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POLYMER-SUPPORTED CATALYSTS FOR THE REACTION OF ETHANOL WITH POLYMETHYLHYDROGENDISILOXANE

R.V. PARISH* and M.I. VANIA

Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester, M60 1QD (Great Britain)

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Summary

The ligand groups PPh_2, PEt_2, and $AsPh_2$ have been bonded to macroreticular polystyrene and treated with $[IrCl(C_8H_{14})_2]_2$ and Et_3SiH. The resulting materials were used to catalyse the reaction between ethanol and polymethylhydrogendisiloxane, $Me_3SiO[Si(Me)(H)O]_nSiMe_3$ (n = ca. 50). The arsine system showed very little useful activity. The Et_2P system had good activity initially, rather less on recovery and reuse in five more reactions, and then suddenly decreased in activity. For PPh_2, the catalyst showed a steady decline in two dozen reaction cycles. In each case, the separated liquid products showed catalytic activity, demonstrating that leaching of the metal from the support was occurring. The addition of the metal-free supported ligand inhibited the leaching, and stabilised the activity over at least a dozen cycles.

Introduction

Insolubilized metal complexes are useful catalysts, showing many of the best features of homogeneous and heterogeneous systems [1–3]. In our previous studies of the catalysis of *O*-silylation by iridium complexes anchored by means of various ligands to silica [4], deactivation of the catalysts occurred by leaching of the metal into solution. Radio-labelling demonstrated that removal of ligand from the support was also taking place. We now believe that this may in part have been due to initial over-loading of the silica with ligand and, hence, inefficient anchoring [5]. However, we have also investigated the use of modified polystyrene ligands as supports, for which leaching of ligand should be impossible. Several studies with this type of catalyst have been reported [6–9], and we now describe the use of iridium complexes of phosphine and arsine ligands in the catalysis of the reaction between ethanol and polymethylhydrogendisiloxane, $Me_3SiO[Si(Me)(H)O]_nSiMe_3$ (n = ca. 50). Earlier work in these Laboratories has shown that related monomeric complexes are very effective catalysts for this type of reaction [10].

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Experimental

Catalytic runs with 4.3 mmol of Si–H and 8.6 mmol of ethanol in toluene at 45°C (total volume, 6 cm^3) were monitored by following the rate of evolution of hydrogen, as described previously [4].

Polystyrene-supported complexes. Polystyrene beads (macroreticular, 30% cross-linked) were brominated in the presence of iron(III) chloride [11], and washed with acetone, dioxane/water (1/1), and dioxane. The beads were then treated with $LiPPh_2$, $LiPEt_2$, or $LiAsPh_2$, prepared from $ClPPh_2$, $PhPEt_2$ or $AsPh_3$ and lithium shot [12], and washed with methanol and chloroform. Iridium was applied as $[IrCl(C_8H_{14})_2]_2$ in toluene; after stirring for 2–3 h under nitrogen, a slight excess of Et_3SiH was added, and stirring was continued overnight. The catalyst was then Soxhlet-extracted with refluxing toluene for 4 h.

Results

Supported ligands were prepared by treatment of brominated polystyrene with LiR ($R = AsPh_2$, PEt_2, or PPh_2). These materials were then treated with $[IrCl(C_8H_{14})_2]_2$ and triethylsilane. The latter reagent was used to convert the polymer-bound iridium to a silyliridium(III) complex [13] which should be stable to atmospheric oxidation. The activity of the complexes was examined by monitoring the evolution of hydrogen from a 2/1 mixture of ethanol and polymethylhydrogendisiloxane in toluene.

Supported-$AsPh_2$. The iridium-arsine system showed high activity, giving effectively complete reaction in 50 minutes. However, on recovery and reuse, activity declined drastically, and only about 20, 10 and 8% reaction was achieved in 50 minutes in successive runs. After each run, the separated liquid products were examined. Those from the first run were yellow, and exhibited modest homogeneous catalytic activity when further reagents were added. The products of the later runs were virtually inactive.

The arsenic content of the supported ligand was lower than had been anticipated (0.1%), and a considerable excess of iridium was used to prepare the catalyst. It is therefore likely that the solid contained a substantial proportion of loosely bound iridium, which was readily leached during the first run. The remaining arsine-bound iridium appeared to have low activity. After four runs, the As/Ir ratio was ca. 1/1.

Supported-PEt_2. The Et_2P-iridium catalyst showed good initial activity (60% reaction in 30 minutes), which declined to a rather lower level for the following five runs (ca. 45% reaction in 30 minutes), and then fell sharply (ca. 10% reaction in runs 7 and 8). The liquid products showed moderate activity as homogeneous catalysts, which became steadily less in successive runs. For the first three runs, these products were dark coloured, suggesting the leaching of iridium. This was confirmed by chemical analysis: the iridium content of the solid fell from 1.65% initially to 0.73% after eight runs, but the phosphorus content was unchanged. The P/Ir ratio rose from ca. 0.75/1 to ca. 1.7/1, indicating that the fresh catalyst must have contained some iridium not bound to PEt_2 groups.

Supported-PPh_2. Detailed studies were carried out with the PPh_2-iridium system, since it proved to be the most successful. This catalyst showed high initial activity (80% reaction in 20 min), which declined slowly during 27 reuse cycles, being

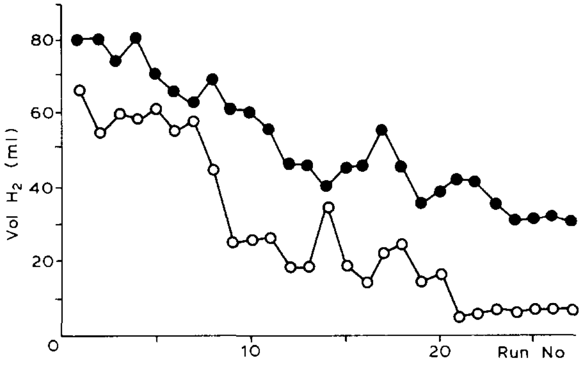

Fig. 1. Amount of dihydrogen liberated after 20 minutes in successive reuse cycles of the PPh_2-iridium catalyst (●), and of the separated liquids (○).

finally about 35% in 20 min (Fig. 1). This decline is considerably slower than for either of the above systems, and also than for the silica-bound PPh_2-iridium system [4], but is probably again due to leaching of the metal from the support. The reactivity of the liquid products paralleled that of the solid (Fig. 1), again suggesting leaching of iridium. To confirm this hypothesis, a fresh sample of the catalyst was treated for 30 min at reaction temperature with successive portions of ethanol in toluene, at the normal reaction concentration. After the liquid was separated from the solid, an aliquot of the polysilane was added. Hydrogen-evolution was observed to be substantial for the first batch of ethanol solution, but fell to quite small amounts by the fourth. This activity is presumably due to loosely bound iridium in the catalyst which is readily dissolved by ethanol; the amount available would decrease rapidly in successive treatments.

Further confirmation that the catalytically active species in solution was an iridium complex was obtained by removing the liquids through a bed of fresh, metal-free, supported ligand (packed in the syringe used to withdraw the liquid). The results of a series of runs with one batch of catalyst are shown in Fig. 2. Here, the liquid products from all the runs were tested for catalytic activity; those from odd-numbered runs were tested directly, and showed the same pattern of declining

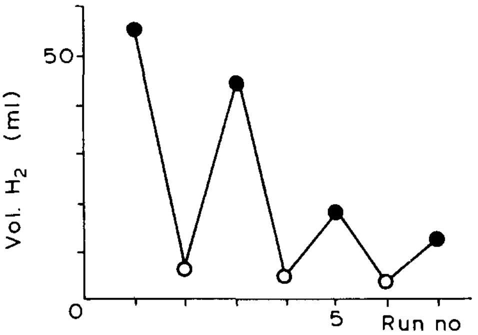

Fig. 2. Activity of liquid products from successive runs (cm^3 H_2 after 25 min) without treatment (●) or after treatment with the ligand (○).

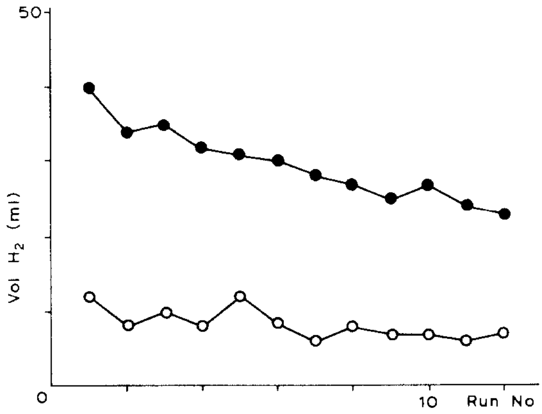

Fig. 3. Dihydrogen liberated after 25 min from the mixed catalyst (●) and from the separated liquid (○).

activity as described above. Samples from the even-numbered runs were drawn off through the ligand, and these were effectively inactive. It is therefore possible to reabsorb the iridium onto the supported ligand. This implies that some mechanism is operating to block ligand sites after the metal has been displaced, or, possibly, is causing the displacement of the metal from the ligand site. The ligand which had been used as absorbent in the even-numbered runs had become an active catalyst, confirming that iridium had indeed been absorbed from the liquid.

These observations suggested an approach to the control of leaching. A sample of the supported-PPh_2-iridium catalyst (0.5 g) was mixed with the untreated supported ligand (0.75 g), and the mixed material used in a series of runs. The activity of this mixed catalyst was approximately half that of fresh, undiluted catalyst, but the decline in activity on reuse was dramatically reduced (Fig. 3). Thus, any iridium which was leached into solution was promptly reabsorbed. In consonance with this, the liquid products from these runs showed very little catalytic activity.

Discussion

To judge from the initial results, polystyrene-supported $AsPh_2$-, PEt_2-, and PPh_2-iridium complexes are all promising catalysts for the reaction of alcohols with polymeric silanes. However, the principal potential benefit of an insoluble catalyst is its ease of recovery and reuse. In each case, the recovered catalyst was less active than the fresh material, a result similar to that found with silica-supported catalysts [4]. The $AsPh_2$ catalyst was very rapidly deactivated, and became effectively inactive after three cycles of reuse. The PEt_2 catalyst was somewhat better, but could not be used for more than about six successive runs. The most successful was the PPh_2 system, which retained useful activity even after more than two dozen runs.

In every case, loss of activity appeared to be associated with loss of iridium into the solution, and separate experiments indicated that the ethanol in the reaction mixture was the prime agent in leaching. In the preparation of the catalysts, an excess of $[IrCl(C_8H_{14})_2]_2$ was employed, and it is likely that some of this complex is retained, loosely bound, in the polymer. Previous work in these laboratories has shown that, in homogeneous systems, rhodium and iridium complexes become more active as the phosphine(arsine)/metal ratio decreases [10,14]. The high initial activity of the fresh catalyst is therefore likely to be due to iridium complexes containing no phosphine (arsine) ligands, and probably in solution rather than on the polymer. Such loosely bound material would be removed in the first one or two runs, and this almost certainly accounts for the initial decline in activity.

During preparation, the catalysts had all been thoroughly washed with toluene. Clearly, the introduction of a small amount of ethanol (8%) gives a significant increase in solubility of the absorbed iridium complex. Successive treatments with ethanol/toluene showed that this type of leaching was effectively complete after two or three runs.

The continued decline in activity beyond this stage seems to be due to further, slower leaching, which could be controlled by addition of the free supported ligand. These experiments suggest that the iridium can be quite firmly bound to the supported ligand, and it is difficult to define the mechanism of leaching. Cleavage of the Ir–P bond might occur during the series of oxidative-addition reductive-elimination reactions by which the catalysis presumably [10] occurs, but it might be expected that any displaced iridium could simply be rebound to the vacated site. Of course, rebinding would be facilitated by the provision of additional sites, as was observed, but it seems likely that the original displacement may occur by an oxidation process. Conversion of PPh_2 groups to $OPPh_2$ would effectively prevent recoordination of the metal. Normal precautions were taken to exclude oxygen, but we cannot be sure that low levels were not present. Only small amounts would be required, and oxidation of phosphine groups is known to be catalysed by metal complexes [15–17]. Such oxidation would explain the facile deactivation of the PEt_2 catalysts, but is unlikely for the $AsPh_2$ system.

The diminished activity of the catalyst to which free ligand had been added is probably due to an increase in the P/Ir ratio for the bound iridium, as the metal is redistributed among the available sites. However, it is also possible that the effective catalyst is actually the iridium species in solution, and that bound to the polymer may have quite low activity. This would be in line with the observed high homogeneous activity of iridium complexes containing no phosphine ligands [10]. Steric interactions of the polysilane with the catalyst surface would also inhibit the reaction. However, whatever the precise mechanism by which these catalysts function, a practical solution to the leaching problem now appears to be available.

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References

1 L.L. Murrell, Advanced Materials in Catalysis, Burton and Garton (Eds.), Academic Press, New York, 1977, Chap. 8.

2 J.P. Collman and L.S. Hegedus, Principles and Applications of Organo-transition Metal Chemistry, University Science Books, California, 1980, p.370.

3 D.C. Bailey and S.H. Lange, Chem. Rev., 81 (1981) 109.

4 R.V. Parish and M.I. Vania, J. Organomet. Chem., 260 (1984) 41.

5 I. Khatib and R.V. Parish, unpublished observations.

6 R.H. Grubbs and R.C. Kroll, J. Am. Chem. Soc., 93 (1971) 3062.

7 K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C Pitkethly, and P J Robinson, J. Organomet. Chem., 87 (1975) 189.

8 C.U. Pittman, S.E. Jacobsen, and H. Hiramoto, J. Am. Chem. Soc., 97 (1975) 4774.

9 J.P. Collman, L.S. Hegadus, M.P Cooke, J. Norton, G. Dulcetti, and D.N. Marquardt, J Am. Chem Soc., 94 (1972) 1789.

10 S.N. Blackburn, R.N. Haszeldine, R.V. Parish, and J.H. Setchfield, J. Organomet. Chem., 192 (1980) 329.

11 G.A. Crosby, N.M. Weinshenker, and H.S. Uh, J. Am. Chem. Soc., 97 (1975) 2232.

12 H.M Relles and R.W. Shluenz, J. Am. Chem. Soc., 96 (1974) 6469

13 S.N. Blackburn, R.N. Haszeldine, R.V. Parish, and J.H. Setchfield, J. Chem Res. (S), (1980) 170 (M 2442).

14 H.M. Dickers, R.N. Haszeldine, L.S. Malkin, A.P. Mather, and R.V. Parish, J Chem. Soc. Dalton Trans., (1980) 308.

15 G. Read and P. Walker, J. Chem. Soc. Dalton Trans., (1977) 883.

16 J. Halpern and A.L. Pickard, Inorg. Chem., 9 (1970) 2798.

17 B.W. Graham, K.R. Laing, C.J. O'Connor, and W.R. Roper, J. Chem. Soc. Dalton Trans., (1972) 1237.