Asymmetric Heterogeneous Catalysis

Enhancing the Enantioselectivity of Novel Homogeneous Organometallic Hydrogenation Catalysts**

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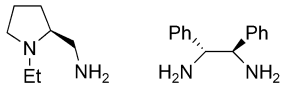
The exigent need to develop new asymmetric hydrogenation catalysts is universally acknowledged, and many new feasible strategies for the design and synthesis of such catalysts continue to be proposed.[1–5] Herein, in addition to describing a new set of efficient, diamino-type ligands for a central rhodium or palladium ion that leads to good enantioselective (*ee*) performance, homogeneously, we also show that significant improvement in the stereoselectivity of the organometallic catalyst may be achieved by heterogenizing it at the inner walls of a mesoporous silica so that advantage is taken of the spatial restrictions imposed by the concave surface at which we have located the active center.

Comparatively few reports have hitherto been published in which Rh^{I} or Pd^{II} complexes without phosphane ligands have been used to activate hydrogen, but a rapidly growing number employing nitrogen containing ligands has appeared of late for the purpose of asymmetric catalysis.[6] One of the incentives for this change is the rather unstable nature and cost of many chiral phosphanes.[6b] It is not, however, the nitrogen-containing ligands that are the key feature of this work. Rather it is the fact that advantage is taken of a concave surface of a silica support, on which the homogeneous organometallic catalyst is tethered, thereby boosting the enantioselectivity to a value higher than that obtained from the same catalyst and the same tether attached to a convex silica support.

The catalysts themselves are pseudo square-planar rhodium(I) or palladium(II) complexes of the bidentate amines: (*S*)-(−)-2-aminomethyl-1-ethyl pyrrolidine **1a** and (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine **1b**, which may readily act as ligands to the metal center. The Rh^{I} catalysts are bonded either to 1,5-cyclooctadiene (COD) or norbornadiene (NBD), whereas for the palladium species we used the allyl (C_3H_5) group as the coordinating alkene. The BF_4^- salts of these organometallic cations are readily handled, air-stable, crystalline materials amenable to X-ray analysis.[7]

For the cations based on **1a** (paired in each case with the BF_4^- anion; see Scheme 1) X-ray structural analysis shows that the square-planar rhodium(I) or palladium(II) center has high steric hindrance. Access to it by a relatively bulky incoming reactant is spatially restricted (see below), and this feature is essential for good enantioselective catalytic behavior.



1a **1b**

Scheme 1. The ligands used in this study.

A fragment of the crystal structure of the Rh^{I} complex with ligand **1a** is shown in Figure 1a, from which it is seen that the BF_4^- anion is hydrogen-bonded to the nitrogen of the amino groups.

By using described procedures[8–12] whereby 3-bromopropyl trichlorosilane serves as a means of anchoring isolated organometallic species to the inner walls of mesoporous silica, we may functionalize an ion-pair of all ligands **1a** and **1b** complexed to metal so as to yield their respective single-site catalysts, as depicted in Figure 1b. We have anchored ligand **1b** to a mesoporous silica (pore diameter 30) and to a nonporous silica (known as cabosil). This permits the comparison of catalytic performance of the organometallic species when it is either at a convex or at a concave siliceous surface (Figure 2). (It is much easier to prepare concave than convex silica surfaces. Since this work began, we have studied a series of silicas in which the pore diameters range from a low of 38 Å to a high of 250 Å; but, to date, the only satisfactory, well-defined convex silica surface that we have been able to investigate is that of the commercial material known as cabosil).

We chose as a test reaction the simple, well-known[12] case of the hydrogenation of *E*-α-phenylcinnamic acid (Scheme 2)

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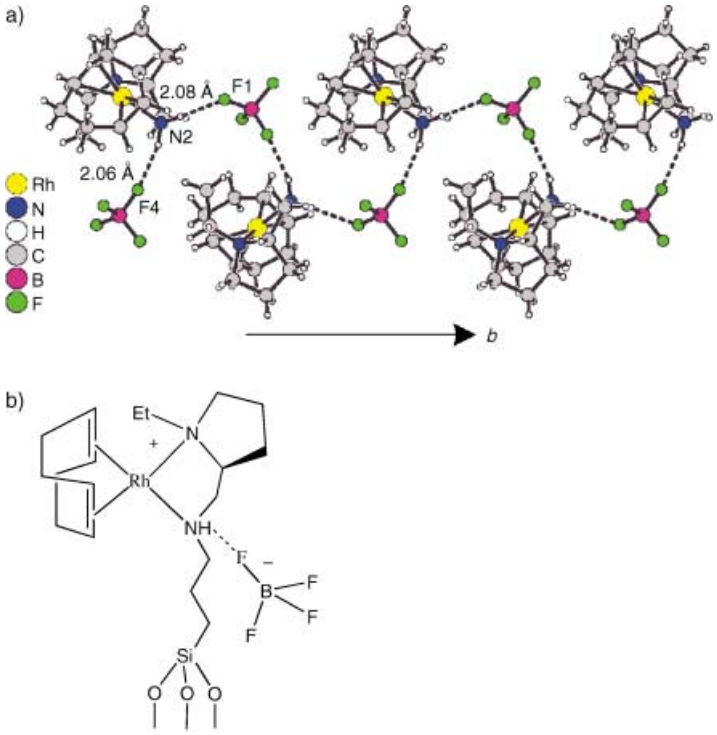


Figure 1. a) Fragment of the crystal structure of the Rh^{I} complex of **1a** illustrating the complex hydrogen-bonded network; the *b* axis is labeled. b) A molecular diagram of the heterogenized single site catalyst.

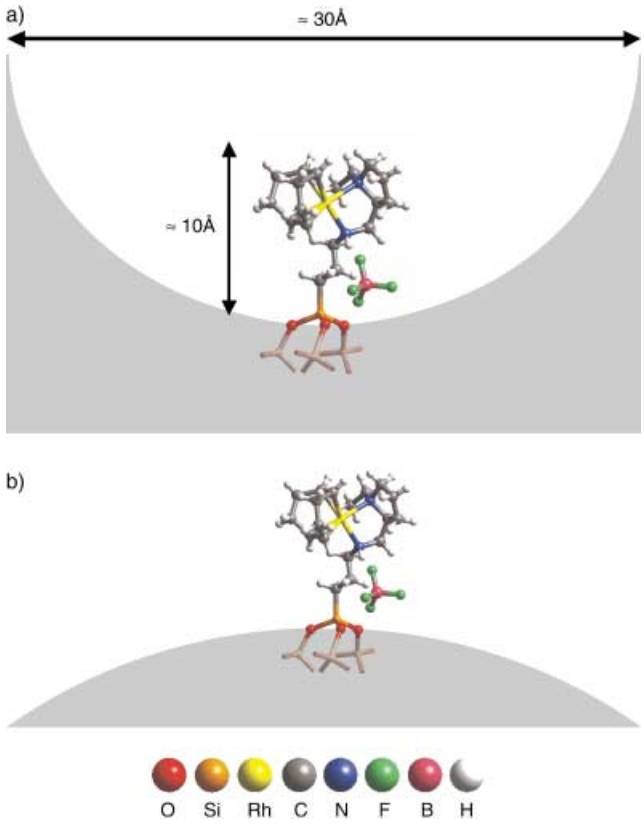
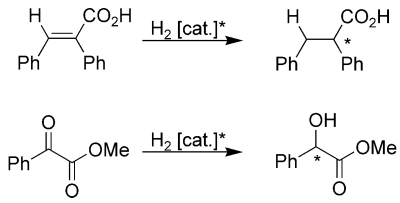


Figure 2. Graphical model (to scale) showing the constraints of the catalyst once anchored on a) MCM-41 (concave) and b) cabosil (convex) surfaces.



Scheme 2. The asymmetric hydrogenation reactions under investigation.

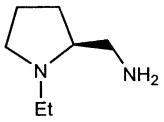
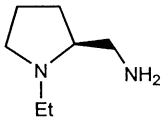
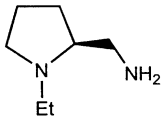
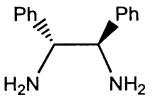
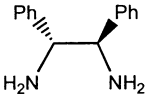
the predominant product being the 2,3-diphenyl propionic acid. We have previously examined[12e] this heterogeneous asymmetric hydrogenation using a Pd diphenylphosphino-ferrocenyl (dppf), tethered catalysts, in which, depending upon the manner of production of the heterogenized catalyst, variable amounts of other products (2,2- and 3,3-diphenylpropionic acids) as well as variable values of *ee* of the 2,3-diphenyl propionic acid were obtained.

Catalytic tests were carried out (see Experimental Section) both on the new Rh^{I} homogeneous catalysts and on their anchored analogues. The homogeneous and heterogeneous palladium complex of ligand **1a** and **1b** where also tested (the crystal structure of the homogeneous catalyst is given as supplementary information). The results are summarized in Table 1. It is to be noted that, in the repeat cycle of experiments (for the case of the heterogenized organometallic catalyst), the *ee* values as well as the conversions and selectivities do not drop significantly in the first and second recycle compared with the respective values for the parent catalyst. This fact, as well as the observation that, compared with the corresponding homogeneous catalyst, there is a significant enhancement of the *ee* value upon heterogenization suggests that the original catalytically active species is the Rh-diamine-diene complex, unlike the situation that seems to prevail in the case of Rh-diphosphane analogues.[13]

Whilst the asymmetric hydrogenation of *E*-α-phenylcinnamic acid was studied to establish proof of principle and to compare with our earlier results[12e] by using tethered Pd-dppf catalysts, we have also investigated another reactant, methyl benzoylformate, that is of considerable commercial value. In this case also the enantioselectivity of the heterogenized organometallic catalyst, for the production of methyl mandelate, at the concave silica surface is much enhanced, (see Table 1) compared to its homogeneous analogue. The improvements in the enantioselective performance of the catalyst clearly demonstrate the benefit of anchoring the catalysts inside the concave surfaces of mesoporous silica. Full details for the reactions are given in recently filed patents.[14]

It is seen that the enantioselectivity achieved with the anchored variants of the catalysts is superior to that achieved with their homogeneous counterparts, (Table 1). Moreover, further evidence to support the view that it is the concavity (and hence restricted access to the active site by the relatively bulky reactants) that is crucial as a determinant of the enhancement of the *ee* value is borne out by the observed

Table 1: The activities, selectivities[a] and enantiomeric excess (*ee*) values for the various homogeneous and heterogeneous catalysts for the hydrogenation of *E*-α-phenylcinnamic acid and methyl benzoylformate.[b]

Amine and diene	Counter-ion	Catalyst	Reaction	Metal	*t* [h]	Conv. [%]	Sel [%].	*ee* [%]
 COD	BF_4^-	homogeneous	α-phenyl cinnamic acid	Rh^I	24	74	77	93
		heterogeneous			24	80	74	96
	BF_4^-	homogeneous		Rh^I	24	95	58	0
		heterogeneous	methyl benzoyl formate		0.25	85	92	92
					1	98	94	91
					24	99	79	80
 NBD	BF_4^-	homogeneous	α-phenyl cinnamic acid	Rh^I	24	88	76	64
		heterogeneous			24	99	66	91
	BF_4^-	homogeneous	methyl benzoyl formate	Rh^I	0.5	85	70	18
		homogeneous 20 °C			0.5	56	59	69
		heterogeneous			2	100	98	99
 allyl	BF_4^-	homogeneous	α-phenyl cinnamic acid	Pd^{II}	24	100	87	76
		heterogeneous			24	93	87	93
	BF_4^-	homogeneous	methyl benzoyl formate	Pd^{II}	2	100	94	0
		heterogeneous			1	96	97	87
					2	97	97	87
 COD	BF_4^-	homogeneous	α-phenyl cinnamic acid	Rh^I	24	57	84	81
		heterogeneous MCM-41			24	98	80	93
		1st recycle			24	90	86	90
		2nd recycle			24	89	84	90
		cabosil			24	95	77	79
 allyl	BF_4^-	homogeneous	α-phenyl cinnamic acid	Pd^{II}	24	95	82	79
		heterogeneous			24	75	100	88

[a] For 2,3-diphenylpropionic acid and methyl mandelate. [b] Also shown is the comparative performance of a heterogeneous catalyst after two recycle experiments for the hydrogenation of *E*-α-phenylcinnamic acid. The heterogeneous analogue of **1b**, where the ligand is anchored onto the commercially available silica (cabosil M5, surface area = 200 $m^2 g^{-1}$), is also given. In all cases the same enantiomer of 2,3-diphenylpropionic acid was formed. Reaction conditions: substrate ≈0.5 g; solvent (methanol) ≈30 mL; homogeneous catalyst ≈10 mg; heterogeneous catalyst ≈50 mg; Pressure = 20 bar; T = 313 K; t = 24 h.

diminished degree of enantioselectivity when a catalyst is anchored to a convex siliceous surface (see Table 1). In the postulated computer graphic models shown (to scale) in Figure 3a and Figure 3b it may be seen that access of the phenylcinnamic acid to the Rh^I ion is favored only when the reactant approaches the active site along the axis of the pore (Figure 3a), whereas no such restrictions exist in the case of the same catalyst anchored at the convex surface.[15]

In previous, similar experiments, on allylic amination, involving catalysts located at the walls of mesoporous silica (e.g., Pd((*S*)-1[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]-ethyl-*N*,*N*′-dimethylethylene-diamine)Cl_2),[8,9,12e] it was the constraints imposed by the space surrounding the metal center (active site) that dominated the enantioselectivity. In the case presented herein, there is a subtle difference; it is the restricted access generated by the concavity of the pore that is the principal determinant. Even though the "capping" cyclooctadiene may be lost during or just prior to the act of catalytic turnover at the Rh^I center, access to the latter of the reactant is nevertheless a key factor, and this is why concavity enhances the catalytic performance observed.[15]

To confirm that the anchored catalysts are truly heterogeneous and that no complications arise from leaching of the organometallic moiety during use, we performed a hot filtration and analyzed the resulting product mixtures (by inductively coupled plasma atomic emission spectroscopy; ICPAES). In a typical reaction at 313 K and 20 bar of H_2 pressure (Table 1), the solid catalyst was filtered from the reaction mixture after 8 h, and the reaction continued for a further 16 h. There was no appreciable change in the conversion of the *E*-α-phenylcinnamic acid during the 16 h period after removal of the solid catalyst, and the product selectivities and enantiomeric excess value were also unaffected. These facts rule out the possibility that colloidal Rh(Pd) or Rh(Pd) black are formed as, if they were, no longer would we observe an enantiomeric excess or essentially unchanged product selectivities.

It is not an easy task to extend the comparison between asymmetric organometallic catalysts tethered on to a range of concave/convex pairs because it is difficult to prepare nonporous convex silicas (like the commercially available cabosil). We have, however, obtained results that confirm the validity of our arguments by using three distinctly different concave silicas.[16]

Experimental Section

All compounds were purchased from Aldrich, unless otherwise stated. The solvents were all predried by using standard methods. The reactions were carried out under an atmosphere of nitrogen by using

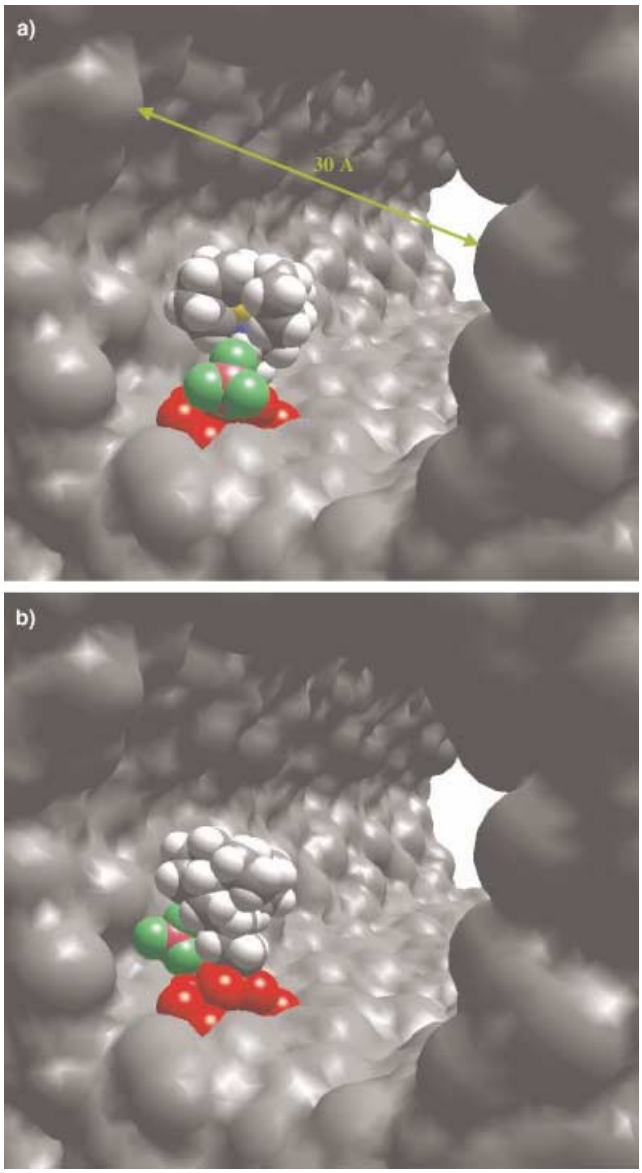


Figure 3. Color portrayal of the anchored Rh^{I}-organometallic -diene, as-prepared catalyst, thus illustrating the hindered access to the metal center because the incoming reactant must approach parallel to the channel (a). When rotation about the C–C bond in the tether occurs so that the Rh^{I} center faces the wall of the pore, as in (b), access to the active site is no longer possible. Whilst it is feasible that some of the diene may be jettisoned during or shortly after hydrogenation, it is not likely that all of it is jettisoned in the original catalyst (as is generally the case in analogous homogeneous catalytic situations) as (I) the repeat cycles (see Table 1) show that catalytic performance is sustained in progressive experiments, and (II) there is a significant enhancement in ee upon anchoring the organometallic catalyst (see text).

standard Schlenk line techniques. All experimental procedures as well as the crystal structures are given in the supporting information, a typical procedure is detailed below. The NMR were performed on a Bruker DPX 500 MHz employing cryo-probe technology.

[Rh(1,5-cyclooctadiene)(1R,2R)-(+)-1,2-diphenylethylenediamine]BF_4: $[RhCl(COD)]_2$ (64 mg, 0.13 mmol) was dissolved in THF (10 mL) to which $AgBF_4$ (50 mg, 0.26 mmol) was added, this solution was stirred for 1 hour at room temperature. The solution was then filtered (to remove AgCl) and (1R, 2R)-(+)-1,2-diphenylethylenediamine (50 mg, 0.26 mmol) was added to the filtrate and the solution left to stir for 1 hour. The resulting solution was slightly concentrated in vacuo and hexane (25 mL) added to precipitate the required product. The product was isolated by filtration and washed with hexane (2 × 20 mL) and diethyl ether (2 × 20 mL) and dried in vacuo giving a yellow powder (185 mg, 90 %). Elemental analysis calcd (%) for $C_{22}H_{28}N_2RhBF_4$: C 51.76, H 5.50, N 5.50; found C 51.44, H 5.57, H 5.29. ^{1}H NMR (CD_3OD): $\delta = 1.95$ (br m, CH_2 4H), 2.46 (br m, CH_2, 4H), 4.01 (s, NCH, 2H), 4.24 (m, CH, 2H), 4.35 (m, CH, 2H), 7.1–7.3 ppm (m, Ph, 10H). ^{13}C NMR (CD_3OD): $\delta = 31.6$ (CH_2), 66.3 (NCH) 81.4 (CH), 128.5, 129.2, 129.6, 140.5 ppm (Ph). ESI (positive ion): 423 [M^+].

Activation of MCM-41: To dry calcined MCM-41 (BET surface area 880 $m^2 g^{-1}$, determined by N_2 adsorption; 2.0 g) in THF (15 mL) dichlorodiphenylsilane (0.48 g, 0.19 mmol) was added and stirred at room temperature for 1 hour (Ph_2SiCl_2) reacts with external Si-OH moieties[10–11] and ensures all proceeding silane species reacts at the internal surface of MCM-41). The solution was then cooled to −78 °C and 3-bromopropyltrichlorosilane (1.10 g, 4.8 mmol) was added. This mixture was allowed to slowly warm up to room temperature and stirred for a further 8 h. The resulting solution was heated at 50 °C for 1 hour. The MCM-41 was filtered and purified by soxhlet extraction with THF and finally dried in vacuo. Elemental analysis found (%): C 4.70, H 0.87, Br 2.14. ^{29}Si CP MAS NMR indicated significant loss of Si–OH moieties indicating grafting had occurred, the XRD of the resulting MCM-41 was analogous to the pure MCM-41 showing no loss of structure occurred.

Tethering with (1R,2R)-(+)-1,2-diphenylethylenediamine: The activated MCM-41 (500 mg) was heated to reflux in THF (15 mL) together with the amine (150 mg) for 24 h. After this time the MCM-41 was filtered and purified by soxhlet extraction with THF and finally dried in vacuo. Elemental analysis found (%): C 9.72, H 1.92, N 0.15, Br 1.30. IR $\tilde{\nu} = 3205$ cm^{-1} broad (weak), N–H stretch. Powder XRD indicated no loss in the structure of the mesopore during this process.

Addition of rhodium: In a Schlenk $[RhCl(COD)]_2$ (30 mg, 0.06 mmol) and $AgBF_4$ (30 mg, 0.12 mmol) were dissolved in THF (10 mL) and stirred for 1 hour. The solution was filtered and the tethered MCM-41 was added to the filtrate and stirred for 4 h during which time the solution became pale and the solid became yellow. This pale yellow solid was filtered and washed with THF (4 × 20 mL), CH_2Cl_2 (4 × 20 mL) and dried in-vacuo. **3b**: C 11.23, H 2.02, N 0.12, Br 1.22. ^{19}F MAS NMR indicated the presence of BF_4^- $\delta = -152.0$ ppm (reference $CFCl_3$), in solution $\delta = -154$ ppm. Powder XRD only showed peaks that correspond to MCM-41 implying that the rhodium is highly dispersed inside MCM-41.

Catalysis procedure: The catalytic reactions (enantioselective hydrogenations) were carried out in a high-pressure stainless-steel catalytic reactor (100 mL) lined with poly ether ether ketone (PEEK). The homogeneous catalyst (10 mg or 50 mg of the mesoporous silica anchored heterogeneous catalyst), which was previously evacuated and stored under inert conditions (nitrogen or argon), was transferred under an inert atmosphere to the catalyst delivery unit, which was subsequently sealed and introduced to the high-pressure reactor (by using dry helium).

The substrate {(E)-α-phenyl cinnamic acid or methyl benzoylformate} (0.5 g), solvent (methanol, 30 g) and a suitable internal standard (cyclododecane) were then introduced into the reactor and the reactor was sealed. The reactor as well as the inlet and outlet ports were purged with dry nitrogen (three times) prior to the introduction of hydrogen (5 bar). A leak test was carried out and the reactor was then pressurized to 20 bar with hydrogen. The reactor was then heated to the desired temperature (313 K) and the contents were stirred with a mechanical stirrer at 400 rpm. (In the cases in which kinetic and rate effects were studied, a minirobot liquid-sampling valve was employed to remove small aliquots of the sample without perturbing the pressure in the reactor).

At the end of the reaction, the heating was turned off the contents of the reactor were cooled (quenched). The reactor was then depressurized. A mass-balance calculation was made at this stage to check for handling and weight losses. The products were analyzed (with a suitable internal standard) by gas chromatography (GC; Varian, Model 3400 CX) employing a HP-1 capillary column (25 m × 0.32 mm) and flame ionization detector with a variable ramp temperature program from 433 K to 493 K, for cinnamic acid. The identities of the products were first confirmed by using authenticated standards and their individual response factors were determined with a suitable internal standard (calibration method). The conversions and selectivities were determined as defined by the following equations and the yields were normalized with respect to the response factors obtained as above:

Conversion % = [(moles of initial substrate − moles of residual substrate)/(moles of initial substrate)] × 100 Selectivity % = [(moles of individual product)/(moles of total products)] × 100

The products were further identified by NMR spectroscopy (^{1}H and ^{13}C in CD_3OD) which showed the loss of the C=C and the gain of a C−C moiety for cinnamic acid and for methyl benzoyl formate a loss of a C=O and a gain of a C−O environment. The enantioselectivity values (*ee*) (for cinnamic acid) were first determined by GC (Hewlett Packard {HP 5890}) with a chiral column {gamma-cyclodextrin dialkyl (Chiraldex) (20 m × 0.25 mm)} and the identities of the chiral products were further confirmed by LC–MS (Shimadzu LCMS-QP8000) equipped with a chiral detector (OR-990, JASCO), again, with a chiral column (CHIRALCEL OJ-R, DAICEL). Enantiomeric excess values were calculated from the peak areas of the enantiomers by using the following formula:

$$ee = ([R] - [S]) \times 100/([R] + [S])$$

Finally, as a further confirmation, the products were isolated from the reaction mixture and esterified to the methyl ester by the following procedure: Boron trifluoride (14 %, 2 mL) in methanol was added to a glass vial containing the sample to be esterified (300 μL), the vial was sealed with a teflon-lined stopper and heated for 1 h at 353 K. The sample was cooled to room temperature and Milli-Q purified water (2 mL) was added with mild shaking. HPLC grade dichloromethane (2 mL) was added before the analysis, which was again performed on the LC–MS (Shimadzu LCMS-QP8000) with the same chiral column (CHIRALCEL OJ-R, DAICEL).

The *ee* values for methyl mandelate were determined by Bayer AG Leverkusen Germany.[14]

Since this work was carried out we have further tested and explored[17] a new method, described by Rege et al.,[18] of anchoring homogeneous catalysts on to high-area supports through the use of the triflate anion. For that purpose two entirely new ligands and (for comparison) two of the ones reported here were used to produce the Rh^I-based asymmetric hydrogenation catalysts. This method is very convenient and it also produces superior heterogeneous asymmetric catalysts than their homogeneous analogues.

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[7] *Crystallographic data:* **1a Rh COD** complex $C_{15}H_{28}BF_4N_2Rh$, $M = 426.11\ g\,mol^{-1}$, yellow prisms $0.28 \times 0.14 \times 0.07$ mm, monoclinic, $a = 9.1422(2)$ Å, $b = 10.8050(4)$ Å, $c = 9.3369(3)$ Å, $\beta = 110.243(2)°$, $V = 865.34(5)$ Å^3, $T = 180(2)$ K, space group $P2_1$, $Z = 2$, 5542 reflections collected, 3400 independent reflections ($R_{int} = 0.0286$), refinement method: full matrix least squares on F^2, final $R_1 = 0.0254$, $wR_2 = 0.0588$, GOF = 1.125. **1a Rh NBD** complex $C_{14}H_{24}BF_4N_2Rh$, $M = 410.07\ g\,mol^{-1}$, yellow prisms $0.25 \times 0.12 \times 0.12$ mm, orthorhombic, $a = 9.3033(2)$ Å, $b = 10.4587(3)$ Å, $c = 16.7856(5)$ Å, $\beta = 90°$, $V = 1633.25$ Å^3, $T = 180(2)$ K, space group $P2_12_12_1$, $Z = 4$, 9724 reflections collected, 3359 independent reflections ($R_{int} = 0.1154$), refinement method: full matrix least squares on F^2, final $R_1 = 0.0591$, $wR_2 = 0.1278$, GOF = 0.991. **1a Pd** complex $C_{10}H_{21}BF_4N_2Pd$, $M = 362.50\ g\,mol^{-1}$, clear prisms $0.30 \times 0.18 \times 0.12$ mm, orthorhombic, $a = 8.0393(3)$ Å, $b = 12.8833(4)$ Å, $c = 13.8562(5)$ Å, $\beta = 90°$, $V = 1435.12(9)$ Å^3, $T = 180(2)$ K, space group $P2_1$, $Z = 2$, 8364 reflections collected, 3190 independent reflections ($R_{int} = 0.0319$), refinement method: full matrix least squares on F^2, final $R_1 = 0.0303$, $wR_2 = 0.0700$, GOF = 1.032, crystallographic data is available in the .cif format. CCDC-193929 (**1a Rh COD**), CCDC-193930 (**1a Rh NBD**), and CCDC-203770 (**1a Pd**) contain the supplementary crystallographic data for this paper. 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.ac.uk).

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[15] Accepted theory amongst experts in homogeneous catalysis states that the diene (in this case COD or NBD) are no longer present in the catalyst when it facilitates hydrogenation. But if this were true the catalytic performance of a given organometallic complex would be independent of the initially coordinated diene. This is patently not the case—see Drexler et al.,[15a] where Rh^{I} hydrogenation catalysts exhibit a thousand fold difference in reactivities on replacing the COD by NBD. In the critical act of catalysis, possibly even homogeneously, but certainly heterogeneously, under the conditions that we employ, the diene may still be implicated.[13] This is why we have depicted the as-prepared heterogeneous catalyst in Figure 3a and 3b; a) H. J. Drexler, W. Baumann, A. Spannerberg, C. Fisher, D. Heller, *J. Organomet. Chem.* **2002**, *621*, 89.
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