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PAPER

P/S ligands derived from carbohydrates in Rh-catalyzed hydrosilylation of ketones†

Noureddine Khiar,*[a] Manuel Pernía Leal,[a] Raquel Navas,[a] Juan Francisco Moya,[a] María Victoria García Pérez[b] and Inmaculada Fernández*[b]

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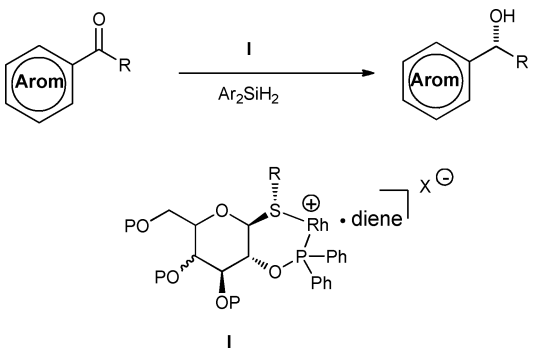
Reported is the synthesis of a number of diastereomerically pure cationic Rh(I)-complexes **I** starting from phosphinite thioglycosides. These complexes were used in the asymmetric hydrosilylation of prochiral ketones. The reactivity and enantioselectivity of the reaction was shown to be dependent on the pyranose ring, the substituent at the sulfur atom, the hydroxylic protective groups and most significantly on the alkene co-ligand.

Introduction

The 'so called' chiral market is in continuous expansion, as a consequence of the importance of chiral compounds in agriculture, fragances, medicine, and material science.[1] Therefore, asymmetric synthesis of enantiopure entities is one of the most dynamic and creative fields in organic synthesis. Within the different ways developed so far to ensure a chiral transition state,[2] enantioselective catalysis is the method of choice, because it combines efficiency, versatility, atom economy, and is well-suited from the "green chemistry" perspective.[3] Enantioselective catalysis is usually achieved by using a chiral organic ligand, which is responsible for the enantiodiscrimination, either alone,[4] or bound to a transition metal.[5] Nevertheless, despite the enormous and continuous efforts devoted to the metal promoted asymmetric catalysis in the last three decades, there are still significant problems which remain unresolved, so reducing its impact in the arena of fine chemicals synthesis.[6] One of the main reasons for this scenario is that the catalyst precursors are generally relatively expensive complex molecules obtained through a multistep synthesis. Among the different candidates, which can be used to circumvent this drawback, carbohydrates are prominent.[7] Indeed, carbohydrates account for the 93% of the renewable biomass on earth, they are the cheapest enantiopure compounds in the market, and compared to other biomolecules, their chiral coding information capacity is by far the most significant.[8] Based on these premises, and within our interest in the synthesis and application of chiral sulfur compounds in asymmetric synthesis,[9] we have recently found that mixed P/S ligands derived from D-sugars are excellent catalyst precursors in Pd-catalyzed allylic substitution and in Rh(I)-catalyzed enamide hydrogenation.[10–11] In the present work we report our results in the hydrosilylation of prochiral ketones with cationic Rh(I)-complexes type **I**, for the asymmetric synthesis of secondary carbinols, Fig. 1.



I

Fig. 1

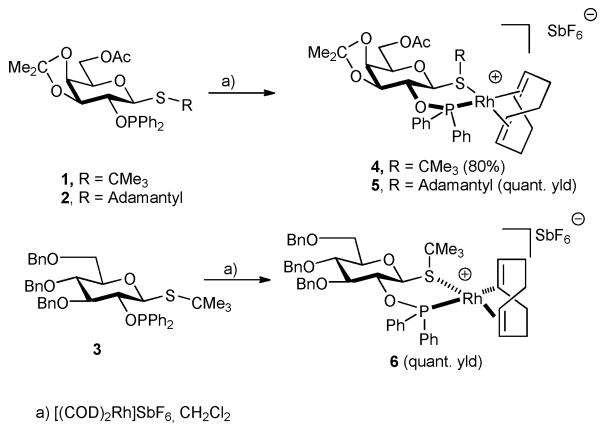
Results and discussion

A large number of chiral ligands,[12] including carbohydrates,[13] have been used in the hydrosilylation of prochiral ketones. While the field has been dominated by the use of ligands with N- or P-coordinating atoms, recently chiral sulfur ligands have emerged as an excellent alternative.[14] One of the most important features in the sulfur carbohydrate based ligands is that the sugar acts as a chiral relay to the nascent stereogenic sulfur centre upon coordination to the metal. Consequently, efficient control of the stereochemical outcome in the coordination step,[15] leads to a well defined chiral environment in very close proximity to the coordination sphere of the metal, and thus to the reaction site.[16] In our previous work we have shown that this control may be exerted, in the case of C_2-symmetric bis-thioglycosides, through stereoelectronic factors, namely the *exo*-anomeric effect,[17] or through steric bias

[a]*Instituto de Investigaciones Químicas (IIQ), CSIC-Universidad de Sevilla, c/. Américo Vespucio, 49., Isla de la Cartuja, 41092 Sevilla, Spain. E-mail: khiar@iiq.csic.es; Fax: +34954460565; Tel: +34954489559*
[b]*Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, c/ Profesor García González, 2, 41012, Sevilla, Spain. E-mail: inmaff@us.es; Fax: +34954556737; Tel: +34954555993*

† Electronic supplementary information (ESI) available: [^{1}H, ^{13}C and ^{31}PNMR spectra of the ligands **1–3**, the catalysts **4–6**, and **9–11**. See DOI: 10.1039/c1ob06305g

in the case of C_1-symmetric phosphinite thioglycosides.[11,18] Based on the success of this catalyst design in the Rh(I)-hydrogenation of enamides, in the present paper, we report our work on the stereoselective synthesis of Rh(I)-complexes **4–6**, Scheme 1, and their application in the cited asymmetric hydrosilylation of aromatic prochiral ketones.



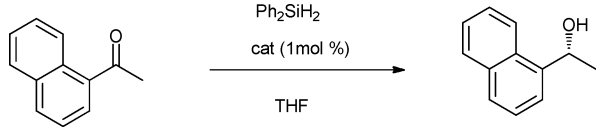
Scheme 1 Synthesis of the catalysts **4–6**.

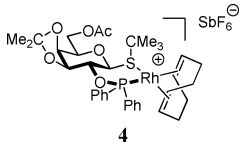
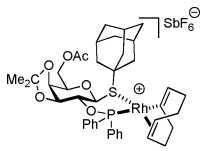
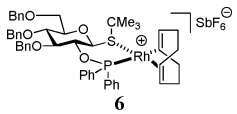
The new ligand **2**, derived from galactose, was designed to determine the effect of enhanced bulkiness of the substituent on the sulfur on the catalytic activity of the process. In contrast, ligand **3**, was designed to determine the effect of the relief of the conformational strain within the ligand as well as the electron density increase of the anomeric sulfur atom, on the catalytic behavior of the ligands. Ligand **2** was obtained in 5 steps from galactose pentaacetate using 1-adamanthane thiol as a glycosyl acceptor, while ligand **3** was obtained in 6 steps, starting from D-glucal.[19]

Before conducting the catalytic study, we first synthesized an advanced catalytic precursor with a well defined structure having a cyclooctadiene coligand and SbF_6 as counterion. Treatment of the starting mixed P/S ligands **1–3** with $Rh(cod)_2SbF_6$[20] in methylene chloride afforded the corresponding Rh(I) complexes in excellent yields, Scheme 1. Interestingly, the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra indicated that complexes **4–6** are obtained as a single diastereoisomer, which highlights the excellent sterochemical control exerted by the *tert*-butyl and the adamantyl groups. With these catalysts, and in order to determine their suitability for the synthesis of chiral carbinols, we used hydrosilylation of 1-naphthyl methyl ketone **7** as the model reaction, Table 1.

As can be seen from Table 1, in the case of the cationic Rh(I) complex **4**, which exhibits an excellent behavior in the enantioselective hydrogenation of enamides, no product was obtained, and only silane polymerization was observed (Table 1, entry 1).[21] Changing the solvent from THF to methylene chloride allows the obtention of the secondary carbinol **8**, in a modest 18% yield and 40% ee. Surprisingly, structurally related Rh(I) complex **5**, with an adamantyl group instead of the *tert*-butyl moiety, leads to the secondary carbinol with a good 60% yield and 45% ee. In contrast, the conformationally and electronically different Rh(I)-complex **6**, still exhibits some limitations in its catalytic efficiency as the final product was obtained with a modest 42% chemical yield, but it shows enhancement in its enantiomeric discrimination as it gave the final product with a good 80% ee.

Table 1 Hydrosilylation of 1-naphthyl methyl ketone **7** with catalysts **4–6**, using Ph_2SiH_2[a]



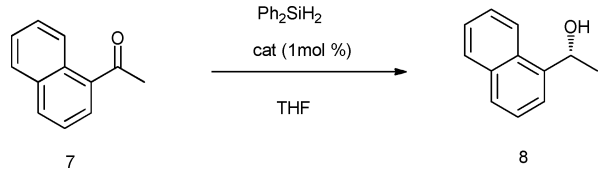
Entry	Catalyst	Yield (%)[b]	Ee[c] (%)
1	 **4**	—[d]	40
2	 **5**	18[e] 60	45
3	 **6**	42	80

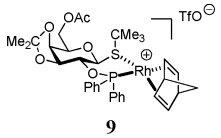
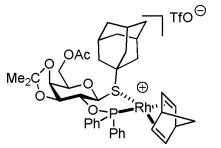
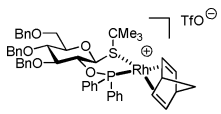
[a] All reactions were conducted in THF using 1 mol% of the catalyst. [b] All the reactions were stopped after 24 h. [c] Determined by chiral HPLC using Chiracel-OB column. [d] Silane polymerization. [e] Reaction conducted in CH_2Cl_2.

In the light of these results, which suggest that these ligands can potentially lead to an efficient catalyst for the hydrosilylation of prochiral ketones, we decided to fine tune some of the structural parameters encoded in their framework. Firstly, and in order to find out if the diene co-ligand and the counterion are simple spectators, or play a prominent role in the catalytic process,[14a] we synthesized the Rh(I)-complexes **9–11** with norbornadiene co-ligand and a triflate counterion. Condensation of the ligands **1–3** with $[(NBD)RhCl]_2$ followed by treatment with silver triflate afforded the Rh(I)-complexes **9–11** as red solids in good yields, Scheme 2. Once again the complexes were obtained as a single diastereoisomer as shown by ^{1}HNMR, ^{31}PNMR and ^{13}CNMR. With these catalysts we then performed the hydrosilylation of the 1-naphthyl methyl ketone using, as before, 1 mol% of the catalyst in THF at room temperature. The results of this study, summarized in Table 2, indicate that all the new Rh-complexes behave better than those that have a COD co-ligand and SbF_6 counterion. Indeed with these catalysts 1-(1-naphthyl)-ethan-1-ol **8** was obtained in better yields and with enhanced enantioselectivity.

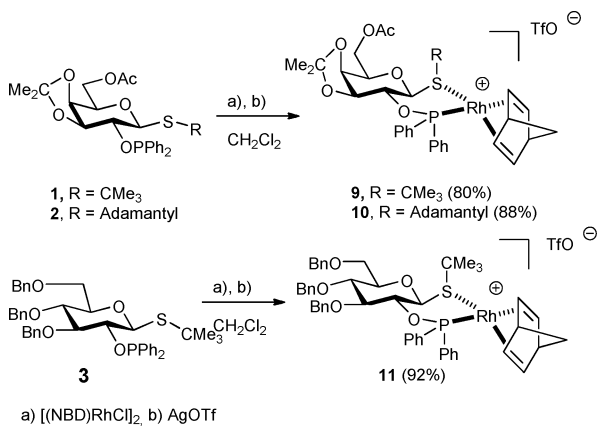
Strained catalysts **9** and **10** derived from galactose afforded mostly the same results, as the product was obtained with acceptable yields (60–65%) and acceptable enantioselectivities 56% and 58% ee, respectively. Interestingly, the use of perbenzylated glucose derived catalyst **11** afforded the desired product in quantitative yield and an excellent 86% ee. With the most efficient catalyst **11**, we then conducted a study in order to unravel the effect of the solvent, temperature and silane structure on the reaction outcome,

Table 2 Hydrosilylation of 1-naphthyl ketone **7** with catalysts **9–11**, using Ph_2SiH_2[a]



Entry	Catalyst	Yield (%)[b]	Ee[c] (%)
1	 **9**	60	56
2	 **10**	65	58
3	 **11**	100	86

[a] All reactions were conducted in THF using 1 mol% of the catalyst. [b] All the reactions were stopped after 24 h. [c] Determined by chiral HPLC using Chiracel-OB column.

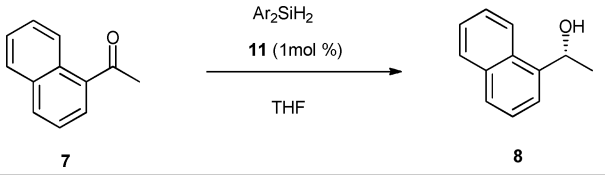


Scheme 2 Synthesis of the catalysts **9–11**.

and to get some indication of the unknown mechanism of the hydrosilylation reaction,[22] Table 3.

With regard to the temperature effect, conducting the reaction at 60 °C leads to the product **8** in quantitative yield but the enantioselectivity drops to 54%. Lowering the temperature to 0 °C (Table 3, entry 3) afforded the secondary carbinol in 96% yield and with ee (85%). Surprisingly, lowering the temperature to –20 °C (Table 3, entry 4), had a dramatic effect both on the yield (28%) and on the enantioselectivity (72% ee). This unusual temperature effect, occasionally referred to as an isoinversion relationship,[23] has already been observed in other catalytic reactions, including hydrosilylation,[24] and may be taken as evidence for two selectivity

Table 3 Influence of solvent, temperature and silane structure on the hydrosilylation of **7** with catalyst **11**[a]



Entry	Solvent	Ar_2SiH_2	T/°C	Yield (%)[b]	ee[c] (%)
1	THF	Ph_2SiH_2	60	100	54
2	THF	Ph_2SiH_2	25	100	86
3	THF	Ph_2SiH_2	0	96	85
4	THF	Ph_2SiH_2	–20	28	72
5	CH_2Cl_2	Ph_2SiH_2	25	83	82
6	CH_2Cl_2	Ph_2SiH_2	0	40	66
7	THF	Ph(1-naphthyl)SiH_2	25	51	91
8	THF	Ph(1-naphthyl)SiH_2	0	28	84

[a] All reactions were conducted using 1 mol% of the catalyst. [b] All the reactions were stopped after 24 h. [c] Determined by chiral HPLC using Chiracel-OB column.

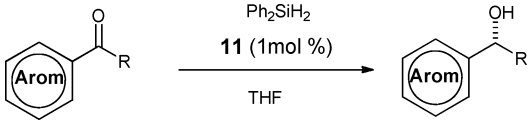
determining stages in a reaction. Indeed, these results, are in accord with Ojima's mechanism for hydrosilylation where the reversible coordination of the ketone to the hydridorhodium complex, together with the irreversible insertion of the carbonyl into the Si–Rh bond,[25] offer two stages for the stereochemical control of the hydrosilylation reaction. With regard to the effect of the solvent, changing THF to methylene chloride has a negative effect on the process, as both reactivity and enantioselectivity dropped. Interestingly, the use of the more hindered silane source, Ph(1-naphthyl)SiH_2 obtained from the reaction of $SiCl_3$ and Ph(1-naphthyl)MgBr gave a product with an excellent 91% ee, but with modest yield (Table 3, entries 7 and 8). From these results, we can conclude that the best conditions at room temperature are Ph_2SiH_2 as silane source, and THF as solvent. Using these conditions, we conducted the asymmetric hydrosilylation of other aromatic prochiral ketones, and the results are given in Table 4.

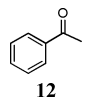
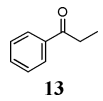
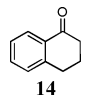
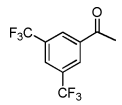
Unhindered acetophenone **12** can be reduced with an acceptable 77% chemical yield and 82% ee (Table 4, entry 1). In the of case 1-phenyl propanone **13** (Table 4, entry 2) the corresponding carbinol has been obtained with lower enantiomeric excess (70% ee). Interestingly, the system is able to reduce the more challenging cyclic ketone **14** (Table 4, entry 3), as the corresponding carbinol has been obtained in quantitative yield and 50% ee. The same result is also obtained with the electronically deficient 3,5-bistrifluoromethyl phenyl ketone **15**, (Table 4, entry 4).

Conclusions

In conclusion, mixed P/S ligands derived from carbohydrates are good catalyst precursors for the asymmetric Rh(I)-catalyzed hydrosilylation of prochiral ketones. Of all the catalysts assayed, the cationic Rh(I)-catalyst **11**, derived from the more electronically rich perbenzylated glucose P/S ligand **3**, gave the best results. With regard to ketone structure, the preliminary results reported here, indicate that catalyst **11** is the most efficient in hydrosilylation of

Table 4 Hydrosilylation of aromatic prochiral ketones with catalyst **11** and Ph(1-naphthyl)SiH_2[a]



Entry	Ketone	Solvent	T/°C	Yield (%)[b]	Ee (%)[c]
1	 **12**	THF	25	75	74
			0	77	82
2	 **13**	THF	25	100	70
			0	100	51
3	 **14**	THF	25	100	50
			0	100	50
4	 **15**	THF	25	100	56
			0	100	50

[a] All reactions were conducted using 1 mol% of the catalyst. [b] All the reactions were stopped after 24 h. [c] Determined by chiral HPLC using Chiracel-OB column.

prochiral ketones with a large steric difference between the two substituents.

Experimental

General methods

All reactions were run under an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents. THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. TLC was performed on Silica Gel GF254 (Merck) with detection by charring with phosphomolybdic acid/EtOH. For flash chromatography, silica Gel (Merck 230–400 mesh) was used. Columns were eluted with positive air pressure. Chromatographic eluents are given as volume to volume ratios (v/v). NMR spectra were recorded with a Bruker AMX_{500} (1H, 500 MHz) and Bruker Avance DRX500 (1H, 500 MHz) spectrometers. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Routine spectra were referenced to the residual proton or carbon signals of the solvent. High-resolution mass spectra were recorded on a Kratos MS-80RFA 241-MC apparatus. Optical rotations were determined with a Perkin-Elmer 341 polarimeter. Elemental analyses were recorded on a leco CHNS-932 apparatus. The organic extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo*.

General procedure for the synthesis of ligands 1–3

To a solution of the corresponding monoalcohol (1.4 mmol) in dry and deoxygented (1/1) THF/NEt_3 (7 mL) solution, was added diphenyl chlorophosphine (276 µl, 1.54 mmol) followed by a catalytic amount of DMAP (30 mg). After 30 min, the suspension was directly loaded on a short pad of silica and eluted with the corresponding deoxygenated eluent. The phosphinite thioglycosides, usually obtained as white solids, were immediately stored in a dry glove box.

***tert*-Butyl 6-*O*-*acetyl*-3,4-*O*-isopropylidene-2-*O*-diphenylphosphinite-1-thio-β-D-galactopyranoside (1).** White solid. m.p.: 116–120 °C; $[\alpha]_D$: +7.1 (1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.56–7.47 (m, 4 H), 7.34–7.29 (m, 6 H), 4.51 (d, 1 H, J = 9.5 Hz), 4.33–4.26 (m, 3 H, H-3), 4.15 (dd, 1 H, J_{HH} = 1.8 Hz and 5.6 Hz), 3.96–3.88 (m, 2 H), 2.03 (s, 3 H), 1.42 (s, 3 H), 1.29 (s, 3 H), 1.22 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.8, 142.9 (d, J_{PC} = 18.4 Hz), 142.1 (d, J_{PC} = 15.2 Hz), 131.3 (d, J_{PC} = 22.1 Hz), 130.5 (d, J_{PC} = 21.3 Hz), 129.0 (d, J_{PC} = 32.5 Hz), 128.0 (d, J_{PC} = 6.4 Hz), 127.9 (d, J_{PC} = 7.2 Hz), 110.5, 83.1 (d, J_{PC} = 3.3 Hz), 80.6 (d, J_{PC} = 18.7 Hz), 79.3 (d, J_{PC} = 2.7 Hz), 73.6 (2C), 63.9, 44.1, 31.3, 27.7, 26.4, 20.8. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ (ppm) 119.8. HRMS Calc. for $[C_{27}H_{35}O_6PNaS]^+$: 541.1792. Found: 541.1788.

(1-Adamantyl) 6-*O*-*acetyl*-3,4-*O*-isopropylidene-2-*O*-diphenylphosphinite-1-thio-β-D-galactopyranoside (2). White solid, m.p.: 133 °C. $[\alpha]_D$: +19.0 (c. 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55–7.53 (m, 2H), 7.48–7.46 (m, 2H), 7.32–7.28 (m, 6H), 4.56 (d, 1H, J = 9.4 Hz), 4.31–4.23 (m, 3H), 4.13 (dd, 1H, J = 5.5 and 2.0 Hz, H-6′), 3.94–3.87 (m, 2H), 2.02 (s, 3H), 1,94 (bs, 3H), 1.79–1.55 (m, 12H), 1.41 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.8, 143.0 (d, J_{PC} = 18 Hz), 142.1 (d, J_{PC} = 18 Hz), 131.5 (d, J_{PC} = 22 Hz), 130.5 (d, J_{PC} = 21 Hz), 129.2, 128.9, 128.0 (d, J_{PC} = 12 Hz), 127.9 (d, J_{PC} = 13 Hz), 110.5, 80.8 (d, J_{PC} = 3 Hz), 80.6 (d, J_{PC} = 19 Hz), 79.2 (d, J_{PC} = 3 Hz), 73.6, 73.5, 63.9, 46.2, 43.8 (3C), 36.2 (3C), 29.8 (3C), 27.7, 26.4, 20.7. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ (ppm)119.6. Elemental Anal. Calc. for $C_{33}H_{41}O_6PS$: C, 66.42%; H, 6.93%; S, 5.37%. Found: C, 66.24%; H, 6.93%; S, 5.74%.

***tert*-Butyl 2-*O*-diphenylphosphinite-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (3).** White solid. m.p.: decomposes $[\alpha]_D^{20}$: 13.6 (c, 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.57–7.48 (m, 4H), 7.32–7.09 (m, 15H), 6.85 (dd, 2H, J = 1.6 and 7.0 Hz), 4.69 (d, 2H, J = 10.9 Hz), 4.61–4.56 (m, 2H), 4.53–4.56 (m, 2H), 4.34 (d, 1H, J = 10.9 Hz), 3.94 (dd, 1H, J = 9.6 and 8.5 Hz), 3.74 (t, 1H, J = 8.5 Hz), 3.69 (dd, 1H, J = 1.7 and 10.7 Hz), 3.61–3.49 (m, 3H), 1.16 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 143.0, 139.9, 138.9, 138.4, 138.3, 131.3, 131.2, 130.8, 130.6, 129.3, 128.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 86.4, 84.1, 82.4, 82.2, 78.6, 69.4, 44.1, 31.4. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ (ppm) 115.6 ppm. Elemental Anal. Calc. for $C_{43}H_{47}O_5PS$: C, 73.06%; H, 6.70%. Found: C, 72.72%, H, 6.58%.

General procedure for the synthesis of the cationic complexes L-Rh(COD)SbF_6, 4–6

To a solution of the corresponding ligand (1 mol equiv.) in dry deoxygenated methylene chloride, was added under argon atmosphere a solution of $[Rh(COD)_2]SbF_6$ (1 mol equiv.) in dry

deoxygenated CH_2Cl_2. The mixture, which changes the colour from red to orange, was stirred for 1 h. The solvent was evaporated. Addition of ether followed by filtration through canula, then evaporation, and finally addition of hexanes afforded the complexes as orange solids.

Complex [1-Rh(COD)]SbF_6, 4

Starting from ligand **1** (32.5 mg, 0.06 mmoles) and $[Rh(COD)_2]SbF_6$ (34.8 mg, 1 equiv.) and following the general procedure afforded complex **4** (80%) as an orange solid. M.p.: decomposes (190 °C). $[\alpha]_D^{20}$: –2.7 (*c* 0.2, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.96–7.92 (m, 2H), 7.60–7.29 (m, 8H), 5.78 (bs, 1H), 5.71 (bs, 1H), 4.80 (t, 1H, J = 5.6 Hz), 4.71 (d, 1H, J = 10.2 Hz), 4.48–4.21 (m, 5H), 4.07 (brs, 1H), 3.88 (bs, 1H), 2.69–2.11 (m, 8 H), 2.04 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H), 1.21 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 170.6, 133.7 (d, J_{PC} = 50.8 Hz), 132.9, 132.7 (d, J_{PC} = 59.6 Hz), 131.9 (d, J_{PC} = 14.3 Hz), 131.7, 130.1 (d, J_{PC} = 11.0 Hz), 129.7 (d, J_{PC} = 11.7 Hz), 128.8 (d, J_{PC} = 10.6 Hz), 114.9, 114.8, 110.9, 110.6, 110.5, 88.5 (d, J_{PC} = 12.2 Hz), 83.8, 82.6 (d, J_{PC} = 10.8 Hz), 80.2, 78.2 (d, J_{PC} = 7.2 Hz), 74.7, 73.8, 63.3, 57.9, 32.1, 31.8, 31.6, 30.9, 29.7, 28.9, 28.1, 26.1, 20.7. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ (ppm) 125.7 (d, J_{PRh} = 94.9 Hz). Elemental Anal. Calc. for $C_{35}H_{47}F_6O_6PRhSSb$: C 43.54%, H 4.91%. Found: C 43.61%, H 5.08%.

Complex [2-Rh(COD)]SbF_6, 5

Starting from ligand **2** (73 mg, 0.12 mmol) and $[Rh(COD)_2]SbF_6$ (67 mg, 0.12 mmol) and following the general procedure afforded complex **5** as an orange solid in quantitative yield. M.p.: decomposes (129 °C). $[\alpha]_D$: –11.3 (c. 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95–7.91 (m, 2H), 7.60–7.52 (m, 3H), 7.40–7.36 (m, 5H), 5.73 (bs, 1H), 5.62(bs, 1H), 4.78 (t, 1H, = 5.7 Hz), 4.72 (d, 1H, J = 10.2 Hz), 4.40–4.32 (m, 4H), 4.22 (dd, 1H, J = 10.3 and 2.2 Hz), 4.08 (bs, 1H), 1.75 (d, 3H, J = 11.9 Hz), 1.63 (s, 3H), 1.51 (brs, 6H), 1.44 (d, 3H, J = 11.7 Hz), 1.42 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 170.6, 133.9, 133.7, 133.4, 133.1, 132.7, 132.0, 131.9, 131.6, 129.9, 129.8, 129.6, 129.5, 128.8, 128.7, 115.2 (dd, J_{PC} = 10.0 and 6.0 Hz), 110.4 (dd, J_{PC} = 10.0 and 5.0 Hz), 88.7 (d, J_{PC} = 12.5 Hz), 84.1, 82.4 (d, J_{PC} = 11.0 Hz), 78.1 (d, J_{PC} = 7.0 Hz), 77.8, 74.5, 73.8, 63.3, 61.1, 43.3, 35.1, 32.2, 31.6, 30.6, 29.0, 28.8, 28.2, 26.2, 20.8. ^{31}P NMR (97.1 MHz, $CDCl_3$): δ (ppm) 125.6 (d, J_{PRh} = 94.2 Hz). HRMS Calc. for $[C_{41}H_{53}O_6PRhS]^+$: 807.2356. Found: 807.2335.

Complex [3-Rh(COD)]SbF_6, 6

Starting from ligand **3** (65 mg, 0.09 mmol) and $[Rh(COD)_2]SbF_6$ (70 mg, 0.09 mmol) and following the general procedure afforded complex **6** as an orange solid in quantitative yield. M.p.: decomposes. $[\alpha]_D^{20}$: –3.8 (*c* 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.90 (m, 2H), 7.60 (m, 3H), 7.30–6.95 (m, 20H), 5.80 (bs, 2H), 4.91 (d, 1H, J = 7.1 Hz), 4.89 (d, 1H, J = 7.5 Hz), 4.75 (d, 1H, J = 7.5 Hz), 4.73 (d, 1H, J = 7.8 Hz), 4.65–4.53 (m, 4H), 4.12 (t, 1H, J = 8.6 Hz), 4.00 (bs, 1H), 3.89 (t, 1H, J = 8.5 Hz), 3.79 (brs, 1H), 3.72 (m, 2H), 3.68–3.62 (m, 1H), 2.85–2.00 (m, 8H), 1.20 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 137.7, 137.6, 137.5, 133.1, 132.2, 132.1,131.5, 130.2, 130.1, 129.7, 129.6, 128.6, 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 115.0, 114.9, 112.1, 112.0, 89.0, 88.9, 84.7, 84.6, 83.5, 83.4, 83.1, 81.2, 79.3, 75.8, 74.9, 73.5, 68.5, 57.9, 32.8, 31.1, 30.9, 29.2, 28.0. ^{31}P-NMR (121.4 MHz): δ (ppm) 123.5 (d, J_{PRh} = 94.9 Hz). HRMS Calc. for $[C_{51}H_{59}O_5PRhS]^+$: 917.2876. Found: 917.2188.

General procedure for the synthesis of the cationic complexes L-Rh(NBD)OTf, 9–11

To a solution of $[Rh(NBD)Cl]_2$ (0.7 equiv.) in dry deoxygenated methylene chloride (1 mL) under argon at 0 °C was added a solution of the ligand (1 equiv.) in dry methylene chloride at 0 °C. The reaction was stirred at 0 °C for 5 min. After that the mixture was added *via* canula over a suspension of silver trifluoromethanesulfonate (1.2 equiv.) and stirred 5 min at room temperature. The reaction was filtered by canula and evaporated until 0.3 mL of solvent, and finally addition of hexanes (5 mL) afforded the complexes as orange solids.

Complex [1-Rh(NBD)]TfO, 9

Starting from ligand **1** (40 mg, 0.07 mmol), $[Rh(NBD)Cl]_2$ (21.3 mg, 0.05 mmol) and AgOTf (24 mg, 0.09 mmol) and following the general procedure afforded 45 mg (80% yield) of complex **9** as an orange solid. M.p.: decomposes (207 °C). $[\alpha]_D$: + 9.0 [*c* 0.2, $CHCl_3$]; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.92–7.88 (m, 2H), 7.60–7.58 (m, 3H), 7.48–7.45 (m, 5H), 5.04 (d, 1H, J_{HH} = 10 Hz), 4.76 (t, 1H, J = 6 Hz), 4.49 (m, 1H), 4.40–4.35 (m, 2H), 4.25 (dd, 1H, J = 3 Hz and 12 Hz), 4.18–4.05 (m, 3H, H-2, 2H), 2.04 (s, 3H), 1.72 (bs, 2H), 1.52 (brs, 2H), 1.48 (s, 3H), 1.43 (s, 9H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.6, 132.6, 132.1, 131.9, 131.8, 130.5, 130.4, 129.4, 129.3, 129.1, 128.9, 110.7, 81.1, 79.4, 78.3, 74.4, 74.0, 68.7, 63.4, 58.3, 53.2, 31.5, 29.0, 27.8, 26.1, 20.7. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ (ppm) 132.2 (d, J_{PRh} = 105.9 Hz). HRMS Calc. for $[C_{34}H_{43}O_6PRhS]^+$: 713.1573. Found: 713.1602.

Complex [2-Rh(NBD)]TfO, 10

Starting from ligand **2** (87 mg, 0.140 mmol), $[Rh(NBD)Cl]_2$ (49.6 mg, 0.1 mmol) and AgOTf (39 mg, 0.154 mmol) and following the general procedure afforded complex **10** (120 mg, 0.13 mmol, 88% yield) as an orange solid. $[\alpha]_D$: + 25.3 [*c.* 1, $CHCl_3$]. M.p.: decomposes (116 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.93–7.89 (m, 2H, Ph_2P), 7.58–7.56 (m, 3H), 7.44–7.39 (m, 5H), 6.05–5.85 (brs, 1H), 5.85–5.70 (bs, 1H), 5.00 (d, 1H, J_{HH} = 10.0 Hz), 4.72 (t, 1H, J = 5.4 Hz), 4.45 (d, 1H, J = 6.6 Hz), 4.40–4.30 (m, 2H), 4.30–3.90 (m, 6H), 2.02–1.95 (m, 6H), 1.90–1.56 (m, 14H), 1.48 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 170.5, 132.6, 133.7, 132.1, 132.0, 131.6, 130.2, 130.1, 129.4, 129.3, 129.0, 128.9, 110.7, 81.4, 78.3, 77.3, 74.3, 73.9, 63.3, 61.7, 53.3, 43.9, 35.2, 30.5, 27.8, 25.9, 20.7. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ (ppm) 130.06 (d, J_{PRh} = 104.5 Hz). HRMS Calc. for $[C_{40}H_{49}O_6PRhS]^+$: 791.2043. Found: 791.2121.

Complex [3-Rh(NBD)]TfO, 11

Starting from ligand **3** (98.5 mg, 0.16 mmol), $[Rh(NBD)Cl]_2$ (36 mg, 0.08 mmol) and AgOTf (40.3 mg, 0.16 mmol) and following the general procedure afforded complex **11** as a yellow solid (144 mg, 92% yield). M.p.: decomposes (183 °C). $[\alpha]_D^{20}$: +15.8 (*c*. 0.1,

acetone). ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.08–8.02 (m, 2H), 7.72–7.62 (m, 2H), 7.40–7.08 (m, 21H), 4.89 (d, 1H, J = 11.0 Hz), 4.88 (d, 1H, J = 11.0 Hz), 4.75 (d, 1H, J = 11.0 Hz), 4.67 (d, 1H, J = 11.0 Hz), 4.63–4.43 (m, 5H), 4.15–4.05 (brs, 2H), 4.03 (t, 1H, J = 9.5 Hz), 3.90 (t, 1H, J = 9.5 Hz), 3.72 (d, 2H, J = 3.5 Hz), 3.65–3.61 (m, 1H), 1.85–1.55 (m, 6H), 1.31 (s, 9H) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ (ppm) 132.9 (d, J_{PRh} = 105.9 Hz). MS (ESI) [$C_{50}H_{55}O_5PRhS^+$]: 901.2 [M^+].

General procedure for the enantioselective hydrosilylation of aromatic prochiral ketones

To a solution of the catalyst **11** (10.4 mg, 0.01 mmol) in THF (1 mL) was added the aromatic ketone (1 mmol) at room temperature and under argon atmosphere. Then diphenylsilane (280 µL, 1.5 mmol, 1.5 equiv.) dissolved in THF (3 mL) was added dropwise by syringe pump during 10 min. The reaction mixture was monitored by TLC, and once the starting ketone was completely consumed, methanol (2 mL) was added with a small amount of pTsOH. After 30 min the solvents were removed under vacuum and the mixture was purified by column chromatography, and the ee's were determined by GC or by HPLC.

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