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Immobilization of (NHC)NN-Pincer Complexes on Mesoporous MCM-41 Support

Carolina del Pozo,[†,§] Avelino Corma,[‡] Marta Iglesias,*[,†] and Félix Sánchez*[,§]

[†]*Instituto de Ciencia de Materiales de Madrid, CSIC, C/Sor Juana Inés de la Cruz 3, Cantoblanco 28049 Madrid, Spain,* [‡]*Instituto de Tecnología Química, CSIC-UPV, Avenida de los Naranjos s/n, 46022 Valencia, Spain, and* [§]*Instituto de Química Orgánica General, CSIC, C/Juan de la Cierva 3, 28006 Madrid, Spain*

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Unsymmetrical pincer-type-ligated {pincer = $[C_6H_3N(CH_2L_1)(CH_2L_2)$-2,6], L_1 = prolinamide, L_2 = NHC} gold and rhodium complexes have proven to be highly effective catalysts for the hydrogenation of alkenes. Immobilization on ordered mesoporous silica (MCM-41) using a grafting process offers significant potential advantages in the application of such catalysts particularly with respect to catalyst separation and recycling. We describe one approach toward such immobilization: covalent bonding to silica via a pendant alkoxysilane group. This approach yields catalysts that are robust, recyclable, and comparable to or even more active than the corresponding species in solution. Spectroscopic evidence (IR spectroscopy, solid-state CP/MAS NMR, SEM), elemental analysis, and studies of catalytic activity support the hypothesis that binding occurs at the prolinamide substituent with no complex degradation. Control experiments showed the true heterogeneous nature of the catalyst in this reaction. Analyses of the hybrid materials revealed that the mesoporous structure of these materials was retained during the immobilization process as well as during catalysis.

Introduction

The process of manufacturing fine chemicals has consistently been a co-producer of environmentally damaging solvent and non-natural chemical waste.[1] Interest in the sustained development of homogeneous catalysts for fine chemical production has led to the opinion that a method for heterogenizing these catalysts must be developed and brought to the industrial area.[2] Several methods for heterogenization of homogeneous catalysts have been explored that are mainly based on inorganic support systems,[3] dendrimers,[4] or functionalized organic polymers.[5] It is generally acknowledged that covalent immobilization, of ligands and complexes, on an inorganic support gives the best recycling results.

A pincer organometallic is generally described as a terdentate ligand bound to a metal center via one sigma and two dative bonds.[6] Previous work has demonstrated the application of pincer metal complexes of the general formula $[M(C_6H_3(CH_2X)_2$-2,6)] (X = SR,[7] NR_2,[6] PR_2[8]) immobilized on dendritic,[9] organic polymeric,[10] and inorganic supports.[11]

*Corresponding authors. (M.I.) E-mail: marta.iglesias@icmm.csic.es. Tel: +34 913349000. Fax: +34 913720623. (F.S.) E-mail: felix-iqo@iqog.csic.es. Tel: +34 915622900. Fax: +34 915644853.

(1) De Vos, D. E.; Vankelecom, I. F. J.; Jacobs, P. A., Eds. *Chiral Catalyst Immobilization and Recycling*; Wiley-VCH: Weinheim, 2000.

(2) (a) Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702–1706. (b) Fodor, K.; Kolmschot, S. G. A.; Sheldon, R. A. *Enantiomer* **1999**, *4*, 497–511.

(3) (a) González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2004**, *346*, 1316–1328. (b) Corma, A.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, A.; Pérez-Ferreras, S.; Sánchez, F. *Adv. Synth. Catal.* **2006**, *348*, 1899–1907. (c) Corma, A.; González-Arellano, C.; Iglesias, M.; Pérez-Ferreras, S.; Sánchez, F. *Synlett* **2007**, 1771–1774. (d) Song, C. E.; Lee, S. *Chem. Rev.* **2002**, *102*, 3495–3524. (e) Notestein, J. M.; Katz, A. *Chem.−Eur. J.* **2006**, *12*, 3954–3965. (f) Corma, A.; Garcia, H. *Adv. Synth. Catal.* **2006**, *348*, 1391–1412.

(4) (a) Newkome, G. R.; He, H.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (b) Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69–82. (c) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717–3756. (d) van Klink, G. P. M.; Dijkstra, H. P.; van Koten, G. *C. R. Chim.* **2003**, *6*, 1079–1085. (e) Ribourbouille, Y.; Engel, G. D.; Gade, L. H. *C. R. Chim.* **2003**, *6*, 1087–1096. (f) Chase, P. A.; Klein Gebbink, R. J. M.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016–4054. (g) van de Coevering, R.; Klein Gebbink, R. J. M.; van Koten, G. *Prog. Polym. Sci.* **2005**, *30*, 474–490. (h) Berger, A.; Klein Gebbink, R. J. M.; van Koten, G. *Top. Organomet. Chem.* **2006**, *20* (Dendrimer Catalysis), 1−38. (i) Andres, R.; De Jesus, E.; Flores, J.-C. *New J. Chem.* **2007**, *31*, 1161–1191. (j) Hwang, S.-H.; Shreiner, C. D.; Moorefield, C. N.; Newkome, G. R. *New J. Chem.* **2007**, *31*, 1192–1217.

(5) (a) Shuttleworth, S. J.; Allin, S. M.; Sharma, P. K. *Synthesis* **1997**, 1217–1239. (b) Bergbreiter, D. E. *Catal. Today* **1998**, *42*, 389–397. (c) Shuttleworth, S. J.; Allin, S. M.; Wilson, R. D.; Nasturica, D. *Synthesis* **2000**, *8*, 1035–1074. (d) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637–4662. (e) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325–3344. (f) Kobayashi, S.; Akiyama, R. *Chem. Commun.* **2003**, 449–460. (g) Mastrorilli, P.; Nobile, C. F. *Coord. Chem. Rev.* **2004**, *248*, 377–395.

(6) (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781. (b) *The Chemistry of Pincer Compounds*; Morales-Morales, M., Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007.

(7) (a) Huck, W. T. S.; Hulst, R.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006–1008. (b) Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *New J. Chem.* **1998**, *22*, 165.

(8) Van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759–1792.

(9) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, 372–659.

(10) (a) Bergbreiter, D. E.; Osborn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058–9064. (b) Bergbreiter, D. E.; Osborn, P. L.; Frels, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 11105–11106.

(11) Mehendale, N. C.; Bezemer, C.; van Walree, C. A.; Klein Gebbink, R. J. M.; van Koten, G. *J. Mol. Catal. A: Chem.* **2006**, *257*, 167–175.

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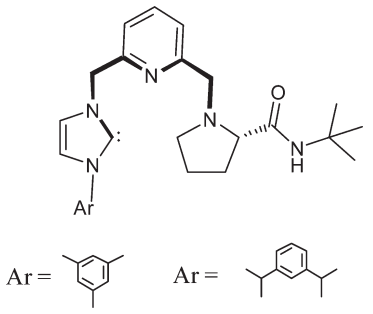


Figure 1

Pincer metal complexes have been applied in a wide range of catalytic reactions: aldol condensation,[12] transfer hydrogenation,[13] etc. Immobilization has been achieved through the 4-position of the aromatic central ring.[14]

Previously we have reported the synthesis of imidazolium salt precursors to unsymmetrical pincer-type chiral ligands (Figure 1) and subsequently prepared examples of transition metal complexes.[15] Rhodium, gold, and palladium complexes incorporating an NHC moiety gave a maximum enantiomeric excess (ee) of up to 98% for hydrogenation of diethyl 2-benzylidenesuccinate.

In this paper we demonstrate the heterogenization on an MCM-41 support through a group attached to the proline group on the ligand. This permits designing a catalyst by modifying the length of the spacer, changing the substituent on the pyridine, etc. The resulting materials have been applied in the hydrogenation of prochiral alkenes and are not substantially diminished compared to the homogeneous catalysts. The roles of the support material and linkers have been investigated, and it was found that the support/tether can have a significant effect on the catalytic reactions. The recycling of the catalytic materials has been studied and shows that the highly stable organometallic catalysts are stable to multiple recycles. It is demonstrated that catalyst immobilization can be a simple, high-yielding process, without complex degradation, and those catalysts immobilized can be recycled.

Results and Discussion

Our research is focused on the synthesis of neutral unsymmetrical pyridine pincer-type ligands with a lateral (*S*)-prolinamide donor function and an N-heterocyclic carbene moiety. Previously, symmetrical NCN-pincer complexes with two ester prolinates or prolinols as the nitrogen donor substituents have been described.[16] We also have reported the synthesis of pincer-type ONN, which contain O_{phenol}, $N_{pyridil}$, and chiral $N_{carboxamide}$ donor group derivatives of the natural amino acid (*S*)-proline as N-donor groups on the pincer backbone.[17] These are commercially available and enantiomerically pure building blocks for the synthesis of chiral ligands, and their stereogenic information can be maintained by choosing the appropriate reaction conditions during the synthesis and purification of the complexes. The stereogenic center (S_C) at the prolinate ring plays an important role, together with the bulkiness of the ester group, in the introduction of stereogenicity on the nitrogen atoms (S_N or R_N) upon coordination to the metal center. We have now incorporated a triethoxysilyl group on the prolinamide substituent in the CNN-pincer backbone. The purpose of incorporating a triethoxysilyl functionality is to obtain CNN-pincer-type ligands that may join to an inorganic carrier by a covalent bond with the SiOH.

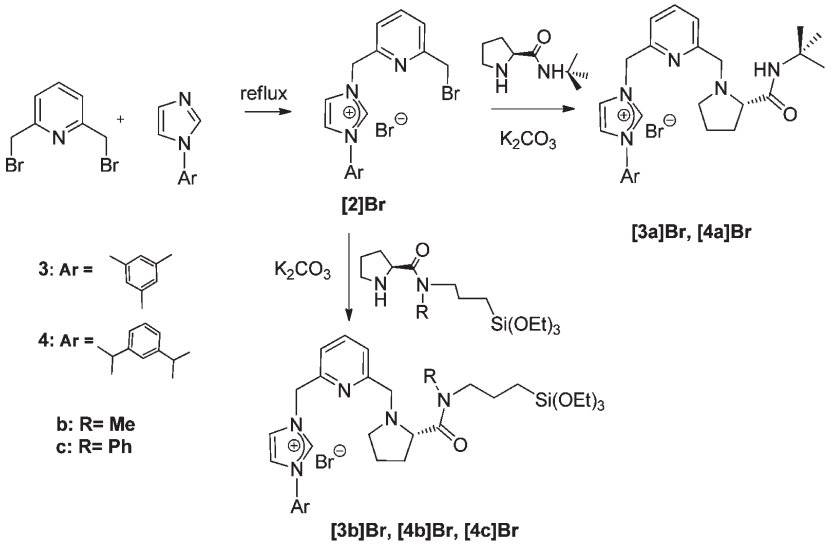
Synthesis of Ligand Precursors (Imidazolium Salts). The syntheses of two classes of hybrid NHC ligands and their metal complex derivatives are presented in Scheme 1. We have recently reported examples of rhodium(I), palladium(II), and god(III) complexes with this class of ligand and here expand the synthetic chemistry to access new derivatives with a triethoxysilyl group for grafting purposes. Scheme 2 shows the synthesis of new complexes.

The imidazolium salts used as precursors for the chelating NHC pyridine pyrrolidine ligands were synthesized by direct alkylation of 1-substituted imidazoles. [**3b**]**Br** and [**4c**]**Br** were prepared by treating [**2-Mes**]**Br** and [**2-^{i}Pr**]**Br** with either (*S*)-*N*-methyl-*N*-(2-(triethoxysilyl)propyl)pyrrolidine-2-carboxamide or (*S*)-*N*-phenyl-*N*-(2-(triethoxysilyl)propyl)pyrrolidine-2-carboxamide (Scheme 1). Specifically, the new (*S*)-1-aryl-3-((6-((2-(methyl(3-(triethoxysilyl)propyl)carbamoyl)pyrrolidin-1-yl)methyl)pyridin-2-yl)methyl)-1*H*-imidazol-3-ium bromide (aryl = mesityl, [**3b**]**Br**; aryl = 2,6-diisopropylphenyl, [**4b**]**Br**) were prepared in two successive nucleophilic substitutions with 1-aryl-1*H*-imidazole and 2,6-bis(bromomethyl)pyridine and the corresponding prolinamide in 70% yield with full retention of the S_C configuration of the carbon stereogenic center (Scheme 1). The ^{1}H NMR spectra in $CDCl_3$ of [**3b**]**Br** and [**4b**]**Br** show that imidazolium C(2)−*H* characteristically resonates at 10.40 and 10.16 ppm. The bridging methylene ($N_{im}CH_2C_{Py}$) moiety appeared as a singlet at 5.88 ([**3b**]**Br**) and 6.08 ([**4b**]**Br**) ppm, and $C_{Py}CH_2N_{pro}$ appeared at 4.1−4.0 ppm ([**3b**]**Br**) and 3.99−3.82 ppm ([**4b**]**Br**) in the ^{1}H NMR spectrum; $C_{Py}CH_2N_{pro}$ appeared at 61.09 ([**3b**]**Br**), 58.28 ([**4b**]**Br**), 52.93 ($N_{im}CH_2C_{Py}$, [**3b**]**Br**), and 50.23 ($N_{im}CH_2C_{Py}$, [**4b**]**Br**) ppm in the ^{13}C NMR spectrum. In the electrospray mass spectrum the imidazolium cation appeared as molecular peaks at m/z 623 ([**3b**]$^+$) and 665 ([**4b**]$^+$), respectively, in 100% abundance.

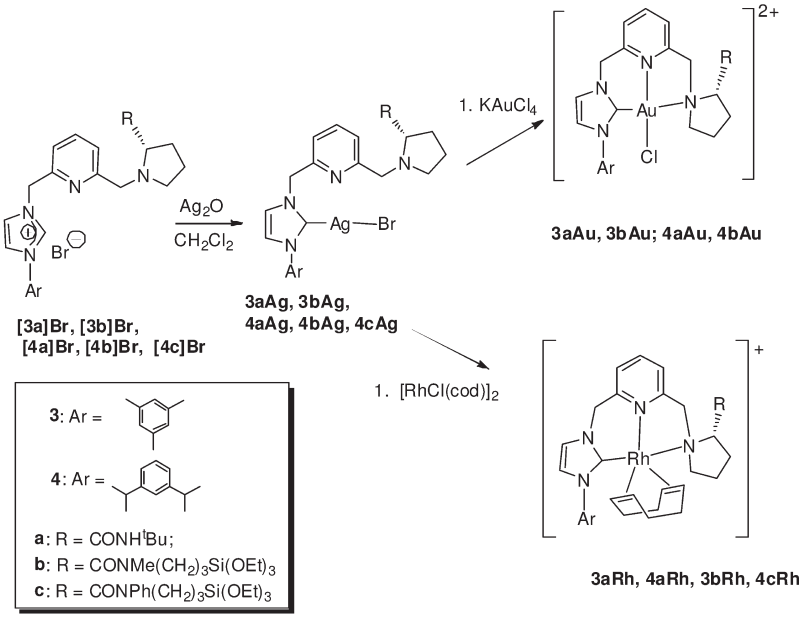
Imidazolium salt (*S*)-1-(2,6-diisopropylphenyl)-3-((6-((2-(phenyl(3-(triethoxysilyl)propyl)carbamoyl)pyrrolidin-1-yl)methyl)pyridin-2-yl)methyl)-1*H*-imidazol-3-ium bromide ([**4c**]**Br**) is obtained in a similar way, and its ^{1}H NMR spectrum shows the characteristic imidazolium C(2)-*H* at 10.34 ppm, the bridging methylene ($N_{im}CH_2C_{Py}$) at 6.23 ppm (51.82 ppm in the ^{13}C NMR spectra), and the $C_{Py}CH_2N_{pro}$ signal at 3.69−3.58 ppm (59.48 in the ^{13}C NMR spectra). The electrospray

(12) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607–1616.
(13) Gagliardo, M.; Chase, P. A.; Brouwer, S.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2007**, *26*, 2219–2227.
(14) (a) Mehendale, N. C.; Bezemer, Ch.; van Walree, C. A.; Gebbink, R. J. M. K.; van Koten, G. *J. Mol. Catal. A: Chem.* **2006**, *257*, 167–175. (b) Mehendale, N. C.; Sietsma, J. R. A.; de Jong, K. P.; van Walree, C. A.; Gebbink, R. J. M. K.; van Koten, G. *Adv. Synth. Catal.* **2007**, *349*, 2619–2630. (c) Huang, Z.; Brookhart, M.; Goldman, A. S.; Kundu, S.; Ray, A.; Scott, S. L.; Vicente, B. C. *Adv. Synth. Catal.* **2009**, *351*, 188–206. (d) McDonald, A R.; Dijkstra, H. P.; Suijkerbuijk, B. M. J. M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2009**, *28*, 4689–4699.
(15) Boronat, M.; Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Organometallics* **2010**, *29*, 134–141.
(16) (a) Gosiewska, S.; Veld, M. H.; Pater, J. J. M. de; Bruijnincx, P. C. A.; Lutz, M.; Spek, A. L.; van Koten, G.; Gebbink, R. J. M. K. *Tetrahedron: Asymmetry* **2006**, *17*, 674–686. (b) Gosiewska, S.; Martinez, S. H.; Lutz, M.; Spek, A. L.; van Koten, G.; Gebbink, R. J. M. K. *Eur. J. Inorg. Chem.* **2006**, *22*, 4600–4607. (c) Gosiewska, S.; Herreras, S. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G.; Gebbink, R. J. M. K. *Organometallics* **2008**, *27*, 2549–2557.
(17) Debono, N.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2007**, *349*, 2470–2476.

Scheme 1. Synthesis of Imidazolium Salts (Ligand Precursors)



Scheme 2. Synthesis of Soluble Complexes



mass spectrum shows a molecular peak at 726 (imidazolium cation).

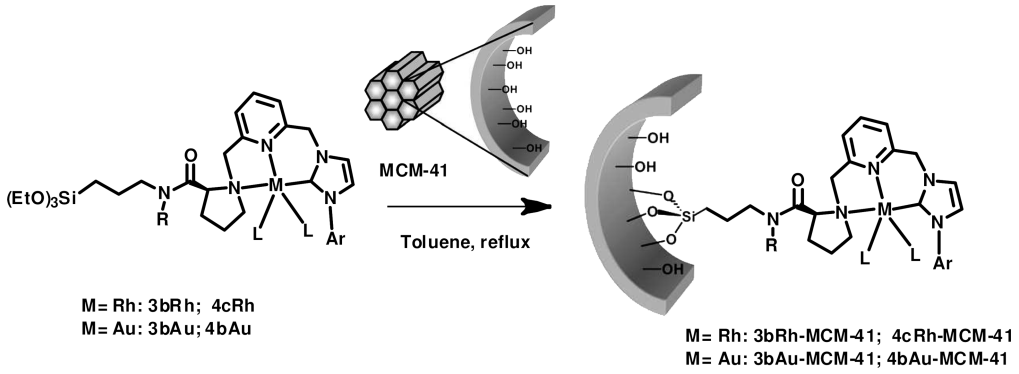
Synthesis of Complexes. The gold and rhodium CNN complexes with a triethoxysilyl group (**3bAu**, **4bAu**, **3bRh**, **4cRh**) shown in Scheme 2 were used in the MCM-41 heterogenization studies. Complexes **3aAu**, **4aAu**, **4aRh**, and **3aRh** (used as reference systems) have been previously prepared.[15]

Salts [**3**]**Br** and [**4**]**Br** are precursors to NHCs, and their gold and rhodium complexes were synthesized by Lin's method of transmetalation from intermediate silver(I) complexes **3Ag** and **4Ag** (Scheme 2).[18] Metalation of the imidazolium salts [**3**]**Br** and [**4**]**Br** using Ag_2O was monitored by ^{1}H NMR spectroscopy, but the silver complexes were not isolated. Instead, $[RhCl(cod)]_2$ (cod = cycloocta-1,5-diene) or $KAuCl_4$ was added directly to the dichloromethane solution of **3Ag** or **4Ag**. Precipitation of silver chloride was observed immediately, but the mixtures were allowed to stir at room temperature for 2−24 h before workup. Consistent with the formation of the Ag complex, the ^{1}H NMR spectra showed the absence of the downfield-shifted signal of the imidazolium ring (NC*H*N) along with the appearance of a diagnostic silver-bound carbene (N*C*N-Ag) peak at $\delta \sim 170$ ppm in the ^{13}C NMR spectrum of **3Ag** and **4Ag**.

Rhodium Complexes. Reaction of **3bAg** and **4cAg** with $[RhCl(cod)]_2$ at room temperature gave the rhodium complexes (**3bRh**, **4cRh**) in high yields. The ^{1}H and ^{13}C NMR spectra are as expected for complexes of the general formula [Rh(NHC-ligand)(cod)Cl]. The cyclooctadiene resonances are observed as four broad lines between 1.8 and 4.5 ppm due to fluxionality in the conformation of the cod chelate. Complexes **3bRh** and **4cRh** exhibit a doublet carbene signal

(18) (a) Garrison, J. C.; Youngs, W. *J. Chem. Rev.* **2005**, *105*, 3978–4008. (b) Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663–1667. (c) Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979–1982. (d) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975.

Scheme 3. Immobilization of Pincer-Type Complexes on MCM-41



in the ^{13}C spectrum at 181.28 and 179.61 ppm in addition to four other signals attributable to the carbon atoms of the cod ligand. Elemental analysis and the ESI-MS spectrum are consistent with the proposed formulation shown in Scheme 2.

Gold Complexes. Chelated organogold(III) complexes can also be prepared by transmetalation from the silver compounds described before.[19] Treatment of the silver complexes **3bAg** and **4bAg** with $KAuCl_4$ in ethanol gives the gold(III)-chloro complexes **3bAu** and **4bAu**, respectively, in >90% yield, as yellow-orange solids. The ^1H NMR spectra showed the absence of the (NCHN) resonance at 10.40 ([**4a**]**Br**) and 10.16 ([**4b**]**Br**) ppm owing to the loss of the acidic imidazolium proton along with the appearance of a diagnostic gold-bound carbene (N*C*N-Au) peak at 181.29 (**3aAu**), 190.78 (**3bAu**), 197.62 (**4aAu**), and 191.78 (**4bAu**) ppm in the ^{13}C NMR spectrum. Subsequent abstraction of the chloride anion from all complexes by treatment with $AgPF_6$ yielded the cationic complexes in good yields. One new stereogenic center was generated upon coordination of ligand **3b** or **4b** to the metal (gold, rhodium). In all cases the cationic complexes were obtained as single diastereoisomers.

Covalent Attachment of Pincer Complexes Containing Pendant Alkoxy Silane Groups to MCM-41. During the past few years we have developed a modular system that combines functionalized ligands with different supports and linkers in order to have systematic access to a variety of immobilized chiral catalysts.[20] We have applied this methodology to immobilize the new pincer complexes onto an MCM-41 mesoporous silica support (Brunauer−Emmett−Teller (BET) surface area 1030 $m^2\ g^{-1}$, micropore surface (*t*-plot) 0 $m^2\ g^{-1}$, external (or mesoporous) surface area 1030 $m^2\ g^{-1}$). MCM-41 is a short-range amorphous material that contains a large number of silanol groups available for grafting; however, it presents a long-range ordering of hexagonal symmetry with regular, monodirectional channels of 3.5 nm diameter.

Table 1. Elemental Analysis of the Heterogenized Complexes

entry	sample	Ar	R	wt %[a] M (mmol g^{-1})[b]
1	**3bRh-(MCM-41)**	mesityl	Me	0.6 (0.06)
2	**4cRh-(MCM-41)**	2,6-diisopropylphenyl	Ph	0.6 (0.06)
3	**3bAu-(MCM-41)**	mesityl	Me	1.8 (0.09)
4	**4bAu-(MCM-41)**	2,6-diisopropylphenyl	Me	1.2 (0.06)

[a] % by weight. [b] In parentheses, mmol per gram support.

In this paper we present the heterogenization of triethoxysilyl-pincer-type CNN complexes to study the effect of the NHC on the catalytic activity to compare the catalytic activity with that obtained with the respective soluble complexes.

The solid was functionalized according to the procedure shown in Scheme 3. Supported complexes were obtained by refluxing a mixture of gold and rhodium pincer complexes containing either a pendant $-NR(CH_2)_3Si(OEt)_3$ group (R = Me, Ph), **3bAu**, **3bRh**, **4bAu**, or **4cRh** and the support in toluene for 16 h. In a typical process, attachment of **3bAu**, **3bRh**, **4bAu**, or **4cRh** to MCM-41 was achieved by heating 300 mg of silica with 16 mg (20 mmol) of **3bAu**, **3bRh**, **4bAu**, or **4cRh** in toluene at 100 °C (Scheme 3). After one night, the original colored solution became colorless and the silica acquired a yellow color. Continuous extraction (Soxhlet) of the resulting material with CH_2Cl_2 or ethanol was performed for 24 h in order to remove any noncovalently attached organic material. After drying, the functionalized silicas **3bAu**, **3bRh**, **4bAu**, and **4cRh** were obtained as off-white solid particles. No detectable **3bAu**, **3bRh, 4bAu**, and **4cRh** remained in solution, which indicated that the silanol groups on the silica surface produced a siloxane linkage and ethanol. This supported catalyst, which contained 0.6−0.9 wt % of metal, was isolated, washed with ethanol, dichloromethane, and diethyl ether three times, respectively, and dried under high vacuum. The impact of the immobilization of **3bAu**, **3bRh**, **4bAu**, and **4cRh** on the structure of complexes was studied by using IR spectroscopy, CP/MAS NMR spectroscopy (^{13}C, ^1H), and elemental analysis, while scanning electron microscopy (SEM) showed a uniform dispersion of the complexes on the surface of the support (see Supporting Information).

Elemental content analysis has been used to characterize the materials. Nitrogen content analysis gives us an indication of how the synthetic procedures that have been carried out on the materials affect the substituents. Silicon and oxygen analyses give little information because they are present in large excess with respect to the organometallic species. The "loading" of catalytic sites was calculated from the rhodium

(19) (a) Li, C. K.-L.; Sun, R. W.-Y.; Kui, S. Ch.-F.; Zhu, N.; Che, Ch.-M. *Chem.—Eur. J.* **2006**, *12*, 5253–5266. (b) Parish, R. V.; Wright, J. P.; Pritchard, R. G. *J. Organomet. Chem.* **2000**, *596*, 165–176. (c) Bonnardel, P. A.; Parish, R. V.; Pritchard, R. G. *Dalton Trans.* **1996**, 3185–3193. (d) Wong, K. H.; Cheung, K. K.; Chang, M. C.W.; Che, C. M. *Organometallics* **1998**, *17*, 3505–3511.

(20) (a) Corma, A.; del Pino, C.; Iglesias, M.; Sánchez, F. *Chem. Commun.* **1991**, 1253–1255. (b) Corma, A.; Iglesias, M.; Martín, M. V.; Rubio, J.; Sánchez, F. *Tetrahedron: Asymmetry* **1992**, *3*, 845–848. (c) Corma, A.; Fuerte, A.; Iglesias, M.; Sánchez, F. *J. Mol. Catal. A* **1996**, *107*, 225–234, and references therein. (d) Alcón, M. J.; Corma, A.; Iglesias, M.; Sánchez, F. *J. Mol. Catal. A* **2003**, *194*, 137–152. (e) Debono, N.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2007**, *349*, 2470–2476. (f) Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Appl. Catal. A* **2010**, *375*, 49–54.

Table 2. Catalytic Hydrogenation of Substituted Succinates with Rh(I) and Au(III) Catalysts[a]

		(*E*)-diethyl 2-benzylidene succinate		diethyl itaconate	
entry	catalyst	TOF[b]	ee (%)[c]	TOF[b]	ee (%)[d]
1	**3aRh**	829	82 (*S*)	4962	< 10 (*S*)
2	**3bRh-(MCM-41)**	5000	98 (*S*)	40 000	5 (*S*)
3	**4aRh**	500	99 (*R*)	4000	18 (*R*)
4	**4cRh-(MCM-41)**	7680	99 (*S*)	33 333	5 (*S*)
5	**3aAu**	1000	70 (*S*)	4470	10 (*S*)
6	**3bAu-(MCM-41)**	3500	100 (*S*)	40 000	6 (*S*)
7	**4aAu**	480	90 (*R*)	3500	15 (*R*)
8	**4bAu-(MCM-41)**	3333	99 (*S*)	25 000	5 (*S*)

[a] Conditions: 4 atm, 40 °C, S/C ratio 1000:1. [b] TOF: h^{-1}. [c] Measured by HPLC (λ: 254 nm, hexane/^{i}PrOH, 95:5, column Chiralcel OD). [d] Measured by HPLC (λ: 230 nm, hexane/^{i}PrOH, 98:2, column Chiralcel AD-H).

and gold contents measured by ICP-MS (see Table 1). The substituent on the alkyl chain (Me, Ph) does not affect the amount of complex in the support (entries 1, 2).

The presence of functional groups characteristic of metal complexes in the materials was checked by FTIR spectroscopy. The stretching vibration modes of the mesoporous framework (Si−O−Si) of the grafted material complex−MCM-41 are observed at around 1241, 1066, and 806 cm^{-1}, while new bands appear at ca. 2967 and 2850 cm^{-1}, assigned to the ν(C−H) stretching of the aliphatic groups in complex−MCM-41. The carbonyl ν(C═O) stretching modes are observed at 1647−1630 cm^{-1}. A strong ν(O−H) stretch appeared in heterogenized compounds from 3200 to 3700 cm^{-1}, confirming the presence of surface silanol groups and the inability to react all silanols with bulky complex−MCM-41. In the IR spectrum of the rhodium-based complex **4cRh-MCM-41** the 1650−1620 cm^{-1} frequencies may be assigned to ν(C═O) and ν(C═C) shifted to lower wavenumbers (relative to the free ligands) because of coordination, the carbonyl stretching signal is found at 1631 cm^{-1}, and the N−H vibration is at 3313 cm^{-1} (broad), whereas a diluted solution of **4cRh** in CH_2Cl_2 has these vibrations at 1733, 1698, and 3345 cm^{-1} (sharp), respectively. The **3bAu-MCM-41** complex shows in its IR spectrum a band at 1647 assigned to ν(C═O). The DFTR spectra for all complexes were measured in the 200−600 nm range. The complexes showed several band maxima in the UV region, agreeing with the assignment of the bands as intraligand transitions in the aromatic ring, and charge-transfer transitions. The diffuse-reflectance spectra of the complexes were almost identical before and after the heterogenization process, indicating that the complexes maintain their geometry and their electronic surroundings without significant distortion even after heterogenization.

The materials were also characterized by cross-polarization magic-angle spinning (CP MAS) ^{13}C solid-state NMR spectra. The solid-state ^{13}C CP MAS NMR spectra of supported complexes are quite similar, since the spectra are dominated by the resonances of the aliphatic and aromatic groups. These signals appear at ca. 10.0 ($SiCH_2$) and 26.1 ($CH_2CH_2CH_2$), and the last one shifts to ca. 55 ppm ($N-CH_2$), aromatic region δ = 130.3−156.4 ppm, and M−C δ = 175.7, δ = 165.6 ppm (CO), for **4cRh-MCM-41**. All peaks corresponding to the ^{13}C NMR spectra of homogeneous complexes were present in the ^{13}C spectra of their heterogenized counterparts.

Catalytic Activity. Hydrogenation of Olefins. Table 2 shows data for the hydrogenations of diethyl itaconate and (*E*)-diethyl 2-benzylidenesuccinate with Au and Rh complexes carried out under standard conditions (EtOH as the solvent, 4 atm H_2, 40 °C). The nature of the metal center influences the catalytic activities. In general, a supported rhodium(I) catalyst is more active than gold(III) with the same ligand. In all cases no metal was detected during the hydrogenation reaction. High enantiomeric excesses were achieved with **3bRh-MCM-41**, **4cRh-MCM-41**, **3bAu-MCM-41**, and **4bAu-MCM-41** (ee >98%) for the hydrogenation of (*E*)-diethyl 2-benzylidenesuccinate, as detected from the HPLC analysis of hydrogenated products. As shown in Table 2, the substituent on the spacer (Me, Ph) does not have a significant effect on the activity nor on the enantioselectivity.

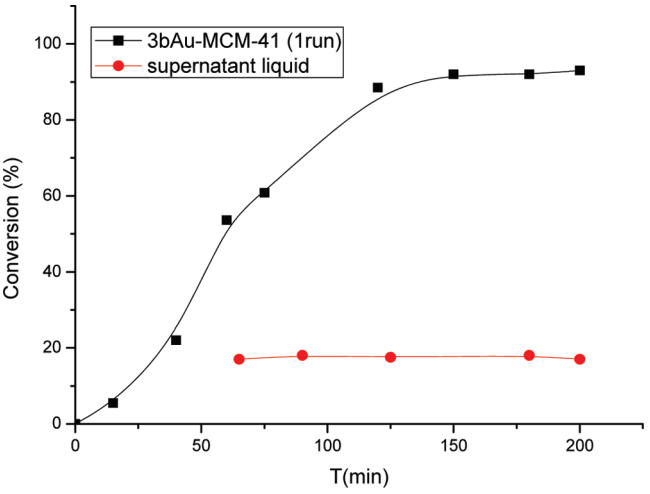


Figure 2. Kinetic traces for the hydrogenation of (*E*)-diethyl 2-benzylidenesuccinate in the presence of **3bAu-MCM-41** and with the supernatant liquid after filtration.

For soluble compounds (**3aRh**, **4aRh**, **3aAu**, **4aAu**) Table 2 also shows the effect of modifying the NHC N-substituent, indicating that the rate and particularly the enantioselectivity are very sensitive to changes at this position. The catalytic activity diminishes when the bis-3,5-diisopropylphenyl derivative (**4a**) is used as catalyst, but this decrease is accompanied by a significant increase of the enantioselectivity (>90%) and inversion of stereochemistry. Hydrogenation of methylenesuccinates catalyzed by derivatives **3a** (*N*-mesityl) leads to the *S* isomer, while the derivative **4a** (*N*-2,6-diisopropylphenyl) gives rise to the *R* isomer. This fact was also recently observed with NHC-phenolimine iridium complexes for the asymmetric transfer hydrogenation and suggests decisive alkyl−aryl interactions.[21] The substitution of the functional group in the substrate has a substantial influence on the enantioselectivity. The most enhanced selectivity was observed with bulkier (*E*)-diethyl 2-benzylidenesuccinate.

(21) Dyson, G.; Frison, J.-C.; Whitwood, A. C.; Douthwaite, R. E. *Dalton Trans.* **2009**, 7141–7151.

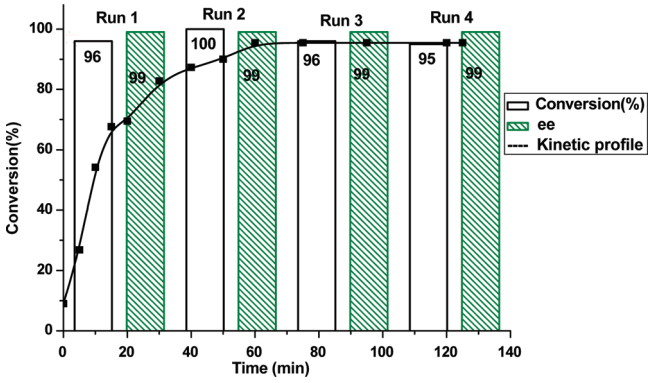


Figure 3. Recycling of **4cRh-MCM-41**.

The reactions catalyzed by supported complexes show a significant increase in reactivity, as shown in Table 2. The enantioselectivity compared with that obtained when using the soluble complex also increases, especially with substrates that have a higher steric hindrance. Hydrogenations with heterogenized catalysts always lead to the *S* isomer, regardless of whether the organometallic precursor has a mesityl or an isopropyl group. The conclusion that can be drawn from the few inversion reactions observed to date with heterogeneous catalysts is that, in the heterogeneous asymmetric reactions, the reversal of enantioselectivity could be attributed to the confinement effect of the porous support.[22]

As a proof of principle, 10 mg of complex **3bAu-MCM-41** was tested. The heterogeneity of the catalyst was assessed by a hot filtration test.[23] Catalysis using 0.9 mmol of substrate was run to 20% conversion (Figure 2). At this stage stirring was stopped and a small part of the clear supernatant solution was removed and stirred separately. At the same time stirring of the remaining reaction mixture was continued. It was found that in the latter reaction mixture catalysis in the presence of the hybrid material went further to completion, whereas the reaction does not occur with the supernatant. These observations indicate that the activity in the parent reaction and in the reaction mixture after sampling is associated with the catalytic activity of the (insoluble) hybrid material, i.e., with Au catalysis of the grafted NCN catalyst, thereby demonstrating the true heterogeneous nature of the catalyst.

Recyclability. The supported catalyst has to be physically and chemically stable during the reaction process. To evaluate the catalyst life and the stability of the supported catalyst, four cycles were carried out (Figure 3). We found that the material displayed minimal loss of activity after 4 runs and also determined if any metal leaching occurred after each run.

To confirm these results, the solid was separated by centrifugation at a conversion value of about 17%. The supernatant was then allowed to react. The residue containing the catalyst was washed twice with ethanol and diethyl ether (3 mL), and each time, after centrifugation, the organic phase was removed. Finally, fresh reagents were added to the remaining solid and the mixture was allowed to react for another run (Figure 2).

Conclusions

We have shown that (NHC)NN-pincer Rh and Au complexes were successfully immobilized on ordered mesoporous silicas. During immobilization the integrity of both the organometallic moiety and the inorganic support remained unchanged. It was found that hybrid mesoporous materials showed a good activity and recycling ability. It must be noted that both CNN-pincer rhodium and gold complexes results in an excellent hybrid material, which performs as a true heterogeneous catalyst and can be recycled and reused up to at least four times without loss of activity. The fact that in consecutive catalysis runs the structure and integrity of both the organometallic moiety and the inorganic support persisted nicely meets the objective set to merge properties of a homogeneous and a heterogeneous catalytic system into one sustainable hybrid catalyst.

Experimental Section

General Remarks. All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. Solvents were carefully degassed before use. C, H, and N analyses were carried out by the analytical department of the Instituto de Química Orgánica (CSIC) with a Lecco apparatus. Metal contents were analyzed by atomic absorption using a Perkin-Elmer AAnalyst 300 atomic absorption apparatus and plasma ICP Perkin-Elmer OPTIMA 2100 DV. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range 4000−200 cm^{-1}) in KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on Varian XR300 and Bruker 200 spectrometers. Chemical shifts are referenced to tetramethylsilane (internal standard). High-resolution ^{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. Gas chromatography analysis was performed using a Hewlett-Packard 5890. The enantiomeric excess was measured by HPLC (Agilent 1200) using a Chiralcel OD chiral column (diethyl 2-benzylidenesuccinate (λ: 254 nm, hexane/^{i}PrOH, 95:5, 0.5 mL/min) and Chiralcel AD-H (diethyl itaconate, λ: 230 nm, hexane/*i*PrOH, 98:2, 0.4 mL/min).

Preparation of Precursors. (*S*)-1-Mesityl-3-((6-((2-(methyl-(2-(triethoxysilyl)propyl)carbamoyl)pyrrolidin-1-yl)methyl)pyridin-2-yl)methyl)-1*H*-imidazol-3-ium Bromide ([3b]Br). A mixture of 3-{[6-(bromomethyl)pyridin-2-yl]methyl}-1-mesityl-1*H*-imidazol-3-ium bromide[15] (5 mmol, 2.25 g), sodium carbonate (10 mmol, 1.06 g), and (*S*)-*N*-methyl-*N*-(2-(triethoxysilyl)propyl)pyrrolidine-2-carboxamide[17] (5 mmol, 1.66 g) in acetone was stirred at room temperature for 12 h. The crude product was washed with diethyl ether to afford the product as a yellow solid (2.46 g, 70%). Anal. Calcd for $C_{34}H_{52}BrN_5O_4Si$ (702.8): C: 58.1; H: 7.5; N: 10.0. Found: C: 58.5; H: 7.2; N: 10.5. $[\alpha]^{20}_D = -19.6$ (CH_2Cl_2, l). IR (KBr, cm^{-1}): ν 2971.8 (m, CH); 1694.5 (m, C═O); 1638.2 (C═C, C═N); 1119.1 (vs, Si−O). UV−vis (λ, nm): 254, 352. ^1H NMR ($CDCl_3$, ppm): δ 10.40 (1H, s, NC*H*N); 8.17 (1H, s, H_{imi}); 7.74 (1H, s, H_{py}), 7.54−7.50 (1H, m, H_{py}); 7.33 (1H, s, H_{Py}); 7.32−7.21 (2H, m, H_{mes}); 6.95 (1H, d, H_{imi}); 5.88 (2H, s, $N_{imi}CH_2C_{py}$); 4.1−4.0 (2H, m, $C_{Py}CH_2N_{pro}$); 3.70−3.68 (6H, m, CH_2CH_3); 3.55−3.50 (2H, m, CH_2N); 3.49−3.46 (2H, m, CH_3N); 3.20−3.17 (1H, m, C*H*N); 3.00−2.95 (2H, m, CH_2N_{pro}); 2.30 (3H, s, *p*-CH_3); 2.01 (6H, s, *o*-CH_3); 1.80−1.75 (4H, m, $CH_2CH_2N_{pro}$); 1.70−1.60 (2H, m, $CH_2CH_2CH_2$); 1.22 (9H, t, CH_3); 0.52−0.50 (2H, m, CH_2Si). ^{13}C NMR ($CDCl_3$, ppm): δ 141.14 (C_{py}); 138.41 (C_{py}); 138.02 (NCHN); 134.20 (C_{arom}); 130.81 (C_{py}); 129.83 ($2C_{arom}$); 129.20 (C_{arom}); 128.88 (C_{arom}); 123.78 (C_{arom}); 123.38 (CH_{imi}); 122.32 (CH_{imi}); 122.22 (C_{py}); 122.19 (C_{py}); 65.57 ($N_{pro}CH$); 61.09 ($C_{py}CH_2N_{pro}$); 58.39 (CH_2CH_3); 57.73 ($N_{pro}CH_2CH_2$); 52.93 ($N_{imi}CH_2C_{py}$); 50.97 (CH_2N); 33.66 (NCH_3); 30.33 (CH_2CH_2); 29.29 (CH_2CH_2);

(22) Bartók, M. *Chem. Rev.* **2010**, *110*, 1663–1705.
(23) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341.

23.01 ($CH_2CH_2CH_2$); 21.11 (p-CH_3); 18.22 (CH_3CH_2); 17.69 (o-CH_3); 14.74 ($SiCH_2$). EM (m/z): 623 ($M^+ - Br$, 100).

(*S*)-1-(2,6-Diisopropylphenyl)-3-((6-((2-(methyl(2-(triethoxysilyl)-propyl)carbamoyl)pyrrolidin-1-yl)methyl)pyridin-2-yl)methyl)-1*H*-imidazol-3-ium Bromide ([4b]Br). A mixture of 3-{[6-(bromomethyl)-pyridin-2-yl]methyl}-1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium[15] (1 mmol, 493 mg), potassium carbonate (12 mmol, 1.66 g), and ((*S*)-*N*-methyl-*N*-(2-(triethoxysilyl)ethyl)pyrrolidine-2-carboxamide (1 mmol, 332.3 mg) in acetone was stirred at room temperature for 24 h. The crude was washed with diethyl ether to afford the product as a beige solid (558 mg, 75%). Anal. Calcd for $C_{37}H_{58}BrN_5O_4Si$ (744.9): C: 59.7; H: 7.9; N: 10.7. Found: C: 60.5; H: 7.4; N: 10.5. $[\alpha]^{20}_D = -18.7$ (CH_2Cl_2, l). IR (KBr, cm^{-1}): ν 2962.8 (m, CH); 1703.5 (m, C=O); 1655.4 (s, C=C, C=N); 1120.9 (vs, Si−O). ^1H NMR ($CDCl_3$, ppm): δ 10.16 (1H, s, NC*H*N); 8.3 (1H, s, H_{imi}); 7.70 (1H, s, H_{py}), 7.54−7.51 (1H, m, H_{py}); 7.50−7.48 (2H, m, H_{arom}); 7.47 (1H, H_{Py}); 7.28−7.26 (1H, m, H_{arom}); 7.14 (1H, H_{imi}); 6.08 (2H, s, $N_{imi}CH_2C_{py}$); 4.10−4.00 (6H, m, CH_2CH_3); 3.99−3.82 (2H, m, $C_{Py}CH_2N_{pro}$); 3.75−3.60 (3H, m, NCH_3); 3.44−3.43 (2H, m, CH_2N); 3.42−3.38 (1H, m, CHN); 3.10−3.00 (2H, m, CH_2-CH_2N_{pro}); 2.25−2.20 (2H, m, CH_{iPr}); 2.19−2.12 (4H, m, CH_2-CH_2CH); 1.78−1.65 (2H, m, $CH_2CH_2CH_2$); 1.24 (9H, t, CH_3); 1.17 (6H, d, CH_3); 1.09 (6H, d, CH_3); 0.53−0.50 (2H, m, CH_2Si). ^{13}C NMR ($CDCl_3$, ppm): δ 172.25 (CO); 155.25 (C_{py}); 147.69 (C_{py}); 141.04 (NCHN); 134.04 (C_{arom}); 130.16, (C_{py}); 127.72 ($2C_{arom}$); 126.08 (C_{arom}); 120.49 (C_{arom}); 120.32 (C_{arom}); 123.82 (CH_{imi}); 120.21(CH_{imi}); 118.25 (C_{py}); 118.12 (C_{py}); 64.52 ($N_{pro}CH$); 58.28 ($C_{py}CH_2N_{pro}$); 57.86 (CH_2CH_3); 55.54 ($N_{pro}CH_2CH_2$); 50.23 ($N_{imi}CH_2C_{py}$); 50.05 (CH_2N); 32.25 (NCH_3); 29.07 ($CH(CH_3)_2$); 25.00 ($CH(CH_3)_2$); 24.46 (CH_2CH_2); 24.42 (CH_2CH_2); 24.16 (CH_3CH_2); 20.00 ($CH_2CH_2CH_2$); 10.58 (CH_2Si). EM (m/z): 665 ($M^+ - Br$, 100).

(*S*)-1-(2,6-Diisopropylphenyl)-3-((6-((2-(phenyl(3-(triethoxysilyl)-propyl)carbamoyl)pyrrolidin-1-yl)methyl)pyridin-2-yl)methyl)-1*H*-imidazol-3-ium Bromide ([4c]Br). A mixture of 3-{[6-(bromomethyl)pyridin-2-yl]methyl}-1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium[15] (1 mmol, 493 mg), potassium carbonate (12 mmol, 1.66 g), and ((*S*)-*N*-phenyl-*N*-(2-(triethoxysilyl)propyl)pyrrolidine-2-carboxamide (synthesized as described in the Supporting Information) (1 mmol, 394.6 mg) in acetone was stirred at room temperature for 24 h. The crude was washed with diethyl ether to afford the product as a beige solid (565 mg, 70%). Anal. Calcd for $C_{42}H_{60}BrN_5O_4Si$ (806.95): C: 62.5; H: 7.5; N: 8.7. Found: C: 63.0; H: 7.2; N: 8.3. $[\alpha]^{20}_D = -20.0$ (CH_2Cl_2, l). IR (KBr, cm^{-1}): ν 2978.2 (m, CH); 1693.3 (m, C=O); 1654.5 (s, C=C, C=N); 1107.8 (vs, Si−O). ^1H NMR ($CDCl_3$, ppm): δ 10.34 (1H, s, NC*H*N); 7.78 (1H, s, H_{imi}); 7.65 (1H, s, H_{py}), 7.53−7.51 (1H, m, H_{py}); 7.50−7.45 (3H, m, H_{arom}); 7.35−7.34 (1H, m, H_{Py}); 7.32−7.26 (5H, m, H_{arom}); 7.0 (1H, s, H_{imi}); 6.23 (2H, s, $N_{imi}CH_2C_{py}$); 4.09−3.99 (6H, m, CH_2CH_3); 3.69−3.58 (2H, m, $C_{Py}CH_2N_{pro}$); 3.53−3.50 (2H, m, CH_2N); 3.49−3.44 (1H, m, CHN); 3.15−3.10 (2H, m, $CH_2CH_2N_{pro}$); 2.29−2.25 (2H, m, CH_{iPr}); 2.19−2.12 (4H, m, CH_2CH_2CH); 1.70−1.65 (2H, m, $CH_2CH_2CH_2$); 1.24 (9H, t, CH_3); 1.21 (6H, d, CH_3); 1.13 (6H, d, CH_3); 0.49−0.52 (2H, m, CH_2Si). ^{13}C NMR ($CDCl_3$, ppm): δ 145.41 (C_{py}); 138.63 (C_{py}); 138.36 (NCHN); 138.72, (C_{arom}); 137.09 (C_{py}); 132.27 (C_{arom}); 130.26 (C_{arom}); 128.5 (C_{arom}); 127.3 (C_{arom}); 125.3 (C_{arom}); 124.67 (5 C_{arom}); 124.87 (C_{arom}); 123.82 (CH_{imi}); 123.67 (CH_{imi}); 123.25 (C_{py}); 122,1 (C_{py}); 64.98 ($N_{pro}CH$); 59.48 ($C_{py}CH_2N_{pro}$); 57.96 (CH_2CH_3); 55.54 ($N_{pro}CH_2CH_2$); 51.82 ($N_{imi}CH_2C_{py}$); 50.97 (CH_2N); 29.07 ($CH(CH_3)_2$); 25.53 ($CH(CH_3)_2$); 25.37 (CH_2CH_2); 24.42 (CH_2-CH_2); 24.16 (CH_3CH_2); 21.19 ($CH_2CH_2CH_2$); 9.12 (CH_2Si). EM (m/z): 726 ($M^+ - Br$, 100).

Synthesis of Rhodium(I) Complexes. The complexes were synthesized following the general method: a solution of **[4b]Br** (1 mmol, 807.0 mg) and Ag_2O (0.5 mmol, 115.5 mg) in dichloromethane was stirred at room temperature under a N_2 atmosphere. The mixture was filtered through Celite in order to remove unreacted Ag_2O and other insoluble solids. $[RhCl(cod)]_2$ (0.5 mmol, 246 mg) was added to the solution of the resulting silver salt in CH_2Cl_2. After stirring overnight at room temperature, the solution was filtered through Celite. The solvents were removed in vacuo, and the residue was washed several times with diethyl ether. Cationic complexes with PF_6 as counterion were generated by halide abstraction via addition of $AgPF_6$ in a CH_2Cl_2/H_2O solvent system.

[Rh(cod)(3b)]Cl (3bRh): yellow, 94% yield. Anal. Calcd for $C_{42}H_{63}ClN_5O_4RhSi$ (868.5): C: 58.1; H: 7.3; N: 8.1; Rh: 11.9. Found: C: 56.2; H: 7.2; N: 7.8; Rh: 11.1. IR (KBr, cm^{-1}): ν 2963.8 (m, CH); 1664.5, 1658.0, 1594.1 (C=O, C=C, C=N); 1110.3 (vs, Si−O). UV−vis: λ (nm) 289, 355, 417. ^{13}C NMR (CD_3Cl, ppm): δ 181.28 (C−Rh); 172.53 (C=O); 145.28 (C_{Py}); 135.21 (C_{Py}); 129.87 (C_{arom}); 129.70 (C_{arom}); 128.63 ($2C_{arom}$); 128.12 ($2C_{arom}$); 123.16 (C_{py}); 122.8 (C_{imi}); 122.5 (C_{imi}); 121.52 ($2C_{py}$); 100.41 ($C{=}C_{cod}$); 78.47 ($C{=}C_{cod}$); 67.46 ($N_{pro}CH_2C_{py}$, CHN); 64.87 (CH_2CH_3); 56.80 ($N_{imi}CH_2C_{Py}$, CH_2N_{pro}, CH_2N); 34.85 (CH_{2cod}); 31.97 ($N_{pro}CH_3$); 30.84 (CH_{2cod}); 28.36 (CH_2-CH_2CH); 25.93 ($CH_2CH_2CH_2$); 25.48 (CH_3CH_2); 18.25 (p-CH_3); 17.23 (o-CH_3); 14.04 ($CH_2CH_2CH_2$); 14.03 ($CH_2CH_2CH_2$); 9.01 ($SiCH_2$). EM (m/z, %): 870 ($M^+ + 1$), 605 ([$M^+ - CON(CH_3)(CH_2)_3Si(OEt)_3$]).

[Rh(cod)(4c)]Cl (4cRh): yellow, 95% yield. Anal. Calcd for $C_{50}H_{71}ClN_5O_4RhSi$ (972.6): C: 61.8; H: 7.4; N: 7.2; Rh: 10.6. Found: C: 61.4; H: 7.6; N: 7.4; Rh: 10.1. IR (KBr, cm^{-1}): ν 2959 (m, CH); 1733, 1698 (C=O, C=C, C=N); 1109.9 (vs, Si−O). UV−vis: λ (nm) 287, 352, 396. ^1H NMR (CD_3Cl, ppm): δ 7.57−7.40 (11H, m, H_{arom}, H_{Py}); 7.25−7.05 (1H, m, N_{im}); 6.95−6.85 (2H, m, N_{im}); 6.55−6.57 (2H, m, $N_{im}CH_2C_{py}$); 4.35−4.32 (2H, m, CH_{cod}); 4.16−4.12 (2H, m, $C_{py}CH_2N_{pro}$); 3.50−3.45 (6H, m, CH_2CH_3); 3.25−3.10 (5H, m, CH_2N_{pro}, $N_{pro}CH$, CH_2N); 2.43−2.39 (2H, m, CH_{2cod}); 2.25−2.00 (2H, m, $CH_2CH_2N_{pro}$); 2.00−1.78 (8H, m, CH_{2cod}); 1.80−1.75 (6H, m, CH_{iPr}, CH_2CH_2CH, $CH_2CH_2CH_2$); 1.45 (6H, d, CH_3); 1.35 (9H, s, CH_3); 1.17 (6H, d, CH_3); 0.78−0.73 (2H, m, CH_2Si). ^{13}C NMR (CD_3Cl, ppm): δ 179.61 (C−Rh); 155.68 (C=O); 138.43 (C_{Py}); 136.28 (C_{Py}); 134.95 (C_{arom}); 132.50 (C_{arom}); 131.81 (C_{arom}); 129.57 (C_{py}); 129.23 ($2C_{arom}$); 129.01 ($2C_{arom}$); 125.75 ($2C_{arom}$); 124.5 (C_{arom}); 124.0 ($2C_{arom}$); 123.8 (C_{py}); 125.5 (C_{imi}); 123.35 (C_{imi}); 122.23 (C_{py}); 104.29 ($C{=}C_{cod}$); 80.21 ($C{=}C_{cod}$); 68.48 (CH_2CH_3); 68.20 ($N_{pro}CH_2C_{py}$, CHN); 58.94 ($N_{imi}CH_2C_{Py}$, CH_2N_{pro}, CH_2N); 36.10 (CH_{2cod}); 31.92 ($CH(CH_3)_2$); 31.35 (CH_{2cod}); 30.79 ($CH(CH_3)_2$); 30.23 (CH_2CH_2CH); 26.11 (CH_2-CH_3); 18.83 ($CH_2CH_2CH_2$); 14.66 ($SiCH_2$). EM (m/z): 972 (M^+).

Synthesis of Gold Complexes. The milder conditions of the transmetalation pathway make it an attractive choice also for the synthesis of gold(III) complexes. A solution of ligand (2 mmol) and Ag_2O (1 mmol, 231 mg) in dichloromethane was stirred at room temperature under a N_2 atmosphere. The mixture was filtered through Celite in order to remove unreacted Ag_2O and other insoluble solids. An ethanolic solution of $KAuCl_4$ (1 mmol) was added to the solution of the silver salt in CH_2Cl_2. After stirring overnight at room temperature, the solution was filtered through Celite. The solvents were removed in vacuo, and the residue was washed several times with diethyl ether. **[AuCl(3b)]Cl$_2$ (3bAu)**: yellow, 85% yield. Anal. Calcd for $C_{34}H_{51}AuCl_3N_5O_4Si$ (925.2): C: 44.1; H: 5.7; N: 7.6; Au: 21.3. Found: C: 43.6; H: 5.3; N: 7.2; Au: 20.8. IR (KBr, cm^{-1}): ν 2975.3 (m, CH); 1686.8 (sh, C=O), 1650.1 (s, C=C, C=N); 1118.1 (vs, Si−O). UV−vis: λ (nm) 296, 339, 391. ^1H NMR (CD_3Cl, ppm): δ 7.93 (1H, s, H_{imi}); 7.35 (2H, H_{py}), 7.30−7.28 (1H, m, H_{arom}); 7.25−7.14 (1H, m, H_{arom}); 7.02−7.00 (1H, m, H_{py}); 6.92 (1H, d, H_{imi}); 5.59−5.51 (2H, m, $N_{imi}CH_2C_{py}$); 4.54−4.32(2H, m, $C_{Py}CH_2N_{pro}$); 4.03−3.99 (3H, m, CH_3N); 3.70−3.68 (6H, m, CH_2CH_3); 3.25−3.19 (3H, m, CH_2N_{pro}, CHN_{pro}); 3.00−2.95 (2H, m, CH_2N); 2.29 (2H, s, p-CH_3); 2.11 (6H, s, o-CH_3); 1.98−1.75 (4H, m, CH_2CH_2CH); 1.70−1.60 (2H, m, CH_2CH_2-CH_2); 1.22 (9H, s, CH_3); 0.58−0.56 (2H, m, CH_2Si). ^{13}C NMR (CD_3Cl, ppm): δ 190.78 (C−Au); 166.04 (C=O); 145.00 (C_{Py}); 144.32 (C_{Py}); 134.95 (C_{arom}); 134.02 (C_{py}); 133.90 (C_{arom}); 129.29 (C_{arom}); 129.57 (C_{arom}); 129.23 (C_{arom}); 129.01 (C_{arom}); 123.50 (C_{py});

122.55 (C_{py}) 122.05(C_{imi}); 119.5 (C_{imi}); 65.04 ($N_{pro}CH$); 60.35 ($N_{pro}CH_2C_{py}$); 57.54 (CH_2CH_3); 53.58 ($N_{pro}CH_2$, $C_{py}CH_2C_{imi}$); 50.53 (NCH_2); 33.38 ($N_{pro}CH_3$); 28.87 (CH_2CH_2CH); 20.45 ($CH_2CH_2CH_2$); 20.36 (CH_3CH_2); 17.65 (*p*-CH_3); 17.01 (*o*-CH_3); 14.04 ($CH_2CH_2CH_2$); 13.51 ($CH_2CH_2CH_2$); 8.84 ($SiCH_2$). EM (*m*/*z*): 922 ([Au(3b)]Cl_2 + MeOH]).

[AuCl(4b)]Cl_2 (4bAu): yellow, 85% yield. Anal. Calcd for $C_{37}H_{57}Cl_3N_5O_4AuSi$ (967.3): C: 45. 9; H: 6.0; N: 7.2; Au: 20.3. Found: C: 45.4; H: 6.5; N: 6.7; Au: 19.8. IR (KBr, cm^{-1}): ν 2962.8 (m, CH); 1635.3, 1604.0 (s, C═O, C═C, C═N); 1107.1 (vs, Si−O). UV−vis: λ (nm) 296, 339, 391. ^{1}H NMR ($CDCl_3$, ppm): δ 7.78 (1H, s, H_{imi}); 7.35 (1H, s, H_{py}), 7.28−7.27 (2H, m, H_{py}); 7.26 (1H, m, H_{arom}); 7.25−7.14 (2H, m, H_{arom}, H_{Py}); 6.95 (1H, s, H_{imi}); 5.55 (2H, s, $N_{imi}CH_2C_{py}$); 4.54−4.32 (m, NCH_3); 4.07−3.98 (6H, m, CH_2CH_3); 3.98−3.82 (2H, m, $C_{Py}CH_2N_{pro}$); 3.44−3.42 (2H, m, CH_2N); 3.40−3.38 (1H, m, CHN); 3.20−3.05 (2H, m, $CH_2CH_2N_{pro}$); 2.40−2.32 (2H, m, CH^iPr); 2.29−2.20 (4H, m, CH_2CH_2CH); 1.80−1.68 (2H, m, $CH_2CH_2CH_2$); 1.24 (9H, s, CH_3); 1.17 (6H, d, CH_3); 1.12 (6H, d, CH_3); 0.53−0.50 (2H, m, CH_2Si). ^{13}C NMR ($CDCl_3$, ppm): δ 191.78 (C−Au); 172.04 (C═O); 144.59 (C_{Py}); 143.22 (C_{Py}); 134.95 (C_{arom}); 134.02 (C_{py}); 133.90 (C_{arom}); 129.29 (C_{arom}); 128.25 (C_{arom}); 129.23 (C_{arom}); 129.01 (C_{arom}); 123.50 (C_{py}); 122.77 (C_{py}) 121.25 (C_{imi}); 119.51 (C_{imi}); 65.04 ($N_{pro}CH$); 57.28 ($C_{py}CH_2N_{pro}$); 56.86 (CH_2CH_3); 54.54 ($N_{pro}CH_2CH_2$); 52.23 ($N_{imi}CH_2C_{py}$); 51.05 (CH_2N); 32.25 (CH_3N); 29.15 ($CH(CH_3)_2$); 26.00 ($CH(CH_3)_2$); 25.55 (CH_2CH_2); 24.42 (CH_2CH_2); 24.35 (CH_3CH_2); 21.19 ($CH_2CH_2CH_2$); 10.55 (CH_2Si). EM (*m*/*z*): 896 ([Au(**4b**)Cl]).

Synthesis of Heterogenized Complexes. To a suspension of the mesoporous solid, MCM-41 (150 mg), in toluene (25 mL), was added a solution of 1 mmol of the complexes in 5 mL of ethanol. The slurry was heated at 100 °C for 6 h. The mixture was cooled, and the solid was filtered off and washed thoroughly with ethanol and diethyl ether.

3bRh-MCM-41: Found: C: 6.20; H: 3.18; N:0.60; Rh: 0.6; 0.06 mmol/g. IR (KBr, cm^{-1}): ν 1647, 1637, 1630 (C═O, C═N, C═C), 1064 (Si−O). UV−vis: λ (nm) 220, 285, 395. ^{13}C NMR (solid) (ppm): δ 185.5 (C−Rh), 174.5 (C═O); 157.0−120.0 (C_{Py}, C_{Ph}, C_{imi}); 60.0−50.0 ($N_{pro}CH_2C_{Py}$, $N_{imi}CH_2C_{py}$, CH_2N_{pro}, CHN_{pro}, CH_2N); 28.7−22.2 ($CH_2CH_2CH_2$, NCH_3, CH_{3mes}); 10.1 (CH_2Si).

4cRh-MCM-41: Found: C: 7.62; H: 4.40; N: 0.55; Rh: 0.6; 0.06 mmol/g. IR (KBr, cm^{-1}): ν 1631, 1620 (C═O, C═N, C═C), 1059 (Si−O). UV−vis: λ (nm) 217, 288, 329. ^{13}C NMR (solid) (ppm): δ 175.7 (C−Rh); 165.6 (CO); 136.4−129.13 ($C_{Py,}$ C_{arom}); 102.3, 93.7, 71.6 (cod); 62.1−55.8 ($N_{pro}CH_2C_{py}$, $N_{imi}CH_2C_{Py}$, CH_2N_{pro}, CH_2N); 37.7−25.4 (CH_3, $CH_2CH_2CH_2$); 12.7 (CH_2Si).

3bAu-MCM-41: Found: C: 9.81; H: 2.40; N: 1.81; Au: 1.8; 0.09 mmol/g. IR (KBr, cm^{-1}): ν 1647, 1634, 1557 (C═O, C═N, C═C), 1097 (Si−O). UV−vis: λ (nm) 220, 253, 289, 325. ^{13}C NMR (solid) (ppm): δ 168.4 (CO), 156.7−130.3 (C_{Py}, C_{Ph}, C_{imi}); 58.8−55.8 ($N_{pro}CH_2C_{Py}$, $N_{imi}CH_2C_{py}$, CH_2N_{pro}, CHN_{pro}, CH_2N), 35.1−31.5 ($CH_2CH_2CH_2$, NCH_3); 21.0 (CH_{3mes}); 10.5 (CH_2Si).

4bAu-(MCM-41): Found C: 7.24; H: 2.77; N: 1.48; Au: 1.2; 0.06 mmol/g. IR (KBr, cm^{-1}): ν 1639, 1634, 1557 (C═O, C═N, C═C), 1095 (Si−O). UV−vis: λ (nm) 222, 254, 289, 327, 384. ^{13}C NMR (solid) (ppm): δ 172.0 (CO), 155.6−132.0 (C_{Py}, C_{Ph}, C_{imi}); 59.5−56.0 ($N_{pro}CH_2C_{Py}$, $N_{imi}CH_2C_{py}$, CH_2N_{pro}, CHN_{pro}, CH_2N), 35.0−32.0 ($CH_2CH_2CH_2$, NCH_3, C); 21.5 (CH_{3mes}); 10.3 (CH_2Si).

Catalytic Activity. Hydrogenation of Alkenes. The catalytic properties, in hydrogenation reactions, of the complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C, 4 atm of dihydrogen pressure, and 1:100 metal/substrate molar ratio. Specifically, 15 mg of the catalyst **4cRh-MCM-41** (8.2×10^{-4} mmol of Ru) was added to a solution of 230 mg (0.84 mmol) of (*E*)-diethyl 2-benzylidenesuccinate and in ethanol (40 ml, the mixture stirred at 40 °C, 1000 rpm). The evolution of the reaction of hydrogenated product was monitored by gas chromatography.

Recycling Experiments. At the end of the process the reaction mixture was centrifuged, and the catalyst residue was 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 4 runs, up to 95% conversion was reached after 220 min, and ee (%) was maintained after 4 cycles.

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Supporting Information Available: Details of the synthesis and characterization of new compounds, including images of ^{13}C NMR spectra and HPLC traces. This material is available free of charge via the Internet at http://pubs.acs.org.