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PAPER

Development of homogeneous and heterogenized rhodium(I) and palladium(II) complexes with ligands based on a chiral proton sponge building block and their application as catalysts†

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Chiral compounds prepared from proton sponge building block 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine were found to be effective chiral ligands for obtaining complexes of rhodium(I) and palladium(II) by reaction with $[RhCl(cod)]_2$, $PdCl_2(cod)$ or $Pd(OAc)_2$. The complexes bearing triethoxysilane groups were immobilized on mesoporous MCM-41 in order to obtain new heterogeneous catalysts. Both materials are active in the hydrogenation of alkenes and could be recycled without loss of activity or enantioselectivity.

Introduction

Heterogenization of homogeneous single-site catalysts on solid support materials allows combination of the superior activity and selectivity of homogeneous with the simple recovery of heterogeneous catalyst. Heterogenized catalysts can also be used in fixed- or flow-bed reactors, which additionally simplify process development. Therefore, such systems have been extensively studied during the past two decades.[1]

Active centers may be immobilized in several ways, depending on the binding between active center and support. The family of the silicon based porous MCM materials,[2] led to new paths for the reaction between suitable precursors with the Si–OH groups in the internal walls of the large surface of the hexagonally ordered parallel channels. The applications of the resulting inorganic materials containing active sites are important in different fields, ranging from catalysis to optoelectronics.[1,3] Typical approaches for such reactions include direct grafting, where a functionalized complex reacts with the OH groups, or tethering where a step by step route is followed, starting by reaction between the walls and a functionalized organic molecule (ligand) which then binds the metal center.[4]

1,8-bis(dimethylamino)naphthalene (**1**) introduced by Alder[5] and sold by Aldrich as "Proton Sponge®" it is not only the best-known compound of its type but is inexpensive and straightforward to derivatise. While **1** has a high affinity towards H^+, it is indifferent to other electrophiles, which is in contrast to usual nitrogen bases. Some examples of reactivity of **1** apart from routine protonation include, somewhat surprisingly, its role as a hydride donor in its reaction with *mer*-$RhCl_3(dmso)_3$ or $[RuCl(dppb)]_2$(**l-Cl**)$_3$,[6] with fluoroalkyl complexes of iridium,[7] or with $B(C_6F_5)_3$[8] to form the 1,1,3-trimethyl-2,3-dihydroperimidinium cation (TMP^+). There is also a single example of a metal complex coordinating (directly) to **1**, (*via* the amino groups); the reaction with $Pd(hfac)_2$ (hfac: hexafluoroacetylacetonate) immediately generates a poorly-characterized charge-transfer product, which after standing for a week forms the cationic complex $[Pd(hfac)(\mathbf{1})]^+$.[9] The hfac ligand may be substituted for β-diketones and one of these complexes was structurally characterized; coordination causes severe distortion of the proton sponge, the N· · ·N distance opening to 2.94 Å from 2.51 Å. The proton sponge ligand is easily displaced in this complex, even by water. **1** can also act as a weak *carbon* nucleophile, but only in the presence of exceptionally reactive electrophiles.[10] Other examples for proton sponges include 4,9-dichloroquino[7,8-*h*]quinoline (**2**),[11] 1,8- bis(*N*,*N*,*N*,*N*-tetramethylguanidino)naphthalene (**3**)[12] and chiral, atropisomeric, binaphthyl substituted 1,8-bis(dimethylamino)naphthalene derivatives (**4**) in the racemic as well as enantiopure states.[13] Recently, the transition metal complexes of the proton sponge 2 [14] and 3 [15] were reported.

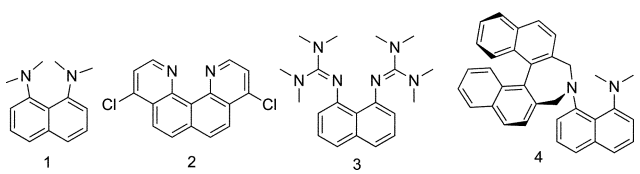

Chart 1

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Several years ago, the formation of a diaminoacetal was reported by condensation of 1,8-diaminonaphthalene with the chromium tricarbonyl complex of benzaldehyde[16] and the synthesis of a Pd complex with a pincer ligand obtained *via* a condensation of isopthalic dicarboxaldehyde and 2 equiv. of 1,8-diaminonaphthalene.[17] The aim of this study is to gain insight into the effects of the ligand properties such as the rigidity or flexibility of chiral chelating ligands and the influence of donor atoms in determining the asymmetric induction in the catalytic process. Specifically, to establish the relation between regioselectivity, induced by chiral chelate ligands in the catalytic process to involve each conformational isomer in the solution, and the enantiomeric excess of the product. We believe that the potential of this chiral building block to influence asymmetric transformations should be investigated. As part of an ongoing project on the design and synthesis of ligands for asymmetric catalytic reactions, we developed a modular synthetic strategy for preparing new ligands based on 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine (type **(*R*,*R*)-A** or type **(*R*,*R*)-B** in Fig. 1). Nitrogen atoms from pyridine, amine or imine moieties are different electronically and are assumed to provide different binding properties to transition metals. Although pyridine is a strong electron-donating ligand, the delocalized π-system provides a tool for tuning the electronic nature of this moiety with substituents. While the different donor abilities of the pyridine, phenol, amine or imine groups can serve as an electronic differentiator for transition metal-catalyzed asymmetric reactions, the *trans*-2,5-disubstituted pyrrolidine moiety can provide a chiral influence for asymmetric discrimination on prochiral substrates.

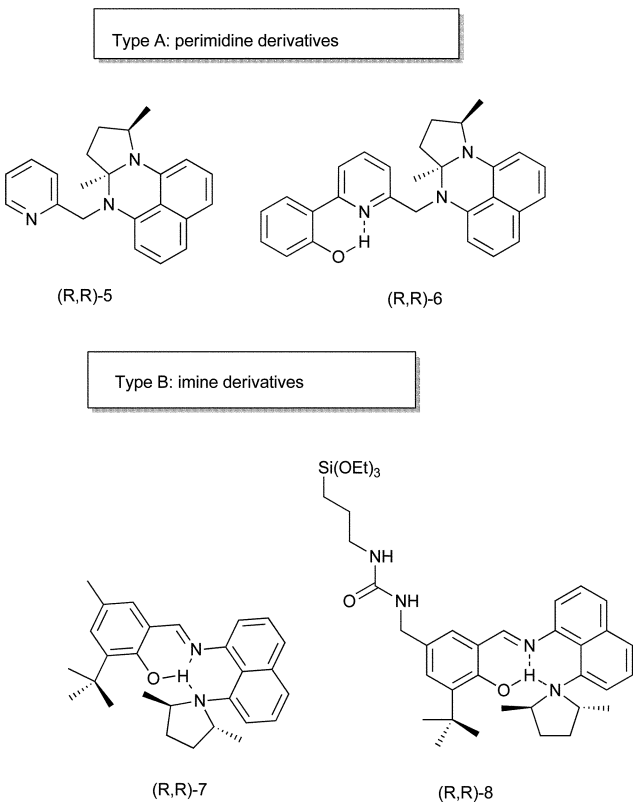


Fig. 1 Chiral perimidine and imine ligands.

Recently, we have shown that complexes with anionic linear Schiff ligands (Chart 2, (a)) have excellent catalytic activity in several reactions.[18] On the other hand, we have also developed a series of novel conformationally restricted ONN-Pincer-type ligands (Chart 2, (b)) resembling coordination environments present in Schiff-base ligands.[19] To study the scope and efficiency of these systems, we modified the substituents on the pyridine ring or on the imine group to create different electronic properties. Herein we report the syntheses, characterization and reactivity of rhodium and palladium complexes with chiral perimidino **(*R*,*R*)-5**, **(*R*,*R*)-6** (Fig. 1, type A), and imino derivatives **(*R*,*R*)-7**, and **(*R*,*R*)-8** (Fig. 1, type B). These compounds were obtained *via* condensation of an aldehyde and the chiral building block (proton sponge precursor) 8-((*R*,*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine that exhibit unusual structures and interesting reactivity. These complexes and their respective heterogenized complexes on MCM-41 were shown to be effective catalysts for enantioselective hydrogenation.

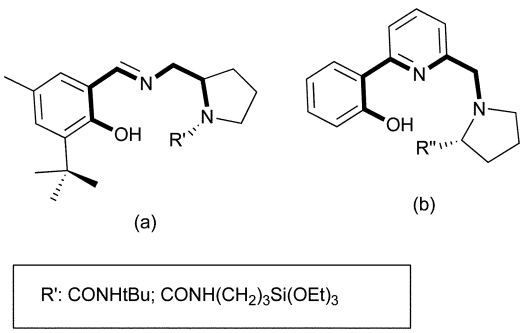


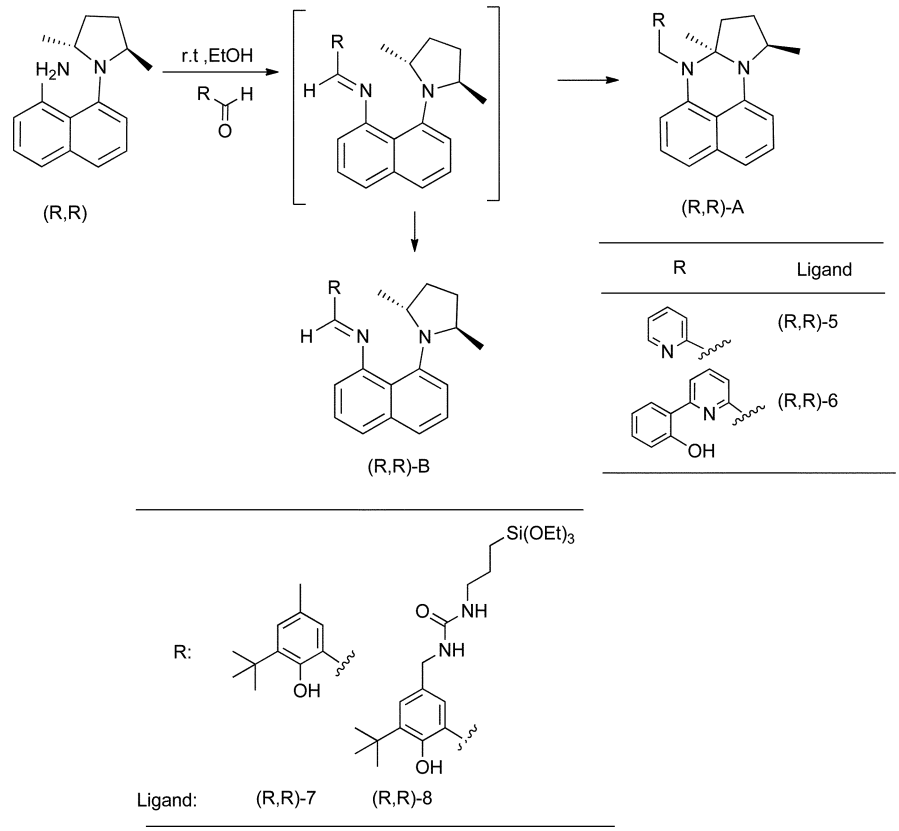
Chart 2

Results and discussion

Synthesis of ligands from 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine

Several groups[20] including those of Alder,[21] Staab,[22] Pozharskii[23] and Lloyd-Jones[24] have investigated and derivatized the proton sponge 1,8-bis(dimethylamino)naphthalene. We have used 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine as a precursor to obtain new chiral ligands. This precursor has been derivatized by reaction with different aldehydes in order to obtain pincer-type ligands containing such functionality. Treatment of different aldehydes (depicted in Scheme 1) with 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine, in ethanol at room temperature in the presence of molecular sieves (4 Å), gave compounds of type **(*R*,*R*)-A** or **(*R*,*R*)-B** (Scheme 1) in moderate to good yield (40–70%). All new compounds have been characterized by ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and ESI mass spectrometry (see experimental).

Initially, we expected an imino compound as a product in all cases. However, the ^{1}H-NMR spectra of type **(*R*,*R*)-A** compounds obtained from pyridine-2-carbaldehyde and 6-(2-hydroxyphenyl)pyridine-2-carbaldehyde did not match with the NMR spectra of the expected imino compounds, as we could see the signals of diastereotopic CH_2-N groups as ABXY system at δ 4.82, 4.57 (**(*R*,*R*)-5**), and 4.70, 4.45 (**(*R*,*R*)-6**) ppm. Thus, we suspected that the products type **(*R*,*R*)-A** were not imino compounds.



Scheme 1 Condensation products of 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine with different aldehydes.

Single crystal X-ray diffraction studies have been performed on **(*R*,*R*)-6**. Fig. 2 shows the molecular structure with the atomic numbering. Crystal data and structure refinement details of **(*R*,*R*)-6)** are given in Table S1.† Each structure consists of a central pyridine ring that is substituted at its 2-position by a phenol group and at its 6-position by an amine-containing CH_2(7a*R*,10*R*)-7a,10-dimethyl-7a,8,9,10-tetrahydro-7*H*-pyrrolo[1,2-a]perimidine) unit. The amine group is inclined essentially orthogonal to the plane of the adjacent pyridyl unit. The phenol moieties are almost co-planar with respect to the pyridine unit [tors.: C(17)–C(16)–C(15)–N(3) –4.7 (3)] and are disposed mutually *cis* as a result of a hydrogen bonding interaction between the phenol hydrogen atom and the neighboring pyridine nitrogen [N(3)–H(1) 1.852(2) Å; O(1)–N(3) 2.576(2) Å]. The *ipso* carbons, C(1) and C(7), deviate slightly from the naphthalene plane 0.032(6) and 0.081(6) Å, respectively. The torsion angle between C(7)–N(2) and C(1)–N(4) is 7.0 (2)°. The N(1)–N(2) distance (2.378(3) Å) is shorter than an idealized value, 2.51 Å. This distortion of N::N could come from the stress caused by the cyclisation. When we use **5** and **6** as chiral chelate ligands, the nitrogen atom N(1) is not in the direction of metal atom and the metal is far away. Thus, **5** and **6** act as chiral N,N or N,N,O ligands, not as N,N,N- or N,N,N,O ligand. The mass spectra of **6** reveal protonated molecular ion peak.

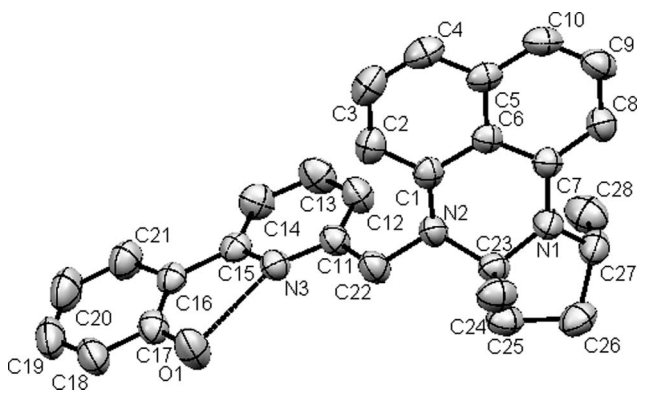
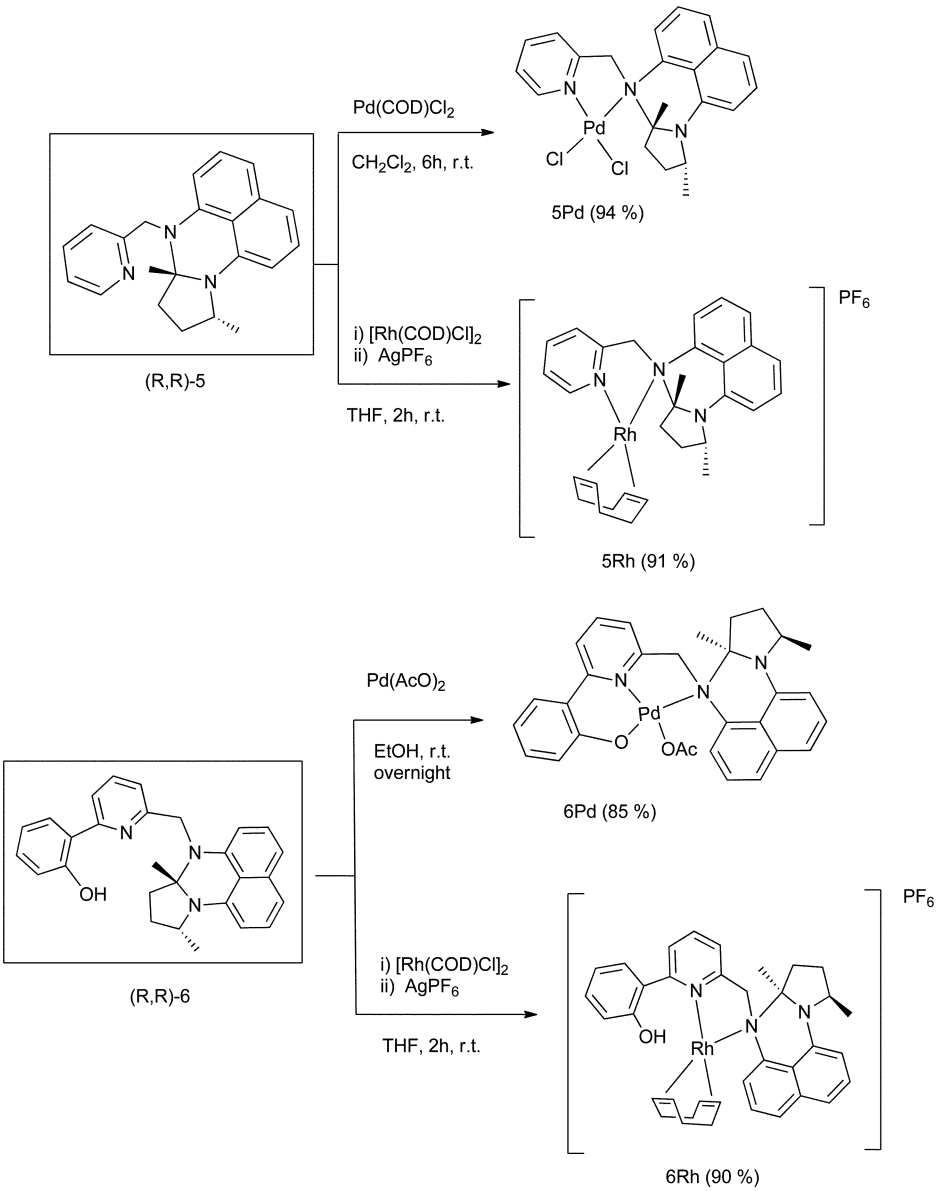


Fig. 2 Molecular structure of **(*R*,*R*)-6**.

Treatment of 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde or *N*-(3-*tert*-butyl-5-formyl-4-hydroxyphenylcarbamoyl)-4-(triethoxysilyl)butanamide and 8-[(2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl]naphthalen-1-amine in ethanol gave **(*R*,*R*)-7** and, **(*R*,*R*)-8**, imino ligands (type **(*R*,*R*)-B)**, as yellow oils in good yields. Mass spectrum of **(*R*,*R*)-7** reveals protonated molecular ion peak while in their IR spectra absorption bands characteristic for their imino functionalities (*ca.* 1618 cm^{-1}) are evident. In their ^1H NMR spectra, the imine compounds gave a singlet at δ 8.26 (**(*R*,*R*)-7**), 8.32 (**(*R*,*R*)-8**) consistent with the presence of CH═N protons, phenol hydrogen atom appears at low field, as a broad singlet at δ 13.86 ppm (**(*R*,*R*)-7**), 14.11 ppm (**(*R*,*R*)-8**), these values suggest that the proton is coordinate between the two nitrogen atoms and the oxygen atom is inside the structure, stabilizing the imino compounds and prevent the cyclization.

To support the spectroscopic data, crystals of **(*R*,*R*)-7** have been the subject of single crystal X-ray diffraction studies. A perspective view is depicted in Fig. 3; crystal data and structure refinement



Scheme 2 Synthesis of perimidine-complexes.

details of **(*R*,*R*)-7** are given in Table S2.† The di amine group is inclined essentially orthogonal to the plane of the phenol unit (46.80°). There is a hydrogen bonding interaction between the phenol hydrogen atom, the neighboring imine nitrogen [N(2)–H(1) 1.850(3) Å; O(1)–N(2) 2.591(3) Å)] and the amine group [N(1)–N(2) 2.756 Å; N(1)–H(1) 2.940(3) Å]. The *ipso* carbons, C(1) and C(3), deviate slightly from the naphthalene plane 0.110 and 0.021 Å, respectively. The torsion angle between C(1)–N(1) and C(3)–N(2) is −13.4 (2)°. In this case the N(1)–N(2) distance (2.756(4) Å) is larger than an idealized value, 2.51 Å. The stereochemistry of **(*R*,*R*)-7** is the same as that of 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine, as expected, **(*R*,*R*)-7** and **(*R*,*R*)-8** act as tridentate ligands when coordinated to metals.

In both families, the absolute configuration of asymmetric carbons is maintained throughout the process; starting from a configuration R we obtain a configuration R.

Synthesis of rhodium and palladium complexes

Several complexes incorporating **(*R*,*R*)-5**, **(*R*,*R*)-6**, **(*R*,*R*)-7**, and **(*R*,*R*)-8** as ligands were prepared by standard methods (Schemes 2, 3).

The reactions of **(*R*,*R*)-5** and **(*R*,*R*)-6** with [Pd(cod)Cl_2] or $Pd(AcO)_2$ were carried out at room temperature in CH_2Cl_2 or EtOH solution in a 1 : 1 complex : ligand ratio. The products, [Pd(L*)X], **5Pd**, **6Pd** (L* = **(*R*,*R*)-5**, X = Cl_2; **(*R*,*R*)-6**, X = OAc), were obtained in almost quantitative yields as stable brown solids by careful precipitation from pentane; which later underwent elemental analysis, ESI-MS and ^{1}H- ^{13}C NMR spectroscopy. Thus, the ESI-MS spectra of **5Pd** and **6Pd** show the peaks from the fragments due to elimination of the ion chloride [M^+ - Cl] (471.3 for **5Pd**) or acetate [M^+-OAc] (585.5 for **6Pd**). All assignments were confirmed by good agreement between the observed and calculated isotopic distributions. The absence of the ν(OH) band

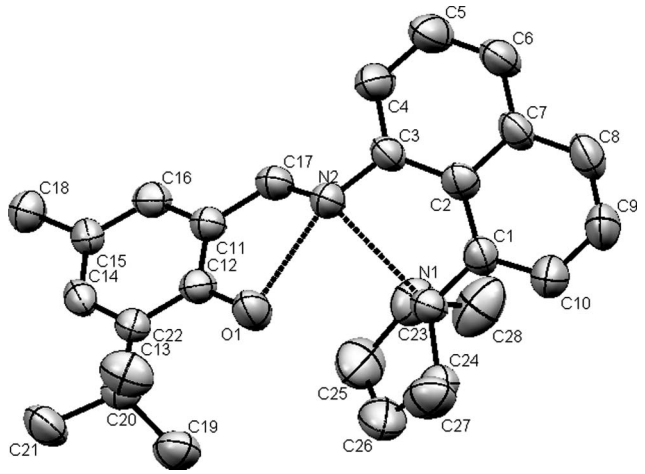
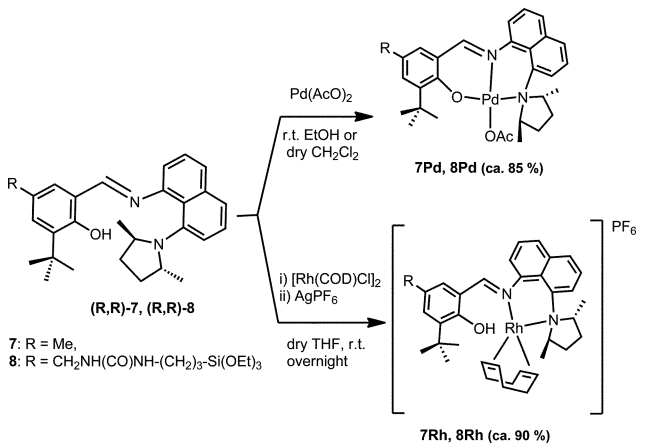


Fig. 3 Molecular structure of **(*R*,*R*)-7**.



Scheme 3 Synthesis of imino-complexes.

(present in the spectra of the free ligand **6** at ~3430 cm^{-1}) is in accordance with loss of the -OH proton. The IR spectrum of **6Pd** also shows strong bands at 1290 and ~1600 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for monocoordinate acetate ligands.[25] New bands at 555 cm^{-1} are ascribed to ν(Pd–O) (**6Pd**).

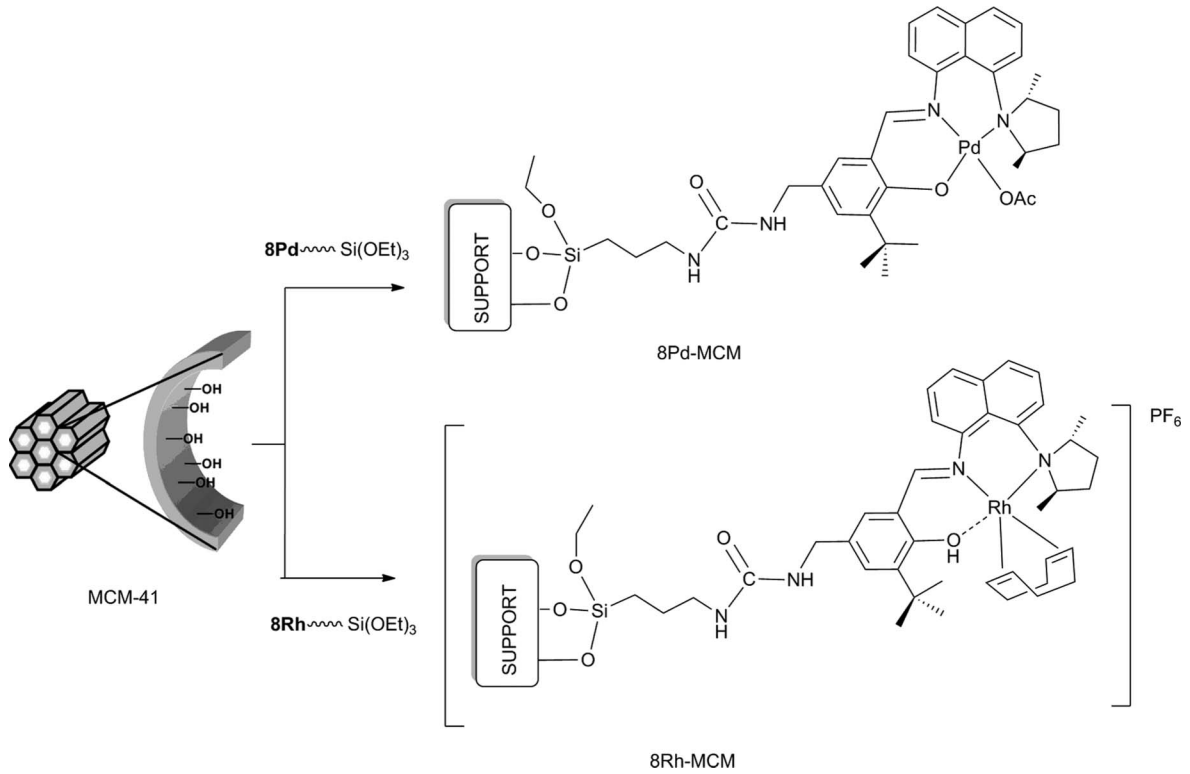
Diamagnetic palladium complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopies. All assignments are based on several correlations in the 2D spectra. They are fully consistent with the structures depicted in Scheme 2. In all cases, the spectra show the simultaneous occurrence of two sets of signals which are attributable on the one hand to the substituted pyridine entity and on the other hand to the amine sponge derivative part of the ligand. In the ^{1}H NMR spectra all the resonances were high field shifted as compared to the uncoordinated ligand and they were in agreement with metallation of the ligand with coordination of the metal atom *via* the pyridine nitrogen atom. Deprotonation of the –OH group was confirmed by the absence of OH resonance in the ^{1}H spectrum. The ^{1}H NMR spectrum shows the signal of the *Me*COO protons as a singlet at $\delta = 1.88$ ppm (**6Pd**). The ^{13}C NMR spectrum of **6Pd** showed the signals assigned to the OAc group.

The cationic complexes, [Rh(cod)(L*)]PF_6, (**5Rh,6Rh**) (L* = **(*R*,*R*)-5**, **(*R*,*R*)-6**), were synthesized by the reaction of $[RhCl(cod)]_2$ with a stoichiometric amount of solid $AgPF_6$ and, subsequently after 1 h the corresponding L*-chiral ligand, in THF solution. Filtration through Celite and evaporation of the solvent yielded a solid product, which was recrystallized by careful addition of diethyl ether. The experimental data allowed us to establish that both **(*R*,*R*)-5** and **(*R*,*R*)-6** ligand act, in the formation of complexes, as chelating ligands. In the ^{1}H NMR spectra the cyclooctadiene resonances are observed as four broad lines between 1.8 and 4.8 ppm due to fluxionality in the conformation of the cyclooctadiene chelate. Complexes exhibit four signals in their ^{13}C spectra attributable to the carbon atoms of the cod ligand. Elemental analysis and the ESI-MS spectra (540.3 for **5Rh** and 632.3 for **6Rh** corresponding to [M^+ - PF_6]) are consistent with the proposed formulation shown in Scheme 2, but a single crystal structure has not yet to be obtained. The –OH group deprotonation was not observed for rhodium complex with ligand **6**, the infrared spectrum presents a signal corresponding to ν(OH) at 3443 cm^{-1}.

The reactions between the imino compounds **(*R*,*R*)-7** or **(*R*,*R*)-8** with $Pd(OAc)_2$ were carried out at room temperature in EtOH solution, respectively, in a 1 : 1 complex : ligand ratio. The products, [Pd(L*)(OAc)], **7Pd**, **8Pd** (L* = **(*R*,*R*)-7**, **(*R*,*R*)-8**) were obtained in almost quantitative yields as stable solids (Scheme 3). These complexes were characterized by electro-spray mass spectrometry. Thus, the ESI-MS spectrum of **7Pd** shows the peak from the fragment due to elimination of the acetate at *m*/*z* 519.3 [M^+-OAc]. All assignments were confirmed by good agreement between the observed and calculated isotopic distributions. In **7Pd**, the absence of the ν(OH) band (present in the IR spectrum of the free ligand **(*R*,*R*)-7** at ~3430 cm^{-1}) is in accordance with loss of the –OH proton. The IR spectrum showed a band at 1585 cm^{-1} assigned to coordinated C═N, about 30 cm^{-1} less than the free ligand, as expected for coordination of the imine. The IR spectrum also shows strong bands at 1320 and 1650 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for monocoordinate acetate ligands.[25] A new band at 541 cm^{-1} is ascribed to ν(Pd–O) for **7Pd**.

Diamagnetic palladium complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy. All assignments are based on several correlations in the 2D spectra. They are fully consistent with the structures depicted in Scheme 3. In all cases, the spectra show the simultaneous occurrence of two sets of signals which are attributable on the one hand to the substituted pyridine entity and on the other hand to the amine sponge derivative part of the ligand. In the ^{1}H NMR spectra all the resonances were high field shifted as compared to the uncoordinated ligand and they were in agreement with metallation of the ligand with coordination of the metal atom *via* the pyridine nitrogen atom. In the ^{1}H NMR of both **7Pd** and **8Pd**, the absence of the OH resonance indicates the deprotonation of the –OH group. The ^{1}H NMR spectrum of **7Pd** showed a singlet at 7.99 due to imine proton shifted upfield 0.27 ppm compared with the free ligand. Also, the acetate group was observed as a singlet at 1.34 ppm. The ^{13}C NMR spectrum of **7Pd** showed the imine carbon at δ 153.7 ppm (160.4 ppm for **8Pd**) and two signals for acetate at δ 29.7 and 197.1.

Cationic complexes, [Rh(cod)(L*)]PF_6, (**7Rh, 8Rh**) (L* = (*R*,*R*)-**7** and (*R*,*R*)-**8**), were synthesized by the reaction of $[RhCl(cod)]_2$ with a stoichiometric amount of solid $AgPF_6$ and, subsequently after 30 min the corresponding L*-chiral ligand, in THF solution.



Scheme 4 Heterogenization of imino complexes.

Filtration through Celite and evaporation of the solvent yielded a solid product, which was recrystallized using Et_2O. The ^1H NMR spectrum of the isolated product **7Rh** showed four broad lines between 1.8 and 4.8 ppm, due to fluxionality in the conformation of the cod chelate, a singlet at δ 5.96 due to the imine (5.93 **8Rh**), and a broad singlet at δ 12.41 (9.82 for **8Rh**) assigned to the uncoordinated OH group. Complexes exhibit four signals in the ^{13}C spectrum attributable to the carbon atoms of the cod ligand. ESI-MS spectrum show the mass for the molecular peak at 625.5 for **7Rh** [M^+ - PF_6]), but a single crystal structure has yet to be obtained. IR spectra show the corresponding to ν(OH) at 3408 cm^{-1}. The ν(C═N) stretch was observed at 1619 cm^{-1}.

When the chiral ligands are coordinated to the metal, this introduces a new chiral centre in the complex at the coordinated N atom and metal centre. We can deduce from NMR data, the coordination of the metal ion is completely stereospecific and gives rise to a single diastereoisomer.

Heterogenization of complexes containing pendant alkoxy silane groups to MCM-41

In the last years we have developed a modular system combining functionalized ligands with different supports and linkers in order to have a systematic access to a variety of immobilized chiral catalysts.[4] The pure siliceous MCM-41 (MCM) parent material was derivatized following the strategy depicted in Scheme 4. This consisted of the grafting of a spacer, $CH_2NHCONH(CH_2)_3Si(OEt)_3$, on the walls of the MCM material. MCM-41 is short range materials containing a large number of silanol groups available for grafting. MCM-41 however, presents a long range ordering with hexagonal symmetry with regular monodirectional channels of 3.5 nm diameter.

Supported complexes were obtained by refluxing a mixture of the precursor **8Pd** or **8Rh** and the support, in toluene, with metal loadings of approximately 0.20–0.30 mmol-metal g^{-1} support. These materials were characterized by elemental content analysis, FT IR, DFTR and CP-MAS solid state, ^{13}C NMR spectroscopy. Complexation reactions yielded materials with the expected ratios of metal to nitrogen loadings. In general these results showed us that little other than the expected reactions are occurring on the functionalized silica surface.

The presence of functional groups characteristic of **8Pd** or **8Rh** in the materials was checked by FTIR spectroscopy. The stretching vibrations modes of the mesoporous framework (Si–O–Si) of the grafted material **8Pd-** or **8Rh-MCM** are observed at around 1240, 1070, and 810 cm^{-1}, as in the parent MCM, while new bands appear at *ca.* 2950 and 2850 cm^{-1}, assigned to the ν(C–H) stretching of the aliphatic linear chain in MCM-Pr and pyrrolidine ring. The presence of ligands leads to the appearance of the ν(C═N, C═O, C═C) stretching modes at 1640–1570 cm^{-1}. A new band at *ca.* 550 cm^{-1} is ascribed to ν(Pd–O). The complexes immobilized on supports have been characterized by diffuse reflectance spectroscopy. The complexes show several band maxima in the UV region agreeing with the assignment of the bands as intraligand transitions in the aromatic ring, and charge-transfer transition. The diffuse reflectance spectra of complexes are almost identical before and after the heterogenization process, indicating that the complexes maintain their geometry and their electronic surrounding even after heterogenization without significant distortion.

The materials were also characterized by cross-polarization magic-angle spinning ^{13}C CP MAS solid state NMR. The solid state ^{13}C CP MAS NMR spectra (Supporting Information) of

Table 1 Catalytic hydrogenation of prochiral olefins with palladium and rhodium-complexes[a]

		Diethyl itaconate		(*E*)-Diethyl 2-benzylidenesuccinate	
Entry	Cat.	ee (%)[c]	TOF[b]	ee (%)[d]	TOF[b]
1	**5**Pd	≤ 5	588	50	118
2	**5**Rh	≤ 5	600	97	36
3	**6**Pd	≤ 5	582	10	109
4	**6**Rh	≤ 5	590	60	92
5	**7**Pd	≤ 5	600	85	158
6	**8**Pd-MCM	≤ 5	1176	80	210
7	**7**Rh	≤ 5	602	95	108
8	**8**Rh-MCM	≤ 5	1164	90	300
9	3Pd (ref. 14a)	6	3368	12	640
10	3Pd-MCM (ref. 14a)	≤ 10	4980	≤ 10	900
11	6bPd (ref. 15a)	≤ 5	2800	15	565
12	13Pd-MCM (ref. 15b)	10	234	30	78

[a] Conditions: 4 atm, 40 °C, S/C ratio 1000 : 1, diethyl itaconate; S/C ratio 100 : 1, (*E*)-diethyl 2-benzylidenesuccinate. [b] TOF: h^{-1}. [c] Measured by HPLC (λ: 230 nm, hexane/iPrOH: 98 : 2, column chiralcel AD-H), (S) isomer. [d] Measured by HPLC (λ: 254 nm, hexane/iPrOH: 95 : 5, column chiralcel OD), (S) isomer.

8Pd-MCM, **8Rh-MCM** materials are quite similar, since the spectra are dominated by the resonances of the aliphatic and aromatic groups. These signals appear at 8.6 and 8.3 ppm (Si–CH_2), 28.6 (CH_2–CH_2–CH_2), 44.0–43.6 ppm (N–CH_2); aromatic region δ = 130.3–156.4 ppm, δ = 160.5, 160.1 ppm (N=CH) and δ = 198 ppm (OAc). The majority of peaks corresponding to the ^{13}C NMR spectrum of homogeneous complexes were present in the ^{13}C spectrum of their heterogenized counterparts.

Catalytic activity

In order to evaluate the catalytic performances of these new Rh(I), Pd(II) complexes we have tested them in hydrogenation reactions. The following paragraphs show the results obtained in experimental conditions that allow us to make a comparative study of different catalysts and substrates. Obviously for preparative application a tuning of conditions has to be done for each case. Certainly for preparative applications it is necessary to adjust the experimental conditions for each case.

We chose two substrates with different steric hindrance, as a model, to make a comparative study between the soluble and systems to check the recyclability heterogenised and later we will study the full catalytic activity by varying the substrates and reactions.

The structurally well defined supported rhodium and palladium catalytic materials were tested in the asymmetric hydrogenation of several substrates. The hydrogenation of (*E*)-diethyl 2-benzylidenesuccinate or diethyl itaconate with Rh- and Pd-complexes were carried out under standard conditions (EtOH as the solvent, 4 atm hydrogen pressure, 40 °C). In all cases, with all catalysts, complete conversion of substrate was observed. Results were summarized in Table 1. Heterogenized catalysts show higher enantioselectivity than the homogeneous catalysts. High enantiomeric excess (98% ee) was observed in the asymmetric hydrogenation of diethyl (*E*)-diethyl 2-benzylidenesuccinate.

Table 2 Recycling experiments of **8Rh-MCM** in the catalytic hydrogenation of (*E*)-diethyl 2-benzylidenesuccinate

Cycle	TOF (h^{-1})[a]	ee (%)[b]
1	300	90
2	285	88
3	290	85

[a] TOF: mmol subs./mmol cat.h. [b] Measured by HPLC (λ: 254 nm, hexane/iPrOH: 95 : 5, column chiralcel OD), (S) isomer.

Table 1 shows the effect of ligand substituents have on activity and enantioselectivity, if we compare the catalytic activity of complex **6Pd**, in this work, with that of previously reported for [(*S*)-*N*-(*tert*-butyl)-1-((6-(2-hydroxyphenyl)pyridine-2-yl)methyl)pyrrolidine-2-carboxamide]Pd (ligand type **(a)** in Chart 1, complex **6bPd** in reference 19a) and with **13Pd-MCM-41** (described in reference 19b), which have the prolinamide as chiral group, it appears that although the latter has a better catalytic activity (TOF: 565 h^{-1} entry 11 *vs.* 109 h^{-1}, entry 3), the enantiomeric excess is comparable in both cases (15% *vs.* 10%).[19a] Similarly in this case the enantioselectivity increases considerably when the catalyst is heterogenized (entry 12).[19b] If we now compare the results obtained with the complexes derived from **(*R*,*R*)-7** (this work) with those previously reported for catalysts with the phenol-imino-amino ligand, 2-(((1-benzylpyrrolidin-2-yl)methylene)amino)-6-(*tert*-butyl)-4-methylphenol as ligand, (ligand type **(b)** in Chart 1, complexes **3Pd**, **3Pd-MCM-41** in reference 18a) we found that the most active catalysts are those with the Schiff base system derived with a proline derivative group (entries 9, 10 in Table 1). However, the highest enantioselectivity is obtained with the catalyst reported in this paper (entries 5, 7).

Catalyst recycling

From an environmental point of view, it is desirable to minimize the amount of waste for each organic transformation. Reusability is an important feature to be monitored for application of heterogenized single-site catalysts. Before reuse, the catalyst was separated from the reaction mixture by filtration and washed with ethanol. After the first run, the reaction reached >99% after 3 h and this remained steady up to the 4th run, proving that the catalyst is highly stable and simple to recycle. Because the homogeneous catalyst shows lower activity than the heterogenized, we confirmed that the presence of site-isolated metal complexes grafted onto MCM-41 was responsible for enhanced conversion and that the reaction is truly heterogeneous.

The catalytic materials were easily separated from the substrate/product solution by simple filtration subsequent washing, and then added fresh substrate, and solvent without further addition of catalyst. The recycling process could be repeated four times with no significant loss in selectivity, and minimal losses in activity (Table 2 and Fig. 4). Furthermore, the filtrate, which was colorless, was placed in a catalyst free autoclave and fresh substrate was added. Dihydrogen pressure was applied, however no further conversion was observed. This demonstrates that no metal leaching from the silica surface is occurring. The metal content (loading) of the recycled catalytic material was the same as the starting catalytic material suggesting little, if any, metal

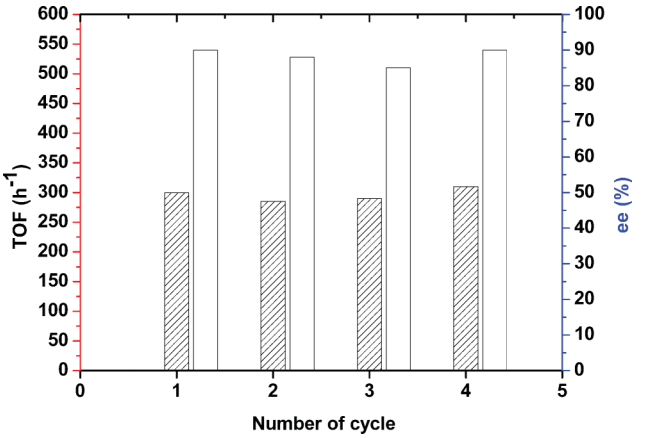


Fig. 4 Recycling of 8Rh-MCM.

leaching. Hot filtration experiments and ICP measurements were independently carried out to rule out the possibility of leaching.

In order to check the stability of metal complexes supported on the solid matrix, we have characterized the solid before and after reaction. As can be deduced from IR, ^{13}C NMR and UV-vis spectra the nature of supported species is very similar and the most important signals for ligands appear in the same position after reaction.

Conclusions

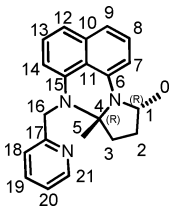
In this work we report the synthesis of the first pincer type complexes derived from a chiral proton sponge precursor, as well as a surprising cyclisation transformation that takes place under mild conditions to afford perimidine derivatives from several aldehydes and 8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-amine with good yields. The complexes derived from both types of ligands present high activity and enantioselectivity in hydrogenation of prochiral olefins. The supported complexes in MCM-41 show better activity than the homogeneous counterpart, and they could be recycled for subsequent cycles without loss of any material's features.

Experimental section

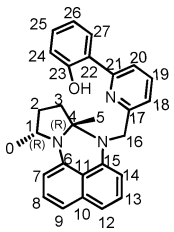
General remarks

All manipulations were carried out by using standard Schlenk vacuum-line techniques under an atmosphere of oxygen-free argon. All solvents for synthetic use were dried and distilled, under an argon atmosphere, by standard procedures.[26] ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 KHz. The reaction was monitored by gas chromatography with helium as carrier gas, 10 psi; injector temperature: 230 °C; detector temperature: 250 °C.

Synthesis of ligands



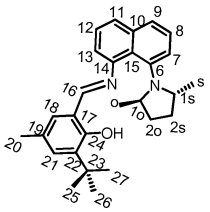
(7a*R*,10*R*)-7a,10-dimethyl-7-(pyridin-2-ylmethyl)-7a,8,9,10-tetrahydro-7*H*-pyrrolo[1,2-*a*]perimi dine ((*R*,*R*)-5). To a solution of 8-[(2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl]naphthalen-1-amine (300 mg, 1.25 mmol) in absolute ethanol (20 mL) and in the presence of molecular sieves (2 g, 4 Å) was added a ethanolic solution (10 mL) of 3 pyridine-2-carbaldehyde (133 mg, 1.25 mmol). The reaction mixture was stirred overnight at room temperature and filtered. The residue was dried under reduced pressure and purified by flash chromatography, R_f 0.25 (5 : 1 heptane/ethyl acetate) to obtain a pale pink solid Yield = 290 mg, 71%. M.p.: 58–60 °C. IR (KBr, cm^{-1}): ν_{CHarom} 3048 (w); ν_{CHalip} 2970 (m), 2922 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1582 (s), 1435 (s), 1418 (s); δ_{CH} 1374 (m), 1337 (s); $\delta_{CHout\ plane}$ 810 (s), 756 (s); ρ_{CH} 639 (m), 607 (w), 517 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (ddd, 1H, H_{21}, J_{HH} = 0.9, 1.6, 4.8 Hz); 7.70 (dt, 1H, H_{19}, J_{HH} = 1.7, 7.5 Hz); 7.58 (d, 1H, H_{18}, J_{HH} = 7.3 Hz); 7.45 (t, 1H, H_{13}, J_{HH} = 7.7 Hz); 7.33–7.22 (m, 4H, H_8, H_9, H_{12}, H_{20}); 6.56 (d, 1H, H_{14}, J_{HH} = 7.3 Hz); 6.25 (dd, 1H, H_7, J_{HH} = 3.0, 5.2 Hz); 4.82 (d, 1H, H_{16}, -CH_2-, ABXY, J_{HH} = 17.6 Hz); 4.57 (d, 1H, H_{16}, -CH_2-, ABXY, J_{HH} = 17.6 Hz); 4.29 (m, 1H, H_1, -CH_{pyrr}); 2.55–2.47 (m, 2H, 2 -CH_{2pyrr}); 2.34 (m, 1H, -CH_{2pyrr}); 1.95 (m, 1H, -CH_{2pyrr}); 1.49 (d, 3H, H_0, -CH_3, J_{HH} = 6.6 Hz); 1.37 (s, 3H, H_5, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6 (C_{17}); 149.1 (C_{21}); 141.9 (C_{15}); 138.9 (C_6); 137.0 (C_{19}); 134.8 (C_{10}); 127.0 (C_{13}); 126.8 (C_9); 121.8 (C_{20}); 120.8 (C_{18}); 117.1 (C_8); 115.3 (C_{12}); 114.9 (C_{11}); 104.5 (C_7); 103.9 (C_{14}); 78.5 (C_4); 53.8 (C_{16}, -CH_2-); 52.6 (C_1); 36.8 (C_3); 29.5 (C_2); 20.0 (C_0, -CH_3); 18.5 (C_5, -CH_3). Anal. Calc. for $C_{22}H_{23}N_3$ (329.4): C, 80.2; H, 7.0; N, 12.8. Found: C, 80.2; H, 7.2; N, 12.5%. ESI-MS *m*/*z* (%): 329.0 [M$^+$], 314.0 [M$^+$–CH_3], 252.0 [M$^+$–Py].



2-(6-{[(7a*R*,10*R*)-7a,10-dimethyl-7a,8,9,10-tetrahydro-7*H*-pyrrolo[1,2-*a*]perimidin-7-yl]methyl} pyridin-2-yl)phenol ((*R*,*R*)-6). To a solution of 8-[(2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl]naphthalen-1-amine (50 mg, 0.208 mmol) in absolute ethanol (2 mL) and in the presence of molecular sieves (2 g, 4 Å) was added a ethanolic solution (4 mL) of 6-(2-hydroxyphenyl)pyridine-2-carbaldehyde (41.4 mg, 0.208 mmol). The reaction mixture was stirred overnight at room temperature and filtered. The residue was dried under reduced pressure and purified by flash chromatography (15 : 1 heptane/ethyl acetate) to afford a pale pink solid. Yield = 33 mg, 38%. M.p.: 90–93 °C. IR (KBr, cm^{-1}): ν_{OH} 3435 (m); ν_{CHarom} 3194 (w), 3051 (w); ν_{CHalip} 2963 (m), 2925 (m), 2867 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1596 (s), 1578 (vs), 1458 (s), 1430 (s); δ_{CH}

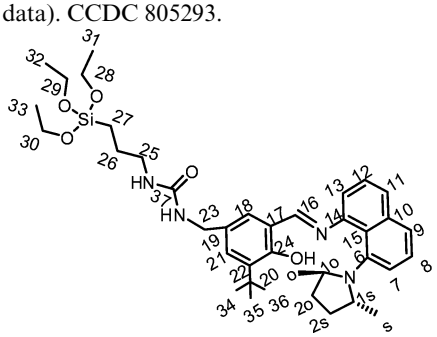
1374 (m), 1335 (m), 1299 (s); $\delta_{CHout\ plane}$ 818 (s), 756 (s); ρ_{CH} 633 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.60 (s br, 1H, OH); 7.84 (dd, 1H, H_{27}, J_{HH} = 1.5, 8.0 Hz); 7.79 (s br, 1H, H_{20}); 7.71 (t, 1H, H_{19}, J_{HH} = 7.7 Hz); 7.39–7.31 (m, 3H, H_9, H_{13}, H_{25}); 7.15 (s br, 1H, H_{18}); 7.13 (d, 1H, H_8, J_{HH} = 4.4 Hz); 7.08 (d, 1H, J_{HH} = 3.7 Hz) and 7.04 (d, 1H, J_{HH} = 4.4 Hz) (H_{12} and H_{24}); 6.95 (dt, 1H, H_{26}, J_{HH} = 1.5, 7.3 Hz); 6.44 (d, 1H, H_{14}, J_{HH} = 7.3 Hz); 6.11 (t, 1H, H_7, J_{HH} = 4.4 Hz); 4.70 (d, 1H, H_{16}, -CH_2-, ABXY, J_{HH} = 17.6 Hz); 4.45 (d, 1H, H_{16}, -CH_2-, ABXY, J_{HH} = 17.6 Hz); 4.16 (m, 1H, H_1, -CH_{pyrr}); 2.42–2.32 (m, 2H, -CH_{2pyrr}); 2.25–2.18 (m, 1H, -CH_{2pyrr}); 1.84–1.81 (m, 1H, -CH_{2pyrr}); 1.37 (d, 3H, H_o, -CH_3, J_{HH} = 5.9 Hz); 1.25 (s, 3H, H_s, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.9 (C_{22}); 157.5 (C_{23}); 156.7 (C_{17}); 141.7 (C_{15}); 138.8 (C_6), 138.7 (C_{19}); 134.9 (C_{10}); 131.5 (C_9); 127.1 (C_{13}); 126.4 (C_{27}); 126.3 (C_{18}); 124.7 (C_{21}); 119.2 (C_{24}); 118.9 (C_{25}); 118.6 (C_{26}); 117.5 (C_8); 117.4 (C_{20}); 115.4 (C_{12}); 114.9 (C_{11}); 104.5 (C_7); 104.1 (C_{14}); 78.5 (C_4); 53.2 (C_{16}, -CH_2-); 52.7 (C_1); 36.9 (C_3); 29.5 (C_2); 20.0 (C_o, -CH_3); 18.6 (C_s, -CH_3). Anal. Calc. for $C_{28}H_{27}N_3O$ (421.5): C, 79.8; H, 6.5; N, 10.0. Found: C, 79.6; H, 6.8; N, 10.2%. ESI-MS m/z (%): 421.0 [M^+], 406.0 [M^+–CH_3].

Crystal data for **RR-6**: $C_{28}H_{27}N_3O$, M = 421.53, orthorhombic, a = 10.414(3) Å, b = 13.565(3) Å, c = 15.401(4) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 2175.6(9) Å^3, T = 296(2)K, space group $P2_12_12_1$, Z = 4, 15489 reflections measured, 2280 independent reflections (R_{int} = 0.0750). The final R_1 values were 0.0376 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0812 ($I > 2\sigma(I)$). The final R_1 values were 0.0475 (all data). The final $wR(F^2)$ values were 0.0846 (all data). CCDC 805292.



2-*tert*-butyl-6-((*E*)-(8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)-naphthalen-1-ylimino)methyl)-4-methylphenol ((*R*,*R*)-7). To a solution of 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (176 mg, 0.915 mmol) in absolute ethanol (20 mL) was added 8-[(2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl]naphthalen-1-amine (200 mg, 0.915 mmol). After stirring at room temperature for 24 h, the reaction mixture was filtered and washed with ethanol. The residue was dried under reduced pressure and purified by flash chromatography (10 : 1 heptane/ethyl acetate) to obtain a microcrystalline orange solid. Yield = 199 mg, 58%. M.p.: 73–75 °C. IR (KBr, cm^{-1}): ν_{OH} 3445 (m); ν_{CHarom} 3049 (w); ν_{CHalip} 2961 (m), 2920 (m), 2870 (m); $\nu_{C=N}$, $\nu_{C=C}$ 1618 (s), 1564 (vs), 1439 (s); $\delta_{CHout\ plane}$ 1370 (m), 1330 (s). UV-Vis: λ_{max} = 302 nm, 343 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.86 (s br, 1H, OH); 8.26 (s, 1H, H_{16}, N=CH); 7.67 (dd, 1H, H_9, J_{HH} = 1.3, 8.4 Hz); 7.50 (d, 1H, H_{11}, J_{HH} = 8.0 Hz); 7.43–7.37 (m, 2H, H_8, H_{12}); 7.18 (d, 1H, J_{HH} = 1.8 Hz) and 6.99 (d, 1H, J_{HH} = 1.8 Hz) (H_{18} and H_{21}); 7.05 (d, 1H, H_{13}, J_{HH} = 7.5 Hz); 6.94 (dd, 1H, H_7, J_{HH} = 1.3, 7.1 Hz); 3.75–3.66 (m, 1H) and 3.51–3.46 (m, 1H) (H_{1s} and H_{1o}, -CH_{pyrr}); 2.30 (s, 3H, H_{20}, -CH_3); 1.96–1.86 (m, 1H) and 1.80–1.70 (m, 1H) (H_{2s} and H_{2o}, -CH_{2pyrr}); 1.46 (s, 9H, $H_{25,26,27}$); 1.39–1.33 (m, 1H) and 1.18–1.09 (m, 1H) (H_{2s} and H_{2o}, -CH_{2pyrr}); 1.25 (d, 3H, -CH_3, J_{HH} = 6.2 Hz) and 0.36 (d, 3H, -CH_3, J_{HH} = 6.2 Hz) (H_o and H_s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0 (C_{16}, N=CH); 158.2 (C_{24}); 147.2 (C_{14}); 143.7 (C_6); 137.2 (C_{22}); 136.9 (C_{10}); 131.0 (C_{19}); 130.8 (C_{18}); 130.1 (C_{21}); 128.1 (C_{15}); 126.5 (C_9); 125.7 (C_{12}); 125.4 (C_8); 122.4 (C_{11}); 119.1 (C_{17}); 118.5 (C_{13}); 118.0 (C_7); 58.8 (C_{1s}); 51.4 (C_{1o}); 34.7 (C_{23}); 31.6 (C_{2o}); 29.4 (3C, $C_{25,26,27}$); 29.2 (C_{2s}); 20.7 (C_{20}, CH_3-Ph); 18.3 (C_o, CH_{3pyrr}); 17.5 (C_s, CH_{3pyrr}). Anal. Calc. for $C_{28}H_{34}N_2O$ (414.6): C, 81.1; H, 8.3; N, 6.8. Found: C, 81.0; H, 8.5; N, 6.5%. ESI-MS m/z (%): 414.0 [M^+], 399.0 [M^+–CH_3], 223.0 [M^+–CH_3–^{t}Bu–Ar-OH–imine].

Crystal data for **RR-7**: C28H34N2O, M = 414.57, monoclinic, a = 9.8047(8) Å, b = 8.8134(8) Å, c = 14.0070(12) Å, α = 90.00°, β = 91.3630(10)°, γ = 90.00°, V = 1210.04(18) Å3, T = 296(2)K, space group $P2_1$, Z = 2, 8037 reflections measured, 4000 independent reflections (R_{int} = 0.0324). The final R_1 values were 0.0636 ($I > 2\sigma(I)$). The final wR(F2) values were 0.1125 ($I > 2\sigma(I)$). The final R_1 values were 0.1082 (all data). The final wR(F2) values were 0.1281 (all data). CCDC 805293.



***N*-(3-*tert*-butyl-5-((*E*)-(8-((2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl)naphthalen-1-ylimino)methyl)-4-hydroxybenzylcarbamoyl)-4-(triethoxysilyl)butanamide (*R*,*R*)-8.** Using a similar procedure to that described for (R,R)-7, from *N*-(3-*tert*-butyl-5-formyl-4-hydroxyphenylcarbamoyl)-4-(triethoxysilyl)butanamide (0.378 g, 0.832 mmol) and 8-[(2*R*,5*R*)-2,5-dimethylpyrrolidin-1-yl]naphthalen-1-amine (200 mg, 0.832 mmol) in absolute ethanol (3 mL). After purification by flash chromatography (4 : 1 heptane/ethyl acetate) an orange oil was obtained. Yield = 405 mg, 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.11 (s br, 1H, OH); 8.32 (s, 1H, H_{16}, N=CH); 7.65 (dd, 1H, H_9, J_{HH} = 1.1, 7.9 Hz); 7.50 (d, 1H, H_{11}, J_{HH} = 7.9 Hz); 7.44–7.37 (m, 2H, H_8, H_{12}); 7.27 (d, 1H, H_{18}, J_{HH} = 2.7 Hz); 7.16 (d, 1H, H_{21}, J_{HH} = 2.7 Hz); 7.05 (d, 1H, H_{13}, J_{HH} = 7.7 Hz); 6.93 (dd, 1H, H_7, J_{HH} = 1.0, 7.2 Hz); 4.34 (s, 2H, H_{23}, -CH_2-); 3.80 (q, 6H, $H_{28,29,30}$, J_{HH} = 7.0 Hz); 3.75–3.69 (m, 1H, H_{1o}, -CH_{pyrr}); 3.54–3.48 (m, 1H, H_{1s}, -CH_{pyrr}); 3.23–3.16 (m, 2H, H_{25}, -CH_2-); 1.98–1.87 (m, 1H, H_{2o}, -CH_{2pyrr}); 1.75–1.70 (m, 1H, H_{2s}, -CH_{2pyrr}); 1.69–1.61 (m, 2H, H_{26}, -CH_2-); 1.46 (s, 9H, $H_{34,35,36}$); 1.42–1.30 (m, 1H, H_{2o}, -CH_{2pyrr}); 1.26 (d, 3H, H_o, -CH_3, J_{HH} = 5.6 Hz); 1.20 (t, 9H, $H_{31,32,33}$, J_{HH} = 7.0 Hz); 1.13–1.10 (m, 1H, H_{2s}, -CH_{2pyrr}); 0.65 (m, 2H, H_{27}, -CH_2-Si); 0.39 (d, 3H, H_s, -CH_3, J_{HH} = 5.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5 (C_{16}, N=CH); 159.9 (C_{37}, C=O); 158.0 (C_{24}); 146.9 (C_{14}); 143.7 (C_6); 138.0 (C_{22}); 136.9 (C_{10}); 130.5 (C_{19}); 129.4 (C_{18}); 129.2 (C_{21}); 128.1 (C_{15}); 126.9 (C_9); 125.8 (2C, C_{12}, C_8); 122.5 (C_{11}); 119.2 (C_{17}); 118.7 (C_{13}); 118.0 (C_7); 58.9 (C_{1s}); 58.5 (3C, $C_{28,29,30}$); 51.5 (C_{1o}); 44.6 (C_{23}, -HN-CH_2-Ph); 43.0 (C_{25}, -CH_2-); 34.9 (C_{20}); 31.6 (C_{2o}); 29.4 (3C, $C_{34,35,36}$); 29.2 (C_{2s}); 23.6 (C_{26}, -CH_2-); 18.4 (C_o, CH_3); 18.3 (3C, $C_{31,32,33}$); 17.5 (C_s, CH_3); 7.6 (C_{27}, -CH_2-Si).

Synthesis of complexes

(*R*,*R*)-5Pd. Pd(cod)Cl_2 (43 mg, 0.152 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **(*R*,*R*)-5** (50 mg, 0.152 mmol) in the same solvent and the mixture was stirred at room temperature

for 6 h. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of pentane and collected by filtration, to afford a stable light brown solid. Yield = 73 mg, 94%. IR (KBr, cm^{-1}): ν_{CHarom} 3049 (w); ν_{CHalip} 2965 (m), 2925 (m) 2875 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1609 (s) 1587 (vs), 1420 (s); δ_{CH} 1373 (m), 1338 (m); $\delta_{CHout\ plane}$ 811 (s), 758 (s); ρ_{CH} 638 (w), 603 (w), 514 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.04 (m, $1H_{Py}$); 7.63 (m, $1H_{Py}$); 7.56 (m, $1H_{Py}$); 7.28 (m, $1H_{Py}$); 7.13 (d, $2H_{Nph}$, J_{HH} = 8.0 Hz); 7.05 (d, $2H_{Nph}$, J_{HH} = 7.3 Hz); 6.38 (dd, $2H_{Nph}$, J_{HH} = 1.0, 6.4 Hz); 5.97 (d, 1H, -CH_2-, ABXY, J_{HH} = 18.1 Hz); 5.61 (d, 1H, -CH_2-, ABXY, J_{HH} = 18.1 Hz); 4.03 (m, 1H, -CH_{pyrr}); 2.89–2.56 (m, 2H, -CH_{2pyrr}); 2.37–2.17 (m, 2H, -CH_{2pyrr}); 1.25 (d, 3H, -CH_3, J_{HH} = 10.2 Hz); 0.89 (s, 3H, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.7 (C_{Py}); 152.1 (C_{Py}); 141.2 (C_{Nph}); 139.0 (C_{Py}); 134.8 (C_{Nph}); 127.1 (C_{Py}); 124.0 ($2C_{Nph}$); 123.7 (C_{Py}); 118.0 ($2C_{Nph}$); 116.7 ($2C_{Nph}$); 105.1 ($2C_{Nph}$); 79.2 (-*C*N-CH_{3pyrr}); 55.6 (-CH_2-); 52.7 (-*C*H-CH_{3pyrr}); 36.6 (-CH_{2pyrr}); 31.0 (-CH_{2pyrr}); 20.0 (-CH_3); 18.1 (-CH_3). Anal. Calc. for $C_{22}H_{23}Cl_2N_3Pd$ (506.8): C, 52.1; H, 4.6; N, 8.3. Found: C, 52.4; H, 4.8; N, 7.8%. ESI-MS *m*/*z* (%): 471.3 [M^+–Cl], 435.3 [M^+–2Cl], 329.3 [M^+–2Cl–Pd].

(*R*,*R*)-5Rh. $AgPF_6$ (38.5 mg, 0.152 mmol) in THF (10 mL) was added to a solution of $[Rh(cod)Cl]_2$ (37 mg, 0.076 mmol) in THF (10 mL) and the mixture was stirred vigorously at room temperature for 30 min. The resulting AgCl was filtered off and the yellow solution was treated with **(*R*,*R*)-5** (50 mg, 0.152 mmol) in the same solvent. The mixture was stirred at room temperature for 2 h. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of Et_2O and collected by filtration, to afford a stable dark green solid. Yield = 95 mg, 91%. IR (KBr, cm^{-1}): ν_{CHalip} 2962 (m), 2924 (m) 2886 (m), 2839 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1614 (s), 1587 (s), 1413 (m); δ_{CH} 1378 (m), 1335 (m); ν_{PF} 842 (vs); $\delta_{CHout\ plane}$ 762 (m); ρ_{CH} 558 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (m, $1H_{Py}$); 7.85 (m, $1H_{Py}$); 7.73 (m, $1H_{Py}$); 7.50 (m, $1H_{Py}$); 7.40 (dd, $2H_{Nph}$, J_{HH} = 1.0, 7.9 Hz); 7.24 (d, $2H_{Nph}$, J_{HH} = 7.9 Hz); 6.53 (d, $2H_{Nph}$, J_{HH} = 7.4 Hz); 5.82 (d, 1H, -CH_2-, ABXY, J_{HH} = 16.2 Hz); 4.41 (d, 1H, -CH_2-, ABXY, J_{HH} = 16.0 Hz); 4.05 (m, 2H, -CH=C_{cod}); 3.87 (m, 1H, -CH_{pyrr}); 3.58 (m, 2H, -CH=C_{cod}); 2.58 (m, 2H, -CH_{2cod}); 2.33 (m, 2H, -CH_{2cod}); 2.21 (m, 2H, -CH_{2cod}); 1.87 (m, 2H, -CH_{2cod}); 1.68 (d, 3H, -CH_3, J_{HH} = 6.0 Hz); 1.58 (m, 2H, -CH_{2pyrr}); 1.32 (m, 2H, -CH_{2pyrr}); 1.15 (s, 3H, -CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (C_{Py}); 146.2 (C_{Py}); 141.0 (C_{Py}); 138.5 (C_{Nph}); 134.5 (C_{Nph}); 128.0 ($2C_{Nph}$); 126.4 (C_{Py}); 123.7 (C_{Py}); 117.5 ($2C_{Nph}$); 115.8 ($2C_{Nph}$); 105.7 ($2C_{Nph}$); 87.0 (2C, -CH=CH_{cod}); 83.0 (2C, -CH=CH_{cod}); 77.2 (-*C*N-CH_{3pyrr}); 57.9 (-CH_2-); 51.6 (-*C*H-CH_{3pyrr}); 39.6 (-CH_{2pyrr}); 30.3 (2C, 2 -CH_{2cod}); 29.9 (2C, 2 -CH_{2cod}); 29.4 (-CH_{2pyrr}); 20.3 (-CH_3); 15.6 (-CH_3). Anal calcd. for $C_{30}H_{35}F_6N_3PRh$ (685.5): C, 52.6; H, 5.1; N, 6.1. Found: C, 52.3; H, 5.0; N, 5.8%. ESI-MS *m*/*z* (%): 540.3 [M^+-PF_6], 432.3 [M^+-PF_6–cod], 330.3 [M^+–cod–Rh].

(*R*,*R*)-6Pd. $Pd(AcO)_2$ (26.7 mg, 0.119 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **(*R*,*R*)-6** (50.1 mg, 0.152 mmol) in the same solvent and the mixture was stirred at room temperature overnight. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of pentane and collected by filtration, to afford a stable brown solid. Yield = 65 mg, 85%. IR (KBr, cm^{-1}): ν_{CHarom} 3055 (w); ν_{CHalip} 2964 (m), 2924 (w), 2891 (vw); $\nu_{C=O}$ 1624 (s); $\nu_{C=C}$, $\nu_{C=N}$ 1596 (vs), 1573 (s), 1467 (s); δ_{CH} 1406 (s), 1378 (m), 1360 (m); ν_{C-O} 1317 (s); $\delta_{CHout\ of\ the\ plane}$ 821 (m), 755 (m); δ_{OCO} 686 (w); ν_{Pd-O} 555 (vw). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.35 (dd, $1H_{Py}$, J_{HH} = 1.1, 7.5 Hz); 7.80 (m, $1H_{Nph}$); 7.79 (m, $1H_{Nph}$); 7.73 (d, $1H_{Py}$, J_{HH} = 7.8 Hz); 7.61 (dd, $1H_{Py}$, J_{HH} = 1.0, 7.9 Hz); 7.55 (d, $1H_{Ph}$, J_{HH} = 8.1 Hz); 7.40 (dd, $1H_{Nph}$, J_{HH} = 1.0, 7.9 Hz); 7.30 (d, $1H_{Nph}$, J_{HH} = 7.9 Hz); 7.20 (m, $1H_{Ph}$); 7.19 (m, $1H_{Ph}$); 6.85 (m, $1H_{Nph}$); 6.68 (m, $1H_{Ph}$); 6.57 (d, $1H_{Nph}$, J_{HH} = 7.5 Hz); 4.57 (d, 1H, -CH_2-, ABXY, J_{HH} = 17.2 Hz); 4.22 (d, 1H, -CH_2-, ABXY, J_{HH} = 17.1 Hz); 4.05 (m, 1H, -CH_{pyrr}); 2.68 (dd, 1H, -CH_{2pyrr}, J_{HH} = 6.8, 12.1 Hz); 2.37 (m, 1H, -CH_{2pyrr}); 1.91 (m, 1H, -CH_{2pyrr}); 1.88 (s, 3H, CH_3CO_2-); 1.65 (s, 3H, -CH_3); 1.62 (m, 1H, -CH_{2pyrr}); 1.35 (d, 3H, -CH_3, J_{HH} = 6.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.0 (CH_3CO_2-); 164.4 (*C*-O, C_{Ph}); 161.0 (C_{Nph}); 153.2 (C_{Nph}); 142.4 (C_{Py}); 138.8 (C_{Nph}); 136.5 (C_{Nph}); 134.3 (C_{Py}); 132.1 (C_{Ph}); 128.5 (C_{Ph}); 127.6 (C_{Py}); 127.1 (C_{Nph}); 126.9 (C_{Py}); 123.6 (C_{Py}); 122.6 (C_{Ph}); 121.8 (C_{Ph}); 120.1 (C_{Nph}); 117.0 (C_{Nph}); 116.2 (C_{Nph}); 116.0 (C_{Ph}); 113.7 (C_{Nph}); 105.4 (C_{Nph}); 86.2 (-*C*N-CH_{3pyrr}); 66.5 (-CH_2-); 51.7 (-*C*H-CH_{3pyrr}); 34.9 (-CH_{2pyrr}); 28.7 (-CH_{2pyrr}); 24.3 (CH_3CO_2-); 22.2 (-CH_3); 20.0 (-CH_3). Anal. Calcd. for $C_{30}H_{29}N_3O_3Pd$ (586.0): C, 61.5; H, 5.0; N, 7.2. Found C, 61.8; H, 4.9; N, 7.7%. ESI-MS *m*/*z* (%): 585.5 [M^+], 526.5 [M–CH_3CO_2], 421.5 [M^+–CH_3CO_2–Pd].

(*R*,*R*)-6Rh. $AgPF_6$ (48 mg, 0.190 mmol) in THF (10 mL) was added to a solution of $[Rh(cod)Cl]_2$ (46.4 mg, 0.095 mmol) in THF (10 mL) and the mixture was stirred vigorously at room temperature for 30 min. The resulting AgCl was filtered off and the yellow solution was treated with **(*R*,*R*)-6** (80 mg, 0.190 mmol) in the same solvent. The mixture was stirred at room temperature for 2 h. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of Et_2O and collected by filtration, to afford a stable (in solid state) dark yellow solid. Yield = 133 mg, 90%. This compound decomposes in solution (the compound turns red) and the NMR spectrum cannot be collected in common solvents, only ^{13}C MAS solid was used for characterization; ^{1}H NMR solid proton spectrum does not provide information because the signals are broad. IR (KBr, cm^{-1}): ν_{OH} 3443 (m); ν_{CHarom} 3101 (vw), 3058 (vw); ν_{CHalip} 2964 (m), 2926 (m), 2880 (m), 2837 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1596 (s), 1578 (s), 1537 (s), 1461 (s); δ_{CH} 1378 (m), 1335 (m), 1299 (m); ν_{PF} 843 (vs); $\delta_{CHout\ of\ the\ plane}$ 760 (m); ρ_{CH} 557 (s). ^{13}C NMR (300 MHz, solid): δ 158.3 (C_{Ph}); 154.5 (C_{Ph}); 152.0 (C_{Py}); 140.2 (C_{Nph}); 138.5 (2C, C_{Nph}, C_{Py}); 135.4 (C_{Nph}); 133.5 (C_{Nph}); 127.6 (2C, C_{Nph}, C_{Ph}); 126.3 ($2C_{Py}$); 119.1 (5C, $3C_{Ph}$, C_{Nph}, C_{Py}); 115.3 ($2C_{Nph}$); 104.6 ($2C_{Nph}$); 80.9 (5C, 2 -CH=CH_{cod}, -*C*N-CH_{3pyrr}); 53.4 (-CH_2-); 53.3 (-*C*H-CH_{3pyrr}); 39.0 (-CH_{2pyrr}); 30.6 (5C, 4 -CH_{2cod}, -CH_{2pyrr}); 19.7 (-CH_3); 19.5 (-CH_3). Anal. Calcd. for $C_{36}H_{39}F_6N_3OPRh$ (777.6): C, 55.6; H, 5.1; N, 5.4; found C, 50.8; H, 4.5; N, 4.4%. (*R*,*R*)-6Rh + 3/2 CH_2Cl_2: C, 50.2; H, 4.5; N, 4.6). ESI-MS *m*/*z* (%): 632.3 [M^+], 523.3 [M^+–H^+–cod].

(*R*,*R*)-7Pd. $Pd(AcO)_2$ (21.6 mg, 0.096 mmol) in EtOH (10 mL) was added to a solution of **(*R*,*R*)-8** (40 mg, 0.096 mmol) in the same solvent and the mixture was stirred at room temperature overnight. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of pentane and collected by filtration, to afford a stable light brown solid. Yield = 48 mg, 85%. IR (KBr, cm^{-1}): ν_{CHarom} 3053 (w); ν_{CHalip} 2960 (vs), 2921 (vs), 2867 (s); $\nu_{C=O}$ 1650 (s); $\nu_{C=C}$, $\nu_{C=N}$ 1585 (vs), 1572 (vs), 1529 (s); δ_{CH} 1457 (s), 1426 (s), 1373 (s), ν_{C-O} 1320 (s); $\delta_{CHout\ plane}$ 819 (m), 765 (m); δ_{OCO} 710 (w); ν_{Pd-O} 541 (vw). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H, N=CH); 7.30 (d, $1H_{Nph}$, J_{HH} = 6.4 Hz); 7.28

(m, 1H$_{Nph}$); 7.27 (d, 1H$_{Nph}$, J_{HH} = 6.4 Hz); 7.26 (d, 1H$_{Nph}$, J_{HH} = 5.9 Hz); 7.10 (d, 1H$_{Ph}$, J_{HH} = 2.2 Hz); 7.05 (d, 1H$_{Ph}$, J_{HH} = 2.2 Hz); 6.41 (d, 1H$_{Nph}$, J_{HH} = 7.5 Hz); 6.31 (d, 1H$_{Nph}$, J_{HH} = 7.5 Hz); 4.00 (dc, 1H, -CH$_{pyrr}$, J_{HH} = 1.3, 6.4 Hz); 2.37–2.30 (m, 1H, -CH$_{2pyrr}$); 2.15–2.11 (m, 1H, -CH$_{2pyrr}$); 2.10–2.00 (m, 1H, -CH$_{2pyrr}$); 1.82–1.76 (m, 1H, -CH$_{2pyrr}$); 1.40 (s, 3H, -CH$_{3Ph}$); 1.34 (d, 3H, -CH$_{3pyrr}$, J_{HH} = 7.0 Hz); 1.34 (s, 3H, CH$_3$CO$_2$-); 1.32 (d, 3H, -CH$_{3pyrr}$, J_{HH} = 6.0 H$_3$); 1.29–1.27 (m, 1H, -CH$_{pyrr}$); 1.09 (s, 9H, 3 -CH$_{3t\text{-}Bu}$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 197.1 (CH$_3$*C*O$_2$-); 153.7 (N=CH); 142.0 (C$_{Nph}$); 141.1 (C$_{Ph}$); 139.2 (C$_{Nph}$); 136.9 (C$_{Ph}$); 136.4 (C$_{Ph}$); 135.1 (C$_{Ph}$); 134.3 (C$_{Nph}$); 130.2 (C$_{Nph}$); 130.3 (C$_{Nph}$); 127.8 (C$_{Nph}$); 126.9 (C$_{Nph}$); 116.1 (C$_{Ph}$); 115.2 (C$_{Ph}$); 114.9 (C$_{Nph}$); 103.3 (C$_{Nph}$); 102.7 (C$_{Nph}$); 52.2 (-*C*H-CH$_{3pyrr}$); 36.4 (-CH$_{2pyrr}$); 29.7 (*C*H$_3$CO$_2$-); 29.7 (-*C*H-CH$_{3pyrr}$); 29.6 (-CH$_{3Ph}$); 29.4 (-CH$_{2pyrr}$); 22.7 (C$_{t\text{-}Bu}$); 20.1 (-CH$_{3pyrr}$); 18.1 (3C, 3 -CH$_{3t\text{-}Bu}$); 14.9 (-CH$_{3pyrr}$). Anal. Calcd. for C$_{30}$H$_{36}$N$_2$O$_3$Pd (579.0): C, 62.2; H, 6.3; N, 4.8; found: C, 62.6; H, 6.3; N, 4.7%. ESI-MS *m*/*z* (%): 519.3 [M$^+$–OAc], 415.5 [**L**].

(*R*,*R*)-7Rh. AgPF$_6$ (24.4 mg, 0.096 mmol) in THF (10 mL) was added to a solution of [Rh(cod)Cl]$_2$ (23.5 mg, 0.048 mmol) in THF (10 mL) and the mixture was stirred vigorously at room temperature for 30 min. The resulting AgCl precipitated was filtered off and the yellow solution was treated with **(*R*,*R*)-8** (40 mg, 0.096 mmol) in the same solvent. The mixture was stirred at room temperature for 2 h. After the solvent had been removed under vacuum to 0.5 mL, the product was precipitated by careful addition of Et$_2$O and collected by filtration, to afford a stable dark beige solid. Yield = 67 mg, 90%. IR (KBr, cm^{-1}): ν_{OH} 3408 (m); ν_{CHarom} 3054 (vw); ν_{CHalip} 2962 (m), 2921 (m), 2882 (m), 2838 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1619 (m), 1591 (s), 1467 (m), 1432 (m); δ_{CH} 1375 (m), 1300 (s), 1231 (m); ν_{PF} 843 (vs); $\delta_{CHout\ plane}$ 755 (w), 731 (w); ρ_{CH} 558 (m), 500 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ 12.41 (s br, OH); 7.44–7.34 (m, 3H$_{Nph}$); 7.26–7.16 (m, 3H$_{Nph}$); 6.53 (m, 1H$_{Ph}$); 6.51 (m, 1H$_{Ph}$); 5.96 (s, 1H, N=CH); 4.79–4.69 (m, 1H, -CH$_{2pyrr}$); 4.41–4.39 (m, 2H, -CH=C$_{cod}$); 4.24–4.19 (m, 1H, -CH$_{2pyrr}$); 4.11–4.07 (m, 2H, -CH=C$_{cod}$); 3.29–3.20 (m, 1H, -CH$_{pyrr}$); 2.66–2.55 (m, 2H, -CH$_{2cod}$); 2.52 –2.38 (m, 2H, -CH$_{2cod}$); 2.31–2.28 (m, 1H, -CH$_{2pyrr}$); 2.22 (s, 3H, -CH$_{3Ph}$); 2.08–1.96 (m, 2H, -CH$_{2cod}$); 1.95–1.84 (m, 2H, -CH$_{2cod}$); 1.46 (d, 3H, -CH$_{3pyrr}$, J_{HH} = 8.8 Hz); 1.40 (s, 9H, -CH$_{3t\text{-}Bu}$); 1.28 (d, 3H, -CH$_{3pyrr}$, J_{HH} = 11.5 Hz); 0.91–0.86 (m, 1H, -CH$_{2pyrr}$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.2 (N=CH); 158.3 (C$_{Ph}$); 148.4 (C$_{Nph}$); 143.6 (C$_{Nph}$); 138.0 (C$_{Ph}$); 134.6 (C$_{Nph}$); 131.7 (C$_{Ph}$); 130.9 (C$_{Ph}$); 127.8 (C$_{Ph}$); 127.6 (C$_{Nph}$); 126.3 (C$_{Nph}$); 126.3 (2C$_{Nph}$); 122.7 (C$_{Nph}$); 120.1 (C$_{Ph}$); 116.1 (C$_{Nph}$); 115.3 (C$_{Nph}$); 83.0 (2C, -CH=CH$_{cod}$); 80.8 (2C, -CH=CH$_{cod}$); 52.5 (-*C*H-CH$_{3pyrr}$); 52.3 (-*C*H-CH$_{3pyrr}$); 35.1 (C$_{t\text{-}Bu}$); 32.7 (-CH$_{2pyrr}$); 30.3 (2C, 2 -CH$_{2cod}$); 29.8 (3C, 3 -CH$_{3t\text{-}Bu}$); 29.7 (2C, 2 -CH$_{2cod}$); 29.5 (-CH$_{2pyrr}$); 20.0 (-CH$_{3Ph}$); 18.5 (-CH$_{3pyrr}$); 8.8 (-CH$_{3pyrr}$). Anal. Calcd. for C$_{36}$H$_{46}$F$_6$N$_2$OPRh (770.6): C, 56.1; H, 6.0; N, 3.6; found: C, 51.8; H, 6.0; N, 3.1%. **7Rh**·CH$_2$Cl$_2$: C, 51.9; H, 5.6; N, 3.3%. ESI-MS *m*/*z* (%): 625.5 [M$^+$ - PF$_6$], 415.5 [L].

(R,R)-8Pd. Pd(AcO)$_2$ (10.11 mg, 0.045 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added to a solution of **(*R*,*R*)-8** (30.5 mg, 0.045 mmol) in the same solvent and the mixture was stirred at room temperature overnight. After the solution was purified through celite and subsequent the solvent was removed under vacuum to 0.5 mL, the product was precipitated by careful addition of pentane and collected by filtration, to afford a stable dark red solid. Yield = 33 mg, 87%. UV-Vis: λ_{max} (nm) = 531, 434, 376, 296. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.32 (s, 1H, N=CH); 7.68 (d, 1H$_{Nph}$, J_{HH} = 8.0 Hz); 7.50 (t, 1H$_{Nph}$, J_{HH} = 7.3 Hz); 7.44–7.40 (m, 2H$_{Nph}$); 7.36 (d, 1H$_{Ph}$, J_{HH} = 2.2 Hz); 7.17 (d, 1H$_{Ph}$, J_{HH} = 2.2 Hz); 7.06 (d, 1H$_{Nph}$, J_{HH} = 6.6 Hz); 6.94 (d, 1H$_{Nph}$, J_{HH} = 7.3 Hz); 4.34 (d, 2H, -CH$_2$-Ph, J_{HH} = 4.4 Hz); 3.78 (c, 6H, -*O*-C*H*$_2$-CH$_3$, J_{HH} = 7.3 Hz); 3.53–3.42 (m, 1H, -CH$_{pyrr}$); 3.24–3.15 (m, 3H, 1H, -CH$_{pyrr}$, 2H, -CH$_2$-); 1.97–1.85 (m, 2H, -CH$_{2pyrr}$); 1.71–1.58 (m, 1H, -CH$_{2pyrr}$); 1.67–1.60 (m, 2H, -CH$_2$-); 1.47 (s, 9H, -CH$_{3t\text{-}Bu}$); 1.30–1.28 (m, 4H) (1H, -CH$_{2pyrr}$) (3H, CH$_3$CO$_2$-); 1.25–1.23 (m, 6H, -CH$_{3pyrr}$); 1.21 (t, 9H, -*O*-CH$_2$-C*H*$_3$, J_{HH} = 7.3 Hz); 0.68–0.60 (m, 2H, -CH$_2$-Si). ^{13}C NMR (125 MHz, CDCl$_3$): δ 197.2 (CH$_3$*C*O$_2$-); 160.4 (N=CH); 159.8 (C=O); 158.2 (C$_{Ph}$); 146.9 (C$_{Nph}$); 138.5 (C$_{Nph}$); 137.9 (C$_{Ph}$); 133.7 (C$_{Nph}$); 130.1 (C$_{Ph}$); 129.4 (C$_{Ph}$); 129.1 (C$_{Ph}$); 128.1 (C$_{Nph}$); 126.8 (C$_{Nph}$); 125.4 (2C$_{Nph}$); 122.4 (C$_{Nph}$); 119.1 (C$_{Ph}$); 118.6 (C$_{Nph}$); 117.9 (C$_{Nph}$); 58.9 (-*C*H-CH$_{3pyrr}$); 58.4 (3C, 3 -*O*-*C*H$_2$-CH$_3$); 51.3 (-*C*H-CH$_{3pyrr}$); 44.5 (-CH$_2$-); 42.9 (-CH$_2$-); 34.8 (C$_{t\text{-}Bu}$); 31.5 (-CH$_{2pyrr}$); 29.7 (*C*H$_3$CO$_2$-); 29.3 (3C, 3 -CH$_{3t\text{-}Bu}$); 29.1 (-CH$_{2pyrr}$); 25.6 (-CH$_{3pyrr}$); 23.5 (-CH$_2$-); 18.2 (3C, 3 -*O*-CH$_2$-*C*H$_3$); 17.4 (-CH$_{3pyrr}$); 7.5 (-CH$_2$-Si).

(*R*,*R*)-8Rh. AgPF$_6$ (8.21 mg, 0.0325 mmol) in dry THF (10 mL) was added to a solution of [Rh(cod)Cl]$_2$ (7.93 mg, 0.0162 mmol) in the same solvent and the mixture was stirred vigorously at room temperature for 30 min. The resulting AgCl precipitated was filtered off and the yellow solution was treated with **(*R*,*R*)-9** (22 mg, 0.0325 mmol) in dry THF. The mixture was stirred at room temperature overnight. After the solution was purified through celite and subsequent the solvent was removed under vacuum to 0.5 mL, the product was precipitated by careful addition of Et$_2$O : pentane (1 : 1) and collected by filtration, to afford a stable dark green solid. Yield = 27.5 mg, 82%. UV-Vis: λ_{max} (nm) = 512, 356, 287. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.82 (s br, OH); 7.37–7.18 (m, 3H$_{Nph}$); 7.12–6.98 (m, 3H, 2H$_{Ph}$, 1H$_{Nph}$); 6.65 (d, 1H$_{Nph}$, J_{HH} = 6.6 Hz); 6.43 (d, 1H$_{Nph}$, J_{HH} = 6.6 Hz); 5.93 (s, 1H, N=CH); 4.73–4.65 (m, 1H, -CH$_{2pyrr}$); 4.44–4.37 (m, 2H, -CH=C$_{cod}$); 4.31–4.05 (m, 5H) (1H, -CH$_{2pyrr}$, 2H, -CH=C-$_{cod}$, 2H, -CH$_{2Ph}$); 3.76 (m, 6H, -*O*-C*H*$_2$-CH$_3$); 3.25 (m, 3H) (1H, -CH$_{pyrr}$, 2H, -CH$_2$-); 2.66–2.54 (m, 2H, -CH$_{2cod}$); 2.45–2.31 (m, 2H, -CH$_{2cod}$); 2.28–2.24 (m, 1H, -CH$_{2pyrr}$); 2.24–2.04 (m, 4H, -CH$_{2cod}$); 1.89–1.83 (m, 2H, -CH$_2$-); 1.51–1.49 (m, 3H, -CH$_{3pyrr}$); 1.37 (m, 9H, 3 -CH$_{3t\text{-}Bu}$); 1.25–1.22 (m, 12H, CH$_{3pyrr}$, -*O*-CH$_2$-C*H*$_3$); 1.12–1.00 (m, 1H, -CH$_{2pyrr}$); 0.89–0.74 (m, 2H, -CH$_2$-Si). ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.4 (N=CH); 155.8 (br, 2C, C$_{Ph}$, C$_{37}$, C=O); 148.9 (C$_{Nph}$); 141.6 (C$_{Nph}$); 138.5 (C$_{Ph}$); 136.6 (C$_{Nph}$); 134.7 (C$_{Ph}$); 128.9 (C$_{Ph}$); 127.0 (C$_{Ph}$); 126.7 (C$_{Nph}$); 125.5 (C$_{Nph}$); 124.9 (C$_{Nph}$); 124.4 (C$_{Nph}$); 122.0 (C$_{Nph}$); 120.3 (C$_{Ph}$); 115.9 (C$_{Nph}$); 115.4 (C$_{Nph}$); 80.4 (2C, -CH=CH$_{cod}$); 79.6 (2C, -CH=CH$_{cod}$); 65.8 (3C, -*O*-*C*H$_2$-CH$_3$); 53.4 (-*C*H-CH$_{3pyrr}$); 52.4 (-*C*H-CH$_{3pyrr}$); 43.0 (-CH$_2$-); 42.5 (-CH$_2$-); 34.7 (C$_{t\text{-}Bu}$); 30.3 (2C, -CH$_{2cod}$); 30.0 (-CH$_{2pyrr}$); 29.7 (2C, -CH$_{2cod}$); 29.4 (3C, -CH$_{3t\text{-}Bu}$); 29.1 (-CH$_{2pyrr}$); 22.7 (-CH$_2$-Si); 19.9 (3C, 3 -*O*-CH$_2$-*C*H$_3$); 16.2 (-CH$_{3pyrr}$); 7.9 (2C, -CH$_{3pyrr}$, -CH$_2$-Si).

Synthesis of heterogenized complexes

A solution of metal complex **(*R*,*R*)-8Pd** or **(*R*,*R*)-8Rh** (0.022 mmol), bearing a triethoxysilyl group, in CH$_2$Cl$_2$ (5 mL) was added to a well-stirred toluene suspension (25 mL) of the mesoporous solid (MCM-41, 150 mg). The slurry was heated at 110 °C for 16 h. After the mixture was cooled, the solid was filtered off, washed thoroughly with ethanol and diethyl ether and dried

under vacuum, to afford the respective heterogenized complexes in almost quantitative yields.

(*R*,*R*)-8Pd–MCM. Stable dark brown-reddish solid. Elemental analysis indicated 1.4 mass% Pd. Found C,5.4; H, 1.4; N, 0.73%. IR (KBr, cm^{-1}): $\nu_{C=O,C=N,C=C}$ 1641 (s), 1575 (s), ν_{Si-O} 1085, ν_{Pd-O} 544 (vw). DFTR: λ_{max} (nm) = 675, 619, 488, 363, 329, 287, 263, 231. ^{13}C NMR (300 MHz, Solid): δ 198.0 (CH_3CO_2-); 160.5 (N=CH); 158.0 (C=O); 140.4–121.0 (15C, $5C_{Ph}$ and $10C_{Nph}$); 120.7 (C_{Ph}); 59.5 (-*O*-CH_2-CH_3); 59.0 ($-CH_{pyrr}$); 51.3 ($-CH_{pyrr}$); 44.0 ($-CH_2$-); 43.00 ($-CH_2$-); 34.6 ($C_{t\text{-}Bu}$); 28.0 (6C, 3 -$CH_{3t\text{-}Bu}$, 2 -CH_{2pyrr}, CH_3CO_2-); 23.6 ($-CH_2$-); 16.0 (4C, 3 -*O*-CH_2-CH_3, -CH_{3pyrr}); 13.3 ($-CH_{3pyrr}$); 8.6 ($-CH_2$-Si).

(*R*,*R*)-8Rh–MCM. Stable dark green solid. Elemental analysis indicated 1.4 mass% Rh. Found C, 5.1; H, 1.4; N, 0.6%. IR (KBr, cm^{-1}): $\nu_{C=O}$ 1638 (s), $\nu_{C=N,C=C}$ 1580; ν_{Si-O} 1085, ν_{P-F} 803 (vs). DFTR: λ_{max} (nm) = 666, 561, 362, 331, 287, 255, 226. ^{13}C NMR (300 MHz, Solid): δ 160.1 (N=CH); 152.0 (C=O); 140.4–115.0 ($16C_{arom}$, $6C_{Ph}$ and $10C_{Nph}$); 80.0 (4C, 2-CH=CH_{cod}); 59.5 (-*O*-CH_2-CH_3); 53.00 (2C, 2-CH_{pyrr}); 43.6 (2C, 2 -CH_2-); 34.3 ($C_{t\text{-}Bu}$); 28.6 (9C, 4-CH_{2cod}, 3-$CH_{3t\text{-}Bu}$, 2-CH_{2pyrr}); 21.5 (-*O*-CH_2-CH_3, -CH_2-); 15.6 ($-CH_{3pyrr}$); 8.3 (2C, -CH_{3pyrr}, -CH_2-Si).

Catalytic activity

Hydrogenation of alkenes. The catalytic properties, in the hydrogenation of (*E*)-diethyl 2-benzylidenesuccinate and diethyl itaconate, of rhodium and palladium complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C temperature, 4 atm dihydrogen pressure and 1/100 or 1/1000 metal/substrate molar ratio. The evolution of the hydrogenated reaction product was monitored by gas chromatography.

Specifically: To a suspension of the catalyst, **8Rh-MCM** (15 mg, 2.0 10^{-3} mmol of Rh) in ethanol (40 mL), was added a solution of 52.4 mg (0.2 mmol) of (*E*)-diethyl 2-benzylidene succinate and the mixture stirred at 40 °C, 1000 rpm. The evolution of the reaction was monitored by gas chromatography.

Recycling experiments. At the end of the process the reaction mixture was centrifuged, and the catalyst residue washed to completely remove any remaining products and/or reactants. The solid was used again and any change in the catalytic activity was observed. In each of the four runs, up to 95% conversion was reached after 220 min and ee (%) was maintained after 4 cycles.

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