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Synthesis of Binuclear Platinum Complexes Containing the Ligands 8-Naphthyridine, 2-Aminopyridine, and 7-Azaindolate. An Experimental Study of the Steric Hindrance of the Bulky Pentafluorophenyl Ligands in the Synthesis of Binuclear Complexes

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The bidentate N-donor ligands 2-aminopyridine (2-ampy), 7-azaindolate (aza) and 1,8-naphthyridine (napy) have been used to study the steric effect of pentafluorophenyl groups in the synthesis of binuclear platinum(II) complexes. The 2-ampy and aza ligands bridge two "$Pt(C_6F_5)_2$" fragments with Pt···Pt distances of 4.1 and 3.4 Å, respectively (complexes **1** and **3**). Under the same reaction conditions the napy ligand shows chelating behavior and makes the mononuclear complex (**A**) highly reactive because of its strained coordination. One of the Pt−N bonds of the chelating complex is broken on reaction with HX {X = Cl (**4**), Br (**5**)} because of protonation while the anion X^- occupies a created vacant site. The resulting mononuclear complex eliminates C_6F_5H when refluxed, and a binuclear complex (**6**) with two napy ligands bridging two "$Pt(C_6F_5)Cl$" fragments is obtained. The reaction of **A** with $HPPh_2$ affords a mononuclear complex (**7**) analogous to complexes **5** and **6**, but reflux gives a binuclear complex (**8**) with the two napy ligands terminally bound and the PPh_2 groups bridging the "$Pt(C_6F_5)$napy" moieties. The reaction of **A** with HC≡CPh gives a binuclear complex; moreover, the final product does not depend on the ratio of complex **A** to HC≡CPh. Complexes **1**, **4**, **6**, **9** have been structurally characterized by X-ray diffraction.

Introduction

Binuclear platinum(II) complexes containing two identical bridging ligands can adopt three extreme structure types (see Chart 1). In one of them (Chart 1a) the two platinum square planar environments may be in the same plane[1−3] or bent (Chart 1b),[4−8] while in the other type, usually known as "face to face" (Chart 1c), the platinum coordination planes are parallel or nearly parallel.[9−14]

The ability of bidentate ligands to facilitate the synthesis of bi- and polynuclear complexes is well-known.[10,11,15−18] Nevertheless, some bidentate ligands with a flexible connection between their donor atoms, such as dppm, en, tmeda,

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(1) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. *J. Chem. Soc., Dalton Trans.* **1979**, 434.
(2) Usón, R.; Forniés, J.; Tomás, M.; Fandos, R. *J. Organomet. Chem.* **1984**, *263*, 253.
(3) Lopez, G.; Ruiz, J.; Garcia, G. G.; Vicente, C.; Marti, J. M.; Hermoso, J. A.; Vegas, A.; Martinez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.
(4) Gerisch, M.; Heinemann, F. W.; Bruhn, C.; Scholz, J.; Steinborn, D. *Organometallics* **1999**, *18*, 564.
(5) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400.
(6) Janka, M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2000**, *19*, 5071.
(7) Freeman, W. A.; Nicholls, L. J.; Liu, C. F. *Inorg. Chem.* **1978**, *17*, 2989.
(8) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Langes, C.; Kopacka, H. A. R.; Bruggeller, P. *Inorg. Chim. Acta* **1999**, *290*, 167.
(9) Blake, A. J.; Reid, G.; Schroder, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 64.
(10) Oskui, B.; Sheldrick, W. S. *Eur. J. Inorg. Chem.* **1999**, 1325.
(11) Azam, K. A.; Ferguson, G.; Ling, S. S. M.; Parvez, M.; Puddephatt, R. J.; Srokowski, D. *Inorg. Chem.* **1985**, *24*, 2799.
(12) Hutton, A. T.; Shabanzadeh, B.; Shaw, B. L. *Chem. Commun.* **1983**, 1053.
(13) Garcia-Herbosa, G.; Connelly, N. G.; Munoz, A.; Cuevas, J. V.; Orpen, A. G.; Politzer, S. D. *Organometallics* **2001**, *20*, 3223–3229.
(14) Daws, C. A.; Hill, M. G.; Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1992**, *31*, 2948–2955.

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prefer to act as chelate ligands when they react with metal complexes if the metal center has two labile ligands in suitable positions.[19−25]

In other cases di- or polydentate ligands prefer to act as bridging ligands rather than chelating [napy, hpp (1,3,4,6,7,8-hexahidro-2*H*-pyramido-1,2-a-pyramidinate), tbo (1,3,6-triazabicyclo-3,3,0-oct-4-ene)].[26−28] However, formation of binuclear complexes using typical binucleating ligands can be precluded by the steric hindrance of the ancillary ligands bonded to the metal center. So, in spite of the well-known ability of the 1,8-naphthyridine to act as a bridging ligand[28−32] we have not been able to prepare the binuclear $[Pt_2(\mu\text{-napy})_2(C_6F_5)_4]$ but obtained instead the mononuclear and very reactive complex *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**)[33] because this complex contains a strained four-membered ring with a small bite angle [N−Pt−N 62.3(3)°]. On the other hand, some examples in which the presence of sterically demanding coligands causes the formation of higher nuclearity complexes are also known.[34]

The formation of the mononuclear complex *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) instead of the binuclear one seems to be due to the position of the bulky pentafluorophenyl rings with respect to the platinum coordination planes (perpendicular or nearly perpendicular), which if bridged by the N donor atoms of the 1,8-naphthyridine ligand should adopt an approximately face to face disposition with the platinum coordination planes nearly parallel, thus producing congestion of the C_6F_5 groups.

Chart 1

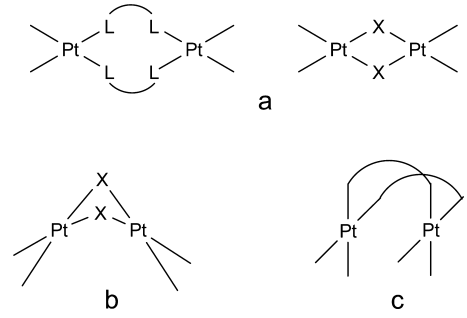
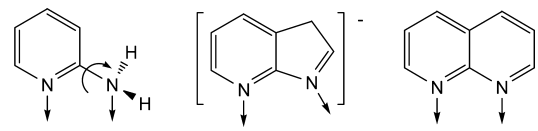


Chart 2



In this paper we report a careful study of the effects of sterically bulky ligands on the formation of diplatinum(II) complexes. With this aim we have synthesized and structurally characterized several binuclear complexes, two of them containing the "$Pt(C_6F_5)_2$" moiety as in **A** but with more flexible bridging ligands such as 2-aminopyridine or 7-azaindole (see Chart 2).

In addition we have also prepared two binuclear platinum complexes with 1,8-naphthyridine as bridging ligands but with only one C_6F_5 group per platinum atom to avoid the steric congestion that precluded the formation of the binuclear complex. Other reactions with *cis*-$[Pt(C_6F_5)_2(napy)]$ have also been studied.

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^{-1} range on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. ^1H, and ^{19}F NMR spectra at room temperature were recorded on a Brüker ARX-300 or a Unity-300 spectrometer in $CDCl_3$ or acetone-d_6 solutions. ^1H, ^{19}F NMR spectra at low and variable temperature were recorded in acetone-d_6 or DMSO-d_6 solutions on a Brüker ARX-300 spectrometer. Positive and negative ion FAB mass spectra were recorded on a VG-Autospec spectrometer operating at about 30 kV, using the standard cesium ion FAB gun and 3-nitrobenzyl alcohol as matrix. $[NBu_4]_2[Pt_2(\mu\text{-Cl})_2(C_6F_5)_4]$,[2] *cis*-$[Pt(C_6F_5)_2(thf)_2]$[35] *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**)[33] and 1,8-naphthyridine (napy)[36] were prepared as described elsewhere. The 2-aminopyridine (ampy), 7-azaindol (azaH) and phenylacetilene were used as purchased from Aldrich; diphenylphosphine was purchased from Fluka.

$[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]$ (1). To a solution of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.200 g, 0.297 mmol) in CH_2Cl_2 (10 mL) was added the equimolar amount of ampy ligand (0.028 g, 0.297 mmol). The solution was immediately evaporated to dryness. The yellow residue was treated with *n*-hexane, filtered off, and washed with $CHCl_3$ and *n*-hexane and air-dried (92% Yield). Anal. Found (Calcd for $C_{34}H_{12}F_{20}N_4Pt_2$): C, 32.65 (32.76); H, 1.10 (0.97); N, 4.24 (4.49).

(15) Forniés, J.; Garcia, A.; Gil, B.; Lalinde, E.; Moreno, M. T. *Dalton Trans.* **2004**, *22*, 3854–3863.
(16) Anillo, A.; Diaz, M. R.; Garcia-Granda, S.; Obeso-Rosete, R.; Galindo, A.; Ienco, A.; Mealli, C. *Organometallics* **2004**, *23*, 471–481.
(17) Liu, Q. D.; Jia, W. L.; Wu, G.; Wang, S. I. *Organometallics* **2003**, *22*, 3781–3791.
(18) Jamali, S.; Rashidi, M.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2003**, *11*, 2313–2317.
(19) Hughes, R. P.; Meyer, M. A.; Tawa, M. D.; Ward, A. J.; Williamson, A.; Rheingold, A. L.; Zakharov, L. N. *Inorg. Chem.* **2004**, *43*, 747.
(20) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Chem. Commun.* **1981**, 851.
(21) Kinoshita, I.; Yasuba, Y.; Matsumoto, K.; Ooi, S. *Inorg. Chim. Acta* **1983**, *80*, L13.
(22) Maresca, L.; Natile, G.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Am. Chem. Soc.* **1982**, *104*, 7661.
(23) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608.
(24) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467.
(25) Deacon, G. B.; Nelson, K. T.; Tiekink, E. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 1819.
(26) Irwin, M. D.; Abdou, H. E.; Mohamed, A. A.; Fackler, J. P., Jr *Chem. Commun.* **2003**, *23*, 2882.
(27) Mohamed, A. A.; Mayer, A. P.; Abdou, H. E.; Irwin, M. D.; Pérez, L. M.; Fackler, J. P., Jr *Inorg. Chem.* **2007**, *46*, 11165.
(28) Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Suenaga, Y.; Yamamoto, M. *Inorg. Chim. Acta* **1998**, *271*, 129.
(29) Dossing, A.; Larsen, S.; van Lelieveld, A.; M. Bruun, R. *Acta Chem. Scand.* **1999**, *53*, 230.
(30) Tiripicchio, A.; Tiripicchio Camellini, M.; Uson, R.; Oro, L. A.; Ciriano, M. A.; Viguri, F. *J. Chem. Soc., Dalton Trans.* **1984**, 125.
(31) Gatteschi, D.; Mealli, C.; Sacconi, L. *J. Am. Chem. Soc.* **1973**, *95*, 2736.
(32) Griffith, W. P.; Yuen Koh, T.; White, A. J. P.; Williams, D. J. *Polyhedron* **1995**, *14*, 2019.
(33) Casas, J. M.; Diosdado, B. E.; Falvello, L. R.; Forniés, J.; Martín, A.; Rueda, A. J. *J. Chem. Soc., Dalton Trans.* **2004**, 2733–2740.
(34) Shen, W.-Z.; Gupta, D.; Lippert, B. *Inorg. Chem.* **2005**, *44*, 8249.
(35) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912.
(36) Paudler, W. W.; Kress, T. J. *J. Org. Chem.* **1967**, *32*, 832.

FAB− MS: *m*/*z* 1247 $[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]^-$. IR ($cm^{-1}$): C_6F_5 X-sensitive mode,[37] 812, 801 s; others, 1623 m, 1619 w, 1465 vs, 1060 vs, 956 vs; ampy: ν(N−H) 3332 m, others, 1584 m, 1504 s, 771 sw. ^{1}H NMR room temperature (acetone-d_6): δ ampy: 8.21 (d, 1H, -NH_2), 8.05 aprox. (d + t overlapped, 2H), 7.89 (d, 1H, -NH_2), 7.65 (d, 1H), 7.03 (t, 1H). ^{19}F NMR room temperature (acetone-d_6): δ −118.60 [m, 4F, *o*-F,$^3J(^{195}Pt, F) = 445$ Hz], −119.70 (m, 4F, *o*-F), −162.77 (t, 2F, *p*-F), −162.88 (t, 2F, *p*-F), −165.19 (m, 2F, *m*-F), −165.30 (d, 2F, *m*-F), −165.37 (t, 2F, *m*-F), −165.44 (d, 2F, *m*-F).^{1}H NMR 223 K (acetone-d_6): δ ampy: 8.50 (d, 2H), 8.10 (m, 4H), 7.96(d, 2H), 7.70(d, 2H), 7.04(t, 2H). ^{19}F NMR 223 K (acetone-d_6): −117.53 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 443$ Hz], −118.98 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 365$ Hz], −119.37 (d, 2F, *o*-F), −120.12 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 470$ Hz], −162.31 (t, 2F, *p*-F), −162.41 (t, 2F, *p*-F), −164.36 (m, 2F, *m*-F), −164.96 (m, 6F, *m*-F).

$[NBu_4][Pt(C_6F_5)_2Cl(Haza)]$ (2). To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ (0.500 g, 0.031 mmol) in CH_2Cl_2 (30 mL) were added 0.073 g (0.062 mmol) of 7-azaindol (1:2 molar ratio). The solution was stirred at room temperature for 30 min and then evaporated to dryness. A mixture of 2 mL of ^{i}PrOH and 30 mL of H_2O was added to the residue, and after 15 min of stirring a white solid was obtained, filtered off, and air-dried (65% Yield). Anal. Found (Calcd for $C_{33}H_{42}F_{12}N_3ClPt$): C, 44.61 (44.43); H, 4.71 (4.57); N, 4.16 (4.54).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 807 s, 796 s; others, 1501 vs, 1056 vs, 959 vs; azaH: ν(N−H): 3421 m, others:1598 m, 546 w, 496 w, 445 w; ν(Pt−Cl): 292 w; NBu_4^+: 888 m. ^{1}H NMR room temperature ($CDCl_3$): δ aza: 8.4 (d, 1H, H*1*), 6.9 (dd, 1H, H2), 7.9 (d, 1H, H*3*), 6.5 (d, 1H, H*4*), 7.3 (m, 1H, H*5*), 10.3 (s, 1H, H*6*); NBu_4: 0.95 (t, 12H, -CH_3), 1.38 (sext., 8H, α-CH_2), 1.61 (m, 8H, β-CH_2), 3.12 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$): δ −118.5 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 487$ Hz], −120.2 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 527$ Hz], −166.4 (m, 2F, *m*-F), −167.1 (m, 2F, *m*-F), −165.4 (t, 1F, *p*-F), −166.4 (t, 1F, *p*-F).

$[NBu_4]_2[Pt_2(\mu\text{-aza})_2(C_6F_5)_4]$ (3). To a solution of $[NBu_4][Pt(C_6F_5)_2Cl(azaH)]$ (**2**) (0.400 g, 0.432 mmol) in CH_2Cl_2 (20 mL) were added 0.54 mL of a solution of NBu_4OH in methanol (0.8 M, 0.432 mmol). The solution was stirred for 15 min, and after that, the solution was evaporated to dryness. Twenty milliliters of ^{i}PrOH were added to the residue precipitating a white solid that was filtered off, washed with 5 mL of ^{i}PrOH and *n*-hexane, and, finally air-dried (80% Yield). Anal. Found (Calcd for $C_{70}H_{82}F_{20}N_6Pt_2$): C, 47.42 (47.30); H, 4.81 (4.65); N, 4.92 (4.72).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 809 s, 796 s; others, 1501 vs, 1056 vs, 957 vs; azaH: 1598 m, 580 w, 468 w, 446 w; NBu_4^+: 888 m. ^{1}H NMR room temperature ($CDCl_3$): δ aza: 8.4 (d, 2H, H*1*), 6.9 (dd, 2H, H2), 7.9 (d, 2H, H*3*), 6.5 (d, 1H, H*4*), 7.3 (m, 1H, H*5*); NBu_4: 0.95 (t, 12H, -CH_3), 1.38 (sext., 8H, α-CH_2), 1.61 (m, 8H, β-CH_2), 3.12 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$): δ −118.5 [d, 4F, *o*-F, $^3J(^{195}Pt, F) = 494$ Hz], −120.3 [d, 4F, *o*-F, $^3J(^{195}Pt, F) = 537$ Hz], −166.4 (m, 4F, *m*-F), −167.1 (m, 4F, *m*-F), −165.4 (t, 2F, *p*-F), −166.4 (t, 2F, *p*-F).

***cis*-$[Pt(C_6F_5)_2Cl(napyH)]\cdot H_2O$ (4).** To a CH_2Cl_2 (30 mL) solution of *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) (0.200 g, 0.303 mmol were added 0.65 mL of a solution of HCl (aq.) in MeOH (0.464 M, 0.303 mmol). The solution was stirred at room temperature for 15 min, and the precipitation of a yellow solid was observed. This solid was filtered off, washed with 5 mL of CH_2Cl_2, and air-dried (76% Yield). Anal. Found (Calcd for $C_{20}H_9ClF_{10}N_2OPt$): C, 33.44 (33.67); H, 0.96 (1.27); N, 3.84 (3.92).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 815 s, 803 s; others, 1501 vs, 1058 vs, 958 vs; napyH: ν(N−H) 3634 s m, others, 1634 s, 1618 s, 1548 s, 825 s, 784 s; ν(Pt−Cl) 341 m; H_2O 3460 m. ^{1}H NMR room temperature (acetone-d_6): δ 10.1 [dd, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 5.6 Hz], 9.6 [dd, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 5.2 Hz, $^3J(^{195}Pt, o\text{-H}) = 29.7$ Hz], 8.6 [dd, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.3 Hz], 8.1 [dd, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.4 Hz], 9.7 [dd, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.7 Hz], 9.3 [dd, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.6 Hz]. ^{19}F NMR (acetone-d_6): δ −117.4 [d, 2F, *o*-F, $^3J(^{195}Pt,F) = 488$ Hz], −119.0 [d, 2F, *o*-F, $^3J(^{195}Pt,F) = 493$ Hz], −165.9 (m, 2F, *m*-F), −167.6 (m, 2F, *m*-F), −165.7 (t, 1F, *p*-F), −165.8 (t, 1F, *p*-F).

***cis*-$[Pt(C_6F_5)_2Br(napyH)]\cdot H_2O$ (5).** To a solution of *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) (0.200 g, 0.303 mmol) in CH_2Cl_2 (30 mL) were added 0.85 mL of a solution of HBr (aq.) in MeOH (0.354 M, 0.303 mmol). The solution was stirred at room temperature for 15 min and then evaporated to dryness. Twenty milliliters of $CHCl_3$ were added to the residue, and the resulting yellow solid was filtered off, washed with 5 mL of $CHCl_3$ and *n*-hexane, and finally air-dried(71% Yield). Anal. Found (Calcd for $C_{20}H_9BrF_{10}N_2OPt$): C, 31.84 (31.69); H, 1.32 (1.19); N, 3.84 (3.69).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 813 s, 803 s; others, 1501 vs, 1058 vs, 959 vs; napyH: ν(N−H) 3629 s m, others, 1632 s, 1607 s, 1546 s, 827 s, 783 s, 636 s; H_2O 3469 m. ^{1}H NMR room temperature (acetone-d_6): δ 10.2 [dd, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 5.5 Hz], 9.7 [dd, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 5.1 Hz], 8.7 [dd, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.1 Hz], 8.2 [dd, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.4 Hz], 9.8 [dd, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.5 Hz], 9.3 [dd, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.5 Hz]. ^{19}F NMR (acetone-d_6): δ −116.6 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 484$ Hz], −118.9 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 487$ Hz], −165.6 (m, 2F, *m*-F), −167.7 (m, 2F, *m*-F), −164.6 (t, 1F, *p*-F), −165.9 (t, 1F, *p*-F).

$[PtCl(C_6F_5)(\mu\text{-napy})_2PtCl(C_6F_5)]$ (6). A suspension of *cis*-$[Pt(C_6F_5)_2Cl(napyH)]$ (**4**) (0.200 g, 0.288 mmol) in CH_2Cl_2 (30 mL) was refluxed for 90 min and then evaporated to dryness. Twenty milliliters of $CHCl_3$ were added to the residue. The resulting yellow solid was filtered off, washed with 5 mL of $CHCl_3$ and *n*-hexane, and, finally air-dried (62% Yield). Anal. Found (Calcd for $C_{28}H_{12}Cl_2F_{10}N_4Pt_2$): C, 31.83 (31.86); H, 0.89 (1.15); N, 5.31 (5.31).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 804 s; others, 1500 vs, 1056 vs, 963 vs; ν(Pt−Cl) 340 m; napy: 847 s, 837 s, 791 s, 667 s. ^{1}H NMR room temperature (acetone-d_6): δ 10.4 [d, 2H, *o*-H, ^3J(*o*-H, *m*-H) = 5.1 Hz], 9.6 [d, 2H, *o*-H, ^3J(*o*-H, *m*-H) = 5.6 Hz], 8.1 [dd, 2H, *m*-H, ^3J(*m*-H, *p*-H) = 8.0 Hz], 7.5 [dd, 2H, *m*-H, ^3J(*m*-H, *p*-H) = 8.0 Hz], 8.9 (d, 2H, *p*-H), 8.7 (d, 2H, *p*-H). ^{19}F NMR room temperature (acetone-d_6): δ the signals for the *ortho*-fluor atoms cannot be appreciated over the noise level −166.9 (very broad signal, 4F, *m*-F), −164.4 (t, 2F, *p*-F).^{19}F NMR (acetone-d_6, −80 °C): δ −109.2 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 118$ Hz], −121.7 [d, 2F, *o*-F, $^3J(^{195}Pt, F) = 245$ Hz], −165.6 (m, 2F, *m*-F), −166.5 (m, 2F, *m*-F), −163.3 (t, 2F, *p*-F).

***cis*-$[Pt(C_6F_5)_2(HPPh_2)(napy)]$ (7).** To a suspension of *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) (0.200 g, 0.303 mmol) in CH_2Cl_2 (30 mL) under nitrogen atmosphere were added 52 μL (0.303 mmoles) of $HPPh_2$. The solution was stirred for 15 min at room temperature and then evaporated to dryness. Thirty milliliters of *n*-hexane were added to the residue yielding a solid which was filtered off, washed with *n*-hexane, and finally air-dried(71% Yield). Anal. Found (Calcd for $C_{32}H_{17}F_{10}N_2PPt$): C, 45.63 (45.45); H, 2.15 (2.04); N, 3.36 (3.15).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 803 vs, 782 s, others, 958 vs; $HPPh_2$: 2377 s, 1239 m, 1191 m, 703 m; napy: 834 m,, 632 w. ^{1}H NMR room temperature (acetone-d_6): δ 9.3 [d, 1H, *o*-H], 9.2 [s, 1H, *o*-H], 7.6 [m, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 7.6 Hz], 7.7 [m,

(37) Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 188.

Table 1. Crystal Data and Structure Refinement For $[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]\cdot 2CH_2Cl_2$ (**1**·$2CH_2Cl_2$), *cis*-$[Pt(C_6F_5)_2Cl(napyH)]\cdot H_2O$ (**4**·H_2O), $[Pt_2(C_6F_5)_2Cl_2(napy)_2]\cdot 0.375CH_2Cl_2$ (**6**·$0.375CH_2Cl_2$), and $[Pt_2(C_6F_5)_3(C{\equiv}CPh)(napy)_2]\cdot 2.5Me_2CO$ (**9**·$2.5Me_2CO$)

complex	**1**·$2CH_2Cl_2$	**4**·H_2O	**6**·$0.75CH_2Cl_2$	**9**·$2.5Me_2CO$
empirical formula	$C_{34}H_{12}F_{20}N_4Pt_2$ ·$2CH_2Cl_2$	$C_{20}H_7ClF_{10}N_2Pt$ ·H_2O	$C_{56}H_{12}Cl_4F_{20}N_4Pt_2$ ·$0.375CH_2Cl_2$	$C_{47}H_{17}F_{15}N_4Pt_2$ ·$2.5Me_2CO$
unit cell dimensions				
a (Å)	10.326(2)	13.035(4)	9.4640(10)	12.442(2)
b (Å)	11.2017(13)	13.677(4)	35.601(4)	25.214(4)
c (Å)	18.241(2)	12.292(4)	20.671(4)	16.797(2)
α (deg)	97.550(11)	90	90	90
β (deg)	94.610(6)	108.16(3)	93.550(10)	111.116(7)
γ (deg)	100.28(2)	90	90	90
V (Å^3), Z	2046.2(5), 2	2082.3(11), 4	6951.3(17), 8	4915.8(11), 4
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	200(1)	293(1)	293(1)	173(1)
radiation	graphite monochromated Mo Kα	graphite monochromated Mo Kα	graphite monochromated Mo Kα	graphite monochromated Mo Kα
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
cryst dimens (mm)	0.45 × 0.30 × 0.25	0.50 × 0.25 × 0.25	0.32 × 0.19 × 0.13	0.55 × 0.40 × 0.40
abs coeff (mm^{-1})	7.218	6.973	8.331	5.787
transmissn factors	1.000−0.379	0.439−0.360	0.865−0.420	0.512−0.228
abs cor	516 azimuthal scan data	432 azimuthal scan data	432 azimuthal scan data	10141 symmetry equivalent reflections
diffractometer	Siemens P4	Siemens P3m	Enraf Nonius CAD4	Siemens SMART
2θ range for data collect.(deg)	4.04−25.00	3.28−50.00	4.12−49.96	3.06−52.08
no. of rflns collected	7600	3853	13030	23535
no. of indep rflns	7172 [R(int) = 0.0197]	3667 [R(int) = 0.0320]	12191 [R(int) = 0.0935]	8531 [R(int) = 0.0383]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.039	1.041	1.006	1.710
final R indices ($I > 2\sigma(I)$)[a]	$R1$ = 0.0462, $wR2$ = 0.1390	$R1$ = 0.0291 $wR2$ = 0.0695	$R1$ = 0.0780 $wR2$ = 0.1654	$R1$ = 0.0336 $wR2$ = 0.0966
R indices (all data)	$R1$ = 0.0554, $wR2$ = 0.1514	$R1$ = 0.0399 $wR2$ = 0.0755	$R1$ = 0.2236 $wR2$ = 0.2258	$R1$ = 0.0391 $wR2$ = 0.1014

[a] $R1 = \sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{0.5}$

1H, *m*-H, ^3J(*m*-H, *p*-H) = 7.6 Hz], 8.4 [d, 1H, *p*-H], 8.5 [d, 1H, *p*-H]. ^{19}F NMR room temperature (acetone-d_6): δ −116.7 [d, 2F, *o*-F, $^3J(^{195}Pt, F_o)$= 446 Hz], −117.3 [d, 2F, *o*-F, $^3J(^{195}Pt, F_o)$= 355 Hz], −164.5(t, 1F, *p*-F), −163.2 (t, 1F, *p*-F), −164.9 (m, 2F, *m*-F), −166.1 (m, 2F, *m*-F).^{31}P-{^{1}H} NMR room temperature (acetone-d_6): δ −8, 43 [$^1J(^{195}Pt, P)$ = 2469 Hz, $^4J(F_o(trans), P)$ = 211 Hz, $^4J(F_o(cis), P)$ = 74 Hz].

[Pt(C$_6$F$_5$)(napy)(μ-PPh$_2$)$_2$Pt(C$_6$F$_5$)(napy)] (8). A suspension of *cis*-$[Pt(C_6F_5)_2(HPPh_2)(napy)]$ (**7**) (0.100 g, 0.120 mmol) in toluene (20 mL) was refluxed for 3 h, and gradually the suspension turned into an orange solution. This was evaporated to dryness, and the residue was treated with 5 mL of ^{i}PrOH, yielding a solid which was filtered off, washed with *n*-hexane, and finally air-dried (57% Yield). Anal. Found (Calcd for $C_{52}H_{32}F_{10}N_4P_2Pt_2$): C, 46.30 (46.09); H, 2.41 (2.38); N, 3.75 (4.13).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[37] 802 s, others, 965 s; PPh_2: 777 m, 699 m, 510 m, 469 m; napy: 832 m. ^{1}H NMR room temperature (acetone-d_6): δ 9.3 [d, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 5.0 Hz], 9.1 [d, 1H, *o*-H, ^3J(*o*-H, *m*-H) = 4.7 Hz], 7.7 [m, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.1 Hz], 7.6 [m, 1H, *m*-H, ^3J(*m*-H, *p*-H) = 8.2 Hz], 8.5 [d, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.6 Hz], 8.4 [d, 1H, *p*-H, ^3J(*p*-H, *o*-H) = 1.6 Hz]. ^{19}F NMR room temperature (acetone-d_6): δ −114.2 [d, 2F, *o*-F, $^3J(^{195}Pt, F_o)$= 446 Hz], −114.3 [d, 2F, *o*-F, $^3J(^{195}Pt, F_o)$ = 355 Hz], −168.6 (t, 2F, *p*-F), −166.8 (m, 4F, *m*-F). ^{31}P-{^{1}H} NMR room temperature (acetone-d_6): δ −137, 64 [$^2J(P_A, P_{A'})$ = 174 Hz, $^1J(^{195}Pt, P_A)$ = 2671 Hz, $^1J(^{195}Pt, P_{A'})$ = 1823 Hz].

[Pt(C$_6$F$_5$)$_2$(μ-napy)(μ-C≡CPh)Pt(C$_6$F$_5$)(napy)] (9). To a solution of $[Pt(C_6F_5)_2(napy)]$ (**A**) (0.300 g, 0.455 mmol) in CH_2Cl_2 (30 mL) under nitrogen atmosphere were added 46.5 μL (0.277 mmol) of HC≡CPh. The solution was stirred at room temperature for 2 h and then evaporated to dryness. To the residue were added 30 mL of *n*-hexane yielding a solid that was filtered off, washed with *n*-hexane and, finally air-dried(82% Yield). Anal. Found (Calcd for $C_{42}H_{17}F_{15}N_4Pt_2$): C, 40.15 (40.27); H, 1.10 (1.37); N, 4.36 (4.47).

IR (cm^{-1}): C_6F_5 X-sensitive mode, [37] 811 m, 802 m, 792 m; others, 1501 s, 1058 s, 965 s, 956 s; napy: 839 m, 634 w; CCPh: 2020 w, 1990 m, 751 m. ^{1}H NMR room temperature (acetone-d_6): δ 10.3 [br, 1H], 9.6 [d, 1H], 9.9 [dd, 1H], 8.9 [dd, 3H], 8.0 [br, 1H], 8.7 [dd, 1H], 7.6 [dd, 1H], 7.2 [dd, 3H], 9.2 [br, 1H], 8.9 [dd, 1H], 7.8 [dd, 4H]. ^{19}F NMR (acetone-d_6): δ −113.0 [d, 2F, *o*-F], −116.2 [d, 2F, *o*-F], −119.8 [d, 2F, *o*-F], −164.6 (m, 2F, *m*-F), −166.0 (m, 2F, *m*-F), −167.4 (m, 2F, *m*-F), −163.7 (t, 1F, *p*-F), −165.1 (t, 1F, *p*-F), −166.0 (t, 1F, *p*-F).

X-ray Structure Determinations. Crystal data and other details of the structure analyses are presented in Table 1. Suitable crystals were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 or Me_2CO solutions of the complexes **1**, **4**, **6**, and **9**. Crystals were mounted at the end of a glass fiber. The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-93 or SHELXL-97.[38,39] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except as noted below. For **1**, **6**, and **9**, all hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon atoms (1.5 times for methyl hydrogen atoms). For **4**, all hydrogen atoms, except for those in water molecules, were located in the Fourier maps and refined with a common displacement parameter. For **1**, one CH_2Cl_2 moiety was

(38) Sheldrick, G. M. *SHELXL-97, Fortran program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.
(39) Sheldrick G. M., *SHELXL-93, program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1993.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]\cdot 2CH_2Cl_2$ (**1**·$2CH_2Cl_2$)

Pt(1)−C(7)	2.009(8)	Pt(1)−N(4)	2.177(7)
Pt(1)−N(1)	2.102(6)	Pt(2)−C(13)	2.017(9)
Pt(2)−C(19)	2.014(9)	Pt(2)−N(2)	2.169(8)
Pt(2)−N(3)	2.096(7)	Pt(1)−C(1)	2.018(8)
N(1)−C(29)	1.352(10)	N(1)−C(25)	1.367(11)
N(2)−C(29)	1.434(11)	N(3)−C(34)	1.326(11)
N(3)−C(30)	1.371(11)	N(4)−C(34)	1.402(11)
C(7)−Pt(1)−C(1)	91.5(3)	C(7)−Pt(1)−N(1)	88.2(3)
C(1)−Pt(1)−N(1)	177.3(3)	C(7)−Pt(1)−N(4)	177.6(3)
C(1)−Pt(1)−N(4)	88.7(3)	N(1)−Pt(1)−N(4)	91.8(3)
C(19)−Pt(2)−C(13)	89.3(4)	C(19)−Pt(2)−N(3)	90.3(3)
C(13)−Pt(2)−N(3)	176.3(3)	C(19)−Pt(2)−N(2)	176.3(3)
C(13)−Pt(2)−N(2)	89.0(3)	N(3)−Pt(2)−N(2)	91.5(3)
C(29)−N(1)−Pt(1)	122.2(5)	C(29)−N(2)−Pt(2)	113.4(6)
C(34)−N(3)−Pt(2)	125.1(6)	C(30)−N(3)−Pt(2)	116.0(6)
C(34)−N(4)−Pt(1)	113.6(5)	N(1)−C(29)−N(2)	116.5(7)
N(3)−C(34)−N(4)	117.3(8)		

found to be disordered over two sets of positions and their occupancies fixed to 0.5. The anisotropic parameters for the chlorine and carbon atoms of these disordered molecules were constrained to be the same. The C−Cl distances in the CH_2Cl_2 molecules were restrained to chemically reasonable values. For **6**, three very diffuse molecules of CH_2Cl_2 were found in the density maps. They were refined isotropically and with common sets of isotropic displacement parameters for all the atoms in each molecule. Again, the C−Cl distances were restrained to sensible values. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 1.

Results and Discussion

Synthesis of $[(C_6F_5)_2Pt(\mu\text{-N-N})_2Pt(C_6F_5)_2]^{n-}$ (N-N = 2-aminopyridine, $n = 0$; 7-azaindolate, $n = 2$). Reaction of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ with 2-aminopyridine (ampy) in CH_2Cl_2 (molar ratio 1:1) allows the isolation of complex $[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]$ (**1**) in high yield. Its binuclear nature is suggested by the FAB+ mass spectrum (*m*/*z*: 1247).

The molecular structure of complex **1** has been established by an X-ray diffraction study. Important crystallographic data and data collection parameters are summarized in Table 1. Selected bond distances and angles are given in Table 2.

The molecular structure along with the atom labeling scheme is given in Figure 1. **1** is a binuclear compound in which two "$Pt(C_6F_5)_2$" moieties are bridged by two ampy ligands. The more important structural observation is that the two square planar platinum environments form a dihedral angle of 79.9(3)°, so that the disposition of the coordination planes does not cause the C_6F_5 groups to clash as would occur if the coordination planes were forced by the bridging ligand to be approximately parallel (as would presumably occur for napy). The complex exhibits a HT configuration and the long Pt···Pt distance [4.077(1)Å] precludes any intermetallic interaction. Within each platinum environment the Pt−N(amine) distances are slightly longer than those for Pt−N (pyridine) indicating that the latter are slightly stronger bonds (see Experimental Section). The angles formed by each C_6F_5 ring and its respective platinum coordination planes are 58.3(3)° (C(1)), 84.9(3)° (C(7)), 86.8(4)° (C(13)), and 85.0(3)° (C(19)).

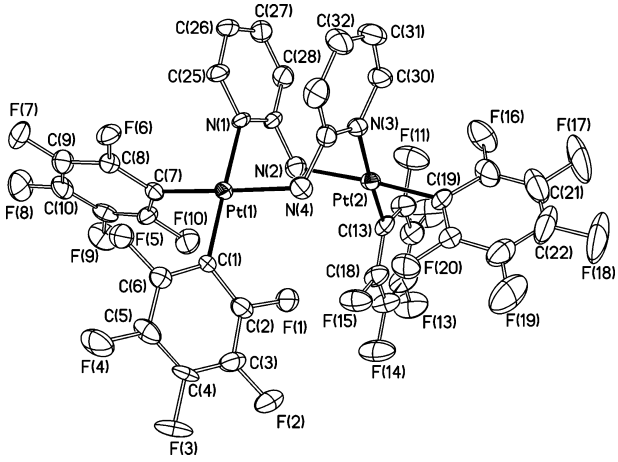


Figure 1. Molecular structure of the complex $[Pt_2(\mu\text{-ampy})_2(C_6F_5)_4]$ (**1**) (50% probability ellipsoid level).

Complex **1** is one of the few examples which contains neutral ampy ligands acting as bridges.[40,41] Noteworthy are the marked out of plane binding modes of the two metal ions from the aminopyridine planes. Relevant spectroscopic data for complex **1** are given in the Experimental Section.

The synthesis of the binuclear anionic complex $[NBu_4]_2[Pt_2(\mu\text{-aza})_2(C_6F_5)_4]$ (**3**) containing two azaindolate bridging ligands has been carried out in a two step process. The reaction of the binuclear $[NBu_4]_2[Pt_2(\mu\text{-Cl})_2(C_6F_5)_4]$ with azaindol (Haza) in CH_2Cl_2 (molar ratio 1:2) gives the mononuclear $[NBu_4][Pt(C_6F_5)_2Cl(Haza)]$ (**2**), which is fully characterized by its IR, ^1H, and ^{19}F NMR spectra (see Experimental Section).

Deprotonation of the 7-azaindole in $[NBu_4][Pt(C_6F_5)_2Cl(Haza)]$ (**2**) (in CH_2Cl_2) with NBu_4OH in MeOH solution results in the deprotonation of the coordinated 7-azaindole, the displacement of the chloro ligand, and the formation of the binuclear complex $[NBu_4]_2[Pt_2(\mu\text{-aza})_2(C_6F_5)_4]$ (**3**). Its IR spectrum shows, as expected, no signal corresponding to ν(N−H) and two strong absorptions, at 807 and 796 cm^{-1}, indicating *cis*- disposition of the pentafluorophenyl groups. However, these data are compatible with complex **3** being either mono- or binuclear (i.e., HH or HT configuration). NMR data for complex **3** are given in Experimental Section.

The final confirmation of the binuclear nature of **3** was obtained by an X-ray diffraction study. Unfortunately we have not been able to obtain crystals of sufficient quality as to carry out a complete X-ray structure analysis. Nevertheless, from the data available, the molecular skeleton can be established and shows that the anion of **3** is binuclear with the aza- ligands bridging the two metal atoms in an HT disposition. Figure 2 shows a schematic representation of the skeleton of the anion. As can be seen the orientation of the platinum coordination planes does not result in steric clashing of the C_6F_5 ligands, thus allowing formation of this binuclear complex.

Considering that the reaction between *cis*-$[Pt(C_6F_5)_2(thf)_2]$ and napy does not produce the binuclear complex but the

(40) Charland, J. P.; Beauchamp, A. L. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 581.
(41) Darensbourg, D. J.; Frost, B. J.; Larkins, D. L. *Inorg. Chem.* **2001**, *40*, 1993.

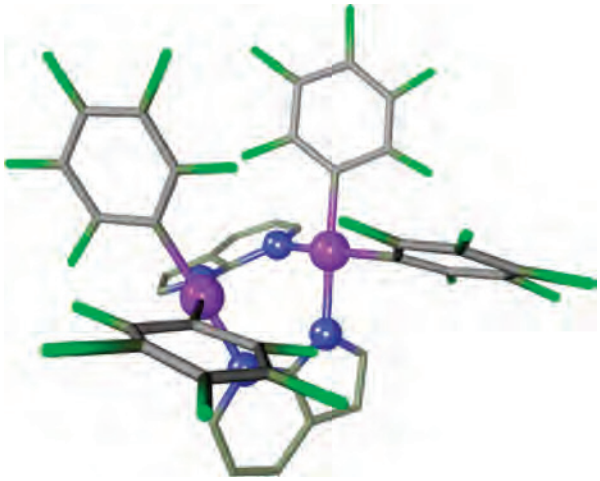


Figure 2. Schematic representation of the anion $[Pt_2(\mu\text{-aza})_2(C_6F_5)_4]^{2-}$ (**3**).

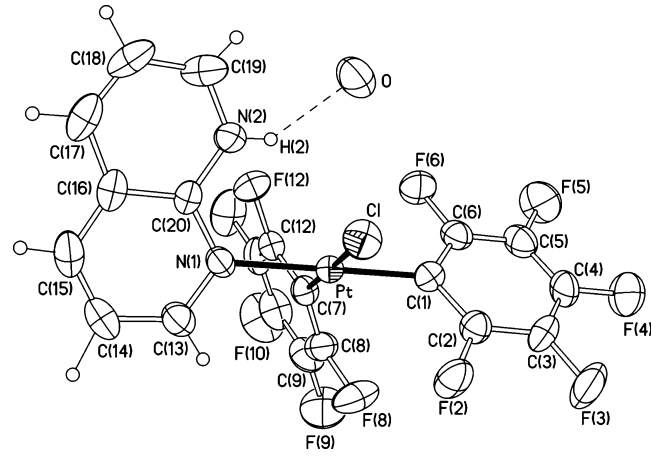


Figure 3. Molecular structure of the complex *cis*-$[Pt(C_6F_5)_2Cl(napyH)]$ (**4**) (50% probability ellipsoid level).

Table 3. Selected Bond Distances (Å) and Angles (deg) for *cis*-$[Pt(C_6F_5)_2Cl(napyH)]\cdot H_2O$ (**4**·H_2O)

Pt−C(7)	1.996(6)	Pt−Cl	2.378(2)
Pt−C(1)	1.994(6)	Pt−N(1)	2.099(5)
C(1)−Pt−C(7)	88.7(2)	C(7)−Pt−N(1)	90.3(2)
C(1)−Pt−Cl	92.0(2)	N(1)−C(20)−N(2)	117.7(5)

mononuclear **A**, due, in all likelihood, to the bulkiness of the C_6F_5 groups, we have attempted to prepare binuclear platinum complexes containing the 1,8 napy ligand as a bridge by using other smaller ligands bonded to platinum. One of the simplest complexes with small ancillary ligands would result from the reaction between $PtCl_2$ and 1,8 napy, which in appropriate molar ratios could produce the binuclear derivative. Unfortunately, the reaction between $PtCl_2$ and 1,8 napy is very slow. Refluxing the mixture in 1,2 dichloroethane for 12 h gives a yellow solid which is rather insoluble in all common solvents. The C, H, and N analyses agree with the values expected for $[PtCl_2(napy)]_x$. However, its very low solubility does not allow study of its NMR spectrum nor production of crystals for an X-ray crystal study. Its binuclear character is suggested by the FAB+ mass spectrum that show peaks corresponding to the $[Pt_2Cl_3(napy)_2]+$ fragment ($m/z = 757$).

Usually substitution of one C_6F_5 group bonded to a platinum center can be readily achieved by reacting the pentafluorophenyl platinum complex with HX (X = Cl, Br) solutions, in a process which produces breaking of the Pt−C_6F_5 bond, and formation of HC_6F_5 and a Pt−X bond.[2] However, the reaction between **A** in CH_2Cl_2 and HCl in MeOH/H_2O (1:1 molar ratio) rather leads to protonation of the napy ligand and formation of *cis*-$[Pt(C_6F_5)_2Cl(napyH)]\cdot H_2O$ as a yellow solid. Spectroscopic data are in agreement with this formula. An IR absorption around 3630 cm^{-1} is due to the ν(N−H) vibration and the ν(Pt−Cl) is observed at 341 cm^{-1}, and two absorptions due to the X-sensitive mode of the C_6F_5 groups (see Experimental Section) are observed at 815 (s) and 803(s) cm^{-1}. A broad absorption at around 3460 cm^{-1} is due to the presence of H_2O which can not be eliminated.

The ^1H and ^{19}F NMR spectra in acetone-d_6 are also in agreement with the proposed formula (see Experimental Section). The signal due to the hydrogen atom bonded to the nitrogen atom cannot be detected, probably because its acidic character and exchange processes involving the H_2O present. The ^{19}F NMR spectrum shows signals due to two inequivalent C_6F_5 groups (see Experimental Section).

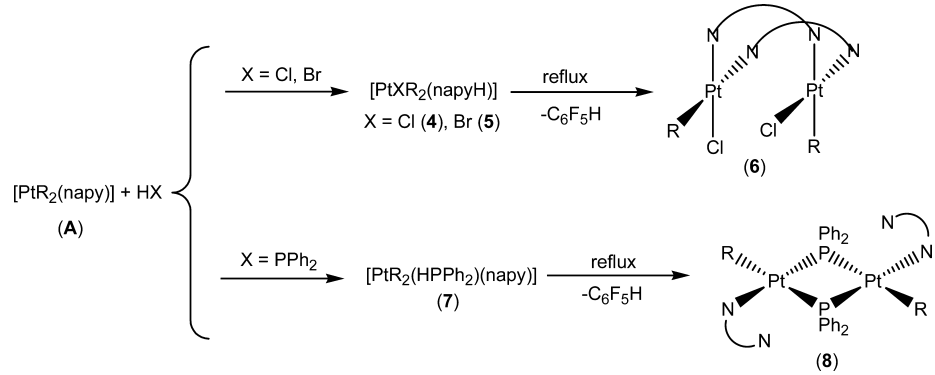
An X-ray diffraction study of complex **4** has also been carried out (Figure 3, Table 3). The Pt−C, Pt−N, and Pt−Cl distances are in the range found for other platinum(II) complexes.[33,42−44] The position of all the hydrogen atoms of the complex were determined from the electron density maps and freely refined. It was also found that the hydrogen atom bonded to the nitrogen establishes a hydrogen bond with a water molecule, which explains the formation of a persistent hydrate complex, observed in the IR and ^1H NMR.

Formation of **4** demonstrates the high reactivity of the strained four-membered chelate ring in **A**. The bromo derivative **5** can be formed by a similar reaction (see Experimental Section).

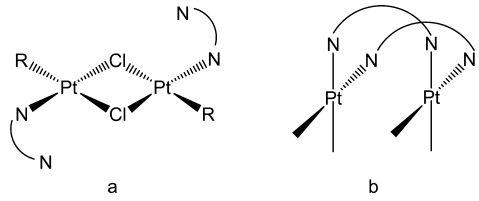
Complex **4** is moderately stable at room temperature both in solid state and in solution. However, when a suspension of **4** in CH_2Cl_2 is refluxed for 90 min, a yellow solid $[PtCl(C_6F_5)(\mu\text{-napy})_2PtCl(C_6F_5)]$ (**6**) is obtained (see Scheme 1). All the available structural data are in agreement with this formulation. The FAB+ mass spectrum shows a peak corresponding to $[Pt_2Cl_2(C_6F_5)_2(napy)_2]^+$. The IR spectrum shows only one absorption at 804 cm^{-1} due to the X-sensitive mode of the C_6F_5 groups (suggesting only one C_6F_5 group per Pt atom), and the ν(Pt−Cl) appears at 340 cm^{-1}. The ^1H NMR spectrum shows six signals assigned to the 1,8-naphthyridine protons indicating the inequivalence of the pyridine rings. One of the *ortho*-protons shows platinum satellites [9.6 ppm, d, $^3J_{Pt-H}$= 52.9 Hz] while the other, which

(42) Ara, I.; Casas, J. M.; Forniés, J.; Rueda, A. J. *Inorg. Chem.* **1996**, *35*, 7345.
(43) Casas, J. M.; Forniés, J.; Martín, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1559–1563.
(44) Casas, J. M.; Forniés, J.; Martín, A.; Rueda, A. J. *Organometallics* **2002**, *21*, 4560–4563.

Scheme 1



Scheme 2



appears at higher frequencies, does not clearly show platinum satellites. The ^{19}F NMR spectrum at low temperature shows signals due to one type of C_6F_5 groups with hindered rotation around the Pt−C bond (see Experimental Section).

All these structural data are consistent with the proposed formula for **6** $[Pt_2(C_6F_5)_2Cl_2(napy)_2]$ with a symmetrical structure. Two possible structures might account for the spectroscopic data (see Scheme 2a,b). The X-ray structure of **6** (see Figure 4) shows that the complex is binuclear with bridging napy ligand and face to face platinum coordination planes. Two essentially identical molecules are found in the asymmetric unit, and we will focus on one, since structural parameters are very similar for both (Table 4). The Pt−C, Pt−N, and Pt−Cl distances are in the range found in other Pt complexes containing ligands of this type,[33,42−44] and the angles around the platinum atoms for mutually *cis* ligands are between 87.7(8)° and 94(1)°. The pentafluorophenyl groups and hence the chloro ligands are arranged in such a way that they

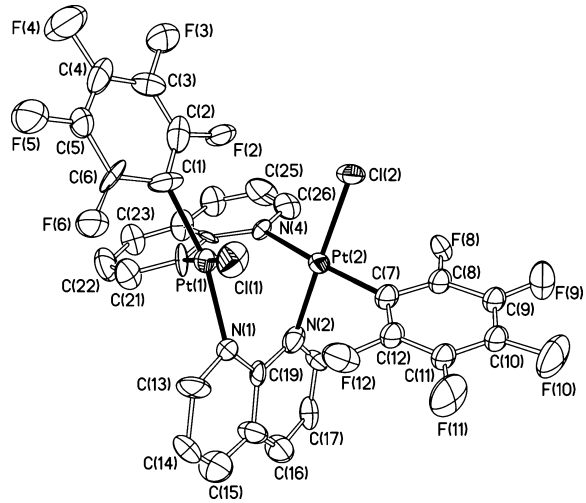


Figure 4. Molecular structure of the complex $[Pt_2(C_6F_5)_2Cl_2(napy)_2]$ (**6**) (50% probability ellipsoid level).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Pt_2(C_6F_5)_2Cl_2(napy)_2]\cdot 0.375CH_2Cl_2$ (**6**·0.375CH_2Cl_2)

Pt(1)−Pt(2)	2.997(2)	Pt(2)−C(7)	1.97(3)
Pt(1)−C(1)	2.02(3)	Pt(2)−N(2)	2.02(2)
Pt(1)−Cl(1)	2.262(8)	Pt(2)−N(4)	2.13(2)
Pt(1)−N(1)	2.12(2)	Pt(2)−Cl(2)	2.302(7)
Pt(1)−N(3)	2.03(2)		
Pt(3)−Pt(4)	3.050(2)	Pt(4)−C(35)	1.99(3)
Pt(3)−C(29)	1.98(3)	Pt(4)−N(6)	2.11(2)
Pt(3)−Cl(3)	2.298(9)	Pt(4)−N(8)	2.04(3)
Pt(3)−N(5)	2.08(3)	Pt(4)−Cl(4)	2.282(8)
Pt(3)−N(7)	2.09(2)		
C(1)−Pt(1)−Pt(2)	119(1)	N(2)−Pt(2)−N(4)	89.5(9)
N(3)−Pt(1)−N(1)	89.4(9)	N(4)−Pt(2)−Cl(2)	92.0(6)
C(1)−Pt(1)−Cl(1)	88(1)	C(7)−Pt(2)−Cl(2)	88.7(8)
N(1)−Pt(1)−Cl(1)	92.0(7)	C(7)−Pt(2)−Pt(1)	118.8(9)
N(1)−Pt(1)−Pt(2)	74.2(6)	N(2)−Pt(2)−Pt(1)	83.3(7)
N(3)−Pt(1)−Pt(2)	81.3(5)	N(4)−Pt(2)−Pt(1)	74.0(7)
Cl(1)−Pt(1)−Pt(2)	100.4(2)	Cl(2)−Pt(2)−Pt(1)	97.6(2)
C(29)−Pt(3)−Pt(2)	99.8(9)	N(6)−Pt(4)−N(8)	94(1)
N(5)−Pt(3)−N(7)	89(1)	N(6)−Pt(4)−Cl(4)	90.0(9)
C(29)−Pt(3)−Cl(3)	93(1)	C(35)−Pt(4)−Cl(4)	87.7(8)
N(7)−Pt(3)−Cl(3)	91.4(8)	C(35)−Pt(4)−Pt(3)	118(1)
N(5)−Pt(3)−Pt(4)	77.0(9)	N(6)−Pt(4)−Pt(3)	74.4(8)
N(7)−Pt(3)−Pt(4)	79.7(9)	N(8)−Pt(4)−Pt(3)	77.5(9)
Cl(3)−Pt(3)−Pt(4)	112.7(2)	Cl(4)−Pt(4)−Pt(3)	109.2(3)

avoid steric clashes between the C_6F_5 ligands. This arrangement also produces a closer packing of the ligands that viciates the movement of the C_6F_5 rings which would make the F*o* of each group equivalent and the F*m* as well.

Each platinum center is bonded to two N-atoms, one from each napy ligand, but the Pt−N distances are slightly different [Pt(1)−N(3) = 2.03(2) Å; Pt(1)−N(1) = 2.12(2) Å; Pt(2)−N(2) = 2.02(2) Å; Pt(2)−N(4) = 2.13(2) Å] in agreement with the higher *trans*-influence of the C_6F_5 ligand. Each napy ligand is essentially planar and is oriented almost perpendicular to one of the platinum coordination planes (dihedral angles: plane Pt(1)-plane napy N(3,4) = 87.7(4)°; plane Pt(2)-plane napy N(1,2) = 85.6(4)°] but rotated with respect to the other platinum plane [dihedral angles: plane Pt(1)-plane napy N(1,2) = 62.7(5)°; plane Pt(2)-plane napy N(3,4) = 64,1(4)°]. It is notable that the two Pt−N bonds of each ligand are not in the plane of their respective napy plane; these "mis-directed" Pt−N bonds allow reduction of interligand steric interactions. The platinum coordination planes are not completely parallel (dihedral angle = 35.9(5)°) while the Pt(1)−Pt(2) distance is 2.997(2) Å. This is a short intermetallic distance for a compound that does not require the presence of a Pt−Pt bond. Notably the Pt···Pt distance

in complex **1** is 4.077(1) Å, and long distances have also been observed in other complexes of this general type. Although the shortest Pt···Pt distance found in a binuclear Pt(II) complex bridged by two identical bidentate ligands in a face to face disposition is 2.789(1) Å (in $[Pt_2(C_4H_6NO)_2(bipy)_2](ClO_4)_2$), [10] more typical Pt···Pt separations are around 3.0 Å for ligands with N-, or O- donor atoms[45−47] or even longer (3.2−4.0 Å) for ligands with P donor atoms.[5,12,48] This short Pt···Pt distance is presumably enforced by the proximity of the nitrogen atoms in the skeleton of the napy ligand which requires proximity of the platinum centers to which they are bonded. The formation of "mis-directed" Pt−N bonds allows a longer Pt···Pt distance, but even in this situation the metal centers are very close. In all likelihood, the whole structure is a compromise between the formation of a binuclear complex, which is presumably thermodynamically favored, and the necessity of avoiding the steric repulsions between the metal atoms and the C_6F_5 groups.

With the aim of investigating further the reactivity of complex **A** toward other reagents ZH to produce elimination of C_6F_5H and incorporation of the nucleophile Z^- to the platinum coordination environment, we have studied the reaction between *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) and PPh_2H at room temperature in a 1:1 molar ratio. This results in the formation of *cis*-$[Pt(C_6F_5)_2(HPPh_2)(napy)]$ (**7**) (Scheme 1), a complex which contains PPh_2H and monodentate napy as ligands. The structure of **7** can be inferred from the spectroscopic data.

The FAB+ mass spectrum shows a peak corresponding to the cation *cis*-$[Pt(C_6F_5)_2(HPPh_2)(napy)]^+$ ($m/z = 845$). The IR spectrum of this complex shows an absorption at 2377 cm^{-1} corresponding to the ν(H−P) vibration of $HPPh_2$ and other absorptions due to the same ligand at 520, 475, and 427 cm^{-1}. The ^1H NMR data are given in the Experimental Section. At 6.3 ppm there is a doublet due to the hydrogen atom bonded to the phosphorus [$^1J(^{31}P,H) = 378$ Hz], which also shows platinum satellites [$^2J(^{195}Pt,H) = 35$ Hz]. The ^{19}F NMR spectrum shows signals corresponding to two chemically inequivalent C_6F_5 groups. The ^{31}P NMR spectrum shows a signal at −8.4 ppm with platinum satellites [$^1J(^{195}Pt,^{31}P) = 2469$ Hz].

Deprotonation of the PPh_2H does not take place at room temperature, but when a toluene solution of **7** is refluxed, deprotonation of the phosphine and concomitant elimination of C_6F_5H takes place, thus resulting in the formation of $[Pt_2(C_6F_5)_2(PPh_2)_2(napy)_2]$ (**8**) (Scheme 1).

All the spectroscopic data (see Experimental Section) are in agreement with the proposed structure (Scheme 1) for **8** with bridging PPh_2 and terminal monodentate napy ligands.

The ^{31}P {^1H} NMR spectrum is the result of the superimposition of the spectra of the three isotopomers. It consists of a central singlet at −137.7 ppm with no ^{195}Pt centers (spin system A_2), eight signals (as two doublets of doublets) due to the AA′ part of the AA′X spin system from the isotopomer with one ^{195}Pt center. The parameters $^2J(P_A, P_{A'})$, $^1J(^{195}Pt, P_A)$, and $^1J(^{195}Pt, P_{A'})$ can be extracted from this subspectrum. Finally, the isotopomer with two ^{195}Pt centers, for which only two signals appear, are separated by $N = {}^1J(^{195}Pt, P_{A'}) + {}^1J(^{195}Pt, P_A)$.[49−51] The chemical shift of the P atoms appear at high field as it should be expected for a 32 valence electron skeleton, that is, the two PPh_2 are supporting two Pt atoms not joined by a Pt−Pt bond. In agreement with this, the value of the coupling between the two P atoms (174 Hz) is in the range usually found for the phosphido groups in a "Pt(μ-$PPh_2)_2$Pt" fragment.[52−54] The assignment of the two values (see Experimental Section) can be carried out unambiguously by comparison with other analogous complexes.[55]

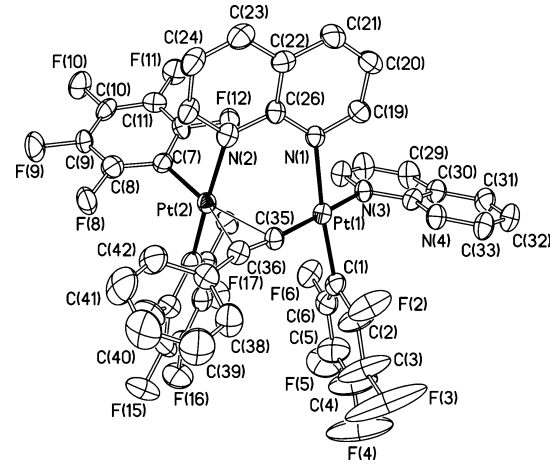


Figure 5. Molecular structure of the complex $[Pt_2(C_6F_5)_3(C{\equiv}CPh)(napy)_2]$ (**9**) (50% probability ellipsoid level).

Complexes **A**, **6**, and **8** are noteworthy examples of the structural differences induced by the type of ligands in complexes of similar stoichiometry $[Pt(C_6F_5)Z(napy)]_x$ ($Z = C_6F_5$, $x = 1$, **A**; $Z = Cl$, $x = 2$, **6**; $Z = PPh_2$, $x = 2$, **8**).

Finally, *cis*-$[Pt(C_6F_5)_2(napy)]$ (**A**) reacts with HCCPh either in 1:1 or 2:1 molar ratio to produce, under mild conditions, $[Pt_2(C_6F_5)_3(C{\equiv}CPh)(napy)_2]$ (**9**). The structure of **9** has been established by single crystal X-ray diffraction (see Figure 5). Relevant crystallographic details are summarized in Table 1 while selected bond distances and angles are listed in Table 5. Complex **9** is binuclear and each platinum center displays square planar coordination environments, with one napy and an acetylide acting as bridging ligands. One of the platinum centers is coordinated to two C_6F_5 groups in *cis* positions, one N atom of the bridging napy ligand, and η^2 to the C≡C

(45) Grehl, M.; Krebs, B. *Inorg. Chem.* **1994**, *33*, 3877–3885.
(46) Engelking, H.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **1996**, 2409–2416.
(47) Oskui, B.; Mintert, M.; Sheldrick, W. S. *Inorg. Chim. Acta* **1999**, *287*, 72–81.
(48) Wing-Wah Yam, V.; Yu, K.-L.; Man-Chung Wong, K.; Cheung, K.-K. *Organometallics* **2001**, *20*, 721.
(49) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.
(50) Fornies, J.; Fortuño, C.; Gil, R.; Martin, A. *Inorg. Chem.* **2005**, *44*, 9534.
(51) Forniés, J.; Fortuño, C.; Ibañez, S.; Martín, A. *Inorg. Chem.* **2006**, *45*, 4850.
(52) Falvello, L. R.; Forniés, J.; Fortuño, C.; Durán, F.; Martin, A. *Organometallics* **2002**, *21*, 2226.
(53) Alonso, E.; Forniés, J.; Fortuño, C.; Martin, A.; Orpen, A. G. *Organometallics* **2003**, *22*, 2723.
(54) Ara, I.; Chaouche, N.; Fornies, J.; Fortuño, C.; Kribii, A. *Organometallics* **2006**, *25*, 1084.
(55) Ara, I.; Chaouche, N.; Fornies, J.; Fortuño, C.; Kribii, A.; Martín, A. *Eur. J. Inorg. Chem.* **2005**, 3894.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Pt_2(C_6F_5)_3(C{\equiv}CPh)(napy)_2]\cdot 2.5Me_2CO$ (**9**·2.5Me_2CO)

Pt(1)−C(1)	2.005(6)	Pt(2)−C(13)	2.010(6)
Pt(1)−C(35)	1.939(5)	Pt(2)−C(7)	2.012(6)
Pt(1)−N(1)	2.146(5)	Pt(2)−N(2)	2.115(5)
Pt(1)−N(3)	2.085(4)	Pt(2)−C(35)	2.230(5)
Pt(1)−Pt(2)	3.065(5)	Pt(2)−C(36)	2.305(5)
C(35)−C(36)	1.225(8)		
C(35)−Pt(1)−C(1)	88.1(2)	C(13)−Pt(2)−C(7)	88.6(2)
C(35)−Pt(1)−N(1)	91.2(2)	C(7)−Pt(2)−N(2)	90.7(2)
C(1)−Pt(1)−N(3)	89.8(2)	C(13)−Pt(2)−C(35)	95.3(2)
N(3)−Pt(1)−N(1)	91.8(2)	N(2)−Pt(2)−C(35)	84.4(2)
C(35)−Pt(1)−Pt(2)	45.8(2)	C(13)−Pt(2)−C(36)	93.4(2)
N(1)−Pt(1)−Pt(2)	77.3(1)	N(2)−Pt(2)−C(36)	88.4(2)
N(3)−Pt(1)−Pt(2)	128.5(1)	C(35)−Pt(2)−C(36)	31.3(2)
C(1)−Pt(1)−Pt(2)	107.2(2)	C(35)−Pt(2)−Pt(1)	38.6(1)
C(13)−Pt(2)−Pt(1)	95.3(2)	C(36)−Pt(2)−Pt(1)	69.8(1)
C(7)−Pt(2)−Pt(1)	126.6(2)	N(2)−Pt(2)−Pt(1)	81.9(1)
C(35)−C(36)−C(37)	164.2(6)		

of the acetylide ligand, while the other is bonded to one C_6F_5 group, the acetylide ligand (σ-bound) and one of the N atoms of the bridging napy and to the N atom of the other, monodentate, napy ligand. The dihedral angle between the metal coordination planes is 81.4(3)°; the Pt(1)···Pt(2) distance is 3.065(1) Å, which seems to indicate that there is no intermetallic bond. Both napy ligands are planar. The Pt−N distances for the bridging napy are almost equal within experimental error (Table 5). The Pt(2)−N(2) vector lies almost in the napy plane but the Pt(1)−N(1) deviates significantly from this plane by 13.4(2)°. The Pt(1)−N(1)−N(2)−Pt(2) torsion angle is 13.3(3)°. This is the result of mis-directed bonding between the napy ligands and the Pt centers imposed by the coordination of the rest of the ligand and the steric strain. The C≡C distance 1.228(8) Å is in agreement with the η^2-interaction[56,57] as is the C(35)−C(36)−C(37) angle [164.2(6)°]. Finally, the η^2-Pt(2)−C≡CPh interaction is slightly asymmetric [Pt(2)−C(35) = 2.230(5) Å and Pt(2)−C(36) = 2.305(5) Å].

The overall process involves substitution of a C_6F_5 group on one platinum by the action of the HC≡CPh while the other remains; bridging by the acetylide group of one of the substrates and the napy of the other leads to formation of the binuclear entity. Finally, the tendency of the Pt(II) substrates to four coordination leads to cleavage of one Pt−N bond of the napy ligand (which as we have seen before is strained when acting as a chelating ligand) and results in a monodentate napy ligand.

The spectroscopic data of **9** are in agreement with this stoichiometry. Thus, the infrared spectrum shows an absorption at 839 cm^{-1} corresponding to the napy ligand. The acetylide ligand gives two absorptions at 1990 cm^{-1} [ν(C≡C)] and 751 cm^{-1}. The ^{1}H NMR spectrum shows two signals [7.8 ppm (3H) and 7.3 ppm (2H)] for the hydrogen atoms of the phenyl ring. The napy resonances are difficult to assign because of the inequivalence of the two napy ligands. Six well defined signals corresponding to a bridging napy are observed besides other six poorly resolved signals whose chemical shift suggests that this ligand is terminal. The ^{19}F NMR spectrum indicates the existence of three chemically inequivalent C_6F_5 groups.

(56) Forniés, J.; Gómez-Saso, M. A.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1992**, *11*, 2873.
(57) Carpenter, P.; Lukehart, C. M. *Inorg. Chim. Acta* **1991**, *190*, 7.

Conclusions

Attempts to synthesize binuclear complexes with two bridging "*cis*-$Pt(C_6F_5)_2$" fragments have succeeded with the 2-ampy and the 7-aza bidentate ligands. The first one apparently works because of the high flexibility between the two N-donor atoms of the ligands and the second because, although the donor atoms are in rigid positions, they have a large bite angle. The distances between the platinum centers in the binuclear complexes are 4.1 and 3.4 Å for 2-ampy and 7-aza, respectively, in agreement with the structural characteristics of these ligands.

The rigid napy ligand, with a more restricted bite angle, gives a mononuclear complex with the "$Pt(C_6F_5)_2$" fragment having the bidentate ligand in a strained chelating form. Our hypothesis that the steric requirement of the C_6F_5 groups is the cause of the formation of a mononuclear complex with the napy ligand instead of the binuclear alternatives was confirmed because the substitution of one pentafluorophenyl group for a chloro ligand in each platinum ion and the decrease in spatial requirements led to formation of a binuclear complex with a short Pt···Pt distance of 2.98 Å and a bridging 1,8-naphthyridine ligand.

The substitution of one C_6F_5 anion by the more bulky PPh_2 group (also potentially a bridging ligand) in complex **A** affords a binuclear complex of type 1a (see Chart 1) with monodentate napy ligands.

Use of the less bulky bridging ligand −C≡CPh produces substitution of one pentafluorophenyl group, independent of the Pt/napy ratio (1:1 or 2:1), affording an asymmetrical binuclear complex with two different bridging ligands: the acetylide in a $\sigma-\pi$ coordination and one of the two napy ligands.

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Supporting Information Available: Further details of the structure determinations of **1**·2CH_2Cl_2, **4**·H_2O, **6**·0.375CH_2Cl_2, and **9**·2.5Me_2CO including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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