Dalton Communications

Effects of Catalyst Site Accessibility on Catalysis by Rhodium(I) Complexes of Amphiphilic Ligands $[Ph_2P(CH_2)_nPMe_3]^+$ ($n = 2, 3, 6$ or 10) tethered to a Cation-exchange Resin†

Eric Renaud and Michael C. Baird*
Department of Chemistry, Queen's University, Kingston K7L 3N6, Canada

The effects of catalyst site accessibility on the activities of supported olefin hydrogenation catalysts have been assessed utilizing the complexes $[Rh(nbd)L_2][NO_3]_3$ [nbd = η^4-norbornadiene; L = $Ph_2P(CH_2)_nPMe_3^+$; $n = 2, 3, 6$ or 10] tethered to a cation-exchange resin *via* the tetraalkylphosphonium moieties of the co-ordinated ligands; the most active catalysts are those containing the longer-chain ligands, where the catalyst sites are farthest removed from steric hindrance by the resin surface.

We have previously described the utilization of rhodium(I) complexes of the series of cationic, water-soluble tertiary phosphines $Ph_2PCH_2CH_2NMe_3^+$ [1a–c] and $Ph_2P(CH_2)_nPMe_3^+$ ($n = 2, 3, 6$ or 10)[1d] as catalysts for mono- and bi-phasic catalysis of olefin hydrogenation. Utilizing aqueous solutions of complexes of the type $[Rh(nbd)L_2][NO_3]_3$ [nbd = η^4-norbornadiene; L = $Ph_2PCH_2CH_2NMe_3^+$ or $Ph_2P(CH_2)_nPMe_3^+$] it was possible to hydrogenate both water-soluble olefins in aqueous solutions and olefins dissolved in water-immiscible solvents. Interestingly, in the case of biphasic catalysis utilizing $[Rh(nbd)\{Ph_2P(CH_2)_nPMe_3\}_2][NO_3]_3$ as catalyst precursors, a definite chain-length effect was observed, the system where $n = 6$ being the most active of the series.[1d]

The complex $[Rh(nbd)(Ph_2PCH_2CH_2NMe_3)_2][NO_3]_3$ also forms a novel, interesting biphasic catalyst system when bound ionically *via* the tetraalkylammonium group‡ to a cation-exchange resin, the supported complex acting as a very effective catalyst for the hydrogenation and hydroformylation of olefins in acetone solution.[1c] In view of the intense current interest in the design and utilization of supported catalysts,[2] we decided to investigate both the catalytic activities of resin-supported rhodium complexes of $Ph_2P(CH_2)_nPMe_3^+$ and the effects of chain length on relative catalyst activities. We present here preliminary results of an investigation of the catalytic properties of the complexes $[Rh(nbd)\{Ph_2P(CH_2)_nPMe_3\}_2][NO_3]_3$ ($n = 2, 3, 6$ or 10) supported on the sodium form of a strong acid, macroreticular cation-exchange resin (Rohm & Haas Amberlyst 15, purchased from Aldrich).

The complexes were loaded onto the ion-exchange support by adding an aqueous solution of the former (0.05 mmol) to a well stirred suspension of the resin (5 g) in water under nitrogen. Interestingly, the rates of sorption of the catalyst precursors exhibited significant chain-length dependences, the yellow colour of the complexes of the smaller ligands ($n = 2$ or 3) disappearing within 10 min while the solutions of the complexes where $n = 6$ or 10 took 15 and 30 min, respectively, to decolourize. The aqueous phase was then removed by syringe, the rhodium-containing resins washed successively with distilled water, methanol and diethyl ether, and dried by heating at 50 °C under reduced pressure. The catalyst loadings (0.42% w/w) were thus about 0.4% of the possible total loading, calculated assuming interactions only of the trimethylphosphonium groups with the sulfonate groups of the resin.

Catalytic runs were generally carried out at 21 °C in the glass pressure vessel of a Parr hydrogenation apparatus. In our initial experiments, hex-1-ene (10 cm^3) dissolved in methanol (30 cm^3) was added to the resin-supported catalyst precursor (ratio of substrate to catalyst ~1600:1) under nitrogen. The reactor bottle was flushed with hydrogen and then held under 3 atm pressure of hydrogen for 2 h, under which conditions the consumption of olefin substrate was incomplete. The pressure was released, and quantitative analyses of the products were carried out utilizing gas chromatography. The results of representative experiments 1–4 are shown in Table 1, from which it can be seen that the catalyst systems exhibit a very pronounced ligand chain-length dependence, the activities increasing with increasing chain length. The overall results strongly imply that, as proposed above and previously for the $Ph_2PCH_2CH_2NMe_3^+$ system,[1c] the catalysts are bound to the resin *via* the tetraalkylphosphonium groups, the catalyst sites of the longer-chain ligand systems being subject to relatively little steric hindrance by the surface of the resin. Motion of the rhodium centres becomes increasingly free and the catalyst sites therefore become increasingly more accessible as the length of the tether increases, and thus the long-chain ligand systems behave essentially as homogeneous catalysts while retaining the advantages[2] of heterogeneous catalysts. Although direct comparison of activities with liquid-phase catalysts[1c,d] is difficult, the longer-chain supported systems with $n = 6$ or 10 appear to exhibit somewhat lower catalytic activities than do the liquid–liquid biphasic systems, as anticipated, but also result in proportionately less isomerized products. As is also

---

† *Non-SI unit employed*: atm = 101 325 Pa.

‡ It may be assumed that binding of the cationic complexes described in refs. 1*c* and 1*d* to a cation-exchange resin occurs *via* the small tetra-alkylammonium and -phosphonium moieties rather than *via* the rhodium(I) complex ions because the latter would be much more sterically hindered by the relatively bulky nbd and PPh_2 groups. In addition, the chain-length effects observed here would not be evident were the catalysts all bound *via* the rhodium ions.

Table 1 Representative results of catalytic hydrogenation by [Rh(nbd){$Ph_2P(CH_2)_nPMe_3$}$_2$]

		Product (%)			
Experiment	Ligand *n*	Hexane	Hex-1-ene	*trans*-Hex-2-ene	*cis*-Hex-2-ene
(*a*) Hex-1-ene					
1	2	5	90	2	2
2	3	13	80	3	4
3	6	19	69	6	7
4	10	28	58	6	8
5	2	35	0	55	10
6	3	42	1	47	10
(*b*) Styrene		Ethylbenzene			
7	2	5			
8	3	15			
9	6	26			
10	10	21			
(*c*) Cyclohexene		Cyclohexane			
11	2	1			
12	3	1			
13	6	0			
14	10	3			

apparent, hydrogenation is accompanied by very little olefin isomerization.

Experiments 5 and 6 involve catalytic reactions in which hex-1-ene (20 cm^3) was hydrogenated in the absence of methanol and (10 cm^3) in the presence of diethyl ether (30 cm^3), respectively, for 2 h. As can be seen, much more active catalysts are formed but olefin isomerization becomes competitive; why this should be is not yet clear. Experiment sets 7–10 and 11–14 involve the hydrogenation of styrene and cyclohexene (10 cm^3), respectively, each in methanol (30 cm^3) for 2 h. As can be seen, a pronounced chain-length effect is still apparent with both olefins, although the catalysts are relatively ineffective for the bulky cyclohexene. However, the resin-supported catalysts appear to exhibit somewhat higher activities for styrene hydrogenation than were observed previously in liquid–liquid biphasic systems.[1d]

Our experiments appear to be the first in which the role(s) of tether length of a series of electronically similar, supported catalysts has been systematically investigated. Our results to date clearly confirm our initial hypothesis [1c] that the activities of supported catalysts should be strongly affected by increasing the degrees of motional freedom and hence the accessibility of the catalyst centres.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (operating grant to M. C. B.) and Alcan Aluminium (Graduate Fellowship to E. R.) for financial assistance, the International Nickel Company and Johnson Matthey for loans of rhodium trichloride.

References

1 (*a*) R. T. Smith, K. U. Ungar and M. C. Baird, *Transition Met. Chem.*, 1982, **7**, 288; (*b*) R. T. Smith, K. U. Ungar, L. J. Sanderson and M. C. Baird, *Ann. N.Y. Acad. Sci.*, 1983, **415**, 253; (*c*) R. T. Smith, K. U. Ungar, L. J. Sanderson and M. C. Baird, *Organometallics*, 1983, **2**, 1137; (*d*) E. Renaud, R. B. Russell, S. Fortier, S. J. Brown and M. C. Baird, *J. Organomet. Chem.*, 1991, **419**, 403.

2 See T. G. Southern, *Polyhedron*, 1989, **8**, 407; D. Sinou, *Bull. Soc. Chim. Fr.*, 1987, 480; D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 109; M. Barton and J. D. Atwood, *J. Coord. Chem.*, 1991, **24**, 43; F. R. Hartley, *Supported Metal Complexes*, D. Reidel, Dordrecht, 1985.

Received 9*th June* 1992; *Communication* 2/03046B