (0.174 mmol). Yield: 0.225 g (95%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 23.2 (s). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.85–7.11 (m, Ar, 14H), 5.22 (d, $^3J_{HH} = 6.6$ Hz, H–C_6H_4, 1H), 5.01 (d, $^3J_{HH} = 6.2$ Hz, H–C_6H_4, 2H), 4.39

(d (br), $^3J_{HH} = 4.5$ Hz, H–C_6H_4, 1H), 2.77 (pt, $J = 4.2$ Hz, CH_2P, 1H), 2.66 (sep, $^3J_{HH} = 6.8$ Hz, C*H*–$(CH_3)_2$, 1H), 2.01 (m, CH_2P, 1H), 1.73 (s, C*H*$_3$–C_6H_4, 3H), 0.99 (d, $^3J_{HH} = 7.0$ Hz, CH–(C*H*$_3$)$_2$, 3H), 0.96 (d, $^3J_{HH} = 6.9$ Hz, CH–(C*H*$_3$)$_2$, 3H), −0.32 (s, CH_3Si, 9H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 134.6–123.2 (m, Ar), 107.5 (s, *C*–$CH(CH_3)_2$), 95.4 (s, *C*–CH_3), 92.5 (s, C_6H_4), 89.0 (s (br), C_6H_4), 88.6 (d, $^2J_{CP} = 2.3$ Hz, C_6H_4), 82.7 (s (br), C_6H_4), 30.5 (s, *C*H$(CH_3)_2$), 23.3 (s, CH(*C*H$_3$)$_2$), 21.1 (s, CH(*C*H$_3$)$_2$), 18.0 (s, CH_3), 17.0 (s (br), CH_2P), 0.9 (d, $^3J_{CP} = 2.0$ Hz, CH_3Si). EA: Anal. Calc. for $C_{34}H_{39}Cl_2PRuSi$: C, 60.17; H, 5.79. Found: C, 60.29; H, 5.93%. MS (ES(+), *m*/*z*): 643.0 (643.2 calcd) $[M-Cl]^+$.

4.2.9. Synthesis of *Ru-2P*$_2$

Experimental conditions and workup were identical to those of the preparation of **Ru-1P**$_1$ using 0.100 g of dendrimer **2P**$_2$ (0.064 mmol) and 0.078 g of the ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ (0.127 mmol). Yield: 0.173 g (97%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), δ (ppm): 23.2 (s). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K), δ (ppm): 8.80–7.10 (m, Ar, 56H), 5.23 (d, $^3J_{HH} = 6.0$ Hz, H–C_6H_4, 4H), 5.06 (d, $^3J_{HH} = 6.0$ Hz, H–C_6H_4, 4H), 4.82 (d, $^3J_{HH} = 6.0$ Hz, H–C_6H_4, 4H), 4.44 (d (br), $^3J_{HH} \approx 4$ Hz, H–C_6H_4, 4H), 2.80 (pt, $J = 14.4$ Hz, CH_2P, 4H), 2.60 (sep, $^3J_{HH} = 6.8$ Hz, C*H*–$(CH_3)_2$, 4H), 2.00 (m, CH_2P, 4H), 1.71 (s, C*H*$_3$–C_6H_4, 12H), 0.94 (d, $^3J_{HH} = 6.8$ Hz, CH–(C*H*$_3$)$_2$, 12H), 0.88 (d, $^3J_{HH} = 7.0$ Hz, CH–(C*H*$_3$)$_2$, 12H), 0.12 to (−0.15) (m, CH_2Si, 16H), −0.23 (s, CH_3Si, 12H), −0.68 (s, CH_3Si, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 134.6–122.9 (m, Ar), 107.7 (s, *C*–$CH(CH_3)_2$), 94.7 (s, *C*–CH_3), 92.5 (s (br), C_6H_4), 89.6 (s, C_6H_4), 88.3 (s (br), C_6H_4), 82.7 (s (br), C_6H_4), 30.5 (s, *C*H$(CH_3)_2$), 23.3 (s, CH(*C*H$_3$)$_2$), 21.1 (s, CH(*C*H$_3$)$_2$), 18.0 (s, CH_3), 15.6 (s (br), CH_2P), 9.8 (s, CH_2Si_0), 2.9 (s, CH_2Si_1), −1.0 (s, CH_3Si), −2.3 (s, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), δ (ppm): 3.62 (d, $^2J_{SiP} = 7.4$ Hz, Si_1). EA: Anal. Calc. for $C_{140}H_{160}Cl_8P_4Ru_4Si_5$: C, 60.16; H, 5.77. Found: C, 58.35; H, 5.89%. MS (ES(+), *m*/*z*): 2758.5 (2759.6 calcd) $[M-Cl]^+$, 1362.9 (1362.0 calcd) $[M-2Cl]^{2+}$.

4.3. Catalytic reactions

4.3.1. Hydrogenation

Hydrogenation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to an isobutanol bath. The temperature was controlled using a thermostat to ±0.5 °C. Internal temperature was monitored using a thermopar coupled to a digital recorder, whereas the internal pressure was continuously measured as a function of time with a Linseis L-200 recorder.

Dimethyl itaconate (0.01 mol), the precursor complex (2×10^{-5} mol [Rh]) and, eventually, PPh_3 (2×10^{-5} mol) were dissolved in 20 ml of thf. The resulting solution was immediately placed in the autoclave, which had previously been purged by successive vacuum/nitrogen cycles and thermostated at 20 °C. $H_{2(g)}$ was admitted until a pressure of 10 bar was reached. After the time indicated for each reaction, the autoclave was slowly depressurized and the quantitative distribution of products and their e.e. were determined by GC analysis.

4.3.2. Hydrogen transfer

The precursor complex (6×10^{-6} mol [Ru]) was dissolved in 3 ml of a freshly prepared solution 0.02 M of *t*-BuOK in propan-2-ol at room temperature. The resulting solution was stirred for 30 min. Then 10 ml of a 0.12 M solution of acetophenone in propan-2-ol was added. The solution was stirred at 82 °C. Aliquots of the catalytic reaction were passed through a short column (silica gel) eluted with ethyl acetate before evaluation by GC of the quantitative distribution of products and their e.e.

Acknowledgements

Financial support for this research was provided by the DGICYT (Projects BQU2003-01131 and CTQ2004-01546). L.-.I.R. is indebted to the Ministerio de Ciencia y Tecnología for a scholarship.

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