

Synthesis and catalytic properties of neutral and cationic rhodium- and iridium-containing carbosilane dendrimers

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Received 5th December 2002, Accepted 29th January 2003

First published as an Advance Article on the web 11th February 2003

The reaction of phosphanyl-terminated carbosilane dendrimers containing only one phosphorus ligand per arm with $[MCl(cod)]_2$ ($M = Rh, Ir$; $cod = cycloocta-1,5-diene$) resulted in the grafting of $MCl(cod)$ moieties on the surface of the dendrimer. However, dendrimers displaying two phosphorus ligands per arm gave very unstable species which were not isolated. On the other hand, the last group of dendrimers reacted with $[MCl(cod)]_2$, in the presence of silver salts, to afford cationic dendrimers in which a metal fragment is attached simultaneously to both phosphorus atoms of the same arm. The substitution of cod with 1,1'-bis(diphenylphosphino)ferrocene ($dppf$) in one example of the latter group yielded a bimetallic Rh/Fe layer-containing dendrimer. The new metallodendrimers were tested as catalysts in the hydrogenation of 1-hexene.

Introduction

Metallodendrimers constitute a very interesting class of macromolecules because of their useful properties in areas such as catalysis, electrochemistry and photophysics, among others.¹ Although metals have served as branching centers and building block connectors, a number of them have also been incorporated on the surface after dendritic construction. This is the case, for example, of dendrimers containing Au , Pd , Pt , Co , Rh , Fe , W , Ru , Ti , Zr or Nb .² In the vast majority of the cases, the species were obtained by direct complexation of alkyne-,³ nitrogen-,⁴ or phosphine-terminated dendrimers.⁵ Very recently, we described the synthesis of the very stable (both kinetically and thermodynamically) diphenylphosphino-terminated carbosilane dendrimers which, after reaction with metal complexes, such as $AuCl(tht)$ ($tht = tetrahydrothiophene$) or $[MCl_2(cod)]$ ($M = Pd, Pt$), gave dendrimers decorated on the surface by transition metals. Interestingly, gold-complexed dendrimers were found to be suitable species for the synthesis of the first transition metal clusters grafted on the periphery of the dendrimers.⁶ In addition, we found that palladium dendrimers retain the catalytic properties of the mononuclear species in the hydrovinylolation of styrene.⁷ Here, we report an extension of our studies concerning the synthesis of neutral and cationic rhodium- and iridium-containing dendrimers and their catalytic behavior in the hydrogenation of 1-hexene.

Results and discussion

The carbosilane dendrimers used for this study are shown in Chart 1. The synthesis and characterization of **1**, **2** and **3** have been reported elsewhere.⁸ Dendrimer **4** was obtained similarly by the repetitive stepwise synthetic route of hydrosilylation of the vinylic end-groups of the dendrimer with chlorosilanes, followed by alkenylation with vinylmagnesium chloride. Unlike **3**, the third hydrosilylation step involved the use of $HSiMeCl_2$. Finally, the reaction with the tetramethylenediamine complex of (diphenylphosphino)methylolithium in thf permitted the incorporation of terminal CH_2PPh_2 groups. Dendrimer **4** was obtained as a colorless oil in moderate yields, accompanied with minor quantities of PPh_2CH_3 which were removed by column chromatography on silica gel. The $^{31}P\{^1H\}$ NMR spectrum showed one signal at -21.4 ppm in agreement with the values for **1–3**. The $^{29}Si\{^1H\}$ NMR spectrum revealed four different types of silicon atoms, as expected. The signal corresponding to the external silicon atoms appeared as a triplet ($J(PSi) = 14.0$ Hz). Both the 1H and ^{13}C NMR spectra were consistent with the structure proposed.

Neutral metal complexes dendrimers

The complexation ability of the diphenylphosphino groups of dendrimers shown in Chart 1 was verified by allowing them to react with $[MCl(cod)]_2$ ($M = Rh, Ir$) in thf . Majoral and co-workers described the grafting of rhodium (but not iridium) units to some phosphino-terminated dendrimers by an identical method.^{5f} The complete disappearance of the signal at about $-(22-25)$ ppm in the ^{31}P NMR spectra due to the diphenylphosphane dendrimers indicated that the reaction occurred quantitatively in all cases. However, according to the nature of the dendrimer employed, two kinds of metallodendrimers are formed: those showing one only $MCl(cod)$ unit grafted per branch (**1a,b** and **3a,b**) and those displaying two metal fragments bonded per arm (**2a,b** and **4a** (Chart 2)). Dendrimers of the first type were easily isolated and spectroscopically characterized. The reaction was monitored by ^{31}P NMR spectroscopy, which showed that complexation induces the expected deshielding effect with the occurrence of a doublet at 25 ppm ($J(PRh) = 148$ Hz) and a singlet at about 15 ppm for the rhodium and iridium complexes, respectively. In contrast, the metallodendrimers **2a,b** and **4a** could not be isolated because they rapidly decomposed in solution even at low temperatures. Thus, ^{31}P NMR spectroscopy showed, after mixing the reagents, the emergence of a doublet at 39 ppm ($J(PRh) = 196$ Hz) along with another minor doublet ($J(PRh) = 150$ Hz) at about 17 ppm. Interestingly, the first (probably **2a** or **4a**) disappeared rapidly to give broad signals at about 28–30 ppm, which is typical for oxidized phosphorus species, while the second remained unaltered. According to the ^{31}P NMR parameters we assigned the last doublet to cationic species containing only one metal center per branch ($2 : 1 P : Rh$ molar ratio) (see below). Most probably, the high steric congestion on the periphery of these species is responsible for their instability. The orange compounds **1a,b** and **3a,b** are pure within the limits of the NMR spectroscopic detection. They are soluble in most common organic solvents and were fully characterized by elemental analyses, 1H , ^{13}C , ^{31}P and ^{29}Si NMR and FAB or ES mass spectrometry. For example, only one signal in the ^{31}P NMR spectrum as well as the two signals for **1a,b** and the four for **3a,b** in the ^{29}Si NMR spectra, confirmed the structures proposed. Moreover, the presence of the cyclooctadiene ligand and the methyl, phenyl, methylene and ethylene protons in the expected integrated ratio is corroborated from the 1H and ^{13}C NMR spectra. Although molecular parent ion peaks were not shown in the FAB or ES mass spectrum, several fragments were detected. For example, the FAB mass spectrum of **1a** contained two ion peaks at m/z 2120.8 (calc. 2120.5) and 1042.3

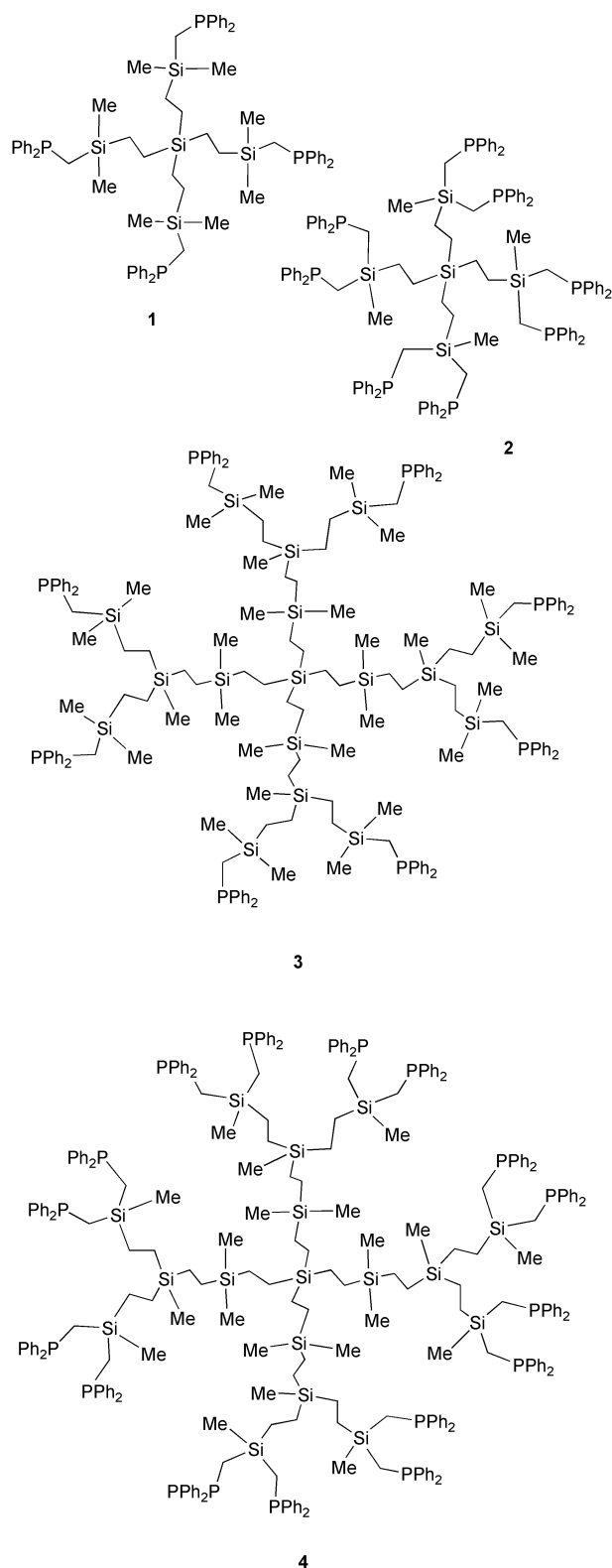


Chart 1

(calc. 1042.5) corresponding to $[M - Cl]^+$ and $[M - 2Cl]^+$, respectively, in accordance with the proposed formula. Other fragments for **1a** and for **1b** and **3a** derivatives are listed in the Experimental section. Unfortunately, neither FAB and ES mass spectrometry nor MALDI-TOF techniques gave fragments for **3b**, which could not be identified. This fact has precedents in the literature.⁹

Cationic metallodendrimers

The instability of the rhodium or iridium complexed dendrimers **2a,b** and **4a,b** can be attributed to the high congestion

on the surface of the dendrimers given that each branch should support two metal units $MCl(cod)$. In order to minimize this effect we envisaged the synthesis of the corresponding metallodendrimers containing only one metal per branch; for this, it was necessary to abstract the chlorine ligands of the dinuclear $[MCl(cod)]_2$ by using silver salts. Thus, we reacted **2** or **4** with $[MCl(cod)]_2$ in the presence of $AgCF_3SO_3$ or $AgBF_4$ in thf at room temperature. The process was monitored by ^{31}P NMR spectroscopy that showed that the reaction proceeded readily to completion. All the NMR data were in agreement with the formation of the cationic dendrimers $[2a]^{4+}(CF_3SO_3)_4$, $[2b]^{4+}(CF_3SO_3)_4$, $[4a]^{8+}(CF_3SO_3)_8$ and $[4b]^{8+}(BF_4)_8$ (Chart 3). ^{31}P NMR spectra exhibited doublets ($J(PRh) = 145.3$ and 145.4 Hz) at 18.9 and 19.3 ppm for $[2a]^{4+}$ and $[4a]^{8+}$, respectively, and singlets at 18.9 and 19.3 ppm for $[2b]^{4+}$ and $[4b]^{8+}$, respectively. It is worth noting that the $M(cod)$ units can be grafted on the surface of the dendrimers through two P atoms belonging to the same or different branches. On the other hand, the possible interaction through two different molecules of dendrimer was ruled out because of the very low solubility expected for the resulting polymers. Since in all cases the ^{31}P NMR spectra showed only one signal, it can be concluded that only a single stereoisomer is, in fact, formed. By comparison with our recent studies on platinum and palladium-containing dendrimers, we tentatively assigned compounds $[2a,b]^{4+}$ and $[4a,b]^{8+}$ to the stereoisomer that displays the metal centers bonded to the phosphine ligands of the same branch.

The $^{29}Si\{^1H\}$ NMR spectrum showed the two or the four different silicon environments expected for $[2a,b]^{4+}$ or $[4a,b]^{8+}$, respectively, and their 1H NMR spectra were consistent with the structures proposed, showing characteristic data of complexed cyclooctadiene. However, the low solubility of $[4a]^{8+}$ and $[4b]^{8+}$ precluded obtaining their ^{13}C NMR spectra. In order to overcome this, we planned to substitute the cyclooctadiene ligand for carbonyl groups, which were expected to increase the solubility of the final species. This process is known to occur for monometallic rhodium or iridium complexes.¹⁰ Thus, CO was bubbled through a thf solution of $[4a]^{8+}$ for 2 h and ^{31}P NMR and IR spectroscopies showed that the substitution process occurred easily to yield $[4a']^{8+}$. The $\nu(CO)$ IR pattern in the $1966\text{--}2064\text{ cm}^{-1}$ region confirmed the nature of the resulting compound. Unfortunately, as found for $[4a]^{8+}$, the poor solubility in the common organic solvents precluded registering its ^{13}C NMR spectrum.

Reaction with 1,1'-bis(diphenylphosphino)ferrocene (dppf)

One of the most interesting goals in metallodendrimer chemistry is the formation of molecular multiple layer structures, which can be useful for the construction of nanoscale molecular architectures.¹¹ Since the dendrimers reported here display metal centers containing cyclooctadiene ligands, we reacted them with dppf, in an attempt to displace the molecule of cod and to form a double metal layer dendritic system. The reaction did not proceed with the cationic dendrimers, apparently because of the positive charge on metal atoms. However, the neutral dendrimer **1a** gave, after reaction with dppf in thf, the new double metallic layer dendritic system **1a-dppf** (Chart 4) which is a yellow air-sensitive solid. It was characterized by NMR spectroscopy. The ^{31}P NMR spectrum confirmed its formation, showing two double doublet signals at 24.3 ppm ($J(PRh) = 141$ Hz; $J(PP) = 36$ Hz), and at 22.5 ppm ($J(PRh) = 151$ Hz; $J(PP) = 39$ Hz) for the dppf ligand and a signal for the phosphorus nucleus of the dendrimer at 44.4 ppm ($J(PRh) = 192$ Hz; $J(PP) = 36$ Hz; $J(PP) = 39$ Hz). The synthesis of **1a-dppf** is not clean because another unidentified rhodium-containing species, displaying one signal at 47.0 ppm ($J(PRh) = 200$ Hz), was always present. However, this minor product could be easily separated by washing the solid **1a-dppf** with methanol.

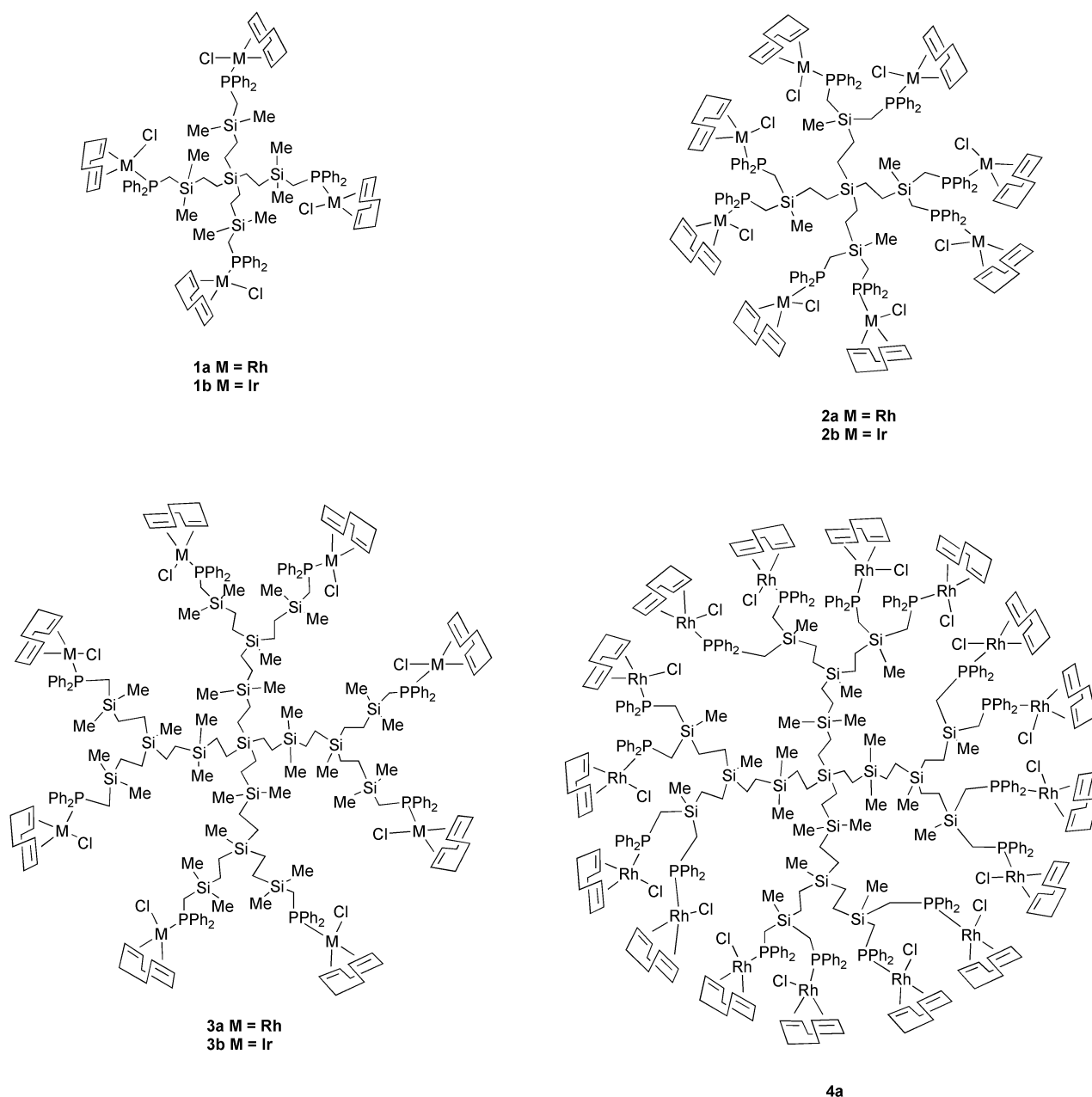


Chart 2

Eventually, traces of dppf were also eliminated by washing the solid with diethyl ether.

Catalytic studies

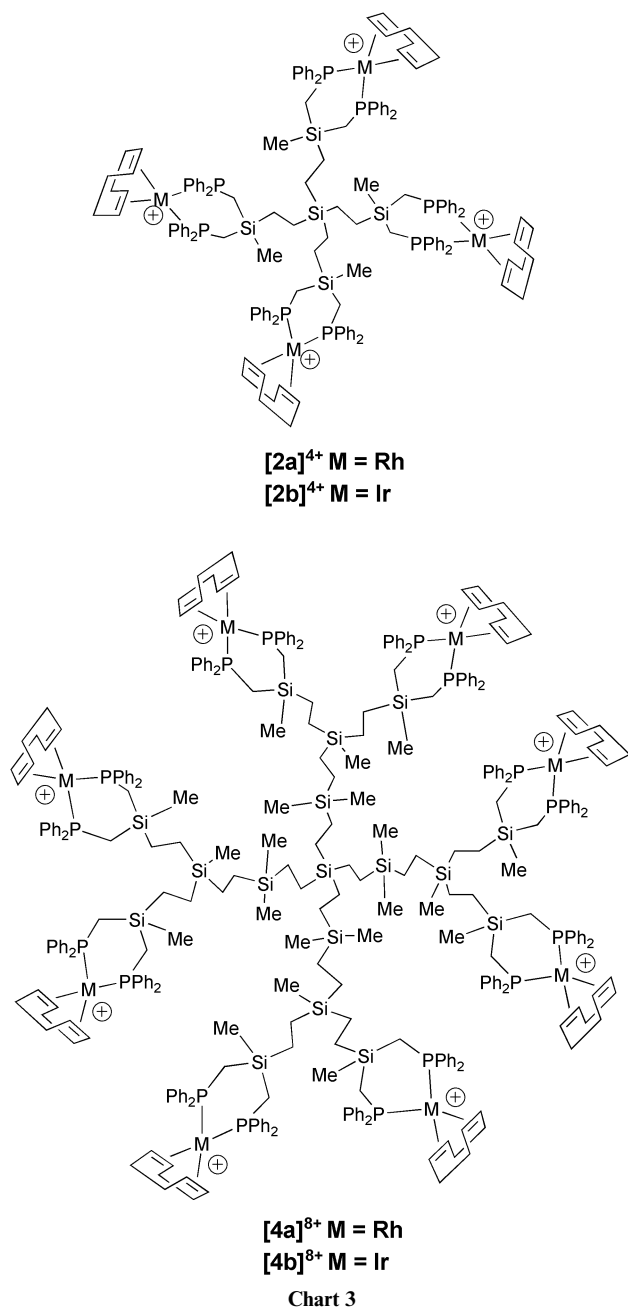
In recent years, the attachment of homogeneous catalysts to soluble dendrimer supports has received considerable attention owing to its potential advantages related to the fixation and recovery or recycling of the catalyst.¹² The dendrimers have a well-defined structure with the possibility of attaching a known large number of active sites on the periphery, retaining basically 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. The results have been generally similar, but with a slightly lower range of selectivities to those obtained with the homogeneous mononuclear species, which indicates that the catalytic centres act as independent sites. Several reports concerning the catalytic hydrogenation of olefins in the presence of metallodendrimers have been published,¹³ including the use of dendrimers containing 8 or 16 terminal chiral diphosphine ligands in asymmetric

hydrogenation processes. The results showed no significant decrease of the enantioselectivity compared with mononuclear analogues.^{14–16} Very recently, asymmetric hydrogenation has been tested using a group of cationic rhododendrimers containing up to 32 metal centres, the largest chiral phosphine dendrimer reported up to now.¹⁷ In this case, a decrease in both activity and selectivity of the dendrimer catalysts was observed when going to the higher generations. The length of the spacer between the phosphorus atoms and the carbon–silicon linkage could be an important factor in the control of the selectivity of the reaction as reported in the catalysed hydroformylation of alkenes.¹⁸

In this work, the Rh(I) bound metallodendrimers were employed as efficient catalysts for olefin hydrogenation under standard conditions (25 °C, 10 bar H₂, 1 h, acetone) and using 1-hexene as substrate in a 1 : 500 metal-to-substrate ratio. For good reproducibility of the catalytic results the catalyst had to be freshly prepared under an inert atmosphere.

As shown in Table 1, the catalytic activity (TOF) of neutral Rh(I) dendrimers **1a** and **3a** was found to be higher than both monomeric [RhCl(cod)(PPh₃)] and dimeric [RhCl(cod)]₂ complexes (entries 6, 7, 10, 11, 1 and 2). There was a slight decrease



in turnover frequency upon growth of the Rh(I) metal-lodendrimer (entries 6, 7, 10, 11). Kakkar *et al.* have reported similar results.¹³

The cationic Rh(I) metalodendrimer **[2a]⁴⁺** is less active than the corresponding ionic monomeric Rh(I) species $[\text{Rh}(\text{cod})(\text{dppp})][\text{CF}_3\text{SO}_3]$ (dppp = 1,3-bis(diphenylphosphino)propane), but shows a higher activity than the neutral dendritic species of the same generation **1a** (entries 6, 7, 8, 9). Fig. 1 shows mol% values of the hydrogenation reaction products of 1-hexene *vs.* time using **[2a]⁴⁺** as precursor. The same behaviour is observed for the monomeric neutral species $[\text{RhCl}(\text{cod})(\text{PPh}_3)]$ or $[\text{RhCl}(\text{cod})]_2$, in agreement with the results already reported by Schrock and Osborn¹⁹ and Crabtree *et al.*²⁰

When hydrogenation reactions were run in the same conditions but for 2 h the turnover frequencies are similar except for compound **3a** which shows a decrease presumably due to a partial decomposition of the third-generation Rh(I) dendrimer (entries 10, 11). Moreover, a decrease of the *cis*- and *trans*-2-hexene products was observed in agreement with a slow hydrogenation of the secondary olefin formed in the isomerization process. The results also reflect the expected relative

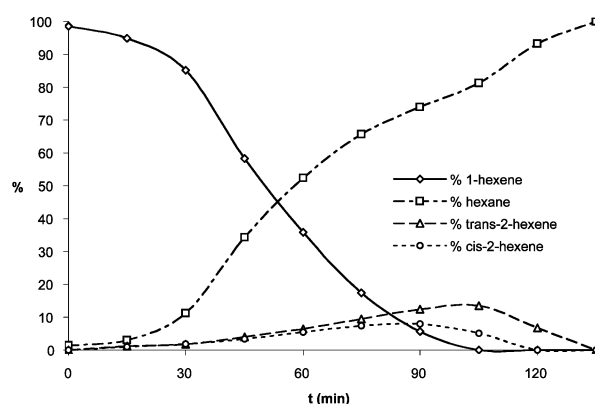
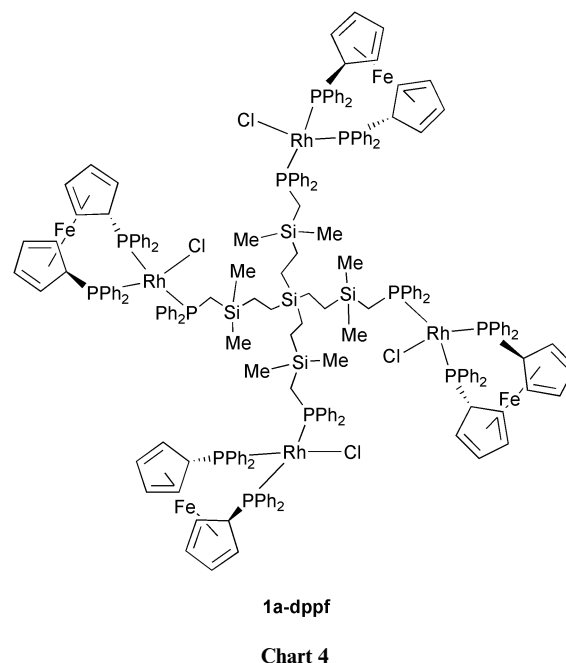


Fig. 1 Mol% of hydrogenation reaction products of 1-hexene *vs.* time using **[2a]⁴⁺** as precursor.

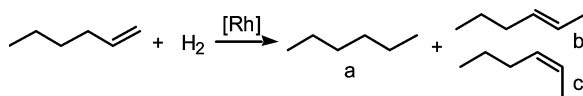
hydrogenation ability of the catalyst towards hexenes: 1-hexene > *cis*-2-hexene > *trans*-2-hexene.

Neutral dendritic species showed higher catalytic activities if the hydrogenation mixture is exposed to the air for 30 min after 1 h reaction and reintroduced into the autoclave for another hour in the same conditions. The ionic **[2a]⁴⁺** dendrimer was less sensitive to the air exposure. This can be related to the observation reported by Marciniec *et al.*²¹ for the catalytic hydrosilylation reaction of 1-hexene, the presence of oxidants probably shortens the induction period of the active catalyst.

The iridium dendrimers were also tested as hydrogenation catalyst for 1-hexene in the same conditions. Compound **1b** showed similar turnover frequency to that observed for Rh(I) metalodendrimer **1a** but unreproducible results have been found. This is related to the low solubility observed for the Ir(I) dendrimers under the reaction conditions.

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 Et₂O), CaCl₂ and stored over molecular sieves (acetone) or dried with CaCl₂ and distilled from CaH₂ (CH₂Cl₂) under N₂ prior to use. Elemental analysis (C, H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC). ¹H

Table 1 Hydrogenation reaction of 1-hexene

Run	Precursor [Rh]	t/h	Conversion (%)	a (%)	b + c (%)	b/c	TOF
1	[RhCl(cod)(PPh ₃)]	1	6	74.5	25.5	1.3	30
2		2	17	68	32	1.4	42
3	[RhCl(cod)] ₂	1	8	75.5	24.5	0.8	38
4		2	28	85	15	1.05	70
5	[Rh(cod)(dppf)][CF ₃ SO ₃]	1	99	98.5	1.5	6.7	472
6	1a	1	14	83	17	0.9	72
7		2	29	86.5	13.5	1.05	68
8	[2a] ⁴⁺ [CF ₃ SO ₃] ₄	1	47	75	25	1.2	220
9		2	99	99.5	0.5	0.6	250
10	3a	1	12	82.5	17.5	0.9	57
11		2	17	83.5	16.5	1.0	45

Reaction performed in acetone solution at 25 °C. Hydrogen pressure 10 bar. Ratio Rh/1-hexene 1/500. TOF = mol_a mol_{Rh}⁻¹ h⁻¹.

(250 MHz), ¹³C (62.86 MHz), ²⁹Si (49.66 MHz) and ³¹P (101.26 Mz) NMR spectra were recorded at 25 °C on a Bruker 250 spectrometer and ¹⁹F (282.23 MHz) NMR spectra on a Varian Unity 300 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe₄ for ¹H, ¹³C and ²⁹Si, 85% H₃PO₄ for ³¹P, CF₃COOH for ¹⁹F) 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 (FAB and ES) spectra were recorded on a Fisons VGQuattro spectrometer using as a matrix NBA (3-nitrobenzylalcohol) for FAB spectra. MALDI-TOF spectra were recorded on a Voyager DE-RP (Perspective Biosystems) time-of-flight (TOF) spectrometer using as a matrix DBH (2,5-dihydrobenzoic acid).

The starting materials [RhCl(cod)]₂,²² [IrCl(cod)]₂,²³ and phosphine-terminated dendrimers **1**, **2** and **3** were prepared following published procedures.^{6,7} Other reagents were purchased from commercial suppliers.

Syntheses

Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³(C³H₃)(CH₂PPh₂))₂)₄ (**4**). A solution of Si(CH₂CH₂SiMe₂CH₂CH₂SiMe(CH₂CH₂SiMeCl₂))₄ (2.29 g, 1.28 mmol) in 10 mL of thf was added dropwise to a solution of LiCH₂PPh₂·TMEDA (7.2 g, 0.022 mol) in 20 mL of thf at -10 °C. After stirring for 4 h part of the solvent was removed under vacuum and hexane was slowly added (40 mL). The suspension was filtered through Celite and the solvent was removed. The crude product was purified by chromatography on a silica gel column eluting with 3 : 10 thf–hexane, under N₂, to give **4** as a colourless oil (50% overall yield); δ_H (CDCl₃): -0.27 (s, C²H₃), -0.23 (s, C¹H₃), -0.03 (s, C³H₃) (60H), 0.18–0.4 (m, 64H, CH₂Si), 1.64 (s br, 32H, CH₂P) and 7.26–7.38 (m, 160H, C₆H₅); δ_C (CDCl₃): -6.5 (s, C²H₃), -4.1 (s, C¹H₃), -2.8 (s, C³H₃), 1.2, 3.0, 4.5 (s br), 7.1 (s br), 8.2 (CH₂Si), 12.6 (d, J(PC) = 28 Hz, CH₂P), 128.4 (s br, C₆H₅), 131.0 (d, J(PC) = 42.8 Hz, *ipso*-C₆H₅), 132.6 (d, J(PC) = 18.6 Hz, *o*-C₆H₅) and 140.9 (s br, C₆H₅); δ_{Si} (CDCl₃): 9.4 (Si⁰), 8.3 (Si²), 5.9 (Si¹) and 4.4 (t, ²J(Psi) = 14.0 Hz, Si³); δ_P (CDCl₃): -21.4 (s, PPh₂).

Si⁰(C¹H₂C²H₂Si¹(CH₃)₂CH₂PPh₂RhCl(cod))₄ (**1a**). To a solution of **1** (0.22 g, 0.19 mmol) in CH₂Cl₂ (10 mL) was added [RhCl(cod)]₂ (0.19 g, 0.38 mmol) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated to dryness and the residue was washed with diethyl ether. The product was then dried under vacuum. Complex **1a** was obtained as a yellow solid (360 mg, 88%) (Found: C, 54.64; H, 5.72. C₁₀₀H₁₃₆Cl₄P₄Rh₄Si₅ requires C, 55.71; H, 6.36% *M*

2155.95); δ_H (CDCl₃): 0.35 (m, 40H, CH₃, CH₂Si), 1.74 (d, 8H, J(HP) = 14.9 Hz, CH₂P), 1.8–2.01 (m, 16H, cod CH₂), 2.38 (s br, 16H, cod CH₂), 3.01 (s br, 8H, cod CH=CH), 5.42 (s br, 8H, cod CH=CH) and 7.24–7.64 (m, 40H, C₆H₅); δ_C (CDCl₃): -0.6 (d, ³J(CP) = 2.9 Hz, CH₃), 2.9 (s, C¹H₂), 10.0 (d, ³J(CP) = 3.8 Hz, C²H₂), 12.8 (d, J(CP) = 13.1 Hz, CH₂P), 28.7 (s, cod CH₂), 32.9 (d, J(CRh) = 2.4 Hz, cod CH₂), 69.8 (d, J(CRh) = 14.0 Hz, cod CH=CH), 103.7 (dd, J(CRh) = 12.5 Hz, ²J(CP) = 7.0 Hz, cod CH=CH), 128.0 (d, ³J(CP) = 9.5 Hz, *m*-C₆H₅), 129.7 (s, *p*-C₆H₅), 133.9 (d, ²J(CP) = 10.9 Hz, *o*-C₆H₅) and 135.2 (d, ¹J(CP) = 39.7 Hz, *ipso*-C₆H₅); δ_{Si} (CDCl₃): 9.41 (Si⁰), 3.30 (Si¹); δ_P (CDCl₃): 25.2 (d, J(PRh) = 147.8 Hz, PPh₂). MS (ES⁺): *m/z* = 2120.8 [M - Cl]⁺, 1874.4 [M - Cl - RhCl(cod)]⁺, 1042.3 [M - 2Cl]²⁺, 919.2 [M - 2Cl - RhCl(cod)]²⁺, 795.8 [M - 2Cl - 2RhCl(cod)]²⁺, 683.2 [M - 3Cl]³⁺. MS (FAB⁺): *m/z* = 2121.3 [M - Cl]⁺, 1800.1 [M - Cl - 3cod]⁺, 1627.9 [M - Cl - 2RhCl(cod)]⁺.

Reaction of 1a with 1,1'-bis(diphenylphosphino)ferrocene (1a-dppf). A solution of dppf (0.09 g, 0.16 mmol) in 5 mL of thf was added slowly to a solution of **1a** (0.09 g, 0.04 mmol) in 10 mL of thf at -50 °C. The reaction was monitored by ³¹P NMR. The solvent was evaporated to dryness and the solid **1a-dppf** was washed with methanol and diethyl ether twice and dried under vacuum (105 mg, 66%); δ_P (thf): 44.4 (ddd, J(CRh) = 192 Hz; ²J(PP) = 36 Hz; ²J(PP) = 39 Hz, PPh₂), 24.3 (dd, J(PRh) = 141 Hz, ²J(PP) = 36 Hz, dppf) and 22.5 (dd, ¹J(PRh) = 152 Hz, ²J(PP) = 39 Hz, dppf); δ_{Si} (thf): -0.16 (s, Si¹); δ_H (CDCl₃): -0.6–0.3 (m, CH₂, CH₃), 1.8 (m br, CH₂P), 3.4, 4.0, 4.3, 4.7 (s, Cp) and 7.04–8.1 (m, C₆H₅).

Si⁰(C¹H₂C²H₂Si¹(CH₃)₂CH₂PPh₂IrCl(cod))₄ (**1b**). Experimental conditions and workup were identical to those for the preparation of **1a**. **1b** (501 mg, 92%) (Found: C, 46.90; H, 5.52. C₁₀₀H₁₃₆Cl₄Ir₄P₄Si₅ requires C, 47.78; H, 5.45%; *M* 2513.19); δ_H (CDCl₃): 0.2–0.3 (m, 40H, CH₃, CH₂Si), 1.68 (s br, 8H, cod CH₂), 1.84 (d + m, 16H, J(HP) = 13.8 Hz, CH₂P, cod CH₂), 2.14–2.16 (m, 16H, cod CH₂), 2.68 (s br, 8H, cod CH=CH), 5.00 (s br, 8H, cod CH=CH) and 7.2–7.8 (m, 40H, C₆H₅); δ_C (CDCl₃): -0.8 (s, CH₃), 2.8 (s, C¹H₂), 9.7 (d, ³J(CP) = 3.5 Hz, C²H₂), 12.1 (d, J(CP) = 19.4 Hz, CH₂P), 29.3 (s, cod CH₂), 32.3 (s, cod CH₂), 52.9 (s, cod CH=CH), 91.9 (d, ²J(CP) = 13.5 Hz, cod CH=CH), 127.9 (d, ³J(CP) = 9.7 Hz, *m*-C₆H₅), 129.8 (s, *p*-C₆H₅), 133.3 (d, ²J(CP) = 10.6 Hz, *o*-C₆H₅) and 134.4 (d, J(CP) = 47.8 Hz, *ipso*-C₆H₅); δ_{Si} (CDCl₃): 9.5 (Si⁰) and 3.2 (Si¹); δ_P (CDCl₃): δ 15.6 (s, PPh₂). MS (ES⁺) (CH₂Cl₂): *m/z* = 2477.0 [M - Cl]⁺, 2143.5 [M - Cl - IrCl(cod)]⁺, 1053.4 [M - 2Cl - IrCl(cod)]²⁺. MS (FAB⁺) (CH₂Cl₂): *m/z* = 2477.0

$[M - Cl]^+$, 2143.3 $[M - Cl - IrCl(cod)]^+$, 1807.6 $[M - Cl - 2IrCl(cod)]^+$.

Si(CH₂CH₂Si(CH₃)(CH₂PPh₂RhCl(cod))₂)₄ (2a). Experimental conditions and workup were identical to those for the preparation of **1a**. The synthesis was assayed in CH₂Cl₂ and in thf but the product could not be isolated pure in the solid state; δ_P (thf): 39.3 (d, J (PRh) = 196.3 Hz, PPh₂) and 17.3 (d, J (PRh) = 151.1 Hz, PPh₂) with integrals in the ratio 1 : 0.04.

Si(CH₂CH₂Si(CH₃)(CH₂PPh₂IrCl(cod))₂)₄ (2b). Experimental conditions and workup were identical to those for the preparation of **2a**; δ_P (thf): -8.35 (s br, PPh₂) and 8.2 (s, PPh₂) with integrals in the ratio 1 : 0.06.

Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³-(C³H₃)₂CH₂PPh₂RhCl(cod))₂)₄ (3a). Experimental conditions and workup were identical to those for the preparation of **1a** but using thf as solvent (310 mg, 81%) (Found: C, 56.11; H, 7.42. C₂₂₈H₃₄₀Cl₈P₈Rh₈Si₁₇ requires C, 55.74; H, 6.97%; M 4913.34); δ_H (CDCl₃): -0.12 (s, C²H₃), -0.09 (s, C¹H₃) (36H), 0.3–0.5 (m, 112H, CH₂Si, C³H₃), 1.73 (d, 16H, 2J (HP) = 14.7 Hz, CH₂P), 1.83 (m, 16H, cod CH₂), 1.97 (m, 16H, cod CH₂), 2.31 (m, 32H, cod CH₂), 3.01 (s, 16H, cod CH=CH), 5.42 (s, 16H, cod CH=CH), 7.31 (m, 48H, C₆H₅) and 7.60 (m, 32H, C₆H₅). δ_C (CDCl₃): -6.3 (s, C²H₃), -4.19 (s, C¹H₃), -0.48 (s, C³H₃), 2.8, 3.8, 4.5, 4.8, 6.9 (s, CH₂Si), 10.1 (s br, C⁶H₂Si), 13.0 (d, J (CP) = 10.3 Hz, CH₂P), 28.9 (s, cod CH₂), 33.1 (s, cod CH₂), 70.0 (d, J (CRh) = 14.0 Hz, cod CH=CH), 104.0 (dd, J (CRh) = 18.2 Hz, 2J (CP) = 6.7 Hz, cod CH=CH), 128.2 (d, 3J (CP) = 9.7 Hz, *m*-C₆H₅), 129.9 (s, *p*-C₆H₅), 133.3 (d, 2J (CP) = 10.9 Hz, *o*-C₆H₅) and 135.4 (d, J (CP) = 39.4 Hz, *ipso*-C₆H₅); δ_{Si} (CDCl₃): 8.7 (Si⁰), 7.3 (Si²), 4.96 (Si¹) and 3.3 (Si³). δ_P (CDCl₃): 24.2 (d, J (PRh) = 149.1 Hz). MS (ES⁺): m/z = 1531.8 $[M - 3Cl - 2cod]^+$. MS (MALDI⁺): m/z = 610.99 $[M - 8Cl - 7cod - 2Rh]^+$.

Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³-(C³H₃)₂CH₂PPh₂IrCl(cod))₂)₄ (3b). Experimental conditions and workup were identical to those for the preparation of **3a** (220 mg, 94%) (Found: C, 49.02; H, 6.39. C₂₂₈H₃₄₀Cl₈Ir₈P₈Si₁₇ requires C, 48.66; H, 6.09%; M 5627.78); δ_H (CDCl₃): -0.16 (s, C²H₃), -0.08 (s, C¹H₃) (36H), 0.22 (s, C³H₃), 0.3–0.45 (m, 112 H, CH₂Si), 1.54 (m, 16H, cod CH₂), 1.8 (m, 32H, cod CH₂, CH₂P), 2.19 (m, 32H, cod CH₂), 2.65 (s, 16H, cod CH=CH), 5.00 (s, 16H, cod CH=CH) and 7.34–7.59 (m, 80H, C₆H₅); δ_C (CDCl₃): -6.3 (s, C²H₃), -4.1 (s, C¹H₃), -0.5 (s, C³H₃), 1.2, 2.8, 4.8, 6.9 (s, CH₂Si), 10.0 (s br, C⁶H₂Si), 12.3 (d, J (CP) = 19 Hz, CH₂P), 29.6 (s, cod CH₂), 33.6 (s, cod CH₂), 53.1 (s, cod CH=CH), 92.2 (d, 2J (CP) = 14.1 Hz, cod CH=CH), 128.1 (d, 3J (CP) = 9.5 Hz, *m*-C₆H₅), 130.1 (s, *p*-C₆H₅), 133.5 (d, 2J (CP) = 10.5 Hz, *o*-C₆H₅) and 134.5 (d, J (CP) = 47.8 Hz, *ipso*-C₆H₅); δ_{Si} (CDCl₃): 8.75 (Si⁰), 7.3 (Si²), 4.9 (Si¹) and 2.4 (Si³); δ_P (CDCl₃): 14.8 (s, PPh₂).

Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³-(C³H₃)(CH₂PPh₂RhCl(cod))₂)₄ (4a). Experimental conditions and workup were identical to those for the preparation of **2a**; δ_P (thf): 39.5 (d, J (PRh) = 196.5 Hz, PPh₂) and 17.2 (d, J (PRh) = 151.0 Hz, PPh₂) with integrals in the ratio 1 : 0.1.

[Si⁰(C¹H₂C²H₂Si¹(CH₃)(CH₂PPh₂)₂Rh(cod))₄][CF₃SO₃]₄ ([2a]⁴⁺(CF₃SO₃)₄). [RhCl(cod)]₂ (0.16 g, 0.33 mmol) was dissolved in 10 mL of thf and AgCF₃SO₃ was added (0.17 g, 0.67 mmol). The mixture was stirred at room temperature for 1 h in the dark and the AgCl formed was removed by filtration through Celite. The solution was added to a solution of dendrimer **2** (0.315 g, 0.165 mmol) in 10 mL of thf and stirred for 1 h. The resulting orange solution was concentrated to small volume and diethyl ether was added. The solid was filtered off,

washed twice with Et₂O and dried (443 mg, 80%) (Found: C, 54.72; H, 5.36. C₁₅₂H₁₇₂F₁₂O₁₂P₈Rh₄S₄Si₅ requires C, 54.54; H 5.18%; M 3347.10); δ_H (CDCl₃): -0.71, -0.41 (m, 28H, CH₃, CH₂Si), 1.57 (s br, 16H, CH₂P), 2.25 (m, 32H, cod CH₂), 4.36 (s, 16H, cod CH=CH) and 7.25–7.71 (m, 80H, C₆H₅); δ_C (CDCl₃): -2.53 (CH₃), 0.87 (C¹H₂), 7.83 (C²H₂), 10.8 (s br, CH₂P), 30.4 (cod CH₂), 100.0 (d, 2J (CP) = 25 Hz, cod CH=CH), 121.0 (q, J (CF) = 320 Hz, CF₃SO₃) and 129.4–133.3 (m, C₆H₅). δ_{Si} (CDCl₃): 0.81 (Si¹); δ_P (CDCl₃): 18.90 (d, J (PRh) = 145.3 Hz); δ_F (CDCl₃): -80.2 (s, CF₃SO₃).

[Si⁰(C¹H₂C²H₂Si¹(CH₃)(CH₂PPh₂)₂Ir(cod))₄][CF₃SO₃]₄ ([2b]⁴⁺(CF₃SO₃)₄). Experimental conditions and workup were identical to those for the preparation of **[2a]⁴⁺(CF₃SO₃)₄** (174 mg, 88%) (Found: C, 49.01; H, 4.72. C₁₅₂H₁₇₂F₁₂Ir₄O₁₂P₈S₄Si₅ requires C, 49.29; H, 4.68%; M 3704.34); δ_H (CDCl₃): -0.71, -0.1 (m, 28H, CH₃, CH₂Si), 1.8–2.16 (m, 48H, CH₂P, cod CH₂), 3.95 (s, 16H, cod CH=CH) and 7.30–7.64 (m, 80H, C₆H₅). δ_C (CDCl₃): -2.5 (s, CH₃), 0.92 (s, C¹H₂), 7.9 (s, C²H₂), 10.7 (s br, CH₂P), 31.0 (s, cod CH₂), 88.0 (d, 2J (CP) = 30 Hz, cod CH=CH), 120.7 (q, J (CF) = 319 Hz, CF₃SO₃) and 129.1–133.5 (m, C₆H₅). δ_{Si} (CDCl₃): 0.31 (Si¹). δ_P (CDCl₃): 18.90 (d, J (PRh) = 145.3 Hz, PPh₂). δ_F (CDCl₃): -80.0 (s, CF₃SO₃). MS (ES⁺): m/z = 777.8 $[M]^+$, 2202.3 $[M - 3Ir(cod)]^+$. MS (ES⁻): m/z = 149.4 $[CF_3SO_3]^-$.

[Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³-(C³H₃)(CH₂PPh₂)₂Rh(cod))₂)₄][CF₃SO₃]₈ ([4a]⁸⁺(CF₃SO₃)₈). Experimental conditions and workup were identical to those for the preparation of **[2a]⁴⁺(CF₃SO₃)₄** (281 mg, 73%) (Found: C, 54.33; H, 5.66. C₃₃₂H₄₁₂F₂₄O₂₄P₁₆Rh₈S₈Si₁₇ requires C, 54.66; H, 5.69%; M 7295.30); δ_H (CDCl₃): -0.69, -0.47, -0.19 (m, 60H, C²H₃, C¹H₃, C³H₃), 0.06 (m, 64H, CH₂Si), 1.57 (s br, 32H, CH₂P), 2.23 (m, 64H, cod CH₂), 4.37 (s br, 32H, cod CH=CH) and 7.5 (m, 160H, C₆H₅). δ_{Si} (CDCl₃): 8.5 (Si²), 5.9 (Si¹) and 0.79 (Si³); δ_P (CDCl₃): 19.3 (d, J (PRh) = 145.4 Hz, PPh₂); δ_F (CDCl₃): -79.9 (s, CF₃SO₃).

Reaction of [4a]⁸⁺(CF₃SO₃)₈ with CO. In a suspension of **[4a]⁸⁺(CF₃SO₃)₈** in 15 mL of thf is bubbled CO for 2 hours. The yellow solid **[4a]⁸⁺(CF₃SO₃)₈** is filtered off and dried under vacuum. IR: ν_{max}/cm^{-1} (CO) 1966s, 1999m and 2064w (KBr).

[Si⁰(C¹H₂C²H₂Si¹(C¹H₃)₂C³H₂C⁴H₂Si²(C²H₃)(C⁵H₂C⁶H₂Si³-(C³H₃)(CH₂PPh₂)₂Ir(cod))₂)₄][BF₄]₈ ([4b]⁸⁺(BF₄)₈). Experimental conditions and workup were identical to those for the preparation of **[2a]⁴⁺(CF₃SO₃)₄** (123 mg, 71%) (Found: C, 51.44; H, 5.50%; C₃₂₄H₄₁₂B₈F₃₂Ir₈P₁₆Si₁₇ requires C, 51.80; H, 5.53%; M 7512.04); δ_H (CDCl₃): -0.65–0.1 (m, 124H, CH₂Si, C²H₃, C¹H₃, C³H₃), 1.8–2.1 (m, 96H, CH₂P, cod CH₂), 3.98 (s br, 32H, cod CH=CH) and 7.26–7.7 (m, 160H, C₆H₅); δ_P (CDCl₃): 7.6 (s, PPh₂); δ_{Si} (CDCl₃): 8.5 (Si²), 5.9 (Si¹) and 0.9 (Si³); δ_F (CDCl₃): -148.4 (s, BF₄).

Catalytic reactions

Hydrogenation reactions were performed in a Berghoff autoclave in a 50 mL glass vessel adapted to a Teflon liner. The internal temperature was monitored by means of a thermocouple. Gas chromatography was run on a HP 5890 Series II chromatograph equipped with an Ultra 2 column 50 m × 0.2 mm × 0.33 μ m, for quantitative determination of hexane, 1-hexene, and *cis*, *trans*-2-hexene. A solution of 10 mL of acetone and 1-hexene (1.39 mol) was introduced in a thermostated autoclave, which had previously been purged with successive applications of vacuum and argon. After this a freshly prepared solution of the catalyst is introduced in the autoclave under N₂ atmosphere (in a ratio of Rh/1-hexene = 1/500) and hydrogen was admitted until a pressure of 10 bar was reached. The catalyst solution is prepared under N₂

atmosphere, dissolving 0.0150 g (6.96×10^{-3} mmol) of **1a**, 0.0230 g (6.96×10^{-3} mmol) of **[2a]⁴⁺**(CF₃SO₃)₄ or 0.0170 g (3.48×10^{-3} mmol) of **3a** in 5 mL of freshly distilled and deoxygenated acetone. After the desired time the autoclave was slowly depressurised and the conversion determined by GC analysis.

Acknowledgements

Financial support for this work was generously given by the DGICYT (Projects BQU2000-0644 and PB97-0407-C05-04) and the CIRIT (Project 2001SGR 00054). I. A. is indebted to the Ministerio de Ciencia y Tecnología for a scholarship.

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