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ORGANOAMIDOMETALLICS—IV.* SYNTHESES OF N,N′-BIS(POLYFLUOROPHENYL)ETHANE-1,2-DIAMINATO(2−)PLATINUM(II) COMPLEXES WITH TWO DIFFERENT FLUOROCARBON GROUPS

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Abstract—The N,N′-bis(polyfluorophenyl)ethane-1,2-diaminato(2−)platinum(II) complexes $[\overline{\mathrm{Pt}(\mathrm{N}(p\text{-}\mathrm{HC_6F_4})\mathrm{CH_2CH_2N}}\mathrm{R})(\mathrm{py})_2]$ (R = p-HC_6F_4, p-BrC_6F_4, C_6F_5 or p-MeC_6F_4; py = pyridine) have been prepared by decarboxylation reactions between $[PtI_2(p\text{-}HC_6F_4NHCH_2CH_2NH_2)]$, thallium(I) 2,3,5,6-tetrafluorobenzoate and a suitable polyfluorobenzene, RF, in hot dry pyridine. When R $\neq p$-HC_6F_4, the two different polyfluorophenyl groups can be distinguished by different F3,5 resonances in the ^{19}F NMR spectra. The reactant and analogous complexes $[PtX_2(RNHCH_2CH_2NH_2)]$(R = p-HC_6F_4, X = I or Cl; R = C_6F_5, X = I) were prepared by treatment of K_2PtX_4 (X = I or Cl) with the appropriate N-polyfluorophenylethane-1,2-diamine.

Novel N,N-bis(polyfluorophenyl)ethane-1,2-diaminato-(2−)platinum(II) complexes, $[Pt(NRCH_2)_2(py)_2]$ (py = pyridine), have been prepared by decarboxylation reactions between $PtCl_2(en)$ (en = ethane-1,2-diamine) and thallium(I) pentafluorobenzoate or thallium(I) 2,3,5,6-tetrafluorobenzoate and a suitable reactive polyfluorobenzene in hot pyridine.[2,3] The synthetic path is completely new in organoamidometallic chemistry.[4-6] The products are moisture-stable, by contrast with simple platinum(II) organoamides, e.g. $[Pt(NRCH_2)_2(bpy)]$ (R = H or Me, bpy = 2,2′-bipyridyl),[7,8] and have appreciable antitumour activity.[9] Of necessity, the decarboxylation syntheses result in substitution of the same polyfluorophenyl group on each nitrogen of the ethane-1,2-diaminate ligand. We now report a preparative route to analogous complexes with two different polyfluorophenyl groups.

RESULTS AND DISCUSSION

The synthetic strategy required the initial preparation of platinum(II) halide complexes of N-polyfluorophenylethane-1,2-diamines. The ligands $RNHCH_2CH_2NH_2$ [R = p-HC_6F_4 (**1a**) or C_6F_5 (**1b**)] were obtained by nucleophilic substitution reactions between ethane-1,2-diamine and the appropriate polyfluorobenzene with (R = p-HC_6F_4) or without (R = C_6F_5) an added base. Compound **1b** has previously been prepared in higher yield in a pyridine medium,[10] with characterization by F, N analyses and ^{19}F NMR spectroscopy.[10,11] Although the melting point of **1b** was well below the reported value,[10] identification was unequivocal on the basis of microanalyses (C, H, F, N), ^{1}H and ^{19}F NMR spectra and the mass spectrum. Reaction of **1a** and **1b** with the appropriate potassium tetrahalogenoplatinate(II) complex gave $[PtX_2(RNHCH_2CH_2NH_2)]$ [R = p-HC_6F_4, X = I (**2a**) or Cl (**2b**); R = C_6F_5, X = I (**2c**)]. Considerable variation in yield was observed, depending on the solvent system used (see Experimental).

Syntheses of N,N′-bis(polyfluorophenyl)ethane-1,2-diaminato(2−)platinum(II) complexes, $[\overline{\mathrm{Pt}(\mathrm{N}(p\text{-}\mathrm{HC_6F_4})\mathrm{CH_2CH_2N}}\mathrm{R})(\mathrm{py})_2]$ (**3**), were effected by heating **2a** with thallium(I) 2,3,5,6-tetrafluorobenzoate and a polyfluoroaromatic compound, RF, in hot pyridine. Details of the reactions are given in Table 1. The method was initially validated by synthesis of the known[2,3] symmetrical organoamide **3a** before application to complexes

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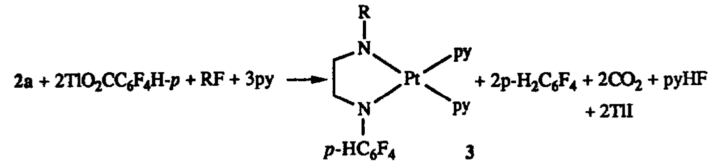
with two different polyfluorophenyl groups, **3b**–**3d**.



3 (1)

3a R=p-HC$_6$F$_4$
3b R=p-BrC$_6$F$_4$
3c R=C$_6$F$_5$
3d R=p-MeC$_6$F$_4$

On the basis of the reaction path to the symmetrical complexes [Pt(NRCH$_2$)$_2$(py)$_2$],[3] reaction (1) can be envisaged as occurring by deprotonation to give the nucleophilic species, [Pt(N(p-HC$_6$F$_4$)CH$_2$CH$_2$NH)(py)$_2$], which attacks the polyfluoroarene, RF, giving **3**. Deprotonation is effected by highly carbanionic p-HC$_6$F$_4$ groups, generated by decarboxylation, and the resulting 1,2,4,5-tetrafluorobenzene is relatively unreactive to nucleophilic substitution.[12]

Yields of pure complexes were low, despite near quantitative decarboxylation, owing to formation of dark coloured impurities which could be difficult to remove. Two complexes, **3b** and **3c**, were isolated as ether solvates, the composition being indicated by both duplicate microanalyses and ^{1}H NMR integrations. Parent ions were observed in the spectra of the unsymmetrical complexes **3b**–**3d**. However, only a single CH_2N resonance and a single set of pyridine resonances were observed, despite the presence of two different polyfluorophenyl groups. The (average) ^3J[PtH(py)] and ^3J[PtH(CH$_2$)] coupling constants (Table 2) are of similar magnitude to those of the symmetrical complexes, [Pt(NRCH$_2$)$_2$(py)$_2$],[3] e.g. **3a** (Table 2). Clear differentiation between the two different polyfluorophenyl groups was observed in the F3,5 resonances (Table 2). The F3,5 chemical shifts of the individual polyfluorophenyl groups of **3b**–**3d** are in close agreement with those of the corresponding symmetrical complexes (Table 2). On the other hand, little differentiation was observed in the F2,6 resonances, since the dominant influence on the chemical shift is the amido nitrogen, which is *ortho* to F2,6 in each case.

The synthesis method, reaction (1), developed for organoamides **3b**–**3d** with two different polyfluorophenyl groups could presumably be extended to other similar complexes, for example, by use of **2c** as a reactant, or by preparation and use of other reactants **2** incorporating different fluorocarbon groups.

EXPERIMENTAL

General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Carbon dioxide was determined gravimetrically as barium carbonate. Decarboxylation was monitored using a small volume barium hydroxide trap additional to the main trap and reactions were terminated when carbon dioxide evolution ceased. Spectroscopic methods are as for Part I.[3] Listed IR bands of compounds examined as Nujol and hexachlorobutadiene mulls are restricted to those of medium or greater intensity, except for N—H and Pt—halogen stretching frequencies. Proton chemical shifts are in ppm downfield from internal Me$_4$Si and fluorine chemical shifts in ppm from internal CFCl$_3$. For platinum-containing ions in the mass spectra, only the most intense peak [containing ^{195}Pt or ^{275}(PtBr)] of

Table 1. Synthesis of N,N′-bis(polyfluorophenyl)ethane-1,2-diaminato(2−)platinum(II) complexes[a]

Reagents				Reaction			
2a (mmol)	TlO$_2$CC$_6$F$_4$H-p (mmol)	RF	mmol	Temperature (°C)	Time (min)	Product	Yield (%)
1.00	2.00	C$_6$F$_5$H	18.0	105–107	25	**3a**	30
1.00	2.00	C$_6$F$_5$Br	16.0	105–110	22	**3b** 0.5C$_4$H$_{10}$O	15
1.00	2.00	C$_6$F$_6$	17.4	100–110	15	**3c** 0.4C$_4$H$_{10}$O	19
0.30	0.60	C$_6$F$_5$Me	4.3	115	25	**3d**	17

[a] Reactions were carried out in pyridine (10 cm^3) and gave 85–100% CO$_2$.

Table 2. Some NMR data for $[\overline{Pt(N(p\text{-}HC_6F_4)CH_2CH_2N}R)(py)_2]$ complexes

Complex	δ(F3,5)[a]	δ(F3,5)[b]		^3J[PtH(py)]	^3J[PtH(CH$_2$)]
3a	−144.8	−144.8		34	29
3b	−144.5	−140.8	(−141.0)[c]	31	[f]
3c	−144.6	−168.7	(−168.9)[d]	30	[f]
3d	−144.9	−150.0	(−150.1)[e]	35	30

[a] For p-HC$_6$F$_4$.
[b] For R.
[c] δ(F3,5) of $[Pt(N(p\text{-}BrC_6F_4)CH_2)_2(py)_2]$.[3]
[d] δ(F3,5) of $[Pt(N(C_6F_5)CH_2)_2(py)_2]$.[3]
[e] δ(F3,5) of $[Pt(N(p\text{-}MeC_6F_4)CH_2)_2(py)_2]$.[3]
[f] Not resolved.

the cluster is given. For bromine-containing ions without platinum, the listed peak is for the ^{79}Br ion. Visible spectra are for solutions in 95% ethanol in the range 350–700 nm.

Solvents and reagents

Petrol refers to the fraction b.p. 60–85°C unless indicated otherwise. Pentafluorobenzene and hexafluorobenzene (Bristol Organics) and ethane-1,2-diamine were dried over molecular sieves (Grade 4A) before use. Triethylamine was refluxed over and distilled from acetic anhydride under nitrogen. Purification of other solvents and sources or preparations of other reagents have been given in earlier papers.[3,13]

Synthesis of N-(polyfluorophenyl)ethane-1,2-diamines

N-(2,3,5,6-Tetrafluorophenyl)ethane-1,2-diamine (**1a**). Pentafluorobenzene (170 mmol) and ethane-1,2-diamine (84 mmol) were refluxed over anhydrous K_2CO_3 for 7 h under nitrogen. Evaporating the mixture to dryness under high vacuum gave a solid which was partitioned between ether and water. Repeated ether extraction and evaporation of the ether *in vacuo* gave a light yellow oil which crystallized upon cooling. The solid was twice recrystallized from ether–petrol giving colourless crystals (yield, 32%), m.p. 44–45°C (Found: C, 45.7; H, 3.7; F, 36.3; N, 13.8. $C_8H_8F_4N_2$ requires: C, 46.2; H, 3.9; F, 36.5; N, 13.5%). ^{19}F NMR ($CDCl_3$): −142.1, m, 2F, F3,5; −160.7, m, 2F, F2,6. ^{1}H NMR ($CDCl_3$): 1.15, s, 2H, NH$_2$; 2.91, t, ^3J(HH) 6 Hz, 2H, CH$_2$NH$_2$; 3.37, qt, ^3J[HH(CH$_2$)] 6 Hz, ^3J[HH(NH)] 6 Hz, ^5J(HF) 1 Hz, 2H, CH$_2$N(H)C$_6$F$_4$H; 4.40, br, 1H, N(**H**)C$_6$F$_4$H; 6.36, tt, ^3J(HF) 10 Hz, ^4J(HF) 7 Hz, 1H, HC$_6$F$_4$. IR: 3474w, 3381w and 3285(br) ν(NH), 2943m, 1650s, 1526vs, 1509vs, 1470s, 1358m, 1156s, 1142s, 924m cm^{-1}. Mass spectrum: m/z 208 [17%, M$^+$], 179 [78, $C_7H_5F_4N^+$], 178 [100, $HC_6F_4NHCH_2{}^+$]. Similarly, reaction of pentafluorobenzene (79 mmol) and ethane-1,2-diamine (26 mmol) in refluxing triethylamine (9 cm^3, 65 mmol) for 19 h under anhydrous conditions gave **1a** (21%) (IR identification).

Hydrochloride derivative. Hydrogen chloride and nitrogen were bubbled through a stirred ether solution of **1a** (9.6 mmol). The precipitated white solid (**1a**·HCl) was refluxed in acetone–petrol for a few minutes, collected and dried (yield, 70%), m.p. 275–280°C (dec.) (Found: C, 39.4; H, 3.6; N, 11.2. $C_8H_9ClF_4N_2$ requires: C, 39.3; H, 3.7; N, 11.5%). ^{19}F NMR [$(CD_3)_2SO$]: −141.2, m, 2F, F3,5; −158.8, m, 2F, F2,6. ^{1}H NMR [$(CD_3)_2SO$]: 3.00, t, ^3J(HH) 6 Hz, 2H, CH$_2$NH$_3{}^+$; 3.59, m, 2H, CH$_2$N(H)C$_6$F$_4$H; 6.20, m(br), 1H, N(**H**)C$_6$F$_4$H; 7.00, tt, ^3J(HF) 11 Hz, ^4J(HF) 7 Hz, 1H, HC$_6$F$_4$; 8.29, s(br), 3H, NH$_3{}^+$. IR: 3318s and 3058s(br) ν(NH), 2909m, 1651m, 1602m, 1544s(br), 1513s(br), 1471s, 1457s, 1448s, 1365s, 1282m, 1157s(br), 1110s, 1037s, 1028s, 958m, 925s, 862m, 829s, 801s, 710s, 692m, 550m(br) cm^{-1}.

N-(Pentafluorophenyl)ethane-1,2-diamine (**1b**). Stirring hexafluorobenzene (170 mmol) and ethane-1,2-diamine (170 mmol) under nitrogen with gentle heating promoted a vigorous exothermic reaction. After 10 min, the near solid mixture was dissolved in ethanol (50 cm^3) which was refluxed for 2 h. Filtration and evaporation of the solution to dryness *in vacuo* gave a dark brown solid. Recrystallization from ether–petrol at 0°C gave colourless crystals (yield, 30%), m.p. 46°C, ref. 10 m.p. 70–71°C (Found: C, 42.8; H, 3.0; F, 41.7; N, 12.7. Calc. for $C_8H_7F_5N_2$: C, 42.5; H, 3.1; F, 42.0; N, 12.4%). ^{19}F NMR ($CDCl_3$): −160.2, m, 2F, F2,6; −165.2, m, 2F, F3,5; −172.7, m, 1F, F4, in satisfactory agreement with values[10,11] using CCl$_4$ as solvent. ^{1}H NMR ($CDCl_3$): 1.16, s, 2H, NH_2; 2.91, m, ${}^{3}J$(HH) 6 Hz, 2H, CH_2NH_2; 3.31, qt, ${}^{3}J[HH(CH_2)]$ 6 Hz, ${}^{3}J$[HH(NH)] 6 Hz, ${}^{5}J$(HF) 1 Hz, 2H, $CH_2N(H)C_6F_5$; 4.17, br, 1H, N(H) C_6F_5. IR: 3473w, 3392w, 3326w and 3212w ν(NH), 2945m, 2867m, 1518vs, 1488vs, 1470s, 1356m, 1021m, 990m, 976m, 954m cm^{-1}. Mass spectrum: *m*/*z* 226 [22%, M^+], 197 [68, $C_7H_4F_5N^+$], 196 [100, $C_6F_5NHCH_2^+$].

Synthesis of N-(polyfluorophenyl)ethane-1,2-*diamineplatinum*(II) *complexes*

Bis - *iodo*[N - (2,3,5,6 - *tetrafluorophenyl*)*ethane*-1,2-*diamine*]*platinum*(II) (**2a**). K_2PtCl_4 (1.2 mmol) and KI (5.3 mmol) were stirred in water (50 cm^3) with gentle heating for 0.5 h. Addition of a solution of **1a** (1.3 mmol) in ethanol (10 cm^3) and stirring overnight gave an orange precipitate, which was washed with a minimum of ethanol and then ether, recrystallized twice from acetone–petrol (b.p. 80–100°C), and refluxed in ether for 2 h giving an orange solid (yield, 16%), m.p. 188–189°C (Found: C; 14.3; H; 1.5; F, 11.3; N, 4.3. $C_8H_8F_4I_2N_2Pt$ requires: C, 14.6; H, 1.2; F, 11.6; N, 4.3%). UV–vis spectrum [λ_{max} (ε)]: 321 (750), 379 (820) nm. IR: 3249m and 3189s ν(NH), 3128m, 3103m, 3070m, 1562m, 1526vs, 1500m, 1473s, 1460m, 1445m, 1429m, 1257m, 1208m, 1175s, 1150m, 1062m, 1038m, 1011m, 930s, 845s, 711m, 687m, 650m, 541m, 193w and 178w ν(Pt—I) cm^{-1}. Mass spectrum: *m*/*z* 254 [43%, I_2^+], 208 [12, $C_8H_8F_4N_2^+$], 179 [81, $C_7H_5F_4N^+$], 178 [100, $HC_6F_4NHCH_2^+$]. A similarly prepared solution of K_2PtI_4 (0.60 mmol) in water (50 cm^3) was treated with **1a** (0.63 mmol) in acetone (10 cm^3) giving a brown oil that dissolved upon addition of more acetone (60 cm^3). After stirring for 0.5 h, the solution was evaporated to dryness *in vacuo* leaving an orange solid. The solid was extracted with acetone, the solution was filtered and again evaporated to dryness. Dissolution in ethanol and precipitation by petrol gave an orange precipitate of **2a** (yield, 73%) (IR identification). An analogous preparation in aqueous t-butanol gave crude **2a** in 86% yield (IR identification).

Dichloro[*N* - (2,3,5,6 - *tetrafluorophenyl*)*ethane*-1,2-*diamine*]*platinum*(II) (**2b**). A solution of K_2PtCl_4 (1.2 mmol) in water (15 cm^3) was stirred for 2 days with **1a** (1.5 mmol) in t-butanol (15 cm^3) giving a cream precipitate which was collected, washed with water then petrol, and dried (yield, 88%), m.p. > 250°C (dec.) (Found: C, 20.6; H, 1.5; N, 6.2. $C_8H_8Cl_2F_4N_2Pt$ requires: C, 20.3; H, 1.7; N, 5.9%). UV–vis spectrum [λ_{max} (ε)]: 313 (380), 378 (87) nm. IR: 3277m and 3202s ν(NH), 3125m, 3076m, 1648m, 1566m, 1531 and 1527vs, 1505m, 1477m, 1352m, 1288m, 1261m, 1220m, 1178s, 1170s, 1062m, 1038m, 1029m, 932vs, 846s, 713m, 690m, 658m, 337m and 331m ν(Pt—Cl) cm^{-1}. Mass spectrum: *m*/*z* 208 [12%, $C_8H_8F_4N_2^+$], 188 [11, $C_8H_7F_3N_2^+$], 178 [100, $HC_6F_4NHCH_2^+$].

Bis - *iodo*[*N* - (*pentafluorophenyl*)*ethane* - 1,2-*diamine*]*platinum*(II) (**2c**). K_2PtCl_4 (1.2 mmol) and KI (5.1 mmol) in water (50 cm^3) were stirred for 0.5 h and then **1b** (1.3 mmol) in acetone (25 cm^3) was added. After stirring overnight, the mixture was evaporated to dryness *in vacuo*. The solid was recrystallized from ethanol–petrol (b.p. < 40°C) to give the title compound (yield, 20%), m.p. 183–184°C (dec.) (Found: C, 14.7; H, 1.0; F, 14.3; N, 4.3. $C_8H_7F_5I_2N_2Pt$ requires: C, 14.2; H, 1.0; F, 14.1; N, 4.2%). UV–vis spectrum [λ_{max} (ε)]: 321 (880) 380 (960) nm. IR: 3246m ν(NH), 3182m, 3127m, 3110m, 1530s, 1523vs, 1456s, 1352m, 1206m, 1138m, 1131m, 1051m, 1012m, 996s, 982s, 669m, 190w and 172w ν(Pt—I) cm^{-1}. Mass spectrum: *m*/*z* 254 [11%, I_2^+], 226 [26, $C_8H_7F_5N_2^+$], 206 [13, $C_8HF_5N^+$], 197 [94, $C_7H_4F_5N^+$], 196 [100, $C_6F_5NHCH_2^+$].

Synthesis of N,N′-bis(*polyfluorophenyl*)*ethane*-1,2-*diaminato*(2−)*platinum*(II) *complexes*

Amounts of reagents, reaction conditions and yields of products are given in Table 1. In each case bis-iodo[N-(2,3,5,6-tetrafluorophenyl)ethane-1,2-diamine]platinum(II), thallium(I) 2,3,5,6-tetrafluorobenzoate, dry pyridine (10 cm^3) and the appropriate polyfluorobenzene were heated with stirring under purified nitrogen. After reaction, the mixture was evaporated to dryness *in vacuo* and the residue washed with petrol (2 × 20 cm^3) and extracted with ether or acetone. The resulting solution was filtered, evaporated to dryness and the residue was washed with a minimum of ethanol (2 × 2 cm^3) on a glass sinter, and recrystallized as indicated below. ${}^{3}J$(PtH) values are given in Table 2.

[*N*,*N′* -*bis*(2,3,5,6 -*tetrafluorophenyl*)*ethane* - 1,2-*diaminato*(2−)]*dipyridineplatinum*(II) (**3a**). Extraction with acetone and recrystallization from ether–petrol gave the yellow title compound, m.p. 188–190°C (dec.), ref. 3 m.p. 173°C (dec.). ^{1}H and ^{19}F NMR, IR and mass spectra of the solid were identical with those of the authentic compound.

[*N* - (4 - *bromo* - 2,3,5,6 - *tetrafluorophenyl*) - *N′*-(2,3,5,6 - *tetrafluorophenyl*)*ethane* - 1,2 - *diaminato*(2−)]*dipyridineplatinum*(II)–*ether* (1 : 0.5) (**3b**·0.5Et$_2$O). Extraction with acetone and recrystallization from ether–petrol gave the title compound, m.p. 178–182°C (dec.) (Found: C, 38.1; 37.8; H, 2.2, 2.3; N, 6.7, 7.0. $C_{24}H_{15}BrF_8N_4Pt \cdot 0.5C_4H_{10}O$ requires: C, 37.9; H, 2.5; N, 6.8%).

^{19}F NMR [(CD$_3$)$_2$CO]: −140.8, m, 2F, F3,5 (C$_6$F$_4$Br); −144.5, m, 2F, F3,5 (C$_6$F$_4$H); −148.9, m, 2F, F2,6 (C$_6$F$_4$Br); −150.5, m, 2F, F2,6 (C$_6$F$_4$H). ^{1}H NMR [(CD$_3$)$_2$CO]: 1.10, t, 3H, Me; 3.16, br, 4H, CH$_2$N; 3.39, q, 2H, CH$_2$O; 6.26, tt, ^3J(HF) 10 Hz, ^4J(HF) 7 Hz, 1H, HC$_6$F$_4$; 7.27, m, 4H, H3,5(py); 7.85, m, 2H, H4(py); 8.61, m, 4H, H2,6(py). UV–vis spectrum [λ_{max} (ε)]: 364 (9300) nm. IR: 2892m, 2836m, 1642s, 1619s, 1604s, 1578m, 1493vs, 1479vs(sh), 1470vs, 1448s, 1438s, 1333m, 1277m, 1160m, 1151m, 1128s, 1089m, 1068m, 940s, 908m, 829m, 761m, 694m cm^{-1}. Mass spectrum: *m/z* 786 [0.7%, M$^+$], 706 [0.6, Pt(C$_{14}$H$_4$BrF$_8$N$_2$)py$^+$], 625 [0.3, Pt(C$_{14}$H$_2$BrF$_8$N$_2$)$^+$], 528 [0.5, Pt(BrC$_6$F$_4$NC)py$^+$], 434 [11, HC$_6$F$_4$NH(CH$_2$)$_2$NHC$_6$F$_4$Br$^+$], 432 [8, HC$_6$F$_4$N(CH$_2$)$_2$NC$_6$F$_4$Br$^+$], 256 [28, BrC$_6$F$_4$NHCH$_2$$^+$], 178 [100, HC$_6F_4$NHCH$_2$$^+$].

[*N*-(*pentafluorophenyl*)-*N*′-(2,3,5,6-*tetrafluorophenyl*)*ethane* - 1,2 - *diaminato*(2−)]*dipyridineplatinum*(II)-*ether* (1:0.4) (**3c**·0.4Et$_2$O). Extraction with acetone and recrystallization twice from ether–petrol gave the title compound, m.p. 192–196°C (dec.) (Found: C, 40.8, 40.6; H, 2.5, 2.6; N, 7.9, 7.7. C$_{24}$H$_{15}$F$_9$N$_4$Pt·0.4C$_4$H$_{10}$O requires: C, 40.7; H, 2.5; N, 7.4%). ^{19}F NMR [(CD$_3$)$_2$CO]: −144.6, m, 2F, F3,5 (C$_6$F$_4$H); −150.8, complex m, 4F, F2,6 (C$_6$F$_4$H and C$_6$F$_5$); −168.7, m, 2F, F3,5 (C$_6$F$_5$); −177.1, m, 1F, F4 (C$_6$F$_5$). In CDCl$_3$, two F2,6 resonances were observed: −150.6, m, *p*-HC$_6$F$_4$; −151.0, m, C$_6$F$_5$. ^{1}H NMR (CDCl$_3$): 1.21, t, 2.4H, Me; 3.11, br m, 2H, CH$_2$NC$_6$F$_5$; 3.23, br m, 2H, CH$_2$NC$_6$F$_4$H; 3.48, q, 1.6H, CH$_2$O; 6.06, tt, ^3J(HF) 10 Hz, ^4J(HF) 7 Hz, 1H, HC$_6$F$_4$; 7.09, m, 4H, H3,5(py); 7.66, m, 2H, H4(py); 8.54, m, 4H, H2,6(py). UV–vis spectrum [λ_{max} (ε)]: 358 (6100) nm. IR: 2898m, 2843m, 1631s, 1605m, 1581m, 1504vs, 1494vs, 1468s, 1449vs, 1440vs, 1333m, 1162m, 1132s, 1113m, 1093m, 1062s, 1011s, 990m, 950s, 906s, 873s, 760s, 694s, 570m, 487m cm^{-1}. Mass spectrum: *m/z* 725 [0.3%, M$^+$], 644 [0.2, Pt(C$_{14}$H$_3$F$_9$N$_2$)py$^+$], 564 [0.2, Pt(C$_{14}$H$_2$F$_9$N$_2$)$^+$], 467 [0.7, Pt(C$_6$F$_5$NC)py$^+$], 449 [0.8, Pt(HC$_6$F$_4$NC)py$^+$], 372 [11, HC$_6$F$_4$N(CH$_2$)$_2$NC$_6$F$_5$$^+$], 370 [8, HC$_6F_4(CH)_2C_6F_5$$^+$], 196 [31, C$_6F_5$NHCH$_2$$^+$], 178 [49, HC$_6F_4$NHCH$_2$$^+$], 79 [100, py$^+$].

[*N* - (2,3,5,6 - *tetrafluoro* - 4 - *methylphenyl*) - *N*′-(2,3,5,6 - *tetrafluorophenyl*)*ethane* - 1,2 - *diaminato*(2−)]*dipyridineplatinum*(II) (**3d**). Ether extraction and recrystallization from ether–petrol gave **3d**, m.p. 183–184°C (dec.) (Found: C, 41.5; H, 2.3; F, 20.6; N, 7.8. C$_{25}$H$_{18}$F$_8$N$_4$Pt requires: C, 41.6; H, 2.5; F, 21.1; N, 7.8%). ^{19}F NMR [(CD$_3$)$_2$CO]: −144.9, m, 2F, F3,5 (C$_6$F$_4$H); −150.0, m, 2F, F3,5 (C$_6$F$_4$Me); −151.1, br m, 4F, F2,6 (HC$_6$F$_4$ and C$_6$F$_4$Me). ^{1}H NMR [(CD$_3$)$_2$CO]: 1.94, m, 3H, Me; 3.14, m, 4H, CH$_2$; 6.22, m, 1H, HC$_6$F$_4$; 7.25, m, 4H, H3,5(py); 7.84, m, 2H, H4(py); 8.58, m, 4H, H2,6(py). UV–vis spectrum [λ_{max} (ε)]: 356 (5200) nm. IR: 1648m, 1630s, 1606m, 1578m, 1494 and 1483vs, 1448vs, 1426m, 1379m, 1332m, 1274m, 1168m, 1131s, 1092m, 1057m, 920s, 872s, 760s, 694s cm^{-1}. Mass spectrum: *m/z* 721 [0.4%, M$^+$], 463 [1.0, Pt(MeC$_6$F$_4$NC)py$^+$], 449 [0.7, Pt(HC$_6$F$_4$NC)py$^+$], 368 [32, MeC$_6$F$_4$N(CH$_2$)$_2$NC$_6$F$_4$H$^+$], 366 [23, MeC$_6$F$_4$N(CH)$_2$NC$_6$F$_4$H$^+$], 192 [92, MeC$_6$F$_4$NHCH$_2$$^+$], 178 [53, HC$_6F_4$NHCH$_2$$^+$], 79 [100, py$^+$].

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