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New N–H---Pt Interactions. The Nature of the Bond

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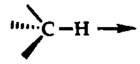
Acetylated 8-aminoquinoline, **7**, is shown to be a ligand which, once complexed to Pt(II) containing cyclometalated ligands, gives rise to cationic complexes containing new three-center N–H---Pt bonds. The presence of this bonding can be deduced by ^{1}H and ^{15}N NMR spectroscopy in that the magnitudes of the spin–spin couplings $^1J(^{195}\text{Pt},^1\text{H})$ and $^1J(^{15}\text{N},^1\text{H})$ can be used to analyze these interactions. In solution these new three-center bonds are not very strong, and there is exchange between coordinated and uncoordinated **7** as shown by phase-sensitive ^{1}H NOESY. The solid-state structure of the cyclometalated complex $[\text{Pt}\{(2,6\text{-CH}_2\text{Ph}_2)\text{C}_6\text{H}_3\}(\mathbf{7})](\text{CF}_3\text{SO}_3)$ (**6**) was determined by X-ray diffraction and reveals that the hydrogen of the N–H is ca. 2.2(1) Å from the metal. Crystal data for **6**: monoclinic *Cc*, a = 15.429(1) Å, b = 14.194(1) Å, c = 19.185(2) Å, β = 101.89(1)°, V = 4111.4 Å^3, and Z = 4. The combination of X-ray distances and NMR coupling constants provides insight both into new and previously postulated N–H---Pt bonds.

Introduction



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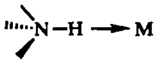

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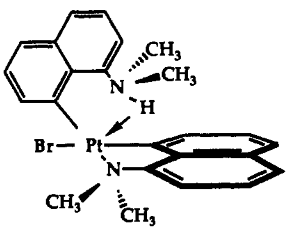
There are now a relatively large number of metal complexes which demonstrate agostic bonding involving a C–H bond and an ML$_n$ fragment,[1–4] e.g., **1**. Within the group of **1** compounds, we now know that the C–H bond can be stretched in varying amounts and that such bonds can have very different physical and spectroscopic characteristics.[5–8] Nitrogen analogues such as **2**, are not well-known and those few which have been suggested[9–13] have not been the subject of detailed study. For the complexes **3** and **4**, we have shown[14] that $^1J(^{15}\text{N},^1\text{H})$, in analogy with $^1J(^{13}\text{C},^1\text{H})$,[1] can be a useful analytical tool. Specifically, the magnitude of $^1J(^{15}\text{N},^1\text{H})$ in **3** decreases by ca. 20% relative to the uncoordinated ligand.[14] If the metal is also NMR active, e.g., ^{195}Pt, the decrease of $^1J(^{15}\text{N},^1\text{H})$ is accompanied by the observation of $^1J(^{195}\text{Pt},^1\text{H})$, and taken together, these two coupling constants help us to characterize and classify the nature of the bonding. Earlier reports concerned with NH agostics were based primarily on X-ray diffraction results[9,10] and in one case on a neutron diffraction study.[11]



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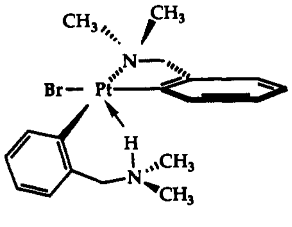

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We report here two new examples of platinum(II) complexes which exhibit NH---Pt bonding and use $^1J(^{15}\text{N},^1\text{H})$ to suggest that these relatively weak bonds are likely to be what has become known as "remote"[1] or "pregostic"[15] interactions.

The new complexes, **5** and **6**, were prepared as shown in Scheme 1 and a summary of their most important ^{1}H NMR and IR parameters is given in Table 1. The selection of the acetylated 8-amino-quinoline, **7**, as a potential N–H donor was based on the expectation that (i) when coordinated via the quinoline nitrogen, the amide N–H bond would be forced to reside close to the metal, thereby facilitating the development of an NH---Pt bond, and (ii) the carbonyl of the amide function would delocalize the nitrogen lone-pair, making the amide nitrogen a relatively poor donor. These complexes represent the first designed molecules showing NH---Pt bonding.

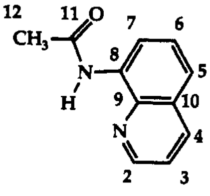

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Table 1. Selected Spectroscopic Data[a] for **5–7**

compd	δ(NH)	$^1J(^{15}N,^1H)$, Hz	$^1J(^{195}Pt,^1H)$, Hz	δ(H2)[b]	$\delta(CH_3)$[c]	IR
5	13.02	84.3	55	9.86	2.36	3446, 1690, 1517[d]
6	10.64	88.3	33	9.19	1.38	3350, 1690, 1520[e]
7	9.77	88.3		8.82	2.30	3353, 1677, 1518[f] 3308, 1658, 1522[g]

[a] Values are for CD_2Cl_2 solutions $\delta(^{15}N)$: **5**, –253.8; **6**, –254.9; **7**, –255.8. [b] Proton *ortho* to N of quinoline, $^3J(^{195}Pt,^1H)$ values of ca. 18 Hz and 17.7 Hz, for **5** and **6**, respectively. [c] CH_3 from quinoline ligand. [d] $CHCl_3$ solution; NH and amide bands. [e] CsI; NH and amide bands. [f] $CHCl_3$ solution; NH and amide bands. [g] CsI; NH and amide bands.

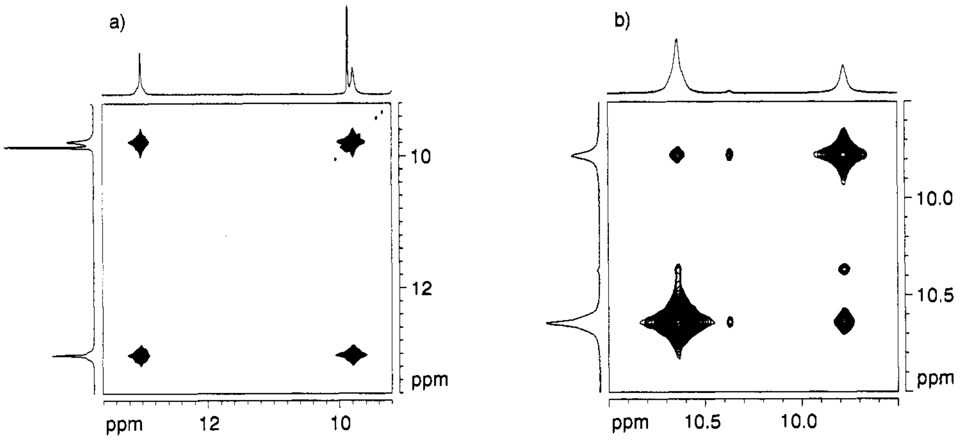
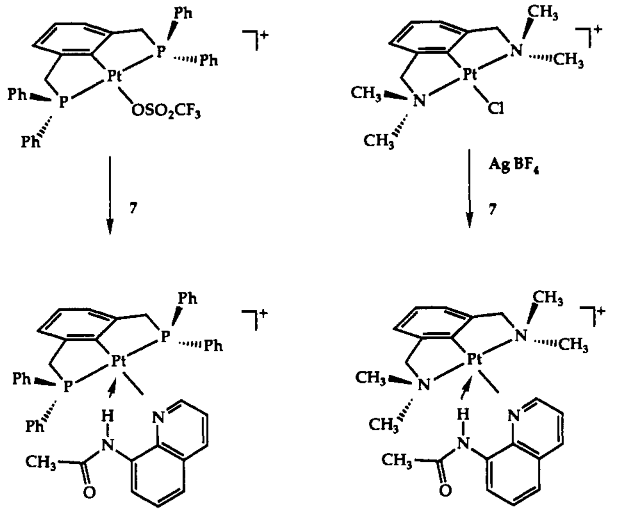


Figure 1. Section of the phase sensitive ^1H 2-D NOESY for both **5**, spectrum a, and **6**, spectrum b, showing exchange in the NH proton region. There is exchange between the "coordinated" NH and the free ligand for both complexes. It is interesting that, for **6**, there is a third, barely visible compound which is also in exchange with both the free ligand and its corresponding complex. Exchange with H_2O is not shown.

Scheme 1



6 CF_3SO_3 salt **5** BF_4 salt

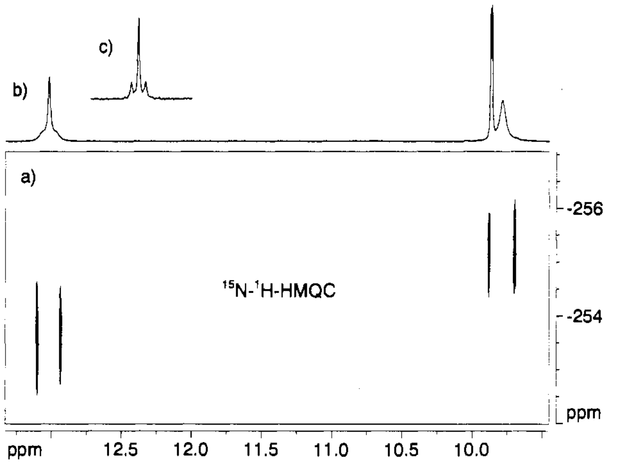


Figure 2. (a) $^{15}N,^1H$ HMQC correlation spectrum (500 MHz) for **5** showing the correlation to the NH proton of **5**, at low field and the broad NH proton of the ligand **7**. (b) Section of the conventional proton spectrum showing (from low to high field) the NH of **5**, the proton of **5** *ortho* to the quinoline nitrogen and the NH proton of uncoordinated **7**. (c) NMR spectrum for the NH proton of **5** at 200 MHz.

In CD_2Cl_2 solution, **5** and **6** exist in equilibrium with the starting complex and free ligand, **7**, as shown by phase-sensitive ^1H, 2-D NOESY spectroscopy; see Figure 1. These spectra also reveal that ligand **7** exchanges its NH proton with H_2O at a much faster rate than does either **5** or **6** (although both exchanges are slow on the NMR time scale). Figure 2 shows a section of the conventional ^1H as well as the 2-D ^{15}N, ^1H 500-MHz correlation spectrum for **5**. In Figure 2b the NH proton of the complex, whose position is now at much higher frequency relative to the uncoordinated ligand, clearly shows ^{195}Pt satellites (although these are sharper at 200 MHz;[16] see Figure 2c). The cross-peaks shown in Figure 2a readily afford $^1J(^{15}N,^1H)$ for both the complex and the free ligand. These and the analogous spectra for **6** demonstrate that the amide N–H proton (a) is coupled to the ^{195}Pt, with values of 55 and 33 Hz for **5** and **6**, respectively, (b) shows only very modest decreases in $^1J(^{15}N,^1H)$, ca. 4 and "0" Hz for **5** and **6**, relative to the 88.3-Hz value in the free ligand, and (c) is markedly shifted to higher frequency relative to the uncomplexed ligand.

The Pt, H spin–spin coupling is too large to arise from anything other than a direct interaction between these two spins; however, in bridging hydrides of Pt(II), $^1J(^{195}Pt,^1H)$ is typically 200–400 Hz.[17] Taken together with the small changes in $^1J(^{15}N,^1H)$ and $\delta(^{15}N)$, summarized in Table 1, the data clearly indicate a weak interaction, so that we classify this as a remote NH---Pt bond,

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(16) (a) *Transition Metal NMR Spectroscopy;* Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991. (b) Pregosin, P. S. *Annual Report on NMR Spectroscopy;* Academic Press: London, 1986; Vol. 17. This T_2 dependence on B_0 strength is well-known and involves relatively rapid ^{195}Pt relaxation at the higher field.

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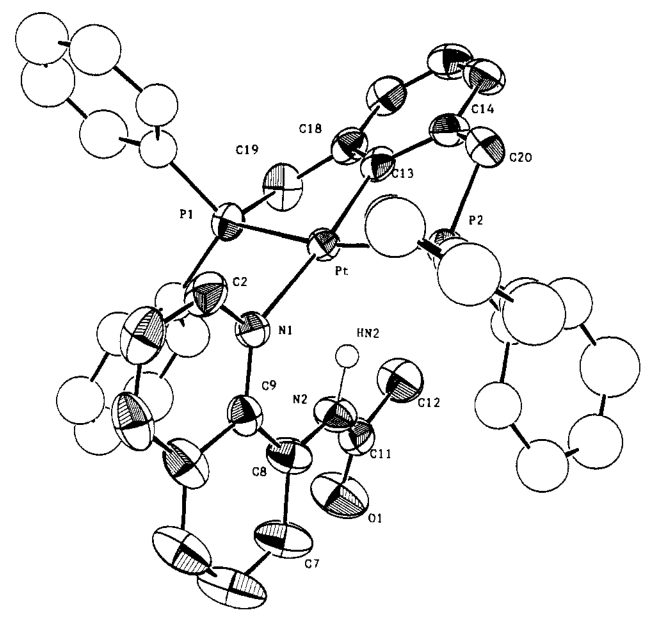


Figure 3. ORTEP view of the cation of **6**.

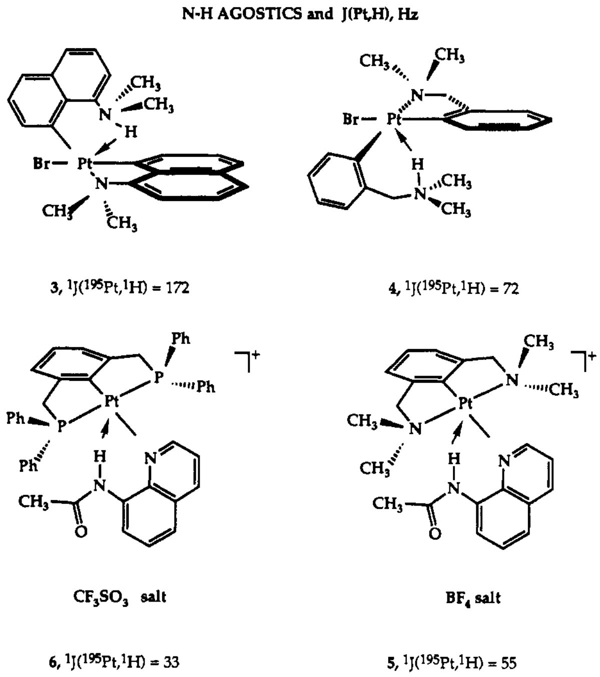
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **6**

Pt-P(1)	2.286(1)	N(2)-C(11)	1.368(9)
Pt-P(2)	2.292(1)	C(15)-C(16)	1.379(10)
Pt-N(1)	2.150(4)	C(11)-O(1)	1.202(9)
Pt-C(13)	2.029(6)	Pt-HN(2)	2.2(1)
N(2)-C(8)	1.395(3)	N(2)-HN(2)	0.9(1)
P(1)-Pt-P(2)	164.98(5)	Pt-C(13)-C(14)	119.1(4)
N(1)-Pt-C(13)	175.1(2)	Pt-N(1)-C(9)	129.4(4)
P(1)-Pt-C(13)	81.7(2)	P(1)-C(19)-C(18)	105.8(4)
P(2)-Pt-C(13)	83.4(2)	P(2)-C(20)-C(14)	107.0(4)
P(1)-Pt-N(1)	94.4(1)	N(2)-C(8)-C(9)	121.5(6)
P(2)-Pt-N(1)	100.5(1)	O(1)-C(11)-C(12)	122.3(7)
Pt-P(1)-C(19)	101.9(2)	C(8)-N(2)-C(11)	128.3(6)
Pt-P(2)-C(20)	101.0(2)	Pt-HN(2)-N(2)	147(9)
Pt-C(13)-C(18)	121.4(4)		
Pt-P(2)-C(20)-C(14)	-31.1(5)	N(1)-C(9)-C(3)-N(2)	-6.5(1.0)
Pt-P(1)-C(19)-C(13)	-31.4(5)	C(3)-N(2)-C(11)-O(1)	0.3(1.0)

in analogy with our earlier[5-8] remote C–H---Pt agostics, in which ligands similar to **7** were involved. We believe that the differences between **5** and **6** arise from the differing steric environments encountered by the NH proton; i.e., considering the substituents above the coordination plane, the NMe is smaller than the PPh, thereby allowing the NH to come somewhat closer to the platinum. 2-D ^1H NOESY studies[18] support the placement of the N–H proton in a pseudo-fifth-coordination position and define the relative position of the acetyl CH_3 with respect to the quinoline moiety.

The solid-state structure of **6** was determined by X-ray diffraction, and an ORTEP view of the cation is shown in Figure 3. The immediate coordination sphere consists of two *trans* P-atoms, the cyclometalated carbon and the quinoline nitrogen, all with relatively routine metal–ligand atom separations. This type of cyclometalated ligand has been used on a number of occasions previously,[19-22] and Gorla et. al.[19] have recently reported detailed crystallographic results for three new structures. Our Pt-P(1), Pt-P(2), and Pt-C(13) separations, 2.286(1), 2.292(1), and 2.029(6) Å, respectively, are in agreement with their values. We note that the metal–carbon bond distance, Pt-C(13), can, in principle, be much shorter.[23] The Pt-N(1) separation, 2.150(4) Å, is somewhat long, but in good agreement with what one expects[5-7,24] for a pyridine or quinoline type ligand, trans to a relatively strong donor. The platinum–amide nitrogen separation is 3.077(5) Å and the amide N–H proton has been found at a distance of 2.2(1) Å from the metal in a pseudo-fifth-coordination position.

Scheme 2



The neutron diffraction study[11] of $[NPr^n_4]_2\{PtCl_4\}\cdot$*cis*-$[PtCl_2(NH_2Me)_2]$, in which two different complex types co-crystallize, showed the Pt-atom of the $PtCl_4$ unit to be 2.262(11) Å from one of the NH atoms of the coordinated NH_2Me of the second platinum. Moreover, the bonding NH---Pt hydrogen–platinum distance in **3** is 2.11(5) Å.[13] Consequently, although our 2.2(1)-Å value has a large experimental uncertainty, it fits well with what is known for such complexes. Assuming that in a bridging hydride complex the Pt–H separation is on the order of 1.65–1.75 Å,[25] we again conclude that for **3** and **4** we are probably dealing with a relatively weak metal-hydrogen interaction. Given the various NH---Pt separations now known, it would seem that the 2.61 Å NH---Co distance found[12b] in $(Et_3NH)[Co(CO)_4]$ is too long to be a covalent bonding interaction. The quinoline framework in **6** makes an angle of 92.7(1)° with the coordination plane, as might be expected for such a ligand.[7,26]

Scheme 2 shows the $^1J(^{195}Pt,^1H)$ values for **3**-**6**, 172, 72, 55, and 33 Hz, respectively, and indicates that the nature of the bonding can vary quite significantly. In a similar vein, the changes in the values $^1J(^{15}N,^1H)$ reflect the one-bond Pt–H interaction, but in a reverse fashion; i.e., the N, H coupling decreases the most when the Pt, H coupling is at a maximum. Consequently, we can envision a sliding scale for this type of NH---Pt bond and suggest that these NMR parameters will be valuable in helping to estimate its relative strength. Moreover, we note the larger $^1J(^{195}Pt,^1H)$ values for **3** and **4**, in which the metal is formally

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Table 3. Experimental Data for the X-ray Diffraction Study of **6**

chem formula	$C_{44}H_{37}F_3N_2O_4P_2PtS$
mol wt	1003.89
T, °C	24
space group	Cc (No. 9)
a, Å	15.4292(7)
b, Å	14.1940(8)
c, Å	19.1849(23)
β, deg	101.890(7)
Z	4
V, Å^3	4111.4 (6)
ρ(calcd), g cm^{-3}	1.622
μ, cm^{-1}	36.293
λ, Å	0.710 69 (graphite monochromated, Mo Kα)
transm coeff	0.9991–0.9084
R^a	0.021
$R_w{}^b$	0.031

[a] $R = \sum||F_o| - 1/k|F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - 1/k|F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o{}^2) + f^2(F_o{}^2)^2]^{1/2}/2F_o$ with f = 0.055.

Table 4. Positional and Isotropic Equivalent Displacement Parameters for **6**[a]

atom	x	y	z	B, Å^2
Pt	0.000	0.12427(1)	0.250	2.461(2)
S	0.5600(1)	0.2432(1)	0.4876(1)	4.62(4)
P1	0.0392(1)	−0.0278(1)	0.23228(8)	2.92(3)
P2	−0.0055(1)	0.2760(1)	0.28979(8)	2.97(3)
F1	0.040(1)	0.6259(5)	0.3820(6)	13.4(4)
F2	0.1574(6)	0.6034(6)	0.4606(7)	12.4(3)
F3	0.0320(6)	0.5601(5)	0.4786(5)	12.0(2)
O1	−0.2152(4)	−0.0397(5)	0.3873(3)	6.4(1)
O2	0.4683(5)	0.2524(6)	0.4784(5)	9.0(2)
O3	0.6020(5)	0.3040(5)	0.4466(4)	8.4(2)
O4	0.5993(7)	0.2354(7)	0.5608(5)	10.1(3)
N1	−0.1247(3)	0.1160(3)	0.1756(3)	2.74(9)
N2	−0.1556(3)	0.0558(4)	0.3146(3)	3.6(1)
C1	0.5718(9)	0.1285(6)	0.4503(8)	7.2(3)
C2	−0.1168(5)	0.1361(5)	0.1112(4)	4.0(1)
C3	−0.1841(7)	0.1283(5)	0.0511(4)	4.6(2)
C4	−0.2650(6)	0.1020(6)	0.0594(4)	4.6(2)
C5	−0.3657(5)	0.0627(7)	0.1383(5)	5.9(2)
C6	−0.3824(5)	0.0475(7)	0.2040(6)	6.7(2)
C7	−0.3119(5)	0.0468(6)	0.2618(5)	5.3(2)
C8	−0.2246(4)	0.0637(5)	0.2552(4)	3.7(1)
C9	−0.2087(4)	0.0885(4)	0.1871(3)	3.0(1)
C10	−0.2815(5)	0.0837(5)	0.1268(4)	4.2(1)
C11	−0.1541(4)	0.0062(5)	0.3760(4)	3.7(1)
C12	−0.0687(6)	0.0125(6)	0.4277(4)	5.1(2)
C13	0.1221(4)	0.1252(4)	0.3144(3)	3.0(1)
C14	0.1598(4)	0.2126(5)	0.3412(3)	3.5(1)
C15	0.2442(4)	0.2138(6)	0.3850(4)	4.3(1)
C16	0.2885(5)	0.1301(5)	0.4035(4)	4.2(1)
C17	0.2503(4)	0.0455(5)	0.3799(4)	3.9(1)
C18	0.1672(4)	0.0420(5)	0.3349(3)	3.4(1)
C19	0.1222(5)	−0.0514(5)	0.3133(4)	4.2(1)
C20	0.1126(4)	0.3037(5)	0.3165(4)	3.8(1)
C111	−0.0479(5)	−0.1139(4)	0.2220(4)	3.6(1)*
C112	−0.1127(6)	−0.1114(5)	0.1579(5)	4.5(1)*
C113	−0.1859(6)	−0.1692(7)	0.1493(5)	5.4(2)*
C114	−0.1946(7)	−0.2300(7)	0.2046(5)	6.1(2)*
C115	−0.1326(7)	−0.2332(8)	0.2632(6)	6.8(2)*
C116	−0.0593(6)	−0.1739(7)	0.2743(5)	5.2(2)*
C121	0.0923(4)	−0.0475(4)	0.1584(3)	3.4(1)*
C122	0.1076(5)	0.0241(5)	0.1146(4)	3.9(1)*
C123	0.1432(7)	0.0043(7)	0.0555(6)	5.8(2)*
C124	0.1673(7)	−0.0823(8)	0.0431(6)	6.4(2)*
C125	0.1568(8)	−0.1557(9)	0.0885(7)	7.0(2)*
C126	0.1191(7)	−0.1391(6)	0.1458(6)	5.8(2)*
C211	−0.0567(5)	0.3697(4)	0.2314(4)	3.7(1)*
C212	−0.1007(5)	0.4443(6)	0.2544(5)	5.0(2)*
C213	−0.1380(7)	0.5138(8)	0.2077(6)	6.6(2)*
C214	−0.1297(7)	0.5098(8)	0.1394(6)	6.4(2)*
C215	−0.0875(6)	0.4389(7)	0.1133(6)	6.1(2)*
C216	−0.0494(6)	0.3667(5)	0.1598(5)	4.9(2)*
C221	−0.0557(4)	0.2827(5)	0.3669(4)	3.6(1)*
C222	−0.1474(5)	0.2763(6)	0.3560(4)	4.6(1)*
C223	−0.1904(6)	0.2757(7)	0.4134(5)	6.0(2)*
C224	−0.1406(7)	0.2823(8)	0.4786(6)	6.8(2)*
C225	−0.0515(9)	0.2887(9)	0.4934(8)	8.5(3)*
C226	−0.0046(6)	0.2883(7)	0.4353(5)	6.0(2)*
HN2	−0.103(7)	0.089(8)	0.313(6)	8(2)*

[a] Esd's are given in parentheses. Starred B values are for atoms that were refined isotropically. B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\text{beta}(1,1) + b^2\text{beta}(2,2) + c^2\text{beta}(3,3) + ab(\cos \text{gamma})\text{beta}(1,2) + ac(\cos \text{beta})\text{beta}(1,3) + bc(\cos \text{alpha})\text{beta}(2,3)]$.

negative and the nitrogen atom formally positive, and the smaller magnitudes of $^1J(^{195}\text{Pt},^1\text{H})$ for **5** and **6**, where the metal is formally positive and the nitrogen neutral.

These results are consistent with both covalent and electrostatic[13] contributions to this type of bonding. Calculations[13b 27] suggest that NH---M interactions, e.g., M = Pd,[13b] Ni,[27] of the type we and others[9–13] describe, may be strongly electrostatic in nature; however, the same calculations[13b] show developing covalent character for M = Pt. Moreover, it is possible that complexes such as **3**–**6** should be thought of as three-center, four-electron bonds,[13b] and thus as special cases of hydrogen bonding and not "agostic";[28] however, if this is the case, then one must be prepared to invoke some rehybridization of the contributing metal orbitals (to include s-character) in order to rationalize the coupling to ^{195}Pt, especially for **3**. Clearly our few data are insuffcent for a definitive conclusion; nevertheless, it appears that we can begin to understand the significance of an observed solid-state NH---M separation, in terms of the extent of the bonding, i.e., relatively weak when longer than ca. 2.2 Å.

We expect that **7** will provide entry to a wider variety of complexes showing NH---M bonding, especially in conjunction with metals in lower oxidation states.

Experimental Section

General Data. All manipulations were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents were dried by conventional procedures and distilled prior to use. IR spectra (Nujol mulls), or solution cells) were recorded on a Perkin-Elmer 883 spectrometer. NMR spectra were measured using Bruker AC 200 and AMX 500 NMR spectrometers. ^{1}H-NOESY and ^{15}N,H correlations (AMX 500) were measured using standard pulse sequences as described previously.[14,18,29] The mixing time for the ^{1}H 2-D NOESY spectra was chosen to be 0.8 s.

Preparation of 5. The starting chloro complex (20 mg, 47.4 μmol) was suspended in 2 mL of acetone containing 0.02 mL of H_2O and stirred for 15 min; addition of $AgBF_4$ (10 mg, 51.4 μmol) was followed by stirring for an additional 10 min. Removal of AgCl by filtration and distillation of the solvent gives a yellow oil, which solidifies to the aquo complex as a white solid when covered with Et_2O. Treatment of the aquo complex (10 mg, 20.3 μmol) with 3.7 mg of **7** in 0.6 mL of CD_2Cl_2 gave the solution used for the NMR measurement. The product is in equilibrium with ligand and the aquo complex. ^{13}C NMR (CD_2Cl_2): δ 168.2 (CO), 155.4 (C(2)), 25.1 ($COCH_3$).

Preparation of 6. The starting cyclometalated triflate complex (10 mg, 12 μmol) and ligand **7** (2.3 mg, 12.2 μ-mol) were dissolved in CD_2Cl_2 for the NMR study. The product **6** was crystallized by covering the CD_2Cl_2 solution with ether and allowing the ether to slowly diffuse into the CD_2Cl_2 solution (yield ca. 70%). Anal. Calcd for $C_{44}H_{37}N_2O_4F_3P_2SPt$: C, 52.64; H, 3.71; N, 2.79. Found: C, 52.02; H, 3.72; N, 2.55. ^{13}C NMR (CD_2Cl_2): δ 167.5 (CO), 153.4 (C(2)), 24.6 ($COCH_3$).

Preparation of 7. 8-Aminoquinoline (2.0 g (13.9 mMol) was dissolved in 20 mL of CH_2Cl_2 and the solution cooled to −78 °C. Acetyl chloride (0.985 mL = 1.083 g, 13.9 mmol) was injected into the quinoline solution using a syringe and the resulting solution stirred vigorously. While the mixture was warming to room temperature an orange solid precipitated. On addition of 20 mL of H_2O (to destroy unreacted acetyl chloride) the solid dissolved leaving an orange solution. Addition of 150 mL of 1 M NaOH was followed by extraction three times with 150 mL

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of CH_2Cl_2. The organic fractions were combined and the solvent removed. The solid which remained was sublimed under vacuum at 40 °C. That which sublimes represents impurity and the crude solid which remains is analytically pure (85% yield). Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.74; H, 5.40; N, 14.68. ^{13}C NMR (CD_2Cl_2): δ 168.9 (CO), 148.6 (C(2)), 25.2 (CH_3).

Crystallography. Crystals of compound **6** were obtained by crystallization from CH_2Cl_2/Et_2O and are air stable.

An Enraf-Nonius CAD4 diffractometer was used for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least squares fit of the 2θ values of 25 high order reflections ($9.4 < \theta < 15.5°$). Selected crystallographic and other relevant data are listed in Table 3 and in Table S1.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three other reflections every 300 measurements.

Data were corrected for Lorentz and polarization factors and empirically, for absorption (azimuthal (Ψ) scans of six reflections having $\chi > 85.5°$, $9.2 < \theta < 21.5°$).[30] The standard deviations on intensities were calculated in term of statistics alone, while those on F_o were calculated as reported in Table 3.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods using anisotropic displacement parameters for all atoms except the carbon atoms of the phenyl rings. Toward the end of the refinement the hydrogen atom bonded to atom N2 was located and included in the refinement while the contribution of the remaining hydrogen atoms in their idealized positions (C–H = 0.95 Å, $B = 1.3B(\text{carbon})$ Å^2) was taken into account but not refined. The function minimized was: $[\Sigma w(|F_o| - 1/k|F_c|)^2]$ with $w = [\sigma^2(F_o)]^{-1}$. No extinction correction was found to be necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[31]

Upon convergence the final Fourier difference map showed no significant peaks. All calculations were carried out by using the Enraf-Nonius MOLEN crystallographic programs.[32]

The handedness of the crystal was tested by refining the two enantiomorphs. The two sets of coordinates gave significantly different values for the agreement factors, based on the Hamilton's test[33] (R_w = 0.033 and R_w = 0.045 respectively) thus establishing the absolute configuration of the molecule. Final atomic coordinates and equivalent thermal factors are given in Table 4.

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Supplementary Material Available: ORTEP plot with full numbering scheme, tables of experimental data (Table S1), calculated positional parameters for the hydrogen atoms (Table S2), and anisotropic displacement parameters (Table S3), and an extended list of bond lengths, angles, and torsion angles (Table S4) (14 pages). Ordering information is given on any current masthead page.

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