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# Rhodium complexes with chiral counterions: achiral catalysts in chiral matrices

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**Abstract**

The neutral complexes [Rh(I)(NBD)((1*S*)-10-camphorsulfonate)] (**2**) and [Rh(I)((*R*)-*N*-acetylphenylalanate)] (**4**) reacted with bis-(diphenylphosphino)ethane (dppe) to form the cationic Rh(I)(NBD)(dppe) complexes, **5** and **6**, respectively, accompanied by their corresponding chiral counteranions. Analogously, **4** reacted with 4,4′-dimethylbipyridine to yield complex **7**. Complexes **5** and **6** disproportionated in aprotic solvents to form the corresponding bis-diphosphine complexes **8** and **9**, respectively. **8** was characterized by an X-ray crystal structure analysis. In order to form achiral Rh(I) complexes bearing chiral countercations new sulfonated monophosphines **13**–**16** with chiral ammonium cations were synthesized. Tris-triphenylphosphinosulfonic acid ($H_3$TPPS, **11**) was used to protonate chiral amines to yield chiral ammonium phosphines **14**–**16**. Thallium-tris-triphenylphosphinosulfonate ($Tl_3$TPPS, **12**) underwent metathesis with a chiral quartenary ammonium iodide to yield the proton free chiral ammonium phosphine **13**. Phosphines **15** and **16** reacted with $[Rh(NBD)_2]BF_4$ to afford the highly charged chiral zwitterionic complexes $[Rh(NBD)(TPPS)_2][(R)\text{-}N,N\text{-dimethyl-1-(naphtyl)ethylammonium}]_5$ (**17**) and $[Rh(NBD)(TPPS)_2][BF_4][(R)\text{-}N,N\text{-dimethyl-phenethylammonium}]_6$ (**18**), respectively. Complexes **5**, **6**, and **18** were tested as precatalysts for the hydrogenation of de-hydro-*N*-acetylphenylalanine (**19**) and methyl-(*Z*)-(α)-acetoamidocinnamate (MAC, **20**) under homogeneous and heterogeneous (silica-supported and self-supported) conditions. None of the reactions was enantioselective.


*Keywords:* Rhodium; Chiral counterions; Catalysis; Hydrogenation

## 1. Introduction

In the 1980s chiral ammonium salts were shown to act as enantioselective phase transfer catalysts in a number of organic transformations [1,2] and recently optical yields of up to 99% have been achieved [3]. Moreover, it was demonstrated that chiral spectator ions also induce chirality in the course of reactions catalyzed by achiral metal complexes. Achiral Pd complexes in the presence of cinchonidinium alkaloids led to enantioselectivities of up to 8% ee in allylic alkylation reactions [4]. The use of achiral rhodium catalysts in combination with steroid derived surfactants gave up to 8.5% ee in the hydrogenation of de-hydro-aminoacids [5] while aziridinations and cyclopropanations catalyzed by achiral Cu complexes associated with chiral binaphtol based counteranions gave up to 28% ee [6]. In view of our interest in ordered catalytic systems [7] we set out to achieve crystalline precatalysts chirally modified by counterions. We disclose here the synthesis and characterization of new chiral ammonium salts of sulfonated monophosphines and rhodium complexes thereof. The resulting cationic and anionic rhodium complexes are associated, respectively, with chiral counteranions and chiral countercations forming the chiral matrix. The potential of such highly charged rhodium salts as 'molecular solid state organometallic catalysts' [8] is explored, since their extremely low solubility in the reaction medium fulfills one of the basic prerequisites of heterogeneous self-supported catalysis. We present the

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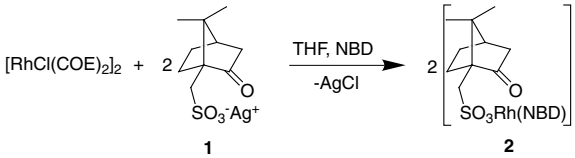
results of catalytic hydrogenations of prochiral de-hydro-aminoacids that were performed in homogeneous solution, supported on silica gel, and without support.

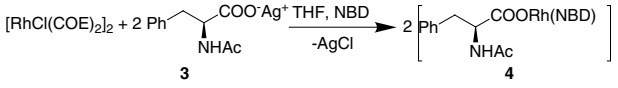
## 2. Results and discussion

### 2.1. Complexes containing chiral anions

In a first approach to form chiral rhodium salts the chloride ligand of the precursor $[Rh_2Cl_2(COE)_2]$ (COE = cyclooctene) was exchanged with the silver salts of camphorsulfonate (**1**) (Eq. (1)) and (*R*)-acetylphenylalanate (**3**) (Eq. (2)) in presence of an excess of norbornadiene (NBD) to afford the neutral (1*S*)-10-camphorsulfonato and (*R*)-*N*-acetylphenylalanato Rh(I) complexes **2** and **4**, respectively. Both complexes were soluble in aliphatic and ether solvents. Despite using an excess of NBD in the syntheses of **2** and **4** only mono NBD complexes of rhodium formed, probably due to effective bidentate ligation of the camphorsulfonate and phenylalanate anions, respectively, to the Rh(I) centers.

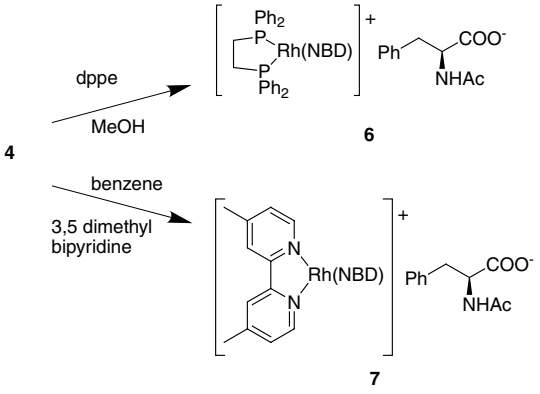



(1)

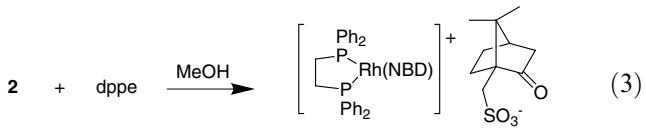



(2)

1,2-Bis(diphenylphosphino)ethane (dppe) cleanly reacted with compounds **2** and **4** in methanol solution to afford **5** (Eq. (3)) and **6**, respectively. Additionally, **4** reacted with 4,4′-dimethyl-2,2′-dipyridyl giving complex **7** (see Scheme 1). The outer-sphere-chiral complexes **5**–**7** formed in excellent isolated yields.



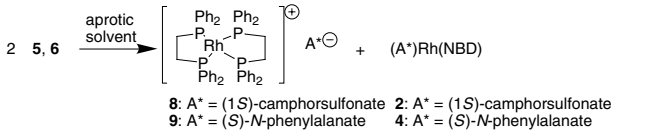

Scheme 1.




(3)

Compounds **5** and **6** disproportionated in aprotic solvents such as THF according to Eq. (4) yielding compounds **8** and **9**, along with the phosphine free neutral complexes **2** and **4**, respectively. Complexes **8** and **9** were identified by separate high yield syntheses in methanol solution from 2 equiv of dppe and **2** or **4**, respectively. It was shown recently that the lipophilicity of $[Rh(dppe)_2]^+A^-$ salts is controlled by modifications of the anion $A^-$ [9]. X-ray quality crystals of **8** were grown from a THF solution of **5**. Fig. 1 shows its solid state structure with a selection of bond parameters. The space group was monoclinic Cc (No.9) with a unit cell of $a = 14.736(3)$, $b = 23.615(5)$, $c = 35.138(7)$, $b = 97.90(3)°$ with two molecules per asymmetric unit.

In view of a possible application as self-supported organometallic catalysts [8], the solubility of compounds **6**–**8** was tested and was found to be low only in alkanes and perfluoroalkanes




(4)

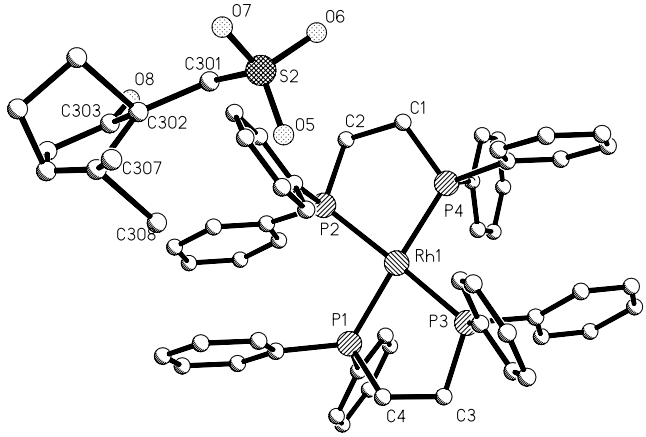
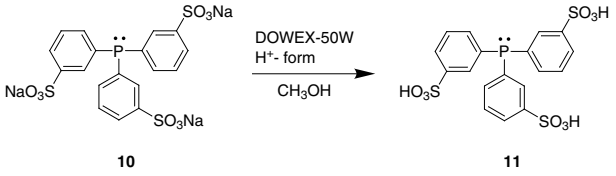


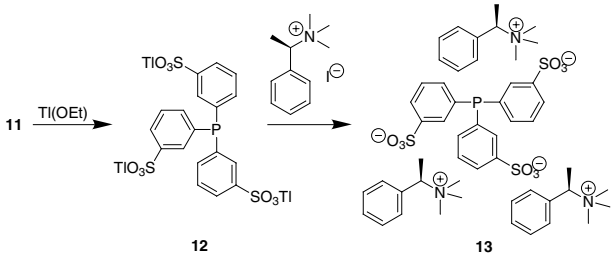

Fig. 1. Structure of complex **8** in the solid state. Selected bond lengths (Å) and angles (°) are as follows: Rh(1)–P(2) 2.280(7), Rh(1)–P(1) 2.290(7), Rh(1)–P(3) 2.293(8), Rh(1)–P(4) 2.317(8), S(2)–O(7) 1.4239, S(2)–O(5) 1.4339, S(2)–O(6) 1.4896, S(2)–C(301) 1.7865, P(1)–Rh(1)–P(2) 97.5(2), P(1)–Rh(1)–P(3) 81.9(3), P(2)–Rh(1)–P(4) 83.0(3), P(3)–Rh(1)–P(4) 100.1(2), O(7)–S(2)–O(5) 117.3, O(7)–S(2)–O(6) 110.6, O(5)–S(2)–O(6) 111.3, O(7)–S(2)–C(301) 104.7, O(5)–S(2)–C(301) 111.1, O(6)–S(2)–C(301) 100.3.

### 2.2. Sulfonated phosphine ligands containing chiral cations

In order to improve the chiral matrix (i.e. to augment the number of chiral units per rhodium atom) we decided to modify the commercially available monophosphine sodium-tris-triphenylphosphinosulfonate ($Na_3TPPS$, **10**) by exchanging the sodium ion for chiral ammonium ions [10]. Direct ion exchange of **10** with (*R*)-*N*,*N*,*N*-trimethyl-1-phenethylammonuim iodide under varying conditions failed. The exchange via the $Ag_3TPPS$ salt was not possible either since $Ag_3TPPS$ was not accessible from **10** by different exchange methods. However, the strongly acidic Dowex-50W ion exchange resin allowed to exchange the sodium cations with protons (Eq. (5)) on a gram scale in excellent yields. Surprisingly, the NMR spectrum of **11** in $CD_3OD$ did not reveal the presence of phosphonium species. Reactions of phosphine **11** with $Ag_2O$ gave inseparable mixtures, presumably due to the formation of silver–phosphine complexes. On the other hand, **11** reacted cleanly with thalliumethoxyde in ethanol solution to afford thallium-tris-triphenylphosphinosulfonate ($Tl_3TPPS$, **12**). Reacting **12** with *N*,*N*,*N*-trimethyl-1-phenethylammonuim iodide finally led to the desired ammonium phosphine **13** (Eq. (6)) along with precipitated TlI




**10** **11** (5)



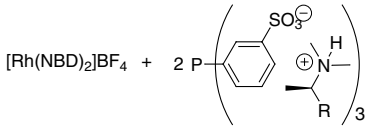

**12** **13** (6)

Phosphines **12** and **13** were prepared in excellent yields and on gram scales. In the $^1H$ NMR spectrum **13** revealed an apparent doublet of triplets (dt) at 1.72 ppm attributed to the methyl group adjacent to the stereogenic carbon atom. Concentration effects were excluded. Irradiating the protons of this methyl group caused the quartet at 4.69 ppm (H on stereogenic C atom) to disappear, whereas the aromatic region of the *ortho*-protons of the *N*,*N*,*N*-trimethyl-1-phenethylammonuim cation remained unchanged. It is thus concluded that there is no $^5J$ coupling between the methyl protons and the aromatic *ortho*-protons. The dt may be explained by the presence of three conformers, each of them displaying a doublet at a different chemical shift.

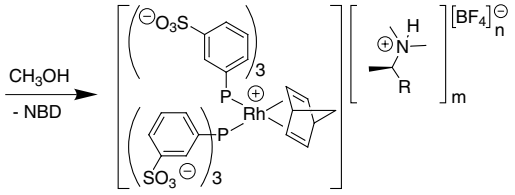
Cinchonidine and its derivatives [11,12] and 1-(naphtyl)ethylamine (NEA) [13,14] were shown to be powerful chiral modifiers in heterogeneously catalyzed reactions [15]. Therefore, phosphine **11** was used to directly protonate chiral amines such as hydroquinidine, (*R*)-NEA, and (*R*)-phenethylamine giving compounds **14**–**16** (see Scheme 2). These reactions were carried out on gram scales and in excellent yields. Compounds **10**–**16** are water soluble [16].

### 2.3. Complexes containing chiral cations

With phosphine ligands **13**–**16** at hands, we undertook complexation studies in order to synthesize achiral rhodium complexes with chiral countercations. Ligands **13** and **16** were reacted with $[RhCl(COE)_2]_2$ in a ratio of 6:1 to afford mainly the corresponding Wilkinson's catalysts along with dimeric species and unreacted ligand. Unfortunately, these mixtures were inseparable. Hydroquinidinium phosphine ligand **14** did not react cleanly neither with $[RhCl(COE)_2]_2$ nor with $[Rh(NBD)_2]BF_4$ in varying stoichiometries and solvents. In general, we found it difficult to separate and purify mixtures of these highly ionic species. However, ligands **15** and **16** reacted cleanly with $[Rh(NBD)_2]BF_4$ in methanol solution to afford fivefold negatively charged zwitterionic complexes **17** and **18**, respectively, in excellent isolated yields (Eq. (7)). Charge-neutral zwitterionic Rh(I) complexes have been shown to catalyze various transformations [17–20]. Complexes **17** and **18** were found to be soluble in protic solvents including water and to be insoluble in aliphatic, aromatic, and notably in ether solvents such as THF. We note that washing complex **17** with THF effectively removed one mole of the [(*R*)-*N*,*N*-dimethyl-1-(1naphtyl)ethylammonium]$BF_4$ salt. Surprisingly, this did not happen with complex **18**.



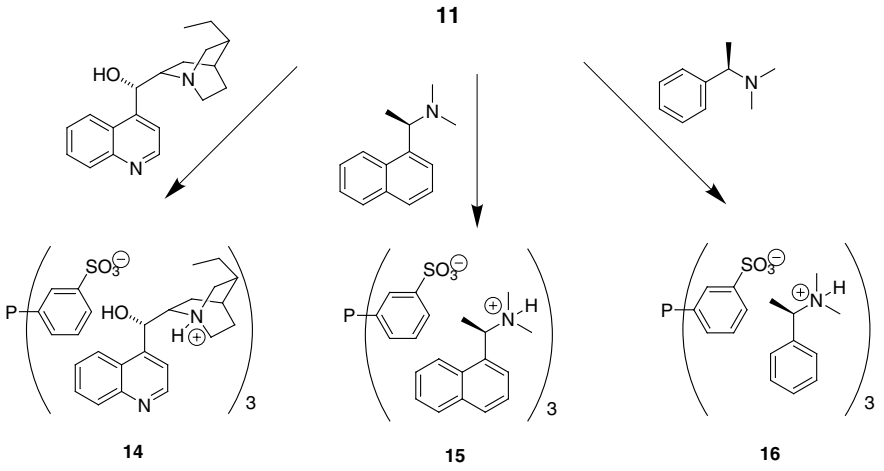

**15** (R = naphtyl)
**16** (R = phenyl)




(7)

**17** (R = naphtyl, m = 5, n = 0)
**18** (R = phenyl, m = 6, n = 1)

Complexes **17** and **18** differ in several ways from 'first generation' complexes such as **5**–**9** containing chiral counteranions. First, chiral countercations are



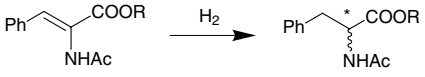

Scheme 2.

non-coordinating, especially considering the cationic nature of the rhodium centers. Second, complexes **17** and **18** form highly charged species, thus effectively lowering the solubility in aprotic solvents which is an important prerequisite when complexes are to be used as truly heterogeneous, "self-supported" organometallic species [8]. Finally, the high number of chiral counterions in **17** and **18** (five and six, respectively) leads to a denser chiral matrix. Unfortunately, **17** and **18** were only isolated as amorphous powders.

Ligand **13** and complex **17** were grafted via H-bonding onto Merck 60® silica using Bianchini's method [20] in amounts of 0.10 mmol/g (Merck 60®) and 0.14 mmol/g (Merck 60®), respectively. Qualitatively, slight leaching of **17** was observed in $CH_2Cl_2$ and no leaching was detected in toluene and THF, whereas it strongly leached in protic solvents.

### 2.4. Catalytic hydrogenations

The 'first generation' catalysts **5** and **6** were tested in the hydrogenation of de-hydro-*N*-acetylphenylalanine (**19**, Eq. (8)). In homogeneous phase at 273 K no enantioselection was observed and **5** and **6** were ca. half as active as the reference system $[Rh(dppe)(NBD)]BF_4$ [21]. The lower activity of **5** and **6** is probably due to the stronger coordination of the camphorsulfonato and the acetylphenylalanato anions, respectively, as compared to $BF_4^-$. Under unsupported heterogeneous conditions in pentane or perfluorohexane solvents, 5 mol% of **6** and **7** hydrogenated methyl-(*Z*)-α-acetoamidocinnamate (MAC, **20**) in 70–80% yield in 24 h without enantioselectivity (0% ee, determined by chiral HPLC [22]). The mother liquors were not catalytically active and rhodium concentrations determined by ICP were less than $10^{-4}$ mol%. Nevertheless, we believe that the observed catalytic activity is due to the presence of small amounts of dissolved complex since the highly ionic and 'truly' insoluble catalyst precursors **17** and **18** showed no activity under similar conditions (vide infra). Complexes **2** and **4** were not stable under hydrogenation conditions forming metallic rhodium precipitate. Complex **18** was tested in different forms for the hydrogenation of MAC (see Table 1).




**19** (R = H)
**20** (R = $CH_3$)

**21** (R = H)
**22** (R = $CH_3$)

(8)

The fivefold negatively charged zwitterionic complex **18** was indeed an active hydrogenation catalyst (entry 1). However, in none of the experiments was any significant enantioselection observed. In the unsupported solid state

Table 1
Catalytic hydrogenation of **20** (0.05–0.5 M) at RT using 5 mol% of catalyst precursor **18**

| Entry | Form | Solvent | Reaction time | $p(H_2)$ (bar) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | Solution | $CH_2Cl_2$ | 20 min | 1 | 72 |
| 2 | Powder | Toluene | 18 h | 6 | 0 |
| 3 | Powder | Toluene | 3 h | 6 | 2 |
| 4 | Powder | Toluene/THF | 18 h | 6 | 0.2 |
| 5 | Ground powder and ultrasound | Toluene/THF | 18 h | 6 | 3.4 |
| 6 | Immobilized on Merck-60 | Toluene | 18 h | 5 | 26[b] |
| 7 | Immobilized on Merck-60 | THF | 18 h | 5 | 21[b] |

[a] Determined by NMR and HPLC.
[b] Mother liquors were catalytically inactive.

only very finely ground **18** in combination with ultra sonication during the reaction exhibited some activity (entry 5). Complex **18** dispersed on Merck 60® (0.14 mmol/g) (entries 6, 7) turned out to be a relatively active catalyst system. The apparently higher activity of the unsupported "heterogeneous" systems **6** and **7** as compared to unsupported **18** may be explained by the significantly higher solubilities of **6** and **7** in the reaction media and thus by a homogeneous contribution to the overall reactivity. In contrast, **18** apparently formed a 'truly' heterogeneous system. It seems therefore that a negative activity test of the mother liquor of a given heterogeneous catalyst system is not sufficient a proof for its heterogeneicity.

## 3. Conclusions

New chiral ammonium sulfonato phosphine ligands **13**–**16** as well as achiral rhodium complexes with chiral counteranions (**5**–**7**) and countercations (**17**, **18**) were synthesized and characterized. The cationic complexes **5** and **6**, and, notably, the pentaanionic complex **18** effectively hydrogenated prochiral de-hydro-aminoacids under homogeneous and silica-supported conditions. However, none of the aforementioned complexes induced chirality. The zwitterionic complexes **17** and **18** showed extremely low solubilities in aprotic solvents such as THF, which is a prerequisite for truly heterogeneous self-supported catalyst systems. Unfortunately, these complexes did not catalyze the hydrogenation of MAC (**20**) under self-supported conditions, although the use of very fine powders may improve activities (entry 5 of Table 1). The immobilization of catalyst precursor **18** via H-bonding on silica gel proved promising from a reactivity and recyclability standpoint. Future efforts will be directed at synthesizing clean complexes of ligand **14** which contains the most promising chiral modifier. The confinement of such catalyst precursors within well defined mesoporous silica may lead to enantioselective systems [23,24] which is the object of future studies. On the other hand, the use of microcrystalline material instead of amorphous powders (of, e.g., **17** or **18**) is another strategy, since the chiral order on a crystalline catalyst surface may impart enantioselectivity. Such crystalline self-supported organometallic catalysts must remain stable under the reaction conditions. For example, microcrystals of compound **8** collapsed under 1 bar of $H_2$ thus destroying any order that may have been present on the crystal surfaces.

## 4. Experimental

### 4.1. General considerations

(*S*)-*N*-acetylphenylalanine (Aldrich), chiral amines, **10**, TlOEt (Strem), were used as received. α-Acetamidocinnamic acid (**20**, Aldrich) was recrystallized from water, dried in vacuo at 373 K, and kept in the glove box. MAC (**21**) was synthesized by reacting a methanol solution of **20** with a $CH_2N_2$ solution in $Et_2O$ at 273 K. $[RhCl(COE)_2]_2$, $[Rh(NBD)_2]BF_4$, [Ag((1*S*)-10-camphorsulfonate] (**1**) [25] were prepared according to published procedures. All reactions involving Ag compounds were carried out in the dark. The syntheses were routinely carried out in a glove box. NMR spectra were recorded on a Bruker DPX-250 spectrometer. Optical rotations were measured on a AVIV-202 polarimeter. Elemental analyses were performed at the microanalytical laboratory of the Hebrew University, Jerusalem. *Caution:* The Tl containing compounds described here are water soluble and highly toxic.

### 4.2. [Rh((1*S*)-10-camphorsulfonate)(NBD)] (2)

NBD (0.25 ml) was added dropwise to a stirred slurry of $[Rh_2Cl_2(COE)_4]$ (255 mg, 0.355 mmol) in THF (5 ml). The resulting dark yellow solution was stirred for 20 min. Then [Ag((1*S*)-10-camphorsulfonate] (**1**, 253 mg, 0.711 mmol) was added portionwise and the resulting mixture was stirred for 24 h. The volatiles were removed in vacuo and the residue was taken up in $CH_2Cl_2$ (5 ml). The mixture was filtered through Celite and the solution was evaporated to dryness. Washing the solid with cold $Et_2O$ and drying in vacuo afforded a yellow powder (246 mg, 81%). Elemental analysis (calculated for $C_{17}H_{23}SO_4Rh$): C, 47.82 (47.89); H, 5.39 (5.44)%.

### 4.3. [Ag((*S*)-*N*-acetylphenylalanate)] (3)

A slurry of (*S*)-*N*-acetylphenylalanine (2.410 g, 11.630 mmol) in $CH_3CN$ (40 ml) was added to solid $Ag_2O$ (1.348 g, 5.815 mmol) and the mixture was stirred for 24 h. The resulting white precipitate was filtered off, washed with $Et_2O$ ($2 \times 40$ ml), and dried in vacuo affording a white powder (3.47 g, 95%). Elemental analysis (calculated for $C_{11}H_{12}NO_3Ag$): C, 41.80 (42.06); H, 3.91 (3.85); N, 4.73 (4.46)%. $^1H$ NMR ($CD_3OD$): $\delta$ 1.85 (s, 3 H), 2.80–2.95 (m, 1 H), 3.10–3.25 (m, 1 H), 4.45–4.55 (m, 1 H), 7.05–7.20 (m, 5 H).

### 4.4. [Rh((*S*)-*N*-acetylphenylalanate)(NBD)] (4)

NBD (0.25 ml) was added dropwise to a stirred slurry of $[Rh_2Cl_2(COE)_4]$ (295.1 mg, 0.4115 mmol) in THF (5 ml). The resulting dark yellow solution was stirred for 20 min. Then [Ag((*R*)-acetylphenylalanate)] (**3**, 258.8 mg, 0.8240 mmol) was added portionwise and the resulting mixture was stirred for 24 h. The volatiles were removed in vacuo and the residue was taken up in $CH_2Cl_2$ (5 ml). The mixture was filtered through Celite and the solution was evaporated to dryness. Washing the solid with cold $Et_2O$ and drying in vacuo afforded a

yellow powder (284 mg, 86%). Elemental analysis (calculated for $C_{18}H_{20}NO_3Rh \cdot 0.5C_4H_{10}O$): C, 55.14 (54.80); H, 5.40 ](5.75); N, 2.80 (3.20)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.29 (s, br, 2 H), 1.81 (s, 3H), 2.55–2.65 (m, 1H), 2.75–2.85 (m, 1H), 4.01 (s, br, 4 H), 4.11 (s, br, 2 H), 4.20–4.30 (m, 1 H), 7.00–7.25 (m, 5 H). The spectrum showed the presence of 0.5 equiv of $Et_2O$.

### 4.5. [Rh(dppe)(NBD)][(S)-10-camphorsulfonate] (5)

A solution of dppe (138.1 mg, 0.346 mmol) in $CH_3OH$ (4 ml) was added dropwise to a stirred solution of [Rh((1*S*)-10-camphorsulfonate)NBD] (148.2 mg, 0.348 mmol) in $CH_3OH$ (4 ml). The resulting orange solution was stirred for 6 h and then stripped to an orange solid. Slurrying and washing with $Et_2O$ (8 ml) afforded a yellow powder (274 mg, 96%). Elemental analysis (calculated for $C_{43}H_{47}SO_4P_2Rh \cdot H_2O$): C, 60.97 (61.28); H, 5.82 (5.86)%. $^{31}$P NMR ($CD_3OD$): $\delta$ 54.5 (d, $J_{Rh-P} = 157.0$ Hz). $^1$H NMR ($CD_3OD$): $\delta$ 0.82 (s, 3 H), 1.09 (s, 3 H), 1.30–1.50 (m, 1 H), 1.50–1.60 (m, 1 H), 1.80 (s, 2 H), 1.86 (d, $J = 18$ Hz, 1 H), 1.90–2.10 (m, 2 H), 2.31 (d of m, $J = 18$ Hz, 1 H), 2.41 (d, $J_{H-P} = 28.1$ Hz, 4 H), 2.50–2.70 (m, 1 H), 2.73 (d, $J = 15$ Hz, 1 H), 3.28 (d, $J = 15$ Hz, 1 H), 4.14 (m, 2 H), 5.36 (m, 4 H), 7.50–7.65 (m, 20 H).

### 4.6. [Rh(dppe)(NBD)][(S)-N-acetylphenylalanate] (6)

A solution of dppe (320.2 mg, 0.804 mmol) in $CH_3OH$ (8 ml) was added dropwise to a stirred solution of [Rh((*S*)-*N*-acetylphenylalanate)(NBD)] (323.5 mg, 0.806 mmol) in $CH_3OH$ (8 ml). The resulting orange solution was stirred for 6 h and then stripped to an orange solid. Slurrying and washing with $Et_2O$ (16 ml) afforded a yellow powder (598 mg, 93%). Elemental analysis (calculated for $C_{44}H_{44}NO_3P_2Rh$): C, 67.88 (66.09); H, 5.46 (5.55); N, 0.82 (1.75)%. $^{31}$P NMR ($CD_3OD$): $\delta$ 54.9 (d, $J_{Rh-P} = 157.0$ Hz). $^1$H NMR ($CD_3OD$): $\delta$ 1.80 (s, 2 H), 1.84 (s, 3 H), 2.42 (d, $J_{H-P} = 28.1$ Hz, 4 H), 2.89 (m, 1 H), 3.17 (m, 1 H), 4.16 (m, 2 H), 4.48 (m, 1 H), 5.38 (m, 4 H), 7.10–7.20 (m, 5 H), 7.50–7.65 (m, 20 H).

### 4.7. [Rh(4,4′-dimethyl-2,2′-dipyridyl)(NBD)][(R)-acetylphenylalanate] (7)

A solution of 4,4′-dimethyl-2,2′-dipyridyl (97.0 mg, 0.526 mmol) in benzene (4 ml) was added dropwise to a stirred solution of [Rh((*S*)-*N*-acetylphenylalanate)(NBD)] (**4**, 207.0 mg, 0.516 mmol) causing the formation of a red oily precipitate. This mixture was stirred for 6 h, evapaorated to dryness, washed and slurried in $Et_2O$ (10 ml), and dried in vacuo to afford a red powder (275 mg, 91%). Elemental analysis (calculated for $C_{30}H_{32}N_3O_3Rh \cdot 0.5H_2O$): C, 60.40 (60.61); H, 5.32 (5.59); N, 7.25 (7.07)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.50 (m, 2 H), 1.84 (s, 3 H), 2.53 (s, 6 H), 2.80–2.95 (m, 1 H), 3.10–3.25 (m, 1 H), 4.00–4.10 (m, 2 H), 4.40–4.45 (m, 4 H), 4.45–4.55 (m, 1 H), 7.05–7.20 (m, 5 H), 7.40–7.45 (m, 2 H), 7.55–7.60 (m, 2 H), 8.19 (s, 2 H).

### 4.8. [Rh(dppe)$_2$][(1S)-10-camphorsulfonate] (8)

A solution of dppe (281.9 mg, 0.708 mmol) in $CH_3OH$ (7 ml) was added dropwise to a stirred solution of [Rh((1*S*)-10-camphorsulfonate)(NBD)] (**2**, 150.2 mg, 0.352 mmol) in $CH_3OH$ (4 ml). The resulting orange solution was stirred for 2 h. The volatiles were evaporated and the solid was washed and slurried in $Et_2O$ (15 ml). Drying in vacuo afforded an orange powder (366 mg, 92%). $^{31}$P NMR ($CD_3OD$): $\delta$ 56.4 (d, $J_{Rh-P} = 133$ Hz). $^1$H NMR ($CD_3OD$): $\delta$ 0.82 (s, 3 H), 1.09 (s, 3 H), 1.30–1.50 (m, 1 H), 1.50–1.60 (m, 1 H), 1.87 (d, $J = 18$ Hz, 1 H), 1.90–2.10 (m, 2 H), 2.19 (m, 8 H), 2.31 (d of m, $J = 18$ Hz, 1 H), 2.50–2.70 (m, 1 H), 2.73 (d, $J = 15$ Hz, 1 H), 3.28 (d, $J = 15$ Hz, 1 H), 7.15–7.40 (m, 40 H). X-ray quality single crystals of **8** were grown from a concentrated and filtered THF solution of **5**.

### 4.9. [Rh(dppe)$_2$][(S)-N-acetylphenylalanate] (9)

A solution of dppe (164.4 mg, 0.413 mmol) in $CH_3OH$ (4 ml) was added dropwise to a stirred solution of [Rh((*S*)-*N*-acetylphenylalanate)(NBD)] (**4**, 82.5 mg, 0.206 mmol) in $CH_3OH$ (2 ml). The resulting orange solution was stirred for 6 h and then stripped to an orange solid which was dried in vacuo. Elemental analysis (calculated for $C_{63}H_{60}NO_3P_4Rh \cdot 2CH_3OH$): C, 66.74 (66.72); H, 5.80 (5.86); N, 0.80 (1.20)%. $^{31}$P NMR ($CD_3OD$): $\delta$ 56.3 (d, $J_{Rh-P} = 133$ Hz). $^1$H NMR ($CD_3OD$): $\delta$ 1.84 (s, 3 H), 2.19 (m, 8 H), 2.91 (m, 1 H), 3.19 (m, 1 H), 4.50 (m, 1 H), 7.10–7.45 (m, br, 45 H).

### 4.10. TPPS-H$_3$ (11)

A solution of TPPS-Na$_3$ (1018 mg, 1.791 mmol) in $CH_3OH$ (5 ml) and water (3 ml) was applied to a conditioned DOWEX-50W acid ion exchange column ($d = 1$ cm, $l = 10$ cm, $CH_3OH$) and eluted with $CH_3OH$ (80 ml). The solution was pumped down to a golden syrup and dried in vacuo overnight. Slurrying and washing with $Et_2O$ ($3 \times 15$ ml) and drying in vacuo afforded a white fine powder (800 mg, 87%). Elemental analysis (calculated for $C_{18}H_{15}O_9PS_3$): C, 42.85 (43.03); H, 2.94 (3.01)%. $^1$H NMR ($CD_3OD$): $\delta$ 7.30–7.45 (m, 6H), 7.80–7.90 (m, 6H). The acid protons are not accounted for due to D–H scrambling. $^{31}$P{$^1$H} NMR($CD_3OD$): $\delta$ −5.48 (s), an impurity at 29.0 ppm amounts usually to <5% by integration and is already present in commercial TPPS-Na$_3$.

### 4.11. TPPS-$Tl_3$ (**12**)

A solution of TPPS-$H_3$ (351 mg, 0.694 mmol) in EtOH (8 ml) was added to TlOEt (519 mg, 2.08 mmol) and EtOH (2 ml) causing immediate precipitation of a white solid. The mixture was stirred for 48 h. The white solid was filtered off, washed with EtOH (20 ml), and dried in vacuo affording a fine white powder (730 mg, 95%). Elemental analysis (calculated for $C_{18}H_{12}O_9PS_3Tl_3$): C, 19.66 (19.43); H, 1.13 (1.09)%. $^1$H NMR (DMSO-$d_6$): $\delta$ 7.00–7.15 (m, 3H), 7.30–7.40 (m, 3H), 7.50–7.65 (m, 6H). $^{31}P\{^1H\}$ NMR(DMSO- $d_6$): $\delta$ −6.15 (s), an impurity at 24.6 ppm amounts usually to <3% by integration.

### 4.12. Modified synthesis of (*R*)-*N*,*N*,*N*-trimethyl-1-phenethylammonuim iodide

A solution of $CH_3I$ (3.35 g, 23.6 mmol) in $CHCl_3$ (10 ml) was added to a stirred solution of (*R*)-*N*,*N*-dimethyl-1-phenethylamine (3.16 g, 21.2 mmol) in $CHCl_3$ (20 ml). The resulting solution was stirred for 5 h, pumped down to a colorless foam, washed and slurried in $Et_2O$ (30 ml), and dried in vacuo yielding a white powder (5.89 g, 95%). $^1$H NMR ($CDCl_3$): $\delta$ 1.81 (d, 3 H, $J = 7$ Hz), 3.34 (s, 9H), 5.37 (q, 1 H, $J = 7$ Hz), 7.35–7.45 (m, 3 H), 7.55–7.65 (m, 2 H).

### 4.13. TPPS-tris-(*R*)-(+)-*N*,*N*,*N*-trimethyl-1-phenethylammonuim salt (**13**)

A solution of (*R*)-(+)-*N*,*N*,*N*-trimethyl-1-phenethylammonuim iodide (475.6 mg, 1.633 mmol) in $CH_3OH$ (10 ml) was dropwise added to a stirred white slurry of TPPS-Tl salt (627.3 mg, 0.5436 mmol) in $CH_3OH$ (10 ml). At equivalence point a floculating orange-yellow precipitate formed. The mixture was stirred for 6 h in the dark. The yellow solid was filtered off over celite and extracted with $CH_3OH$ (2 × 5 ml). The combined colorless filtrate was pumped down to an off-white glassy solid which was washed and slurried in $Et_2O$ (2 × 10 ml) and then dried in vacuo yielding a white finely divided powder (520 mg, 96%). Elemental analysis (calculated for $C_{51}H_{66}N_3O_9PS_3$): C, 61.84 (61.73); H, 6.69 (6.70); N, 4.20 (4.23)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.72 (“dt”, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 9 H), 2.96 (s, br, 27 H), 4.69 (q, $J = 7$ Hz, 3 H), 7.25–7.60 (m, 18 H), 7.75–7.90 (m, 9 H), the spectrum indicates the presence of 2 mol% $Et_2O$. $^{31}P\{^1H\}$ NMR($CD_3OD$): $\delta$ −5.61 (s), an impurity at 28 ppm amounts usually to <5% by integration. $[\alpha]_D^{25} = 19.0$ ($c = 1.034$, $C_2H_5OH$).

### 4.14. TPPS-tris-hydroquinidinium salt (**14**)

A solution of TPPS-H3 (328.0 mg, 0.6409 mmol) in $CH_3OH$ (3 ml) was added dropwise to a solution of hydroquinidine (628.2 mg, 1.924 mmol) in $CH_2Cl_2$ (10 ml). The resulting colorless solution was stirred overnight and then evaporated to a glassy solid. Slurrying and washing in $Et_2O$ (10 ml) afforded 860 mg (91%) of a finely divided white powder. Elemental analysis (calculated for $C_{78}H_{93}N_6O_{15}PS_3$): C, 63.15 (63.23); H, 6.41 (6.33); N, 5.66 (5.67)%. $^1$H NMR ($CD_3OD$): $\delta$ 0.85–0.95 (m, 9 H), 1.10–1.20 (m, 3H), 1.50–1.60 (m, 6H), 1.70–1,90 (m, 12H), 2.30–2.40 (m, 3H), 3.05–3.20 (m, 3H), 3.25–3.40 (m, 6H), 3.40–3.60 (m, 3H), 3.80–3.95 (s, br, 12H), 6.03 (s, 3H), 7.30–7.40 (m, 12H), 7.70–7.85 (m, 12H), 7.85–7.95 (m, 3H), 8.65–8.70 (m, 3H). The N–H and O–H protons are not accounted for due to H–D scrambling. $^{31}P\{^1H\}$ NMR($CD_3OD$): $\delta$ −5.69 (s), an impurity at 28.4 ppm amounts usually to <5% by integration. $[\alpha]_D^{25} = 19.0$ ($c = 1.034$, $C_2H_5OH$).

### 4.15. TPPS-tris-(*R*)-*N*,*N*-dimethyl-1-(naphtyl)ethylammonium salt (**15**)

A solution of (*R*)-*N*,*N*-dimethyl-1-(naphtyl)ethylamine (496.0 mg, 2.489 mmol) in $CH_3OH$ (5 ml) was added dropwise to a stirred solution of TPPS-$H_3$ (410.1 mg, 0.8014 mmol) in $CH_3OH$ (5 ml). The resulting solution was stirred for 4 h. The volatiles were removed in vacuo affording a golden oil. Slurrying and washing with $Et_2O$ (2 × 10 ml) afforded a white powder (838 mg, 95%). Elemental analysis (calculated for $C_{60}H_{66}N_3O_9PS_3$): C, 65.05 (65.49); H, 6.03 (6.05); N, 3.89 (3.82)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.72 (d, $J = 7$ Hz, 9 H), 2.70 (s, br, 18 H), 5.25 (q, $J = 7$ Hz, 3 H), 7.20–7.30 (m, 6 H), 7.50–7.65 (m, 9 H), 7.70–7.85 (m, 9 H), 7.90–8.00 (m, 6 H), 8.20–8.30 (m, 3 H). $^{31}P\{^1H\}$ NMR($CD_3OD$): $\delta$−5.55 (s), an impurity at 28 ppm amounts usually to <5% by integration. $[\alpha]_D^{25} = 11.0$ ($c = 2.011$, $CH_3OH$).

### 4.16. TPPS-tris-(*R*)-*N*,*N*-dimethyl-1-phenethylammonuim salt (**16**)

A solution of (*R*)-*N*,*N*-dimethylphenethylamine (372 mg, 2.49 mmol) in $CH_3OH$ (5 ml) was dropwise added to a stirred solution of TPPS-$H_3$ (420.5 mg, 0.8168 mmol) in $CH_3OH$ (5 ml). The resulting solution was stirred for 4 h. The volatiles were removed in vacuo affording a golden foaming oil. Slurrying and washing with $Et_2O$ (2 × 10 ml) afforded a white powder (729 mg, 94%). Elemental analysis (calculated for $C_{48}H_{60}N_3O_9PS_3$): C, 60.74 (60.67); H, 6.40 (6.36); N, 4.40 (4.42). $^1$H NMR ($CD_3OD$): $\delta$ 1.62 (d, $J = 7$ Hz, 9 H), 2.66 (s, br, 18 H), 4.38 (q, $J = 7$ Hz, 3 H), 7.30–7.45 (m, 21 H), 7.80–7.90 (m, 6 H). $^{31}P\{^1H\}$ NMR($CD_3OD$): $\delta$ −5.62 (s), an impurity at 28 ppm amounts usually to <5% by integration. $[\alpha]_D^{25} = 12.7$ ($c = 1.004$, $CH_3OH$).

### 4.17. [Rh(NBD)TPPS$_2$][(R)-N,N-dimethyl-1-(naphtyl)ethylammonium]$_5$ (17)

A solution of TPPS-tris-(*R*)-*N*,*N*-dimethyl-1-naphtylammonuim salt (**15**, 408.5 mg, 0.3712 mmol) in $CH_3OH$ (4 ml) was added dropwise to solid $[Rh(NBD)_2]BF_4$ (69.0 mg, 0.1845 mmol) under stirring affording an orange solution. Addition of $Et_2O$ (16 ml) caused the precipitation of a red oil. Separation by decantation and drying in vacuo afforded a yellow powder which was washed with THF ($2 \times 16$ ml) to remove [TPPS-(naphtylethylammonium-$Me_2H)_3$]$BF_4$ and dried in vacuo. Elemental analysis (calculated for $C_{113}H_{122}N_5O_{18}P_2RhS_6$): C, 62.06 (61.82); H, 5.70 (5.60); N, 3.21 (3.19)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.25 (br, 2 H), 1.73 (d, $J = 7$ Hz, 15 H), 2.75 (s, 30 H), 3.87 (br, 2 H), 4.47 (br, 4 H), 5.38 (q, $J = 7$ Hz, 5 H), 7.30–8.30 (m, 59 H). $^{31}P\{^1H\}$ NMR($CD_3OD$): $\delta$ 29.2 (d, br, $J = 150$ Hz).

### 4.18. [Rh(NBD)TPPS$_2$][BF$_4$][(R)-N,N-dimethyl-phenethylammonium]$_6$ (18)

(RD193) A solution of TPPS-tris-(*R*)-*N*,*N*-dimethyl-1-phenethylammonuim salt (**16**, 527 mg, 0.555 mmol) in $CH_3OH$ (7 ml) was added dropwise to a solution of $[Rh(NBD)_2]BF_4$ (106 mg, 0.284 mmol) in $CH_3OH$ (1 ml). The reaction mixture was stirred for 2 h and then evaporated to an orange glassy solid. Slurrying and washing with THF ($3 \times 10$ ml), followed by high vacuum drying afforded an orange, finely divided solid (550 mg, 91%). Elemental analysis (calculated for $C_{103}H_{128}BF_4N_6O_{18}P_2RhS_6$): C, 56.62 (56.69); H, 5.99 (5.91); N, 3.79 (3.85)%. $^1$H NMR ($CD_3OD$): $\delta$ 1.48 (br, 2 H), 1.65 (d, $J = 7$ Hz, 18 H), 2.68 (s, 36 H), 4.04 (br, 2 H), 4.39 (q, $J = 7$ Hz, 6 H), 4.57 (br, 4 H), 7.35–7.50 (m, 42 H), 7.88 (m, 6 H), 8.08 (br, 6 H). $^{31}P\{^1H\}$ NMR ($CD_3OD$): $\delta$ 29.2 (d, br, $J = 155$ Hz).

### 4.19. Typical catalytic run

A Fischer–Parr reactor was charged in the glove box with the catalyst precursor, the substrate, and the solvent. The reactor was then taken out of the glove box, pressurized to 5 or 6 bar and depressurized three times with hydrogen, and put under 5 or 6 bar of hydrogen pressure. At the end of the reaction the solid was filtered off and the filtrate directly used for HPLC determination. NMR spectra were taken after removing the volatiles.

## 5. Supplementary Material

CCDC 214524 contains the supplementary crystallographic data for compound **8**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

## References

[1] R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley–Interscience, New York, 1994.
[2] D.L. Hughes, D.-H. Dolling, K.M. Ryan, E.F. Schoenewaldt, E.J.J. Grabowski, J. Org. Chem. 52 (1987) 4745.
[3] T. Ooi, M. Kameda, K. Maruoka, J. Am. Chem. Soc. 125 (2003) 5139.
[4] B.M. Trost, D.L. Van Vranken, C. Bingel, J. Am. Chem. Soc. 114 (1992) 9327.
[5] G. Oehme, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous Phase Organometallic Catalysis, VCH–Wiley, Weinheim, 1998.
[6] D.B. Llewellyn, D. Adamson, B.A. Arndtsen, Org. Lett. 2 (2000) 4165.
[7] K. Töllner, R. Popovitz-Biro, M. Lahav, D. Milstein, Science 278 (1997) 2100.
[8] C. Bianchini, E. Farnetti, M. Graziani, J. Kaspar, F. Vizza, J. Am. Chem. Soc. 115 (1993) 1753.
[9] J. van den Broeke, M. Lutz, H. Kooijman, A.L. Spek, B.-J. Deelman, G. van Koten, Organometallics 20 (2001) 2114.
[10] E. Monflier, P. Bourdauducq, J.-L. Couturier, J. Kervennal, A. Mortreux, J. Mol. Catal. A 97 (1995) 29.
[11] Y. Orito, S. Imai, S. Niwa, J. Chem. Soc. Jpn. (1980) 670.
[12] H.-U. Blaser, H.P. Jalett, W. Lottenbach, M. Studer, J. Am. Chem. Soc. 122 (2000) 12675.
[13] T. Heinz, G. Wang, A. Pfaltz, A. Minder, M. Schürch, T. Mallat, A. Baiker, J. Chem. Soc., Chem. Commun. (1995) 1421.
[14] J.M. Bonello, F.J. Williams, R.M. Lambert, J. Am. Chem. Soc. 125 (2003) 2723.
[15] H.-U. Blaser, Tetrahedron: Asymmetry 2 (1991) 843.
[16] Attempts to exchange the sodium ions of the commercially available tetrasodium salt of the diphosphine ligand 1,2-bis(di-4-sulfonatophenylphosphino)benzene in similar ways were not successful.
[17] M. Stradiotto, J. Cipot, R. McDonald, J. Am. Chem. Soc. 125 (2003) 5618.
[18] B.G. van der Hoven, H. Alper, J. Am. Chem. Soc. 123 (2001) 10214.
[19] C. Dai, E.G. Robins, A.J. Scott, W. Clegg, D.S. Yufit, J.A.K. Howard, T.B. Marder, J. Chem. Soc., Chem. Commun. (1998) 1983.
[20] C. Bianchini, D.G. Burnaby, J. Evans, P. Frediani, A. Meli, W. Oberhauser, R. Psaro, L. Sordelli, F. Vizza, J. Am. Chem. Soc. 121 (1999) 5961.
[21] Complexes analogous to **6** and **7** bearing the COD ligand instead of NBD were very sluggish hydrogenation catalysts.
[22] M.J. Burk, J.E. Feaster, W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 115 (1993) 10125.
[23] A. Joy, S. Uppili, M.R. Netherton, J.R. Scheffer, V. Ramamurthy, J. Am. Chem. Soc. 122 (2000) 728.
[24] B.F.G. Johnson, S.A. Raynor, D.S. Shephard, T. Mashmeyer, J.M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden, M.D. Mantle, Chem. Commun. (1999) 1167.
[25] A. Ohno, A. Tsutsumi, Y. Kawai, N. Yamazaki, Y. Mikata, M. Okamura, J. Am. Chem. Soc. 116 (1994) 8133.