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Convenient One-Step Synthesis of Substituted Phosphine Complexes of Platinum(II) Directly from Hexachloroplatinic Acid

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Cis-$[PtCl_2(PPh_3)_2]$ and $[PtCl_2(P–P)]$ (P–P = $Ph_2P(CH_2)_{1,2\ or 4}\ PPh_2$) are synthesized by treating $H_2[PtCl_6]\cdot H_2O$ with an excess of phosphine in EtOH; by the same procedure, except for the presence of aqueous formaldehyde, trans*-$[PtCl_2(PPh_3)_2]$ can be prepared. By pressurring $H_2[PtCl_6]\cdot 6H_2O$ and an excess of PPh_3 with carbon monoxide and molecular hydrogen in EtOH* trans*-$[PtHCl(PPh_3)_2]$ is obtained; in the presence of propene, even without molecular hydrogen,* trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ forms. All the above complexes are prepared in good yield.*

Introduction

The increasing utility of substituted phosphine complexes of platinum(II) as starting compounds in preparative chemistry and as homogeneous catalysts [1–5] makes the search for new convenient syntheses of these complexes more interesting.

Below, is briefly summarized the literature relating to previous syntheses of the complexes for which a new method of preparation is later described. The usual preparation involves $K_2[PtCl_4]$ as precursor, which in turn is synthesized by reduction of $K_2[PtCl_6]$ with hydrazine [6]. *Cis*-$[PtCl_2(PPh_3)_2]$ is synthesized from $K_2[PtCl_4]$ and PPh_3 [7]; treatment of this complex with hydrazine and acetic acid yields *trans*-$[PtHCl(PPh_3)_2]$ [8]. Also bis-(diphenylphosphine) complexes of platinum(II), for example of the type $[PtCl_2\{Ph_2P(CH_2)_nPPh_2\}]$ are currently prepared from $[PtCl_4]^{2-}$ [9].

Trans-$[PtCl_2(PPh_3)_2]$ can be synthesised by interacting PPh_3 with Zeise's salt, $K[PtCl_3(C_2H_4)]$ (which is also prepared from $[PtCl_4]^{2-}$ [10]) or by treatment of the dimer $[PtCl_2(PPh_3)]_2$ with PPh_3 in benzene [11], which in turn is synthesised by thermally decomposing $H_2[PtCl_4]$ or $H_2[PtCl_6]$ at temperatures ranging between 150 and 450 °C [13–15]. A different method for the preparation of the *trans* derivative consists of adding phosphine to a hot N,N-dimethylformamide-xilene solution of $H_2[PtCl_6]\cdot 6H_2O$, however a substantial quantity of platinum metal is deposited [16].

Our current interest in hydroformylation reactions catalyzed by platinum(II) complexes [17] (the above complexes in combination with $SnCl_2$ have been found excellent catalysts in the highly regioselective hydroformylation of α-olefins [3–5, 18]) prompted us to search for new routes for the synthesis of these complexes directly from $H_2[PtCl_6]\cdot 6H_2O$ (possibly in one step) since the metal is recovered as this derivative from its residues [19, 20].

In the course of studying the hydroformylation of propene catalyzed by a *cis*-$[PtCl_2(PPh_3)_2]$–$SnCl_2$ system, we were able to isolate *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ which has been proved to be an intermediate precursor [17]. Here we report that this complex can be conveniently prepared directly from $H_2[PtCl_6]\cdot 6H_2O$ by treatment with PPh_3, carbon monoxide, propene in EtOH; new procedures for the synthesis of *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$, *trans*-$[PtHCl(PPh_3)_2]$, and $[PtCl_2(P–P)]$ are also described.

Results and Discussion

Cis-$[PtCl_2(PPh_3)_2]$ and $[PtCl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1, 2, or 4) were prepared by heating $H_2[PtCl_6]\cdot 6H_2O$ with the phosphine in the ratio Pt:P = 1:4, in EtOH. This procedure is a convenient extension of the preparation of complexes of the type $[PtCl_2(PR_3)_2]$ (R = alkyl) from $K_2[PtCl_6]$ and an excess of PR_3 [7]. It has been reported that the excess of the phosphorous ligand acts as reducing agent [7].

The above platinum(II) complexes are synthesized in good yields (see experimental) with the exception of $[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$. Carrying out the preparation of this complex in acetone/CH_2Cl_2 the yield can be improved up to 80%.

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In an attempt to prepare *trans*-[PtHCl(PPh$_3$)$_2$], $H_2[PtCl_6]\cdot6H_2O$ and PPh$_3$ in the ratio Pt:P = 1:4 were heated in EtOH with a 40% w/v aqueous formaldehyde solution, following the method reported for the preparation of [MHCl(CO)(PPh$_3$)$_3$] starting directly from $RuCl_3\cdot3H_2O$ or $Na_2[OsCl_6]\cdot6H_2O$ and using formaldehyde as hydride (and carbonyl) source [21]. No hydride (or carbonyl complex formed; unaspectely *trans*-[PtCl$_2$(PPh$_3$)$_2$] precipitated in 85% yield. This procedure offers a substantial improvement in speed and efficiency over those currently available.

The formation of *trans*-[PtCl$_2$(PPh$_3$)$_2$] may occur *via* *trans*-[PtHCl(PPh$_3$)$_2$] as intermediate which would likely yield the final dichloride upon interaction with HCl liberated in the course of the reaction. As a matter of fact, *trans*-[PtHCl(PPh$_3$)$_2$] heated with HCl in EtOH yields *trans*-[PtCl$_2$(PPh$_3$)$_2$]. It is interesting to observe that the procedures for the preparations of *cis*- and *trans*-[PtCl$_2$(PPh$_3$)$_2$] are the same except that in the latter case the reaction occurs in the presence of aqueous formaldehyde. By heating to b.p. a suspension of the *cis* isomer with aqueous formaldehyde in EtOH, in the presence of PPh$_3$, the complex is recovered apparently with no traces of the *trans* isomer. However it has been reported that in solution *cis–trans* isomerization is readily set up in the presence of catalytic amounts of PPh$_3$, the electronic spectra of solutions in chloroform give K ≅ 0.1 at 25 °C for the equilibrium $cis \overset{PPh_3}{\rightleftharpoons} trans$ [11].

Trans-[PtHCl(PPh$_3$)$_2$] has been prepared by pressuring $H_2[PtCl_6]\cdot6H_2O$ and PPh$_3$ (Pt:P = 1:4) with molecular hydrogen and carbon monoxide in EtOH at 100 °C (H$_2$/CO = 1/1; total pressure = 100 atm). Using PPh$_3$ in a stoicheiometric amount the hydride forms in low yield together with platinum metal. Carrying out the reaction in the absence of CO *cis*[PtCl$_2$(PPh$_3$)$_2$] separates out with no detectable amounts of the hydride.

It was reported that [RuCl$_2$(PPh$_3$)$_4$] reacts with molecular hydrogen under pressure to yield [RuHCl(PPh$_3$)$_3$]; the reaction occurs even under atmospheric pressure in the presence of NEt$_3$ [22]. In an attempt to prepare *trans*-[PtHCl(PPh$_3$)$_2$] under milder pressure conditions [PtCl$_2$(PPh$_3$)$_2$] was pressurized with 10 atm of hydrogen and 10 atm of carbon monoxide in the presence of NEt$_3$, however the main product recovered was *cis*-[PtCl$_2$(PPh$_3$)$_2$].

By pressuring $H_2[PtCl_6]\cdot6H_2O$ together with PPh$_3$ in the ratio Pt:P = 1:4 with carbon monoxide and propene (100 and 10 atm, respectively) in EtOH, white crystal of *trans*-[PtCl(COPr-n)(PPh$_3$)$_2$] are recovered in high yield. This complex forms following the scheme:

$$H_2[PtCl_6] + 3PPh_3 \rightarrow [PtCl_2(PPh_3)_2] + Cl_2PPh_3$$

$$[PtCl_2(PPh_3)_2] \xrightarrow{EtOH} [PtHCl(PPh_3)_2] \xrightarrow{propene} [PtCl(Pr)(PPh_3)_2] \xrightarrow{CO} [PtCl(COPr\text{-}n)(PPh_3)_2]$$

The capacity of alcohols to act as a hydride source is well documented [23].

The reaction does not proceed any further with EtOH to yield butanoic ester, contrary to what is observed in the presence of the palladium analog which has been proved to be an intermediate precursor in the catalytic hydrocarboalkoxylation of propene [24]. The structure of *trans*-[PtCl(COPr-n)(PPh$_3$)$_2$] and its catalytic properties when in combination with SnCl$_2$ will be described in a forthcoming paper [17].

In previous articles it has been reported that an acyl derivative can be prepared by reacting lithium tetrachloroplatinate(II) with a terminal olefin and formic acid in DMF, followed by treatment with PPh$_3$:

$$Li_2[PtCl_4] + olefin \xrightarrow[DMF]{HCOOH} [(alkyl)Pt(CO)Cl] \xrightarrow{PPh_3} [PtCl(COR)(PPh_3)_2]$$

However, addition of PPh$_3$ caused partial displacement of carbon monoxide [25].

Experimental

$H_2[PtCl_6]\cdot6H_2O$, phosphines, other reagents and solvents were used as purchased without further purification.

All the platinum(II) derivatives here synthesized have been characterized previously and have been here identified by elemental analysis and by comparison of their IR spectrum with that of an authentical sample prepared by methods reported in literature. IR spectra were recorded on a Perkin-Elmer model 457 spectrometer on Nujol mulls using CsI windows.

High pressure experiments were carried out in a *ca.* 75 ml stainless steel stirred autoclave, thermostatted in an oil bath. Reagents were contained in a pyrex bottle placed in the autoclave to prevent contamination from other metallic species.

Cis-*Dichlorobis(triphenylphosphine)platinum(II)*

An ethanol (5 ml) solution of $H_2[PtCl_6]\cdot6H_2O$ (100 mg, 0.193 mmol) and PPh$_3$ (220 mg, 0.84 mmol) is stirred at room temperature. In a few minutes a white solid forms. The reaction mixture is heated under reflux for 1 hr. After cooling the suspension is filtered. The white precipitate is washed with EtOH and ether and dried under vacuum, mg 149, yield 98%.

Trans-*Dichlorobis(triphenylphosphine)platinum(II)*

$H_2[PtCl_6]\cdot6H_2O$ (100 mg) and PPh_3 (220 mg) are added at room temperature to a mixture of EtOH (5 ml) and a 40% w/v aqueous formaldehyde solution (5 ml). The reaction mixture is refluxed for 1 hr during which a whitish precipitate forms. After cooling the ivory precipitate is collected on a filter, washed with EtOH and ether and dried under vacuum. mg 130, yield 85%.

Dichloro[bis(diphenylphosphine)methane] platinum(II)

$H_2[PtCl_6]\cdot6H_2O$ (100 mg) and bis(diphenylphosphine)methane (160 mg, 0.42 mmol) are added to 5 ml of EtOH at room temperature, with stirring. The reaction mixture is heated under reflux for *ca.* 2 hr. After cooling, the white solid is collected on a filter, washed with EtOH and ether, and dried under vacuum. (110 mg, yield 88%).

Through this procedure the following have been prepared: dichloro[1,2-bis(diphenylphosphino)ethane] platinum(II), (yield = 49%) dichloro[1,4-bis-(diphenylphosphino)butane] platinum(II), trinuclear complex [9], yield 84%.

The yield of the ethane derivative can be improved, up to *ca.* 80%, carrying out the reaction in an acetone/methylenchloride medium.

Trans-*Chlorohydridobis(triphenylphosphine)platinum(II)*

In a typical experiment, $H_2[PtCl_6]\cdot6H_2O$ (100 mg, 0.193 mmol) and PPh_3 (220 mg, 0.84 mmol) are dissolved in 10 ml EtOH in a pyrex bottle placed in an autoclave which is 'washed' with carbon monoxide. After pressurization with 50 atm. of carbon monoxide and 50 atm. of hydrogen at room temperature the autoclave is thermostatted at 100 °C for 4 hr with stirring. After cooling and depressurization the white crystalline solid is collected on a filter and washed with EtOH and ether. The elemental analysis and IR spectrum show it to be *trans*-$[PtHCl(PPh_3)_2]$ in the c form [26]. (mg 125, yield 85%).

Under milder pressure conditions, for example 10 atm. of hydrogen and of CO, the platinum complex is recovered as *cis*-$[PtCl_2(PPh_3)_2]$ (mg 115, yield 75%).

In the presence of minor amounts of PPh_3, for example with a ratio Pt/P = 1/2, some platinum metal forms.

Trans-*Chloro(butanoyl)bis(triphenylphosphine)platinum(II)*

$H_2[PtCl_6]\cdot6H_2O$ (100 mg) and PPh_3 (220 mg) are dissolved in 10 ml EtOH in a pyrex bottle placed in an autoclave. This is 'washed' with carbon monoxide. Propene (10 atm.) and carbon monoxide (100 atm.) are added in that order. The autoclave is thermostatted at 100 °C for 4 hr with stirring. After cooling and depressurization the white crystalline solid is collected on a filter and washed with EtOH and ether. The elemental analysis and the IR spectrum |ν(C=O) at 1659 cm^{-1} [17]| show it to be pure *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ (mg 135, yield 85%).

No optimization of temperature and pressure conditions was attempted.

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