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REACTIONS OF TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0) WITH ALCOHOLS: NEW PLATINUM(IV) HYDRIDO COMPLEXES

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Summary

The reactions of tetrakis(triphenylphosphine)platinum(0) with tin(II) and tin(IV) chlorides in various alcohols are described. Ethanol, 1-propanol and 1-butanol afford octahedral platinum(IV) hydridoalkoxy complexes, $(Ph_3P)_2Pt$ having been inserted into the Sn–Cl and R–OH bonds. Isopropanol produces an alkoxy complex but with no hydride ligand. Methanol gives a different and still unidentified complex apparently of the composition $Pt(PPh_3)_2(SnCl_3)_2Cl_2(CH_3OH)$. The IR and ^1H and ^{31}P NMR spectra of some of these complexes are discussed.

Introduction

Tetrakis(triphenylphosphine)platinum(0) is known to undergo dissociation in solution to bis(triphenylphosphine)platinum(0), which then may undergo oxidative addition reactions with a variety of reactants yielding tetracoordinate square planar platinum(II) complexes, and invariably retaining the two phosphine ligands [1]. In some unusual cases the platinum(0) may be oxidized all the way to platinum(IV). We have found this to occur in the reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$ in ethanol. We have also observed that platinum reacts with ethanol in the Pt/Sn system with splitting of the O–H bond and formation of a hydridoalkoxyplatinum complex [1]. It was of interest to find out whether this behaviour was unique for ethanol, and so we have further studied the Pt/Sn/ethanol system and examined the behaviour of other alcohols under similar conditions. The results may have a bearing on the mechanisms of catalytic reactions involving Pt/Sn systems.

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Results and discussion

The reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ in ethanol affords the octahedral complex chloroethoxyhydridotrichlorostannatobis(triphenylphosphine)platinum(IV), $[Pt(Ph_3P)_2(SnCl_3)(H)(Cl)(OC_2H_5)]$. The identity of the compound is supported by its elemental analysis, molecular weight determination, and IR and NMR spectra. The IR spectrum shows ν(Pt–H) at 2120, ν(Sn–Cl) at 330 and ν(Pt–Cl) at 300 cm^{-1} (sh). The ^{1}H NMR shows signals indicative of the OC_2H_5 group, and a low field signal (−16.6 ppm) indicative of a Pt–H bond. The ^{31}P NMR spectrum shows a shift of +13.7 ppm relative to H_3PO_4 with ^1J(PtP) of 1843 Hz; the value of the coupling constant is comparable to those usually found for Pt^{IV} phosphine complexes [2]. When $SnCl_4 \cdot 5H_2O$ is used instead of $SnCl_2 \cdot 2H_2O$ the product is only slightly different. The ν(Pt–H) band appears at 2140 cm^{-1} in the product from $SnCl_4 \cdot 5H_2O$ and the ^{1}H NMR spectrum of the product from $SnCl_2$ shows an additional signal at 1.75 ppm and its IR spectrum shows an additional strong band at 1550 cm^{-1}. It is likely that the two compounds differ in the relative positions of the hydride and the $SnCl_3$ group; these may be adjacent in the compound derived from the reaction of $SnCl_2$, possibly allowing some intramolecular hydrogen bonding between the chloride of $SnCl_3^-$ and the hydride. The other product has the hydride in a position *trans* to $SnCl_3^-$, and so no such hydrogen bonding is possible. The alcohols studied fall into three classes in respect of their mode of reaction.

(i) Alcohols affording hydridoalkoxyplatinum(IV) complexes. These include ethanol, 1-propanol and 1-butanol. These alcohols give octahedral $Pt(Ph_3P)_2(SnCl_3)(H)(Cl)(OR)$ complexes on reaction with $Pt(Ph_3P)_4$ and $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 5H_2O$. Slight differences between the products obtained using Sn^{II} or Sn^{IV} are observed in all these alcohols as discussed for the case of ethanol above; the Sn^{II} product possibly exhibiting intramolecular hydrogen bonding. The formulation of these products is consistent with their elemental analyses and their IR and NMR spectra.

It is obvious that insertion of Pt into the RO–H bond takes place in these reactions. It is not known whether $Pt(PH_3P)_2$ first inserts into the O–H bond followed by insertion of Pt^{II} in a Sn–Cl bond, or whether the opposite sequence takes place. Insertions of $Pt(Ph_3P)_2$ into the O–H bond in the absence of Sn salts are known (e.g. the reaction of phenol with $Pt(Ph_3P)_2$ [1]). Insertions of $Pt(Ph_3P)_2$ into the Sn–Cl bond in the absence of alcohol are also known (vide infra).

(ii) Alcohols affording non-hydrido alkoxyplatinum(IV) complexes. This behaviour is typified by the reaction of isopropanol with $Pt(Ph_3P)_4$ and $SnCl_2 \cdot 2H_2O$. The binuclear complex $[Pt(Ph_3P)(SnCl_3)_2(Cl)(OC_3H_7)]_2$ is obtained in which the two Pt atoms are bridged by chloride ions. The IR spectrum of the complex shows no absorption in the 2000–2200 cm^{-1} range (the ν(Pt–H) region). It shows two strong ν(C–O) bands at 1115 and 1090 cm^{-1}, and a very strong broad band at 330 cm^{-1}, in the ν(Sn–Cl) region. There is no band in the O–H region indicating the absence of molecular isopropanol. The ^{1}H NMR shows the signals characteristic of the isopropyl group.

(iii) Methanol, which gives a complex apparently of the composition $Pt(Ph_3P)_2(SnCl_3)_2Cl_2(CH_3OH)$. The methanol molecule is tightly held by the complex, whose physical properties are quite different from those of the known complex $[Pt(Ph_3P)_2(SnCl_3)_2Cl_2]$ [3]. The product will be investigated further.

Tetrakis(triphenylphosphine)platinum(0) did not react with any of the alcohols, in the absence of $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 5H_2O$. However, when $Pt(Ph_3P)_4$ was treated with $SnCl_2 \cdot 2H_2O$ in benzene (i.e. in the absence of alcohol) the dimeric Pt^{II} complex $[Pt(Ph_3P)(SnCl_3)Cl]_2$ was obtained. Treatment of this last complex with ethanol did not give a hydrido complex.

Experimental

The following procedure was used for the reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 5H_2O$ in the alcohols. To a suspension of $Pt(Ph_3P)_4$ [4] (0.50 g) in the alcohol (30 ml) was added $SnCl_2 \cdot 2H_2O$ (or $SnCl_4 \cdot 5H_2O$) (0.50 g). Upon stirring the mixture became clear, and stirring was continued for 7 h. A white precipitate separated, and this was filtered off, washed with ethanol then with ether, and dried in a vacuum oven at room temperature.

(i) Ethanol. The compound obtained from $Pt(Ph_3P)_4$ and $SnCl_2 \cdot 2H_2O$ turns pink at 160°C and melts at 188–189°C. (Found: C, 44.20; H, 3.52; C, 13.72; mol. wt. 1141 (by mass spectrometry). $C_{38}H_{36}P_2PtSnCl_4O$ calcd.: C, 44.46; H, 3.54; Cl, 13.82%; mol. wt. 1026.26. It is soluble in DMSO and chloroform, insoluble in carbon tetrachloride, slightly soluble in benzene, and decomposes in carbon disulfide and acetone. IR (Nujol): 2950s, 2870s, 2120m, 1550s, 815w, 330s, 330sh cm^{-1}. ^1H NMR: 1.05 (t, CH_3), 3.40 (q, CH_2); -16.6 (s, Pt–H), 1.75 ppm. ^{31}P NMR: 13.7 ppm (ext. H_3PO_4), $^1J(PtP)$ 1843 Hz.

With $SnCl_4 \cdot 5H_2O$ the product obtained turns pink at 140°C and melts at 160°C. (Found: C, 44.01; H, 3.66; Cl, 13.68. $C_{38}H_{36}P_2PtSnCl_4O$ calcd.: C, 44.46; H, 3.54; Cl, 13.82%). IR (Nujol): 2950s, 2870s, 2140m, 325s, 300sh cm^{-1}. ^1H NMR: 1.05 (t, CH_3), 3.40 (q, CH_2), -16.6 (s, Pt–H) ppm. ^{31}P NMR: 13.7 ppm (ext. H_3PO_4), $^1J(PtP)$ 1843 Hz.

(ii) 1-Propanol. The product obtained from $Pt(Ph_3P)_4$ and $SnCl_2 \cdot 2H_2O$ turns pink at 172°C and melts at 192°C. (Found: C, 43.99; H, 3.74; C, 13.90. $C_{39}H_{38}P_2PtSnCl_4O$ calcd.: C, 45.04; H, 3.66; Cl, 13.67%). It is soluble in DMSO and chloroform but insoluble in carbon tetrachloride. The compound obtained from $Pt(Ph_3P)_4$ and $SnCl_4 \cdot 5H_2O$ turns pink at 148°C and melts at 160°C. (Found: C, 45.02; H, 4.07; Cl, 14.13. $C_{39}H_{38}P_2PtSnCl_4O$ calcd.: C, 45.04; H, 3.66; Cl, 13.67%). IR (Nujol): 2900s, 2860s, 2110m, 1550s, 330sh cm^{-1}. ^1H NMR: 3.20 (t, O–CH_2), 1.25 (2H), 0.70 (t, CH_3), 7.30 (phenyl) ppm. ^{31}P NMR: 13.5 ppm (ext. H_3PO_4); $^1J(PtP)$ 1843 Hz.

(iii) 1-Butanol. The reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ gave a white compound which starts to decompose at 150°C and melts at 167°C. (Found: C, 45.60; H, 3.60; Cl, 12.63. $C_{41}H_{40}P_2PtSnCl_4O$ calcd.: C, 46.16; H, 3.79; Cl, 13.32%). IR (Nujol): 2920s, 2900s, 2850s, 2110m, 1550s, 830w, 330s, 300sh cm^{-1}. ^1H NMR: 3.55 (t, CH_2), 1.10 (4H), 0.85 (t, CH_3), 7.40 (phenyl) ppm.

(iv) Methanol as a solvent. The reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ in methanol gave a white compound that begins to decompose (turning pink) at 148°C and melts at 160°C. (Found: C, 33.98; H, 2.51; C, 23.05, $C_{37}H_{34}P_2PtSn_2Cl_8O$ calcd.: C, 34.92; H, 2.69; C, 22.31%). IR (Nujol): 3400s, 2900s, 2840s, 1660b, 1150m, 325s, 300sh cm^{-1}.

(v) Isopropanol. The reaction of $Pt(Ph_3)P_4$ with $SnCl_2 \cdot 2H_2O$ gave a complex which decomposes at 200°C and melts at 250°C. (Found: C, 24.91; H, 2.20; Cl,

23.97). $C_{42}H_{44}P_2Pt_2Sn_4Cl_1O_2$ calcd.: C, 25.17; H, 2.21; C, 24.76%). IR (Nujol): 2920s, 284s, 1115s, 1090s, 330vs, 300sh cm^{-1}. ^{1}H NMR: 330 (1H), 0.90 (d, 6H) ppm.

(vi) Benzene. The reaction of $Pt(Ph_3P)_4$ with $SnCl_2 \cdot 2H_2O$ in benzene gave an orange product which decomposes at 290°C. (Found: C, 29.66; H, 2.01; Cl, 18.44. $C_{36}H_{30}P_2Pt_2Sn_2Cl_8$ calcd.: C, 30.08; H, 2.09; Cl, 19.78%).

Spectra

The IR spectra were obtained with using Nujol mulls on Perkin–Elmer 225 Grating Infrared Spectrophotometer over the range 200–4000 cm^{-1}. The ^{1}H NMR spectra in the organic range were recorded with a Perkin–Elmer 360 spectrometer. The hydride ^{1}H NMR and ^{31}P NMR spectra were recorded with a XL-100 spectrometer. Deuterated DMSO was normally used as solvent.

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