Synthesis and Reactivity of Hydroxo-bridged Binuclear Platinum Complexes. Crystal Structure of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$†

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The reaction of $[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2]$ with NBu_4OH(aq) in acetone leads to the formation of the hydroxo-complexes $[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (X = F **1** or Cl **2**). These react with weak protic acids such as acetylacetone (Hacac), benzoylacetone (Hbzac) and 8-hydroxyquinoline (Hquin) yielding the mononuclear complexes $[NBu_4][Pt(C_6X_5)_2(L\text{–}L)]$ (X = F, L–L = acac **3**, bzac **4**, or quin **5**; X = Cl, L–L = acac **6**, bzac **7**, or quin **8**). Treatment of complexes **1** and **2** with PhCN in the presence of HBF_4 gives the mononuclear compounds *cis*-$[Pt(C_6X_5)_2(PhCN)_2]$ (X = F **9** or Cl **10**). When the benzonitrile complexes are treated with aniline the corresponding *cis*-$[Pt(C_6X_5)(NH_2Ph)_2]$ (X = F **11** or Cl **12**) are formed. The benzamido derivatives $[NBu_4][Pt(C_6X_5)_2(HNOCPh)(H_2O)]$ (X = F **13** or Cl **14**) are formed when complexes **9** and **10** are treated with NBu_4OH(aq) in acetone, and thermal treatment of **13** yields $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}HNOCPh)\}_2]$ **15**. Complexes **9** and **10** react with methanol in the presence of NBu_4OH to give the corresponding imido ester derivatives $[Pt(C_6X_5)_2\{HN{=}C(OMe)Ph\}_2]$ (X = F **16** or Cl **17**). Spectroscopic (IR, ^1H and ^{19}F) data have been used for structural assignments, and an X-ray structure determination carried out for $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ has established the centrosymmetric binuclear nature of the anion $[(C_6F_5)_2Pt(\mu\text{-}OH)_2Pt(C_6F_5)_2]^{2-}$. The structure has been solved and refined up to R = 0.049 and R' = 0.056 based on 2278 observed reflections. The Pt atoms are four-co-ordinated and show slight deviations from a square-planar arrangement.

In the last few years there has been growing interest in the synthesis of late transition-metal hydroxides owing to their reactivity and potential relevance to catalysis.[1] Some hydroxo-bridged binuclear complexes of nickel,[2,3] palladium[4] and platinum[4–6] have been described. By far the most common method of preparing these hydroxo complexes is through metathesis reactions.

On the other hand, we have recently shown[7] that complexes $[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni or Pd) can be conveniently prepared from the corresponding benzonitrile complexes *cis*-$[M(C_6F_5)_2(PhCN)_2]$ and NBu_4OH in acetone. However, this method is not valid for platinum because in acetone–water the bonded benzonitrile undergoes nucleophilic attack by OH^-.

In this paper the synthesis and reactivity of $[\{PtR_2(\mu\text{-}OH)\}_2]^{2-}$ and *cis*-$[PtR_2(PhCN)_2]$ (R = C_6F_5 or C_6Cl_5) are described, together with an X-ray diffraction study which has confirmed the dinuclearity of the hydroxo(pentafluorophenyl)-platinum complex. A preliminary report of this work has been given.[7]

Results and Discussion

In acetone the chloro-bridged complexes[8,9] $[\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2]^{2-}$ undergo interchange reactions with 20% NBu_4OH(aq) without formal cleavage of the bridging system to yield **1** and **2** [equation (1)]. Both complexes are white solids and the conductance data for their acetone solutions (Table 1) are consistent with the proposed formulae.[10] Their IR spectra show the characteristic absorptions of the C_6F_5 (1500, 1450, 1050 and 950 cm^{-1})[8,11] and C_6Cl_5 (1315, 1285, 1220 and 670 cm^{-1})[12] groups, respectively. A split band at *ca.* 800 cm^{-1} (X-sensitive mode of C_6F_5)[13] indicates the *cis* nature of the $Pt(C_6F_5)_2$ fragment.[14] Similarly, the presence of the *cis*-$Pt(C_6Cl_5)_2$ fragment in complex **2** is manifested by two split bands at *ca.* 830 (X-sensitive mode of C_6Cl_5)[15] and 610 (Pt–C stretch)[12] cm^{-1}. The absorptions found at 3600 and 3560 cm^{-1} are assigned to the OH bridges in complexes **1** and **2**, respectively. Further evidence for the presence of the OH groups is given by the high-field resonances found at δ −1.21 and −0.26 in the ^1H NMR spectra of **1** and **2**, respectively, which are in agreement with previous results for similar compounds.[16,17] The ^{19}F NMR spectrum of **1** (Table 2) indicates the equivalence of the C_6F_5 groups.

$$[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2] + 2NBu_4OH \longrightarrow [NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2] + 2NBu_4Cl \quad (1)$$

$$X = F\ \mathbf{1}\ \text{or}\ Cl\ \mathbf{2}$$

The structure of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ has been determined by single-crystal X-ray diffraction. It consists of binuclear centrosymmetric $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ anions (Fig. 1) and $[NBu_4]^+$ cations, which are held together by electrostatic interactions. Positional parameters and selected geometrical features are collected in Tables 3 and 4 respectively.

The Pt atoms and the four atoms co-ordinated to it deviate slightly from the mean plane defined by them. These deviations are, however, significant in terms of the attained accuracy $[\Sigma(D/S)^2$ = 12.96 for atoms defining the plane *vs.* χ^2 = 5.99 for two degrees of freedom (where D is the individual atomic deviation from the least-squares plane, and S is the standard deviation of D)], the most significant being that of Pt [0.003(1)

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† Bis(tetrabutylammonium) di-μ-hydroxo-bis[bis(pentafluorophenyl)-platinate].

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Table 1 Analytical data, yields, and physical properties for the platinum complexes

Complex	Yield (%)	M.p.[a] (θ/°C)	Analysis[b] (%) C	H	N	Λ_M[c]	Selected IR bands[d] (cm^{-1}) X-Sensitive	Others
1 $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$	90	265	41.2 (42.6)	4.8 (4.7)	1.6 (1.8)	177	805, 795	3600 ν(OH)
2 $[NBu_4]_2[\{Pt(C_6Cl_5)_2(\mu\text{-}OH)\}_2]$	87	224	35.7 (35.3)	4.0 (3.9)	1.4 (1.5)	145	840	3560 ν(OH)
3 $[NBu_4][Pt(C_6F_5)_2(acac)]$	57	280	45.0 (45.5)	5.1 (5.0)	1.3 (1.6)	106	805, 795	1575 ν(CC) + ν(CO) 1510 ν(CO) + ν(CC)
4 $[NBu_4][Pt(C_6F_5)_2(bzac)]$	60	249	48.4 (48.9)	4.9 (4.9)	1.5 (1.5)	118	805, 795	1580 ν(CC) + ν(CO) 1500 ν(CO) + ν(CC)
5 $[NBu_4][Pt(C_6F_5)_2(quin)]$	73	298	48.0 (48.5)	4.9 (4.6)	3.0 (3.1)	109	805, 795	1565
6 $[NBu_4][Pt(C_6Cl_5)_2(acac)]$	56	234	38.1 (38.3)	4.0 (4.2)	1.2 (1.4)	88	840	1575 ν(CC) + ν(CO) 1510 ν(CO) + ν(CC)
7 $[NBu_4][Pt(C_6Cl_5)_2(bzac)]$	53	232	41.5 (41.6)	4.0 (4.1)	1.1 (1.3)	83	840	1580 ν(CC) + ν(CO) 1500 ν(CO) + ν(CC)
8 $[NBu_4][Pt(C_6Cl_5)_2(quin)]$	54	280	40.9 (41.1)	3.8 (3.9)	2.4 (2.6)	98	840	1565
9 *cis*-$[Pt(C_6F_5)_2(PhCN)_2]$	75	238	42.8 (42.5)	1.7 (1.4)	3.3 (3.8)		810, 800	2265, 2258 ν(C≡N)
10 *cis*-$[Pt(C_6Cl_5)_2(PhCN)_2]$	73	245	34.5 (34.7)	1.1 (1.1)	3.0 (3.1)		845, 835	2275 ν(C≡N)
11 *cis*-$[Pt(C_6F_5)_2(NH_2Ph)_2]$	77	236	40.5 (40.3)	2.2 (2.0)	4.0 (3.9)		805, 795	3340, 3280, 3260 ν(NH) 1595, 1575 δ(NH_2)
12 *cis*-$[Pt(C_6Cl_5)_2(NH_2Ph)_2]$	79	237	32.7 (32.8)	1.3 (1.6)	3.0 (3.2)		840, 830	3320, 3270, 3250 ν(NH) 1590, 1570 δ(NH_2)
13 $[NBu_4][Pt(C_6F_5)_2(HNOCPh)(H_2O)]$	63	98	46.0 (46.2)	4.9 (4.9)	3.3 (3.1)	102	805, 790	3380 ν(NH), 3180 ν(OH) 1635 ν(C=O), δ(H_2O)
14 $[NBu_4][Pt(C_6Cl_5)_2(HNOCPh)(H_2O)]$	91	102	38.7 (39.1)	4.3 (4.1)	2.7 (2.6)	79	840, 830	3380 ν(NH) 1635 ν(C=O), δ(H_2O)
15 $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}HNOCPh)\}_2]$	100	197	47.2 (47.1)	4.9 (4.8)	3.5 (3.1)	198	800, 790	3280 ν(NH) 1630 ν(C=O)
16 *cis*-$[Pt(C_6F_5)_2\{HN{=}C(OMe)Ph\}_2]$	70	169	43.7 (43.8)	2.6 (2.4)	4.0 (3.7)		805, 795	3350 ν(NH) 1630 ν(C=N)
17 *cis*-$[Pt(C_6Cl_5)_2\{HN{=}C(OMe)Ph\}_2]$	88	192	34.7 (34.9)	2.1 (1.9)	2.7 (2.9)		840, 830	3340 ν(NH) 1635 ν(C=N)

[a] With decomposition. [b] Calculated values in parentheses. [c] In Ω^{-1} cm^2 mol^{-1} (in acetone solution, $c \approx 5 \times 10^{-4}$ mol dm^{-3}). [d] Nujol mulls.

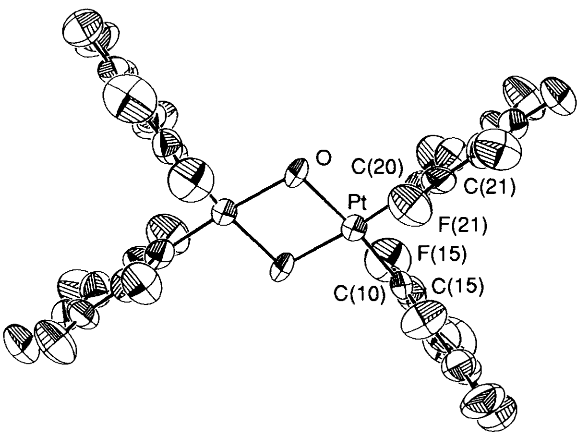


Fig. 1 An ORTEP drawing[18] of the $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ anion

Å]. The two oxygen atoms forming the bridge and the Pt atoms are, due to symmetry restrictions, on the same plane. The structural parameters of the Pt_2O_2 ring [Pt–O 2.07(2) Å; O–Pt–O 78.6(5) and Pt–O–Pt 101.4(6)°] agree with the corresponding values found in bis(μ-hydroxo-platinum) dimers[19,20] and the recently reported palladium analogue of complex **1** [Pd–O 2.068(6) and 2.077(6) Å; O–Pd–O 81.2(4) and Pd–O–Pd 98.8(4)°].[21]

The two pentafluorophenyl rings bonded to Pt are planar and rotated by 90.9(5)° from each other, but the F atoms in one of them are out of the ring planes with deviations up to 0.07(1) Å [for F(13)]. The rings present distortions as indicated by the values of the C–C–C angles which range from 108(1) to 130(2)°. This type of distortion has already been observed in other fluorophenyl rings.[22]

Both complexes **1** and **2** react with the weak acids acetylacetone (Hacac), benzoylacetone (Hbzac) and 8-hydroxyquinoline (Hquin) to give compounds **3**–**8** [equation (2)], where the

$$[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2] + 2HL\text{-}L \longrightarrow 2[NBu_4][Pt(C_6X_5)_2(L\text{-}L)] + 2H_2O \quad (2)$$

X = F, L–L = acac **3**, bzac **4**, or quin **5**
X = Cl, L–L = acac **6**, bzac **7**, or quin **8**

deprotonated L–L$^-$ acts as a chelating bidentate ligand. The IR spectra again show split bands at *ca.* 800 or 830 cm^{-1}, respectively, attributed to the *cis*-$Pt(C_6X_5)_2$ fragments, and measurements of the molar conductivity in acetone (Table 1) indicate that complexes **3**–**8** behave as 1:1 electrolytes.[10] The ^1H and ^{19}F NMR data for these compounds are listed in Table 2.

The labile complexes *cis*-$[PdR_2(PhCN)_2]$ (R = C_6F_5 or $C_6H_2F_3$-2,4,6)[23–25] have been used as starting materials for the synthesis of neutral mononuclear and neutral or anionic binuclear compounds. The benzonitrileplatinum complex **9** has now been prepared by adding benzonitrile to the solution resulting from the arylation of $PtCl_2$ with $MgBr(C_6F_5)$ in tetrahydrofuran, as represented by equation (3). Complexes **9**

$$PtCl_2 + 2MgBr(C_6F_5) + 2PhCN \longrightarrow \underset{\mathbf{9}}{cis\text{-}[Pt(C_6F_5)_2(PhCN)_2]} + MgCl_2 + MgBr_2 \quad (3)$$

Table 2 Proton and ^{19}F NMR data (J in Hz) for the platinum complexes

Complex	$\delta(SiMe_4)$[a]	$\delta(CFCl_3)$
1[b]	-1.21 (s, 2 H, OH)	-121.8 [d, 8 F_o, $J(F_oF_m)$ 25.1, J_{PtF} 534] -167.1 (m, 12 F_m + 4 F_p)
2[c]	-0.26 (s, 2 H, OH)	
3[b]	5.30 (s, 1 H, CH) 1.74 (s, 6 H, CH_3)	-120.0 [d, 4 F_o, $J(F_oF_m)$ 23.5, J_{PtF} 510] -166.1 [t, 2 F_p, $J(F_mF_p)$ 19.5] -167.4 (m, 4 F_m)
4[c]	7.80 [dd, 2 H, Ph, $J(H_oH_m)$ 8.1, $J(H_oH_p)$ 1.1] 7.36 (m, 3 H, Ph) 6.07 (s, 1 H, CH) 1.84 (s, 3 H, CH_3)	-119.0 [d, 2 F_o, $J(F_oF_m)$ 31, J_{PtF} 517] -119.4 [d, 2 F_o, $J(F_oF_m)$ 31, J_{PtF} 517] -167.3 (m, 2 F_p) -168.1 (m, 4 F_m)
5[c]	8.37 (dd, 1 H, J 8.5, 1.4) 8.10 (br, 1 H, J 4.9) 7.34 (m, 2 H) 6.81 (br d, J 7.8) 6.71 (dd, J 7.9, 0.8)	-117.4 [d, 4 F_o, $J(F_oF_m)$ 26.6, J_{PtF} 485] -166.8 (m, 2 F_p + 4 F_m)
6[b]	5.29 (s, 1 H, CH) 1.76 (s, 6 H, CH_3)	
7[b]	7.77 (m, 5 H, Ph) 5.91 (s, 1 H, CH) 1.88 (s, 3 H, CH_3)	
8[b]	8.09 (d, 1 H, J 8.6) 7.91 (d, 1 H, J 5.0) 7.39–7.08 (m, 3 H, Ph) 6.71 (d, 1 H, J 7.5)	
9[b]	7.71 (m, 3 H, Ph) 7.55 (m, 2 H, Ph)	-121.1 (m, 4 F_o, J_{PtF} 480) -162.0 (m, 2 F_p) -165.2 (m, 4 F_m)
10[b]	7.55 (m, 3 H, Ph) 7.56 (m, 2 H, Ph)	
11[b]	7.24–6.82 (m, Ph) 4.48 (s, NH_2, J_{PtH} 41)	-121.3 [d, 4 F_o, $J(F_oF_m)$ 20.7, J_{PtF} 491] -161.7 (m, 2 F_p) -164.4 (m, 4 F_m)
12[b]	7.72–7.05 (m, Ph) 4.39 (s, NH_2, J_{PtH} 45)	
13[c]	7.66 (m, 2 H, Ph) 7.32 (m, 3 H, Ph) 5.9 (br, NH) 2.8 (br, H_2O)	-118.2 [d, 2 F_o, $J(F_oF_m)$ 26.6, J_{PtF} 458] -118.8 [d, 2 F_o, $J(F_oF_m)$ 26.6, J_{PtF} 562] -167.3 [t, 1 F_p, $J(F_mF_p)$ 19.8] -167.5 [t, 1 F_p, $J(F_mF_p)$ 19.8] -167.9 (m, 4 F_m)
14[b]	7.69 (m, 2 H, Ph) 7.31 (m, 3 H, Ph) 5.83 (br, NH) 2.8 (br, H_2O)	
15	9.10 (br, 4 H, Ph) 7.24 (br, 6 H, Ph)	-118.8 (br, 8 F_o) -168.3 (br, 4 F_p + 8 F_m)
16[b]	8.69 (d, 4 H, Ph, J 6.8) 7.64 (m, 6 H, Ph) 6.54 (br, 2 H, NH) 3.22 (s, 6 H, CH_3)	-123.0 [d, 4 F_o, $J(F_oF_m)$ 20.7, J_{PtF} 465] -163.6 [t, 2 F_p, $J(F_mF_p)$ 20.4] -165.6 (m, 4 F_m)
17[b]	8.70 (d, 4 H, Ph) 7.62 (m, 6 H, Ph) 7.17 (br, 2 H, NH) 3.14 (s, 6 H, CH_3)	

[a] Additional peaks from $[NBu_4]^+$, with the correct relative intensities, are found in spectra of the ionic complexes. [b] In $CDCl_3$. [c] In $(CD_3)_2CO$.

and **10** can be prepared from the hydroxo complexes **1** and **2**, respectively. The reaction represented by equation (4) may be

$$[\mathrm{NBu_4}]_2[\{\mathrm{Pt(C_6X_5)_2(\mu\text{-}OH)}\}_2] + 4\mathrm{PhCN} + 2\mathrm{HBF_4} \longrightarrow 2\,cis\text{-}[\mathrm{Pt(C_6X_5)_2(PhCN)_2}] + 2\mathrm{NBu_4BF_4} + 2\mathrm{H_2O} \qquad (4)$$

X = F **9** or Cl **10**

considered as an acid–base reaction in which the $\mathrm{Pt(C_6X_5)_2}$ moiety is trapped by the organonitrile to form the benzonitrile complex.

Both complexes **9** and **10** are non-conducting in acetone solution and their IR spectra show split bands at *ca.* 800 or 830 cm^{-1} for the X-sensitive mode which are characteristic of the *cis*-$\mathrm{Pt(C_6X_5)_2}$ fragments. The shifts to higher wavenumbers observed for ν(C≡N) (Table 1, unco-ordinated PhCN absorbs at 2230 cm^{-1}) are indicative of an end-on co-ordination of benzonitrile.[26]

Table 3 Selected bond lengths (Å) and angles (°) for $[\mathrm{NBu_4}]_2[\{\mathrm{Pt(C_6F_5)_2(\mu\text{-}OH)}\}_2]$

Pt–O	2.07(2)	C(14)–F(14)	1.35(2)
Pt–C(10)	1.97(2)	C(15)–F(15)	1.43(2)
Pt–C(20)	1.97(1)	C(20)–C(21)	1.36(2)
C(10)–C(11)	1.40(2)	C(20)–C(25)	1.41(2)
C(10)–C(15)	1.39(2)	C(21)–C(22)	1.38(2)
C(11)–C(12)	1.35(3)	C(22)–C(23)	1.32(3)
C(12)–C(13)	1.34(2)	C(23)–C(24)	1.34(3)
C(13)–C(14)	1.37(3)	C(24)–C(25)	1.37(2)
C(14)–C(15)	1.32(2)	C(21)–F(21)	1.37(2)
C(11)–F(11)	1.39(2)	C(22)–F(22)	1.35(2)
C(12)–F(12)	1.36(2)	C(23)–F(23)	1.38(2)
C(13)–F(13)	1.35(3)	C(24)–F(24)	1.36(2)
		C(25)–F(25)	1.36(2)
C(10)–Pt–C(20)	89.9(5)	F(14)–C(14)–C(15)	123(1)
O$^{\mathrm{I}}$–Pt–C(10)	96.4(6)	C(14)–C(15)–F(15)	116(1)
O–Pt–C(20)	95.1(6)	C(21)–C(20)–C(25)	112(1)
O–Pt–O$^{\mathrm{I}}$	78.6(5)	C(20)–C(21)–C(22)	127(2)
Pt–O–Pt$^{\mathrm{I}}$	101.4(6)	C(21)–C(22)–C(23)	117(2)
C(11)–C(10)–C(15)	108(1)	C(22)–C(23)–C(24)	121(2)
C(10)–C(11)–C(12)	126(1)	C(23)–C(24)–C(25)	120(2)
C(11)–C(12)–C(13)	120(1)	C(20)–C(25)–C(24)	123(2)
C(12)–C(13)–C(14)	118(2)	F(21)–C(21)–C(22)	113(1)
C(13)–C(14)–C(15)	118(2)	F(22)–C(22)–C(23)	120(2)
C(10)–C(15)–C(14)	130(2)	F(23)–C(23)–C(24)	119(2)
F(11)–C(11)–C(12)	116(1)	F(24)–C(24)–C(25)	119(2)
F(12)–C(12)–C(13)	120(2)	C(24)–C(25)–F(25)	118(2)
F(13)–C(13)–C(14)	120(2)		

Symmetry code: I $-x$, $-y$, $-z$.

Complexes **9** and **10** are labile enough to be used for preparing neutral mononuclear compounds. For example, in dichloromethane the benzonitrile is readily displaced by aniline to give complexes **11** and **12**, according to equation (5). The

$$cis\text{-}[\mathrm{Pt(C_6X_5)_2(PhCN)_2}] + 2\mathrm{NH_2Ph} \longrightarrow cis\text{-}[\mathrm{Pt(C_6X_5)_2(NH_2Ph)_2}] + 2\mathrm{PhCN} \qquad (5)$$

X = F **11** or Cl **12**

substitution reaction takes place without isomerization and the isolated compounds are characterized as the *cis* isomers, for they show in the IR spectra the split bands (X-sensitive mode) attributed to the *cis*-$\mathrm{Pt(C_6X_5)_2}$ fragments.

The nickel and palladium analogues of complex **1** were obtained by the reaction between *cis*-$[\mathrm{M(C_6F_5)_2(PhCN)_2}]$ and $\mathrm{NBu_4OH}$ in acetone. However, under the same experimental conditions, complexes **9** and **10** react with $\mathrm{NBu_4OH}$ in a 1 : 1 molar ratio following a different pathway: nucleophilic attack of $\mathrm{OH^-}$ on co-ordinated benzonitrile is favourably competitive and, instead of the substitution of benzonitrile by $\mathrm{OH^-}$, the reaction product is an aquabenzamido complex [equation (6)].

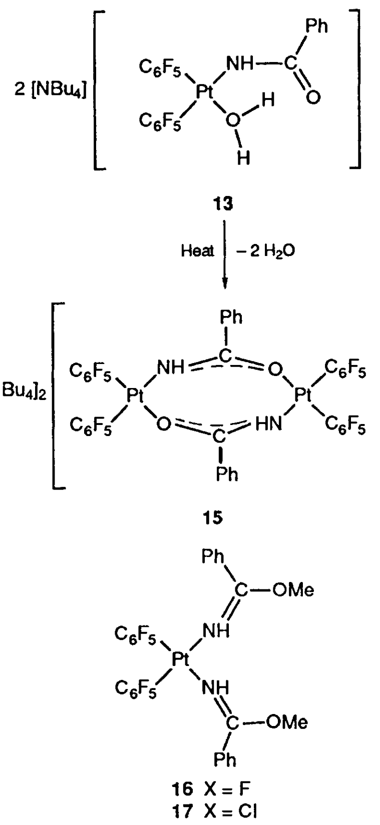
$$cis\text{-}[\mathrm{Pt(C_6X_5)_2(PhCN)_2}] + \mathrm{NBu_4OH} + \mathrm{H_2O} \longrightarrow [\mathrm{NBu_4}][\mathrm{Pt(C_6X_5)_2(HNOCPh)(H_2O)}] + \mathrm{PhCN} \qquad (6)$$

X = F **13** or Cl **14**

The IR data (X-sensitive mode) indicate that the perhalogenophenyl groups in complexes **13** and **14** are mutually *cis* and the ^{19}F NMR spectrum of **13** shows the presence of two inequivalent $\mathrm{C_6F_5}$ groups (*trans* to $\mathrm{H_2O}$ and *trans* to HNOCPh). In acetone solution both **13** and **14** behave as 1 : 1 electrolytes.[10] The mass spectra of each show peaks at *m*/*z* 105 and 121 assignable to the PhCO and $\mathrm{PhCONH_2}$ fragments, respectively, and the IR spectra show ν(NH) and ν(C=O) bands at *ca.* 3300 and 1600 cm^{-1}, respectively. An alternative imino–enol formulation Pt–N=C(OH)Ph is excluded by the absence of ν(OH) bands at *ca.* 3500 cm^{-1}. The ^{1}H NMR data are also consistent with the N-benzamido formulation.[27] The observation of the OH stretching mode of the co-ordinated water as a broad band with its absorption maximum at *ca.* 3200 cm^{-1} suggests that this molecule is involved in hydrogen bonding. When the reaction represented by equation (6) is carried out with a molar ratio of benzonitrile complex: $\mathrm{NBu_4OH}$ = 1 : 2 the same reaction products are obtained.

Table 4 Atomic parameters for $[\mathrm{NBu_4}]_2[\{\mathrm{Pt(C_6F_5)_2(\mu\text{-}OH)}\}_2]$

Atom	*x*	*y*	*z*
Pt	−0.115 19(5)	0.548 48(5)	0.004 95(4)
O	0.000 1(1)	0.560 48(9)	−0.054 40(8)
C(10)	−0.216 4(1)	0.527 82(9)	0.066 23(9)
C(11)	−0.197 8(1)	0.562 6(1)	0.136 76(9)
F(11)	−0.101 16(8)	0.614 42(8)	0.165 98(5)
C(12)	−0.264 8(1)	0.547 4(1)	0.180 27(9)
F(12)	−0.237 4(1)	0.587 45(9)	0.247 16(5)
C(13)	−0.360 39(1)	0.497 2(1)	0.156 6(1)
F(13)	−0.430 85(8)	0.484 53(9)	0.198 04(6)
C(14)	−0.384 1(1)	0.456 5(1)	0.089 25(9)
F(14)	−0.477 82(8)	0.402 3(1)	0.065 99(6)
C(15)	−0.314 1(1)	0.473 3(1)	0.050 18(8)
F(15)	−0.345 05(8)	0.433 33(8)	−0.021 09(5)
C(20)	−0.213 5(1)	0.655 6(1)	−0.048 67(8)
C(21)	−0.218 0(1)	0.753 8(1)	−0.025 15(9)
F(21)	−0.154 77(8)	0.781 55(7)	0.040 16(5)
C(22)	−0.278 0(1)	0.834 4(1)	−0.061 9(1)
F(22)	−0.276 6(1)	0.929 57(7)	−0.034 10(6)
C(23)	−0.342 2(1)	0.814 1(1)	−0.125 7(1)
F(23)	−0.405 51(9)	0.891 33(9)	−0.164 33(6)
C(24)	−0.346 0(1)	0.719 6(1)	−0.154 1(1)
F(24)	−0.411 7(1)	0.700 0(1)	−0.220 04(7)
C(25)	−0.283 8(1)	0.641 3(1)	−0.116 9(1)
F(25)	−0.289 01(9)	0.547 08(9)	−0.148 19(5)
N	0.217 01(9)	0.777 84(9)	0.152 31(7)
C(30)	0.242 1(1)	0.680 8(1)	0.195 33(9)
C(31)	0.298 3(2)	0.694 8(1)	0.275 0(1)
C(32)	0.309 9(2)	0.599 8(2)	0.316 9(1)
C(33)	0.363 2(2)	0.613 6(2)	0.393 8(1)
C(40)	0.152 7(1)	0.850 0(1)	0.186 69(8)
C(41)	0.044 8(1)	0.810 9(1)	0.199 10(9)
C(42)	−0.004 1(2)	0.889 2(2)	0.239 5(1)
C(43)	−0.115 6(2)	0.851 1(2)	0.248 7(1)
C(50)	0.322 2(1)	0.835 2(1)	0.150 72(8)
C(51)	0.401 5(1)	0.777 5(1)	0.116 86(9)
C(52)	0.492 4(1)	0.845 0(2)	0.109 80(9)
C(53)	0.581 5(2)	0.791 2(2)	0.083 0(1)
C(60)	0.149 9(1)	0.748 1(1)	0.077 53(9)
C(61)	0.117 2(2)	0.838 1(2)	0.025 7(1)
C(62)	0.066 7(2)	0.804 3(2)	−0.049 3(1)
C(63)	0.027 0(2)	0.888 6(2)	−0.098 9(1)



Scheme 1 Suggested structures for complexes **13** and **15**–**17**

Complex **13** is stable up to 98 °C and thermogravimetry indicates that above this temperature the H_2O molecule is lost (observed weight loss 2.1%; calculated value 2.0%) to give an intermediate species **15** which is stable in the range 98–197 °C. The molar conductivity of the acetone solution shows that this new complex behaves as a 2:1 electrolyte[10] and the IR bands at 3280w and 1630vs cm^{-1} are attributed to $\nu(NH)$ and $\nu(C{=}O)$ of a co-ordinated benzamido ion whose presence in complex **15** is also corroborated by the mass spectrum (peaks at *m*/*z* 105 and 121 owing to PhCO and $PhCONH_2$, respectively). The ^1H NMR spectrum shows two resonances for the phenyl protons, but while the *meta*- and *para*-hydrogen resonance is found at the same frequency as in the spectrum of complex **13**, the *ortho*-hydrogen resonance is observed at lower field. We have been unable to detect a NH resonance, perhaps because it is masked by the phenyl resonances or by H/D exchange. Scheme 1 shows the structures proposed for complexes **13** and **15**. Thermal dehydration of complex **14** begins at 102 °C, but above this temperature the thermogravimetric curve indicates that a stable intermediate similar to **15** is not formed.

The activation of nitriles with respect to attack by nucleophiles in the co-ordination sphere of metal ions has attracted considerable interest,[28–30] and the reactions of $[PtCl_2(PhCN)_2]$ with a number of carbanions have been reported.[31–33] Recently, it has been demonstrated[34] that $[PtCl_2(PhCN)_2]$ reacts with methanol in the presence of a catalytic amount of base to yield the mono- and bis-imido ester derivatives $[PtCl_2(PhCN)\{HN{=}C(OMe)Ph\}]$ and $[PtCl_2\{HN{=}C(OMe)Ph\}_2]$. Similarly, complexes **9** and **10** also react with methanol in the presence of $NBu_4OH(aq)$ to give the corresponding bis-imido ester complexes **16** and **17**, according to equation (7). The IR absorption from the X-sensitive mode of the C_6X_5 group reveals the *cis* nature of **16** and **17**, and the bands at *ca.* 3350 and 1630 cm^{-1} provide evidence for the NH and C=N groups of the imido ester.[35] Both compounds behave as non-electrolytes in acetone solution. Since the imido ester ligand can adopt either the *E* or *Z* conformation, complexes **16** and **17** might be expected to exist as *EE*, *EZ*, or *ZZ* isomers. The ^1H (and ^{19}F for **16**) NMR patterns exhibited by both complexes (Table 2) rule out the *EZ* isomer, and the positions of the OCH_3 and Ph resonances indicate[34] that the *EE* conformation (Scheme 1) should be assigned to **16** and **17**.

$$cis\text{-}[Pt(C_6X_5)_2(PhCN)_2] + 2\,MeOH \longrightarrow [Pt(C_6X_5)_2\{HN{=}C(OMe)Ph\}_2] \qquad (7)$$

$$X = F\ \mathbf{16}\ \text{or Cl}\ \mathbf{17}$$

Experimental

Carbon, H and N analyses were carried out with a Perkin-Elmer 240 C microanalyser. Decomposition temperatures were determined on a Mettler TG-50 thermobalance with a heating rate of 10 °C min^{-1}. Conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Philips PW 9501/01 conductimeter. The spectroscopic instruments used were a Perkin-Elmer model 1430 for IR and a Bruker model AC 200E (^1H) or Varian model FT 80A (^{19}F) spectrometer for NMR spectra, but the NMR spectra of complexes **13** and **15** were recorded with a Varian Unity 300 spectrometer. Mass spectra were measured on a Hewlett-Packard 5993 C instrument at 70 eV (*ca.* 1.12×10^{-17} J).

The precursors $[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2]$ were prepared as described in the literature.[8,9] Solvents were routinely dried by standard techniques before use.

Preparation of Complexes.—$[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (X = F **1** *or* Cl **2**). A 20% solution of $NBu_4OH(aq)$ (0.350 mmol) was added to an acetone (8 cm^3) solution of $[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2]$ (0.175 mmol). After stirring at room temperature for 30 min the solution was concentrated under reduced pressure until a white solid began to precipitate. Addition of a small amount of water caused complete precipitation of white crystals, which were collected by filtration, washed with water and air-dried.

$[NBu_4][Pt(C_6X_5)_2(L\text{–}L)]$ (X = F, L–L = acac **3**, bzac **4**, *or* quin **5**; X = Cl, L–L = acac **6**, bzac **7**, *or* quin **8**). The ligand HL–L (0.126 mmol) was added to a solution of $[NBu_4]_2[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (0.063 mmol) in acetone (18 cm^3), boiled under reflux for 6 h, then concentrated under reduced pressure. On addition of methanol–water the complexes **3**–**8** precipitated and were filtered off and air-dried.

cis-$[Pt(C_6X_5)_2(PhCN)_2]$ (X = F **9** *or* Cl **10**). A freshly prepared solution of $MgBr(C_6F_5)$ [from Mg (0.183 g, 7.52 mmol) and C_6F_5Br (7.52 mmol) in tetrahydrofuran (thf) (10 cm^3)] was added to $PtCl_2$ (0.5 g, 1.88 mmol) and the mixture boiled under reflux under a nitrogen atmosphere for 4 h. After cooling at room temperature, the solvent was removed under vacuum and the residue extracted with acetone. The resulting solution was filtered through a chromatography column containing magnesium sulfate and silica gel. The solution was taken to dryness to give an oily residue which was treated with diethyl ether (20 cm^3), CH_2Cl_2 (20 cm^3) and benzonitrile (0.388 g, 3.76 mmol). The solution was stirred for 30 min and filtered through magnesium sulfate and silica gel to give a yellow solution, from which most of the solvent was removed under vacuum. Addition of hexane resulted in the precipitation of white solid **9** which was filtered off and air-dried (yield *ca.* 47%).

Compounds **9** and **10** were alternatively prepared from the corresponding hydroxo-complexes. In separate experiments **1** or **2** (0.42 mmol) was added to a solution of 50% $HBF_4(aq)$ (1.68 mmol for **9** or 4.2 mmol for **10**) in thf (12 cm^3). After stirring for 5 min, benzonitrile (1.68 mmol for **9** or 8.4 mmol for **10**) was added and the solution stirred for 30 min. The solvent was then evaporated under vacuum and the residue treated with ethanol (for **9**) or diethyl ether (for **10**) whereupon white crystals of **9** or **10** were formed. They were removed by filtration and air-dried. The yield given in Table 1 for **9** is based on this method.

cis-[$Pt(C_6X_5)_2(NH_2Ph)_2$] (X = F **11** *or* Cl **12**). Aniline (0.436 mmol) was added to a dichloromethane (6 cm^3) solution of *cis*-[$Pt(C_6X_5)_2(PhCN)_2$] (0.109 mmol). After refluxing for 2.5 h, the solution was concentrated under vacuum and addition of hexane resulted in the precipitation of white crystals of complex **11** or **12**, which were filtered off and air-dried.

[NBu_4][$Pt(C_6X_5)_2(HNOCPh)(H_2O)$] (X = F **13** *or* Cl **14**). A 20% solution of NBu_4OH(aq) (0.204 mmol) was added to a solution of *cis*-[$Pt(C_6X_5)_2(PhCN)_2$] (0.204 mmol) in acetone (6 cm^3). After stirring for 30 min, the solution was concentrated under reduced pressure. Addition of water caused the precipitation of a white solid which was recrystallized from $CHCl_3$–hexane.

[NBu_4]$_2$[{$Pt(C_6F_5)_2(\mu$-HNOCPh)}$_2$] **15**. This yellow compound was readily formed on heating at *ca.* 100 °C a sample of complex **13**.

cis-[$Pt(C_6X_5)_2${HNC(OMe)Ph}$_2$] (X = F **16** *or* Cl **17**). A 20% solution of NBu_4OH(aq) (0.167 mmol) was added to a MeOH (8 cm^3) solution of *cis*-[$Pt(C_6X_5)_2(PhCN)_2$] (0.167 mmol). After stirring for 30 min the solution was concentrated under reduced pressure until the formation of a white precipitate of the required complex, which was filtered off, washed with water and air-dried.

The individual yields of the complexes are listed in Table 1.

Crystal Structure Determination of [NBu_4]$_2$[{$Pt(C_6F_5)_2(\mu$-OH)}$_2$].—*Crystal data:* $C_{56}H_{74}F_{20}N_2O_2Pt_2$, $M = 1577$, rectangular prism (0.40 × 0.20 × 0.10 mm), monoclinic, space group $P2_1/c$, unit-cell determination by least-squares fit from 25 reflections ($\theta < 20°$), $a = 12.593(1)$, $b = 12.965(4)$, $c = 19.381(1)$ Å, $\beta = 104.47°$, $U = 3064(1)$ Å^3, $Z = 2$, $D_c = 1.7107$ g cm^{-3}, $F(000) = 1552$, $\mu = 47.07$ cm^{-1}.

5950 Reflections up to $\theta = 25°$ (5337 independent) were measured on a CAD4 diffractometer with graphite-monochromated Mo-Kα radiation and using the ω–2θ scan mode. 2278 Reflections were considered as observed [$I > 3\sigma(I)$]. Two standard reflections were tested every 60 min without significant variation. Scattering factors and anomalous dispersion coefficients were taken from the literature.[36] The heavy-atom (Pt) method and the DIRDIF[37] system was followed by normal Fourier synthesis. Most H atoms were found on a difference map, others were located at the calculated positions.[38] Full-matrix least-squares refinement,[39] 370 variables, 382 degrees of freedom, ratio of freedom 2.0, non-H atoms anisotropic, H atoms isotropic. Least-squares weights were applied so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$ with $w = k/(\sigma_1{}^2\sigma_2{}^2)$ where $k = 1$, $\sigma_1 = f(F_o)$ and $\sigma_2 = g(\sin\theta/\lambda)$.[40] Final R and R' were 0.049 and 0.056 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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