Inorg. Chem. **2005**, *44*, 9444–9452

Inorganic Chemistry

Article

Synthesis and in Solution and Solid State Structural Study of Intramolecular Pt···H Interactions in Pentafluorophenyl Platinum(II) Complexes Containing the Ligands Triazene, Formamidine, and 2-Aminopyridine

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Received May 18, 2005

The preparation of the $[NBu_4][Pt(C_6F_5)_3L]$ complexes (L = triazene, **1**; formamidine, **2**; 2-aminopyridine, **3**) have been carried out. These ligands contain a hydrogen atom, with more or less acidic character, in a position suitable for establishing an intramolecular hydrogen bonding interaction with the metal center. This interaction has been detected in solution for **1**; its ^1H NMR spectrum shows that the resonance assignable to this hydrogen has platinum satellites. For **2**, this coupling is not observed, and the interaction, if it exists, has to be weaker because of the less acidic character of the hydrogen atom. The 2-aminopyridine ligand is more flexible than the triazene or formamidine, and also in this case, no evidence of the interaction in solution is obtained. Nevertheless, if another potential proton acceptor is present, such as ClO_4^- in $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (**4**), a conventional N–H···O–Cl hydrogen bond is formed. The crystal structures of complexes **1**–**4** have been determined by X-ray diffraction.

Introduction

It is well-known that hydrogen bonding plays a very important role in several different areas of chemistry such as crystal engineering, molecular recognition,[1,2] molecular biology and catalysis,[3,4] molecular aggregation in the solid state, and host−guest exchange.[5,6]

Atoms involved in "traditional" hydrogen bonding belong to the second and third periods of groups 14−17. However, metals can also establish interactions with hydrogen atoms in two different ways:[7] (i) agostic interactions,[8,9] in which the metal center receives electron density from the D−H bond (D = hydrogen donor atom), and (ii) hydrogen bonding, in which the metal donates electron density to the hydrogen atom. These hydrogen bonds are supported by electron-rich metals, especially in low oxidation states. In fact, all of the M···H−D (D = hydrogen donor) systems that have been reported until now involve d^8 or d^{10} metals.[10−16]

The basic character of the platinum(II) centers makes them suitable starting materials for preparing complexes containing such interactions because Pt^{II} is an electron-rich center and its complexes are square planar which enables the close location of a hydrogen atom above and below the coordination plane. In addition, the acidic nature of this hydrogen also favors the interaction.

Most of the Pt → H interactions reported so far are intramolecular.[17,18] Van Koten reported a series of complexes

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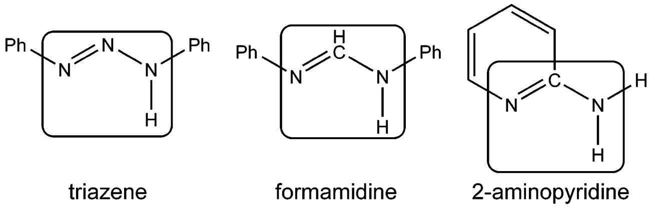
10.1021/ic050800g CCC: $30.25

Chart 1



containing N−H···Pt interactions,[17,19] among which, is the shortest Pt···H distance found for an intramolecular interaction (Pt···H distance = 2.11(5) Å, Pt···H−N = 168(4)°). [17] In this case, the hydrogen atom belongs to a cationic fragment, that enhances its acidic nature. In most of the cases, the proton donor atom is found to be nitrogen, and there are only a couple of examples of O−H···Pt interactions.[18] On the other hand, fewer intermolecular Pt → H interactions are known; a classic example is the one found in $[NPr_4][PtCl_4][cis\text{-}PtCl_2(NH_2Me)_2]$.[20] The structure of this complex was determined by neutron diffraction, and a short Pt···H distance of 2.262(11) Å and an N−H···Pt angle of 164.4(7)° were found. It has been proposed that the presence of this D−H···Pt interaction may facilitate proton transfer to the platinum center followed by coordination of the conjugated base (D^-) to the platinum in a oxidative addition process.[16,19,21,22]

A Pt → H interaction can easily be understood in terms similar to those for a classical hydrogen bond. The metal center has a full orbital with an electron pair that can interact with an electropositive hydrogen atom, or in other words, the electron pair is donated to create a 3-center 4-electron system.[16,18]

In addition to the electrostatic attraction between the electropositive H atom and the electron pair on platinum, a significant covalent contribution to this interaction has been suggested by theoretical studies.[19]

The choice of suitable ligands in terms of their structural features or the electronic properties of their donor atoms is essential for the synthesis of complexes with Pt → H interactions. Ligands containing aminic groups in suitable positions usually yield this type of interaction. Triazene, formamidine, and 2-aminopyridine (see Chart 1) are nitrogen donors, and they contain NH groups which can act as proton donors. The N═E−NHR skeletons of the ligands (circled in the chart) are quite similar, but a small change can influence the acidity or the final orientation of the hydrogen atom and thus can be an important factor in establishing the Pt → H interaction. They have been used to prepare complexes of stoichiometry $[PtR_3L]^-$ ($R = C_6F_5$), and the results are described in this paper.

Free triazene and formamidine ligands have the configurations shown in Chart 1.[23−28] The triazene or more frequently the triazenide ligands are easily coordinated to transition metals.[29−32] However, examples of its coordination to Pt are scarce.[33,34] In addition to this, amidines have rarely been used as ligands, despite the fact that the first example was prepared with platinum in 1865,[35] and very few crystal structures of monodentate neutral formamidine complexes are known.[35] The neutral 2-aminopyridine ligand is present in a great number of complexes in which it acts as a monodentate N-pyridine donor.[36−45]

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, AV-400, Unity-300, or Gemini-300 spectrometer in solution of deuterated solvents. ^1H and ^{19}F NMR spectra at variable temperatures were recorded in acetone-d_6 or CD_2Cl_2 solutions on a Brüker ARX-300 spectrometer. Positive and 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 the matrix. $[NBu_4]_2[Pt(C_6F_5)_3Cl]$,[46] $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$,[47] and $AgClO_4$[48] were prepared as described elsewhere. The triazene, formamidine, and 2-aminopyridine ligands were used as purchased from Aldrich.

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Caution: Perchlorate salts are potentially explosive. Only small amounts have to be handled and with great caution.

Synthesis of $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (1). $AgClO_4$ (0.063 g 0.302 mmol) was added to a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ (0.367 g, 0.302 mmol) in acetone (20 mL). The mixture was stirred at room temperature for 30 min. The precipitated AgCl was eliminated by filtration and 0.060 g (0.302 mmol) of PhN=NNHPh were added to the resulting solution. The solvent was evaporated to dryness; then, 4 mL of OEt_2 were added to the oily residue, and the mixture was evaporated to dryness. The addition of 10 mL of ^{i}PrOH to the residue yielded complex **1** as a yellow solid that was filtered off and washed with *n*-hexane. Yield: 75%. Anal. Found (calcd for $C_{46}H_{47}N_4F_{15}Pt$): C, 48.59 (48.63); H, 4.45 (4.17); N, 4.72 (4.92). IR (cm^{-1}): C_6F_5 ν(C−C) 1632 m, ν(C−F) 1054 vs, 955 vs; X-sensitive mode[49] 804 s, 788 w, 771 s; $C_{12}H_{11}N_3$ 1599 s, 1316 m, 1244 s, 1170 w, 1157 w, 762 s, 697 m, 686 m, 659 m, 537 m, 504 w, 433 w, ν(N−H) 3061 m; NBu_4^+ 883 m. ^{1}H NMR (acetone-d_6, room temperature): δ ($C_{12}H_{11}N_3$) 13.92 [s, 1H, $J_{Pt-H} = 48.3$ Hz], 8.61 (d, 2H), 7.62 (m, 4H), 7.49 (t, 2H), 7.33 (m, 2H); (NBu_4) 3.54 (m, 8H), 1.91 (m, 8H), 1.51 (sext, 8H), 1.05 (t, 12H). ^{19}F NMR (acetone-d_6, 293 K): δ −115.27 [d, 4F, *o*-F, $^3J_{Pt-Fo} = 359$ Hz], −117.83 [d, 2F, *o*-F, $^3J_{Pt-Fo} = 523$ Hz], −165.11 (t, 2F, *p*-F), −166.84 (t, 1F, *p*-F), −165.63 (m, 4F, *m*-F), −167.42 (m, 2F, *m*-F). ^{19}F NMR (acetone-d_6, 208 K): δ −114.98 (d, 2F, *o*-F), −115.27 (d, 2F, *o*-F), −117.82 [d, 1F, *o*-F, $^3J_{Pt-Fo} = 593$ Hz], −118.02 [d, 1F, *o*-F, $^3J_{Pt-Fo} = 487$ Hz], −163.65 (t, 2F, *p*-F), −165.39 (t, 1F, *p*-F), −164.47 (m, 4F, *m*-F), −166.22 (m, 2F, *m*-F). FAB$^-$ (*m/z*): $[Pt(C_6F_5)_3(C_{12}H_{11}N_3)]^-$ 893.

Complex 1 Isolated with Distilled Water. The preceding reaction, precipitated with distilled water instead ^{i}PrOH, renders complex **1** containing water molecules that make the ^{1}H NMR different, especially for the signal of the NH hydrogen atom which appears 1.5 ppm lower and does not show platinum satellites.

^{1}H NMR (acetone-d_6, room temperature): δ $C_{12}H_{11}N_3$ 12.48 (s, 1H), 8.04 (d, 2H), 7.58 (m, 6H), 7.41 (m, 2H); NBu_4 3.54 (m, 8H), 1.91 (m, 8H), 1.51 (sext, 8H), 1.05 (t, 12H); H_2O 2.95 (s).

Synthesis of $[NBu_4][Pt(C_6F_5)_3(PhN{=}CHNHPh)]$ (2). $AgClO_4$ (0.036 g, 0.173 mmol) was added to a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ (0.211 g, 0.173 mmol) in thf (15 mL). The mixture was stirred at room temperature for 30 min. The precipitated AgCl was eliminated by filtration, and PhN=CHNHPh (0.034 g 0.173 mmol) was added to the resulting solution. The solvent was evaporated to dryness. The residue was treated with ^{i}PrOH giving complex **2**. Yield: 32%. Anal. Found (calcd for $C_{47}H_{48}N_3F_{15}Pt$): C, 49.30 (49.73); H, 4.13 (4.26); N, 3.72 (3.70). IR (cm^{-1}): C_6F_5 ν(C−F) 1054 vs, 954 vs; X-sensitive mode[49] 803 s, 786 w, 768 s; $C_{13}H_{12}N_2$ 1651 vs, 1600 s, 1590 s, 1313 m, 1206 m, 742 w, 695 w, 530 w, 504 w; NBu_4^+ 883 w. ^{1}H NMR, (acetone-d_6, room temperature): δ $C_{13}H_{12}N_2$ 10.63 (d, 1H), 8.79 [d, 1H, $^3J_{Pt-H} = 31.7$ Hz], 8.00 (d, 2H), 7.50 (m, 4H), 7.36 (m, 2H), 7.24 (t, 1H), 7.18 (t, 1H); NBu_4 3.58 (m, 8H), 1.96 (m, 8H), 1.56 (sext, 8H), 1.09 (t, 12H). ^{1}H NMR (acetone-d_6, 195 K): δ $C_{13}H_{12}N_2$ 10.71 (d, 1H), 8.93 (d, 1H), 8.12 (d, 2H), 7.45 (m, 4H), 7.28 (m, 2H), 7.16 (t, 1H), 7.08 (t, 1H); NBu_4 3.41 (m, 8H), 1.75 (m, 8H), 1.31 (sext., 8H), 0.90 (t, 12H). ^{19}F NMR (acetone-d_6, room temperature): δ −115.89 [d, 4F, *o*-F, $^3J_{Pt-Fo} = 386$ Hz], −117.46 [d, 2F, *o*-F, $^3J_{Pt-Fo} = 560$ Hz], −166.85 (m, 6F, 4*m*-F + 2*p*-F), −168.72 (m, 3F, 2*m*-F + 1*p*-F). ^{19}F NMR (acetone-d_6,195 K): δ −114.82 [d, 2F, *o*-F, $^3J_{Pt-Fo} = 347$ Hz], −115.36 [d, 2F, *o*-F, $^3J_{Pt-Fo} = 395$ Hz], −116.84 (d, 1F, *o*-F), −117.27 (d, 1F, *o*-F), −165.08 (m, 6F, 4*m*-F + 2*p*-F), −166.55 (m, 3F, 2*m*-F + 1*p*-F).

Synthesis of $[NBu_4]_{(x+1)}[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)_x$ [$x = 0$ (3), $x = 1$ (4)]. Method A ($x = 0$). 2-Aminopyridine (0.020 g 0.212 mmol) was added to a yellow solution of $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (0.200 g, 0.106 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred for 1 h. The solvent was evaporated to dryness, and the residue was treated with *n*-hexane. The white solid was filtered and washed with *n*-hexane. Yield: 80%. Anal. Found (calcd for $C_{39}H_{42}N_3F_{15}Pt$): C, 45.47 (45.35); H, 4.28 (4.10); N, 4.06 (4.07). IR (cm^{-1}): C_6F_5 ν(C−F) 1054 vs, 952 vs; X-sensitive mode[49] 801 s, 788 m, 772 s; $C_5H_6N_2$ 1630 m, 1590 m, 772 m, ν(N−H) 3511 m, 3339 m; NBu_4^+ 884 w

Method B ($x = 1$). $AgClO_4$ (0.256 g, 1.233 mmol) and 0.116 g (1.233 mmol) of the solid ligand 2-aminopyridine were added to a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ (1.500 g, 1.233 mmol) in acetone (15 mL). The mixture was stirred at room temperature for 30 min. The precipitated AgCl was filtered off, and the resulting solution was evaporated to dryness. The oily yellow residue was treated with ^{i}PrOH. The white solid was filtered and washed with ^{i}PrOH and *n*-hexane. Yield: 78%. Anal. Found (calcd for $C_{55}H_{78}N_4F_{15}ClO_4Pt$): C, 47.97 (48.05); H, 5.68 (5.71); N, 3.90 (4.07). IR (cm^{-1}): C_6F_5 ν(C−F) 1054 vs, 952 vs; X-sensitive mode[49] 801 s, 788 m, 772 s; $C_5H_6N_2$ 1630 m, 1590 m, 772 m, ν(N−H) 3511 m, 3435 m, 3339 m; NBu_4^+ 884 w; ClO_4^- 1163 m, 625 s. ^{1}H NMR (acetone-d_6, 293 K): δ $C_5H_6N_2$ 8.38 [d, 1H, $^3J_{Pt-Ho} = 33.3$ Hz], 7.31 (t, 1H), 6.77 (s, 2H), 6.54 (d, 1H), 6.44 (t, 1H); NBu_4 3.45 (m, 16H), 1.83 (m, 16H), 1.43 (sext, 16H), 0.97 (t, 24H). ^{1}H NMR (acetone-d_6, 213 K): δ $C_5H_6N_2$ 8.34 (d, 1H), 7.36 (t, 1H), 7.04 (s, 2H), 6.55 (d, 1H), 6.51 (t, 1H); NBu_4 3.42 (m, 16H), 1.76 (m, 16H), 1.35 (sext, 16H), 0.92 (t, 24H). ^{1}H NMR (acetone-d_6, 193 K): δ $C_5H_6N_2$ 8.33 (d, 1H), 7.37 (t, 1H), 7.14 (s, 1H), 7.05 (s, 1H), 6.55 (d, 1H), 6.53 (t, 1H); NBu_4 3.40 (m, 16H), 1.74 (m, 16H), 1.32 (sext, 16H), 0.90 (t, 24H). ^{1}H, NMR, (CD_2Cl_2, 293 K): δ $C_5H_6N_2$ 8.40 [d, 1H, $^3J_{Pt-Ho} = 34.3$ Hz], 7.28 (t, 1H), 6.43 (d + t, 2H), 5.97 (s, 2H); NBu_4 3.11 (m, 16H), 1.61 (m, 16H), 1.41 (sext, 16H), 1.00 (t, 24H). ^{1}H NMR (CD_2Cl_2, 193 K): δ $C_5H_6N_2$ 8.26 (s, 1H), 7.27 (m, 1H), 6.42 (m, 2H); NBu_4 2.99 (m, 16H), 1.48 (m, 16H), 1.27 (sext, 16H), 0.88 (t, 24H). ^{1}H NMR (CD_2Cl_2, 178 K): δ $C_5H_6N_2$ 8.21 (s, 1H), 7.24 (d, 1H), 6.93 (s, 1H), 6.39 (m, 2H), 4.95 (s, 1H); NBu_4 2.97 (m, 16H), 1.44 (m, 16H), 1.23 (sext, 16H), 0.84 (t, 24H). ^{19}F NMR (acetone-d_6, 323 K): δ −116.43 [d, 2F, *o*-F, $^3J_{Pt-Fo}$= 536 Hz], −116.68 [d, 4F, *o*-F, $^3J_{Pt-Fo}$= 401 Hz], −166.85 (m, 6F, 4*m*-F + 2*p*-F), −168.79 (m, 3F, 2*m*-F + 1*p*-F). ^{19}F NMR (acetone-d_6, 193 K): δ −114.95 [d, 2F, *o*-F, $^3J_{Pt-Fo}$= 403 Hz], −166.27 (d, 1F, *o*-F), −116.50 (d, 1F, *o*-F), −117.98 [d, 2F, *o*-F, $^3J_{Pt-Fo}$= 355 Hz], −164.99 (m, 6F, 4*m*-F + 2*p*-F), −166.85 (m, 3F, 2*m*-F + 1*p*-F). ^{19}F NMR (CD_2Cl_2, 313 K): δ −118.07 [d, 2F, *o*-F, $^3J_{Pt-Fo}$= 549 Hz], −118.31 [d, 4F, *o*-F, $^3J_{Pt-Fo}$= 395 Hz], −166.27 (m, 6F, 4*m*-F + 2*p*-F), −168.13 (m, 3F, 2*m*-F + 1*p*-F). ^{19}F NMR (CD_2Cl_2, 253 K): δ −118.42 (m, 8F, *o*-F), −165.59 (m, 6F, 4*m*-F + 2*p*-F), −167.42 (m, 3F, 2*m*-F + 1*p*-F). ^{19}F NMR (CD_2Cl_2, 178 K): δ −116.85 [d, 2F, *o*-F, $^3J_{Pt-Fo}$= 398 Hz], −118.06 (d, 1F, *o*-F), −119.00 (d, 1F, *o*-F), −120.05 [d, 2F, *o*-F, $^3J_{Pt-Fo}$)= 321 Hz], −164.48 (m, 6F, 4*m*-F + 2*p*-F), −166.37 (m, 3F, 2*m*-F + 1*p*-F).

X-ray Structure Determination. Crystal data and other details of the structural analyses are presented in Table 1. Suitable crystals were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of the complexes. Crystals were mounted at the end of glass fibers. For **1**, the unit cell dimensions were initially determined from the positions of 184 reflections in 60 intensity frames measured at 0.3° intervals in ω and subsequently refined on the basis of the positions of the 7687 reflections from the main dataset. For **2**, the unit cell dimensions were initially determined from the positions of 184 reflections in 90 intensity frames measured at 0.3° intervals in ω

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Table 1. Crystal Data and Structure Refinement for $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (**1**), $[NBu_4][Pt(C_6F_5)_3(PhN{=}CHNHPh)]$ (**2**), $[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)]$ (**3**), and $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (**4**)

	1	**2**	**3**	**4**
empirical formula	$C_{46}H_{47}F_{15}N_4Pt$	$C_{47}H_{48}F_{15}N_3Pt$	$C_{39}H_{42}F_{15}N_3Pt$	$C_{55}H_{78}ClF_{15}N_4O_4Pt$
fw	1135.97	1134.97	1032.85	1374.75
temp	173(2) K	100 K	293(2) K	298(1) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2(1)/n$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
unit cell dimensions	$a = 10.2376(6)$ Å	$a = 10.2221(7)$ Å	$a = 10.0918(12)$ Å	$a = 10.8046(12)$ Å
	$b = 18.1822(11)$ Å	$b = 18.3393(13)$ Å	$b = 11.5285(17)$ Å	$b = 20.285(2)$ Å
	$c = 25.2453(16)$ Å	$c = 25.027(3)$ Å	$c = 19.238(2)$ Å	$c = 28.824(3)$ Å
	$\beta = 100.8950(10)°$	$\beta = 101.522(9)°$	$\alpha = 72.960(12)°$	$\beta = 95.822(18)°$
			$\beta = 86.775(13)°$	
			$\gamma = 68.819(12)°$	
vol	4614.5(5) Å^3	4597.1(7) Å^3	1992.3(4) Å^3	6284.8(12) A^3
Z, calculated density	4, 1.635 Mg/m^3	4, 1.640 Mg/m^3	2, 1.722 Mg/m^3	4, 1.453 Mg/m^3
abs coeff	3.139 mm^{-1}	3.150 mm^{-1}	3.625 mm^{-1}	2.364 mm^{-1}
$F(000)$	2256	2256	1020	2792
cryst size	0.45 × 0.34 × 0.19 mm	0.26 × 0.20 × 0.14 mm	0.45 × 0.35 × 0.25 mm	0.35 × 0.30 × 0.28 mm
GOF on F^2	1.008	0.870	1.038	1.112
Final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0417	R1 = 0.0627	R1 = 0.0253	R1 = 0.0721
	wR2 = 0.0968	wR2 = 0.1494	wR2 = 0.0693	wR2 = 0.1299
R^a indices (all data)	R1 = 0.0588	R1 = 0.1044	R1 = 0.0289	R1 = 0.2038
	wR2 = 0.1140	wR2 = 0.1912	wR2 = 0.0710	wR2 = 0.1680
largest diff. peak and hole	1.95 and −0.89 e·Å^{-3}	3.52 and −2.11 e·Å^{-3}	0.95 and −0.57 e·Å^{-3}	0.96 and −1.10 e· Å^{-}3

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

and subsequently refined on the basis of the positions of 7687 reflections from the main data set. For these two structures, the diffraction frames were integrated using the SAINT package[50] and corrected for absorption with SADABS.[51] For **3**, the unit cell dimensions were determined from 25 centered reflections in the range of $23.0 < 2\theta < 31.8°$. An absorption correction was applied based on the 488 azimuthal scan data. For **4**, the unit cell dimensions were determined from 116 centered reflections, including symmetry equivalents, in the range of $20.4 < 2\theta < 28.8°$. An absorption correction was applied based on 440 azimuthal scan data. Lorentz and polarization corrections were applied for all the structures.

The structures were solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-93 or SHELXL-97.[52,53] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except as noted below. For **1**, **2**, and **4**, all hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the values of U_{iso} for their attached carbon atoms (1.5 times for methyl hydrogen atoms). For **4**, the aminic hydrogen atoms were not included in the model. For **3**, the positions of the hydrogen atoms of the 2-aminopyridine ligand were found in difference density maps and freely refined with a common isotropic displacement parameter. In **1**, one of the methyl groups of the $NBu_4{}^+$ cation is disordered over two positions which were refined with an occupancy of 0.5/0.5. The C−C distances between these disordered carbon atoms and the adjacent C atom were AFIX constrained to idealized values. No H atoms were attached to the disordered C atoms and its adjacent C atom. In **3**, two carbon atoms of the $NBu_4{}^+$ cation (C(38) and C(39)) are disordered over two positions, which were refined with occupancies of 0.6/0.4, and their anisotropic displacement parameters were constrained to be the same. Also, the interatomic distances for this fragment were DFIX, SAME, SADI restrained to idealized values. No attempts were made to include the hydrogen attached to these carbon atoms. In **4**, some C−C distances of one of the $NBu_4{}^+$ cations and the Cl−O distances of the $ClO_4{}^-$ anion were restrained to idealized values. The anisotropic displacement parameters of the four oxygen atoms of the $ClO_4{}^-$ anion were constrained to be the same. Full-matrix least-squares refinement of these models against F^2 converged to the final residual indices given in Table 1.

Results and Discussion

Synthesis and Characterization of $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (1). Complex **1** was obtained by substitution of the halide in $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ for the neutral triazene ligand using $AgClO_4$ as the halide scavenger (eq 1).

$$[NBu_4]_2[Pt(C_6F_5)_3Cl] + AgClO_4 + PhN{=}NNHPh \rightarrow [NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)] + AgCl + NBu_4ClO_4 \quad (1)$$

The IR spectrum of **1** shows a signal at 3061 cm^{-1} assignable to ν(N−H) of the triazene ligand. The homologous signal in the free ligand appears at 3203 cm^{-1}. It is known that hydrogen bonds can be detected by infrared and Raman spectroscopy mainly because of a decrease of the ν(X−H) frequency resulting from the weakening of the X−H bond and the broadening of the band.[54] Thus, the IR of **1** seems to indicate the existence of a hydrogen bonding interaction involving the amminic hydrogen of the triazene ligand.[55]

The ^{1}H NMR room-temperature spectrum confirms the presence of such an interaction with the Pt center (platinum satellites). Thus, the resonance corresponding to the hydrogen atom appears in the spectrum of **1** as a singlet at 13.92 ppm, compared to 11.35 ppm for the free ligand. The displacement

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(50) *SAINT Integration Software*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(51) Sheldrick, G. M. *SADABS*, version 2.03; University of Göttingen: Göttingen, Germany.

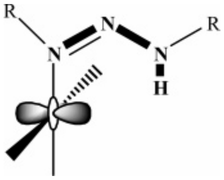
(52) Sheldrick, G. M. *SHELXL-97, Fortran Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany 1997.

(53) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993.

(54) Martín, A. *J. Chem. Educ.* **1999**, *76*, 578.

(55) Del Bene, J. E.; Jordan, M. J. T. *J. Am. Chem. Soc.* **2000**, *122*, 4794−4797.

Scheme 1



of the signal of the interacting hydrogen to higher frequencies ($\Delta\delta = 2.57$ ppm) is the result of the deshielding caused by the electron density donated from the platinum center, which is contained in the d_{z^2} orbital, perpendicular to the coordination plane.[16-18,54] This signal shows platinum satellites [$J_{Pt-H} = 48.30$ Hz] which is unequivocal evidence of the existence of a Pt−H interaction in solution.[16,18,56,57] The magnitude of the coupling constant has been related to the strength of the Pt → H interaction. In the literature, some examples of higher values of J_{Pt-H} can be found for this class of interaction.[17,18,58] However, it is necessary to take into consideration that, in addition to the acidic character of the interacting hydrogen, another important factor that must be considered is the rigidity of the skeleton of the ligand that contains the proton donor fragment. Some ligands are able to force the hydrogen into an optimal position, above the platinum coordination plane, to establish the interaction with the $5d_{z^2}$ orbital. The complexes for which larger J_{Pt-H} values have been reported contain more rigid ligands than the triazene; thus, they can force the Pt → H interaction more effectively (Scheme 1). In some examples with larger J_{Pt-H} values, the interacting hydrogen atom belongs to an OH fragment, which is more polar than NH, and thus the H is more acidic, which again favors the interaction.

If a solution of complex **1** in acetone-d_6 is treated with water and its ^{1}H NMR recorded, the signal corresponding to the hydrogen atom that interacts is shifted toward lower frequency; no platinum satellites are observed in this case. This experiment suggests that the Pt → H interaction is disrupted and new hydrogen bonds are formed with water molecules.

The two phenyl groups of the triazene ligand are inequivalent in the ^{1}H NMR spectrum. On the basis of a ^{1}H−^{1}H COSY experiment all signals have been assigned, even if some of them appear overlapped. The resonance corresponding to the hydrogen atoms ortho to the nitrogen atom coordinated to the platinum center appears at δ 8.61 as a doublet. This signal appears at lower frequencies than the other signals of the ligand because these hydrogen atoms are closer to the platinum center.

The room-temperature ^{19}F NMR spectrum of complex **1** shows two signals for the *o*-fluorine atoms of the three C_6F_5 groups in a 2:1 intensity ratio with Pt−F_o coupling constants of 361 and 528 Hz. The *p*-fluorine atoms appear as two triplets in a 2:1 intensity ratio, and two complex signals in the same ratio also appear for the *m*-fluorine atoms. According to this, there are two different types of C_6F_5 groups, cis and trans, as expected. The equivalence of the *o*-fluorine atoms and the *m*-fluorine atoms of each C_6F_5 should be a consequence of rotation around the Pt−C bond at that temperature, since the presence of Pt···H−N bonds excludes rotation of the N.

In a variable-temperature ^{19}F NMR study it has been found that the −117.83 ppm signal from the room-temperature spectrum, which corresponds to the *o*-fluorine atoms of the C_6F_5 group trans to the triazene ligand, splits into two doublets at 273 K, showing the inequivalence of the two *o*-F at this temperature. The two mutually *trans*-C_6F_5 groups show the same signal pattern as at room temperature, but at 223 K, the two *o*-fluorine atoms of the mutually *trans*-C_6F_5 groups also become inequivalent and generate two doublets each.

Synthesis and Characterization of [NBu$_4$][Pt(C$_6$F$_5$)$_3$(PhN═CHNHPh)] (2). Complex **2** is obtained in a manner similar to that for complex **1**, but formamidine was used as the neutral N-donor ligand.

The formamidine ligand is structurally very similar to triazene, with a ═CH− fragment (which is isolobal with N) instead of the ═N− fragment. Nevertheless, there are differences in the acidity of the hydrogen atom of the N−H fragment, which is stronger in the triazene ligand, as reflected in the ^{1}H NMR spectra of both free ligands. The N−H signal for triazene (vide supra) appears at 11.35 ppm, while in the formamidine ligand, it appears at lower frequencies, 9.23 ppm. This difference in the acidity of the hydrogen should cause a different behavior in the NMR spectra of **2**.

Thus, the ^{1}H NMR spectrum of **2** (acetone, room temperature or 195 K) shows signals corresponding to the formamidine ligand and the NBu_4^+ cation. The signal for the NH group appears as a doublet at 10.63 ppm, and no platinum satellites are observed. This chemical shift represents a $\Delta\delta$ of 1.40 ppm toward higher frequencies than in the free ligand spectrum (cf. $\Delta\delta = 2.57$ ppm, $J_{Pt-H} = 48.3$ Hz in **1**). The resonance corresponding to C−H appears as a doublet at 8.79 ppm with Pt−H coupling (31.7 Hz). This coupling is transmitted through the ligand skeleton. The hydrogen atoms of the phenyl groups appear at aromatic frequencies. The ortho hydrogen atoms of the phenyl group closer to the platinum atom show a doublet at 8.00 ppm. The other atoms of the phenyl groups show signals between 7.50 and 7.08 ppm. These observations do not categorically show that a Pt → H interaction exists for **2** in solution. The displacement toward higher frequencies of the signal of the N−H hydrogen atom is compatible with this interaction, despite the fact that the magnitude of the displacement is less important than for **1**. The most conclusive evidence, which would be the existence of Pt−H coupling, is not observed. Thus, if a Pt → H interaction exists in **2**, it must be weaker than in **1**.

The ^{19}F NMR spectrum of complex **2** at room temperature shows a pattern similar to that described for complex **1**: two doublets (ratio 2:1) corresponding to the *o*-fluorine atoms, with Pt−H coupling constants of 386 and 560 Hz, respectively. The *p*-fluorine and *m*-fluorine atoms appear to be

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(56) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **2000**, *12*, 3560.

(57) Jordan, M. J. T.; Del Bene, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 2101.

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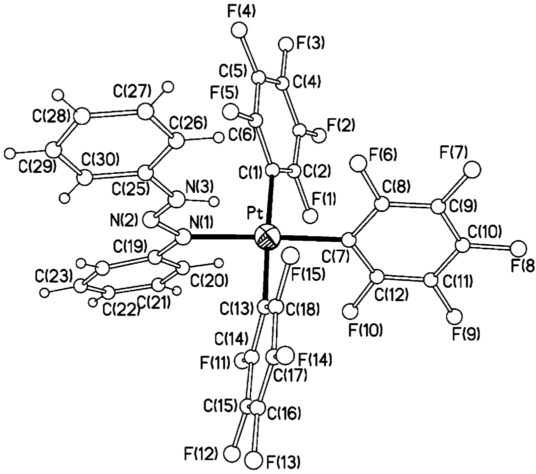

Figure 1. Structure of the complex anion of $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (**1**).

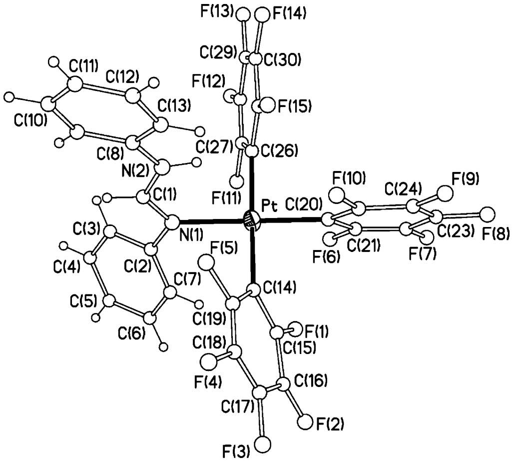

Figure 2. Structure of the complex anion of $[NBu_4][Pt(C_6F_5)_3(PhN{=}CHNHPh)]$ (**2**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (**1**)

Pt−C(7)	2.008(6)	N(1)−N(2)	1.276(7)
Pt−C(1)	2.063 (6)	N(1)−C(19)	1.459(9)
Pt−C(13)	2.076(6)	N(2)−N(3)	1.301(7)
Pt−N(1)	2.087 (5)	N(3)−C(25)	1.370(9)
C(7)−Pt−C(1)	89.1(2)	N(2)−N(1)−C(19)	113.2(6)
C(7)−Pt−C(13)	89.2(2)	N(2)−N(1)−Pt	123.7(4)
C(1)−Pt−N(1)	92.7(2)	C(19)−N(1)−Pt	123.1(4)
C(13)−Pt−N(1)	89.0(2)	N(1)−N(2)−N(3)	113.9(5)
N(2)−N(3)−C(25)	120.9(6)		

partially overlapped. Also, at low temperature, the spectra is similar to the one described for **1**.

The IR absorption ν(N−H) cannot be observed, in contrast to the infrared spectrum of complex **1**, which shows an absorption at 3061 cm^{-1}.

Crystal Structure of Complexes $[NBu_4][Pt(C_6F_5)_3(PhN{=}NNHPh)]$ (1) and $[NBu_4][Pt(C_6F_5)_3(PhN{=}CHNHPh)]$ (2). The structures of the anions of complexes **1** and **2** with the atom numbering scheme are shown in Figures 1 and 2, respectively. Important crystallographic data and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2 for **1** and Table 3 for **2**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4][Pt(C_6F_5)_3(PhN{=}CHNHPh)]$ (**2**)

Pt−C(20)	2.004(8)	N(1)−C(1)	1.285(13)
Pt−C(14)	2.025(7)	N(1)−C(2)	1.416(13)
Pt−C(26)	2.052(7)	N(2)−C(1)	1.355(13)
Pt−N(1)	2.126(7)	N(2)−C(8)	1.375(14)
C(20)−Pt−C(14)	88.7(3)	C(1)−N(1)−Pt	118.2(6)
C(20)−Pt−C(26)	90.1(3)	C(2)−N(1)−Pt	121.7(6)
C(14)−Pt−N(1)	92.8(3)	C(1)−N(2)−C(8)	126.7(7)
C(26)−Pt−N(1)	88.6(3)	N(1)−C(1)−N(2)	122.7(8)
C(1)−N(1)−C(2)	120.1(8)		

As expected, in both complexes the platinum atoms lie at the center of a square-planar environment. The Pt−C distances are within the range found for other similar compounds.[59−61] The shortest Pt−C distance corresponds to the C_{ipso} of the C_6F_5 group trans to the neutral ligand because of the trans influence of the N-donor ligands. The three C_6F_5 rings are not perpendicular to the molecular plane. The dihedral angles for **1** are 74.7(2), 74.1(2), and 64.1(2)°, and the dihedral angles for **2** are 78.2(4), 75.7(4) and 64.5(4)°.

For **1**, the N−N bond lengths [N(1)−N(2) = 1.276(7) Å, N(2)−N(3) = 1.301(7) Å] are equal within the experimental error and indicate delocalization of the charge over the N_3 framework. The dihedral angles between the N_3 framework and phenyl groups of the triazene ligand are 11.8(4) and 9.9(5)°.

The hydrogen atoms were not observed in the difference maps. Atom H(3), attached to N(3) of the triazene fragment, was placed on the external bisector of the angle N(5)−N(3)−C(25) with an N−H distance of 0.88 Å. The resulting Pt → H contact parameters, Pt···H(3) = 2.45 Å and Pt···H(3)−N(3) = 123°, are within the ranges found previously for this type of interaction.[17,20,62−66]

Similar positioning of the analogous H atom in **2** [H(2)] led to a Pt···H(2) distance of 2.59 Å, longer than in **1** but still within the expected range. The Pt···H(2)−N(2) angle, 119°, is similar to those found in other intramolecular Pt → H systems, including **1**. One *ortho*-H atom in **1**, namely that attached to C(20) (Figure 1) could in principle have approached Pt in the same fashion as does H(3). But in fact, the triazene ligand and this phenyl group are oriented in such a way that the (C)H(20)···Pt distance, 2.80 Å, is significantly longer than the H(3)···Pt distance formed by the same ligand. So it appears that the latter contact is favored at the expense of the former. Similarly in **2**, the [C(7)]H(7)···Pt distance (Figure 2), 2.97 Å, is much longer than that of [N(2)]H(2)···Pt.

A significant difference between the structures of **1** and **2** is the different orientation of the phenyl groups of the neutral ligand. Where in **1** these phenyl rings are essentially coplanar with the N_3 skeleton, for **2**, they are substantially rotated with respect to the N−C−N plane, with dihedral angles of 36.5(8)° and 14.6(9)°. The environment of C(1) is planar,

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(60) Usón, R.; Forniés, J.; Tomás, M.; Ara, I. *J. Organomet. Chem.* **1988**, *358*, 525.

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but the C(1)−N distances are different [C(1)−N(1) = 1.285(13) Å and C(1)−N(2) = 1.355(13) Å] which might indicate that the double bond is more localized in **2** than for **1**. All of these observations point to the fact that while in **1** there seems to be a significant degree of electron delocalization, not only in the N_3 system but also involving the phenyl groups, in **2** there is no such delocalization or at least not to such an extent. This would affect the electronic properties of the hydrogen located in a suitable position to interact with the metal center.

Synthesis and Characterization of $[NBu_4]_{(x+1)}[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)_x$ [$x = 0$ (3), $x = 1$ (4)]. The reaction of 2-aminopyridine with $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (2:1 molar ratio) in CH_2Cl_2 produces cleavage of the C_6F_5 bridging system and coordination of L, yielding $[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)]$ (**3**) (eq 2).

$$[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + 2(\text{2-aminopyridine}) \rightarrow 2[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)] \quad (2)$$

On the other hand, if the preparation of **3** is attempted starting from $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ in a manner similar to that described for the preparation of **1** and **2**, removal of the NBu_4ClO_4 is not possible, even by washing the resulting solid with ^{i}PrOH, a solvent in which this salt is soluble. This solid is better formulated as $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (**4**).

Thus, depending on the starting material, $[NBu_4]_{(x+1)}[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)_x$ with $x = 0$ (**3**) or $x = 1$ (**4**) is obtained. The presence of NBu_4ClO_4 cannot be considered as an impurity, since it has an structural role that will be discussed later.

The infrared spectra of **3** and **4** show three signals in the X-sensitive zone[49] corresponding to the presence of three C_6F_5 groups. In **4**, signals at 1163 and 625 cm^{-1} from the ClO_4^- anion are also observed.

The ^{1}H NMR spectra of **3** and **4** (CD_2Cl_2, 293 K) are identical except for the relative intensities of the signals corresponding to the NBu_4^+ cation and the 2-aminopyridine ligand (1:1 for **3** and 2:1 for **4**). These spectra confirm the coordination of the ligand to the platinum center through the pyridinic nitrogen atom since the resonance corresponding to the hydrogen atom in the 6 position of the aromatic ring shows platinum satellites ($J_{Pt-H} = 34.2$ Hz, 8.40 ppm). The rest of the aromatic hydrogen atoms appear at 7.28 ppm (triplet) and 6.43 ppm (doublet + triplet). The aminic hydrogen atoms give a single resonance at 5.97 ppm showing their equivalence at room temperature, and no Pt satellites are observed. The two mechanisms that can account for this observation are a fast rotation of the NH_2 fragment around the C−N bond or a pyramidal inversion process,[67] and either one would render the mutually trans C_6F_5 equivalent. At 193 K, this signal becomes broader because the dynamic process slows down.

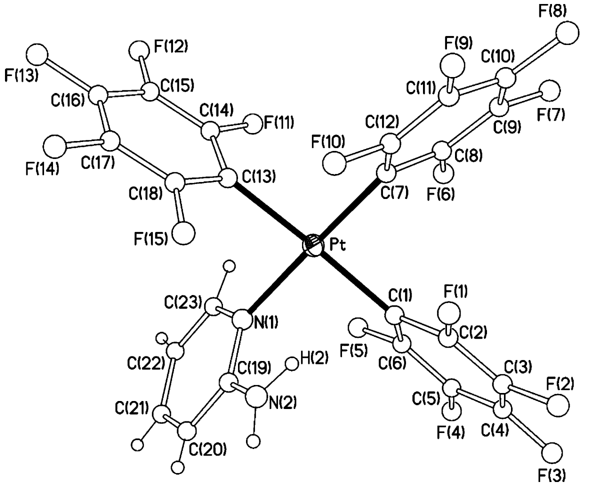

Figure 3. Structure of the complex anion of $[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)]$ (**3**).

The ^{19}F NMR spectra of **3** and **4** are essentially identical and show, at room temperature, two signals corresponding to two types of C_6F_5 groups: the trans pentafluorophenyl groups are equivalent. The *o*-F−Pt coupling constants are 401 and 536 Hz, respectively, corresponding to the two types of C_6F_5 groups in the molecule, one group trans to the neutral ligand and two equivalent mutually trans C_6F_5 groups. The signal of the *o*-fluorine atoms of the mutually trans C_6F_5 rings begins to split at 233−253 K, indicating that at lower temperatures the *o*-fluorine atoms belonging to the same C_6F_5 group become inequivalent. At 193 K, there are four signals in the *o*-fluorine region with an integration corresponding to 2, 1, 1, and 2 atoms. Within the C_6F_5 rings, the two *o*-fluorine atoms are inequivalent, while the *o*-fluorine atoms corresponding to the mutually trans C_6F_5 groups are equivalent in pairs. This equivalence is not caused by the symmetry of the molecule because the aminic hydrogen atoms would be equivalent and that is not the case. At 193 K, the signal corresponding to the aminic hydrogen atoms disappears. At lower temperature (178 K), two new broad signals appear at 6.93 and 4.95 ppm. One of these hydrogen atoms is more deshielded than the other, but the frequency of the signal does not suggest a Pt−H interaction. It seems more likely that at low temperature the rotation around the Pt−C, Pt−N, and C−NH_2 bonds is slower, resulting in different chemical environments for the two aminic hydrogen atoms.

Crystal Structures of $[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)]$ (3) and $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (4). The structures of the anions of complexes **3** and **4**, with the atom numbering scheme, are shown in Figures 3 and 4, respectively. Important crystallographic data and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 4 for **3** and Table 5 for **4**. For the structure of **3**, H atoms were located on difference maps, and their coordinates were refined. In the case of **4**, the quality of the diffraction data collected did not allow for the experimental

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(67) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 404.

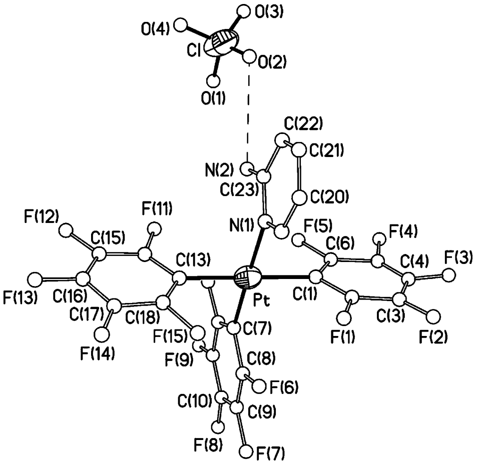

Figure 4. Structure of the anions of $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (**4**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4][Pt(C_6F_5)_3(C_5H_6N_2)]$ (**3**)

Pt−C(7)	2.013(4)	N(1)−C(19)	1.350(5)
Pt−C(13)	2.051(4)	N(1)−C(23)	1.358(5)
Pt−C(1)	2.056(4)	N(2)−C(19)	1.339(5)
Pt−N(1)	2.096(3)	N(2)−H(2)	0.93(5)
N(2)−H(1)	0.86(5)		
C(7)−Pt−C(13)	94.04(14)	C(23)−N(1)−Pt	119.5(3)
C(7)−Pt−C(1)	88.68(14)	C(19)−N(2)−H(2)	118(3)
C(13)−Pt−N(1)	87.12(13)	C(19)−N(2)−H(1)	119(3)
C(1)−Pt−N(1)	90.17(13)	H(2)−N(2)−H(1)	120(4)
C(19)−N(1)−Pt	122.1(3)	N(2)−C(19)−N(1)	117.5(4)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4]_2[Pt(C_6F_5)_3(C_5H_6N_2)](ClO_4)$ (**4**)

Pt−C(7)	2.007(11)	N(1)−C(19)	1.374(15)
Pt−C(13)	2.072(13)	N(1)−C(23)	1.367(15)
Pt−C(1)	2.091(13)	N(2)−C(23)	1.360(19)
Pt−N(1)	2.085(9)		
C(7)−Pt−C(13)	91.3(4)	C(23)−N(1)−Pt	120.2(10)
C(7)−Pt−C(1)	90.3(4)	C(19)−N(1)−Pt	117.8(9)
C(13)−Pt−N(1)	90.4(4)	N(2)−C(23)−N(1)	121.2(13)
C(1)−Pt−N(1)	88.1(4)	N(2)−C(23)−C(22)	126.8(14)
C(23)−N(1)−C(19)	121.9(12)		

location of the hydrogen atoms, and therefore, the H atoms for the aminic group were not included in the model.

In the two complexes, the platinum atoms lie at the centers of square-planar environments with Pt−C and Pt−N distances within the ranges found in similar compounds.[47,68−72]

The 2-aminopyridine ligand is coordinated to the platinum center through the pyridinic N atom. In the case of complex **3**, the $-NH_2$ fragment is located above the square plane in such a way that the Pt···H(2) distance is 2.58(3) Å and Pt···H(2)−N(2) = 120(1)°. Both parameters are consistent with the existence of a weak Pt−H interaction. However, nothing can be inferred about a possible Pt···H−N interaction in **4** because of our inability to locate the NH_2 hydrogen atoms for this structure. Nevertheless, the Pt−N(2) distance is similar in both complexes (3.144(3) Å in **3** and 3.188(9) Å in **4**) which, from the merely geometric point of view, does not rule out the existence of such an interaction.

The most remarkable features of the structure of **4** are the presence of a perchlorate anion and the formation of an N−H···O−Cl hydrogen bond, which can be inferred from the N(2)···O(2) distance of 3.275(16) Å.

In square-planar complexes of Pt containing the 2-aminopyridine ligand, it is commonly found that the pyridinic ring lies nearly perpendicular to the square plane;[41,45] but in the anion of complex **3,** the dihedral angle is 67.0(1)°. This seems to indicate that the Pt···H(2) interaction affects the dihedral angle of the ligand containing the interacting hydrogen. The C_6F_5 groups in **3** are twisted 53.1(1)° [C(1)], 61.7(1)° [C(7)], and 80.5(1)° [C(13)] with respect to the square plane [C(1) is cis to the pyridinic ligand]. The small value of the dihedral angle found for the C(1) ring is probably the result of the steric effect caused by the relatively bulky NH_2 substituent on the pyridinic ligand.

In **4**, the dihedral angle between the pyridinic ring and the coordination plane is now 86.6(4)°; the two planes are almost perpendicular, and the dihedral angles of the pentafluorophenyl rings are 77.9(5), 85.8(4), and 86.6(4)°. These values are consistent with the conclusion that the hydrogen bonding takes place only to an oxygen atom of the perchlorate anion.[73]

The existence in **4** of this N−H···O−Cl intermolecular hydrogen bond explains the crystallization of the perchlorate and complex anions together. This hydrogen bond has to have an appreciable strength, since it is not broken even by donor solvents such as ^{i}PrOH. Also, complex **4** illustrates the fact that the presence of competing proton acceptors can obviate the formation of weak Pt → H interactions.

A comparison of the values of the N−C distances involving the pyridinic nitrogen atom in both complexes [N(1)−C(19) = 1.350(5) Å (**3**), 1.374(15) Å (**4**); N(1)−C(23) = 1.358(5) Å (**3**), 1.367(15) Å (**4**)] and the aminic one [N(2)−C(19) = 1.339(5) Å (**3**); N(2)−C(23) = 1.360(19) Å (**4**)] reveals that all three are equal within the experimental error. This observation is consistent with an electron density delocalization of the π system of the ring and the free electron pair of the aminic group also in the N−C−N fragment, as previously reported.[74]

Concluding Remaks

To understand the different behavior displayed by complexes **1**−**4** in regard to their M → H hydrogen bonds, it is important to consider the various factors that determine the strengths of these interactions which are either moderate or weak.[75] The capacity of Pt(II) to donate electron density to

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an extent necessary to establish stable interactions has been previously reported. In complexes **1**−**4**, the topological and electronic properties of the Pt donor sites are so similar that we must look to other factors to explain the differences among these systems.

The acidity of the hydrogen atom is an important discriminant, the more acidic the hydrogen, the more favorable the hydrogen bond. Complex **1**, with the more acidic H atom of triazene, forms a Pt → H interaction stable enough to be detected in solution (where well-known factors render less favorable interactions unobservable). In contrast, the less acidic H atom of formamidine in **2** forms a Pt → H hydrogen bond that can be observed in the crystal but not in solution.

The flexibility of the ligand carrying the proton donor is a more obvious factor in the formation of these interactions. The ligand must be able to bind to Pt and, at the same time, position the hydrogen atom appropriately to permit hydrogen bond formation. The extra degree of freedom in the aminopyridine ligand of **3** and **4**, namely, rotation of the donor group about a C−N single bond, adds such flexibility to these systems. Complexes **3** and **4** demonstrate the well-established competitive nature of such interactions. The presence of an energetically more favorable alternative for the donor group in **4**, the possibility of forming a hydrogen bond to perchlorate, prevails over the weaker interaction to Pt that is observed in **3**.

Acknowledgment. This work has been suported by the Spanish Ministerio de Educación y Ciencia (Spain) y Fondos FEDER (Projects BQU2002-03997-C02-02 and BQU2002-00554). B.E.D. thanks the CICYT for a grant.

Supporting Information Available: Further details of the structure determinations of **1**−**4** 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.

IC050800G