Chemistry of Metal-Diene Complexes.

A Convenient One Step Synthesis of Mono- and Dihydrido-Platinum(II) Complexes Containing Bulky Phosphine Ligands from (COD)PtCl$_2$

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Received April 29, 1982

The chemistry of platinum hydrides has received a great deal of interest in recent years probably due to their recognition as probable intermediates in the homogeneously catalyzed reactions. Although a variety of synthetic methods are available for the chloro–platinum(II) hydride complexes, PtH(Cl)L$_2$, containing sterically less bulky phosphine ligands, none of these usual methods are effectively applicable for the sterically bulky phosphines and generally lead to extensive decomposition or at best poor yields [1–4]. On the other hand, the platinum(II) dihydrides, PtH$_2$L$_2$, can only be isolated by stabilizing them using bulky phosphine ligands [5–8]. In a recent report we have described some new synthetic routes to these platinum(II) dihydride complexes which involve the sodium borohydride reduction of corresponding dioxygen-, carbonato-, or peroxycarbonato-platinum(II) complexes [9]. The multi-step preparation of these complexes makes these methods unattractive. In the course of our recent investigations on the metal–diene complexes, we have reported a two-step preparation of chloro–platinum(II) hydrides [10] as well as platinum(II) dihydrides [11] containing sterically bulky phosphines using (COD)PtCl$_2$ (COD = 1,5-cyclooctadiene). We now describe a convenient one-step preparation of these complexes by the sodium borohydride reduction of (COD)PtCl$_2$ in the presence of two equivalent of tertiary phosphines per platinum. This method is particularly suited to the preparation of platinum(II) hydrides containing bulky ligands.

The reaction of one equivalent of NaBH$_4$ per platinum with a 1:2 mixture of (COD)PtCl$_2$ and tertiary phosphines, R$_3$P (R$_3$P = $\mathrm{Pr^i_3P}$, $\mathrm{Bu^tPh_2P}$, Cy$_3$P, $\mathrm{Bu^t_2MeP}$, $\mathrm{Bu^t_2Bu^nP}$ and $\mathrm{Bu^t_3P}$) in dry ethanol proceeds exceedingly rapidly at ambient temperatures to produce the corresponding chloro–platinum hydrides, *trans*-PtH(Cl(PR$_3$)$_2$ (*1*) in high yields. Thus, when sodium borohydride is mixed with a 1:2 mixture of (COD)PtCl$_2$ and R$_3$P in ethanol at room temperature, an immediate reaction is observed with gas evolution (eqn. 1).

$$\mathrm{(COD)PtCl_2 + 2R_3P + NaBH_4} \xrightarrow{\text{ethanol}} \textit{trans}\text{-}\mathrm{PtH(Cl)(PR_3)_2 + NaCl + C_8H_{12} + \tfrac{1}{2}B_2H_6}\uparrow \qquad (1)$$

The reactions are usually complete within a few minutes of the addition of NaBH$_4$. The chloro–platinum(II) hydrides (1) can easily be isolated by removing the ethanol and then extracting the reaction mixture with benzene or methylene chloride. Further recyrstallization in benzene/hexane (or benzene/ethanol or CH$_2$Cl$_2$/hexane) gives the analytical pure crystalline products. They have been fully characterized analytically as well as spectroscopically. The infrared spectrum of complex (*1*) shows a medium intense band due to νPt–H in the region 2170–2370 cm^{-1} (R$_3$P = $\mathrm{Pr^i_3P}$, 2220; $\mathrm{Bu^tPh_2P}$, 2260; Cy$_3$P, 2170, $\mathrm{Bu^t_2MeP}$, 2220 and $\mathrm{Bu^t_3P}$, 2370 cm^{-1}). Proton NMR spectra contain a triplet at δ −13.0 to −17.9 ppm (JP–H = 12.7 Hz and JPt–H = 1000–1256 Hz) due to the hydridic proton suggesting the *trans*-disposition of phosphines in these complexes. This is further supported by the ^{31}P NMR spectrum which shows only one main singlet at δP = 36.9 to 75.0 ppm (w.r. to H$_3$PO$_4$) associated with platinum satellites, JPt–P = 2950–2800 Hz.

The platinum(II) dihydride complexes, *trans*-PtH$_2$(PR$_3$)$_2$ (*2*) can also be prepared readily and conveniently in almost quantitatively yields by reacting about 10 fold excess of sodium borohydride with a 1:2 mixture of (COD)PtCl$_2$ and R$_3$P (R$_3$P = $\mathrm{Pr^i_3P}$, $\mathrm{Bu^tPh_2P}$, Cy$_3$P, $\mathrm{Bu^t_2MeP}$, $\mathrm{Bu^t_2Bu^nP}$ and $\mathrm{Bu^t_3P}$) in dry ethanol at room temperature (eqn. 2).

$$\mathrm{(COD)PtCl_2 + 2R_3P} + \xrightarrow[\text{ethanol}]{\mathrm{NaBH_4}\ \text{(excess)}} \textit{trans}\text{-}\mathrm{PtH_2(PR_3)_2 + 2NaCl + C_8H_{12} + B_2H_6}\uparrow \qquad (2)$$

This method represents a general preparative route to the platinum(II) dihydrides containing sterically bulky ligands and is far more convenient than any of the available methods. The reactions are complete within 2–3 hr and the complexes (*2*) can be isolated by removing the ethanol and then extracting the reaction mixture with benzene. Sometimes, when the reaction (eqn. 2) is not complete, a mixture of dihydride and monohydride complexes is obtained. In these instances, the mixture should be further treated with a fresh amount of NaBH$_4$ in ethanol in order

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0020-1693/82/0000-0000/$02.75

to obtain the platinum(II) dihydride according to eqn. 3:

$$PtH(Cl)(PR_3)_2 \xrightarrow{NaBH_4} PtH_2(PR_3)_2 + NaCl + ½B_2H_6\uparrow \quad (3)$$

Recrystallization of platinum(II) dihydride complexes (*2*) can be carried out from benzene/ethanol (or ethanol/H_2O in the case of PR_3 = PPr^i_3). The complex (*2*) (PR_3 = PPr^i_3) is sublimable under reduced pressure at 50–55 °C/0.1 mm.

These Pt(II) dihydrides obtained by the above method are white solids highly soluble in solvents such as benzene, CH_2Cl_2, toluene and less soluble in hexane and ethanol. They react with CCl_4 or $CHCl_3$ giving the chloro–platinum hydrides (*1*). They show Pt–H infrared stretching absorptions in the region 1710–1820 cm^{-1} (R_3P = Pr^i_3P, 1744, Bu^tPh_2P, 1770; Cy_3P, 1710; Bu^t_2MeP, 1730; $Bu^t_2Bu^nP$, 1735; Bu^t_3P, 1820 cm^{-1}.) The relatively low frequency range is consistent with the high *trans*-influence of the hydride ligand. The Pt–H resonances in the proton NMR spectra are observed at δ −2.50 to −3.70 ppm which is again to lower field compared with the corresponding chloro–platinum(II) hydride complexes (*1*) also reflecting the higher *trans*-influence of the hydride ligand. Each of the hydride signals appears as a triplet with ^{195}Pt satellites indicating a *trans*-disposition of the two hydrogen ligands [JP–H ~ 17.0 Hz; JPt–H = 774 to 792 Hz). ^{31}P NMR spectra of these complexes contain only one main signal (δP = 50.1 to 99.2 ppm w.r. to H_3PO_4) with platinum satellites (JPt–P = 2874 to 3071 Hz).

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