A Convenient Preparation of the Amminetrichloroplatinate(II) Anion

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Although the $[Pt(NH_3)Cl_3]^-$ ion has been known for some time, and is of considerable interest as a starting material in Pt(II) coordination chemistry, no convenient, high yielding synthesis of this complex has been reported [1–3]. We now report that *cis*-$Pt(NH_3)_2Cl_2$ reacts with tetraethylammonium chloride in hot dimethylacetamide to give $[Pt(NH_3)Cl_3]^-$ which can be isolated in 74% yield as its tetraphenylphosphonium salt or used *in situ* to prepare other mixed ligand complexes. The preparation of several related $[Pt(RNH_2)X_3]^-$ (R = ethyl, i-propyl, X = Cl, R = H, X = Br) complexes is also described.

Experimental

The *cis*-$Pt(NH_2R)X_2$ (X = Cl, R = H, ethyl and i-propyl; X = Br, R = H) complexes were prepared by the Dhara method [4, 5]. K_2PtCl_4 (Johnson Matthey), tetraethylammonium chloride and bromide (Aldrich) and tetraphenylphosphonium chloride (Aldrich) were all used as received. Infrared spectra were recorded using a Perkin-Elmer model 283 spectrophotometer. Elemental analysis were performed by Atlantic Microlab Inc., Atlanta, Ga.

Preparation of the Complexes

Note: This procedure should be carried out in a well ventilated fume hood.

Tetraphenylphosphonium amminetrichloroplatinate(II)

A solution of *cis*-$Pt(NH_3)_2Cl_2$ (1.17 g, 3.9 mmol) and tetraethylammonium chloride·xH_2O (0.78 g, 4.7 mmol) in dimethylacetamide (200 ml) was heated to 100 °C (±2 °C) for 6 h. (Prolonged heating above 105 °C results in extensive decomposition of the reaction mixture.) During this time a slow stream of N_2 was bubbled through the reaction mixture using a gas dispersion tube. At the end of this 6 h period, the reaction volume was approximately 50 ml. After the orange solution had cooled to room temperature, ethyl acetate/hexane (450 ml, 1:1 *v*/*v*) was added and the cloudy reaction mixture was chilled for 12 h at −10 °C. This procedure yielded a clear, colorless solution and a thick, orange oil. The clear solution was discarded and the oil dissolved in water (20 ml). A small amount of unreacted *cis*-$Pt(NH_3)_2Cl_2$ was removed by filtration and tetraphenylphosphonium chloride (1.5 g, 4.0 mmol) in water (50 ml) was added. This mixture was stirred for 30 min and the resulting light orange solid was collected, washed with water (20 ml) and dried *in vacuo*.

Yield of $[Ph_4P][Pt(NH_3)Cl_3]$ = 1.89 g, 2.9 mmol, 74% based on Pt. This material was recrystallized by chilling (−10 °C) a methylene chloride/ether (1:5 *v*/*v*) solution. *Anal.* Calc. for $C_{24}H_{23}Cl_3NPPt$: C, 43.81; H, 3.53; Cl, 16.16; N, 2.13. Found: C, 44.05; H, 3.48; Cl, 16.27; N, 2.16%. IR(KBr): ν(Pt–Cl) 325 cm^{-1}(m), 340(sh).

cis-(Ammine)pyridinedichloroplatinum

Starting with 2.0 g of *cis*-$Pt(NH_3)_2Cl_2$ (6.7 mmol) a solution of $[Et_4N][Pt(NH_3)Cl_3]$ in water (20 ml) was prepared as described above. Pyridine (0.56 ml) was added and the mixture was stirred and heated to 75 °C for 3 h. During this time, a yellow solid precipitated. This material was collected, washed with ethanol (20 ml) and ether (20 ml) and dried *in vacuo*. Yield of *cis*-$Pt(NH_3)$(pyridine)Cl_2 = 0.68 g, 1.9 mmol, 28% based on Pt. *Anal.* Calc. for $C_5H_8N_2Cl_2Pt$: C, 16.58; H, 2.23; Cl, 19.57; N, 7.74. Found: C, 16.66; H, 2.23; Cl, 19.48; N, 7.71%. IR(KBr): ν(Pt–Cl) 325(m), 335(m).

Tetraphenylphosphonium i-propylaminetrichloroplatinate(II)

This complex was prepared similarly to $[Ph_4P][Pt(NH_3)Cl_3]$ in 50% yield starting with *cis*-Pt(i-propylamine)$_2$Cl$_2$. *Anal.* Calc. for $C_{27}H_{29}Cl_3NPPt$: C, 46.32; H, 4.18; Cl, 15.20; N, 2.00. Found: C, 46.45; H, 4.17; Cl, 15.25; N, 1.98%. IR(KBr): ν(Pt–Cl) 325(s), 335(sh).

Tetraphenylphosphonium ethylaminetrichloroplatinate(II)

This complex was prepared similarly to $[Ph_4P][Pt(NH_3)Cl_3]$ in 44% yield starting with *cis*-Pt(ethylamine)$_2$Cl$_2$. *Anal.* Calc. for $C_{26}H_{27}Cl_3NPPt$: C, 45.52; H, 4.00; N, 2.01. Found: C, 45.55; H, 4.00; N, 2.01%. IR(KBr): ν(Pt–Cl) 325(s), 335(sh).

Tetraphenylphosphonium amminetribromoplatinate(II)

This complex was prepared in 47% yield similarly to $[Ph_4P][Pt(NH_3)Cl_3]$ starting with *cis*-$Pt(NH_3)_2Br_2$ and tetraethylammonium bromide. *Anal.* Calc. for

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$C_{24}H_{23}Cl_3NPPt$: C, 36.43; H, 2.94; Br, 30.29; N, 1.77. Found: C, 36.08; H, 3.02; Br, 30.55; N, 1.80%.

Results and Discussion

The $[Ph_4P]^+$ salts of the monobase anions $[Pt(NH_2R)X_3]^-$ (X = Cl, R = H, C_2H_5, i-C_3H_7; X = Br, R = H) can be prepared in 44–74% yield by the reaction of the corresponding *cis*-$Pt(NH_2R)_2X_2$ complexes with tetraethylammonium halide in hot dimethylacetamide. If isolation of the anions is not required, they can be conveniently used *in situ* to prepare mixed ligand complexes. The preparation of the known complex, *cis*-$PtNH_3$(pyridine)Cl_2 is given as an example [6]. This method has also been used to prepare a number of *cis*-[$Pt(NH_3)$(nitroimidazole)Cl_2] complexes [7].

Though there have been several reports of the synthesis of $[Pt(NH_3)Cl_3]^-$, we felt that an improved procedure would be of interest. The method of Elleman *et al.*, which is based on reacting *cis*-$Pt(NH_3)_2Cl_2$ in concentrated HCl with a Pt metal catalyst, is quite laborious and involves the production of $[Pt(NH_3)_4][PtCl_4]$ (Magnus green salt) as a by-product of the reaction [1]. The Kong and Rochon preparation of $K[Pt(B)Cl_3]$ (B = nitrogen base) entails the reaction of K_2PtCl_4 with B in hot dimethylformamide. This procedure works well for heterocyclic amines but $K[Pt(NH_3)Cl_3]$ was isolated in only 30% yield [3].

Since the driving force of our synthetic procedure is the loss of the NH_2R ligand via evaporation, the preparation will only work for relatively volatile amines. For example, we could not use the procedure to prepare [Pt(cyclohexylamine)$Cl_3]^-$ from the corresponding bis(amine)complex.

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