

Rapid Homogeneous Hydrogenation of Olefins by Hydrido-Cobalt and -Rhodium Complexes of Chelating Triphosphines

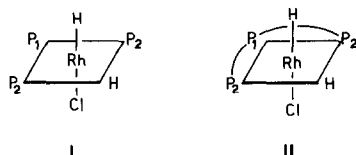
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An objective of our current research is to synthesize transition metal complexes of polydentate ligands that may be efficient homogeneous catalysts. A polyphosphine ligand offers several advantages over comparable monodentate ligands, *e.g.*, i) more control on the coordination number, stoichiometry, and stereochemistry of the resulting complex; ii) an increased basicity (or nucleophilicity) at the metal;^{1,2} and iii) detailed structural and bonding information from the M–P and P–P coupling constants.³ We report some of our results which indicate that cobalt and rhodium complexes containing chelating triphosphine ligands can be rapid and efficient hydrogenation catalysts for olefins. Such complexes may provide a wider range of catalyst selectivity and stereospecificity than can be obtained with comparable complexes of monophosphines;² these points are currently being studied.

The Wilkinson complex, $\text{RhCl}(\text{PPh}_3)_3$, is an efficient hydrogenation catalyst under mild conditions,⁴ but the stoichiometrically analogous complex $\text{RhCl}(\text{ttp})^1$ adds H_2 irreversibly at room temperature and is not a catalyst under comparable mild conditions.⁵ The difference in catalytic behavior of these two rhodium complexes is explicable on the basis of the hydrogenation mechanism proposed for $\text{RhCl}(\text{PPh}_3)_3$, which involves dissociation of a triphenylphosphine ligand, thereby opening a coordination site for the olefin molecule.⁴ Phosphorus-31 n.m.r. studies have shown that the triphenylphosphine ligand *trans* to a hydride (P_1 in **I**) is the most labile;⁶ thus, it is this triphenylphosphine that probably dissociates in the catalysis cycle. The comparable phosphorus atom of the chelating triphosphine in $\text{RhClH}_2(\text{ttp})$ is the central phosphorus atom (P_1 in **II**), which could not dissociate without breaking two chelate chains.



One can still take advantage of a chelating triphosphine ligand on a planar d^8 metal (*e.g.*, $\text{Rh}(\text{I})$) if the fourth position is an important ligand in the catalysis cycle (*e.g.*, hydride for hydrogenation reactions). Thus, a complex such as $\text{HCo}(\text{ttp})$ or $\text{HRh}(\text{ttp})$ should undergo coordination of an olefin, hydride transfer to produce the metal-alkyl, oxidative-addition of H_2 , a second hydride transfer, elimination of the alkane, and regeneration of the $\text{HM}(\text{ttp})$ catalyst. As documented below, the main point of this work is that the catalyst cycle does not require dissociation of a phosphorus group of the triphosphine ligand in order to have a sequence of 16- and 18-electron complexes.⁷ In this light, the hydrogenation mechanisms reported for $\text{HRh}(\text{PPh}_3)_4$ ⁸ and $\text{H}_3\text{Co}(\text{PPh}_3)_3$ ⁹ are probably either incorrect or incomplete.

Several of the cobalt and rhodium hydrido complexes prepared during this study are listed in the Table, along with the rate of H_2 uptake at 25 °C and 1 atm hydrogen pressure. The cobalt hydride complexes $\text{HCo}(\text{triphosphine})\text{L}$ ($\text{L} = \text{CO}, \text{PPh}_3, \text{PhPMe}_2$) were prepared by treating an ethanolic solution of L and $\text{Co}(\text{triphosphine})\text{Cl}_2$ with excess sodium borohydride. Similarly, $\text{HRh}(\text{ttp})$ was obtained by treating $\text{RhCl}(\text{ttp})$ with excess NaBH_4 in ethanol. The trihydride $\text{H}_3\text{Co}(\text{ttp})$ was prepared by reducing $\text{CoCl}_2(\text{ttp})$ with $\text{NaAl}(\text{O}-i\text{-C}_4\text{H}_9)_2\text{H}_2$ in diethyl ether followed by hydrolysis with ethanol. Preparation of $\text{H}_3\text{Co}(\text{etp})$, which readily gives “ $\text{HCo}(\text{etp})$ ” in solution, was accomplished in a similar manner. The hydridic nature of the M–H bond in all the reported complexes has been confirmed by infrared and/or proton n.m.r. spectroscopy.

None of the $\text{HCo}(\text{triphosphine})\text{CO}$ complexes (which are 18-electron cases) hydrogenate 1-octene under mild conditions (Table); this behavior is consistent with spectroscopic data (infrared and ^1H and ^{31}P n.m.r.) that show no detectable CO or phosphine dissociation from these five-coordinate complexes in solution at room temperature. Also, the non-hydrogenation by the $\text{HCo}(\text{triphosphine})\text{CO}$ complexes suggests that the catalytic activity of the remaining cobalt complexes results from dissociation of the monophosphine from $\text{HCo}(\text{triphosphine})\text{L}$ and H_2 from $\text{H}_3\text{Co}(\text{ttp})$ and $\text{H}_3\text{Co}(\text{etp})$ to form “ $\text{HCo}(\text{triphosphine})$ ” in solution. Slow catalytic activity is shown by $\text{HCo}(\text{ttp})\text{PPh}_3$, whereas $\text{HCo}(\text{ttp})\text{PhPMe}_2$ is inactive. This relative behavior can be rationalized on the basis of the cone angles of the two monodentate phosphines, since the more bulky triphenylphosphine ligand should dissociate to a greater extent than dimethylphenylphosphine.¹⁰ The initial hydrogenation rate with $\text{H}_3\text{Co}(\text{ttp})$ is very rapid; however, the rate decreases markedly with

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TABLE. Hydrogenation of 1-Octene with Cobalt and Rhodium Complexes.^a

Complex ^b	Hydrogen Uptake, ml	Time, hr
HCo(ttp)CO	0 ± 10	24
HCo(etp)CO	0 ± 10	18
HCo(tripod)CO	0 ± 10	24
HCo(ttp)PPhMe ₂	0 ± 10	30
HCo(ttp)PPh ₃	50 ± 5	8.5
H ₃ Co(ttp)	700 ± 50	5
H ₃ Co(etp) ^c	1220 ± 50 ^d	3.5
HRh(ttp)	1010 ± 50 ^d	3
(BH ₃)Rh(etp)	300 ± 40 ^e	8

^a Hydrogenation experiments were carried out at ambient H₂ pressures (~ 730 torr) and 25 °C in benzene solutions with a catalyst concentration of *ca.* 10⁻³ M and 1-octene concentration of *ca.* 1M. ^b The abbreviations ttp, etp, and tripod are used for the triphosphine ligands bis(3-diphenylphosphinopropyl)phenylphosphine (PhP(CH₂CH₂CH₂PPh₂)₂), bis(2-diphenylphosphinoethyl)phenylphosphine (PhP(CH₂CH₂PPh₂)₂), and CH₃C(CH₂PPh₂)₃, respectively. ^c We believe that the principal reaction is with "HCo(etp)" which is generated *in situ*. ^d The quantity of H₂ represents *ca.* 100% of the theoretical amount required for complete reduction of the olefin to the alkane. ^e We thank P. R. Blum for this result.

time. This rate decrease is attributed to the isomerization of 1-octene to *cis*- and *trans*-2-octene in the presence of the complex (confirmed by v.p.c. analysis¹¹), which undergo hydrogenation more slowly.

The most rapid hydrogenation rates were with "HCo(etp)", which was generated *in situ*, and with an isolated sample of HRh(ttp). Under the conditions reported in the Table, 1-octene is converted quantitatively to n-octane at comparable rates by these two hydrides, as determined by both v.p.c. and ¹H n.m.r. However, the relative stabilities of these two catalysts differ markedly in solution. The HRh(ttp) complex retains high catalytic activity for at least two days in benzene solution, whereas the activity of "HCo(etp)" ceases when the olefin is depleted. A second batch of olefin is not hydrogenated by the cobalt catalyst if the reaction mixture sets overnight in the absence of olefin.

The high hydrogenation rates of these catalysts, which contain strongly bound triphosphine ligands are somewhat surprising if the recent kinetic studies using HRh(PPh₃)₄ and H₃Co(PPh₃)₃ are correct, as the kinetic studies were interpreted to show that the most active form of the rhodium catalyst is HRh(PPh₃)₂⁸ and that catalytic hydrogenation of cyclohexene by H₃Co(PPh₃)₃ requires dissociation of triphenylphosphine.⁹

The effect of different chelate chain lengths may be seen by comparing the rates of hydrogenation of 1-octene by HCo(ttp) and HCo(etp), where the latter is faster. This result is in contrast with a previous study that used the diphosphines Ph₂P(CH₂)_nPPh₂ (n = 1-6);¹² that study showed markedly higher hydrogenation rates for n = 3 as compared to the case of n = 2. We have been unable to obtain a direct comparison of the two ligands in the rhodium complexes, as the only well-characterized complex obtained by BH₄⁻ reduction of RhCl(etp) is the BH₃ species Rh(BH₃)(etp) instead of the expected HRh(etp) complex. The latter complex catalyzes hydrogenation at a slower rate than does HRh(ttp) (Table).¹¹

References

- 1 T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4194 (1973).
- 2 J. A. Tiethof, J. L. Peterson and D. W. Meek, *Inorg. Chem.*, **15**, in press.
- 3 A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973); B. L. Haymore, J. A. Ibers and D. W. Meek, *Inorg. Chem.*, **14**, 541 (1975).
- 4 J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
- 5 T. E. Nappier, Jr., *Ph.D. Dissertation*, The Ohio State University, 1972.
- 6 C. A. Tolman, P. Meakin, D. L. Lindner and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
- 7 C. A. Tolman, *Chem. Soc. Revs.*, **1**, 337 (1972).
- 8 J. Hjørkjaer, *Adv. in Chem. Ser.*, **132**, 133 (1973).
- 9 J. L. Hendrikse and J. W. E. Coenen, *J. Catal.*, **30**, 72 (1973).
- 10 C. A. Tolman, W. C. Seidel and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974); C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
- 11 We thank P. R. Blum for these results.
- 12 J. C. Poulin, T. P. Dang, and H. B. Kagan, *J. Organomet. Chem.*, **84**, 87 (1975).