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Spectroscopic characterization of "dihydrodichlorobis(triphenylphosphine)-platinum(IV)" as *trans*-hydridochlorobis(triphenylphosphine)platinum(II)

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Recently there has been renewed interest in the preparation and reactions of platinum hydrides especially with respect to determination of stereochemistry[1,2] and the isolation of platinum(IV) compounds[3]. These compounds have been prepared by the oxidative addition reaction of protonic acids to $(PPh_3)_4Pt$[4], although with HF[5] and 5-phenyltetrazole[6] the product is $(PPh_3)_2PtX_2$ (X = F or 5-phenyltetrazolate) rather than the hydride. A plausible intermediate in this latter reaction is a platinum(IV) dihydride $(PPh_3)_2PtH_2X_2$, which can then lose H_2 to yield the product. There are very few examples of platinum(IV) dihydrides, but it has been claimed[4] that in the presence of excess acid two molecules of HCl will add to $(PPh_3)_4Pt$ to give $(PPh_3)_2PtH_2Cl_2$. In view of the importance of platinum(IV) hydrides in the above reactions, we have studied in detail the nature of this complex.

An apparently diagnostic method for confirmation would be chlorine analysis, but in this case it cannot be considered reliable since the complex $(PPh_3)_2PtH_2Cl_2$ is reported to lose HCl even in the solid state. In view of this we have considered it more useful to study the nature of this species in solution as well as in the solid state, and for the reasons given below consider the complex to be the crystalline modification of *trans*-$(PPh_3)_2PtHCl$ originally thought to be the *cis* isomer[7].

(a) The compound *trans*-$(PPh_3)_2PtHCl$ (ν(Pt—H) in $CHCl_3$, 2236 cm^{-1}) as a solution in $CHCl_3$ shows a triplet in the ^1H NMR spectrum at τ 26.3 (*J*(P—H) 13.5 Hz, *J*(Pt—H) 1210 Hz) which corresponds closely to that previously reported[1,2,8]. When HCl is bubbled through the solution the high field line remains a triplet at τ 26.5 (*J*(P—H) 13.6 Hz, *J*(Pt—H) 1212 Hz). Addition of ether to this solution causes crystallization of the "platinum(IV) hydride" (ν(Pt—H) in Nujol mull 2232, 2260, 2270 (sh)). Although the above ^1H NMR spectrum could be assigned to $(PPh_3)_2PtH_2Cl_2$ with the two PPh_3 groups *trans* to each other and the hydrides *trans* to the chlorides, it is surprising that the ^1H NMR spectral data are so similar (the slight differences in coupling constant and chemical shift can be explained by the change in the nature of the solvent when HCl is present).

(b) The ^{1}H NMR spectrum (in $CHCl_3$) of *trans*-$(PPh_3)_2PtHCl$ (ν(Pt–H) in $CHCl_3$, 2236 cm^{-1}) was recorded and the center line of the hydride integrated. Hydrogen chloride was bubbled through the solution and the high field line again integrated under identical conditions. Comparison of the area after addition of HCl showed no increase, which would have been expected if a dihydride were formed, yet when the complex was isolated from the HCl saturated solution the IR spectrum showed bands at 2232, 2260, 2270 (sh) indicative of the "platinum(IV) dihydride".

(c) A sample of the "platinum(IV) hydride" was prepared (ν(Pt–H) in Nujol, 2232, 2260, 2270 (sh)), dissolved in $CHCl_3$ containing HCl and the IR spectrum obtained again. This solution spectrum showed a single band at 2236 cm^{-1}, diagnostic of *trans*-$(PPh_3)_2PtHCl$, yet when the complex was isolated again from ether the spectrum in Nujol mull showed the three bands initially found.

(d) Hexamethylbenzene (83.6 mg) was dissolved in $CHCl_3$ (50.0 ml) and in a 1 ml aliquot of this solution was dissolved *trans*-$(PPh_3)_2PtHCl$ (140.5 mg). Integration of the center line of the hydride resonance against that of the methyl protons gave a relative area for hydride/methyl of 0.59/1 (theoretical for the monohydride is 0.66/1)★. Through this solution was passed HCl for 1¾ hours and, after adding $CHCl_3$ to equalize the volume of the initial solution, the integration was carried out again, giving a value of 0.63/1. Isolation of the complex from this $CHCl_3$/HCl solution gave the "platinum(IV) hydride" (ν(Pt–H) 2232, 2260, 2270(sh)), although the ^{1}H NMR spectrum showed no significant increase in hydride content.

(e) The "platinum(IV) hydride" remains unchanged after heating at 70° for three days, and the Cl analysis (5.11) corresponds to that required for *trans*-$(PPh_3)_2PtHCl$ (4.69).

From these results it is clear that the suggested platinum(IV) hydride is really the platinum(II) hydride *trans*-$(PPh_3)_2PtHCl$ in a different crystalline form. The IR spectrum of this form as a mull in hexachlorobutadiene shows bands at 2232, 2267, 2277 cm^{-1} which is very close to that reported for the *cis* hydride (2225, 2260 cm^{-1}) in the same medium[7]. In addition this IR spectrum looks identical with "complex C" reported in ref. 2 which has been found to be *trans*-$(PPh_3)_2PtHCl$. In conclusion it can be seen that the platinum(IV) dihydride, $(PPh_3)_2PtH_2Cl_2$ is the crystallographic modification of *trans*-$(PPh_3)_2PtHCl$ which was also considered previously to be *cis*-$(PPh_3)_2PtHCl$. In view of this result it is probable that the complex in the corresponding bromo system, which has several bands in the hydride region of the IR spectrum, is a crystallographic modification of *trans*-$(PPh_3)_2PtHBr$[8].

The analogous triethylphosphine complex $(PEt_3)_2PtH_2Cl_2$ [9] has also been suggested as an adduct in the reaction of *trans*-$(PEt_3)_2PtHCl$ with HCl. The characterization of this complex is again based solely on its infrared spectrum in Nujol. However, our results cannot be extrapolated to this study because the greater basicity of PEt_3 as compared to PPh_3 may result in the facile protonation of *trans*-$(PEt_3)_2PtHCl$ to yield the platinum(IV) dihydride.

★The accuracy in the integration of the species is probably of the order of ± 5%.

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