Journal of Organometallic Chemistry, 260 (1984) 41–49
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AN EVALUATION OF SILICA-SUPPORTED CATALYSTS FOR THE REACTION BETWEEN ETHANOL AND POLYMETHYLHYDROGENSILOXANE

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(Received August 5th, 1983)

Summary

Catalysis of the reaction between $Me_3SiO[Si(H)Me)O]_nSiMe_3$ ($n \approx 50$) and ethanol by silica-supported rhodium and iridium catalysts has been investigated. Donor groups in the anchored ligands were PPh_2, S^-, or $C_5H_4^-$. The rhodium–PPh_2 system showed marked inhibition by dihydrogen. The supported iridium catalysts all showed high activity which declined rapidly during successive cycles of re-use, but the iridium–PPh_2 catalyst was the least affected. In every case, the separated liquid products showed activity as homogeneous catalysts, indicating that leaching of the metal from the support was occurring. That ligand was also being leached was shown by labelling with tritium. The results demonstrate the necessity to test supported catalysts through more than one cycle.

Introduction

There are considerable practical advantages in using insolubilized metal complexes as catalysts, combining the best features of homogeneous and heterogeneous systems [1–3]. A popular method of insolubilization is to anchor the complex, via a suitable ligand, to silica, and such materials have been used in hydrogenation, hydroformylation, and *O*-silylation [4–10].

We have previously described the use of anchored-phosphine complexes of iridium(I) for the catalysis of the reaction of tertiary silanes, R_3SiH, with primary alcohols [9], and we now report a range of related catalysts which have been evaluated for the reaction of polymethylhydrogensiloxane with ethanol (eq. 1, $n \approx 50$).

$$Me_3SiO[Si(H)(Me)O]_nSiMe_3 + n\,EtOH \rightarrow Me_3SiO[Si(OEt)(Me)O]_nSiMe_3 + n\,H_2 \tag{1}$$

0022-328X/84/$03.00

Experimental

Silica gel (Fisons, 60–120 mesh) was activated by refluxing with concentrated hydrochloric acid for 4 h [11], and then washed with water, until the washings were neutral, and acetone. After drying in a vacuum pistol, the silica was stored at 200°C. The surface area of this material (BET) was 440 m^2 g^{-1}.

Ligands or preformed metal complexes were anchored to the silica by refluxing in toluene under nitrogen for 4–5 h, removing the product alcohol by a Dean and Stark apparatus. The solid was filtered off and extracted with boiling toluene in a Soxhlet apparatus for 4–5 h, and dried under vacuum at 80°C.

The supported ligands were stirred in toluene for 4 h at room temperature with the metal complex, $[RhCl(C_8H_{14})_2]_2$, $[IrCl(C_8H_{14})_2]_2$, or $[IrCl(cod)]_2$. The solids were filtered off, Soxhlet-extracted with toluene for 4 h and dried under vacuum at 80°C.

Catalytic reactions were conducted at constant pressure (1 atm) in a 100 cm^3 flask equipped with nitrogen inlet, suba-seal, gas-burette, and pivotted magnetic stirrer bar (to minimise crushing of the catalyst during reaction). The catalyst (1.0 g) was placed in the reaction vessel and the system was purged with nitrogen. Toluene (5 cm^3, sodium-dried) and the polysilane (0.28 cm^3, 4.3 mmol SiH) were injected through the suba-seal and the nitrogen flow continued for 10 minutes. The gas-burette was adjusted, the nitrogen flow stopped, and ethanol (0.50 cm^3, 8.6 mmol) was injected. The reaction was usually monitored by recording the evolution of hydrogen, although in some cases small samples of liquid were withdrawn by syringe and the IR absorption at 2150 cm^{-1} compared with those of standard solutions of the polysilane. At the conclusion of a run, the solids were allowed to settle and the liquids withdrawn as completely as possible with a syringe. For a further run with the same catalyst sample, the vessel was purged with nitrogen and fresh solvent and reactants were introduced as described above.

The tritium-labelled ligand $(EtO)_3SiCH(T,H)CH_2PPh_2$ was prepared as follows. Tritiated water (1.0 cm^3, 0.5 Ci, Amersham International) was warmed with dried methanol (25 cm^3) and sodium methoxide (8.0 g) for 2 h, after which methanol was distilled off. A solution of $LiPPh_2$ in THF (100 cm^3) was prepared in the usual way from triphenylphosphine (13.1 g, 0.05 mol), lithium shot (0.77 g, 0.11 mol), and t-butyl chloride (5.4 cm^3, 0.05 mol). Tritiated methanol (2.0 cm^3, ca. 0.05 mol) was added and the mixture allowed to stand overnight. Volatile liquids were removed by rotary evaporation, and the residue extracted with deoxygenated water (40 cm^3) and with chloroform (4 × 20 cm^3). The combined chloroform extracts were dried over magnesium sulphate, and the chloroform removed under reduced pressure, to give an approximate 70% yield of crude $Ph_2P(T,H)$. Approximately equimolar quantities (0.04 mol) of labelled diphenylphosphine and vinyltriethoxysilane were stirred under nitrogen and irradiated with a high-intensity UV lamp for about 80 h. The ligand was recovered by distillation (150–160°C/3 mmHg).

Results

A variety of silica-supported rhodium and iridium catalysts was prepared and evaluated under comparable conditions for the reaction of $Me_3SiO[Si(H)$-

(Me)O]$_n$SiMe$_3$ ($n \approx 50$; the polysilane) with ethanol. Toluene solutions were used with an Si–H concentration of ca. 0.9 mol dm^{-3} and an Si–H/EtOH/M ratio (M = Rh, Ir) of 1.0/2.0/ca. 0.05×10^{-3}.

Phosphine-rhodium systems. The phosphine $(EtO)_3Si(CH_2)_2PPh_2$ was supported on silica and treated with $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene). At 50°C, the activity was low and the reaction ceased after the evolution of about 10% of the expected amount of hydrogen. Pretreatment with nitrogen increased the activity (to ca. 25% reaction), while pretreatment with dihydrogen drastically reduced the activity (ca. 4% reaction). The implied inhibition by the product, dihydrogen, was further demonstrated by purging the system with nitrogen several times during one run; a temporary increase in activity followed each purging (see Fig. 1). A reaction carried out under a slow continuous flow of nitrogen (monitored by observing the decrease in intensity of the IR band at 2150 cm^{-1}) was relatively slow, and did proceed beyond 35%.

Similar inhibition has been found with $[IrCl(CO)L_2]$ as catalyst (L = tertiary phosphine), both homogeneously [12] and anchored to silica [9], but was not observed with homogeneous rhodium-phosphine systems [9,13,14]. The mechanism usually postulated for *O*-silylation involves oxidative-addition of Si–H to the metal followed by nucleophilic attack by the alcohol on the coordinated silyl group. Separation of the alkoxysilane leaves a dihydridometal complex which must lose dihydrogen and react again with the silane. Inhibition by dihydrogen, as observed here, could occur in the last stage.

On re-use, the above catalyst showed even less activity; analytical data, although of low accuracy, indicated that the rhodium-content dropped to about half the initial value after three cycles of use. The loss of activity is therefore probably due to leaching of the metal into solution.

A catalyst was also prepared by treating $[RhCl(C_8H_{14})_2]_2$ with two molar equivalents of $(EtO)_3Si(CH_2)_2PPh_2$ followed by an excess of Et_3SiH and then by reaction with silica gel. This procedure would be expected [15] to give the complex $RhCl(H)(SiEt_3)[Ph_2P(CH_2)_2Si(OEt)_3]_2$, which would become anchored to the silica (the rhodium(III)-silyl derivative was used to reduce the possibility of oxidative degradation of the rhodium complex during the anchoring). Under reaction conditions, this complex would rapidly undergo either silane exchange with the polysilane

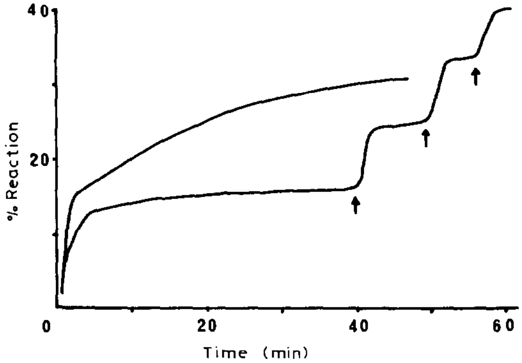

Fig. 1. Reaction with the supported rhodium catalyst. The upper curve is for reaction under constant, slow flushing with nitrogen. The lower curve shows the effect of discontinuous flushing with nitrogen at the times indicated.

[16] or reaction with ethanol to liberate $EtOSiEt_3$. In either case, an active rhodium complex should result. This catalyst showed moderate activity (30% reaction in 50 minutes at 45°C), but was subject to severe deactivation by loss of rhodium into solution.

Mercapto-iridium systems. The reaction of $[IrCl(C_8H_{14})_2]_2$ with one molar equivalent of $(MeO)_3Si(CH_2)_3SH$, followed by an excess of Et_3SiH, gave a red-brown complex, the IR spectrum of which showed the absence of ν(S–H) and the presence of ν(Ir–H) (2200 cm^{-1}). Analytical data suggested the retention of cyclooctene and the probable empirical formula is $Ir(H)(SiEt_3)[S(CH_2)_3Si(OMe)_3](C_8H_{14})$. Six-coordination of iridium(III) might be achieved by dimerisation via bridging mercapto groups. A similar product was obtained by treatment of $[IrCl(C_8H_{14})_2]_2$ with Et_3SiH followed by $(MeO)_3Si(CH_2)_3SH$. Reaction of silica gel with these products gave catalysts with similar characteristics.

These catalysts were initially very active (90% reaction in 40 min at 45°C), but activity declined markedly on re-use, and became effectively zero after four cycles. The separated liquid products were brown, suggesting the presence of soluble iridium-containing species. The addition of fresh quantities of reactants to the products from the first two cycles gave considerable evolution of hydrogen. The products from the third and fourth cycles, however, showed no activity. All solutions slowly deposited metallic iridium.

Similar results were obtained when the catalyst was prepared by treatment of $[IrCl(C_8H_{14})_2]_2$ with the sodium salt of $HS(CH_2)_3Si(OMe)_3$, followed by Et_3SiH and silica gel.

Catalysts prepared by analogous routes but starting from $[IrCl(cod)]_2$ (cod = cycloocta-1,5-diene) showed very low activity, and were also subject to metal leaching.

A phosphine-containing catalyst was obtained by the addition of two molar equivalents of Ph_3P to a mixture of $[IrCl(C_8H_{14})_2]_2$ and $HS(CH_2)_3Si(OMe)_3$, followed by reaction with silica gel. This material was very active (90% reaction in 45 min at 45°C), and the rate of reaction increased during the run. On re-use, the increased activity was maintained during the next run, but declined slowly during further cycles. The liquid products removed after each run showed catalytic activity which paralleled that of the solid, showing that leaching of iridium was again responsible for the loss of activity.

Cyclopentadienyl-iridium systems. The ligand $(MeO)_3Si(CH_2)_3C_5H_5$ was treated in turn with sodium metal, $[IrCl(C_8H_{14})_2]_2$, and silica gel. The initial activity of this product was very high, giving 100% reaction in 20 min at 45°C. However, on re-use the activity decreased substantially, and after four cycles was very low. The liquid products from each run had a brown colour, and addition of the reactants gave further reaction at a similar rate in each case. Loss of iridium from the catalyst was confirmed by chemical analysis, the level falling from 0.6% in the fresh catalyst to 0.3% after five runs.

Phosphine-iridium systems. Two systems were investigated, prepared by treating the silica-supported phosphine with $[IrCl(C_8H_{14})_2]_2$ or by treating the iridium(I) complex with two molar equivalents of $(EtO)_3Si(CH_2)_2PPh_2$, with Et_3SiH, and finally with silica gel. The latter procedure should give [17] the complex $IrH(Cl)(SiEt_3)[Ph_2P(CH_2)_2Si(OEt)_3]_2$ which then becomes anchored to silica (cf. the discussion on the analogous rhodium system above).

The first batch of catalyst obtained from iridium(I) and the silica-supported phosphine (Ir, 1.0%; P, 0.5%; P/Ir, 3.1) was initially inactive, but reaction commenced after about 10 min, after which the rate increased rapidly to give 100% reaction in the next 10 min (at 25°C). In a second run, similar behaviour was observed but the induction period was only about 5 min. Subsequent runs showed no induction period, but there was progressive loss of activity so that, by the sixth run, only 70% reaction was obtained after 60 min. The liquid products from each run were yellow-brown, suggesting leaching of an iridium complex, and analysis after six cycles showed that the iridium-content of the solid had fallen to 0.7%.

A second batch of this catalyst gave considerably slower reactions, even though the iridium-content was much higher (Ir, 2.9%; P, 0.8%; P/Ir, 1.7); this is in line with our previous observations with this type of catalyst [9]. In this case, no induction period was found, and activity decreased with every cycle of use. After four runs, the iridium-content had fallen to 1.7% (P, 0.5%; P/Ir, 1.8).

In an attempt to obtain greater reproducibility, the complex $IrH(Cl)(SiEt_3)[Ph_2P(CH_2)_2Si(OEt)_3]_2$ (ν(Ir–H), 2200 cm^{-1}) was anchored to silica. This catalyst was moderately active (75% reaction in 30 min at 45°C). On re-use, there was a decrease in activity, initially quite marked (50% reaction in 30 min in the fifth run), later steadying (15–20% reaction in 30 min in the ninth and tenth runs). Analytical data suggested that loss of iridium over ten cycles was slight (initially

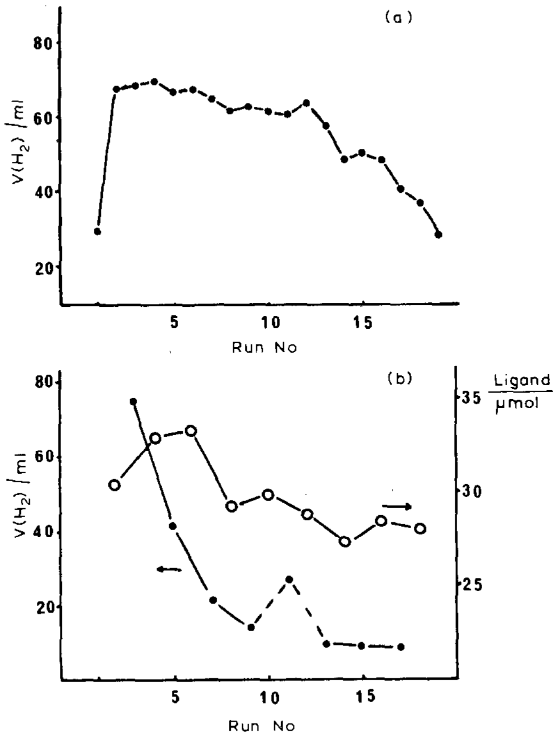

Fig. 2. Re-use of the supported iridium-phosphine complex. (a) Volume of dihydrogen liberated during 20 minutes for successive runs. (b) The catalytic activity and ligand-content of the liquid products from the runs shown in (a).

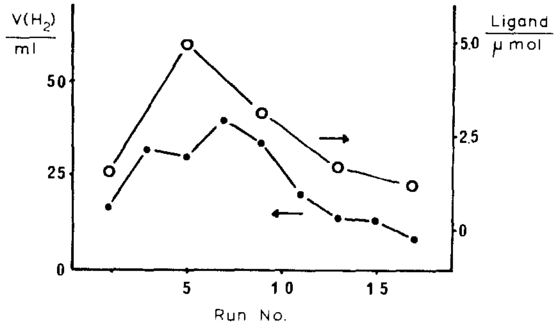

Fig. 3. Reaction of the supported iridium-phosphine complex with ethanol: catalytic activity and ligand-content of the separated liquid.

0.37% Ir; finally 0.34% Ir). However, the separated liquid products showed activity which paralleled the reaction rate during the run from which they were derived, suggesting that leaching of iridium was occurring, especially in the early runs. To reduce the leaching, the catalyst was mixed with 20% of its weight of the silica-supported phosphine. This mixture exhibited relatively low activity (20% reaction in 30 min at 45°C), but the liquid products were completely inactive.

The rate of leaching was unaffected by curing the catalyst at 80°C/3 mmHg for 4 h a procedure which has been reported to give firmer attachment of the trialkoxysilyl groups to silica [18]. Leaching also occurred when the catalyst was stirred with an ethanol/toluene mixture (10/1) at 45°C for 1 h; addition of the polysilane to the filtered liquid gave a slow, steady evolution of hydrogen. No such leaching occurred when the catalyst was stirred with a toluene-polysilane mixture. It is likely, therefore, that the leaching removes ligand as well as metal. To confirm this, a radioactive label was incorporated into the ligand. The tritiated ligand $(EtO)_3SiCH(T,H)CH_2PPh_2$ was prepared from tritiated diphenylphosphine and vinyltriethoxysilane and was treated with $[IrCl(C_8H_{14})_2]_2$, Et_3SiH, and silica as before. This catalyst showed an initial increase in activity followed by a slow decline (Fig. 2a). The liquid products were alternately tested for catalytic activity or counted to determine the tritium content, with parallel results: reactivity and tritium content were initially high, and both fell with progressive re-use of the catalyst (Fig. 2b).

A sample of the tritiated catalyst was also treated with several aliquots of toluene/ethanol mixture, and the separated liquids were tested either for reactivity to the polysilane or for tritium content. There was again a clear parallel (Fig. 3).

Discussion

Silica-supported catalysts involving a variety of ligand groups have been investigated. Several were highly active in the reaction of $Me_3SiO[Si(H)(Me)O]_nSiMe_3$ ($n \approx 50$) with ethanol, but all suffered from loss of activity on re-use. In several cases, it was shown that the diminution in activity was accompanied by leaching of the metal into solution, and it may reasonably be presumed that this was the case for all the catalysts. Up to 30% of the total metal appeared to be lost by this route. The most complete studies were made with supported-phosphine complexes of iridium, and these will be discussed in detail; it is likely that the same arguments apply to the other catalysts.

Loss of metal from the support could involve cleavage of the metal–ligand bond or removal of the complex as a whole. In catalysts obtained by treatment of the supported-phosphine with $[IrCl(C_8H_{14})_2]_2$, the metal may be bound in several ways. Some of the iridium complex may absorb directly onto to the silica surface, some may be bound to one or two phosphine groups, and the phosphine ligands themselves may be anchored by one, two, or three Si–O–Si linkages. In a separate experiment, $[IrCl(C_8H_{14})_2]_2$ was found to absorb onto silica gel (not treated with the phosphine); the resulting material had high catalytic activity, but underwent severe leaching as evidenced by the colour and reactivity of the liquid products and the very low activity of the solid in further tests. The iridium content also decreased dramatically (0.4% to 0.09% after three runs). Such loosely bound iridium would clearly be rapidly lost, which might account for some of the initial rapid deactivation of catalysts obtained from the supported ligands.

A recent solid-state ^{31}P NMR study [19] of platinum complexes produced by treatment of the supported phosphine with $PtCl_2(NCPh)_2$ showed that all available phosphine groups became coordinated, but a large variety of complexes were present. Although these were not identified, it is likely that either one or two phosphine groups were coordinated, and various stereochemical arrangements are possible. In the iridium system, one, two, or three phosphine groups could be bound to iridium(I), the olefinic ligand might or might not be retained, and dimeric complexes are also possible. All these species could have different catalytic activity. It is thus not surprising that there is no correlation between the activity of the catalysts and the iridium-content or the Ir/P ratio. The latter figure probably has little direct significance, since the NMR study also showed that a considerable amount of phosphine oxide was formed during the reaction of $(EtO)_3Si(CH_2)_2PPh_2$ with silica [19]. Phosphine oxide groups are unlikely to coordinate to iridium.

Loss of iridium could occur by oxidation of the phosphine, which process can be catalysed by metal complexes [20–22]. Leaching of this type has been observed in hydroformylation reactions [6]. While normal precautions were taken to exclude oxygen, we cannot discount this as a route to deactivation. However, the addition of the supported ligand to the reaction mixture completely inhibited the loss of iridium over three reaction cycles and it seems unlikely that oxidation plays a major role.

It is possible, with both types of catalyst, that the anchoring Si–O–Si bonds could be solvolysed by the reagent ethanol. The degree of anchoring of the ligand to the silica surface is not known. In principle, one-, two-, or three-point attachment is possible. Under the conditions used, refluxing toluene with azeotropic removal of ethanol, two- or three-point attachment is expected [1,18]. As a further check, a sample of the catalyst obtained from silica and $IrH(Cl)(SiEt_3)[Ph_2P(CH_2)_2Si(OEt)_3]_2$ was heated under vacuum at 80°C for 4 h, a procedure which is expected to give more complete anchoring [18]. The performance of this material, however, was virtually identical to that of the unheated catalyst. The radiochemical experiments with tritium-labelled ligand indicate that the ligand is being leached as well as the iridium, and that this is due to the presence of ethanol in the reaction mixture. However, ethanolysis of the Si–O–Si anchor bonds seems unlikely under the present conditions, since experiments by Murrell [1] with a supported rhodium complex showed no cleavage by methanol even at 175°C.

The most probable cause of leaching is that not all the complex (or ligand) was fully anchored initially. The silica gel was dehydrated at 200°C and one atmosphere pressure, which may have allowed trace amounts of moisture to remain. Reaction of the ligand with water would lead to polymerisation, and the resulting polymers could either bind to the silica surface by formation of Si–O–Si linkages or remain loosely absorbed or hydrogen bonded [18]. Such loosely bound material would not be removed by extraction with toluene, but would be readily dissolved by the more polar ethanol. We favour this as the most likely mechanism of leaching.

When leaching occurs, the liquid products were very active in further catalysis. This suggests that the initial activity of the catalysts is probably due to the material in solution rather than to the insolubilized complexes. This is confirmed by the low eventual activity of catalysts used over many cycles and by the low activity of the catalyst when mixed with the supported ligand. This higher activity of soluble complexes than the supported complexes may reflect a difference in the P/Ir ratio since, in homogeneous systems, activity decreases markedly as this ratio increases [12]. There is also probably a steric effect which inhibits the reaction of internal Si–H groups of the polysilane at a solid surface. Reaction with a monomeric catalyst would be more facile.

The possibility that leaching can occur, and that the catalytic activity observed is actually due to homogeneous catalysis by leached material, makes it imperative that tests with this type of catalyst should be conducted through more than one cycle of re-use, and that the liquid products should also be tested.

Acknowledgement

We are indebted to Dow Corning Ltd. for financial assistance and for gifts of chemicals.

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