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Reactions of Trimethyloxonium Tetrafluoroborate and Dihalo-Bis-Ligandplatinum(II) Complexes

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The reaction of several platinum complexes, PtX_2L_2 ($L = P(C_6H_5)_3$, $P(C_2H_5)_3$, $P(C_6H_5)_2CH_3$, p–$CNC_6H_4CH_3$, $X = Cl$; and $L = CNCH_3$; $X = Cl, Br, I$) and trimethyloxonium tetrafluoroborate gave the appropriate $[Pt_2X_2L_4](BF_4)_2$ species; in this reaction the oxonium salt appears to be acting as halide acceptor, a function previously not ascribed to this reagent.

Introduction

We wish to report the novel reaction of trimethyloxonium tetrafluoroborate with several square planar platinum(II) complexes, PtX_2L_2 ($L = P(C_6H_5)_3$, $P(C_2H_5)_3$, $P(C_6H_5)_2CH_3$, p–$CH_3C_6H_4NC$, $X = Cl$; and $L = CH_3NC$, $X = Cl, Br, I$). The products obtained in these reactions are the halide bridged cationic species, $[Pt_2X_2L_4](BF_4)_2$. The cationic triphenyl- and triethyl-phosphine complexes were known previously,[1-4] having been prepared by several different but related reactions involving the complex PtX_2L_2 and a halide ion acceptor. The other complexes are new; in particular one might point to the new isocyanide complexes $[Pt_2X_2(CNR)_4](BF_4)_2$ prepared here.

Experimental Section

Preparations of *cis*–$PtCl_2L_2$ ($L = P(C_6H_5)_3$,[5] $P(C_6H_5)_2CH_3$,[6] $P(C_2H_5)_3$,[7] CH_3NC,[8] and p–$CH_3C_6H_4NC$[9] are described in the literature. The complexes $PtX_2(CNCH_3)_2$ (X = Br and I) were prepared from the chloride complex and either NaBr or NaI in ethanol, in the manner described by Chatt and Shaw.[10] Trimethyloxonium tetrafluoroborate was prepared by the standard method.[11]

Infrared data were recorded on Perkin Elmer 421 (4000-600 cm^{-1}) and Beckman IR-10 (600-300 cm^{-1}) spectrometers using Nujol mulls. Pmr spectra were obtained with a Varian T-60 spectrometer using TMS ($\tau = 10.0$) as an internal standard. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Rearctions of cis–$PtCl_2\{P(C_6H_5)_3\}_2$ *and Trimethyloxonium Tetrafluoroborate.* A suspension of *cis*–$PtCl_2\{P(C_6H_5)_3\}_2$ (1.58 g, 2.00 mmol) and $[(CH_3)_3O]BF_4$ (0.600 g, 4.00 mmol) in 50 ml dichloromethane was refluxed for 6 hrs. The mixture became pale yellow during this time. The solution was evaporated to dryness and the residue was redissolved in acetonitrile . The resulting solution was filtered and concentrated; a white crystaline product $[Pt_2Cl_2\{P(C_6H_5)_3\}_4](BF_4)_2$ (1.68 g, 99% yield) precipitated on addition of ethanol. This product was recrystallized from acetonitrile/ethanol; mp, 246-250° d. (lit.,[4] 300 d.). It was identified by comparison of its infrared spectrum with that of a known sample, and by elemental analysis.

Reaction of $PtCl_2\{P(C_2H_5)_3\}_2$ and Trimethyloxonium Tetrafluoroborate. A mixture of $PtCl_2\{P(C_2H_5)_3\}_2$ (1.04 g, 2.0 mmol) and $[(CH_3)_3O]BF_4$ (0.56 g, 3.8 mmol) in 40 ml dichloromethane was refluxed 9 hr., then cooled, and solvent evaporated. The residue was extracted with methanol, diluted with an equal volume of ethyl ether, filtered and hexane added until the solution became slightly cloudy. On standing white needles of the known compound $[Pt_2Cl_2\{P(C_2H_5)_3\}_4](BF_4)_2$ precipitated. Yield: 0.60 g, 55%; mp 231-234° (The literature[4] claims no sharp melting point, with decomposition over 250°.) However the infrared spectrum of our compound was identical to that reported.[2]

Reaction of $PtCl_2\{P(C_6H_5)_2CH_3\}_2$ and Trimethyloxonium Tetrafluoroborate. A mixture of $PtCl_2\{P(C_6H_5)_2CH_3\}_2$ (0.48 g, 0.72 mmol) and $[(CH_3)_3O]BF_4$ (020 g, 1.3 mmol) was reacted for 6 hrs. and worked up as above. The product, $[Pt_2Cl_2\{P(C_6H_5)_2CH_3\}_4](BF_4)_2$, not previously reported, was obtained as pale yellow crystals; Yield: 0.20 g, 35% mp 123-126° C.

Anal. Calcd. for $C_{52}H_{52}B_2F_8Cl_2P_4Pt_2$: C, 43.5; H, 3.65. Found: C, 43.1; H, 3.40.

Infrared Spectrum. 3142vw, 3066vw, 1509w, 1482w, 1439s, 1315vw, 1180w, 1098vs, 1048vs, b, 995m, 897s, 889s, 740s, 705sh, 692s, 644w, 605w, 520m, 507m, 485w.

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Reaction of $PtX_2(CNCH_3)_2$ (X = Cl, Br, I) and Trimethyloxonium Tetrafluoroborate. To a suspension of $PtCl_2(CNCH_3)_2$ (0.50 g, 1.43 mmol) in 40 ml of dichloromethane was added $[(CH_3)_3O]BF_4$ (0.42 g, 2.8 mmol). The mixture was refluxed for 0.5 hrs. giving a yellow oil and a colorless solution. After 1 hr., enough acetonitrile was added to dissolve the oil; slow removal of solvent gave a crystalline, white solid, $[Pt_2Cl_2(CNCH_3)_4](BF_4)_2 \cdot NCCH_3$; Yield: 0.47 g, 85%. White needles could be obtained on recrystallization from methanol/ethyl ether/hexane; these showed preliminary softening at 140°, and melted 150-157°. (One mole of acetonitrile was retained in the product, presumably as a solvent of recrystallization; its presence was verified by the pmr spectrum.)

This compound slowly decomposes in air; it is stable in methanol solution at room temperature but decomposes rapidly if heated.

Anal. Calcd. for $C_8H_{12}B_2Cl_2F_8N_4Pt_2 \cdot C_2H_3N$: C, 14.3; H, 1.80; N, 8.34 Found: C, 15.1; H, 1.79; N, 8.35.

Infrared Spectrum. $\nu_{C\equiv N}$ 2305s, 2288s cm^{-1}. Other bands: (IR-10), 1512w, 1290w, 1048vs, b, 985 w, 520w, 510w.

NMR Spectrum (acetonitrile-d_3): τ6.60 (mult.), $CNCH_3$; τ7.93 (singlet), $NCCH_3$; Integrated intensity ratio of these two peaks is 4:1.

Reactions of trimethyloxonium tetrafluoroborate with $PtBr_2(CNCH_3)_2$ and $PtI_2CNCH_3)_2$ gave analogous products: $[Pt_2Br_2(CNCH_3)_4](BF_4)_2$ was obtained as white crystals in 78% yield; mp 130-135°. It was recrystallized from acetonitrile/ethanol. Its identity is proposed from the similarity of the infrared spectrum with that of the chloride analogue. This compound is more air and temperature sensitive than the latter species, however, rapidly decomposing to a beige powder in air. A methanol solution darkened quickly on heating, or after about half an hour at room temperature. This instability prevented analysis.

Infrared Spectrum: $\nu_{C\equiv N}$ 2300s, 2282s cm^{-1}. other bands: 1507w, 1286vw, 1200mw, 1180w, 1048vs, b, 970vw, 898m, 851vw, 773vw.

$[Pt_2I_2(CNCH_3)_4](BF_4)_2$ was obtained as pale yellow crystals in 80% yield, mp 120° d. It was crystallized from acetonitrile/methanol. The compound decomposed rapidly in air, or in prolonged contact with alcohol, and darkened slowly on standing. This instability prevented analysis.

Infrared Spectrum: $\nu_{C\equiv N}$ 2264s, 2251s, cm^{-1}. other bands: 1180w, 1150w, 1115w, 1050vs, b; Nujol mull, low resolution: 500m, 485vw, 470vw.

Reaction of $PtCl_2(p\text{-}CNC_6H_4CH_3)_2$ and Trimethyloxonium Tetrafluoroborate. The reaction of 0.104 g (0.23 mmol) $PtCl_2(p\text{-}CNC_6H_4CH_3)_2$ and 0.15 g (1 mmol) $[(CH_3)_3O]BF_4$ in 25 ml dichloromethane was run for 3.5 hrs. (reflux). The product, $[Pt_2Cl_2(p\text{-}CNC_6H_4CH_3)_4](BF_4)_2 \cdot NCCH_3$, was obtained, using a workup as described above, as fine off-white needles, 0.053 g, 46% yield; mp 176-178°. The compound was stable in air and in solution.

Anal. Calcd. for $C_{32}H_{28}B_2Cl_2F_8N_4Pt_2 \cdot C_2H_3N$: C, 35.7; H, 2.73; N, 6.12. Found: C, 35.8; H, 2.73; N, 6.49.

Infrared Spectrum: $\nu_{C\equiv N}$ 2262s, 2227s cm^{-1}. other bands: 1512sh, 1505s, 1327w, 1287w, 119m, 1172w, 1136m, 1117m, 1048vs, b, 969w, 949w, 900m, 820s, 780m, 736mw, 635m, 605mw, 532w, 510m, 498m, 470m, 435w. A sharp peak at 3165 cm^{-1} is assigned to CH_3CN and is completely absent in the IR spectrum of the starting material.

Results and Discussion

When various square planar platinum complexes PtX_2L_2 were treated with trimethyloxonium tetrafluoroborate in dichloromethane, the halogen bridged dimeric species $[Pt_2X_2L_4](BF_4)_2$ were obtained in good yield, according to the reaction:

$$2PtX_2L_2 + 2[(CH_3)_3O]BF_4 \rightarrow [Pt_2X_2L_4](BF_4)_2 + (CH_3)_2O + 2CH_3Cl$$

Several of the complexes prepared in this way had been reported before ($[Pt_2Cl_2\{P(C_6H_5)_3\}_4](BF_4)_2$ and $[Pt_2Cl_2\text{-}\{P(C_2H_5)_3\}_4](BF_4)_2$[2,4] and their characterization was accomplished by comparison with known samples. The phosphine complex from diphenylmethylphosphine was previously unreported. New isocyanide complexes of platinum, $[Pt_2X_2(CNCH_3)_4](BF_4)_2$ (X = Cl, Br, I) and $[Pt_2Cl_2\text{-}(p\text{-}CNC_6H_4CH_3)_4](BF_4)_2$ were obtained in the reactions of trimethyloxonium tetrafluoroborate with the appropriate dihalo-bis-isocyanideplatinum complex. Of these, only the chlorides were sufficiently stable to be fully characterized. The bromide and iodide species were thermally unstable, both as solids and in solution, and were air sensitive as well. They were identified by virtue of the similarities of the infrared spectra for the three $[Pt_2X_2(CNCH_3)_4](BF_4)_2$ species.

We note parenthetically that the choice of dichloromethane as a solvent in these reactions is important. The obvious alternatives are polar solvents (acetonitrile, acetone, ethanol) which themselves react with the oxonium salt.

The relative ease of obtaining and handling the trimethyloxonium tetrafluoroborate, and the lack of undersirable side products, makes this a convenient route to the complexes described here; presumably this reaction could be extended to halo complexes of other metals as well. Secondarily we note that this reaction illustrates a behavior of trimethyloxonium salts not previously experienced. In this reaction the trimethyloxonium reagent, which is ordinarily used as a strong, alkylating agent, has appearently served as a halide acceptor. We might note, however, that on one previous instance this reagent has been used as a hydride abstracting reagent.[12]

In retrospect, the behavior of trimethyloxonium tetrafluoroborate as a halide acceptor seems not unreasonable. One can view this as a metathetic reaction involving initial halide and tetrafluoroborate exchange between reactants. The trimethyloxonium ha-

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lide, once formed, would rapidly decompose to methyl ether and methyl halide; the escape of these reagents from the system would force the reaction to completion.

Although this mechanism seems quite reasonable, and has some precedent, an alternative may be suggested: The same products could arise if one postulated initial alkylation of the metal to give $PtX_2CH_3L_2^+$ which then eliminates CH_3X and dimerizes to give the product. Alkylation of the metal is not without some merit. Oxonium salts will alkylate most basic reagents, and indeed d^8 square planar complexes are expected to be somewhat basic. For example, the complexes $MCl(CO)\{P(C_6H_5)_3\}_2$ (M = Rh, Ir) are known to coordinate with boron trihalides.[13] However PtX_2L_2 species are apparently not very basic and coordination to Lewis acids is as yet unreported.

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