DIHYDRIDE COMPLEXES OF PLATINUM(II) AND PALLADIUM(II)

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SUMMARY

The dihydride complexes of platinum(II), *trans*-PtH$_2$L$_2$ (L = PCy$_3$, PCy$_2$-i-Pr, and PCy$_2$Et(Cy = cyclohexyl)), have been prepared by the reaction of platinum(II) acetylacetonate with trialkylaluminium in the presence of bulky tertiary phosphine ligands in ether. A *trans*-square planar structure is proposed on the bases of IR and ^{1}H NMR spectral studies. The dihydride complexes react with carbon tetrachloride giving equimolar quantities of chloroform and the corresponding monohydride complexes of the type *trans*-PtHClL$_2$ (L = PCy$_3$ and PCy$_2$-i-Pr). The analogous dihydride complex of palladium(II), *trans*-PdH$_2$(PCy$_3$)$_2$, has been isolated from the similar reaction using tricyclohexylphosphine as a ligand. Comparison of the dihydride complexes with the corresponding mono-hydride complexes is described.

INTRODUCTION

Monohydride complexes of platinum(II), palladium(II), and nickel(II), stabilized by various tertiary phosphines, are known and well characterized. Though preparation of dihydride complex of formula *trans*-PtH$_2$(PPh$_3$)$_2$ had been reported[1], it was corrected later that the complex is the carbonate complex Pt(CO$_3$)(PPh$_3$)$_2$[2]. Recently formation of platinum(II) dihydride complex, *trans*-PtH$_2$(PEt$_3$)$_3$, prepared by oxidative addition of hydrogen to Pt(PEt$_3$)$_3$, has been reported; thermally this complex is quite unstable, and could not be isolated[3]. During a study of platinum and palladium complexes, we isolated the stable dihydride complexes of platinum(II) and palladium(II), *trans*-MH$_2$(PCy$_3$)$_2$ (M = Pt or Pd; Cy = cyclohexyl), which are the first examples of the dihydride complexes of this type[4]. They have higher stability but are less soluble in most organic solvents. In order to determine the structure of the dihydride complexes by ^{1}H NMR study, we investigated the preparation of the more soluble dihydride complexes using phosphine ligands with properties similar to those of tricyclohexylphosphine.

RESULTS

Treatment of platinum(II) acetylacetonate in ether with triisobutyl- or triethylaluminum in the presence of tricyclohexylphosphine gives the dihydride complex as a white precipitate:

$$\text{Pt(Acac)}_2 + 2\ \text{PCy}_3 \xrightarrow[\text{Et}_2\text{O}]{\text{AlR}_3} \text{PtH}_2(\text{PCy}_3)_2$$
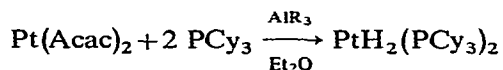
The reaction was continued over a period of one week at room temperature and the yield was increased when an excess of the aluminum compound was used. The complex is diamagnetic and the analysis is in accord with the formula of $\text{PtH}_2(\text{PCy}_3)_2$. Though its low solubility in organic solvents prevented ^{1}H NMR measurement, a molecular weight determination by cryoscopic method in benzene was carried out at low concentration (0.011 mol/l) and it appeared that the complex is monomeric. Reaction of the dihydride with carbon tetrachloride was examined to confirm the presence of hydridic protons and 89% of the expected quantity of chloroform and 76% of trans-$\text{PtHCl}(\text{PCy}_3)_2$ were obtained according to the equation:

$$\text{PtH}_2(\text{PCy}_3)_2 + \text{CCl}_4 \rightarrow \text{PtHCl}(\text{PCy}_3)_2 + \text{CHCl}_3$$
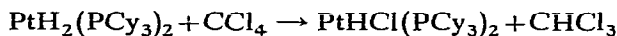
Formation of approximately equimolar quantities of chloroform and the mono-hydride complex provides strong evidence that the dihydride complex has two hydridic protons. The IR spectrum of $\text{PtH}_2(\text{PCy}_3)_2$ shows a strong absorption at 1910 cm^{-1} assigned to the Pt–H stretching frequency. A single absorption due to a Pt–H stretch is consistent with a trans-structure, but the value is higher than the trans-dihydride absorption range (1615–1750 cm^{-1}) so far reported[5]. Since accidental degeneracy is often observed for the complexes with a heavy central metal atom, the possibility that the dihydride complex might have a cis-structure should not be excluded. Though it required further evidence, e.g. ^{1}H NMR measurement, for determination of the definite structure, the complex is less soluble. Then we investigated the preparation of dihydride complexes which have higher solubility, using other phosphine ligands with the steric and electronic properties similar to those of tricyclohexylphosphine. When triisopropylphosphine was used, formation of dihydride complex was not observed, but fortunately the expected dihydride complexes were obtained as viscous oils when isopropyl- or ethyldicyclohexylphosphine were used. Purification of the oily products is difficult. Chromatographic methods were unsuccessful and partial purification was achieved by repeated extraction with n-hexane and evaporation of the solvent. The IR spectrum of $\text{PtH}_2(\text{PCy}_2\text{Pr})_2$ shows a strong absorption at 1920 cm^{-1} assigned to the Pt–H stretch and the 100 MHz ^{1}H NMR spectrum in the hydride region consists of a triplet (1/2/1) at τ 16.9 (J(P–H) 20 Hz) with [195]Pt satellites (J(Pt–H) 610 Hz), consistent with a trans-square planar configuration, and a weak triplet (1/2/1) at τ 13.3 (J 18Hz) which remains unresolved. A sample of $\text{PtH}_2(\text{PCy}_2\text{Pr})_2$, the IR spectra of which showed only few impurities, gave equimolar quantities of chloroform and $\text{PtHCl}(\text{PCy}_2\text{Pr})_2$ on reaction with carbon tetrachloride. $\text{PtH}_2(\text{PCy}_2\text{Et})_2$ also shows v(Pt–H) at 1925 cm^{-1} in the IR spectrum and a triplet (1/2/1) at τ 15.6 (J(P–H) 18 Hz) with [195]Pt satellites (J(Pt–H) 596 Hz) in the ^{1}H NMR spectrum.

From the reactions using tri-n-butylphosphine and triphenylphosphine, no dihydride complex has been obtained. Phosphine exchange reaction of $\text{PtH}_2(\text{PCy}_3)_2$ with triisopropylphosphine did not occur.

When palladium(II) acetylacetonate was used in place of platinum(II) acetylacetonate, the analogous dihydride complex, $\text{PdH}_2(\text{PCy}_3)_2$, was isolated as a pale-yellow precipitate, and from the reaction solution the zerovalent complex

TABLE 1

CHARACTERIZATION DATA OF COMPLEXES

Complex	Analysis Found (calcd.)			$\nu(M-H)$ (cm^{-1})	τ	$J(P-H)$ (Hz)	$J(Pt-H)$ (Hz)	Solv.	Decomp.^{c} (°C)	Yield (%)
	C(%)	H(%)	Mol.wt.							
PtH$_2$(PCy$_3$)$_2$	57.3 (57.0)	9.0 (9.1)	769 (757)	1910				^{b}	195	54
PtH$_2$(PCy$_2$Pr)$_2$			^{a}	1920	16.9^c	20	610	C$_6$H$_6$	^{f}	~72
PtH$_2$(PCy$_2$Et)$_2$			^{a}	1925	15.6^c	18	596	C$_6$H$_6$	^{f}	~90
PdH$_2$(PCy$_3$)$_2$	64.2 (64.6)	9.9 (10.3)	^{b}	1740				^{b}	76	3.5
PtHCl(PCy$_3$)$_2$	54.0 (54.6)	8.2 (8.5)	788 (798)	2150	26.5^c	14	1200	C$_6$H$_6$	^{g}	76
PtHCl(PCy$_2$Pr)$_2$			^{a}	2175	28.7^c	13	1290	CHCl$_3$	^{f}	~88
PdHCl(PCy$_3$)$_2$	61.6 (61.4)	9.3 (9.6)	760 (703)	2010	24.0^d	5	—	C$_6$H$_6$	210	62
Pd(PCy$_3$)$_2$	65.0 (64.8)	9.5 (10.0)	^{b}						90	25

^{a} Not isolated as pure compounds. ^{b} Not sufficiently soluble. ^{c} A triplet with ^{195}Pt satellites. ^{d} A triplet. ^{e} In argon atmosphere. ^{f} Viscous oil. ^{g} Stable at 240°.

Pd(PCy$_3$)$_2$ was obtained as colorless crystals.

$$Pd(Acac)_2 + 2\ PCy_3 \xrightarrow[Et_2O]{AlR_3} PdH_2(PCy_3)_2 + Pd(PCy_3)_2$$
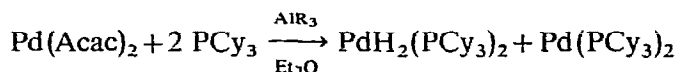
The IR spectrum of PdH$_2$(PCy$_3$)$_2$, which is also less soluble, shows a strong absorption at 1740 cm^{-1} assigned to Pd–H stretching, characteristic of a *trans*-dihydride absorption[5]. Oxidative addition of hydrogen chloride to Pd(PCy$_3$)$_2$ gave *trans*-PdHCl(PCy$_3$)$_2$ at room temperature[6].

$$Pd(PCy_3)_2 + HCl \xrightarrow[Et_2O]{} PdHCl(PCy_3)_2$$
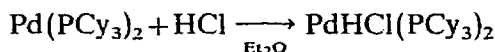
PdHCl(PCy$_3$)$_2$ can also be prepared by the reaction of PdCl$_2$(PCy$_3$)$_2$ with NiH(BH$_4$)(PCy$_3$)$_2$[7]. When other phosphines such as P(i-Pr)$_3$, PCy$_2$-i-Pr, PCy$_2$Et, PBu$_3$ or PPh$_3$ were used, no dihydride complex of palladium was obtained.

DISCUSSION

In the triad of nickel, palladium, and platinum, the stability of hydride or alkyl complexes decreases generally in the order Pt > Pd > Ni. This trend is also observed in this study. PtH$_2$(PCy$_3$)$_2$ and PdH$_2$(PCy$_3$)$_2$, which remain unchanged in air after several hours, decompose at 195 and 76° respectively. When PCy$_2$-i-Pr or PCy$_2$Et was used, the platinum dihydride complexes were obtained while the palladium analogues were not obtained. The tertiary phosphines used have essentially the same basicity except PPh$_3$, but they are different in size[8]. The bulky PCy$_3$ effectively stabilizes the dihydride complexes of platinum and palladium. The slightly smaller phosphines such as PCy$_2$-i-Pr and PCy$_2$Et gave the dihydride complexes only in the case of platinum, but the smaller phosphines such as P(i-Pr)$_3$ and PBu$_3$ gave no

evidence for formation of the dihydride complexes under the conditions studied. At very low temperature, however, the quite unstable dihydride complexes with the smaller phosphines, at least in the case of platinum, may be formed, because PEt_3 is able to form $trans$-$PtH_2(PEt_3)_3$. Thus the stabilization effect of PCy_3 is remarkable and this may be attributed to the steric effects of bulky cyclohexyl rings. Green $et\ al.$ have reported that the bulkiness of the secondary alkyl phosphines contributes to the stability of the nickel(II) and palladium(II) hydride complexes $trans$-$MHX(PR_3)_2$ (M = Ni or Pd; X = anionic ligands; R = Cy or i-Pr)[7]. This steric effect is more prominent in the situation of the dihydride complexes since even $P(i$-$Pr)_3$ is not large enough to stabilize a dihydride complex.

Spectral data indicate that both the mono- and dihydride complexes obtained here have a $trans$-square planar configuration. For the dihydride complexes a single absorption due to a metal–hydrogen stretching mode is consistent with a $trans$-structure. If the two hydrogens lay in cis-positions mutually, the two absorptions due to metal–hydrogen stretching should occur. It is known that metal–hydrogen stretching frequencies are quite sensitive to the nature of the other ligands, particularly the $trans$-ligand, on the metal. Substitution of chlorine in $MHClL_2$ by hydrogen causes a remarkable low shift of metal–hydrogen stretching frequencies due to the strong $trans$-effect of hydrogen arising from its inductive effect compared with chlorine. The decrease of $v(Pt$–$H)$ from $PtHClL_2$ to PtH_2L_2 is 240 cm^{-1} (L = PCy_3) and 255 cm^{-1} (L = PCy_2-i-Pr), which is essentially equal to the decrease (270 cm^{-1}) of $v(Pd$–$H)$. It is considered, therefore, that both the platinum and palladium dihydride complexes have the same structure. The similar variation of $v(M$–$H)$ is observed for octahedral hydride complexes, $trans$-$MHCl[C_2H_4(PEt_2)_2]_2$ and $trans$-$MH_2[C_2H_4(PEt_2)_2]_2$ (M = Ru or Os)[9]. $v(Ru$–$H)$ is 1938 cm^{-1} for the monohydride and 1615 cm^{-1} for the dihydride, and $v(Os$–$H)$ is 2039 cm^{-1} for the mono-hydride and 1721 cm^{-1} for the dihydride, respectively. The decrease of $v(M$–$H)$ from the monohydride to the dihydride is 323 cm^{-1} for ruthenium and 318 cm^{-1} for osmium. Though $trans$-PtH_2-$(PEt_3)_3$ has been reported to show $v(Pt$–$H)$ at 1766 cm^{-1}, there is a significant difference in the structures between $PtH_2(PEt_3)_3$ and PtH_2L_2, that is, the former is trigonal bipyramidal whereas the latter is square planar. ^1H NMR spectra of $PtH_2(PCy_2Pr)_2$ and $PtH_2(PCy_2Et)_2$ provide definite evidence for the structure: spin–spin interaction between the hydridic protons and the two equivalent ^{31}P nuclei (1/2/1 triplet; $J(P$–$H)$ 18–20 Hz) is consistent with a $trans$-square planar configuration. For platinum(II) hydride complexes, the coupling constants with phosphorus in cis-positions to hydrogen are small (7.5–20 Hz) while with phosphorus in the $trans$-position are large, $e.g.$ 156 Hz for $[PtH(PEt_3)_3]ClO_4$[10]. The ^1H NMR spectra of the monohydride complexes $MHClL_2$ (M = Pt or Pd; L = phosphine ligands) also show the hydride resonance as a triplet (1/2/1) with or without ^{195}Pt satellites, indicating clearly a $trans$-structure for the complexes. It is noteworthy that the platinum dihydride complexes show extremely low τ values. According to Buckingham and Stephens[11], the high-field shifts in $trans$-$PtHX(PEt_3)_2$ are attributed mainly to paramagnetic shielding of the proton by the platinum $5d$-electrons which depends on the inverse cube of the Pt–H bond distance associated with the $trans$-effect of the ligand X. Variation of chemical shifts from $PtHClL_2$ to PtH_2L_2 presumably indicates the increase of the Pt–H bond distance in PtH_2L_2 which corresponds to the decrease of $v(Pt$–$H)$, due to the mutual $trans$-effect of the two hydridic protons arranged in $trans$. Also, the great

difference in the coupling constants between the hydrogens and ^{195}Pt nucleus obtained for the dihydride and monohydride complexes may be a good demonstration of the strong *trans*-effect of hydrogen.

EXPERIMENTAL

All procedures were carried out in nitrogen atmosphere. IR spectra were recorded (Nujol mulls) on a Japan Spectroscopic DS-301 spectrophotometer and ^{1}H NMR spectra were recorded on a Japan Electron Optics Lab. JNM-PS-100 spectrometer and the τ values of the hydride band were determined by reference to benzene or chloroform as an internal standard.

Tricyclohexylphosphine and ethyldicyclohexylphosphine. These compounds were prepared according to the methods in the literatures[12,13].

Isopropyldicyclohexylphosphine. Eleven g (47 mmol) of PCy$_2$Cl in 120 ml of ether was added to an ether solution (220 ml) of i-PrMgBr, prepared from 11.5 g (48 mmol) of magnesium and 36 ml (48 mmol) of i-PrBr. After addition of NH$_4$Cl (13 g) in 70 ml of water, white magnesium salts precipitated and were separated by filtration. The filtrate was concentrated until no more salt precipitated. When 5 ml of CS$_2$ was added to the concentrated solution, 9 g (28 mmol) of reddish brown PCy$_2$-i-Pr)$\div$CS$_2$ adduct precipitated (Found: C, 61.1; H, 9.6%. C$_{16}$H$_{29}$S$_2$P calcd.: C, 60.7; H, 9.2%). When the adduct was suspended in 30 ml of EtOH and heated, the adduct was dissolved in solution losing CS$_2$ (and CS$_2$ and EtOH were distilled). To the residue was added 20 ml of EtOH and then distilled again, and then PCy$_2$-i-Pr was distilled at reduced pressure (108°/1 mm). 5.6 g (23 mmol) of PCy$_2$-i-Pr was obtained (49% based on PCy$_2$Cl). PCy$_2$-i-Pr is colorless liquid and burns in air.

trans-PtH$_2$(PCy$_3$)$_2$. To an ether suspension (10 ml) containing 0.26 g (0.66 mmol) of Pt(Acac)$_2$ and 0.38 g (1.3 mmol) of PCy$_3$, was added 0.7 ml of AlEt$_3$ at —60°. The temperature was allowed to rise to room temperature and the reaction mixture was stirred over a period of one week. During this time the white dihydride precipitated. 0.27 g (0.36 mmol) of PtH$_2$(PCy$_3$)$_2$ was obtained after repeated washing with n-hexane and ether (54% yield).

trans-PtH$_2$(PCy$_2$Pr)$_2$ and trans-PtH$_2$(PCy$_2$Et)$_2$. These complexes were prepared by the same procedure used for preparation of PtH$_2$(PCy$_3$)$_2$. The complexes were extracted with n-hexane after decomposition of excess alkylaluminum with methanol, and evaporation of the solvent gave the dihydrides as viscous oils.

trans-PdH$_2$(PCy$_3$)$_2$ and Pd(PCy$_3$)$_2$. The two complexes were obtained analogously using 0.26 g (0.86 mmol) of Pd(Acac)$_2$, 0.46 g (1.6 mmol) of PCy$_3$, and 0.4 ml of AlEt$_3$ in ether (10 ml). 0.02 g (0.03 mmol; 3.5%) of PdH$_2$(PCy$_3$)$_2$ precipitated and was collected by filtration; 0.14 g (0.21 mmol; 25%) of Pd(PCy$_3$)$_2$ was obtained after addition of n-hexane to the filtrate and cooling.

Reaction of PtH$_2$(PCy$_3$)$_2$ with CCl$_4$. 0.13 g (0.17 mmol) of PtH$_2$(PCy$_3$)$_2$ was treated with 0.25 ml of CCl$_4$ in 1 ml of toluene at room temperature. 0.018 g (0.15 mmol; 89%) of CHCl$_3$ was obtained by GLC; from the reaction residue 0.10 g (0.13 mmol; 76%) of PtHCl(PCy$_3$)$_2$ was obtained after evaporation of solvents and washing with n-hexane.

Reaction of PtH$_2$(PCy$_2$Pr)$_2$ with CCl$_4$. By the same procedure 90% of CHCl$_3$ and 88% of PtHCl(PCy$_2$Pr)$_2$ were produced.

Reaction of Pd(PCy₃)₂ with HCl. To an ether suspension (5 ml) containing 0.28 g (0.42 mmol) of $Pd(PCy_3)_2$ was added 0.6 ml of 4.6% alcoholic aqueous hydrochloric acid (HCl, 0.44 mmol) at room temperature. The complex dissolved in solution, and then 0.18 g (0.26 mmol; 62%) of $PdHCl(PCy_3)_2$ was obtained as a white precipitate.

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