New Methoxo-, Hydroxo- and Pyrazolate-bridged Platinum(II) Complexes. Crystal Structure of $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-dmpz})]$ (dmpz = 3,5-dimethylpyrazolate)†

Gregorio López,[*,a] **José Ruiz,**[a] **Gabriel García,**[a] **Consuelo Vicente,**[a] **Venancio Rodríguez,**[a] **Gregorio Sánchez,**[a] **Juan A. Hermoso**[b] **and Martín Martínez-Ripoll**[b]
[a] *Departamento de Química Inorgánica, Universidad de Murcia, 30071-Murcia, Spain*
[b] *Instituto de Química-Física 'Rocasolano'-CSIC, Serrano 119, 28006-Madrid, Spain*

The hydroxo complex $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ reacts with azoles (1:1 molar ratio) in benzene to give the double bridged complexes $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L\text{-}L)]^{2-}$ [L–L = pyrazolate (pz) **1**, 3,5-dimethylpyrazolate (dmpz) **2**, 3-methylpyrazolate (mpz) **3** or indazolate (indz) **4**]. When the same reaction is carried out in methanol with the reactants in 1:2 molar ratio the corresponding di-μ-azolate derivatives $[\{Pt(C_6F_5)_2(\mu\text{-}L\text{-}L)\}_2]^{2-}$ [L–L = pz **5**, dmpz **6**, mpz **7** or indz **8**] are obtained. On treatment of $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with methanol the di-μ-methoxo complex $[\{Pt(C_6F_5)_2(\mu\text{-}OMe)\}_2]^{2-}$ **9** was obtained. The di-μ-azolate complexes **5**–**8** can be alternatively prepared by treatment of **9** with the respective azoles (1:2 molar ratio) in methanol. Reaction of complex **1** with methanol leads to the formation of $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OMe)(\mu\text{-}pz)]^{2-}$ **10**. All the complexes have been isolated as the $[NBu_4]^+$ salts. Spectroscopic (IR, ^1H and ^{19}F NMR) data have been used for structural assignments, and an X-ray structure determination carried out for $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-dmpz})]$ has established the binuclear nature of the anion. The structure was solved and refined to $R = 0.057$ and $R' = 0.089$ based on 10 057 observed reflections. The Pt atoms are four-co-ordinated, Pt(1)–O 2.113(7), Pt(1)–N(1) 2.04(1), Pt(1)–C(10) 2.02(1), Pt(1)–C(20) 1.96(2), Pt(2)–O 2.077(9), Pt(2)–N(2) 2.075(9), Pt(2)–C(30) 1.97(2), Pt(2)–C(40) 2.00(1) Å, and show deviations from a square-planar arrangement towards a tetrahedral disposition.

Binuclear anionic hydroxo complexes of the type $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ [M = Ni (R = C_6F_5),[1] Pd (R = C_6F_5,[2] C_6Cl_5[3] or $C_6H_2F_3$-2,4,6[4]) or Pt (R = C_6F_5)][5] have recently been reported. As expected,[6] their chemical behaviour towards some protic electrophiles is consistent with the high-field proton resonances of the OH bridges in these complexes, and the nickel complex has been used as a basic catalyst in the cyclotrimerization of malononitrile.[7] σ-Ligand metathesis reactions of the type represented by equation (1) have been used as a

$$M\text{-}OH + H\text{-}X \longrightarrow M\text{-}X + H_2O \qquad (1)$$

synthetic strategy and relevant examples can be found in a review by Bryndza and Tam.[6] The result is the formation of new M–X bonds with the concomitant release of water. With $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ as starting material, mononuclear $[MR_2(L\text{-}L)]^-$ (M = Pd or Pt) or binuclear $[\{PdR_2(\mu\text{-}L\text{-}L)\}_2]^{2-}$ complexes have been obtained depending on the endo- or exo-bidentate nature of the $(L\text{-}L)^-$ ligand.[2–5] In this paper we show that the reaction of $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with some azoles is a convenient route for the preparation of the complexes $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-azolate})]^{2-}$ and $[\{Pt(C_6F_5)_2(\mu\text{-azolate})\}_2]^{2-}$.

Although late transition-metal alkoxides are regarded as important intermediates in various transition-metal catalysed synthetic organic reactions, examples of isolated late transition-metal alkoxides are still limited.[6,8–13] The reactions of both $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ and $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ with methanol have been studied in order to obtain methoxo-bridged platinum complexes.

Results and Discussion

When the hydroxo-bridged complex $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ was treated with azoles, HL–L, it yielded the double-bridged complexes $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L\text{-}L)]^{2-}$ [L–L = pyrazolate (pz) **1**, 3,5-dimethylpyrazolate (dmpz) **2**, 3-methylpyrazolate (mpz) **3**, or indazolate (indz) **4**] or $[\{Pt(C_6F_5)_2(\mu\text{-}L\text{-}L)\}_2]^{2-}$ (L–L = pz **5**, dmpz **6**, mpz **7** or indz **8**). Scheme 1 summarizes the above mentioned reactions. These reactions imply protonation of the hydroxo groups and replacement by μ-azolates, and they confirm the stability of azolates as exo-bidentate ligands.[14,15] Similar reactions carried out with the palladium analogue $[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ in dichloromethane led to the isolation of di-μ-azolate palladium complexes for a palladium hydroxo complex : azole ratio = 1:2, but for a 1:1 molar ratio 1:1 mixtures of the μ-hydroxo-μ-azolate and di-μ-azolate complexes were obtained in solution, which we were not able to separate. For platinum mixed μ-hydroxo-μ-azolate complexes are obtained when the reaction is carried out in benzene in 1:1 molar ratio or with excess of azole. However, di-μ-azolate complexes are obtained in methanol using a 1:2 molar ratio of reactants. Moreover, when the mixed μ-hydroxo-μ-azolates are treated with azole in methanol the corresponding di-μ-azolate complexes are formed.

The above-mentioned results suggested the possible formation of an intermediate methoxo complex for which the presence of the electronegative C_6F_5 group should enhance the π stabilization of the Pt–OMe bond.[16] Some methoxo complexes of rhodium and iridium have been obtained by the reaction of the corresponding hydroxo complex with methanol.[17] In fact, the di-μ-methoxo complex **9** was isolated when the hydroxo complex was treated with methanol (Scheme 1). On the other hand, treatment of complex **1** with methanol leads to a 2:1 molar mixture of the new complex $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OMe)(\mu\text{-}pz)]$ **10** and unreacted **1**.

All the isolated complexes show the characteristic infrared

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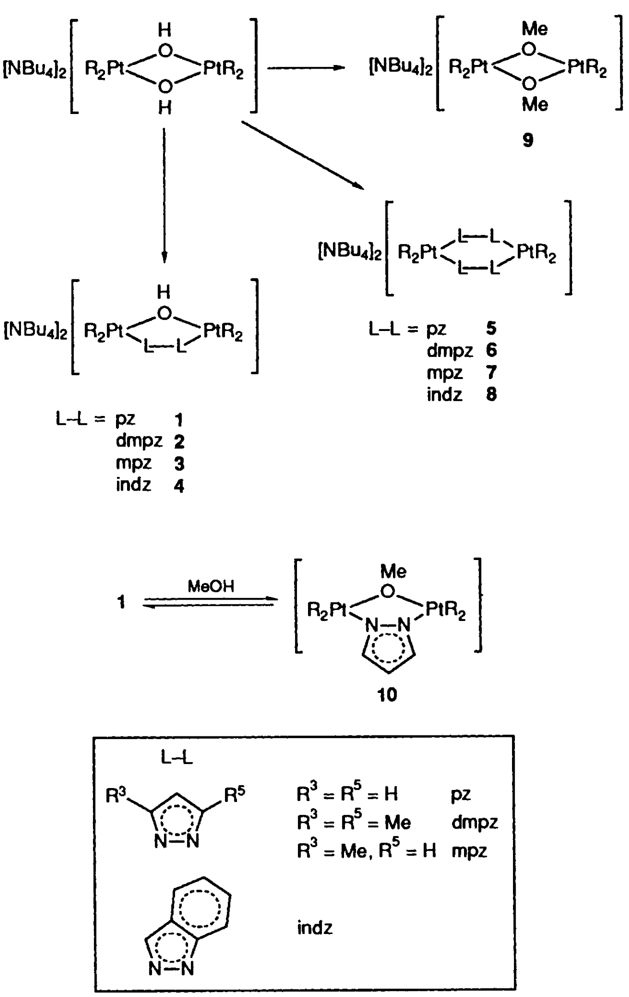
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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] X-sensitive	ν(OH)
1	68	257	43.6 (43.5)	5.0 (4.7)	3.6 (3.4)	177	800, 790	3620
2	66	259	44.4 (44.3)	5.3 (4.9)	3.1 (3.4)	163	800, 790	3600
3	80	262	44.1 (43.9)	5.1 (4.8)	3.6 (3.4)	180	800, 785	3610
4	71	260	45.0 (45.1)	4.6 (4.7)	3.6 (3.3)	160	800, 790	3610
5	75	298	44.5 (44.4)	4.8 (4.7)	4.9 (5.9)	*e*	795, 785	
6	63	295	46.0 (45.7)	5.3 (5.0)	5.1 (4.9)	*e*	795, 785	
7	69	298	45.3 (45.1)	5.0 (4.9)	4.9 (4.9)	*e*	795, 785	
8	67	304	47.9 (47.3)	4.9 (4.7)	4.7 (4.7)	*e*	795, 785	
9	90	213	43.0 (43.4)	5.0 (4.9)	1.3 (1.7)	*e*	800, 790	

[a] Decomposition temperatures. [b] Calculated values in parentheses. [c] In ohm^{-1} cm^2 mol^{-1}. [d] In Nujol mulls (cm^{-1}). [e] Dissociated in acetone.



Scheme 1 Synthesis of the platinum complexes, R = C_6F_5

absorptions of the pentafluorophenyl group[18] at *ca.* 1630m, 1495vs, 1460vs, 1050s, 950vs and 800s cm^{-1}. The absorption at 800 cm^{-1}, which is related to the so-called 'X-sensitive mode' in C_6F_5-containing molecules, is observed as a split band (Table 1) suggesting that the $Pt(C_6F_5)_2$ moiety has *cis* geometry.[19]

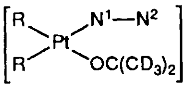
The ^{1}H NMR spectra of complexes **1**–**8** are consistent with the presence of bridging azolate ligands[2,17,20,21] and one set alone is observed for the protons of the heterocyclic ligand. We have been unable to locate the hydroxo resonance (at δ −1.21 in $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$) in the ^{1}H spectra of complexes **1**–**4**, but an infrared absorption at *ca.* 3600 cm^{-1} supports the presence of OH groups in these complexes. Both the high wavenumber and the sharpness of this band suggest that the OH bridge is not involved in hydrogen bonding.

The ^{19}F NMR spectra of **1** and **2** show two signals of the same intensity in the *o*-F region, in accordance with the presence of two pairs of equivalent C_6F_5 groups freely rotating around the Pt–C bonds. Complexes **3** and **4** should give rise to four resonance signals in 2:2:2:2 ratio in the *o*-F region due to the asymmetric nature of mpz and indz, but three signals of ratio 2:2:4 are instead observed (Table 2) indicating that two signals are coincident, probably those derived from the C_6F_5 groups *trans* to the OH bridge. In accordance with the proposed formulae, complexes **1**–**4** behave as 2:1 electrolytes[22] in acetone solution (Table 1). The ^{19}F NMR spectra of a $CDCl_3$ solution of complex **5** shows the expected single signal for the *o*-F atoms (Table 2), but two signals each of relative intensity 4 [−113.6 (4 F_o, J_{PtF_o} 480 Hz), −118.4 (4 F_o, J_{PtF_o} 508 Hz), −168.0 (4 F_p + 8 F_m)] are observed in $(CD_3)_2CO$ solution, which are attributed to the dissociation product $[Pt(C_6F_5)_2(pz)\{(CD_3)_2CO\}]^-$. However, the ^{1}H NMR spectrum in $(CD_3)_2CO$ is the same as in $CDCl_3$ giving no evidence of monodentate pz.[23] The existence of rapid pyrazolate exchange (on the NMR time-scale) between molecules containing monodentate pz could account for the experimental result, but both the ^{1}H and ^{19}F NMR spectra in $(CD_3)_2CO$ recorded in the temperature range −70 to +50 °C gave no indication for the existence of such a dynamic behaviour. Similar dissociation processes have been observed for nickel–azolate systems[24] and the existence of a dynamic process involving mpz exchange (not detected by ^{1}H NMR spectroscopy) has been reported[2] for $[\{Pd(C_6F_5)_2(\mu\text{-}mpz)\}_2]^{2-}$. The insolubility of complex **6** in $CDCl_3$ prevented us from obtaining NMR data for the undissociated species. In $(CD_3)_2CO$ only one signal is observed for the *o*-F atoms of the C_6F_5 rings but its position seems to be consistent with the presence of a neutral complex resulting from dissociation into $2[Pt(C_6F_5)_2\{(CD_3)_2CO\}_2]$ + 2 dmpz$^-$. It should be noted that in this case the H^4 signal of dmpz is seen as a rather broad peak. Complexes **7** and **8** are also insoluble in $CDCl_3$ and the

Table 2 NMR data (J in Hz) for the platinum complexes

Complex	^1H δ($SiMe_4$)[a]	^{19}F δ($CFCl_3$)
1[b]	6.78 (d, 4 H, H^3,H^5, J 2.1) 5.74 (t, 1 H, H^4, J 2.1)	−118.9 (4 F_o, J_{PtF_o} 535) −119.8 (4 F_o, J_{PtF_o} 466) −165.6 (2 F_p) −166.7 (2 F_p + 8 F_m)
2[b]	5.45 (s, 1 H, H^4) 1.50 (s, 6 H, CH_3)	−118.7 (4 F_o, J_{PtF_o} 530) −119.4 (4 F_o, J_{PtF_o} 480) −166.0 (2 F_p) −167.6 (2 F_p + 2 F_m) −168.5 (6 F_m)
3[c]	6.79 (d, 1 H, H^5, J 1.7) 5.62 (d, 1 H, H^4, J 1.7) 1.52 (s, 3 H, CH_3)	−118.6 (2 F_o) −119.0 (2 F_o) −119.6 (4 F_o) −165.4 (1 F_p) −165.8 (1 F_p) −167.5 (2 F_p + 8 F_m)
4[b]	7.47 (s, 1 H) 7.38 (d, 1 H, J 9.1) 6.72 (m, 2 H) 6.36 (d, 1 H, J 9.1)	−118.6 (2 F_o) −118.9 (2 F_o) −119.7 (4 F_o) −165.2 (2 F_p) −166.1 (1 F_p) −167.0 (1 F_p + 8 F_m)
5[b]	7.11 (d, 4 H, H^3, H^5, J 1.8) 5.77 (t, 2 H, H^4, J 1.8)	−117.6 (8 F_o, J_{PtF_o} 508) −167.2 (4 F_p + 8 F_m)
6[c]	5.29 (s, 2 H, H^4) 2.10 (s, 12 H, CH_3)	−111.5 (8 F_o, J_{PtF_o} 480) −170.0 (4 F_p + 8 F_m)
7[c]	7.50 (d, 2 H, H^5, J 1.6) 5.56 (d, 2 H, H^4, J 1.6) 1.83 (s, 6 H, CH_3)	−111.4 (2 F_o, J_{PtF_o} 508) −114.3 (2 F_o, J_{PtF_o} 395) −117.4 (2 F_o, J_{PtF_o} 564) −118.0 (2 F_o, J_{PtF_o} 452) −168.3 (2 F_p) −169.1 (2 F_p) −169.5 (8 F_m)
8[c]	8.25 (s, 2 H) 7.39 (d, 4 H, J 7.8) 6.75 (pseudo t, 2 H, J 7.5) 6.58 (pseudo t, 2 H, J 7.4)	−111.8 (2 F_o, J_{PtF_o} 452) −114.4 (2 F_o, J_{PtF_o} 423) −117.6 (2 F_o, J_{PtF_o} 564) −118.2 (2 F_o, J_{PtF_o} 400) −168.5 (4 F_p + 8 F_m)
9[b]	2.82 (s, 6 H, OCH_3)	−119.7 (8 F_o, J_{PtF_o} 531) −166.8 (4 F_p) −168.0 (8 F_m)
10[b]	6.66 (d, 2 H, H^3, H^5, J 2.1) 5.68 (t, 1 H, H^4, J 2.1) 3.16 (s, 3 H, OCH_3)	−118.5 (4 F_o) −118.8 (4 F_o) −166.2 (2 F_p) −167.2 (2 F_p + 8 F_m)

[a] Additional peaks of $[NBu_4]^+$ are found at δ *ca.* 3.7 (t, NCH_2), 1.8 (m, NCH_2CH_2), 1.5 (m, CH_2CH_3) and 1.0 (t, CH_3), the relative intensities being 16:16:16:24 respectively. [b] In $CDCl_3$. [c] In $(CD_3)_2CO$.



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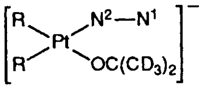

II

^{19}F NMR spectra of $(CD_3)_2CO$ solutions show four peaks for the *o*-F atoms which may be assigned to the structures **I** and **II** resulting from the dissociation of **7** and **8**; both structures are different because of the asymmetry of the mpz and indz groups (N^1–N^2), but again only one set of proton signals are observed in the ^1H NMR spectra of both compounds. Complex **9** provides in $CDCl_3$ solution the expected ^1H and ^{19}F NMR patterns for its symmetric binuclear structure. The NMR data given in Table 2 for complex **10** were obtained from the ^1H and ^{19}F spectra of the $CDCl_3$ solution containing a mixture of complexes **1** and **10**. The relative intensities of the signals indicated that **1** and **10** were present in a 1:2 molar ratio.

Although binuclear species involving di-μ-azolate bridges usually exhibit a boat conformation for the $M(NN)_2M$ six-membered central ring, for M(μ-X)(μ-azolate)M complexes both planar (*e.g.*, $[\{PtCl(C_2H_4)\}_2(\mu\text{-}Cl)(\mu\text{-}pz)]$)[25] and puckered (*e.g.*, $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]$)[24] central five-membered rings have been found. The X-ray structure determination carried out for complex **2** shows that the PtO(NN)Pt five-membered central ring is not planar. The asymmetric unit consists of one binuclear $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]^{2-}$ anion (Fig. 1) and two $[NBu_4]^+$ cations, crystallized with one benzene molecule and held together by electrostatic interactions. Positional parameters are given in Table 3 and selected geometrical features in Tables 4 and 5.

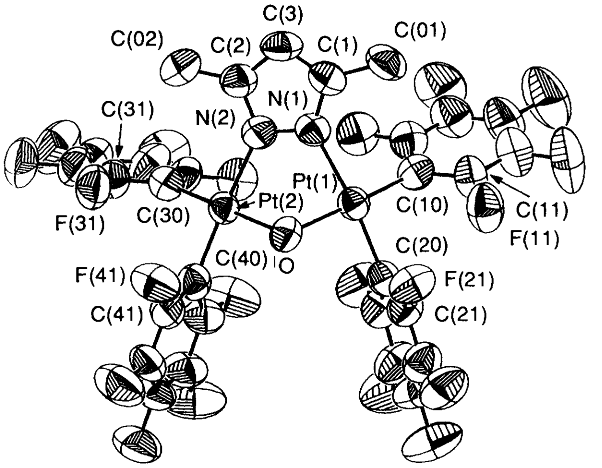

Fig. 1 An ORTEP drawing[26] of the $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]^{2-}$ anion

Each Pt atom is co-ordinated to four atoms which lie on a plane slightly distorted towards a tetrahedral arrangement (see Table 6). The central ring is roughly in an envelope configuration with the O atom at the flap above the plane defined by the other four atoms [1.25(1) Å]. The dmpz group deviates slightly from planarity in terms of the attained accuracy $[\Sigma(d/s)^2 = 8.45$ for the atoms defining the plane *vs.* $\chi^2 = 5.99$ for two degrees of freedom, where d is the atomic deviation from the least-squares plane, and s the standard deviation of d].

The four pentafluorophenyl rings bonded to the Pt atoms are planar and rotated from each other by 81.1(5)° [Pt(1)] and 90.3(5)° [Pt(2)]. The C_6F_5 rings show distortions in their endocyclic bond angles, especially at the *ipso*-carbon [109(1)–116(1)°] and at the two adjacent bond angles [123(2)–130(1)°]. This type of distortion has been observed in other substituted benzene derivatives[27] and for pentafluorophenyl groups in metal complexes.[28]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer in the range 4000–200 cm^{-1} using Nujol mulls between polyethylene sheets. The C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyser. Proton and ^{19}F NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solutions with a Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as standards respectively. Conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Philips PW 9501/01 conductimeter. Solvents were dried and distilled before use. The hydroxoplatinum complex $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ was prepared by a procedure described elsewhere.[5] Analytical and significant IR data, yields, decomposition temperatures and molar conductivities for the new complexes are in Table 1, ^1H and ^{19}F NMR data in Table 2.

Preparation of Complexes **1**–**4**.—The appropriate azole HL–L (0.063 mmol) was added to a solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.063 mmol) in benzene (4 cm^3). The resulting solution was boiled under reflux for 6–7 h and then concentrated under reduced pressure. On addition of hexane complexes **1**–**4** precipitated as white solids which were filtered off and air-dried.

Table 3 Atomic parameters for $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$

Atom	*x*	*y*	*z*
Pt(1)	0.169 41(2)	0.021 38(3)	−0.182 85(4)
O	0.195 8(3)	0.127 1(6)	−0.009 3(7)
N(1)	0.158 1(5)	0.150 2(8)	−0.237 3(9)
C(1)	0.116 8(6)	0.178 0(10)	−0.3210(10)
C(01)	0.074 0(7)	0.101 1(15)	−0.411 9(16)
C(3)	0.126 3(6)	0.280 4(11)	−0.307 0(13)
C(2)	0.172 2(6)	0.315 8(9)	−0.212 3(12)
C(02)	0.202 6(9)	0.421 2(10)	−0.159 4(15)
N(2)	0.189 5(4)	0.236 9(7)	−0.170 3(9)
Pt(2)	0.257 60(2)	0.214 01(3)	−0.042 53(4)
C(10)	0.147 3(6)	−0.079 9(10)	−0.349 2(12)
C(11)	0.190 2(4)	−0.094 2(10)	0.420 3(12)
F(11)	0.240 7(4)	−0.039 8(7)	−0.384 6(8)
C(12)	0.184 0(6)	−0.166 7(13)	−0.530 3(13)
F(12)	0.219 5(6)	−0.182 2(11)	−0.599 4(10)
C(13)	0.130 8(8)	−0.229 4(12)	−0.574 8(16)
F(13)	0.122 1(6)	−0.302 1(11)	−0.682 4(12)
C(14)	0.090 4(7)	−0.217 5(11)	−0.508 7(18)
F(14)	0.040 7(6)	−0.275 7(9)	−0.548 3(14)
C(15)	0.100 7(6)	−0.141 9(10)	−0.395 6(14)
F(15)	0.059 7(4)	−0.134 0(7)	−0.333 9(10)
C(20)	0.181 9(6)	−0.094 3(9)	−0.116 2(11)
C(21)	0.232 0(6)	−0.155 1(10)	−0.126 9(13)
F(21)	0.268 7(6)	−0.135 4(10)	−0.187 3(12)
C(22)	0.243 7(8)	−0.237 3(12)	−0.082 8(16)
F(22)	0.289 0(7)	−0.292 5(11)	−0.097 8(13)
C(23)	0.2072 2(8)	−0.263 0(11)	−0.017 6(16)
F(23)	0.217 6(7)	−0.341 5(8)	0.026 3(12)
C(24)	0.160 9(7)	−0.204 9(12)	−0.002 2(17)
F(24)	0.124 5(6)	−0.228 6(11)	0.059 6(15)
C(25)	0.152 0(5)	−0.125 9(10)	−0.049 9(14)
F(25)	0.102 3(4)	−0.073 2(9)	−0.029 8(12)
C(30)	0.314 8(5)	0.294 4(10)	−0.080 9(11)
C(31)	0.349 8(7)	0.377 0(11)	0.000 3(14)
F(31)	0.347 7(5)	0.406 0(8)	0.119 1(9)
C(32)	0.387 6(9)	0.437 5(14)	−0.029 4(20)
F(32)	0.420 6(8)	0.515 8(12)	0.057 1(15)
C(33)	0.393 0(10)	0.414 3(16)	−0.145 4(21)
F(33)	0.430 2(9)	0.471 5(14)	−0.174 6(18)
C(34)	0.361 6(9)	0.333 7(15)	−0.226 6(16)
F(34)	0.366 3(7)	0.308 5(12)	−0.342 6(11)
C(35)	0.323 2(6)	0.274 4(11)	−0.197 6(14)
F(35)	0.293 3(5)	0.195 0(8)	−0.284 8(7)
C(40)	0.317 4(5)	0.176 2(8)	0.079 2(10)
C(41)	0.320 8(6)	0.213 5(11)	0.201 5(12)
F(41)	0.287 4(4)	0.287 6(8)	0.244 3(8)
C(42)	0.359 3(7)	0.181 0(14)	0.284 8(13)
F(42)	0.360 8(6)	0.223 7(11)	0.403 1(8)
C(43)	0.395 2(7)	0.106 4(19)	0.251 4(18)
F(43)	0.431 3(6)	0.073 5(15)	0.330 8(13)
C(44)	0.394 1(7)	0.067 2(16)	0.132 0(18)
F(44)	0.430 8(7)	−0.005 8(15)	0.093 8(15)
C(45)	0.355 9(7)	0.102 6(13)	0.048 6(14)
F(45)	0.359 2(6)	0.059 0(9)	−0.066 9(9)
N(3)	0.387 8(5)	0.777 5(13)	−0.381 6(13)
C(50)	0.379 8(7)	0.894 3(16)	−0.345 6(19)
C(51)	0.431 0(9)	0.962 3(21)	−0.343 3(24)
C(52)	0.418 2(13)	1.069 8(22)	−0.333 1(37)
C(53)	0.464 7(14)	1.133 6(25)	−0.345 9(42)
C(60)	0.402 2(8)	0.741 4(20)	−0.505 34(19)
C(61)	0.364 2(11)	0.767 2(25)	−0.601 7(23)
C(62)	0.383 8(16)	0.725 1(40)	−0.718 2(28)
C(63)	0.350 7(35)	0.769 9(67)	−0.809 1(45)
C(70)	0.436 0(9)	0.750 4(20)	−0.296 4(24)
C(71)	0.433 2(14)	0.774 6(30)	−0.169 8(26)
C(72)	0.486 6(25)	0.739 1(40)	−0.102 6(39)
C(73)	0.501 5(25)	0.765 9(51)	0.005 4(51)
C(80)	0.332 1(7)	0.726 6(18)	−0.383 3(19)
C(81)	0.327 5(10)	0.608 9(21)	−0.411 2(19)
C(82)	0.261 1(15)	0.579 5(27)	−0.414 0(27)
C(83)	0.255 5(20)	0.464 4(47)	−0.435 5(37)
N(4)	0.084 9(5)	0.269 9(8)	0.178 1(11)
C(90)	0.128 2(5)	0.322 7(9)	0.134 5(11)
C(91)	0.165 7(6)	0.412 7(10)	0.226 8(13)
C(92)	0.203 4(6)	0.456 4(11)	0.162 8(15)
C(93)	0.245 7(9)	0.540 6(13)	0.246 8(20)
C(100)	0.039 1(7)	0.348 5(11)	0.209 7(16)
C(101)	−0.010 1(9)	0.315 1(17)	0.252 3(23)
C(102)	−0.050 7(11)	0.403 7(31)	0.280 9(36)
C(103)	−0.100 2(19)	0.392 8(34)	0.330 5(39)
C(110)	0.114 5(8)	0.241 5(14)	0.290 9(16)
C(111)	0.159 0(7)	0.168 8(14)	0.274 7(17)
C(112)	0.187 7(11)	0.148 3(25)	0.391 5(25)
C(113)	0.236 0(11)	0.088 6(45)	0.392 4(44)
C(120)	0.058 6(7)	0.172 9(11)	0.079 3(16)
C(121)	0.023 6(7)	0.186 9(11)	−0.035 7(16)
C(122)	0.004 9(7)	0.085 0(12)	−0.127 5(17)
C(123)	−0.037 0(10)	0.092 0(19)	−0.237 5(20)
C(200)	0.995 0(11)	0.420 8(13)	0.895 2(18)
C(201)	1.045 8(9)	0.476 5(18)	0.951 1(23)
C(202)	0.949 4(8)	0.446 0(13)	0.948 0(22)
C(210)	0.489 9(16)	0.510 9(23)	0.390 1(26)
C(211)	0.535 8(15)	0.558 8(22)	0.470 4(39)
C(212)	0.452 5(14)	0.450 2(24)	0.418 0(37)

Preparation of Complexes **5**–**8**.—The corresponding azole (0.186 mmol) was added to a methanol (10 cm^3) solution of the di-μ-hydroxo complex (0.093 mmol). The solution was boiled under reflux for *ca.* 7 h, during which time the white complexes **5**–**8** precipitated spontaneously. They were collected by filtration and air-dried. Complexes **5**–**8** were also prepared in lower yields either by treating the corresponding complexes **1**–**4** with azole HL–L (1:1 molar ratio) in methanol followed by precipitation with hexane or by the reaction of complex **9** with the corresponding azole (1:2 molar ratio) in methanol and subsequent precipitation with hexane.

Preparation of Complex **9**.—A solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.126 mmol) in methanol (6 cm^3) was stirred at room temperature. Complex **9** was obtained as a white solid when the solution was vacuum-evaporated to dryness.

Reaction of **1** *with Methanol*.—A solution of complex **1** (0.093 mmol) in methanol (8 cm^3) was stirred at room temperature for 7 h. Complete evaporation to dryness under reduced pressure afforded a white solid, which was identified by NMR spectroscopy as a mixture of complex **1** and the new complex **10**.

X-Ray Structure Determination of Complex **2**.—Crystallographic data and other parameters are given in Table 7. Heavy-atom (Pt) method followed by normal Fourier synthesis. Full-matrix least-squares refinement. Some of the H atoms were located on a difference synthesis map, others were fixed at the expected positions.[33] All non-hydrogen atoms were refined anisotropically. Most H atoms were refined isotropically but the thermal parameters of some of them were kept fixed.

In the final cycles of refinement weighting schemes[34] 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 $w = k/(\sigma_1{}^2 \cdot \sigma_2{}^2)$ where $k = 1$, $\sigma_1 = f(F_o)$ and $\sigma_2{}^2 = g(\sin\theta/\lambda)$.[26]

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

Table 4 Selected bond lengths (Å) for $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$

Pt(1)–O	2.113(7)	C(22)–F(22)	1.32(3)
Pt(1)–N(1)	2.04(1)	C(22)–C(23)	1.40(3)
Pt(1)–C(10)	2.02(1)	C(23)–F(23)	1.33(2)
Pt(1)–C(20)	1.96(2)	C(23)–C(24)	1.36(3)
Pt(2)–O	2.077(9)	C(24)–F(24)	1.36(3)
Pt(2)–N(2)	2.075(9)	C(24)–C(25)	1.36(3)
Pt(2)–C(30)	1.97(2)	C(25)–F(25)	1.41(2)
Pt(2)–C(40)	2.00(1)	C(30)–C(31)	1.39(2)
N(1)–C(1)	1.38(2)	C(30)–C(35)	1.41(2)
N(1)–N(2)	1.34(1)	C(31)–F(31)	1.38(2)
C(1)–C(01)	1.47(2)	C(31)–C(32)	1.40(3)
C(1)–C(3)	1.37(2)	C(32)–F(32)	1.35(2)
C(3)–C(2)	1.37(2)	C(32)–C(33)	1.37(4)
C(2)–C(02)	1.50(2)	C(33)–F(33)	1.35(4)
C(2)–N(2)	1.35(2)	C(33)–C(34)	1.33(3)
C(10)–C(11)	1.44(2)	C(34)–F(34)	1.36(2)
C(10)–C(15)	1.32(2)	C(34)–C(35)	1.39(3)
C(11)–F(11)	1.34(1)	C(35)–F(35)	1.34(2)
C(11)–C(12)	1.37(2)	C(40)–C(41)	1.39(2)
C(12)–F(12)	1.28(2)	C(40)–C(45)	1.38(2)
C(12)–C(13)	1.44(2)	C(41)–F(41)	1.33(2)
C(13)–F(13)	1.35(2)	C(41)–C(42)	1.38(2)
C(13)–C(14)	1.36(3)	C(42)–F(42)	1.36(2)
C(14)–F(14)	1.34(2)	C(42)–C(43)	1.34(3)
C(14)–C(15)	1.41(2)	C(43)–F(43)	1.33(3)
C(15)–F(15)	1.33(2)	C(43)–C(44)	1.37(3)
C(20)–C(21)	1.46(2)	C(44)–F(44)	1.36(3)
C(20)–C(25)	1.34(2)	C(44)–C(45)	1.40(3)
C(21)–F(21)	1.33(2)	C(45)–F(45)	1.35(2)
C(21)–C(22)	1.38(3)		

Table 5 Selected bond angles (°) for $[NBu_4]_2[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$

C(10)–Pt(1)–C(20)	89.8(6)	C(21)–C(20)–C(25)	109(1)
N(1)–Pt(1)–C(10)	95.1(5)	C(20)–C(21)–C(22)	125(1)
O–Pt(1)–C(20)	90.1(4)	C(20)–C(21)–F(21)	120(1)
O–Pt(1)–N(1)	85.0(4)	C(21)–C(22)–C(23)	119(2)
Pt(1)–O–Pt(2)	98.4(3)	C(21)–C(22)–F(22)	122(2)
Pt(1)–N(1)–N(2)	118.5(8)	C(22)–C(23)–C(24)	117(2)
Pt(1)–N(1)–C(1)	134.1(9)	C(22)–C(23)–F(23)	121(2)
C(2)–N(2)–Pt(2)	135.7(9)	C(23)–C(24)–C(25)	120(2)
N(1)–N(2)–Pt(2)	113.6(8)	C(23)–C(24)–F(24)	119(2)
O–Pt(2)–N(2)	83.4(3)	C(20)–C(25)–C(24)	130(1)
N(2)–Pt(2)–C(30)	94.8(5)	C(24)–C(25)–F(25)	114(1)
O–Pt(2)–C(40)	89.9(4)		
C(30)–Pt(2)–C(40)	91.9(5)	C(31)–C(30)–C(35)	112(1)
		C(30)–C(31)–C(32)	125(2)
C(1)–N(1)–N(2)	106(1)	C(30)–C(31)–F(31)	120(1)
N(1)–C(1)–C(3)	109(1)	C(31)–C(32)–C(33)	120(2)
N(1)–C(1)–C(01)	122(1)	C(31)–C(32)–F(32)	120(2)
C(10)–C(1)–C(3)	129(1)	C(32)–C(33)–C(34)	118(2)
C(1)–C(3)–C(2)	106(1)	C(32)–C(33)–F(33)	120(2)
C(3)–C(2)–N(2)	108(1)	C(33)–C(34)–C(35)	122(2)
C(3)–C(2)–C(02)	130(1)	C(33)–C(34)–F(34)	119(2)
C(02)–C(2)–N(2)	122(1)	C(30)–C(35)–C(34)	123(2)
N(1)–N(2)–C(2)	110(1)	C(34)–C(35)–F(35)	118(1)
C(11)–C(10)–C(15)	116(1)	C(41)–C(40)–C(45)	113(1)
C(10)–C(11)–C(12)	124(1)	C(40)–C(41)–C(42)	124(1)
C(10)–C(11)–F(11)	124(1)	C(40)–C(41)–F(41)	120(1)
C(11)–C(12)–C(13)	116(1)	C(41)–C(42)–C(43)	121(2)
C(11)–C(12)–F(12)	127(2)	C(41)–C(42)–F(42)	120(2)
C(12)–C(13)–C(14)	121(2)	C(42)–C(43)–C(44)	118(2)
C(12)–C(13)–F(13)	119(2)	C(42)–C(43)–F(43)	121(2)
C(13)–C(14)–C(15)	119(2)	C(43)–C(44)–C(45)	121(2)
C(13)–C(14)–F(14)	122(2)	C(43)–C(44)–F(44)	120(2)
C(10)–C(15)–C(14)	124(2)	C(40)–C(45)–C(44)	123(2)
C(14)–C(15)–F(15)	117(1)	C(44)–C(45)–F(45)	115(2)

Table 6 Deviations from planarity (*d*) within the two platinum co-ordination spheres

	Plane 1				
Atom	Pt(1)	O	N(1)	C(10)	C(20)
d/Å	−0.0137(9)	0.026(8)	−0.02(1)	0.03(2)	−0.02(1)
	Plane 2				
Atom	Pt(2)	O	N(2)	C(30)	C(40)
d/Å	−0.0296(6)	−0.006(8)	0.02(1)	−0.00(1)	0.02(1)

Table 7 Crystal data and data collection parameters for $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$

Crystal data	
Formula	$C_{73}H_{92}F_{20}N_4OPt_2$
M	1811.70
Crystal habit	Rectangular prism
Crystal size (mm)	0.40 × 0.17 × 0.13
Symmetry	Triclinic, $P\bar{1}$
Unit cell determination	Least-squares fit from 25 reflections ($\theta < 30°$)
Unit cell dimensions	$a = 23.870(2)$, $b = 13.603(1)$, $c = 12.032(1)$ Å $\alpha = 107.61(1)$, $\beta = 102.41(1)$, $\gamma = 89.40(1)°$
U/Å^3, Z	3630.3(4), 2
D_c/g cm^{-3}, $F(000)$	1.6573, 1804
μ/cm^{-1}	80.23
Experimental data	
Technique	Four circle diffractometer: Philips PW1100 Bisecting geometry Graphite oriented monochromator: Cu-Kα radiation ω–2θ scans (λ = 1.5418 Å)
Total measurements	Up to 65°
Number of reflections:	
Measured	12 287
Independent	12 269
Observed	10 057 [$I > 3\sigma(I)$]
Standard reflections	2 every 90 min, no variation
Solution and refinement *	
Solution	Patterson functions and DIRDIF[29] system
Refinement	Least squares on F_o with 5 blocks
Parameters:	
Number of variables	842
Degrees of freedom	877
Ratio of freedom	2.0
Absorption correction[30]	
Minimum	0.835
Maximum	1.577
Mean	1.009
Final *R* and *R′* ‡	0.057, 0.089
Computer and programs	VAX 6410 X-RAY System,[31] DIRDIF[29]

* Scattering factors and anomalous dispersion taken from ref. 32. $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

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