Catalytic Activity of Osmium Complexes in the Homogeneous Hydrogenation of Aldehydes

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Although the mononuclear osmium complexes can be efficient catalyst precursors for a number of reactions, only a few of them have been utilyzed for the homogeneous catalytic system.[1,2] OsHCl(CO)(PPh$_3$)$_3$ has been shown to be a good catalyst for hydrogenation of olefin.[3,4] OsH$_2$(PEtPh$_2$)$_4$, OsH$_2$(CO)(PEtPh$_2$)$_3$ and OsH$_3$(PEtPh$_2$)$_3$ have been used for the catalytic isomerization and hydrogenation of octene, while OsH$_3$(PPh$_3$)$_3$ and OsHCl$_2$(AsPh$_3$)$_3$ for the catalytic hydrogenation and hydroformylation of olefin.[5] Sanchez-Delgado, *et al.* have observed that OsHX(CO)(PPh$_3$)$_3$ (X = Cl, Br) are excellent catalysts for hydrogenation of aldehydes and ketones.[6,7]

Recently we have synthesized several osmium complexes containing arsine ligands and have found that these complexes are efficient catalysts for hydrogenation of aldehydes.[8] We wish to describe here catalytic activity of these complexes.

Experimental Section

All manipulations were carried out under nitrogen or argon, using conventional Schlenck techniques or a dry box. Na$_2$OsCl$_6$·6H$_2$O, AsPh$_3$ and arphos (Strem Chemicals Inc.) were used without further purification. ^{1}H-NMR spectra were obtained on a Bruker WP-60 or Varian EM-390 instrument, and FT-IR spectra on a Nicolet spectrometer.

OsHCl(CO)(AsPh$_3$)$_3$, OsHCl(CO)(AsPh$_3$)(Arphos) and OsCl(CO)(OCOCH$_3$)(AsPh$_3$)$_2$. Preparation of these complexes were described previously.[8]
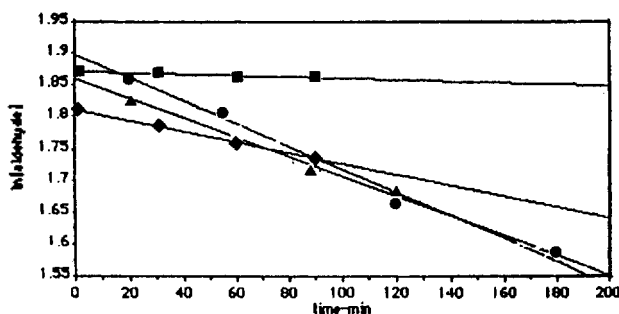
Catalytic Hydrogenation of Porpionaldehyde. In each experiment the catalyst, propionaldehyde, toluene, butan-1-ol (internal standard) and a stirring bar were placed in a glass-lined stainless steel autoclave fitted with a sampling valve. The autoclave was charged to 20 atm hydrogen pressure, then introduced into a thermostatted silicon oil bath at 130 °C and stirring was commended. The hydrogen pressure being about 26 atm after 20 min. Zero-time is set up when the hydrogen pressure was raised to exactly 30 atm and the samples are collected every 20 or 30 min. to be analyzed immediately by GC on a Varian 3700 chromatograph fitted with a flame ionization detector and coupled to an automatic data system Vista CDS-401.

Results and Discussion

The catalytic activity of each of the osmium complexes containing arsine ligands, OsHCl(CO)(AsPh$_3$)$_3$,OsHCl(CO) (AsPh$_3$)(Arphos) and OsCl(CO)(OCOCH$_3$)(AsPh$_3$)$_2$. has been investigated in the hydrogenation of propionaldehyde to propan-1-ol conducted at 130 °C and hydrogen pressure of 30
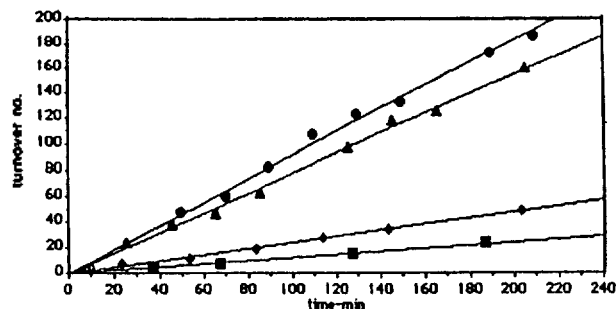
Figure 1. Turnover number in the hydrogenation of propional dehyde with osmium complexes. ● OsHCl(CO)(AsPh$_3$)$_3$(Ph$_2$PCH$_2$CH$_2$AsPh$_2$). ■, OsHCl(CO)(AsPh$_3$)$_3$ + 1 eq. ▲, Ph$_2$PCH$_2$CH$_2$AsPh$_2$. ◆ OsCl(CO)(OCOCH$_3$)(AsPh$_3$)$_2$.

Figure 2. Hydrogenation of propionaldehyde with osmium complexes. ●·OsHCl(CO)(AsPh$_3$)$_3$, ■·OsHCl(CO)AsPh$_3$)$_3$(Ph$_2$PCH$_2$CH$_2$AsPh$_2$), ▲, OsHCl(CO)(AsPh$_3$)$_3$ + 1 eq. ◆, Ph$_2$PCH$_2$CH$_2$AsPh$_2$.

atm. All the osmium complexes have shown good catalytic activity under such reaction conditions. More than 90% of mass balance have been observed and most of propionaldehyde have been converted to propan-1-ol.

Figure 1, shows that turnover number of propan-1-ol, in which the rate of hydrogenation is linear to over 50% conversion. Initial rates for the hydrogenation process were obtained from the slopes of such plots. Under our experimental conditions the kinetics of the reactions are adequently represented by a pseudo-first order rate law, $-d$[aldehyde]/ $dt = k_{obs}$[aldehyde], and plots of ln[aldehyde] *vs* time are also linear as sown in Figure 2.

The catalytic activity of OsHCl(CO)(AsPh$_3$)$_3$ can be explained *via* the mechanism shown in Scheme I as suggested by Sanchez-Delgado, *et al.* for the catalytic reaciton of RuHCl(CO)(PPh$_3$)$_3$. The arsine ligand trans to the hydride ligand is first dissociated to make room for the aldehyde to be able to coordinate to the osmium ion in the first step. The bonding of the arsine ligand to metal ion is known to be weaker than that of the phosphine ligand to metal ion,[9,10] and than the metal complex containing arsine should be more efficient catalyst than the metal complex containing phosphine in place of arsine, since the sixteen-electron species is much more easily formed in the case of the arsine complex. Once the aldehyde group is coordinated to the sixteen-electron intermediate, the oxidative addition of H$_2$ and the transfer of hydride yield an M-alkoxy intermediate. An alcohol is than separated by a reductive elimination process.
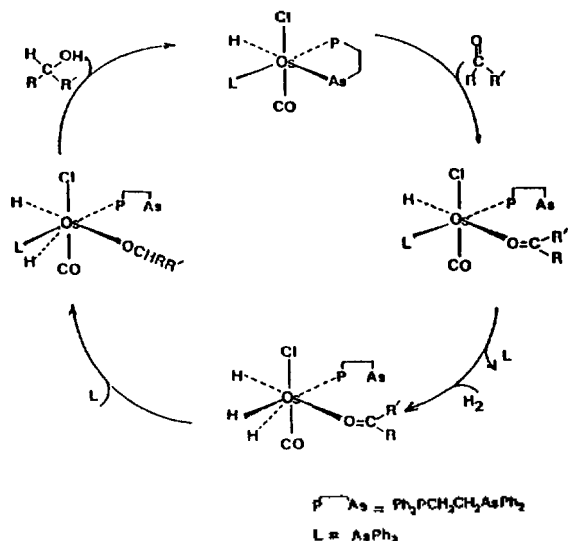
The mechanism in Scheme 2 illustrates the catalytic ac-

Scheme 1.

L = AsPh₃

Scheme 2.
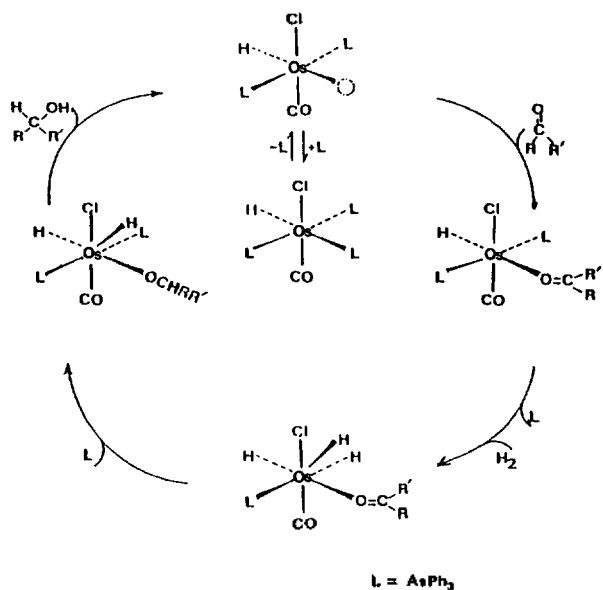
P͡As = Ph₂PCH₂CH₂AsPh₂
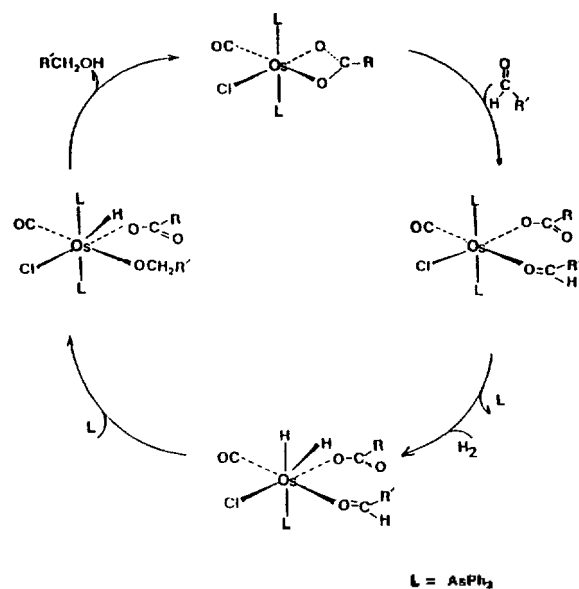
L = AsPh₃

Scheme 3.

L = AsPh₃

tivity of OsHCl(CO)(AsPh₃)(Ph₂PCH₂CH₂AsPh₂). In the first step the Os–As bond of the osmium–arphos chelate ring is broken, while the Os–P bond of the same chelate ring remains intact, for the phosphorus donor atom is more strongly bonded to the osmium metal ion than the arsenic donor atom.

From Figure 1, it is noted that the catalytic activity of OsHCl(CO)(AsPh₃)(Ph₂PCH₂CH₂AsPh₂) is much lower than that of OsHCl(CO)(AsPh₃)₃, which suggests that for osmium the bidentate ligand does not easily dissociate due to the chelate effect. The osmium, a 5d metal, has considerably stronger bonding with the arphos ligand, and, therefore, the osmium–arphos complex is much more thermally stable than the osmium–monodentate arsine complex, which makes the formation of the sixteen–electron intermediate much more difficult.

The effect of addition of arphos ligand to the OsHCl (CO)(AsPh₃)₃ has also been studied in this work. Figure 1 shows that when one equivalent weight of arphos was added to OsHCl(CO)(AsPh₃)₃, the catalytic activity of the mixture

was slightly decreased than the catalytic activity of the pure OsHCl(CO)(AsPh₃)₃. Such decrease in catalytic activity can be understood by considering the fact that the arphos ligand reacts with OsHCl(CO)(AsPh₃)₃ to give the osmium–arphos chelate during the catalytic reaction process of OsHCl(CO)(AsPh₃)₃. The osmium–arphos chelate thus formed acts as the catalytic precursor, causing disfavored catalytic activity.

From Figure 1, The acetate complex, OsCl(CO)(OCOCH₃)₂ shows a slightly lower catalytic activity than the triarsine–osmium complex. Such observation may be explaned by means of the mechanism shown in Scheme 3. To make from for the incoming aldehyde groups in the first step, the carboxylato chelate ring should be broken. However, since the CH₃ is an electron supplying group, the presence of such group stabilyzes the chelate ring and makes the formation of sixteen–electron intermediate somewhat difficult. Once the acetato ligand becomes a monodenatate ligand, an aldehyde coordinates to the osmium ion followed by an oxidative addition of H₂ and hydride transfer to give a seven–coordinated eighteen–electron species of Os–alkoxy intermediate, which eventually gives the product.

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