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## A NEW ROUTE TO FLUOROCARBON-STABILIZED ORGANOAMIDOPLATINUM(II) <u>COMPOUNDS</u>— SYNTHESIS OF A NEW ISOMER OF [Pt(RNCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)X(L)] (R = p-HC<sub>6</sub>F<sub>4</sub> OR C<sub>6</sub>F<sub>5</sub>; X = Cl OR I; L = UNIDENTATE LIGAND) COMPLEXES

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Abstract—Reaction of the complexes  $PtX_2(RNHCH_2CH_2NMe_2)$  (X = Cl or I; R =  $p-HC_6F_4$  or  $C_6F_5$ ) with TIOR' (R' = Et or Bu') co-precipitates TIX and the organoamides [ $Pt(RNCH_2CH_2NMe_2)X]_2$ ; these react with L (pyridine (py) or Me\_2SO) to give [ $Pt(NRCH_2CH_2NMe_2)X]_2$ ; these react with L (pyridine (py) or Me\_2SO) to give [ $Pt(NRCH_2CH_2NMe_2)X(L)$ ] complexes, which, in three cases (R =  $p-HC_6F_4$  or  $C_6F_5$ , L = Me\_2SO, X = Cl; R =  $p-HC_6F_4$ , L = py, X = I), were obtained as the isomer with L *trans* to the NR group.

The scope of platinum(II) organoamide chemistry<sup>1-3</sup> has been greatly increased by the preparation of polyfluorophenyl(R)-substituted complexes  $[Pt(RNCH_2)_2L_2]$  and  $[Pt(RNCH_2CH_2NMe_2)X(L)]$ (e.g.  $R = p-HC_6F_4$  or  $C_6F_5$ ; L = py; X = Cl or I)<sup>4-8</sup> where the fluorocarbon substitution provides stabilization against hydrolysis (cf. moisture-sensitive  $[Pt(RNCH_2)_2bpy]$  (R = H or Me; bpy = 2,2'-bipyridyl<sup>9</sup>). Their preparation by decarboxylation reactions in pyridine solution, e.g. eq. (1)  $(dmen = N, N-dimethylethane-1, 2-diamine),^{4-8}$  is unprecedented in organoamidometallic chemistry. However, the method has limitations. It is essentially restricted to complexes where L = pyridine or substituted pyridine (but see ref. 8) and to formation of  $[Pt(RNCH_2CH_2NMe_2)X(L)]$  complexes with structure 1 but not 2.

$$PtI_{2}(dmen) + TIO_{2}CC_{6}F_{4}H - p + C_{6}F_{5}H + 2py \longrightarrow$$

$$[Pt(p-HC_{6}F_{4}NCH_{2}CH_{2}NMe_{2})I(py)]$$
(1a)

 $+p-H_2C_6F_4+TII+CO_2+pyHF.$  (1)

We now report a new synthetic route to  $[Pt(RNCH_2CH_2NMe_2)X(L)]$  complexes and the first preparation of compounds with structure 2.



New N,N-dimethyl-N'-polyfluorophenylethane-1,2-diamines and their platinum dihalide complexes<sup>‡</sup> were prepared as shown in Scheme 1. Reaction of the platinum halide complexes with thallium(I) ethoxide or t-butoxide co-precipitated thallium(I) halide and the N,N-dimethyl-N'-polyfluorophenylethane - 1,2 - diaminato(1 – )halogeno-

<sup>\*</sup> Author to whom correspondence should be addressed. † Isomer 1 may be termed *trans* and isomer 2 *cis*, since

donor atoms of similar charge are *trans* and *cis*, respectively.

<sup>&</sup>lt;sup>‡</sup>All new compounds were characterized by microanalysis, <sup>1</sup>H and <sup>19</sup>F NMR spectra, and, where volatile, by mass spectrometry.

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platinum(II) complex, which was identified primarily by observation of the dimer parent ion in the mass spectrum (and appropriate fragment ions).



Treatment of the TlI/3a mixture with slightly less than the stoichiometric amount of py required for dimer cleavage in THF yielded [Pt(p-HC<sub>6</sub>F<sub>4</sub>NCH<sub>2</sub>  $CH_2NMe_2$  (py)] with the previously unknown structure 2a, which was obtained analytically and isomerically pure (81% yield) on recrystallization from ether-petrol. By contrast, cleavage with a large excess (> 500:1) of neat pyridine gave 1a (90%). The two isomers were readily distinguished by values of  ${}^{3}J[PtH(Me)]$  (1a 31, 2a 45 Hz),  $^{3}$ *J*[PtH2,6(py)] (1a 40, 2a 24 Hz), and  $\delta$ F2,6 (1a -150.4, **2a** -146.5 ppm). The relative magnitudes of the coupling constants are consistent with the *trans* influence order,  $py > Cl^{10}$  and N(amido) > N(amine).7 Dissolution of the new isomer, 2a, in a large excess of pyridine gave 1a and  $[Pt(p-HC_6$  $\overline{F}_4$ NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(py)<sub>2</sub>]<sup>+</sup>I<sup>-</sup> (4). The latter gave two, equal intensity, H2,6(py) resonances  $[{}^{3}J(PtH)$ 40 Hz, py trans to -NMe<sub>2</sub>; <sup>3</sup>J(PtH)27Hz, py trans to  $-N(p-HC_6F_4)$ ] downfield from that of 1a, and a F2,6 resonance well displaced from that of 2a. A plausible isomerization path is:

$$2a + py \longrightarrow 4 \longrightarrow 1a + py$$

Substitution by iodide *trans* to the amido nitrogen rather than *trans* to the amine nitrogen is as expected from their *trans* effects.<sup>7,11</sup> Reaction of dimers **3b–3d** with a limited amount of pyridine gave mixtures of isomers **1** and **2**.

Treatment of 3d or 3c/TlCl mixtures with dimethyl sulphoxide for 2 h followed by filtration and addition of water gave [Pt(RNCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>) Cl(Me<sub>2</sub>SO)] (R = p-HC<sub>6</sub>F<sub>4</sub> or C<sub>6</sub>F<sub>5</sub>) with structures 2b or 2c, respectively. Observation of  $\delta$ (Me) of Me<sub>2</sub>SO at 3.3-3.4 ppm is indicative<sup>12</sup> of S- bonding, as is observation of platinum-hydrogen  $(SMe_2)$  coupling  $[{}^{3}J(PtH)$  ca 20 Hz] (see refs 12 and 13). Identification as isomer 2 is based on the magnitude of  ${}^{3}J[PtH(NMe_2)]$  (40-45 Hz) which is consistent with ---NMe<sub>2</sub> trans to halogen (see, for example 2a) and far too large for ---NMe<sub>2</sub> trans to sulphur (see, for example 1a for ---NMe<sub>2</sub> trans to py which has a trans influence less than S-bonded Me<sub>2</sub>SO- cf. v(PtCl) of cis-PtCl<sub>2</sub>(py)<sub>2</sub><sup>14</sup> and cis-PtCl<sub>2</sub>(Me<sub>2</sub>SO)<sub>2</sub><sup>15</sup>). When a solution of 2b in Me<sub>2</sub>SO was stirred for 7 days, only slight conversion into 1b occurred (2b: 1b = 3:1).

The outcome of the cleavage reactions indicates that isomer 2 is the kinetically favoured product. Thermodynamic control favours isomer 1, thus accounting for the earlier isolation of this isomer from decarboxylation reactions in boiling pyridines.<sup>5,7</sup>

Studies are continuing on the cleavage of the dimers 3 and of the factors influencing the structure, 1 or 2, and isomerization of the product. Preliminary results indicate that  $RNH(CH_2)_2NEt_2$  $(R = p-HC_6F_4 \text{ or } C_6F_5)$  ligands and their platinum dihalide complexes can also be prepared, opening a possible route to  $[Pt(RNCH_2CH_2NEt_2)X(L)]$  complexes.

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## REFERENCES

- 1. D. C. Bradley and M. F. Chisholm, Accts Chem. Res. 1976, 9, 273.
- M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*. Ellis Horwood, Chichester (1980).
- 3. M. D. Fryzuk and C. D. Montgomery, *Coord. Chem. Rev.* 1989, **95**, 1.
- G. B. Deacon, B. M. Gatehouse, I. L. Grayson and M. C. Nesbit, *Polyhedron* 1984, 3, 753.
- 5. D. P. Buxton, G. B. Deacon, B. M. Gatehouse, I. L. Grayson and P. J. Wright, *Acta Cryst.* 1985, C41, 1049.
- 6. D. P. Buxton, G. B. Deacon, B. M. Gatehouse, I. L.

Grayson, R. J. Thomson and D. St. C. Black, Aust. J. Chem. 1986, **39**, 2013.

- D. P. Buxton, G. B. Deacon, B. M. Gatehouse, I. L. Grayson and D. St. C. Black, *Aust. J. Chem.* 1988, 41, 943.
- D. P. Buxton, G. B. Deacon and D. St. C. Black, *Polyhedron* 1989, 8, 143.
- G. W. Watt and D. G. Upchurch, J. Am. Chem. Soc. 1968, 90, 914; 1967, 89, 177.
- T. G. Appleton, H. C. Clark and L. E. Manzer, Coord. Chem. Rev. 1973, 10, 335.
- M. K. Cooper and J. M. Downes, *Inorg. Chem.* 1978, 17, 880.

- G. Annibale, L. Cattalini, V. Bertolasi, V. Ferretti, G. Gilli and M. L. Tobe, J. Chem. Soc., Dalton Trans. 1989, 1265.
- J. D. Fotheringham, G. A. Heath, A. J. Lindsay and T. A. Stephenson, *J. Chem. Res. S* 1986, **82** (M, 1986, 801); Y. Ducommun, L. Helm, A. E. Merbach, B. Hellquist and L. I. Elding, *Inorg. Chem.* 1989, **28**, 377.
- 14. A. D. Allen and T. Theophanides, Can. J. Chem. 1964, 42, 1551.
- 15. W. Kitching, C. J. Moore and D. Doddrell, *Inorg. Chem.* 1970, **9**, 541.