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Note

# Carbosilane dendrimers peripherally functionalized with *P*-stereogenic diphosphine ligands and related rhodium complexes

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ABSTRACT

The first carbosilane dendrimer functionalized with *P*-stereogenic diphosphine ligands was prepared along with its cationic rhodium derivative. A mononuclear rhodium model compound was also synthesized. Both species were used as catalysts in the hydrogenation of dimethylitaconate and the results compared with those obtained with the related rhodium-containing *P*-stereogenic monophosphine dendrimers.



## 1. Introduction

The synthesis of efficient, catalytically active species is one of the most studied areas in the chemistry of dendrimers, and in particular in the field of asymmetric dendrimer catalysis [1]. Several strategies have been envisaged for inducing chirality in dendrimers. One of them involves the attachment of a chiral phosphine onto the surface of the dendrimer. Following this method, we have recently described the first examples of carbosilane dendrimers peripherally functionalized with *P*-stereogenic monophosphines **2**, **3**, and the corresponding model compound **1** [2] (Chart 1).

These supramolecules are easily able to incorporate different metal fragments, such as PdCl($\eta^3$-2-Me$C_3H_4$), RhCl(cod) or $RuCl_2$(*p*-cymene), to afford species with potential catalytic behaviour. Thus, the palladium complexes proved to be excellent catalysts in the asymmetric hydrovinylation of styrene, both in organic solvents [2] and in $scCO_2$ [3], in terms of selectivity and enantiomeric excess of 3-phenyl-1-butene. However, the rhodium compounds were less effective in the hydrogenation of dimethylitaconate [4]. With the goal of improving the catalytic results of this latter process, we decided to synthesize analogous carbosilane dendrimers with peripheral chiral *P*-stereogenic diphosphines, instead of monophosphines. This idea was drawn from the literature, which shows that, in general, diphosphine ligands are better catalysts, in the presence of metal salts, than the corresponding monophosphines in processes such as hydrogenation and others [5].

Here we report efficient synthesis of the first *P*-stereogenic diphosphine-functionalized dendrimer, the corresponding rhodium complex and preliminary results of its catalytic behaviour. A mononuclear metal model was also prepared for comparison.

## 2. Results and discussion

### 2.1. Synthesis of diphosphine-functionalized dendrimers

One way to graft phosphine ligands onto a carbosilane dendrimer is to attack dendrimers containing peripheral $SiR_2Cl$ units with the lithium salt $LiCH_2PR_2$ [6]. If the arms of the dendrimer are functionalized with $SiRCl_2$ groups, then the resulting species will display diphosphine ligands on the surface.

Our first attempts at obtaining dendrimers functionalized with chiral diphosphines consisted of making dendrimer **4** react with **LiP–BH$_3$** (Scheme 1). However, the results were not satisfactory due to the incomplete functionalization of all the arms, probably because of strong steric congestion in the molecular system.

In order to overcome this problem, we decided to use compound **5** as a starting dendrimer. Compound **5** contains $-Si(CH_3)_2CH_2CH_2-$ spacers, which were expected to reduce the steric hindrance. In this case, we were able to isolate the dendrimer **6** (Scheme 1).

Dendrimer **6** was obtained along with **P–BH$_3$**. After deprotection with morpholine, **7** and the excess of free monophosphine **P** were separated by column chromatography (Chart 2).

Following the same strategy, the model compound **8** was prepared from commercial $Me_2SiCl_2$. Compound **8** appeared in all attempts mixed with the compound resulting from the substitution

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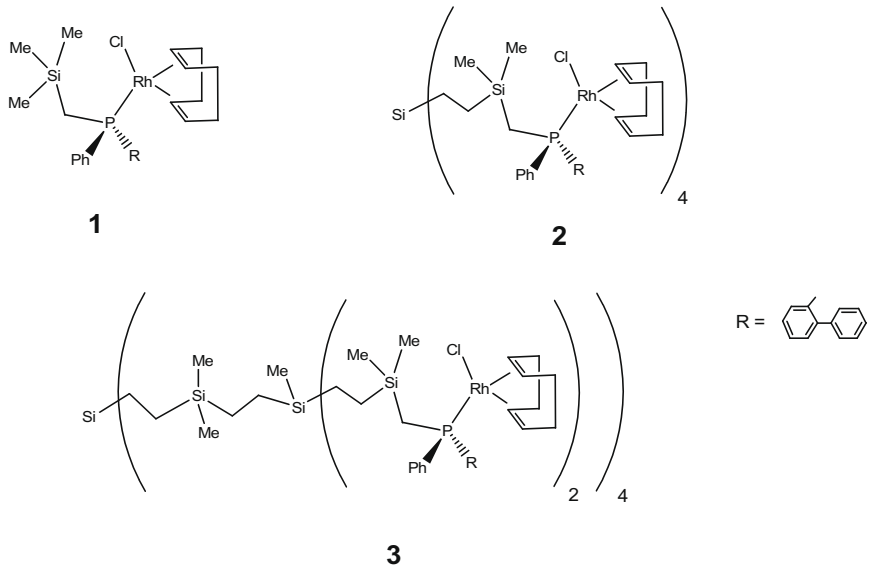



**Chart 1.**

of only one chloride ligand. Column chromatography allowed us to separate the products. However, in spite of numerous attempts, the excess of **P–BH$_3$** could not be eliminated, either in its protected form or after treatment with morpholine. Thus, **9** was obtained with a 56% yield, and contained about 15% **P** (Chart 2).

The presence of a $C_2$ symmetry element justifies that **9** shows only one signal ($\delta = -29.2$ ppm) in the $^{31}$P NMR spectrum. For the same reason, the methyl groups are homotopic and consequently they appear in the $^1$H NMR spectrum as a singlet ($\delta = -0.47$ ppm) and as a triplet in the $^{13}$C NMR spectrum ($\delta = -0.7$ ppm, $^3J_{CP} = 4.5$ Hz). However, the protons bound to the same methylenic carbon are diastereotopic with respect to each other, but they are homotopic in relation to those of the remaining $CH_2P$ group. This situation results in an AA′BB′ spin system. In the $^1$H NMR spectrum these protons appear as a pseudoquadruplet, due to the overlapping of two pseudotriplets ($^2J_{HH} \approx {}^2J_{HP}$). Since the starting phosphine, **P–BH$_3$**, displays *S* configuration, and assuming that no inversion in the stereogenic centre takes place during the synthesis of **8** or the borane deprotection process, the two *P*-sterogenic centres of the diphosphine in the model compound should have the same configuration, that is, they give rise to the isomer *l*. In the hypothetical formation of the isomer meso-(*R*, *S*) (isomer *u*), the symmetry plane generated in this isomer would make both methyl groups diastereotopic and consequently, potentially distinguishable in the NMR spectrum. For **9**, no evidence of formation of the isomer meso-(*R*, *S*) was detected, which, according to Mezzeti and coworkers [7], indicates that the diastereomers ratio *l*:*u* is at least 99:1.

The $^{31}$P NMR spectrum of **7** reveals two very close singlets ($\delta = -29.4$ and $-29.7$ ppm) due to the lack of the $C_2$ symmetry axis. Although the four diphosphine groups in the dendrimer are equivalent to each other, each diphosphine is formed of two *P*-stereogenic groups. So, in spite of showing the same *S* configuration, they do not have identical environments. The same explanation is valid for the other nuclei. For example, the four protons in the Si{$CH_2P$}$_2$ are now different and they appear as a multiplet ($\delta = 1.04$–$0.92$ ppm) in the $^1$H NMR spectrum.

The MALDI-TOF spectrum of **7** and **9** unambiguously confirmed the formation of the new species and showed the molecular peak with no traces of incomplete functionalization.

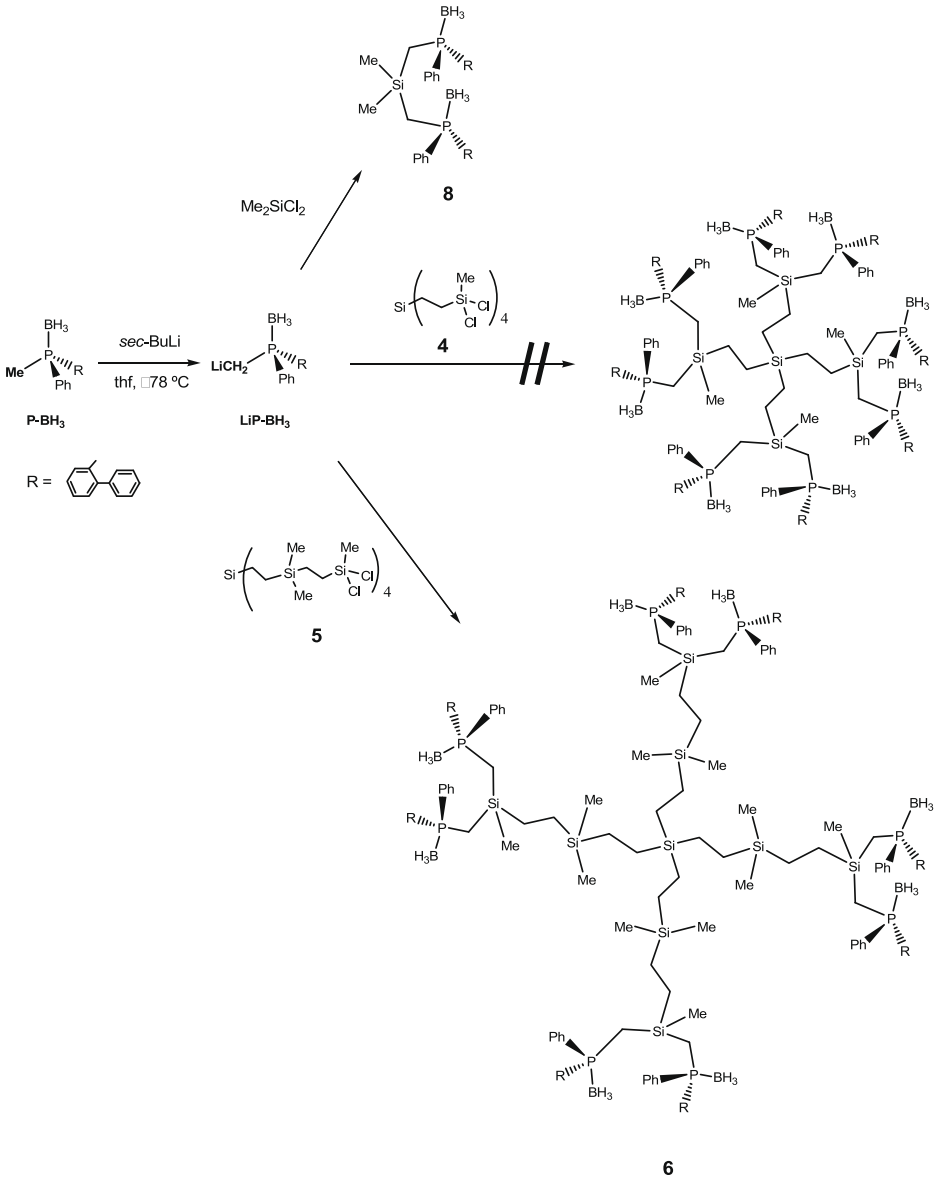
### 2.2. Synthesis and characterization of cationic rhodium complexes

The synthesis of cationic complexes of **7** and **9** requires the prior preparation of a thf solution of the appropriate rhodium (I) salt obtained by reaction of [Rh(μ-Cl)($\eta^4$-cod)]$_2$ with silver triflate. AgOTf acts as a halide abstractor. After filtering the AgCl, the solution was added to a solution of **7** or **9** and stirred for several minutes. Compound **10** precipitated as an orange solid, whereas the complex [Rh(cod)P$_2$]OTf that was also formed remained in solution, allowing the obtention of **10** in pure form. Metallodendrimer **11** was more soluble and was only isolated after the addition of diethyl ether to the mixture. In both cases high yields were obtained (Chart 3).

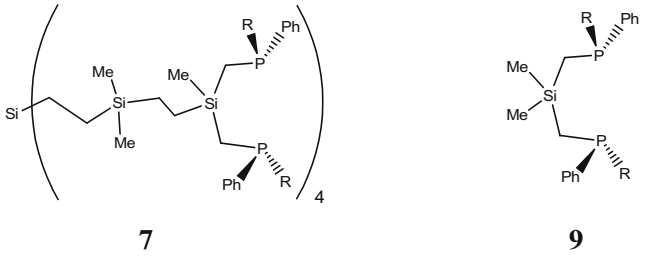
The $^{31}$P NMR spectrum of **10** contains one signal ($\delta = 22.3$ ppm, $^1J_{PRh} = 145.6$ Hz) shifted downfield in relation to the free ligand **9** ($\delta = -29.2$ ppm), as expected. That of **11** shows two doublets, assigned to the two different phosphorous nuclei in the four diphosphine units. The $^1$H NMR spectrum of **10** displays two broad signals derived from the four protons in the CH groups of the diene ligands, since two protons are homotopic with respect to the other two. An identical situation is observed for the protons in the $CH_2P$ unit. One singlet is seen ($\delta = -1.10$ ppm) and attributed to the equivalent methyl groups. Interestingly, the four CH protons from the diene in each arm are different from those in the metallodendrimer **11**, due to the lack of axial symmetry in the diphosphine fragment, although only two broad signals were actually seen in the spectrum.

Degradation of **11** in solution precluded us from taking its $^{13}$C NMR spectrum. For **10**, the most interesting features were the two bands assigned to the CH groups of the diene, in accordance with the previous discussion. The $^{19}$F NMR spectra of both complexes showed a unique signal at $-79$ ppm, corroborating the presence of the triflate ion. ESI(+) mass spectrometry confirmed the identity of the two compounds.

The mass spectrum for **10** contained the molecular peak along with [M−OTf]$^+$ and [M−OTf−cod]$^+$ fragments. In that for **11**, peaks corresponding to [M−3OTf]$^{3+}$ and [M−4OTf]$^{4+}$ units were identified, as well as the successive loss of the ligand cyclooctadiene. It should be noted that for the last fragments, the separation among consecutive peaks was 1/3 or 1/4, respectively, of the massic unity (amu) confirming the charge of the ion.




**Scheme 1.**



**7**



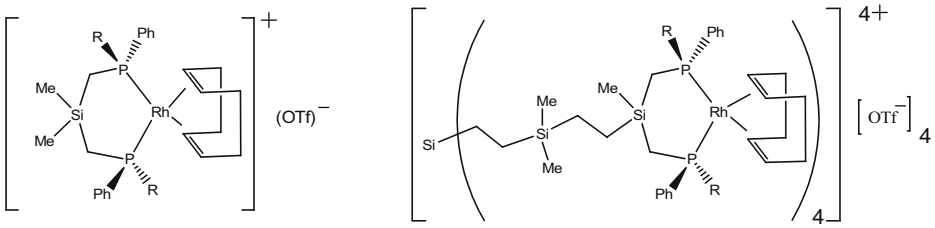
**9**

**Chart 2.**

### 2.3. Hydrogenation of dimethylitaconate

Asymmetric hydrogenation of dimethylitaconate under mild conditions has previously been achieved by using rhodium or ruthenium complexes generated *in situ* via reaction of metal complexes with monodentate or bidentate chiral phosphines. Our previous results that made use of dendrimers functionalized with chiral monophosphines showed that the rhodocomplexes **1**, **2** and **3** were active in terms of conversion, although the enantiomeric excesses produced were zero in all cases [4]. In this paper we have explored the catalytic behaviour of **10** and **11** in the same process in order to compare their catalytic results with those reported for chiral monophosphines. Dichloromethane was the solvent used, since the model compound was insoluble in thf. The conversion was monitored by GC and the results are listed in Table 1. For comparison, we have included results obtained previously with neutral rhodium dendrimers.

Table 1 shows that the conversion decreases in going from the neutral to the cationic derivatives. However, for the latter, the enantioselectivity is no longer zero, though it is still low. Mezzetti et al. have described similar results with other diphosphines [8]. A dendrimeric positive effect in terms of activity was also observed. Thus, the metallodendrimer is approximately three times more active than the model compound. We assume that in the model compound the formation of species like $[Rh(diphosphine)_2]^+$ would block access to the active centre. However, this mechanism is




**10** **11**

**Chart 3.**

**Table 1**
Hydrogenation of dimethylitaconate using catalytic precursors **1**, **2**, **3**, **10** and **11**.

| Catalytic precursor | *t* (h) | Conversion (%) | TOF ($h^{-1}$) | e.e. |
|---|---|---|---|---|
| **1** | 1 | 61.2 | 306 | ~0 |
| | 2 | 98.1 | 245 | ~0 |
| **2** | 2 | 94.4 | 236 | ~0 |
| **3** | 2 | 68.6 | 171 | ~0 |
| **10** | 2 | 13.7 | 7 | 7.6 (*S*) |
| **11** | 2 | 46.7 | 23 | 7.8 (*S*) |

Catalytic conditions for the neutral complexes: [Rh]/substrate 1:500; $T = 20$ °C; 10 bar $H_{2(g)}$; 20 mL thf. Catalytic conditions for cationic complexes: [Rh]/substrate 1:100; $T = 20$ °C; 10 bar $H_{2(g)}$; 20 mL $CH_2Cl_2$.

much less probable in **11** because of the greater volume of the dendrimer.

## 3. Conclusion

The first dendrimer containing *P*-sterogenic diphosphines has been synthesized along with the model compound **9**. The reaction of these species with the dinuclear rhodium complex $[Rh(\mu\text{-}Cl)(\eta^4\text{-}cod)]_2$ in the presence of silver triflate yielded the corresponding metallated species, which were tested as catalysts in the hydrogenation of dimethylitaconate. The complexes proved to be catalytically active and, in terms of enantiomeric excesses, both species improved on previous results involving rhodium dendrimers functionalized with chiral monophosphines.

## 4. Experimental

### 4.1. General data

All manipulations were performed under purified nitrogen using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. 1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and $^{29}Si\{^1H\}$ were obtained using Bruker DXR 250, Varian Unity 300 and Varian Mercury 400 spectrometers. Two-dimensional NMR spectra were recorded on a Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for $^1H$, $^{13}C$ and $^{29}Si$, $CF_3COOH$ for $^{19}F$ and 85% $H_3PO_4$ for $^{31}P$) and coupling constants are given in Hz. MS ESI(+) spectra were recorded using an LC/MSD-TOF (Agilent Technologies) spectrometer. MS MALDI-TOF spectra were recorded with a Voyager DE-RP (Perseptive Biosystems) spectrometer using DBH (2,5-dihydroxybenzoic acid). Conversions and enantiomeric excesses were determined by GC using a Hewlett-Packard 5890 Series II gas chromatograph (30-m Chiraldex DM column) with an FID detector. $[Rh(\mu\text{-}Cl)(\eta^4\text{-}cod)]_2$, **P–BH$_3$**, and the starting chlorocarbosilane dendrimers were prepared as previously described [4]. Other reagents were used as received from commercial suppliers.

### 4.2. Synthesis 7

The phosphine–borane **P–BH$_3$** (0.949 g, 3.271 mmol) was dissolved in 20 ml of thf and cooled to −78 °C. *Sec*-butyllithium (2.40 ml of 1.3 M cyclohexane/hexane solution, 3.120 mmol) was added slowly. After stirring the violet mixture for 2 h, a precooled solution of dendrimer **5** (0.280 g, 0.297 mmol) in thf was added. The temperature was maintained at −78 °C for 3 h and after that the mixture was left stirring for 14 h, slowly reaching room temperature. Afterwards, 20 ml of HCl 0.5 M was added and the thf was removed *in vacuo*. The remaining aqueous suspension was extracted with dichloromethane (3 × 10 ml) and the combined organic portions dried with anhydrous sodium sulphate. After evaporating the $CH_2Cl_2$ to dryness, the crude product was dissolved in morpholine (20 g, 20 ml) and stirred for 14 h at room temperature. Morpholine was then removed and the crude product was passed through a short column of alumina with toluene as the eluent. A mixture of dendrimer **7** and the free phosphine **P** was obtained after evaporating the toluene. The product was purified by flash chromatography under $N_2$ in a silica gel column eluting with hexane:thf 10:2. The target compound was finally obtained as a white foam. Yield: 0.250 g (29%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): −29.4 (*s*), −29.7 (*s*). $^1H$ NMR (400.1 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 7.34–7.06 (*m*, Ar, 112H), 1.04–0.92 (*m*, $CH_2P$, 16H), 0.34–0.24 (*m*, $^1CH_2Si$, 8H), 0.20–0.14 (*m*, $^2CH_2Si$, 8H), 0.06–(−0.18) (*m*, $^3CH_2Si + {}^4CH_2Si$, 16H), −0.24 (*s*, $^1CH_3Si$, 12H), −0.26 (*s*, $^{1'}CH_3Si$, 12H), −0.51 (*s*, $^2CH_3Si$, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 147.9–127.1 (*m*, Ar), 13.2–12.6 (*m*, $CH_2P$), 8.0 (*pt*, $^3J_{CP} \approx 3$ Hz, $^4CH_2Si$), 7.2 (*s*, $^2CH_2Si$), 6.5 (*s*, $^3CH_2Si$), 2.9 (*s*, $^1CH_2Si$), −3.2 (*pt*, $^3J_{CP} = 4.9$ Hz, $^2CH_3Si$),−4.3 (*s*, $^1CH_3Si$), −4.3 (*s*, $^{1'}CH_3Si$). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 9.13 (*s*, $Si_0$), 5.84 (*s*, $Si_1$), 3.98 (*m*, $Si_2$). MS (MALDI-TOF, DBH, *m/z*): 2858.5 (2858.1 calculated) $[M+H]^+$.

### 4.3. Synthesis 9

The phosphine–borane, **P–BH$_3$**, (0.477 g, 1.644 mmol) was dissolved in 20 ml of thf and cooled to −78 °C. *Sec*-butyllithium (1.235 ml of 1.3 M cyclohexane/hexane solution, 1.605 mmol) was added slowly. After stirring the violet mixture for 2 h, $Me_2SiCl_2$ was added (0.095 ml, 1.064 g/ml, 0.783 mmol). The temperature was maintained at −78 °C for 3 h and after that the mixture was left stirring for 14 h, slowly reaching room temperature. Afterwards, 20 ml of HCl 0.5 M was added and the thf was removed *in vacuo*. The remaining aqueous suspension was extracted with dichloromethane (3 × 10 ml) and the combined organic portions dried with anhydrous sodium sulphate. The monosubstituted product was removed by flash chromatography ($SiO_2$, $CH_2Cl_2$). The mixture formed by the excess of **P–BH$_3$** and the model compound was dissolved in morpholine (15 g, 15 ml) and stirred for 14 h at room temperature. Morpholine was then removed and the crude product was passed through a short column of alumina

with toluene as the eluent to eliminate the borane–morpholine adduct. The product was obtained as a white foam. Yield: 0.290 g (56%) (15% mol impure with **P**). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): −29.2 (*s*). $^1H$ NMR (250.1 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 7.37–7.10 (*m*, Ar, 28H), 1.01 (*pq*, *J* = 16.3 Hz, 4H), −0.47 (*s*, $CH_3Si$, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 148.0–127.1 (*m*, Ar), 14.9 (*dd*, $^1J_{CP}$ = 30.1 Hz, $^3J_{CP}$ = 4.5 Hz, $CH_2P$), −0.7 (*t*, $^3J_{CP}$ = 4.5 Hz, $CH_3Si$). MS (MALDI-TOF, DBH, *m/z*): 608.2 (608.2 calculated) $[M]^{+\cdot}$.

### 4.4. Synthesis 10

$[Rh(\mu\text{-}Cl)(\eta^4\text{-}cod)]_2$ (0.117 g, 0.243 mmol) was dissolved in 10 ml of thf and $AgCF_3SO_3$ was added (0.137 g, 0.486 mmol). The mixture was stirred at room temperature for 1 h in the dark and the AgCl that formed was removed by filtration through Celite. The solution was added to a solution of model compound **9** (0.290 g of the impure mixture) in 10 ml of thf and the resulting mixture was stirred for 30 min. The orange precipitate was filtered off, washed three times with thf and recrystallized in $CH_2Cl_2$/diethyl ether. Yield: 0.301 g (70%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CD_2Cl_2$, 298 K), $\delta$ (ppm): 22.3 (*d*, $^1J_{PRh}$ = 145.6 Hz). $^1H$ NMR (400.1 MHz, $CD_2Cl_2$, 298 K), $\delta$ (ppm): 7.86–6.56 (*m*, Ar, 28H), 5.19 (*s* (*br*), CH, 2H), 4.00 (*s* (*br*), CH, 2H), 2.96–2.56 (*m*, $CH_2$, 4H), 2.15 (*m*, $CH_2$, 4H), 1.31 (*s* (*br*), $CH_2P$, 2H), 0.56 (*m*, $CH_2P$, 2H), −1.10 (*s*, $CH_3Si$, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 298 K), $\delta$ (ppm): 145.6–119.7 (*m*, Ar + OTf), 100.9 (*s* (*br*), CH), 98.4 (*s* (*br*), CH), 34.7 (*s* (*br*), $CH_2$), 27.1 (*s* (*br*), $CH_2$), 13.6 (*s* (*br*), $CH_2P$), 0.2 (*s* (*br*), $CH_3Si$). $^{19}F\{^1H\}$ NMR (376.4 MHz, $CD_2Cl_2$, 298 K), $\delta$ (ppm): −79.3 (*s*, OTf). MS (ESI(+), *m/z*): 819.2 (819.2 calculated) $[M-OTf]^+$, 711.1 (711.1 calculated) $[M-OTf-cod]^+$.

### 4.5. Synthesis 11

$[Rh(\mu\text{-}Cl)(\eta^4\text{-}cod)]_2$ (0.052 g, 0.105 mmol) was dissolved in 10 ml of thf and $AgCF_3SO_3$ was added (0.054 g, 0.211 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 the dendrimer **7** (0.151 g, 0.053 mmol) in 10 ml of thf and stirred for 30 min. The resulting orange solution was concentrated to a small volume and diethyl ether was added. The orange solid was filtered off, washed twice with $Et_2O$ and dried. Yield: 0.179 g (79%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 21.7 (*d*, $^1J_{PRh}$ = 144.7 Hz), 21.5 (*d*, $^1J_{PRh}$ = 144.9 Hz). $^1H$ NMR (400.1 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): 8.04–6.43 (*m*, Ar, 112H), 5.15 (*s* (*br*), CH, 8H), 3.97 (*s* (*br*), CH, 8H), 2.93–2.57 (*m*, $CH_2$, 16H), 2.16 (*s* (*br*), $CH_2$, 16H), 1.37 (*s* (*br*), $CH_2P$, 8H), 0.57 (*m*, $CH_2P$, 4H), 0.43 (*m*, $CH_2P$, 4H), 0.29–(−1.00) (*m*, $CH_2Si$, 32H), −0.37 (*s*, $^1CH_3Si + {}^{1'}CH_3Si$, 24H), −1.10 (*s*, $^2CH_3Si$, 12H). $^{19}F\{^1H\}$ NMR (376.4 MHz, $CDCl_3$, 298 K), $\delta$ (ppm): −78.2 (*s*, OTf). MS (ESI(+), *m/z*): 1283.3 (1283.3 calculated) $[M-3OTf]^{3+}$, 1247.3 (1247.3 calculated) $[M-3OTf-cod]^{3+}$, 925.3 (925.3 calculated) $[M-4OTf]^{4+}$, 898.2 (898.2 calculated) $[M-4OTf-cod]^{4+}$, 871.2 (871.2 calculated) $[M-4OTf-2cod]^{4+}$, 844.2 (844.2 calculated) $[M-4OTf-3cod]^{4+}$, 817.2 (817.2 calculated) $[M-4OTf-4cod]^{4+}$.

### 4.6. Catalytic reactions

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 ($10^{-3}$ mol) and the precursor complex ($10^{-5}$ mol [Rh]) were dissolved in 10 ml of $CH_2Cl_2$. The resulting solution was immediately placed in the autoclave, which had previously been purged by successive vacuum/nitrogen cycles and maintained at 20 °C. Hydrogen 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.

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## References

[1] (a) A.M. Caminade, P. Servin, R. Laurent, J.P. Majoral, Chem. Soc. Rev. 37 (2008) 56;
(b) J.K. Kassube, L.H. Gade, Top. Organomet. Chem. 20 (2006) 61.
[2] (a) L.I. Rodríguez, O. Rossell, M. Seco, A. Grabulosa, G. Muller, M. Rocamora, Organometallics 25 (2006) 1368;
(b) L.I. Rodríguez, O. Rossell, M. Seco, G. Muller, Organometallics 27 (2008) 1328.
[3] L.I. Rodríguez, O. Rossell, M. Seco, A. Orejón, A.M. Masdeu-Bultó, J. Organomet. Chem. 693 (2008) 1857.
[4] L.I. Rodríguez, O. Rossell, M. Seco, G. Muller, J. Organomet. Chem. 692 (2007) 851.
[5] K.V.L. Crépy, T. Imamoto, Adv. Synth. Catal. 345 (2003) 79.
[6] (a) M. Benito, O. Rossell, M. Seco, G. Segalés, Inorg. Chim. Acta 291 (1999) 247;
(b) M. Benito, O. Rossell, M. Seco, G. Segalés, Organometallics 18 (1999) 5191.
[7] R.M. Stoop, C. Bauer, P. Setz, M. Wörle, T.Y.H. Wong, A. Mezzetti, Organometallics 18 (1999) 5691.
[8] F. Maienza, F. Santoro, F. Spindler, C. Malan, A. Mezzetti, Tetrahedron: Asymmetry 13 (2002) 1817.