COMMUNICATION

SYNTHESIS AND CRYSTAL STRUCTURE OF [N,N'-BIS(2,3,5,6-TETRAFLUOROPHENYL)-ETHANE-1,2-DIAMINATO(2-)|DIPYRIDINEPLATINUM(II)

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Abstract—The reaction of $PtCl_2en$ (en = ethane-1,2-diamine) with $TlO_2CC_6F_5$ in boiling pyridine unexpectedly yielded a polyfluorophenyl-stabilized ethane-1,2-diaminatoplatinum(II) complex, $Pt[N(p-HC_6F_4)CH_2]_2(py)_2$,1a, the structure of which has been established by X-ray crystallography.

Decarboxylation reactions between $PtCl_2L_2$ [e.g. $L_2 = 2,2'$ -bipyridyl(bpy) or *trans*-(pyridine)₂] complexes and thallous polyfluorobenzoates in boiling pyridine yield R_2PtL_2 (e.g. $R = C_6F_5$ or p-HC₆F₄) and RPtClL₂ organometallics,¹ e.g. $PtCl_2L_2 + 2TIO_2CR \rightarrow R_2PtL_2 + 2CO_2 + 2TICl$. We now report that the corresponding reaction of $PtCl_2en$ (en = ethane-1,2-diamine) with thallous penta-fluorobenzoate does not give $(C_6F_5)_2Pten$ or $C_6F_5PtClen$, but surprisingly an N-(2,3,5,6-tetra-fluorophenyl) substituted ethane-1,2-diaminato-platinum(II) complex is obtained.

Reaction of stoichiometric amounts of the reagents in boiling pyridine for 60 min under nitrogen gave carbon dioxide (95%). Evaporation of the reaction mixture to dryness, extraction with acetone, filtration to remove thallous chloride, and crystallization from acetone/petroleum ether gave 1a as the air-stable, yellow, 1:1 acetone solvate in 37% yield, m.p. $170-171^{\circ}$ (dec.)†. The structure (Fig. 1) was established by X-ray crystallography. Crystal data 1a.Me₂CO: C₂₇H₂₄N₄OF₈Pt,



1a $R = p - HC_6F_4$ **1b** R = H**1c** $R = C_6F_5$

M = 767.59, monoclinic, a = 19.044(8), b =14.006(7), c = 11.223(6) Å, $\beta = 110.73(5)^{\circ}$, U =2800Å³. D_m (flotation) = 1.82(1), $D_c = 1.82 \text{ g cm}^{-3}$ for z = 4. Mo K_{α} , $\lambda = 0.7107$ Å, $\mu = 48.7$ cm⁻¹, F(000) = 1487.64, 298 K. Space group C2/c or Cc, the former confirmed by successful refinement. The molecule possesses a 2-fold axis of symmetry. Tabular crystal $(0.20 \times 0.06 \times 0.11 \text{ mm})$, Philips **PW1100** diffractometer (graphite monochromator); cell parameters from 25 reflections θ 8-15°; absorption correction applied, transmission maximum 0.7449, minimum 0.5926. Sin θ/λ max. $\pm hkl, \pm 23$, 18, 14. Three standard 0.704. reflections (2hr intervals) showed no significant intensity variation. 4274 reflections measured (ω scans, scan width $\pm 1.5^{\circ}$ in 2θ + dispersion allowance), 4083 unique reflections (R_{int} 0.038) with 2806 unobserved (I \ge 3 σ (I)). Structure solution by Patterson and Fourier methods, full-matrix least

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 $^{^{\}dagger}$ New complexes 1a.Me₂CO and 1c were obtained analytically pure with satisfactory 1H and 19F NMR spectra.



Fig. 1. Structure of $C_{24}H_{18}N_4F_8Pt.C_2H_6O$ (1a.Me₂CO)—Acetone not located (see text). Selected bond lengths (Å) and angles (°) are:

Pt-N(1)	1.98(2)	N(1)-Pt-N(1)	90(1)
Pt-N(2)	2.08(2)	N(1)– Pt – $N(2)$	95(1)
N(2)-C(6)	1.45(3)	N(2)-Pt-N(2)	80(1)
N(2)-C(7)	1.35(2)	C(6)-N(2)-C(7)	126(2)
C–N(py)	1.36-1.40	C(6)-N(2)-Pt	109(1)
C-C(py)	1.31-1.37	C(7) - N(2) - Pt	123(1)
C-C(arom)	1.34-1.42	C(6)-C(6)-N(2)	116(2)
C-F(arom)	1.33-1.36		

squares refinement (F magnitudes), 175 parameters refined (all non-hydrogen atoms anisotropic), R 0.054, wR 0.047 ($w = 1/\sigma^2(F)$). Maximum shift to E.S.D. (U₁₂ of N(1)) was 0.026; maximum and minimum peak heights in final difference Fourier synthesis were 2eÅ⁻³ and 1eÅ⁻³ respectively in vicinity of disordered acetone molecule positions. Atomic scattering factors (neutral atoms) from Ref. 2. Programs used were SHELX³ and ORTEP⁴; data reduction methods were as described previously⁵.[†]

The molecule is illustrated in the figure with the numbering scheme used and selected bond lengths. The disordered acetone molecule, whose presence was inferred from analytical, spectroscopic $[\nu_{CO}: 1709 \text{ cm}^{-1}]$, and density measurements was not located. Peaks in the difference Fourier synthesis implied that it was situated about the centre of symmetry at 1/2 0 1/2. A cavity of radius 3.372 Å exists around 1/2 0 1/2 providing ample space for an acetone molecule in any orientation.

It is of interest to note that Pt-N(2) (anionic) is

longer than Pt-N(1) (neutral) and this may be attributed to the electron withdrawing character of the polyfluorophenyl substituent. This is supported by the $(p-HC_6F_4)-N$ distance which is closer to that of an aromatic C----N distance than a single C-N bond.

The reaction path to 1a is considered to involve formation of $[Pten(py)_2](O_2CC_6F_5)_2$ 2 by substitution and metathesis,

$$PtCl_{2}en + 2py + 2TlO_{2}CC_{6}F_{5} \rightarrow 2 + 2TlCl \quad (1)$$

followed by decarboxylation and proton abstraction by the highly carbanionic C_6F_5 groups giving pentafluorobenzene and the ethane-1,2diaminatoplatinum(II) intermediate 1b,

$$\mathbf{2} \rightarrow \mathbf{1b} + 2\mathbf{C}_{6}\mathbf{F}_{5}\mathbf{H} + 2\mathbf{CO}_{2} \tag{2}$$

and then nucleophilic attack by the secondary amine nitrogens of 1b on pentafluorobenzene.

$$1\mathbf{b} + 2\mathbf{C}_6\mathbf{F}_5\mathbf{H} + 2\mathbf{p}\mathbf{y} \rightarrow \mathbf{1a} + 2\mathbf{p}\mathbf{y}\mathbf{HF}.$$
 (3)

Support for this path is provided by the following observations: The complex [Pten(py)₂]Cl₂, obtained from PtCl₂en in boiling aqueous pyridine,⁶, reacts with thallous pentafluorobenzoate in pyridine at room temperature to give **2**, which yields **1a** in

[†]Atomic and thermal parameters, observed and calculated structures together with a list of bond lengths and angles have been deposited with the Editor, from whom copies are available on request. Atomic Co-ordinates have also been deposited with the Cambridge Crystallographic Data Centre.

boiling pyridine [reactions (2) and (3)]. Monitoring reaction (1) by ¹⁹F NMR spectroscopy reveals the presence of pentafluorobenzene in the reaction mixture as required by reactions (2) and (3). Reaction of PtCl₂en with thallous 2,3,5,6-tetrafluorobenzoate in boiling pyridine yields 1,2,4,5tetrafluorobenzene, which is much less reactive than C₆F₅H to nucleophilic attack,⁷ and an airsensitive intermediate, plausibly **1b**, which reacts with added pentafluorobenzene and hexafluorobenzene to give **1a** and **1c** respectively.

The present reactions provide a convenient synthesis of air-stable ethane-1,2-diaminatoplatinum-(II) complexes, which are stabilised by polyfluorophenyl substitution on nitrogen. Previous ethane-1,2-diaminatoplatinum(II) complexes, e.g. Pt(NHCH₂)₂bpy,⁸ have been prepared under forcing conditions, viz. deprotonation of ethane-1,2diamineplatinum(II) complexes by potassium amide in liquid ammonia, and are highly moisture sensitive (e.g. Refs. 8 and 9). Analogous decarboxylation reactions may provide a route to stabilised diorganoamido derivatives of other precious metals.

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