

# Synthesis and Reactivity of (Pentafluorophenyl)platinate(II) Complexes with Bridging 1,8-Naphthyridine (napy) and X Ligands (X = C<sub>6</sub>F<sub>5</sub>, OH, Cl, Br, I, SPh). Crystal Structure of [NBu<sub>4</sub>][Pt<sub>2</sub>(μ-napy)(μ-OH)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]·CHCl<sub>3</sub>

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By reaction of [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with 1,8-naphthyridine (napy), [NBu<sub>4</sub>][Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(napy)] (**1**) is obtained. This compound reacts with *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] to give the dinuclear derivative [NBu<sub>4</sub>][Pt<sub>2</sub>(μ-napy)(μ-C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**2**). The reaction of several HX species with **2** results in the substitution of the bridging C<sub>6</sub>F<sub>5</sub> by other ligands (X) such as OH (**3**), Cl (**4**), Br (**5**), I (**6**), and SPh (**7**), maintaining in all cases the naphthyridine bridging ligand. The structure of **3** was determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group *P*2<sub>1</sub>/*n*, with *a* = 12.022(2) Å, *b* = 16.677(3) Å, *c* = 27.154(5) Å, β = 98.58(3)°, *V* = 5383.2(16) Å<sup>3</sup>, and *Z* = 4. The structure was refined to residuals of *R* = 0.0488 and *R*<sub>w</sub> = 0.0547. The complex consists of two square-planar platinum(II) fragments sharing a naphthyridine and OH bridging ligands, which are in *cis* positions. The short Pt–Pt distance [3.008(1) Å] seems to be a consequence of the bridging ligands.

## Introduction

Aryl groups are typical terminal ligands<sup>1</sup> that, in some cases, can act as bridging ligands forming M(μ-C)M' electron-deficient (3c–2e) bonds which are highly reactive.<sup>2</sup> However, the pentafluorophenyl group has proved to be very reluctant to act as a bridging ligand, probably because of the presence of electron-withdrawing substituents, which reduce the capability of the *ipso*-C atom to participate in this type of bond. In fact, as far as we know, the only complexes with bridging C<sub>6</sub>F<sub>5</sub> groups are the anionic homo- or heterometallic palladium or platinum complexes [NBu<sub>4</sub>]<sub>2</sub>[MM'(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (M = Pd, Pt; M' = Pd, Pt)<sup>3,4</sup> and their preparation has been carried out using two synthetic methods: (i) reaction of [NBu<sub>4</sub>]<sub>2</sub>[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-

Cl] with AgClO<sub>4</sub> (1:1 molar ratio) in CH<sub>2</sub>Cl<sub>2</sub> (a procedure for synthesizing only the platinum complex),<sup>3</sup> (ii) a more general process consisting of reacting [NBu<sub>4</sub>]<sub>2</sub>[M(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and *cis*-[M'(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (1:1 molar ratio) in CHCl<sub>3</sub>.<sup>4</sup> Attempts to prepare other palladium or platinum complexes containing at least one C<sub>6</sub>F<sub>5</sub> bridging group have been unsuccessful: for instance, the reactions between [NBu<sub>4</sub>]<sub>2</sub>[PtX(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (X = Cl, Br, I) and *cis*-[M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (M = Pd, Pt) in CH<sub>2</sub>Cl<sub>2</sub> (1:1 molar ratio) render mixtures of [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [NBu<sub>4</sub>]<sub>2</sub>[M<sub>2</sub>(μ-X)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] instead of the expected [NBu<sub>4</sub>]<sub>2</sub>[MM'(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>X(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] or [NBu<sub>4</sub>]<sub>2</sub>[MM'(μ-C<sub>6</sub>F<sub>5</sub>)(μ-X)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>4</sup>

In this paper we study the reaction of [NBu<sub>4</sub>][Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>L] [L = didentate N-donor ligand napy (1,8-naphthyridine), bpy (2,2'-bipyridine)] with *cis*-[M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (M = Pt, Pd) with the aim of preparing dinuclear [NBu<sub>4</sub>][PtM(μ-L)(μ-C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] complexes containing both C<sub>6</sub>F<sub>5</sub> and L acting as bridging ligands. The reaction takes place successfully when L = napy, but when L = bpy, a rearrangement reaction takes place.

## Experimental Section

**General Methods.** C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded over the 4000–200 cm<sup>-1</sup> range on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Varian XL-200 or a Unity-300 in CDCl<sub>3</sub> or HDA solutions. Negative ion FAB mass spectra were recorded on a VG-Autospec spectrometer operating at ca. 30 kV, using the standard cesium ion FAB gun and 3-nitrobenzyl alcohol as matrix. [NBu<sub>4</sub>]<sub>2</sub>[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Cl],<sup>5</sup> [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>],<sup>3,4</sup> *cis*-[M(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (M = Pd, Pt),<sup>6</sup> and 1,8-naphthyridine<sup>7</sup> were prepared as described elsewhere. F<sub>b</sub> denotes a fluorine substituent of the bridging C<sub>6</sub>F<sub>5</sub> group.

**[NBu<sub>4</sub>][Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(napy)] (**1**).** (a) To a yellow solution of [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.150 g, 0.080 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added napy (0.021 g, 0.160 mmol) (molar ratio 1:2). After 4 h of stirring at room temperature, the resulting pale yellow solution was

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evaporated to dryness. The oily residue was treated with diethyl ether (5 mL) and evaporated to dryness. Upon addition of  $i$ PrOH (20 mL) and after 30 min of stirring, a pale-yellow solid was obtained (**1**) and was filtered off and washed with  $i$ PrOH and  $n$ -hexane. Yield: 53%. Anal. Found (calcd for  $C_{42}H_{42}F_{15}N_3Pt$ ): C, 47.34 (47.19); H, 4.12 (3.96); N, 3.77 (3.93). FAB<sup>+</sup> MS:  $m/z$  827  $[Pt(C_6F_5)_3(napy)]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 802 s, 787 m, 770 m; others, 1626 w, 1493 vs, 1054 s, 953 vs; napy, 832 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.6 [d,  $^3J(^{195}Pt, H) = 34.4$  Hz, 1H,  $o$ -H], 9.0 [d, 1H,  $o'$ -H], 8.2 (d, 1H,  $m$ -H), 8.1 (d, 1H,  $m'$ -H), 7.4 (m, 1H,  $p$ -H), 7.3 (m, 1H,  $p'$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -116.9 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 588.0$  Hz, 2F,  $o$ -F], -118.3 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 380.8$  Hz, 4F,  $o$ -F], -166.9 (m<sub>c</sub>, 6F,  $m$ -F), -168.4 (t, 3F,  $p$ -F).

(b) To a solution of  $[NBu_4][Pt(C_6F_5)_3Cl]$  (1.000 g, 0.822 mmol) in THF (30 mL) was added  $AgClO_4$  (0.170 g, 0.822 mmol), and the mixture was stirred at room temperature for 30 min. The  $AgCl$  formed was filtered off, and the resulting solution was evaporated to dryness. The oily residue was dissolved in  $CH_2Cl_2$  (30 mL) and reacted with napy (0.107 g, 0.822 mmol) at room temperature for 10 h. The resulting mixture was evaporated to dryness and the residue was treated with  $i$ PrOH (50 mL) for 1 h. The pale yellow solid, **1**, was filtered off and washed with  $i$ PrOH and  $n$ -hexane. Yield: 80%.

**[PPN][Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(napy)] (1a) and [PPh<sub>3</sub>Et][Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(napy)] (1b).** To a solution of **1** (0.500 g, 0.470 mmol) in MeOH was added (PPN)-Cl ( $Ph_3PNPPh_3Cl$ ) (0.540 g, 0.940 mmol) (molar ratio 1:2) was added, and **1a** precipitated (84% yield). Complex **1b** (**1**, 0.500 g, 0.470 mmol;  $PPh_3EtBr$ , 0.348 g, 0.470 mmol) was prepared in a similar way (83% yield).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2).** To a solution of **1** (0.100 g, 0.094 mmol) in  $CH_2Cl_2$  (40 mL), was added  $cis$ - $[Pt(C_6F_5)_2(THF)_2]$  (0.063 g, 0.094 mmol) (molar ratio 1:1) was added. The resulting yellow solution was immediately evaporated to dryness, and the residue was treated with  $CHCl_3$  (5 mL) and evaporated to dryness. The final residue was stirred with  $n$ -hexane (20 mL) for 30 min, rendering a yellow solid which was filtered off. Yield: 72%. Anal. Found (calcd for  $C_{54}H_{42}F_{25}N_3Pt_2$ ): C, 40.68 (40.58); H, 2.81 (2.65); N, 2.41 (2.63). IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 815 m, 800 m, 795 m, 753 sh; others, 1634 w, 1608 w, 1497 vs, 1063 s, 959 vs; napy, 834 m, 579 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.9 (d, 2H,  $o$ -H), 8.6 (d, 2H,  $m$ -H), 7.7 (m, 2H,  $p$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -97.5 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 188.2$  Hz, 2F,  $o$ -F<sub>b</sub>], -117.2 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 463.2$  Hz, 4F,  $o$ -F], -122.9 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 473.5$  Hz, 4F,  $o$ -F], -153.0 (t, 1F,  $p$ -F<sub>b</sub>), -164.9 (m<sub>c</sub>, 4F,  $m$ -F), -166.9 (m<sub>c</sub>, 4F,  $m$ -F), -168.4 (m<sub>c</sub>, 2F,  $m$ -F<sub>b</sub>), -162.1 (t, 2F,  $p$ -F), -165.4 (t, 2F,  $p$ -F).

**[PPN][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2a) and [PPh<sub>3</sub>Et][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2b).** Complexes **2a** and **2b** were synthesized from **1a** or **1b** following a similar procedure to that described for **2** (78% and 74% yield respectively).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -OH)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (3).**  $[NBu_4][Pt_2(\mu\text{-napy})(\mu\text{-C}_6\text{F}_5)(\text{C}_6\text{F}_5)_4]$  (**2**) (0.165 g, 0.103 mmol) was dissolved in MeOH (30 mL), and then 2 mL of H<sub>2</sub>O was added. After 24 h of stirring, the solution was evaporated to ca. 5 mL, and an orange solid began to precipitate. The solid was filtered off and 20 mL of H<sub>2</sub>O were added to the resulting solution. Partial evaporation rendered an additional amount of **3**. Total yield: 90%. Anal. Found (calcd for  $C_{48}H_{43}F_{20}N_3OPt_2$ ): C, 39.96 (39.80); H, 2.80 (2.99); N, 3.04 (2.90). FAB<sup>+</sup> mass spectrum:  $m/z$  1205  $[Pt_2(C_6F_5)_4(napy)(OH)]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 812 m, 800 m; others, 1636 w, 1498 vs, 1062 s, 958 vs; napy, 836 m, 579 w. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  9.3 (dd, 2H,  $o$ -H), 8.9 (dd, 2H,  $m$ -H), 7.6 (dd, 2H,  $p$ -H). <sup>19</sup>F NMR (acetone- $d_6$ ):  $\delta$  -117.3 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 475.2$  Hz, 4F,  $o$ -F], -118.6 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 492.4$  Hz, 4F,  $o$ -F], -166.6 (m, 4F,  $p$ -F), -166.9 (m<sub>c</sub>, 4F,  $m$ -F), -167.4 (m<sub>c</sub>, 4F,  $m$ -F).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -Cl)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (4).** To a yellow solution of **2** (0.250 g, 0.156 mmol) in  $CH_2Cl_2$  (30 mL) was added 0.34 mL (0.156 mmol) of 0.464 M HCl. The color of the solution immediately turned dark orange. The solution was evaporated to dryness and the residue was stirred with  $n$ -hexane (20 mL) for 5 min rendering an orange solid, **4**, which was filtered off. Yield: 87%. Anal. Found (calcd for  $C_{48}H_{42}ClF_{20}N_3Pt_2$ ): C, 39.55 (39.31); H, 3.07 (2.89); N, 2.90 (2.86).

FAB<sup>+</sup> MS:  $m/z$  1224  $[Pt_2(C_6F_5)_4(napy)Cl]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 811 m, 800 m; others, 1633 w, 1500 vs, 1062 s, 960 vs; napy, 835 m, 579 w;  $\nu(Pt-Cl)$ , 286 m. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  9.4 (dd, 2H,  $o$ -H), 8.9 (dd, 2H,  $m$ -H), 7.7 (dd, 2H,  $p$ -H). <sup>19</sup>F NMR (acetone- $d_6$ ):  $\delta$  -114.8 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 510.1$  Hz, 4F,  $o$ -F], -116.7 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 422.2$  Hz, 4F,  $o$ -F], -165.2 (t, 2F,  $p$ -F), -166.2 (m<sub>c</sub>, 4F,  $m$ -F), -167.0 (t, 2F,  $p$ -F), -168.2 (m<sub>c</sub>, 4F,  $m$ -F).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -Br)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5).** As described for complex **4**, **2** (0.30 g, 0.19 mmol) was reacted with an aqueous solution of 0.354 M HBr (0.53 mL, 0.19 mmol). Yield: 78%. Anal. Found (calcd for  $C_{48}H_{42}BrF_{20}N_3Pt_2$ ): C, 38.16 (38.16); H, 2.56 (2.80); N, 2.71 (2.78). FAB<sup>+</sup> MS:  $m/z$  1267  $[Pt_2(C_6F_5)_4(napy)Br]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 809 m, 798 m; others, 1632 w, 1504 vs, 1495 vs, 1062 s, 957 vs; napy, 835 m, 580 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.9 (m, 2H,  $o$ -H), 8.6 (m, 2H,  $m$ -H), 7.7 (m, 2H,  $p$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -119.2 [m<sub>c</sub>, 4F,  $o$ -F], -122.0 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 477.6$  Hz, 4F,  $o$ -F], -162.0 (t, 2F,  $p$ -F), -165.0 (m<sub>c</sub>, 8F,  $m$ -F), -166.7 (t, 2F,  $p$ -F).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -I)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (6).** Following the same procedure as above, **2** (0.150 g, 0.094 mmol) in  $CH_2Cl_2$  (20 mL) was reacted with 0.28 mL (0.094 mmol) of 0.350 M HI. Yield: 85%. Anal. Found (calcd for  $C_{48}H_{42}F_{20}IN_3Pt_2$ ): C, 37.25 (37.00); H, 2.61 (2.71); N, 2.60 (2.69). FAB<sup>+</sup> mass spectrum:  $m/z$  1554  $[NBu_4][Pt_2(C_6F_5)_4(napy)I]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 805 m, 794 m; others, 1635 w, 1504 vs, 1500 vs, 1064 s, 958 vs; napy, 835 m, 580 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.2 (dd, 2H,  $o$ -H), 8.5 (dd, 2H,  $m$ -H), 7.3 (dd, 2H,  $p$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -118.5 (m<sub>c</sub>, 4F,  $o$ -F), -120.2 (m<sub>c</sub>, 4F,  $o$ -F), -165.2 (t, 2F,  $p$ -F), -165.4 (t, 2F,  $p$ -F), -166.4 (m<sub>c</sub>, 4F,  $m$ -F), -166.8 (m<sub>c</sub>, 4F,  $m$ -F).

**[NBu<sub>4</sub>][Pt<sub>2</sub>( $\mu$ -napy)( $\mu$ -SPh)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (7).** A 0.175 g (0.110 mmol) sample of **2** was reacted with 12  $\mu$ L (0.110 mmol) of HSPH in 20 mL of  $CHCl_3$ . After 15 min of stirring, the solution was evaporated to dryness and the residue was treated with  $n$ -hexane for 2 h, to render an orange solid (**7**) that was filtered off. Yield: 81%. Anal. Found (calcd for  $C_{54}H_{47}F_{20}N_3Pt_2S$ ): C, 42.44 (42.11); H, 3.28 (3.14); N, 2.54 (2.73); S, 2.58 (2.08). FAB<sup>+</sup> MS  $m/z$  1297  $[Pt_2(C_6F_5)_4(napy)(SPh)]^-$ . IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 808 m, 789 m; others, 1632 w, 1499 vs, 1058 s, 956 vs; napy, 835 m, 578 w; SPh, 697 w, 488 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.5 [dd, 2H,  $o$ -H], 8.4 (d, 2H,  $m$ -H), 7.6 (m, 2H,  $p$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -115.7 (m<sub>c</sub>, 4F,  $o$ -F), -118.1 [m<sub>c</sub>,  $^3J(^{195}Pt, F) = 451.6$  Hz, 4F,  $o$ -F], -166.0 (t, 2F,  $p$ -F), -166.8 (t, 2F,  $p$ -F), -167.2 (m<sub>c</sub>, 8F,  $m$ -F).

**[NBu<sub>4</sub>][PtPd( $\mu$ -napy)( $\mu$ -OH)(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (8).** To a solution of  $[NBu_4][Pt(C_6F_5)_3(napy)]$  (0.20 g, 0.187 mmol) in  $CH_2Cl_2$  (40 mL)  $cis$ - $[Pd(C_6F_5)_2(THF)_2]$  (0.11 g, 0.187 mmol) was added (molar ratio 1:1). The yellow solution was immediately evaporated to dryness and the residue was dissolved in  $CHCl_3$  (5 mL) and evaporated again. The final residue was stirred with  $n$ -hexane (20 mL) for 30 min rendering a solid which was filtered off. Yield: 85%. Anal. Found (calcd for  $C_{48}H_{43}F_{20}N_3OPdPt$ ): C, 42.21 (42.41); H, 2.95 (3.19); N, 2.83 (3.09). IR (cm<sup>-1</sup>):  $C_6F_5$  X-sensitive mode,<sup>8</sup> 799 m, 769 m; others, 1632 w, 1499 vs, 1058 s, 957 vs; napy, 836 m, 579 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.2 [dd, 1H,  $o$ -H], 9.0 [dd, 1H,  $o$ -H], 8.4 (td, 2H,  $m$ -H), 7.5 (m, 1H,  $p$ -H), 7.4 (m, 1H,  $p$ -H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -113.9 (m<sub>c</sub>, 2F,  $o$ -F), -115.1 (m<sub>c</sub>, 2F,  $o$ -F), -118.9 (m<sub>c</sub>, 2F,  $o$ -F), -119.0 (m<sub>c</sub>, 2F,  $o$ -F), -163.1 (t, 1F,  $p$ -F), -163.3 (t, 1F,  $p$ -F), -165.1 (m<sub>c</sub>, 2F,  $m$ -F), -165.4 (t, 1F,  $p$ -F), -165.6 (t, 1F,  $p$ -F), -165.7 (m<sub>c</sub>, 2F,  $m$ -F), -166.5 (m<sub>c</sub>, 2F,  $m$ -F), -166.9 (m<sub>c</sub>, 2F,  $m$ -F).

**Reaction of  $[NBu_4][Pt(C_6F_5)_3(bpy)]$  with  $cis$ - $[Pt(C_6F_5)_2(THF)_2]$ .** To a solution of  $[NBu_4][Pt(C_6F_5)_3(bpy)]$  (0.100 g, 0.091 mmol) in  $CHCl_3$  (30 mL) was added  $cis$ - $[Pt(C_6F_5)_2(THF)_2]$  (0.062 g, 0.091 mmol) (molar ratio 1:1). The solution quickly turned orange and then a precipitate appeared. After 30 min of stirring at room temperature, the solvent was evaporated to dryness and  $CHCl_3$  (10 mL) was added. The pale yellow precipitate (identified by IR spectroscopy as  $[Pt(C_6F_5)_2(bpy)]$ ) was filtered off (65% yield). The resulting solution was evaporated to dryness, and the final residue was stirred with  $n$ -hexane (20 mL) finally rendering a solid, which was filtered off and identified as  $[NBu_4][Pt_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  (56% yield).

**Reaction of **2** with  $CH_3COOH$ .** To a solution of **2** (0.135 g, 0.084 mmol) in 20 mL of  $CH_2Cl_2$  was added 0.24 mL of 0.35 M  $CH_3COOH$ . After 30 min of stirring at room temperature, the solution was evaporated to dryness and the residue treated with  $n$ -hexane, yielding a solid

**Table 1.** Crystal Data for  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]\cdot\text{CHCl}_3$  (1)<sup>a</sup>

chemical formula	$\text{Pt}_2\text{Cl}_3\text{F}_{20}\text{O}_1\text{N}_3\text{C}_{49}\text{H}_{43}$
fw	1567.4
space group	$P2_1/n$ (No. 14)
<i>a</i> , Å	12.022(2)
<i>b</i> , Å	16.677(3)
<i>c</i> , Å	27.154(5)
$\beta$ , °	98.58(3)
<i>V</i> , Å <sup>3</sup>	5383.2(16)
<i>Z</i>	4
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.787
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	5.45
$\lambda$ , Å	0.710 73 (graphite monochromator)
temp, °C	-73
<i>R</i>	0.0488
<i>R</i> <sub>w</sub>	0.0547

$$^a R = \sum |F_o - F_c| / \sum |F_o|. \quad R_w = (\sum w|F_o - F_c|^2 / \sum w|F_o|^2)^{1/2}.$$

identified as a mixture of the starting material and **3**. Longer reaction time (up to 14 h) rendered **3** only. Yield: 95%.

**X-ray Structure Analysis.** A batch of pale yellow crystals of **3**·CHCl<sub>3</sub> was grown by slow diffusion of *n*-hexane into a solution of **3** in chloroform at low temperature (-30 °C). A representative crystal of dimensions 0.30 × 0.15 × 0.23 mm was selected and mounted on a Siemens/STOE AED2 four circle diffractometer. The basic crystallographic parameters for this complex are listed in Table 1. Data were collected at 200 K by the  $\omega$ - $\theta$  scan technique. The cell constants are based on 24 reflections with  $20 < 2\theta < 28^\circ$ , including Friedel pairs. Three standard reflections were measured after every 240 min of beam exposure during data collection, showing no systematic variation in decay. Data reduction included an empirical correction ( $\Psi$ -scan method, 10 reflections, transmission factors = 1.000 and 0.410). The structure was solved by the Patterson heavy-atom method, which revealed the positions of the platinum atoms of the anion. The remaining non-H atoms were located in successive Fourier syntheses and refined with anisotropic temperature factors. H atoms, except those of the methyl groups, were constrained to ride on their C atoms and located at fixed positions with a C-H distance of 0.96 Å and a common isotropic thermal parameter of 0.053(8) Å<sup>2</sup>. During the course of the refinement, regions of electron density that were at nonbonding distances to either the anion or the cation were refined as one molecule of lattice chloroform. One of the Cl atoms was disordered over two sites—Cl(3) and Cl(4)—at half-occupancy. Positional restraints were applied to the C-Cl and Cl...Cl distances. A difference map following convergence had six peaks between 1.32 and 1 e/Å<sup>3</sup>, located in the area of the central heavy atoms. This effect is common in crystals containing strongly scattering and strongly absorbing elements. A total of 4953 data with  $F > 4\sigma F_o$  were used to refine 713 parameters. Final residuals were  $R = 0.0488$  and  $R_w = 0.0547$ , with a quality of fit indicator of 1.06.

All calculations were performed on a Micro Vax 3100 workstation with the SHELXTL PLUS software package.<sup>9</sup>

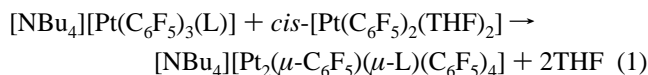
## Results and Discussion

The mononuclear complex  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{napy})]$  (**1**), which is used as the starting material, was obtained by a cleavage reaction of the C<sub>6</sub>F<sub>5</sub>-bridged derivative  $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  with 1,8-naphthyridine in 1:2 molar ratio. This reaction takes place under mild conditions and takes approximately 4 h to complete. Another alternative procedure which renders a better yield consists of reacting  $[\text{NBu}_4]_2[\text{PtCl}(\text{C}_6\text{F}_5)_3]$  with AgClO<sub>4</sub> and 1,8-naphthyridine (1:1:1 molar ratio). The <sup>1</sup>H NMR spectrum of **1** (see Experimental Section) indicates that 1,8-naphthyridine is acting as a monodentate ligand, so that only one N-donor atom is involved in the coordination to the platinum center. This result differs from the fluxional behavior

observed in other 1,8-naphthyridine platinum complexes *cis*- $[\text{PtCl}(\text{PR}_3)(\text{napy})]$  ( $\text{PR}_3 = \text{PEt}_3, \text{PPh}_3, \text{PMe}_2\text{Ph}$ ) studied by Dixon<sup>10</sup> in which, at room temperature, the two N atoms are alternatively coordinated to the platinum center through a five-coordinate transition state and only at low temperature (-70 °C) is the fluxional process slow enough to distinguish two different pyridine rings.

Complex **1** is stable not only in the solid state but also in dichloromethane or acetone solutions at room temperature. This stability in solution is in sharp contrast to the behavior of the analogous  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{phen})]$  complex which rearranges very quickly to  $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{phen})]$  and  $[\text{NBu}_4]_2[\text{Pt}(\text{C}_6\text{F}_5)_4]$  in dichloromethane and more slowly in acetone solutions.<sup>11</sup> The greater tendency of 1,10-phenanthroline to act as a chelating ligand may be the reason for this rearrangement, which was not observed for **1**.

**Synthesis of  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$ .** As we have stated before, and according to our previous experience, a reasonable synthetic strategy for the preparation of a dinuclear platinum compound with only one pentafluorophenyl bridging ligand is to react an anionic complex such as  $[\text{Pt}(\text{C}_6\text{F}_5)_3(\text{L})]^{n-}$  (L being a potentially bridging ligand) with *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ . If such a reaction were to take place according to eq 1, the desired compound could be formed.



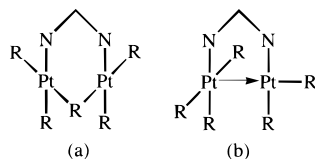
However,  $[\text{NBu}_4]_2[\text{Pt}(\text{C}_6\text{F}_5)_3\text{X}]$  (X = Cl, Br, I) reacts with *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  in CH<sub>2</sub>Cl<sub>2</sub>, rendering mixtures of  $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  and  $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-X})_2(\text{C}_6\text{F}_5)_4]$ , as a result of a rearrangement process, instead of the desired  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)(\mu\text{-X})(\text{C}_6\text{F}_5)_4]$ .<sup>4</sup> Bearing this in mind, and with the aim of preparing dinuclear complexes with one bridging C<sub>6</sub>F<sub>5</sub> ligand by a method similar to that schematized in eq 1, we chose  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{napy})]$  (**1**) as the starting material since (a) napy is a potential dinucleating agent which in **1** acts as a monodentate ligand,<sup>12</sup> and (b) the rigidity of this ligand increases the possibilities of bringing the metal centers together, favoring the formation of the C<sub>6</sub>F<sub>5</sub> bridge or a metal-metal interaction.<sup>13</sup> Thus, the reaction of  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{napy})]$  with *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  (molar ratio 1:1) in CH<sub>2</sub>Cl<sub>2</sub> results, after evaporation to dryness, in the formation of the dinuclear  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  (**2**). We have not been able to isolate suitable crystals of **2** for an X-ray study and attempts to grow crystals of  $[\text{PPN}][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  (**2a**) and  $[\text{PPh}_3\text{Et}][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  (**2b**) have also been unsuccessful. However, the <sup>1</sup>H and <sup>19</sup>F NMR spectra of **2** indicate that in this complex the two metal centers are bridged by both the napy ligand and the C<sub>6</sub>F<sub>5</sub> ligand (eq 1, L = napy).

The <sup>1</sup>H NMR spectrum of **2** shows three signals for the six aromatic protons, indicating a highly symmetric arrangement

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(9) SHELXTL-PLUS Software Package for the Determination of Crystal Structures, Release 4.0. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.

Chart 1

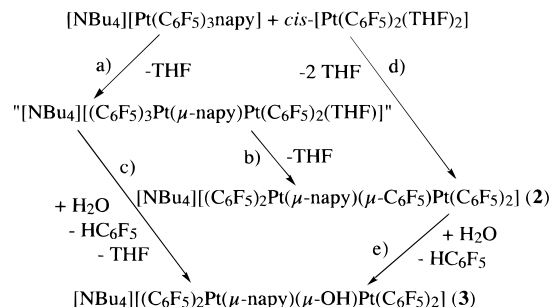


of the napy ligand in which both pyridine rings are equivalent and coordinated to the platinum atoms. The  $^{19}\text{F}$  NMR spectrum unambiguously reflects the structural role of the  $\text{C}_6\text{F}_5$  ligands. The signals at  $-117.2$  [ $^3J(^{195}\text{Pt},\text{F}) = 463.2$  Hz, 4F, *o*-F],  $-122.9$  [ $^3J(^{195}\text{Pt},\text{F}) = 473.5$  Hz, 4F, *o*-F],  $-164.9$  (4F, *m*-F),  $-166.9$  (4F, *m*-F),  $-162.1$  (2F, *p*-F), and  $-165.4$  (2F, *p*-F) ppm are assigned to the two types of terminal  $\text{C}_6\text{F}_5$  ligands. The signals at  $-97.5$  [ $^3J(^{195}\text{Pt},\text{F}) = 188.2$  Hz, 2F, *o*-F],  $-153.0$  (1F, *p*-F), and  $-168.4$  (2F, *m*-F) ppm are due to another type of pentafluorophenyl group. As can be seen the *o*- and *p*-fluorine atoms of this group appear at lower fields than the typical *o*- and *p*-fluorine resonances of terminal  $\text{C}_6\text{F}_5$  groups suggesting the bridging role of this pentafluorophenyl ring. In addition, the *o*-fluorine signal shows platinum satellites the intensity of which (satellites/central signal ratio: 46.07/53.93) unambiguously establishes that this pentafluorophenyl group is bridging two platinum centers according to the theoretical isotopomers ratio [(a)  $\text{Pt}(\mu\text{-C}_6\text{F}_5)\text{Pt}$  (43.82%), (b)  $^{195}\text{Pt}(\mu\text{-C}_6\text{F}_5)\text{Pt}$  (44.74%) while no platinum satellites due to the less abundant isotopomer (c)  $^{195}\text{Pt}(\mu\text{-C}_6\text{F}_5)^{195}\text{Pt}$  (11.42%) are observed in the spectrum] (satellites/central signal ratio: 44.74/43.82 + 5.71).

The formation of **2** indicates that complex **1** acts as a didentate metaloligand toward  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ , producing the displacement of both THF ligands and that the coordination sphere of the platinum center is completed by the formation of an electron-deficient bridging system ( $\mu\text{-C}_6\text{F}_5$ ) (Chart 1a). It is interesting to note the preference of **2** for a structure such as that represented in Chart 1a instead of that shown in Chart 1b, with a donor–acceptor Pt–Pt bond which one could expect taking into account the well-documented basicity of these platinum substrates.<sup>14</sup>

The reaction between **1** and  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  has been followed by  $^{19}\text{F}$  NMR spectroscopy. Equimolar amounts of the reagents were mixed at  $-78^\circ\text{C}$ , and no reaction was observed until  $-30^\circ\text{C}$ . At this temperature some changes in the signals are observed, indicating the beginning of the reaction. However, the resonance due to the *o*-fluorine atoms of the bridging  $\text{C}_6\text{F}_5$  group could not be detected until  $10^\circ\text{C}$ . When the temperature was increased, all of the signals due to **2** were observed in the NMR spectrum of the mixture. All these facts suggest that an intermediate complex [probably a dinuclear compound resulting from the displacement of only one THF group (see Scheme 1.a)] is formed prior to the formation of **2** (Scheme 1.b). In addition a concomitant although minor process also takes place given that at  $-20^\circ\text{C}$  *o*-fluorine and *p*-fluorine signals due to  $\text{C}_6\text{F}_5\text{H}$  begin to be detected. The formation of  $\text{C}_6\text{F}_5\text{H}$  must be the result of hydrolysis of some species present in the solution. Since neither **1** nor  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  hydrolyze under these conditions and **2** is not yet present at this temperature,  $\text{C}_6\text{F}_5\text{H}$  must be the result of the hydrolysis of the suggested intermediate complex (Scheme 1.c). At the end of the experiment ( $40^\circ\text{C}$ ) signals due to  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  (**3**) are also observed. However, we cannot determine if the presence of **3**

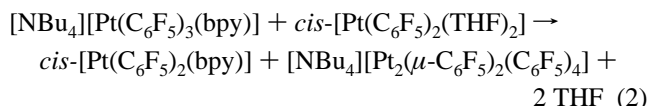
Scheme 1



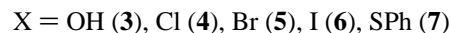
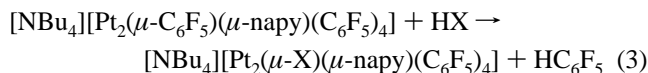
in this solution is the result of the reaction of the hydrolyzed intermediate, of the hydrolysis of **2**, or both.

Finally, it must be pointed out that the reaction conditions of **1** and  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  in the NMR tube are completely different from those used in the preparation of **2** (see Experimental Section) since, in the latter, the reactants are mixed at room temperature (approximately  $20^\circ\text{C}$ ) and the reaction mixture is immediately evaporated to dryness (Scheme 1.d). Both facts favor the displacement and the elimination of THF from the reaction mixture and the formation of complex **2**. It is probably due to this fact that we have not detected any hydrolysis product during the preparation of complex **2**.

We have also studied a similar reaction between  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{bpy})]$ <sup>15</sup> and  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$  (molar ratio 1:1) which results in the formation of  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{bpy})]$  and  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  (eq 2) (identified by elemental analyses and IR spectra) instead of the formation of the dinuclear derivative. This process seems to be a consequence of the greater tendency of the bpy to act as a chelating ligand rather than as a bridging one.<sup>15</sup>



The electron-deficient  $\text{Pt}(\mu\text{-C}_6\text{F}_5)\text{Pt}$  bond in **2** is unstable toward hydrolysis, and when  $\text{H}_2\text{O}$  is added to a methanol solution of **2** and stirred for 24 h,  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  (**3**) is formed in a high yield.<sup>16</sup> Other reactants such as HX (X = Cl, Br, I, SPh) behave in a similar way, yielding the corresponding  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-X})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  complexes (eq 3), and the reaction takes place faster than with water. However, treatment of **2** with an aqueous solution of acetic acid renders **3** instead of the acetato complex.



The  $^1\text{H}$  NMR spectra of complexes **3**–**7** are similar to that described for **2**, showing that the two pyridine rings of the napy ligand are equivalent. The signal of the *ortho* hydrogen atoms shows a shoulder due to coupling with  $^{195}\text{Pt}$ . The  $^{19}\text{F}$  NMR spectra of these complexes show two types of terminal pen-

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(16) We have carried out a  $^{19}\text{F}$  NMR study of this hydrolysis process in  $\text{CD}_2\text{Cl}_2$  (donor solvents cannot be used for this purpose, since complex **2** reacts with them producing the cleavage of the  $\text{Pt}(\mu\text{-C}_6\text{F}_5)\text{Pt}$  bridging system), and it has been observed that the reaction is first order with respect to the platinum binuclear complex.

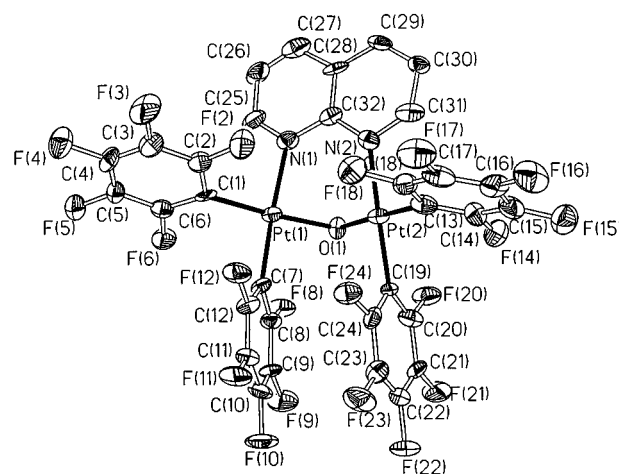
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for the Complex  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$ 

Pt(1)–O(1)	2.092(8)	Pt(2)–O(1)	2.121(8)
Pt(1)–N(1)	2.129(12)	Pt(2)–N(2)	2.116(12)
Pt(1)–C(1)	2.007(14)	Pt(2)–C(13)	2.018(15)
Pt(1)–C(7)	2.005(14)	Pt(2)–C(19)	1.985(13)
Pt(1)···Pt(2)	3.008(1)		
C(1)–Pt(1)–O(1)	175.0(4)	C(1)–Pt(1)–C(7)	92.3(5)
C(7)–Pt(1)–O(1)	92.2(5)	C(1)–Pt(1)–N(1)	90.5(5)
C(7)–Pt(1)–N(1)	176.3(5)	O(1)–Pt(1)–N(1)	85.1(4)
C(13)–Pt(2)–C(19)	87.4(6)	C(13)–Pt(2)–O(1)	177.7(5)
C(19)–Pt(2)–O(1)	92.0(5)	C(13)–Pt(2)–N(2)	94.1(5)
C(19)–Pt(2)–N(2)	177.1(5)	O(1)–Pt(2)–N(2)	86.4(4)
Pt(1)–O(1)–Pt(2)	91.1(3)	Pt(2)–N(2)–C(32)	131.2(10)
C(31)–N(2)–C(32)	114.2(12)	Pt(1)–N(1)–C(32)	126.3(9)
N(2)–C(32)–N(1)	119.2(12)		

tafluorophenyl groups (*trans* to the N-atoms of the napy ligand and *trans* to the X-bridging ligand) (see Experimental Section).

Finally, we have also attempted the synthesis of the heterodinuclear  $[\text{NBu}_4][\text{PtPd}(\mu\text{-C}_6\text{F}_5)(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$  by reacting  $[\text{NBu}_4][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{napy})]$  with *cis*- $[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ . However, in no case have we been able to isolate the product with bridging  $\text{C}_6\text{F}_5$  and we only obtain the hydroxo compound  $[\text{NBu}_4][\text{PtPd}(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4]$ , which could be the result of the hydrolysis of the former due to a greater lability of the Pd–C bonds.

**Crystal structure of  $[\text{NBu}_4][\text{Pt}_2(\mu\text{-OH})(\mu\text{-napy})(\text{C}_6\text{F}_5)_4] \cdot \text{CHCl}_3$ .** Crystallographic data and selected bond distances and angles for complex **2** are given in Tables 1 and 2 respectively. The structure of the complex anion is shown in Figure 1. The core of the anion comprises two platinum atoms 3.008(1) Å apart, bridged by an OH and a napy ligands. Each platinum center has also two terminal *cis*  $\text{C}_6\text{F}_5$  groups which form a square planar environment for both metals. The terminal Pt–C bond distances are equal within experimental error [1.985(13)–2.018(15) Å] as are the two pairs of Pt–O and Pt–N distances [Pt(1)–O(1) = 2.092(8), Pt(2)–O(1) = 2.121(8), Pt(1)–N(1) = 2.129(12) and Pt(2)–N(2) = 2.116(12) Å]. The bond angles around each platinum center range from 85.1(4) to 94.1(5)° for *cis* ligands, the smallest angle corresponding to O–Pt–N, and from 175.0(4) to 177.7(5)° for *trans* ligands. The distance between the two platinum atoms lies at the upper end of the range for Pt–Pt bonding distances [3.008(1) Å] although Pt–Pt interactions have been invoked for systems with longer internuclear separations (e.g., the 3.39 Å stacking separation in  $[\text{PtCl}_2(\text{en})]_4^{17}$ ). We think, however, that in this case the short

**Figure 1.** Perspective drawing of the  $[\text{Pt}_2(\mu\text{-napy})(\mu\text{-OH})(\text{C}_6\text{F}_5)_4]^-$  anion showing 40% probability ellipsoids. Hydrogen atoms are omitted.

Pt···Pt distance is merely a consequence of the steric constraints imposed by the bridging ligands which also cause the coordination planes of the platinum atoms to form an angle of 87.01–(24)°. This fact prevents a suitable overlapping of the orbitals for the formation of the metal–metal bond.

The rigidity of the napy ligand seems in fact to play a key role in the structure of the anion of **3** since in the related anion  $[\text{Pt}_2(\mu\text{-dppm})(\mu\text{-I})(\text{C}_6\text{F}_5)_4]^-$  the Pt···Pt distance is 4.45 Å and the dihedral angle formed by the coordination planes of the two platinum centers is 44.9(1)°. It is also remarkable that, as a consequence of this type of coordination, the napy ligand results clearly distorted with the C(32)–N(1)–Pt(1) and C(32)–N(2)–Pt(2) angles [131.2(10) and 126.3(9)°, respectively] rather different from the expected 120°.

On the basis of the  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra we consider that the structures of complexes **2**, **4**, **5**, **6**, and **7** are similar to that of complex **3**.

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**Supporting Information Available:** Tables of crystallographic data and refinement parameters, atomic coordinates, complete bond distances and angles, anisotropic displacement parameters and H-atom coordinates (12 pages). Ordering information is given on any current masthead page.

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