

Figure 4. PMR spectrum (a) and ^{13}C NMR spectrum (b) of $\text{Na}_4\text{-}[\text{Co}_2(\text{medpa})\text{Cl}_8]$ complex.

complex having a broad d-d transition peak at 630 nm with a large $\text{S} \rightarrow \text{Co}$ charge transfer band at near 400 nm.³⁻⁶ The pmr spectrum of this complex (Figure 4) shows the methyl protons at 1.5 ppm as a doublet, the protons between the nitrogen and sulfur donor atoms at 3.8 ppm as a doublet of doublets and the protons on the heterocyclic ring at 3.3 ppm as multiplets. The ^{13}C NMR of the complex also shows carbons in five different environments, which also suggest that the complex is binuclear.

The reaction of $[\text{Co}_2(\text{medpa})\text{Cl}_8]^{4-}$ with NaNO_2 in 1:8 mole ratio has yielded the $[\text{Co}_2(\text{medpa})(\text{NO}_2)_8]^{4-}$ complex, while the reaction of the chloro complex with en in 1:4 mole ratio has given the $[\text{Co}_2(\text{medpa})(\text{en})_4]^{4+}$ complex. Their visible absorption spectra of these two complexes (Figure 3) show the blue shift with λ_{max} at 570 nm. The pmr spectrum of the nitro complex shows a similar pattern to the chloro complex.

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Catalytic Activity of Osmium(II) Complexes Containing Phosphine Ligands in the Homogeneous Hydrogenation of Propionaldehyde

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The metals in the third transition series (5d metals) are generally known to form very stable bonds with molecules typically involved in catalytic cycles, and are, therefore, not widely used as homogeneous catalysts.^{1,2} Osmium complexes, however, can be effectively used as catalytic precursors for homogeneous hydrogenation, if the ligands of complexes and the reaction conditions are properly selected. Examples of homogeneous catalysis by the osmium complexes have so far been restricted mainly to carbonyl clusters³ and mononuclear hydridophosphine derivatives⁴.

Though homogeneous hydrogenation of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bonds of organic compound by ruthenium(II) complexes has been widely investigated,⁵ the analogous osmium(II) complexes which are expected to have somewhat different properties are relatively less studied. We have previously reported the synthesis and catalytic activities of osmium(II) complexes containing arsine ligands for the hydrogenation of propionaldehyde.^{4b,4c} Recently, we have prepared a series of new carbonyl-hydride osmium(II) complexes containing chelating phosphine ligands, $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ [$\text{L-L}=\text{Ph}_2\text{P}(\text{CH}_2)_n$, PPh_2 ($n=1$ (1), 2(2), 3(3)), $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ (4), and $\text{Ph}_2\text{PFe}(\text{C}_5\text{H}_4-\eta^5)\text{PPh}_2$ (5)] and investigated their catalytic activities for the transfer hydrogenation of trans-cinnamaldehyde with 2-propanol as hydrogen donor.⁵ We wish to report here the homogeneous hydrogenation of propionaldehyde using these osmium(II) complexes as catalysts.

Experimental

All manipulations were routinely carried out under nitrogen using conventional Schlenk techniques. Solvents were dried by known procedures and distilled under nitrogen immediately prior to use. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, PPh_3 , $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, 1,1-bis(diphenylphosphino) ferrocene were purchased from Aldrich and were used without further purification.

IR spectra (KBr discs) were recorded on an Analect FX-6160 FT-IR spectrometer. ^1H NMR spectra were measured on a 300 MHz Varian Gemini-300 NMR spectrometer with CDCl_3 , CD_2Cl_2 , DMSO-d_6 as NMR solvents. Elemental analyses were performed by Micro-Tech Analytical Lab., Skokie, Illinois, USA. The analyses of the products of catalytic reactions were carried out with a Hewlett Packard 5890 Series II gas chromatography using HP-5 (crosslinked 5% PhMe silicone: $\approx 25 \text{ m} \times 0.2 \text{ mm} \times 0.1 \mu\text{m}$ film thickness) column and internal standard (*n*-decane) method. The chromatography was connected to a HP 3394A integrator.

$\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ [$\text{L-L}=\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1, 2, 3$), $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, $\text{Ph}_2\text{PFe}(\text{C}_5\text{H}_4-\eta^5)_2\text{PPh}_2$]. Preparation of these complexes have been described previously.⁵

Catalytic Hydrogenation of Propionaldehyde. In each experiment a 60 mL toluene solution containing propionaldehyde (20 mmol), catalyst (0.02 mmol), and internal standard (*n*-heptane, *ca.* 0.2 g) was introduced into a Parr Series 4560 bench top mini reactor with a gas inlet valve and a sampling valve.

The system was purged twice with hydrogen to 250 psi. The temperature was raised to 110 °C and the internal pressure maintained constant. As soon as the hydrogen pressure was raised to exactly 294 psi (20 atm), stirring was started. This point was regarded as zero time and sampling was performed intermittently using a needle attached to the sampling valve. The temperature was maintained throughout the reaction and the extracted sample was immediately analyzed by GC.

Results and Discussion

The catalytic activity of each of the osmium(II) complexes containing chelating phosphine ligands, $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ [$\text{L-L}=\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1(1), 2(2), 3(3)$), $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ (4), $\text{Ph}_2\text{PFe}(\text{C}_5\text{H}_4-\eta^5)_2\text{PPh}_2$ (5), has been investigated in the hydrogenation of propionaldehyde to propan-1-ol conducted at 110 °C and hydrogen pressure at 20 atm. All the compounds tested have shown good catalytic activity under such reaction condition. More than 90% of mass balances have been observed and most of propionaldehyde have been converted to propan-1-ol.

Figure 1 shows the turnover number in the hydrogenation of propionaldehyde with osmium(II) complexes, which, along with Table 1, indicates that the catalytic activities decrease in the order $5 > 3 > 4 > 1 > 2$. All the hydrogen reactions catalyzed by these complexes obey the pseudo-first order rate law. The observed rate constant, k_{obsd} , was obtained from the equation $-\text{d}[\text{propionaldehyde}]/\text{dt} = k_{\text{obsd}}[\text{propionaldehyde}]$ and the slope of the straight line in the graph of $\ln[\text{propio-$

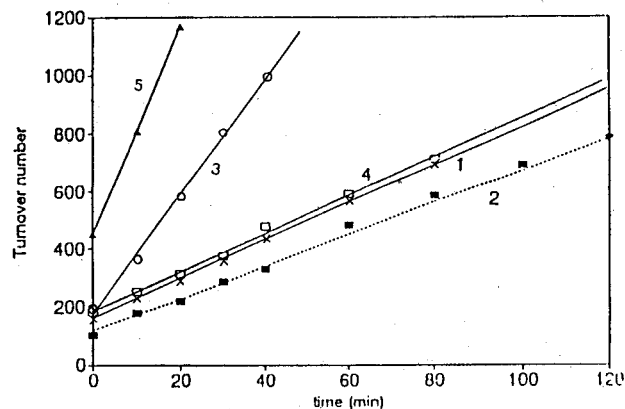
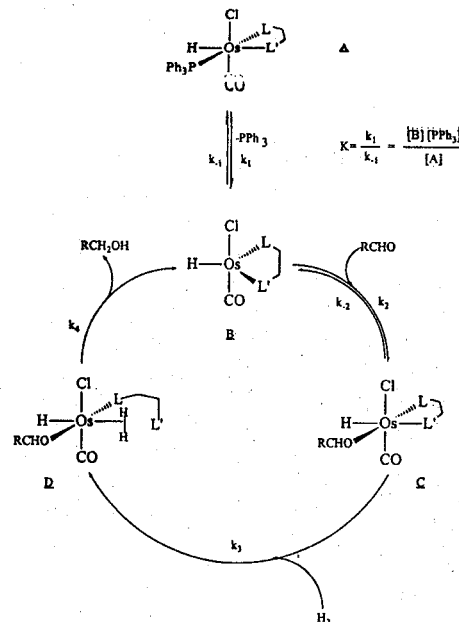


Figure 1. Turnover number vs time in the hydrogenation of propionaldehyde with osmium(II) complexes: $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (1), $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (2), $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$ (3), $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)$ (4), $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{dppf})$ (5) (dppfa 1,1'-bis(diphenylphosphino)ferrocene).

Table 1. Hydrogenation of Propionaldehyde with Osmium Complexes

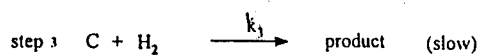
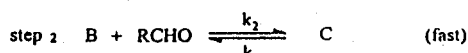
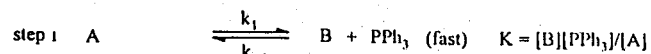
Compound	Rate (mol/L·min) × 10	Relative activity
(1)	1.1	1.3
(2)	0.9	1.1
(3)	4.1	4.9
(4)	1.1	1.3
(5)	6.0	7.2
$\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$	0.8	1.0



Scheme 1.

naldehyde] vs time (min).

All the complexes show higher catalytic activity than $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ which does not have a chelate ring. In



$$\text{Rate} = \frac{-d[\text{RCHO}]}{dt} = \frac{k_2 k_3 K [\text{H}_2] [A] [\text{RCHO}]}{(k_{-2} + k_3 [\text{H}_2]) [\text{PPh}_3]}$$

$$= k_{\text{obsd}} [\text{RCHO}]$$

$$(k_{\text{obsd}} = k_2 k_3 K [A] [\text{H}_2] / (k_{-2} + k_3 [\text{H}_2]) [\text{PPh}_3])$$

Scheme 2.

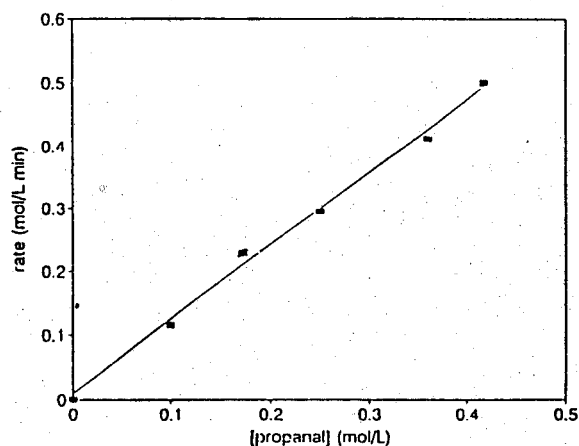


Figure 2. Dependence of rate of hydrogenation of propionaldehyde on the concentration of the propionaldehyde at 110 °C, with 20 atm H₂ and 3.3 × 10⁻⁴ M catalyst precursor.

our recent work we have also found the effectiveness of ruthenium(II) complexes containing chelating bidentate diphosphine ligands in the homogeneous hydrogenation of cyclohexane.⁶ Among the complexes **1**, **2**, and **3** having the different chelate ring sizes, the reaction rate increases 2 < 1 < 3. In the case of the complexes **2**, **4** and **5** with the similar chelate ring size, the catalytic activity increases 2 < 4 < 5.

The reaction mechanism on the hydrogenation of olefine and aldehyde have been widely studied.⁷⁻¹¹ The catalytic activities of the osmium(II) complexes studied in this work can be explained *via* the mechanism shown in schemes I and II. The rate of hydrogenation of propionaldehyde is linearly proportional to the concentration of propionaldehyde (Figure 2). On the other hand, the reaction rate is inversely proportional to the concentration of PPh₃ added to the reaction (Figure 3). It has also been observed that the reaction rate is proportional to the concentration of the catalyst (Figure 4) as well as to the concentration of the hydrogen (Figure 5). Such data are in well accord with the mechanism depicted in Schemes I and II. The initial step involves the dissociation of the monomeric phosphine ligand from the catalyst precursor, since this is the easiest one to be broken, while the

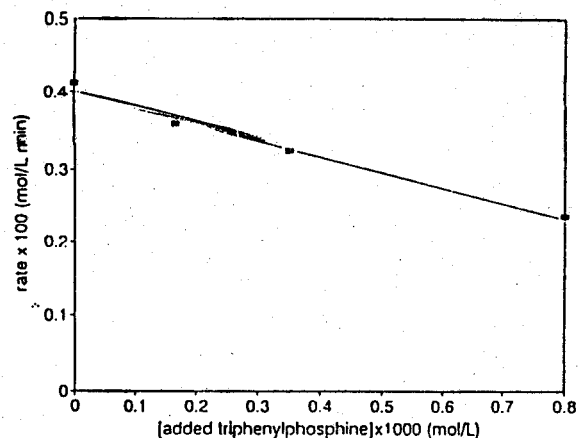


Figure 3. Dependence of rate of hydrogenation of propionaldehyde on the concentration of the added PPh₃ at 110 °C, with 20 atm H₂ and 3.3 × 10⁻¹ M propionaldehyde and 3.3 × 10⁻⁴ M catalyst precursor.

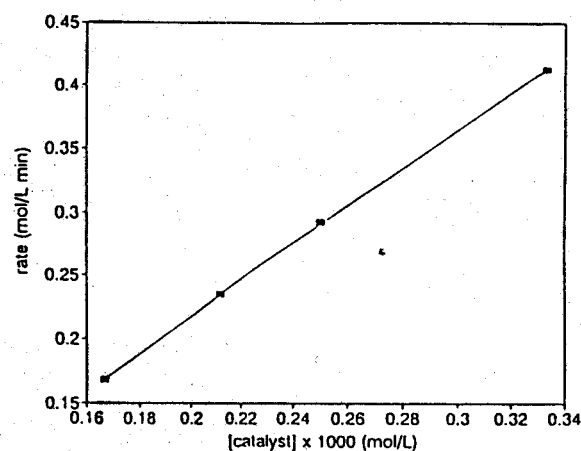


Figure 4. Dependence of rate of hydrogenation of propionaldehyde on the concentration of the catalyst precursor at 110 °C, with 20 atm H₂ and 3.3 × 10⁻¹ M propionaldehyde.

Os-P bond of the chelate ring remains intact. The equilibrium constant *K* for step 1 is known to be affected by the steric effect of other ligand,¹² which is favored by **3** and **5** with the largest chelate ring size among the complexes of **1** through **5**. In the rate-determining step of **3**, one phosphine end of the B chelating diphosphine ring is dissociated for an oxidative addition of H₂, facilitating the transfer of hydride to yield an alcohol eventually through an M-alkoxy intermediate. From Table 1, it is noted that the catalytic activity of OsHCl(CO)(PPh₃)₃ is lower than that of the complexes of **1** through **5**, which suggests that for the osmium complexes the bidentate ligand does not easily dissociate due to the chelate effect in the initial steps. The complex **5** has the largest chelate ring involving ferrocene moiety, and the dissociation of the monomeric phosphine ligand from the catalyst precursor will be easier than the complex **3** in the initial step. We have previously studied the homogeneous hydrogenation of propionaldehyde using osmium complexes containing arsine ligands as well as using ruthenium complexes containing phosphine ligands.^{4b,4c,13} Concerning osmium

complexes, we note that although all of them are efficient catalyst precursors, they are on the average one order of magnitude less active than their ruthenium analogues, which may be considered a normal trend.^{2a}

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