In Situ Generation of the Hydrogenation Catalysts RhH(ttp) and RhH(Cyttp), ttp = PhP(CH$_2$CH$_2$CH$_2$-PPh$_2$)$_2$ and Cyttp = PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$, by Treating the RhCl(triphosphine) Complexes with either AlEt$_3$ or AlEt$_2$Cl

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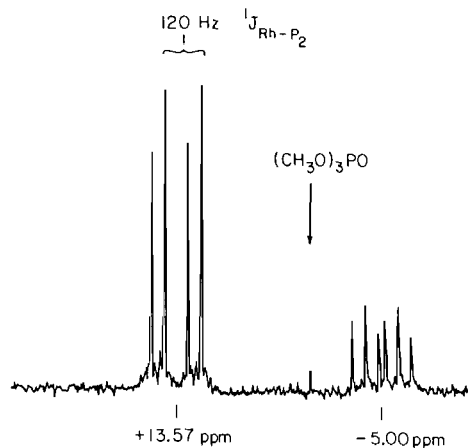
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Fig. 1. Phosphorus-31 broad-band, proton-decoupled spectrum of RhCl(ttp) in the presence of a 20-fold molar ratio of Et$_3$Al in toluene. The (MeO)$_3$PO signal is the secondary standard, which is superimposed on the spectrum. The phosphorus chemical shifts are reported relative to 85% H$_3$PO$_4$ at 0.00 ppm; positive shifts are downfield from the standard.

A great deal of research has been directed toward homogeneous catalysis by transition metal complexes since Wilkinson and co-workers reported the rapid hydrogenation of olefins by RhCl(PPh$_3$)$_3$ [1]. For the Wilkinson complex, it has been generally accepted that dissociation of a PPh$_3$ ligand is necessary for the hydrogenation catalysis at ambient conditions [2, 3]. On the other hand, DuBois and Meek [4] have shown that a similar-type complex RhCl(ttp), where ttp is the chelating PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ ligand, catalyzed the hydrogenation of 1-octene when NaBH$_4$ and ethanol were added. The RhCl(ttp) complex differs significantly from Wilkinson's catalyst since the tridentate ligand remains bonded throughout the reaction [5]; thus, the catalytic activity of RhCl(ttp) was presumed [4] to be due to RhH(ttp), which was generated *in situ* with NaBH$_4$ [6, 7].

Herein, we report that the complex RhCl(ttp) in the presence of either triethylaluminum or diethylaluminum chloride is an effective homogeneous catalyst for hydrogenation of 1-olefins and 1-octyne. Proton and phosphorus-31 NMR spectra are used to identify several different chemical species [including RhH(ttp)] in these catalytically active solutions. The observed rate of hydrogenation of 1-octene to n-octane at 20 ± 0.3 °C and under constant H$_2$ pressure of 750 torr is 6.4 × 10^4 M^{-1} min^{-1}, *i.e.*, 25 times more rapid than the Wilkinson catalyst, RhCl(PPh$_3$)$_3$, under comparable conditions. The rate expression is first order in the rhodium complex, first order in H$_2$, and zero order in olefin. A mechanism involving RhR(ttp), RhH(ttp) associated with an ethylaluminum species, and H$_2$ is proposed to account for the spectroscopic and kinetic data.

Experimental

Solutions containing the aluminum alkyls and RhCl(ttp) are air-sensitive, and they were handled under a nitrogen atmosphere using either Schlenk glassware of an inert atmosphere glovebag. Toluene and 1-octene were distilled from sodium benzophenoneketyl into a dry flask under N$_2$. Toluene solutions (25% w/w) of triethylaluminum, AlEt$_3$, and diethylaluminum chloride AlEt$_2$Cl, used in the kinetic study were transferred in a dry box from stock bottles into vials that contained a septum port and valve (available from Pierce Chemical Co.). The reagent was then transferred *via* a syringe into the reaction flask under an atmosphere of nitrogen in a glovebag.

Most of the hydrogenation experiments were carried out at constant hydrogen pressure using an automatic gas-measuring instrument. Solutions were thermostatted at 20 ± 0.3 °C. For reactions carried out at constant pressure, the system volume was about 125 ml, about 0.5 mM in rhodium, 640 mM in olefin and 25 mM in AlEt$_2$Cl. The total pressure was kept at about 775 torr; p(H$_2$) = 750 torr, p(solvents) = 25 torr. For reactions carried out at constant volume, the volume of the system was about 400 ml. No hydrogen consumption was observed for solutions containing all the reagents except RhCl(ttp), thereby excluding any significant catalysis by either AlEt$_3$ or AlEt$_2$Cl under these conditions.

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TABLE I. $^{31}P\{^1H\}$ NMR Data on RhCl(ttp)–AlEt$_{3-n}$Cl$_n$ Solutions.

	δP_1 ppm	δP_2 ppm	$^2J_{P_1-P_2}$ Hz	$^1J_{Rh-P_1}$ Hz	$^1J_{Rh-P_2}$ Hz
Rh[a] + 2AlEt$_3$	−4.6	14.2	43.8	108.5	121.3
Rh + 2AlEt$_3$ + C$_2$H$_4$	−12.8	11.5	49.9	141.7	114.7
Rh + 2AlEt$_3$ + 1-Octene	−12.4	12.0	49.3	141.9	114.7
	−4.6	14.4	43.0	108.1	121.3
Rh + 2AlEt$_3$ + 1-Pentene	−12.6	11.7	49.3	141.9	114.7
Rh + 2AlEt$_2$Cl + 1-Octene	−12.8	12.2	50.0	139.0	115.8
Rh + 2AlEt$_2$Cl + 1-Pentene	−12.1	12.3	50.0	140.5	116.2

[a]Rh = the RhCl(ttp) complex.

Results and Discussion

The $^{31}P\{^1H\}$ NMR spectrum of a toluene solution of RhCl(ttp) and AlEt$_3$ is shown in Fig. 1. This ^{31}P spectrum also results from a toluene solution of RhCl(ttp) and AlEt$_2$Cl. The NMR pattern is typical of planar rhodium-ttp complexes and results from spin-spin coupling between the terminal phosphorus, the central phosphorus, and the rhodium atom, all of which have a spin of ½ [5, 8]. Table I also gives the $^{31}P\{^1H\}$ NMR data for several solutions containing RhCl(ttp) and the aluminum alkyls.

The proton NMR spectrum for the RhCl(ttp)–AlEt$_3$ solution shows a rhodium hydride resonance at −5.2 ppm. Also, there are two sets of ethyl resonances due to the ethyl groups on aluminum; however, neither of these resonance positions is the same as that of free AlEt$_3$ or AlEt$_2$Cl. On the basis of an extensive NMR study, we have concluded that these ethyl resonances arise from two molecules of either AlEt$_3$ or AlEt$_2$Cl bonding to RhH(ttp) *via* both the hydride and the rhodium atom. The hydride is presumed to come from a β-hydride elimination of ethylene from RhEt(ttp), which is formed by an initial alkylation reaction. The upfield set of ethyl resonances is not present after addition of ethylene; thus, it is assigned to an ethylaluminum species that is coordinated to the hydrido ligand. The downfield set of ethyl resonances is assigned to an ethylaluminum compound coordinated directly to rhodium. This ethylaluminum compound must be in equilibrium with AlEt$_3$ since the position of the ethyl resonances moves closer to that of free AlEt$_3$ upon addition of more AlEt$_3$. Thus, it appears that a toluene solution of RhCl(ttp) and AlEt$_3$ can be characterized by eqn. 1. The exact nature of the ethylaluminum species is not known because of the equilibrium between coordinated and free ethylaluminum species and the likelihood that AlEt$_2$Cl is one of the products in the reaction between RhCl-

(ttp) and AlEt$_3$. Hence, the ethylaluminum species is indicated by EtAl.

$$\text{EtAl} < \atop | \\ (ttp)RhH{-}\overset{\vee}{Al}Et \rightleftharpoons Et\,\overset{\vee}{Al} + (ttp)RhH{-}\overset{\vee}{Al}Et \qquad (1)$$
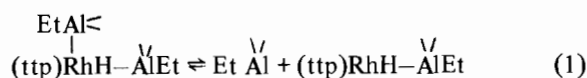
Addition of ethylene to a solution of RhCl(ttp) and AlEt$_3$ results in a new set of $^{31}P\{^1H\}$ NMR parameters as shown in Table I. Furthermore, the ^1H NMR spectrum no longer exhibits the Rh–H resonance at −5.2 ppm, and the set of ethyl resonances assigned to Rh–H–AlEt is not observed. Thus, this new rhodium species is thought to be EtAl–RhEt-(ttp). Similarly, the $^{31}P\{^1H\}$ NMR spectra show that addition of either 1-pentene or 1-octene to a toluene solution of RhCl(ttp) and AlEt$_3$ results in a mixture of two compounds. One compound is proposed to be EtAl–Rh(ttp)H–AlEt, whereas the other is assigned as EtAl–RhR(ttp). The chemical equations representing these reactions are as follows:

$$\text{EtAl} < \atop | \\ RhCl(ttp) + xsAlEt_3 \rightleftharpoons (ttp)Rh{-}H{-}\overset{\vee}{Al}Et + C_2H_4 \qquad (2)$$

$$\text{EtAl} < \atop | \\ (ttp)Rh{-}H{-}\overset{\vee}{Al}Et + olefin \rightleftharpoons \atop \qquad\qquad\qquad \text{EtAl} < \atop | \\ (ttp)Rh{-}R \qquad (3)$$
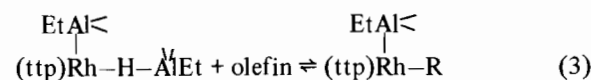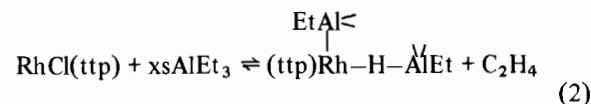
Addition of 1-pentene or 1-octene to solutions containing RhCl(ttp) and AlEt$_2$Cl results in a clean ^{31}P NMR spectrum that contains only one set of parameters; the parameters are consistent with rhodium-alkyl compounds of the type EtAl–RhR(ttp). Thus, a kinetic study on the catalytic hydrogenation of olefins was carried out with AlEt$_2$Cl and RhCl(ttp) in toluene. The observed rate law is −d[H$_2$]/dt = k_{obsd}[Rh]$_T$[H$_2$] in the presence of a large excess of olefin and excess AlEt$_2$Cl. Table II lists the various substrates hydrogenated catalytically by solutions
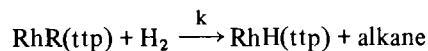
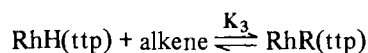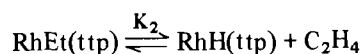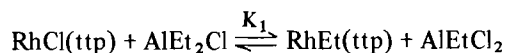TABLE II. Relative Rates of Hydrogenation of Various Substrates.

Substrate	Relative Rate
1-Octene	100[a]
2,3-Dimethyl-1-butene	5.2
2,3-Dimethyl-2-butene	NO RXN.
cis-2-Octene	1.2
trans-2-Octene	0.84
trans-2-Pentene	1.1
Cyclohexene	NO RXN.
1,3-Octadiene (cis + trans)	NO RXN.
1-Octyne	28
Cyclohexanone	NO RXN.
1-Octene (Wilkinson's catalyst)	3.8

[a]The observed rate of hydrogenation of 1-octene to n-octane at 20 ± 0.3 °C and under constant H_2 pressure of 750 torr is $6.4 \times 10^4 \, M^{-1} \, min^{-1}$.

or RhCl(ttp) and AlEt$_2$Cl and the relative rates based on 1-octene being assigned a value of 100. The rates indicate, as is expected, that internal and more hindered olefins react slower than terminal unhindered olefins.

A consideration of the $^{31}P\{^1H\}$ and the ^1H NMR spectra, the rate data, and the fact that solution of RhCl(ttp) and either AlEt$_3$ or AlEt$_2$Cl catalyze the hydrogenation of olefins, leads us to propose the following mechanism for the catalytic hydrogenation of olefins by RhCl(ttp) and excess AlEt$_2$Cl. Association of the ethylaluminum species with the rhodium complex is omitted for clarity.

$$RhCl(ttp) + AlEt_2Cl \overset{K_1}{\rightleftharpoons} RhEt(ttp) + AlEtCl_2$$

$$RhEt(ttp) \overset{K_2}{\rightleftharpoons} RhH(ttp) + C_2H_4$$

$$RhH(ttp) + alkene \overset{K_3}{\rightleftharpoons} RhR(ttp)$$

$$RhR(ttp) + H_2 \overset{k}{\longrightarrow} RhH(ttp) + alkane$$

After the catalysis solutions were treated with H$_2$, the resultant solutions were analyzed by glc; they contained only the saturated alkane in all but one case. In the case of 1-octene, 96% of the olefin was reduced to n-octane and 4% was isomerized to an internal olefin. n-Octane was obtained quantitatively from 1-octyne, even though it should generate 1-

octene as an intermediate. The rate of reactions using solutions of previously used catalyst decreased with successive additions of 1-octene; our observations suggest that the life of the catalyst is related more to the air sensitivity (and concomitant handling problems) of the Et$_2$AlCl than to the instability of the rhodium complex.

Use of a More Bulky Triphosphine

Use of the more sterically hindered catalyst RhCl(Cyttp), where Cyttp represents the tetra-

$$\overset{\overset{\displaystyle Ph}{\displaystyle |}}{}$$

cyclohexyl triphosphine ligand Cy$_2$P(CH$_2$)$_3$P(CH$_2$)$_3$-PCy2, resulted in a calculated second-order rate constant of $6.5 \times 10^4 \, M^{-1} \, min^{-1}$. However, the reaction is definitely dependent on the concentration of the olefin, in contrast to the RhCl(ttp) system. The third-order rate constant for the equation $r = k[H_2][Rh]_T$-[octene] is about $1.2 \times 10^4 \, M^{-2} \, min^{-1}$. The olefin dependence is understandable in terms of the mechanism proposed for catalysis by RhCl(ttp). In the case of the more hindered catalyst RhCl(Cyttp), equilibrium constant K_3 would be smaller than for RhCl(ttp); thus, the hydrogenation mechanism with RhCl(Cyttp) is probably more complicated and involves an olefin complex in the rate step.

Acknowledgements

References

1 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc.*, A, 1711 (1966).
2 B. R. James, 'Homogeneous Hydrogenation', Wiley, New York, 1973.
3 E. L. Muetterties, Ed. 'Transition Metal Hydrides', M. Dekker, New York, 1971.
4 D. L. DuBois and D. W. Meek, *Inorg. Chim. Acta, 19,* L29 (1976).
5 D. W. Meek and T. J. Mazanec, *Acct. Chem. Res., 14,* 266 (1981).
6 S. H. Strauss and D. F. Shriver, *Inorg. Chem., 17,* 3069 (1978).
7 S. E. Diamond and F. Mares, *J. Organomet. Chem., 142,* C55 (1977).
8 J. A. Tiethof , J. L. Peterson and D. W. Meek, *Inorg. Chem., 15,* 1365 (1976).