A Reproducible Synthesis of Aquatris(triethylphosphine)platinum(II) Hexafluorophosphate

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A reproducible synthesis of $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ is described. The fast-atom bombardment mass spectrum shows a parent ion signal and signals from fragments corresponding to loss of H_2O, $PEt_3 + H_2O$, and $PEt_3 + H_2O + nC_2H_4$ (n = 1—3).

We have recently reported[1] the synthesis of the complex $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ but that the conditions for the production of this complex were difficult to reproduce. This complex is of considerable interest since there are very few complexes of platinum(II) to which water is also co-ordinated. A rare structurally characterised example has recently been reported.[2] In addition, the water molecule of $[Pt(H_2O)(PEt_3)_3]^{2+}$ is easily replaced by anionic or neutral groups. For example, we have demonstrated[1] exchange of the water molecule for NO_3^-, ClO_4^-, O_2CMe^-, Cl^-, PEt_3, *etc.* and the extreme lability of the water molecule is demonstrated by the observation that fluoride can be abstracted from the PF_6^- groups in *e.g.* acetone to give $[PtF(PEt_3)_3]^+$.[1] We now report that a change in the synthetic procedure for $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ allows its reproducible synthesis in moderate yield.

Results and Discussion

The original synthesis of $[Pt(H_2O)(PEt_3)_3][PF_6]_2$ involved[1] addition of Ag_2SO_4 to a solution of $[PtCl_2(PEt_3)_2]$ and PEt_3 {*i.e.* $[PtCl(PEt_3)_3]^+$} in dilute sulphuric acid. The major problem associated with isolation of the required product appeared to be that not all of the chloride ion was precipitated by the silver because of the formation of soluble PEt_3 complexes of silver chloride. These were evidently capable of releasing chloride to the platinum complex so that addition of PF_6^- precipitated $[PtCl(PEt_3)_3]PF_6$, despite the fact that this complex was not identified as being present in the reaction solution by *in situ* ^{31}P n.m.r. studies.

In order to circumvent this problem, we have changed the order of addition of the reagents to prevent the presence of excess PEt_3 when AgCl is present.

Thus, both $[PtCl_2(PEt_3)_2]$ and Ag_2SO_4 have a low solubility in dilute sulphuric acid. Stirring them together leads to the formation of insoluble AgCl and soluble $[Pt(PEt_3)_2(SO_4)]$. By employing a slight excess of $[PtCl_2(PEt_3)_2]$ it is possible to ensure that no excess silver remains in solution and that only $[Pt(PEt_3)_2(SO_4)]$ is formed. Addition of a stoicheiometric quantity of PEt_3 to this solution causes quantitative conversion to $[Pt(PEt_3)_3Y]^{n+}$ ($Y = HSO_4, n = 1; Y = H_2O, n = 2$) ($^{31}P$ n.m.r. evidence). Addition of KPF_6 to this solution causes precipitation of $[Pt(H_2O)(PEt_3)_3][PF_6]_2$, in *ca.* 30% yield.‡

The product was identified by comparison of its spectroscopic properties with those of the complex previously prepared.[1]

In addition, we have measured the fast-atom bombardment (f.a.b.) mass spectrum of this product. This spectrum, taken in a glycerol mull, shows a clearly defined parent ion at m/z 567 $[Pt(H_2O)(PEt_3)_3]^+$ and fragment peaks corresponding to $[Pt(PEt_3)_3]^+$, $[Pt(PEt_3)_2]^+$, and successive loss of three C_2H_4 units from $[Pt(PEt_3)_2]^+$. This spectrum is very similar to that of solutions of $[Pt(PEt_3)_3Y]^{n+}$ prepared from $[PtCl_2(PEt_3)_2]$, PEt_3, and Ag_2SO_4 in dilute sulphuric acid and suggests that the peak observed at 567 in these mass spectra may be assigned as arising from $[Pt(H_2O)(PEt_3)_3]^+$.[3]

Experimental

I.r. spectra were recorded on a Perkin-Elmer PE 577 grating spectrometer and n.m.r. spectra on a Bruker Associates WM 250 or JEOL FX 60Q Fourier-transform spectrometer. F.a.b. mass spectra were obtained on glycerol mulls using a VG 7070E mass spectrometer.

Aquatris(triethylphosphine)platinum(II) *Hexafluorophosphate.*—The complex *cis*-$[PtCl_2(PEt_3)_2]$ (0.54 g, 1.07 mmol) was stirred with Ag_2SO_4 (0.33 g, 1.05 mmol) in distilled water (40 cm^3) for 16 h under nitrogen. The resulting white suspension was filtered to remove AgCl, acidified to pH 2 with dilute H_2SO_4, and treated with PEt_3 (0.16 cm^3, 1.08 mmol). ^{31}P N.m.r. studies showed that this solution did not contain any $[PtCl(PEt_3)_3]^+$. Addition of KPF_6 (0.35 g, 2.3 mmol) caused the slow precipitation of the *complex* as white clusters of needles. These were collected, washed with water, and dried in air. Yield *ca.* 0.2 g (30%). The complex was identified by comparison of its i.r. spectrum (Nujol mull, CsI plates) with that of a fully characterised sample.

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‡ The low isolated yield arises because of the solubility of the product in water.