Pentafluorophenyl Complexes of Platinum Containing Intramolecular Pt···H Hydrogen Bridging Interactions. Crystal Structures of $[NBu_4][Pt(C_6F_5)_3(8\text{-hydroxyquinaldine})]$ and $[NBu_4][Pt(C_6F_5)_3(8\text{-methylquinoline})]$

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Anionic complexes with the molecular formula $[NBu_4][Pt(C_6F_5)_3L]$ (L = 8-hydroxyquinoline, C_9H_7NO, (**1**); 8-hydroxyquinaldine, $C_{10}H_{10}NO$, (**2**); 7,8-benzo[*h*]quinoline, $C_{13}H_9N$, (**3**); 8-methylquinoline, $C_{10}H_9N$ (**4**)) were prepared by cleavage of the pentafluorophenyl bridging system in $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ with L (**1**−**4**) or by substitution of the chloride ion by the ligand L in $[NBu_4]_2[Pt(C_6F_5)_3L]$ (**1** and **4**). ^{1}H NMR spectra of **1**−**3** show the presence of a Pt···H interaction in solution with *J*(Pt,H) of 69 (**1**), 88 (**2**), and 22 Hz (**3**). For **4**, no Pt−H coupling is observed. Structures of complexes **2** and **4** were determined by single crystal X-ray diffraction. For **2** a Pt−H distance of 2.19 Å was determined, whereas for **4** the methyl hydrogen atoms were not located and a Pt-H distance in the range of 2.3−2.6 Å was calculated geometrically. Compound **2** ($C_{44}H_{45}F_{15}N_2OPt$) crystallizes in the monoclinic system, space group $P2_1/c$: $a = 18.376(6)$ Å, $b = 11.786(4)$ Å, $c = 20.473(7)$ Å, $\beta = 102.88(6)°$, $V = 4322(3)$ Å^3, $Z = 4$. Compound **4** ($C_{44}H_{45}F_{15}N_2Pt$) crystallizes in the triclinic system, space group $P\bar{1}$ $a = 12.125(2)$ Å, $b = 13.152(2)$ Å, $c = 14.795(7)$ Å, $\alpha = 88.20(3)°$, $\beta = 68.15(3)°$, $\gamma = 86.37(1)°$, $V = 2185.2(5)$ Å^3, $Z = 2$. The existence and nature of the Pt···H interactions both in solution and in the solid state are discussed.

Introduction

In recent years we have reported the preparation of a large number of anionic pentafluoro- and pentachlorophenyl complexes of platinum(II). The basicity of the metal center in these complexes allows their use as precursors in the synthesis of heteropolynuclear complexes containing donor-acceptor Pt → M (M = Ag,[1,2] Sn,[3] Pb,[4] Hg,[5] Tl[6]) bonds in which M behaves as a Lewis acid. In light of these results, we have been prompted to investigate the possibility of formation of similar Pt → H bonds. M → H interactions of this kind have been described only recently[7] and are substantially different from the well-known "agostic interactions".[8] Whereas in the latter the electron density of the C−H bond is donated to the metal center (3 centers−2 electrons, 3c-2e), the M → H interactions can be regarded as "hydrogen bonding" interactions (3 centers−4 electrons, 3c−4e) in which the metal center is the donor of the electron density toward the more or less acidic hydrogen. These bonding modes produce some interesting spectroscopic differences.

Nevertheless, from our previous research it is known that the reactions of the pentahalophenyl complexes of platinum(II) with strong acids HX lead to the cleavage of the Pt−C bond and formation of C_6F_5H but not to the formation of the hydride complexes.[9] This reactivity indicates that it would be advisable to use substrates containing hydrogen atoms with a more moderate acidic character. This can be achieved by using ligands containing hydrogen atoms suitable from the point of view of both their structure and their acidic properties (see Chart 1). We have chosen four quinoline type ligands (see Chart 2) in which there are hydrogen atoms (in bold) with these characteristics.

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Chart 1

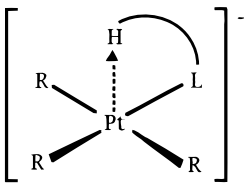
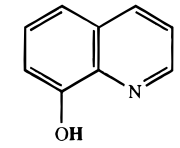
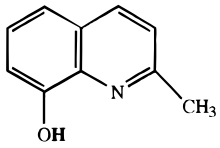


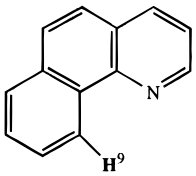
Chart 2



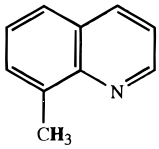
8-hydroxyquinoline (hq)



8-hydroxyquinaldine (hq')



7,8-benzo[*h*]quinoline (bq)



8-methylquinoline (mq)

Experimental Section

General Procedures. C, H, and N analyses were done with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded over the range of 4000−200 cm^{-1} on a Perkin-Elmer 883 or 1710 FTIR spectrophotometer using Nujol mulls between polyethylene sheets. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian XL-200 or a Unity-300 spectrometer in $CDCl_3$ or HDA solutions. $[NBu_4]_2[Pt(C_6F_5)_3Cl]$[9a] and $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[10] were prepared as described elsewhere. 8-Hydroxyquinoline, 8-hydroxyquinaldine, 7,8-benzo[*h*]quinoline and 8-methylquinoline were obtained from commercial sources and used as delivered. All of the reactions in which a silver reagent was used were carried out under exclusion of light.

Preparation of $[NBu_4][Pt(C_6F_5)_3L]$ (L = hq (1), hq′ (2), bq (3), mq (4). To a solution of 0.278 g (0.148 mmol) of $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ in 20 mL of CH_2Cl_2 was added 0.296 mmol of L (**1**, 0.042 g of hq; **2**, 0.047 g of hq′; **3**, 0.053 g of bq; **4**, 40.0 μL of mq). The mixture was stirred at room temperature for 5 h and the solvent was evaporated to dryness. The residue was treated with ^{i}PrOH rendering complexes **1**−**4**. Yield: 85% (**1**), 60% (**2**), 87% (**3**), 87% (**4**).

Complexes **1** and **4** can also be prepared as follows: To a solution of 0.300 g (0.247 mmol) of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ in THF (20 mL) were added equimolar amounts of L (**1**, 0.036 g of hq; **4**, 33.0 μL of mq) and $AgClO_4$ (0.051 g, 0.247 mmol) precipitating AgCl instantaneously. The mixture was stirred at room temperature for 20 min. The precipitated AgCl was eliminated by filtration and the resulting solution was evaporated to dryness. The oily residue was washed with 15 mL of ^{i}PrOH giving **1** and **4** as white solids. Yield: 70% (**1**), 75% (**2**).

Preparation of $[NBu_4][cis\text{-}Pt(C_6F_5)_2(hq^-)]$ (hq^- = 8-Hydroxyquinolinate, 5). A solution of $[NBu_4][Pt(C_6F_5)_3(hq)]$, **1**, in 30 mL of $CHCl_3$ was refluxed for 10 h. The solvent was evaporated to dryness and the yellow residue was treated with ^{i}PrOH rendering **5** (yield 95%).

Preparation of Crystals for X-ray Structure Determinations. Suitable crystals for X-ray purposes were obtained for both complexes **2** and **4** by slow diffusion of n-hexane into a solution of 0.02 g (**2**, 0.016 mmol; **4**, 0.018 mmol) of the corresponding complexes in CH_2Cl_2 (3 mL) at −30 °C.

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Analytical and Spectroscopic data. $[NBu_4][Pt(C_6F_5)_3(hq)]$ 1. Anal. Found (calcd): N, 2.55 (2.58); C, 47.71 (47.65); H, 3.83 (4.00). IR: C_6F_5 X-sensitive 805 (s), 787 (w), 772 (s); C_6F_5 others 1632 (m), 1605 (m), 1500 (vs), 1057 (vs), 957 (vs); hq 1617 (m), 1597 (m), 1581 (m), 1405 (m), 1378 (m), 1265 (m), 1212 (m), 1172 (m), 1099 (m), 827 (s), 779 (s), 760 (m), 744 (m), 565 (m); NBu_4^+ 888 (m). ^1H NMR ($CDCl_3$, room temperature), ppm: hq 7.04 (dd, 1H), 7.22 (dd, 1H), 7.26 (dd, 2H), 7.35 (dd, 1H), 8.06 (dd, 1H), 9.74 (dd, 1H, J(Pt,H) = 30 Hz), 12.22 (s, 1H, *J*(Pt,H) = 69 Hz); NBu_4^+ 0.96 (t, 12H, CH_3), 1.43 (m, 8H, α-CH_2), 1.69 (m, 8H, β-CH_2), 3.25 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F −118.15 and −119.20 (broad signals with poor resolution), −120.25 (4F, J_{Pt-F} = 345 Hz); *m*-F −165.86 (4F), −166.70 (2F); *p*-F −164.94 (2F), −168.16 (1F).

$[NBu_4][Pt(C_6F_5)_3(hq')]$ 2. Anal. Found (calcd): N, 2.43 (2.55); C, 48.37 (48.13); H, 4.11 (4.13). IR: C_6F_5 X-sensitive 806 (s), 788 (m), 774 (s); C_6F_5 others 1636 (m), 1499 (vs), 1055 (vs), 954 (vs); hq′ 1608 (s), 1573 (s), 1518 (s), 1342 (m), 1316 (m), 1287 (m), 1263 (s), 1214 (m), 1173 (m), 1150 (m), 1107 (s), 832 (s), 752 (m), 742 (m), 572 (m); NBu_4^+ 881 (m). ^1H NMR ($CDCl_3$, room temperature), ppm: hq′ 3.47 (s, 3H), 7.00 (dd, 1H), 7.15 (d, 2H), 7.29 (t, 1H), 7.93 (d, 1H), 12.34 (s, 1H, *J*(Pt,H) = 88 Hz); NBu_4^+ 0.92 (t, 12H, CH_3), 1.37 (m, 8H, α-CH_2), 1.63 (m, 8H, β-CH_2), 3.17 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F −118.80 (1F, J_{Pt-F} = 562.9 Hz), −119.35 (4F, J_{Pt-F} = 304.4 Hz), −120.22 (1F, J_{Pt-F} = 433.6 Hz); *m*-F −166.25 (4F), −167.22 (1F), −168.32 (1F); *p*-F −165.18 (2F), −166.87 (1F). ^{13}C NMR ($CDCl_3$, room temperature), ppm: hq′ 162.73, 152.66, 138.31, 133.85, 129.52, 126.42, 123.03, 118.65, 116.01, 31.01 (J_{Pt-C} = 52 Hz); NBu_4^+ 58.36, 23.49, 19.23, 13.12.

$[NBu_4][Pt(C_6F_5)_3(bq)]$ 3. Anal. Found (calcd): N, 2.97 (2.51); C, 50.48 (50.50); H, 4.15 (4.06). IR: C_6F_5 X-sensitive 807 (s), 789 (m), 769 (s); C_6F_5 others 1628 (m), 1602 (m), 1496 (vs), 1056 (vs), 956 (vs); bq 1590 (m), 1399 (m), 1314 (m), 1277 (m), 1173 (m), 1164 (m), 838 (s), 785 (m), 752 (s), 740 (s), 699 (m), 469 (m); NBu_4^+ 888 (m). ^1H NMR (HDA, room temperature), ppm: bq ≈ 7.8 (several signals, 6H), 8.45 (d, 1H), 10.13 (d, 1H, *J*(Pt,H) = 28 Hz), 13.39 (d, 1H, J(Pt,H) = 22 Hz); NBu_4^+ 0.95 (t, 12H, CH_3), 1.36 (m, 8H, α-CH_2), 1.80 (m, 8H, β-CH_2), 3.41 (m, 8H, γ-CH_2). ^{13}C NMR (HDA, room temperature), ppm: bq 155.19, 146.94, 138.26, 135.28, 130.34 (J_{Pt-C} = 28 Hz), 129.90, 129.52, 129.41, 128.79, 127.76, 126.74, 125.87, 121.84 (J_{Pt-C} = 31 Hz); NBu_4^+ 59.16, 24.11, 20.06, 13.49.

$[NBu_4][Pt(C_6F_5)_3(mq)]$ 4. Anal. Found (calcd): N, 2.62 (2.59); C, 49.03 (48.85); H, 3.98 (4.19). IR: C_6F_5 X-sensitive 803 (s), 782 (s), 769 (s); C_6F_5 others 1633 (m), 1607 (m), 1499 (vs), 1056 (vs), 955 (vs); mq: 1601 (m), 1093 (m), 828 (s), 743 (m); NBu_4^+ 882 (m). ^1H NMR ($CDCl_3$, room temperature), ppm: mq 4.10 (s, 3H), 7.19 (m, 1H), 7.30 (t, 1H), 7.50 (t, 2H), 8.06 (d, 1H), 10.13 (d, 1H, *J*(Pt,H) = 25 Hz); NBu_4^+ 0.95 (t, 12H, CH_3), 1.37 (m, 8H, α-CH_2), 1.60 (m, 8H, β-CH_2), 3.12 (m, 8H, γ-CH_2). ^{13}C NMR ($CDCl_3$, room temperature), ppm: mq 156.43, 147.36, 139.26, 137.45, 133.70, 131.20, 127.50, 127.07, 120.73 (J_{Pt-C} = 30 Hz), 21.77; NBu_4^+ 59.08, 24.08, 20.03, 13.50.

$[NBu_4][cis\text{-}Pt(C_6F_5)_2(hq^-)]$ 5. Anal. Found (calcd): N, 2.81 (3.06); C, 47.99 (48.53); H, 4.91 (4.62). IR: C_6F_5 X-sensitive 800 (s), 810 (s); C_6F_5 others 1635 (m), 1606 (m), 1500 (vs), 1059 (vs), 956 (vs); hq^- 1587 (m), 1573 (s), 1405 (m), 1323 (m), 1288 (m), 1228 (m), 1152 (m), 1115 (m), 821 (s), 785 (m), 747 (m), 741 (m), 518 (m); NBu_4^+ 880 (m). ^1H NMR ($CDCl_3$, room temperature), ppm: hq^- 6.78 (d, 1H), 6.86 (d, 1H), 7.14 (dd, 1H), 7.32 (t, 1H), 8.00 (d, 1H, *J*(Pt,H) = 30 Hz), 8.19 (dd, 1H); NBu_4^+ 0.77 (t, 12H, CH_3), 1.09 (m, 8H, α-CH_2), 1.30 (m, 8H, β-CH_2), 2.90 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$, room temperature), ppm: *o*-F −118.88 (2F, J_{Pt-F} = 502.3 Hz), −119.55 (2F, J_{Pt-F} = 536.8 Hz); *m*-F −166.23 (2F), −166.66 (2F); *p*-F −165.09 (1F), −165.64 (1F).

X-ray Structure Analysis of 2. Important crystal data and data collection parameters for complex **2** are listed in Table 1. The complex $[Pt(C_6F_5)_3(hq')]^-$ crystallizes as the tetra-*n*-butylammonium salt in space group $P2_1/c$ with $Z = 4$. A platelike crystal mounted on the tip of a glass fiber with epoxy cement was used for geometric and intensity data collection. Four circle diffractometer data were taken at −123.1 ± 0.1 °C. Lattice dimensions and type were determined by routine procedures and verified by oscillation photography. Cell constants were

Table 1. Crystallographic Data for Complexes $[NBu_4][Pt(C_6F_5)_3(hq')]$ (**2**) and $[NBu_4][Pt(C_6F_5)_3(mq)]$ (**4**)

	2	**4**
formula	$C_{44}H_{45}F_{15}N_2OPt$	$C_{44}H_{45}F_{15}N_2Pt$
molecular weight	1097.928	1081.929
space group	$P2_1/c$	$P\bar{1}$
a, Å	18.376(6)	12.125(2)
b, Å	11.786(4)	13.152(2)
c, Å	20.473(7)	14.795(7)
α, deg	90	88.20(3)
β, deg	102.88(6)	68.15(3)
γ, deg	90	86.37(1)
V, Å^3	4323(3)	2185.2(5)
Z	4	2
d_{calc}, g cm^{-3}	1.69	1.64
μ (Mo Kα) cm^{-1}	33.77	33.37
temperature, °C	-123.1 ± 0.1	20 ± 1
R	0.036 (F_o^2)[a]	0.036 (F_o)[a]
R_w	0.081 (F_o^2)[b]	0.036 (F_o)[c]

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

refined from 2θ values of 48 reflections including Friedel pairs ($20.3 < 2\theta < 32.0°$). During intensity data collection, three standard reflections were measured at regular intervals. These check reflections did not vary appreciably in intensity during the course of data collection. For the diffractometer data, a measured absorption correction was applied, based on 10 complete Ψ-scans of reflections with the diffractometer angle χ near 90°. Since the localization of the hydrogen atoms was to be attempted, the weak reflections were measured carefully. Data were taken to $2\theta = 50°$.

The structure of compound **2** was solved by direct methods and developed and refined in a series of alternating difference Fourier maps and least squares analyses using all of the data and the program SHELXL-93.[11] All non-hydrogen atoms were refined anisotropically. The positions of all the hydrogen atoms were obtained from difference density maps. Weak similarity restraints were applied to some of the hydrogen atoms—the C−H distances within each of the three methyl groups and one of the methylene groups were thus restrained. The isotropic displacement parameters of the hydrogen atoms within each of three methyl groups of the cation and within the methyl group of the hq′ ligand were constrained to be equal. The isotropic displacement parameters of H(1) and H(23) were set to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. Residuals and other final refinement parameters are listed in Table 1.

X-ray Structure Analysis of 4. Table 1 summarizes key information pertinent to data collection and structure refinement. A blocklike crystal was mounted on an Enraf-Nonius CAD4 diffractometer operating at room temperature. The unit cell and orientation matrix for data collection were determined from the least-squares refinement of the setting angles of 25 strong, high-angle reflections. One asymmetric fraction of data ($+h,\pm k,\pm l$) was collected by $\omega - 2\theta$ scans at variable speeds dependent on an initial prescan. There was no significant crystal movement or decay over the data collection period.

The structure of compound **4** was solved by direct methods and developed and refined in a series of alternating difference Fourier maps and least-squares analyses. An empirical absorption correction was applied[12] following isotropic convergence. All non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms, except for those of the C(28) methyl group, were placed in calculated positions and refined as riding atoms (C−H = 0.96 Å) with a common thermal parameter. The computer program package SHELXTL PLUS[13] was used for all crystallographic work. Residuals and other final refinement parameters are listed in Table 1.

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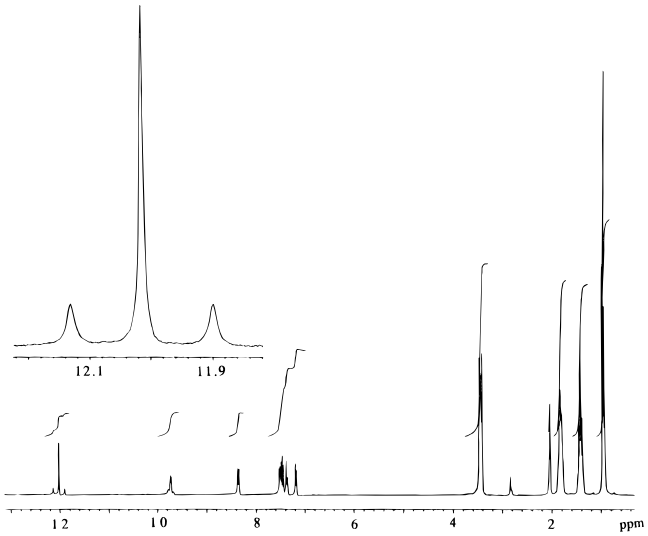

Figure 1. ^{1}H NMR spectrum of complex $[NBu_4][Pt(C_6F_5)_3(hq)]$ (**1**) at 300 MHz.

Results and Discussion

Synthesis of Complexes $[NBu_4][Pt(C_6F_5)_3L]$ [L = 8-Hydroxyquinoline (hq), 1; 8-Hydroxyquinaldine (hq′), 2; 7,8-Benzo[*h*]quinoline (bq), 3; 8-Methylquinoline (mq), 4]. The addition of ligand L to a yellow solution of $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ in CH_2Cl_2 in a 2:1 molar ratio produces its discoloration after 5 h of stirring, thus indicating the cleavage of the (μ-C_6F_5) system and the coordination of L to the metal center. Evaporation of the solvent leads to a solid whose analytical and spectroscopic data are in accord with the appropriate formulation $[NBu_4][Pt(C_6F_5)_3L]$ (eq 1). Complexes

$$[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + 2\,L \xrightarrow{CH_2Cl_2} 2\,[NBu_4][Pt(C_6F_5)_3L] \quad (1)$$
(L = hq, hq', bq, mq)

1 and **4** can also be obtained by substitution of the halide in $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ by the corresponding L ligand. The addition of $AgClO_4$ to a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ and L in tetrahydrofuran (molar ratio 1:1:1) causes the precipitation of AgCl and the ligand L occupies the coordinative vacancy. After removal of the AgCl, the solution is evaporated to dryness rendering the corresponding $[NBu_4][Pt(C_6F_5)_3L]$ (eq 2). The

$$[NBu_4]_2[Pt(C_6F_5)_3Cl] + L + AgClO_4 \xrightarrow{THF} [NBu_4][Pt(C_6F_5)_3L] + AgCl + NBu_4ClO_4 \quad (2)$$
(L = hq, mq)

yield in the preparation of these complexes is very similar for both methods, nevertheless, the reaction time for the second method is only 20 min, considerably shorter than that required for the first one.

A $CHCl_3$ solution of **1** was refluxed for 10 h producing the deprotonation of the ligand 8-hydroxyquinoline and the formation of $[NBu_4][Pt(C_6F_5)_2(hq^-)]$ (hq^- = 8-hydroxyquinolinate, **5**) and C_6F_5H. The anionic hq^- ligand is coordinated in a chelating fashion. This reaction shows the moderate acidic character of the hydrogen of the hydroxylic fragment, which is able to cleave the Pt−C bond only in more extreme reaction conditions such as reflux temperatures.

NMR Studies. The ^{1}H NMR spectrum of **1** (room temperature, $CDCl_3$) is shown in Figure 1. The most striking feature of this spectrum is the existence of a signal at high frequency, 12.22 ppm, corresponding to the hydroxylic hydrogen of the 8-hydroxyquinoline ligand. This signal is found in the spectrum

of the free ligand at 8.52 ppm, 3.70 ppm lower in frequency than in the spectrum of complex **1**. Besides, for complex **1**, this signal shows platinum satellites with a coupling constant of 69 Hz. This value is too high to be only a consequence of the transmission of the effect through the ligand skeleton. The displacement of the signal to higher frequencies and, more important, the presence of the coupling with Pt indicate the existence of a Pt,H interaction in solution. One of the characteristics of the M → H hydrogen bond is the displacement of the signal of the interacting hydrogen to higher frequencies in the ^{1}H NMR spectrum.[7] This displacement seems to be due to the deshielding of the proton that is produced by the electron density belonging to the metal center that is donated to the hydrogen atom. In the case of Pt(II), this electron density is located in the d_{z^2} orbital, perpendicular to the molecular square plane. This behavior in the ^{1}H NMR spectrum differentiates the M → H hydrogen bond from the agostic model in which the signal of the hydrogen involved in the interaction moves to lower frequency with respect to no interaction.[8] The magnitude of the signal displacement in the spectrum of **1** is significant, larger than the one reported by Albinati and co-workers for some platinum complexes for which a Pt···H interaction has been invoked.[14] Moreover, the coupling constant is one of the largest found in the literature for this kind of interaction. Only in van Koten's complexes [PtX{1-$C_{10}H_6$(NMe_2)-8-*C,N*}{1-$C_{10}H_6$-($NHMe_2$)-8-*C,H*}] (X = Cl, Br, $OOCCF_3$) and [PtBr{C_6H_4CH-(R)(NR'_2)-2-*C,N*}{C_6H_4CH(R)(NHR'_2)-2-*C,H*}] (R, R′ = Me, Et)[7b] is the value of the coupling constant larger (*ca.* 170 Hz) indicating a stronger Pt···H interaction. This is probably due to the very acidic nature of the hydrogen atom involved in the interaction, belonging formally to an ammonium fragment. In our complex **1** a lower acidity of the hydrogen is expected. These results seem to indicate that the M → H interactions have a clear electrostatic component.

^{195}Pt,H coupling constants of considerable magnitude have also been found in complexes containing clearly agostic Pt···H interactions. For example for the complex [Pt(C_7H_{11})(^{t}Bu_2-$PC_2H_4P^tBu_2$)][BPh_4], in which the signal of the agostic hydrogen appears at −1.05 in the ^{1}H NMR spectrum, a coupling constant of *J*(Pt,H) = 136 Hz is observed.[15] Thus, the value of the Pt,H coupling constant is indicative of the strength of the metal−hydrogen interaction, but not of its nature.

The ^{1}H NMR spectrum of **2** (room temperature, $CDCl_3$) is similar that of **1**. In this case the signal due to the hydroxylic hydrogen appears at 12.34 ppm and shows platinum satellites with *J*(Pt,H) = 88 Hz, slightly larger than for **1**. The only structural difference between the ligands 8-hydroxyquinoline (in **1**) and 8-hydroxyquinaldine (in **2**) is the presence in the latter of a methyl group in position 2 of the double ring. It might have been anticipated that the location of these methyl protons in **2** resulted in some kind of interaction with the metal center. However, the ^{1}H NMR spectrum does not show any evidence of the existence of such an interaction. Only one signal is observed for the three hydrogen atoms indicating free rotation of the methyl group on the NMR time scale. No Pt···H coupling, but a displacement of the signal by 0.76 ppm with respect the free ligand, is observed probably due to the metal electron density. The ^{13}C NMR spectrum of **2** (room temperature, $CDCl_3$) shows platinum satellites in the signal of the methyl carbon atom (J_{Pt-C} = 52 Hz). It is unlikely that this coupling is produced through a Pt···H−C interaction, but it is transmitted through the aromatic ring as previously observed in other Pt complexes containing 2-methyl-4-R-pyridine ligands.[16]

In complex **3**, the ligand 7,8-benzo[*h*]quinoline shows some differences to those previously described. The presence of a third condensed ring increases the rigidity of the skeleton constraining considerably the position of the H^9 hydrogen atom (see Chart 2) with respect to the hq and hq′ ligands. On the other hand, the polarity of the C−H bond is much less than that of the O−H-bond, and thus this hydrogen atom is less acidic. The signal due to H^9 appears at 13.39 ppm, 4.42 ppm higher in frequency than in the spectrum of the free ligand, and shows platinum satellites with *J*(Pt,H) = 22 Hz. This value indicates that, in this case, the strength of the Pt···H interaction in solution is smaller than for complexes **1** and **2**. It is noteworthy that despite the reduced acidic character of H^9 the interaction still exists, and this could be due to the rigidity imposed by the ligand skeleton. Albinati and co-workers have reported the synthesis of the complexes [$PtCl_2$(L)(bq)] (L = PEt_3, PPh_3, $PTol_3$) in which coupling constants *J*(Pt,H^9) ranging from 14.1 to 16.2 Hz have been observed.[14a] In the ^{13}C NMR spectrum of **3** the signal corresponding to the carbon atom bonded to H^9 appears at 130.34 ppm and shows coupling with the platinum atom [J_{Pt-C} = 28 Hz].

In the ^{1}H NMR spectrum of complex **4** (room temperature, $CDCl_3$), only one signal is observed for the three methyl hydrogen atoms, 4.11 ppm, indicating that the methyl group freely rotates on the NMR time scale. No Pt···H coupling is observed and the signal is moved only 1.28 ppm to higher frequency with respect to the free ligand. The same spectrum measured at −55 °C does not show significant alterations. For the family of complexes [$PtCl_2$(L)(mq)] (L = PEt_3, PPh_3, $PTol_3$, C_2H_4, PhCH=CH_2), also containing the 8-methylquinoline ligand, coupling constants *J*(Pt,H) in the range of 11.2−12.7 Hz have been reported.[14a] In the ^{13}C NMR spectrum of **4** at room temperature the signal due to the methyl carbon atoms equally does not show any kind of coupling. All of these data suggest that in solution there is no Pt···H interaction for complex **4** or, if there is, that it is very weak and is continuously formed and broken faster than the NMR time scale. This result can be rationalized by considering that the polarity of the C−H bond is very small and the hydrogen atoms of the methyl group have the freedom to rotate around the C−C bond.

For complexes **1** and **3**−**5**, coupling between ^{195}Pt and the hydrogen at position 2 of the ligand is observed. This coupling (with a coupling constants of *ca.* 30 Hz) is transmitted throught the Pt−N bond and the skeleton of the ligand, and it is not indicative of any kind of Pt···H interaction.[14] Displacement of the signal of the *ortho* hydrogen atoms in **1**, **3**, and **4** and the methyl hydrogen atoms of the hq′ ligand in **2** to lower fields are also observed in their ^{1}H NMR spectra due to the deshielding produced by the electron density belonging to the metal center, as mentioned above.

The ^{19}F NMR data for complexes **1**-**4** are given in the Experimental Section. Two different types of C_6F_5 groups (intensity 1:2) are to be expected; however, the analysis of the spectra cannot be carried out unambiguously in all cases. In general, the resolution of the signals is poor, especially for the *o*-F atoms, even at low temperature. Taking into consideration the shape of the ligands L, this fact could probably be due to the proximity of the substituents at the 8 position of the quinoline ligands to the fluorine atoms, the closest of which are the *o*-F atoms (see Chart 2). For **2**, the NMR spectrum is clear enough

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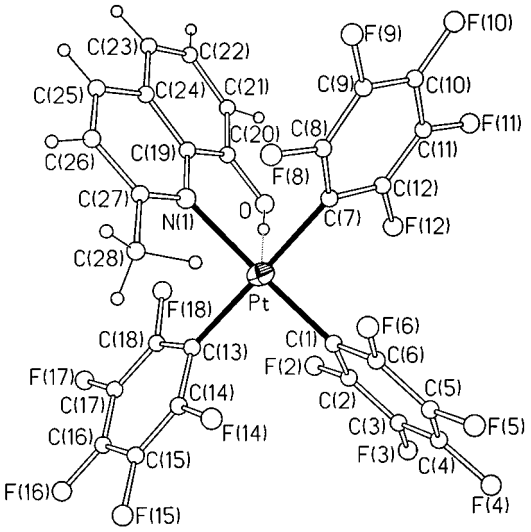

Figure 2. Drawing of anion from the crystal structure of $[NBu_4][Pt(C_6F_5)_3(hq')]$ (**2**) showing the atom labeling scheme. Heavy atoms are represented by their 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Complex $[NBu_4][Pt(C_6F_5)_3(hq')]$ (2)

		Distances	
Pt−C(1)	2.008(5)	Pt−C(7)	2.061(5)
Pt−C(13)	2.070(5)	Pt−N(1)	2.126(4)
Pt···O	2.975(4)	Pt···H(1)	2.19
O−H(1)	0.82		
		Angles	
C(1)−Pt−C(7)	91.1(2)	C(1)−Pt−C(13)	89.9(2)
C(1)−Pt−N(1)	178.0(2)	C(7)−Pt−C(13)	178.3(2)
C(7)−Pt−N(1)	87.1(2)	C(13)−Pt−N(1)	91.9(2)
Pt−N(1)−C(19)	123.0(3)	Pt−N(1)−C(27)	116.8(3)
Pt···H(1)−O	160	C(20)−O−H(1)	109(7)

to identify two different signals (1:2 intensity) due to *p*-F. The C_6F_5 groups *cis* to L show only one signal for the *m*-F atoms and one for the *o*-F atoms whereas for the other C_6F_5 group the two *o*-F and *m*-F atoms are inequivalent.

Crystal Structure of $[NBu_4][Pt(C_6F_5)_3(hq')]$, 2. The structure of the anion of complex **2** with the atom numbering scheme is shown in Figure 2. Important crystallographic data and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. Since an attempt to locate the hydrogen atoms was to be undertaken, we gathered data at a low temperature (150 K) and attempted to spend sufficient time with the weak reflections to have reliable measurements for them. Data were taken from 4 to 50° 2θ (Mo radiation).

As can be expected, Pt lies in the center of a square planar environment. The Pt−C and Pt−N distances are in the range found for other similar compounds.[1,2,14,17] The three C_6F_5 rings are not perpendicular to the molecular plane (dihedral angles of 55.2°, 58.0°, and 62.5°).

All of the hydrogen atoms were located from difference density maps. We took several parallel paths to the localization and refinement of the hydrogen atom that is suspected to interact with the platinum center. In all cases, we used all of the X-ray data and refined on F_o^2 using the program SHELXL-93.[11] In the first effort, the hydrogen atom was located in a difference Fourier map (O−H distance equal to 0.82 Å) and refined. The O−H distance turned out slightly shorter than expected, at 0.61-(7) Å, but in all other respects the refinement was routine. In a second route to the localization of the hydrogen atom, the O−H distance was fixed at 0.82 Å, and the hydrogen atom was constrained to ride in a circle about the extension of the C−O bond. The initial value of the torsion angle C(21)−C(20)−O−H(1) was set by an annular difference Fourier calculation which, as it turned out, gave a clear result. We also checked the localization of the hydrogen atom by making contoured sections of a difference map. The results of all of these approaches were essentially identical.

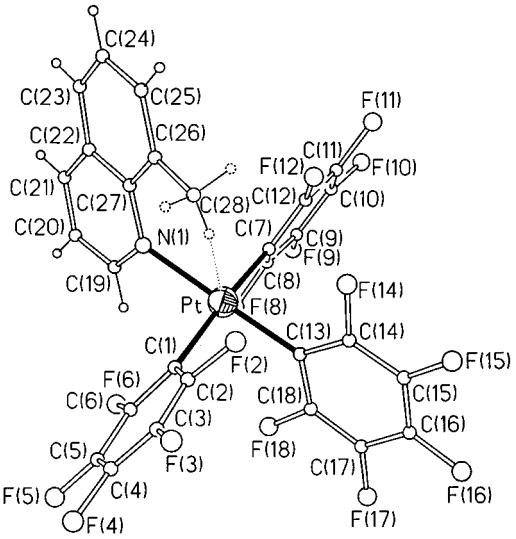

Figure 3. Drawing of anion from the crystal structure of $[NBu_4][Pt(C_6F_5)_3(mq)]$ (**4**), showing the atom labeling scheme. Heavy atoms are represented by their 50% probability ellipsoids. The hydrogen atoms on C(28) are in calculated positions and their contributions were not included in the crystallographic model.

The position of the hydrogen atom of the OH group points to the presence of a Pt···H interaction since the O−H(1) vector is directed toward the platinum atom. If the O−H(1) distance is allowed to refine to 0.61(7) Å, the Pt···H(1) distance is 2.39-(7) Å and the Pt···H(1)−O angle is 163(6)°. When the O−H(1) distance is fixed at 0.82 Å, more in line with common expectation, we obtain a Pt···H(1) distance of 2.19 Å and the Pt···H(1)−O angle is 160°.

A longer distance, 2.69(8) Å, is found between the platinum center and one of the hydrogen atoms of the methyl group of the ligand [H(28a)]. As the C(28)−H(28A) vector is not directed toward the platinum atom [C(28)−H(28A)−Pt = 112-(6)°], we think that in this case there is no Pt···H interaction.

Finally, there are relatively short distances (2.6−2.9 Å) between the *o*-F atoms of the pentafluorophenyl rings *cis* to the hq′ ligand and the hydrogen atoms of both the methyl and the hydroxy groups. These distances could help to explain the unusual patterns seen in the ^{19}F NMR spectra of complexes **1**−**4**.

Crystal Structure of the Complex $[NBu_4][Pt(C_6F_5)_3(mq)]$, 4. The structure of the anion of complex **4** with the atom numbering scheme is shown in Figure 3. Important crystallographic data and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 3. The platinum atom is located in a square planar environment, typical for Pt(II) complexes. The Pt−C_{ipso} distances are in the range found for similar pentafluorophenyl complexes,[1,2] and as for **2**, the shortest Pt−C distance is that to the C_{ipso} of the C_6F_5 group *trans* to the neutral ligand due to the *trans* influence of the N-donor ligands. The pentafluorophenyl rings containing C(7) and C(13) and the quinoline double ring are almost perpendicular to the molecular square plane [86.7-(4)° and 82.8(3)°, respectively]. However, the dihedral angle

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Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Complex $[NBu_4][Pt(C_6F_5)_3(mq)]$ (**4**)

		Distances	
Pt−C(1)	2.058(11)	Pt−C(7)	2.031(10)
Pt−C(13)	1.990(8)	Pt−N(1)	2.140(8)
Pt···C(28)	3.174(9)		
		Angles	
C(1)−Pt−C(7)	174.3(4)	C(1)−Pt−C(13)	87.8(4)
C(1)−Pt−N(1)	94.9(3)	C(7)−Pt−C(13)	89.2(4)
C(7)−Pt−N(1)	88.0(3)	C(13)−Pt−N(1)	177.0(3)
Pt−N(1)−C(19)	110.6(7)	Pt−N(1)−C(27)	129.6(6)

between the molecular square plane and the ring containing C(1) is 68.0(3)°. This fact could be explained by the disposition of the 8-methylquinoline ligand, as is described below.

The Pt−N distance, 2.140(8) Å, is similar to those found in the literature for other Pt(II) complexes with quinoline ligands.[14,17] The angles around the N atom of the ligand are not 120°, as might be expected for sp^2 hybridization; they deviate from this idealized value by about 10° (see Table 3). Moreover, the methyl carbon C(28) is not coplanar with the quinoline double ring; it deviates by 0.28 Å. These distortions lead C(28) to be more distant from the Pt atom and closer to the pentafluorophenyl ring containing C(1) than in an idealized situation. The proximity of the methyl carbon atom C(28) is consistent with the larger dihedral angle of the C(1) ring with respect to the molecular square plane. These features are not observed in complex **2** and are probably caused by the presence of the methyl group in the 2 position of the quinoline double ring.

The C(28) atom sits above the coordination plane; the Pt−C(28) distance is 3.174(9) Å. This distance is in the range found in complexes of Pt(II) and Ir(I) for which a M−H interaction has been postulated.[8b,14,17] Unfortunately, due to the quality of the crystallographic data, it has not been possible to locate and refine the position of the methyl hydrogen atoms from the electron density maps. We only can study the possible Pt···H distances in the cases of the different conformations of the methyl group, locating geometrically the hydrogen atoms (C−H distance of 0.96 Å, H−C−C and H−C−H angles about 109.5°). The Pt···H distances obtained from this method are in the range from 2.28 to 2.60 Å. These distances are short and are in the range in which M−H interactions have been reported in the literature.[8b,14] As in complex **2**, in this study we also have found *o*-F-H distances in the range of 2.6−3.0 Å.

Concluding Remarks

Here we report the synthesis and characterization of $[NBu_4][Pt(C_6F_5)_3L]$ complexes containing ligands L with hydrogen atoms located in such a way that Pt···H interactions could be present. In solution, we have studied carefully their ^{1}H NMR spectra, and in all cases we have detected a significant displacement toward higher frequency of the signal of the hydrogen that could be involved in the Pt···H interaction. Despite the fact that this displacement has sometimes been cited as evidence of the Pt···H interaction,[7] we think that the shift in the signal is not sufficient proof of a significant Pt···H interaction since the shift could in principal also be caused by the anisotropic deshielding effect of the $5d_{z^2}$ orbital electron density. The presence of coupling between the metal center and the hydrogen atoms seems to be much more conclusive. We have observed this coupling for complexes **1**, **2**, and **3**. For complexes **1** and **2**, the value of the coupling constant J(Pt,H) is one of the largest reported for this kind of interaction, around 80 Hz, indicating a strong Pt···H interaction. In **3**, the strength of the interaction seems to be smaller since the observed coupling constant is 22 Hz. For complex **4** no coupling constant, and thus no interaction, is observed.

The formally negative charge on the platinum center must play a decisive role in the establishment of these Pt···H interactions.[7f] With this in mind, the strength of these interactions in complexes **1**−**4** can be rationalized in terms of the electropositive character of the hydrogen atoms and the rigidity of the skeleton of the ligands. For the ligands 8-hydroxyquinoline and 8-hydroxyquinaldine (complexes **1** and **2**), the hydrogen atom belongs to a hydroxylic fragment, and therefore it has moderate acidic characteristics. For the ligand 7,8-benzo[*h*]-quinoline (complex **3**), the hydrogen atom should not be so electropositive; but the rigidity of the three condensed aromatic ring system forces the orientation of H[9] toward the platinum atom. The result is the presence of a Pt···H interaction but weaker than that for **1** and **2** based on the value of *J*(Pt,H). For the ligand 8-methylquinoline (complex **4**), the low polarity of the C−H bonds and the possibility of free rotation of the methyl group seem to preclude any kind of Pt···H interaction. Van Koten and co-workers have also observed a decrease in the value of the coupling constant *J*(Pt,H) in the complexes [PtX(L-*C,N*)-(LH-*C,H*)] in which the ligands are not so rigid.[7b] These conclusions are in agreement with theoretical studies carried out by Dedieu and van Koten[18] in which it is revealed that the main character of the M···H−X interaction is electrostatic in nature with a minor covalent contribution in which a $5d_{z^2}$–6s hybridization is required in the case of Pt(II), the latter being a necessary condition for direct through-bond Pt−H coupling.

In the solid state, the crystal structure of **2** shows that the hydrogen atom is pointing towards the platinum center with a Pt···H distance of 2.19 Å. Since the hydroxylic atom prefers this orientation to any of the others possible, the existence of a Pt···H interaction is quite clear. In the case of complex **4**, the quality of the crystallographic data does not allow the location of the methyl hydrogen atoms to be determined and thus it is not possible to measure a value for the Pt···H distance. Given the position of the carbon atom and considering the possible conformations of the methyl group, we have calculated Pt···H distances between 2.3 and 2.6 Å, in the range reported in the literature for Pt···H interactions. From these data the existence of such an interaction in the solid state could be possible. Nevertheless, it is necessary to be cautious since the geometry of the ligand has been chosen precisely to force the proximity of the hydrogen atoms and the metal. We think that with the available data it is not possible either to confirm or to discard the presence of a Pt···H interaction in **4**.

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Supporting Information Available: Tables of crystallographic data, full atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, full bond distances and bond angles, and hydrogen coordinates and isotropic displacement parameters for **2** and **4** and, for the structure of complex **2**, annular difference Fourier calculation near O atom used to find the electron density corresponding to H(1) and its graphic representation and contoured sections of a difference map showing the electron density corresponding to H(1) (19 pages). Ordering information is given on any current masthead page.

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