

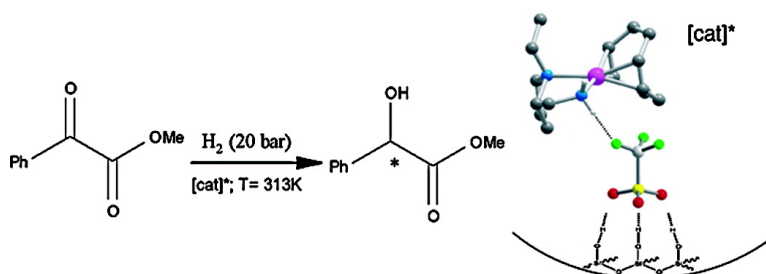
Communication

Constraining Asymmetric Organometallic Catalysts within Mesoporous Supports Boosts Their Enantioselectivity

Robert Raja, John Meurig Thomas, Matthew D. Jones, Brian F. G. Johnson, and David E. W. Vaughan

J. Am. Chem. Soc., **2003**, 125 (49), 14982-14983 • DOI: 10.1021/ja030381r • Publication Date (Web): 15 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Constraining Asymmetric Organometallic Catalysts within Mesoporous Supports Boosts Their Enantioselectivity

Robert Raja,^{*,‡} John Meurig Thomas,^{*,†,§} Matthew D. Jones,[‡] Brian F. G. Johnson,[‡] and David E. W. Vaughan^{||}

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, U.K. W1S 4BS, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, U.K. CB2 1EW, Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, U.K. CB2 3QZ, and Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania, 16802

Received June 25, 2003; E-mail: robert@ri.ac.uk

The availability of surfactant-templated mesoporous siliceous solids with sharply defined diameters that fall within the range of 20–250 Å has opened up new possibilities in heterogeneous catalysis. Such large pores enable¹ quite sizable metal complexes to be tethered on to their inner walls so that appreciable (surface) concentrations of accessible, well-defined—in situ XAFS, FTIR, and multinuclear CP/MAS NMR^{2,3}—active centers may be assembled in a spatially uniform fashion within these high area (ca. 300–800 m² g⁻¹) siliceous supports. It has previously been shown that highly active epoxidation,⁴ as well as a variety of selective hydroxylation^{1c,3} hydrogenation,^{5a,6} and allylic amination⁶ catalysts yielding important organic products, may be designed in this manner.

It has also been argued^{2b,6,7} that, by constraining the tethered asymmetric organometallic catalyst so as to increase the interaction between the pore wall and the active center and hence to restrict access of reactant to the catalyst, an improvement in the enantioselectivity ensues. In essence, the spatial constraint imposed upon the chiral catalyst by the walls of the pores of the support enhances its asymmetry by predisposing access of the prochiral reactant to the active center (Supporting Information).⁸

Because we believe that this approach constitutes a potentially powerful means of effecting highly enantioselective syntheses and other organic processes,⁹ we summarize here a systematic study¹⁰ of a range of porous silicas in each of which there is a very narrow spread of pore diameter and on to the inner walls of which one of four distinct cationic Rh(I) or Pd(II) complexes containing chiral bidentate ligands has been anchored. Partly because of their ease of synthesis,¹¹ diamino ligands (of three kinds; see below), rather than diphosphino ligands, attached to the Rh(I) or Pd(II) center, were used. Rather than employing as porous supports the popular (organic-template-derived) MCM types (which have nonintersecting pores) and related silicas such as SBA-15, we have used¹² a set of commercially available desiccant silicas having narrow pore size distributions (Figure 1 A) (designated Davison 923, 634, and 654). These are made by reacting sodium silicate with a strong mineral acid (usually sulfuric acid), with the pore size being controlled by gel time, final pH, temperature, concentration of reactants, etc.¹² Compared to MCM-41-type silicas, they are much lower in cost, more thermally and mechanically stable, less susceptible to structural collapse, and available in a range of granularities. They also have some intersecting pores that facilitate the diffusion of the reactant species to the immobilized catalyst. The average

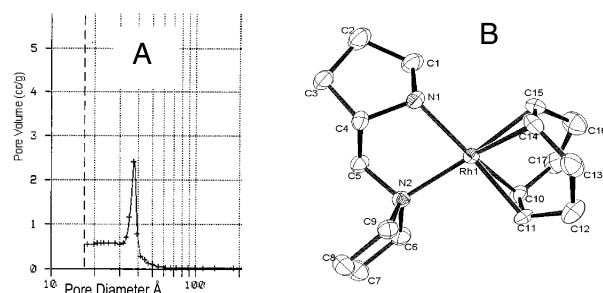


Figure 1. (A) Pore size distribution curve for the mesoporous sample (Davison 923), which has a value of 38 Å mean pore diameter. (B) Molecular structure of the Rh(I) complex to the chiral ligand PMP and COD [(S)-(+)-1-(2-pyrrolidinylmethyl)-pyrrolidine and cyclo-octadiene], CCDC ref 212362; selected distances (Å) and angles (deg); Rh(1)–N(1) = 2.1193(18), Rh(1)–N(2) = 2.1738(19), Rh(1)–C(14) = 2.113(2), Rh(1)–C(10) = 2.126(2), Rh(1)–C(15) = 2.143(2), Rh(1)–C(11) = 2.152(2), N(1)–Rh(1)–N(2) = 82.16(7). The ellipsoids are drawn at the 50% probability level, and the H-atoms and triflate cations have been omitted for clarity.

diameters¹³ of the pores of these silicas were, respectively, 38, 60, and 250 Å, and their respective surface areas are 700, 500, and 300 m² g⁻¹.

Rather than tethering the cationic Rh(I) complex containing the chiral diamino ligand (and cyclooctadiene, COD) using our customary^{2,9} covalent procedure (involving 3-bromopropyl-trichlorosilane to link up with a surface silanol group), we have instead employed the noncovalent immobilization approach recently described by de Rege et al.¹⁴ In this method, a surface-bound triflate (CF₃SO₃⁻) counterion securely anchors the cationic Rh(I)(COD) (Figure 1B) or the Pd(allyl) diamino complex to the inner wall.^{14,15} (This straightforward method circumvents the need for ligand modification to secure covalent tethering, and its advantages are described fully elsewhere.^{15b})

The four constrained chiral catalysts were: [Rh(COD)(S)-(+)-1-(2-pyrrolidinylmethyl)-pyrrolidine]-CF₃SO₃, [Pd(allyl) (S)-(+)-1-(2-pyrrolidinylmethyl)-pyrrolidine] CF₃SO₃, [Rh(COD) (S)-(-)-2-aminomethyl-1-ethyl-pyrrolidine] CF₃SO₃, and [Rh(COD) (1R,2R)-(+)-1,2-diphenyl-ethylenediamine] CF₃SO₃, which we abbreviate to Rh(COD)PMP, Pd(allyl)PMP, Rh(COD)AEP, and Rh(COD)-DED, respectively. The test reaction (see Supporting Information for experimental conditions) was the asymmetric hydrogenation of methyl benzoylformate to its corresponding methyl mandelate.

In their homogeneous form, only the Rh(COD)PMP and Pd(allyl)PMP exhibit any significant enantioselectivity (ee) under the reaction conditions (see Table 1) employed by us, whereas the other two homogeneous catalysts (namely, Rh(COD)AEP and

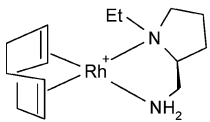
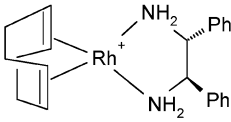
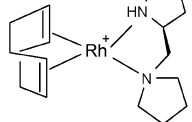
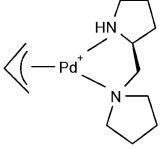
[‡] Department of Chemistry, University of Cambridge.

[†] Davy Faraday Research Laboratory.

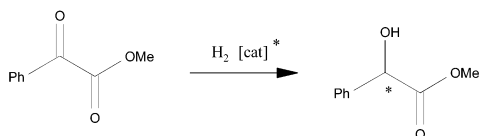
[§] Department of Materials Science and Metallurgy, University of Cambridge.

^{||} Pennsylvania State University.

Table 1. Asymmetric Hydrogenation of Methyl Benzoylformate^a

Catalyst	Counter-ion	Catalyst	Silica Type (pore dimension)	Metal	t (h)	Conv. ^b	TOF ^d (h ⁻¹)	ee ^c
 Rh(COD)AEP	CF ₃ SO ₃ ⁻	Homogeneous	-	Rh(I)	2.0	62	46	0
	CF ₃ SO ₃ ⁻	Heterogeneous	Davison 923 (38 Å)	Rh(I)	0.5	82.6	542	82
			Davison 634 (60 Å)		2.0	93.3	153	77
			Davison 654 (250 Å)		0.5	67.1	440	65
					2.0	93.9	154	61
 Rh(COD)DED	CF ₃ SO ₃ ⁻	Homogeneous	-	Rh(I)	2.0	69.9	60	0
	CF ₃ SO ₃ ⁻	Heterogeneous	Davison 923 (38 Å)	Rh(I)	0.5	77.7	596	50
			Davison 634 (60 Å)		2.0	98.1	188	79
			Davison 654 (250 Å)		0.5	59.7	458	68
					1.0	75.5	290	73
 Rh(COD)PMP	CF ₃ SO ₃ ⁻	Homogeneous	-	Rh(I)	0.5	46.2	145	53
	CF ₃ SO ₃ ⁻	Heterogeneous	Davison 923 (38 Å)	Rh(I)	0.5	92.8	643	85
			Davison 634 (60 Å)		2.0	95.8	166	94
			Davison 654 (250 Å)		0.5	63.0	436	72
					2.0	91.5	159	78
 Pd(allyl)PMP	CF ₃ SO ₃ ⁻	Homogeneous	-	Pd(II)	0.5	96.0	264	55
	CF ₃ SO ₃ ⁻	Heterogeneous	MCM-41 (30 Å)	Pd(II)	0.5	89.8	542	62
			Catalyst Recycled		2.0	98.9	149	67
					2.0	100	151	66

^a Methyl benzoylformate ≡ 0.5 g; solvent (methanol) ≡ 30 mL; catalyst (homogeneous) ≃ 10 mg; (heterogeneous) ≡ 50 mg; H₂ ≡ 20 bar; T = 313 K. ^b Conversion % = [(moles of initial substrate - moles of residual substrate)/(moles of initial substrate)] × 100. ^c Enantiomeric excess values (for the product methyl mandelate) were calculated from the peak areas of the enantiomers using the following formula: ee = ([R] - [S]) × 100/([R] + [S]). ee's for methyl mandelate and conversions were determined at Bayer AG, Business Unit Chemicals, Leverkusen Germany.¹⁷ ^d TOF = [(mol_{substrate-converted})/(mol_{complex}(Rh or Pd/silica))⁻¹ h⁻¹].



Rh(COD)DED did not display any significant ee. This is probably because the bulkiness of PMP in comparison to AEP and DED exerts further spatial congestion in the vicinity of the active center.

Table 1 summarizes the results with all four chiral catalysts and shows that, as expected from arguments given above, chiral restriction does indeed boost the ee values in a manner that logically reflects the declining influence of spatial constraint in proceeding from the 38 Å to the 60 Å to the 250 Å pore diameter silica (see Supporting Information). For the heterogeneous catalysts, the trend with Rh(COD)PMP is mirrored by both AEP and DED ligands, and it is clear that even when some of the asymmetric catalysts exhibit significant ee's under homogeneous conditions, their performance is much enhanced when immobilized in a constrained environment. It is also noteworthy that the noncovalent method of anchoring the organometallic catalyst does not lead to facile leaching when the catalyst is recycled. Further experimental details are given in two recently filed patents.¹⁶

Supporting Information Available: Experimental details, analytical methods employed, and single-crystal structure details are given (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- For selected examples, see: (a) Thomas, J. M. *Nature* **1994**, *368*, 289. (b) Jarupatrakorn, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 8380. (c) Nozaki, C.; Lugmair, C. G.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 13194.
- (a) Maschmeyer, T.; Oldroyd, R. D.; Sankar, G.; Thomas, J. M.; Shannon, I. J.; Kleptko, J.; Masters, A. F.; Catlow, C. R. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1639. (b) Thomas, J. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3588.
- Bell, A. T. *Science* **2003**, *299*, 1688.
- Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159.
- (a) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, *36*, 20 and references therein. (b) Bae, S. J.; Kim, S.-W.; Hyeon, T.; Kim, B. M. *Chem. Commun.* **2000**, 31.
- Johnson, B. F. G.; Raynor, S. A.; Shephard, D. S.; Maschmeyer, T.; Thomas, J. M.; Sankar, G.; Bromley, S. T.; Oldroyd, R. D.; Gladden, L. G.; Mantle, M. D. *Chem. Commun.* **1999**, 1167.
- (a) Thomas, J. M. *Faraday Discuss.* **1995**, *100*, C9. (b) Thomas, J. M.; Maschmeyer, T.; Johnson, B. F. G.; Shephard, D. S. *J. Mol. Catal. A* **1999**, *141*, 139.
- Maschmeyer, T. Oral report to the Davy Faraday Laboratory, March 1995. Unpublished work. See also refs 7(a) and 7(b).
- Jones, M. D.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Lewis, D. W.; Rouzard, J.; Harris, K. D. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4326.
- (a) Haller, G. L. *J. Catal.* **2003**, *216*, 12. (b) Derouane, E. G.; Andre, J. M.; Lucas, A. A. *J. Catal.* **1988**, *110*, 1998. In all these studies, however, there was no reference to enantioselectivity, and the range of pore diameters explored was very narrow (e.g., 25–36 Å in ref 10b).
- Tommasino, M. L.; Thomazeau, C.; Touchard, F.; Lemaire, M. *Tetrahedron: Asymmetry* **1999**, *10*, 1813.
- Acker, A. G. *J. Colloid Surf. Sci.* **1970**, *32*, 41.
- These values were obtained from the dV/d log(D) plots pertaining to the desorption isotherm of N₂ on the silicas.
- de Rege, F. M.; Morita, D. K.; Ott, K. C.; Tumas, W.; Broene, R. D. *Chem. Commun.* **2000**, 1797.
- (a) Bianchini, C.; Burnaby, D. G.; Evans, J.; Frediani, P.; Meli, A.; Oberhauser, W.; Psaro, R.; Sordelli, L.; Vizza, F. *J. Am. Chem. Soc.* **1999**, *121*, 5961. (b) Rouzard, J.; Jones, M. D.; Raja, R.; Johnson, B. F. G.; Thomas, J. M.; Duer, M. J. *Helv. Chim. Acta* **2003**, *86*, 1753.
- Raja, R.; Thomas, J. M.; Jones, M. D.; Johnson, B. F. G. German Patents DE 10305946 and DE 10305943, filed Feb 12, 2003.

JA030381R