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Rhodium bis-phosphine catalysts on mesoporous silica supports: new highly efficient catalysts for the hydrogenation of alkenes†‡

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A bidentate rhodium phosphine complex anchored onto a mesoporous molecular sieve was shown to be an active catalyst for the hydrogenation of alkenes, with the activity dependent on the method of grafting, and in general, exceeding that of related homogeneous catalysts.

Remarkable developments in homogeneous catalysis have taken place over the past two decades.[1] Unfortunately, the recovery of the precious metals and expensive ligands from the reaction medium is often not feasible. For this reason, there have been many approaches to ‘heterogenizing’ homogeneous catalysts by attaching well defined molecular species to polymeric supports.[2] Despite the development of some very effective supported systems,[3] a general strategy for mimicking solution phase behaviour is yet to be developed. Reactions on supports are generally slower and less predictable than their solution counterparts, commonly requiring excesses of reagents, higher temperatures and longer reaction times.[4]

The discovery of mesoporous molecular sieves has provided new possibilities in catalysis.[5] These mesoporous materials have unique structures characterized by high surface areas, large pores, and high long-range order; properties that make them ideal catalyst supports. MCM-41-type silicates have been used as supports for a variety of metals and metal complexes.[6] Recently, Shyu *et al.* described a supported analogue of Wilkinson’s catalyst, prepared by treating MCM-41 with $(EtO)_3Si\text{-}(CH_2)_3\text{-}PPh_2$ and then $RhCl(PPh_3)_3$.[7] Our approach to the preparation of a Rh complex supported on a mesoporous molecular sieve involves the use of a bidentate phosphine in order to minimize leaching, and a cationic complex to prevent dimerization through chloride bridges[8] (Fig. 1). The catalysts thus obtained are highly active for the hydrogenation of olefins, even more than the corresponding homogeneous complexes. The magnitude of the activity and the nature of the grafted species is strongly dependent on the method of grafting. To the best of our knowledge, this is the first report of a bidentate rhodium phosphine complex grafted onto a mesoporous molecular sieve.

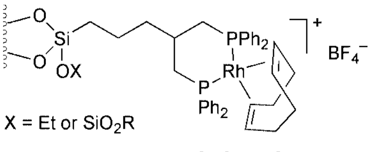
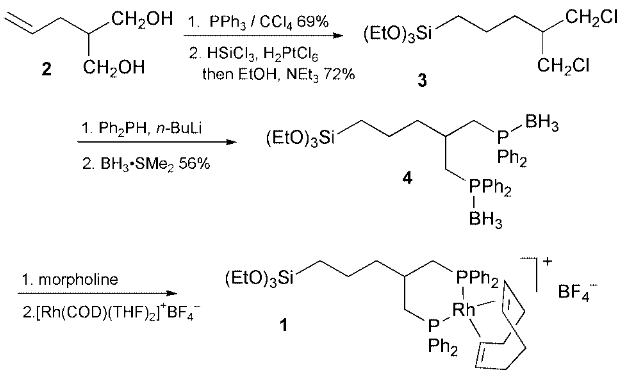


Fig. 1 Supported Rh catalyst.

Catalyst **1** is prepared as shown in Scheme 1.[9] Alkylation of diethyl malonate with allyl bromide (89% yield) and reduction of the ester groups with $LiAlH_4$ (69% yield) provides diol **2**. Treatment of **2** with PPh_3 in CCl_4 followed by hydrosilylation of the pendant olefin using H_2PtCl_6 yields **3**. The phosphine substituents were introduced using Ph_2PLi, and protected prior to isolation. Compound **4** was purified by flash chromatography and then deprotected with morpholine. Treatment with $[Rh(COD)(THF)_2]^+BF_4^-$§ generated the homogeneous Rh complex **1**. This was spectroscopically characterized and then grafted onto the surface of a molecular sieve (SBA-15-type)[5] at 25, 110 and 165 °C (method A). Grafting was also carried out in the presence of an inert spacer, $EtSi(OEt)_3$ (method B).[10] The resulting catalysts were characterized by MAS NMR, TEM, and nitrogen adsorption.



Scheme 1 Synthesis of Rh catalyst **1**.

^{31}P MAS NMR analysis of these materials revealed that as the grafting temperature was increased, the resonance at 14 ppm which corresponded to the homogeneous complex **1** (Fig. 2A) decreased while a new peak at 35 ppm, attributable to a P(V) species, appeared.[11] When the complex was grafted in refluxing mesitylene, the resulting material (**1-mps-165A**) was composed entirely of the P(V) species (Fig. 2B). Grafting in the presence of an inert spacer (method B) proved to be optimal (Fig. 2B).

The various Rh complexes were examined for their ability to catalyze the hydrogenation of isosafrole (**5**), Table 1.¶ With the exception of **1-mps-25A**, all the mesoporous catalysts tested are *more active than the corresponding homogeneous catalysts* (entries 1, 2).

Catalyst **1-mps-25B**, prepared in the presence of $EtSi(OEt)_3$, has the highest activity (3300 turnovers h^{-1}, entry 6). These results are consistent with the results of Shyu,[7] who found that their MCM-41-modified catalyst was *ca.* 3× more active than Wilkinson’s catalyst. Since **1-mps-25B** also had the lowest loading on support, the increased activity may be due to site isolation.[12] The least active catalyst of those examined, **1-mps-25A**, also has the highest Rh loading of 2.0%, consistent with this postulate. Studies are currently underway to measure the proximity of the Rh complexes on support.[12] Simple mixing of $[Rh(COD)_2]^+BF_4^-$ with the mesoporous support in the absence of any phosphine also led to an active hydrogenation catalyst (entry 7). The presence of an intermediate heteropoly acid species to aid in adsorption was not found to be necessary in this case.[13]

Retention of Rh on the surface was also a function of the grafting method. Supported systems with lower loadings of Rh were found to be more prone to leaching as determined by ICP-

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† Electronic supplementary information (ESI) available: NMR data. See http://www.rsc.org/suppdata/cc/b1/b102355c/

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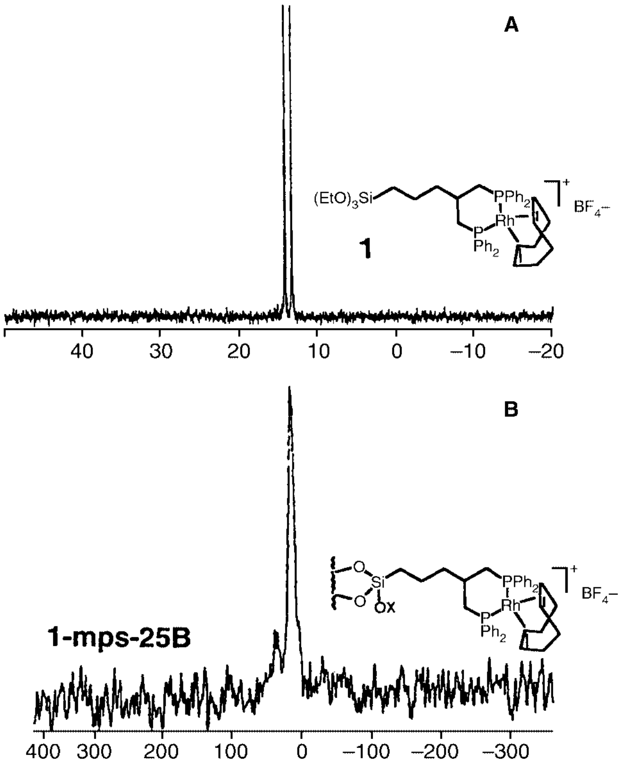

Fig. 2 ^{31}P NMR of homogeneous (**A**) supported (**B**) Rh complexes.

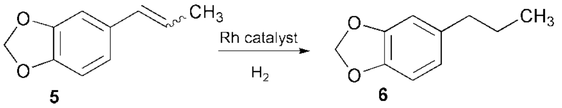

Table 1 Hydrogenation of **5**[a]

Entry	Catalyst[b]	Loading on support[c]	Turnover Frequency[d]
1	**Rh$^+$/DPPP**	n.a.	350
2	**1**	n.a.	750
3	**1-mps-110A**	1.4%	> 1600
4	**1-mps-25A**	2.0%	200
5	**1-mps-165A**	1.4%	1030
6	**1-mps-25B**	0.34%	3300
7	**Rh$^+$/mps**	3.3%	2300

[a] All reactions were carried out at rt, 750 psi of H_2, $[\text{substrate}]_{\text{init}} = 0.06$ M in dry, deoxygenated, distilled THF. Reaction times were between 30 and 90 min. Solutions were prepared in a glove box under argon. [b] mps = mesoporous silicate. [c] Wt%, determined by ICP MS analysis. [d] Turnovers per hour.

MS analysis of the reaction mixture after filtration through a nylon filter. Catalyst **1-mps-25B** (0.3% Rh by weight) lost a significant amount of Rh after the first use (21–36%) and less (*ca.* 5%) in subsequent runs. Catalyst **1-mps-110A** (1.4% Rh by weight) was much more robust, and lost only 2–3% Rh during the first run.

In conclusion, we have demonstrated that rhodium complexes heterogenized on mesoporous molecular sieves are highly active catalysts for the hydrogenation of olefins. With one exception (**1-mps-25A**), the supported complexes are all more active than the corresponding homogeneous catalysts.

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Notes and references

§ Prepared by treatment of $[Rh(COD)Cl]_2$ in THF with $AgBF_4$ and filtration of the resulting solution through Celite-545 (not acid washed).

¶ Isosafrole was purified by column chromatography, distillation, deoxygenated with three freeze, pump, thaw cycles, and purified immediately prior to use by passage through a short plug of dry alumina. The catalyst was found to be extremely sensitive to trace amounts of oxygen and deactivates with time, even when stored in a glove box.

1 R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, John Wiley & Sons, Inc., New York, 1994; I. Ojima, *Catalytic Asymmetric Synthesis*, VCH Publishers, New York, 1993.
2 D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 109; C. U. Pittman, Jr., in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1982, Vol. 8, 553; S. C. Bourque, H. Alper, L. E. Manzer and P. Arya, *J. Am. Chem. Soc.*, 2000, **122**, 956.
3 C. Bianchini, D. G. Burnaby, J. Evans, P. Frediani, A. Meli, W. Oberhauser, R. Psaro, L. Sordelli and F. Vizza, *J. Am. Chem. Soc.*, 1999, **121**, 5961; H.-B. Yu, Q.-S. G. Hu and L. Pu, *Tetrahedron Lett.*, 2000, **41**, 1681; H. Gao and R. J. Angelici, *J. Mol. Catal.*, 1999, **149**, 63; K. Nozaki, Y. Itoi, F. Shibahara, E. Shirakawa, T. Ohta, H. Takaya and T. Hiyama, *J. Am. Chem. Soc.*, 1998, **120**, 4051; A. Corma, M. Iglesias, C. del Pino and F. Sanchez, *J. Chem. Soc., Chem. Commun.*, 1991, 1253; S. Itsuno, K. Kamahori, K. Watanabe, T. Koizumi and K. Ito, *Tetrahedron: Asymmetry*, 1994, **5**, 523; H. Brunner and J. C. Bailar, Jr., *Inorg. Chem.*, 1973, **12**, 1465; B. M. Trost and E. Keinan, *J. Am. Chem. Soc.*, 1978, **100**, 7779; J. Collman, L. Hegedus, M. Cokke, J. Norton, G. Dolcetti and D. Marquardt, *J. Am. Chem. Soc.*, 1972, **94**, 1789.
4 D. J. Gravert and K. D. Janda, *Chem. Rev.*, 1997, **97**, 489 and references cited therein; R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, 1971, **93**, 3062.
5 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
6 P. Sutra and D. Brunel, *Chem. Commun.*, 1996, 2485; Y. V. S. Rao, D. E. De Vos, T. Bein and P. A. Jacobs, *Chem. Commun.*, 1997, 355; C.-J. Liu, S.-G. Li, W.-Q. Pang and C.-M. Che, *Chem. Commun.*, 1997, 65; T. Maschmeyer, R. D. Oldroyd, G. Dankar, J. M. Thomas, I. J. Shannon, J. A. Klepetko, A. F. Masters, J. K. Beattie and C. R. A. Catlow, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1639; B. F. G. Johnson, S. A. Raynor, D. S. Shephard, T. Maschmeyer, J. M. Thomas, G. Sankar, S. Bromley, R. Oldroyd, L. Gladden and M. D. Mantle, *Chem. Commun.*, 1999, 1167; L. Zhang, T. Sun and J. Y. Ying, *Chem. Commun.*, 1999, 1103; K. Kageyama, J.-I. Tamazawa and T. Aida, *Science*, 1999, **285**, 2113; For an excellent review of catalytic applications in general see: J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 56.
7 S.-G. Shyu, S.-W. Cheng and D.-L. Tzou, *Chem. Commun.*, 1999, 2337.
8 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.
9 E. Lindner, A. Enderle and A. Baumann, *J. Organomet. Chem.*, 1998, **555**, 247.
10 N. Bellocq, S. Abramson, M. Lasperas, D. Brunel and P. Moreau, *Tetrahedron: Asymmetry*, 1999, **10**, 3229.
11 L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe and R. E. Wasylishen, *J. Am. Chem. Soc.*, 1982, **104**, 438; K. D. Behringer and J. Blumel, *Inorg. Chem.*, 1996, **35**, 1814.
12 J. P. Collman, J. A. Belmont and J. I. Brauman, *J. Am. Chem. Soc.*, 1983, **105**, 7288.
13 R. Augustine, S. Tanielyan, S. Anderson and H. Yang, *Chem. Commun.*, 1999, 1257; M. Burk, A. Gerlach and D. Semmeril, *J. Org. Chem.*, 2000, **65**, 8933.