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LETTER

Facile platinum(II) promoted amide deprotonation and subsequent cyclization. Comments on a possible L_mPt---H–NH(CO)R agostic moiety

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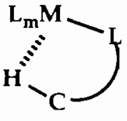
Introduction

There are now many molecules which show 'agostic' bonding of the form **1** [1]. Within this class there are (i) some complexes in which the interactions of the C–H moiety with the metal center are relatively strong, with a subsequent marked reduction in the one-bond C–H coupling constant [2–5] and (ii) a distinct second group in which the M---H–C interaction is relatively weak [6], so that ${}^1J$(C, H) does not change appreciably.



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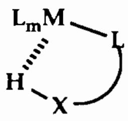

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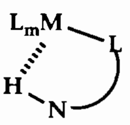

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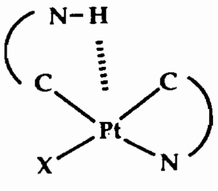
In principle, there is no reason why molecules such as **2** should not exist, and indeed complexes with X = Si [7], H [8] and recently P [9] have been reported. The chemistry for compounds such as **3**, with X = N, is very limited [10, 11]. We have recently proposed [12] some NMR criteria involving ${}^1J({}^{15}N,{}^1H)$, which proved useful in the characterization of two cyclometallated platinum(II) complexes of type **4**.



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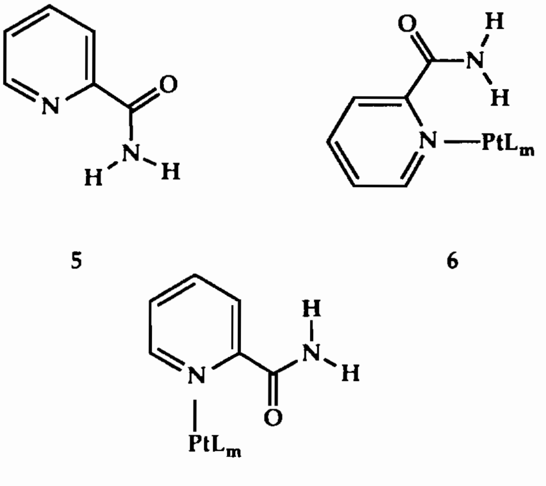
To further prepare complexes containing M---H–N interactions we have considered the platinum(II) chemistry of pyridine-2-carboxamide (**5**), shown in Scheme 1. Coordination of the pyridine nitrogen should force one of the N–H bonds to come close to the platinum center as shown in **6**. This assumption is reasonable since one expects [13] restricted rotation about the carbonyl carbon–nitrogen bond, as is typical in amides, but no isomerism to **7**. Further, in platinum and related chemistry, neutral amides are usually oxygen and not nitrogen ligands [14].

We report here on some Pt(II) chemistry involving **5** and show an unexpected cyclization reaction under mild conditions to afford a novel N,N′ chelate complex with the deprotonated amide nitrogen serving as one donor.



Scheme 1.

Results and discussion

Reaction of the dinuclear complexes *sym–trans*-[Pt(μ-Cl)Cl(PR_3)]$_2$, R = Ph, *p*-Tol, Et, with 2 equiv. of **5** in $CHCl_3$ at *c.* 333 K affords the bidentate nitrogen complexes **8a–8c** as shown in Scheme 2. The reaction proceeds slowly (3–4 days) but is essentially quantitative for **8a** and **8c** and gives a 72% yield for **8b**. This is a unique example of a mild metal promoted deprotonation of an amide in non-aqueous medium in the absence of added base.

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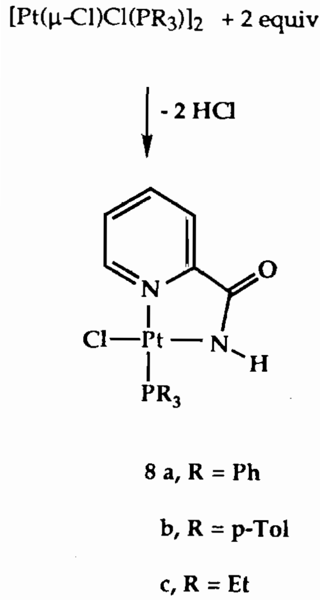


Scheme 2.

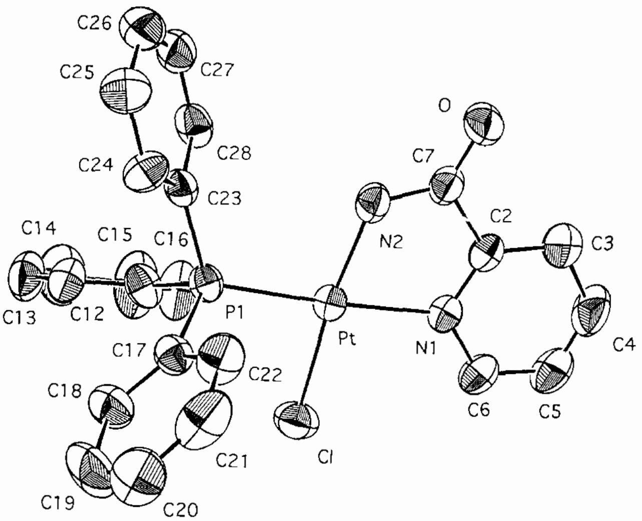


Fig. 1. ORTEP plot of **8a**. Selected bond lengths (Å) and bond angles (°): Pt–Cl, 2.313(2); Pt–P(1), 2.255(1); Pt–N(1), 2.092(4); Pt–N(2), 1.995(5); N(2)–C(7), 1.322(8); C(7)–O, 1.234(7); P(1)–Pt–N(1), 176.5(1); Cl–Pt–N(2), 173.4(1); P(1)–Pt–Cl, 88.9(1); P(1)–Pt–N(2), 97.7(1); Cl–Pt–N(1), 94.6(1); N(1)–Pt–N(2), 78.8(2).

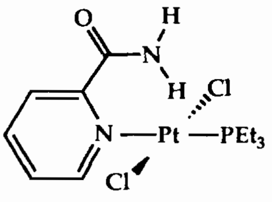
The structure of **8a** was determined by X-ray diffraction* methods and a view of the molecule is shown in Fig. 1. The complex has a distorted square planar geometry with the tertiary phosphine and the pyridine nitrogen in *trans* position to one another. Interestingly, the amide nitrogen exercises a *trans* influence similar to that of a Cl^- or an RCN ligand as demonstrated by the 2.313(2) Å separation observed for the Pt–Cl bond [15]. The N(1)–Pt–(N2) bite angle is *c.* 79°. Generally speaking, we find relatively routine bond angles and bond distances for the remaining ligands, with the longer Pt–N bond distance for N(1) resulting from the difference in *trans* influence between PPh_3 and Cl^-.

The complexes **8** show ^1H and ^{31}P NMR spectra which support their formulation as given. The ^{31}P spectra show singlets accompanied by ^{195}Pt satellites, e.g. for **8a**, $\delta = 7.7$, $^1J(Pt,P) = 3870$ Hz. The NH protons appear at $\delta = c.$ 4.4–5.2 and reveal relatively large two-bond spin–spin interactions of *c.* 80 Hz. We see nothing unusual in this value; however, we find few comparison data [16], perhaps because many 'Pt–NH_2R' complexes have relatively broad NH type resonances, thereby obscuring this coupling. We have used natural abundance 2-D $^{15}N,^1H$ correlation NMR spectroscopy [17] (a method which as yet has not been applied in coordination chemistry) to confirm that only *one* proton resides on nitrogen. Interestingly, the values $^1J(^{15}N,^1H) = 80$–83 Hz in **8a–8c** are relatively small for an sp^2 nitrogen [18] and *c.* 10% less than those for **5**.

We consider this an interesting cyclization reaction for several reasons:

1. This type of reaction is known *in water* for a variety of metal centers, e.g. Cu(II) and Pd(II) [19], but for platinum(II) a base is required [20] and in many cases the complexes were not isolated [20].
2. Should an intermediate Pt---H–N moiety exist, the N–H would be in a pseudo fifth bonding position thus facilitating proton loss. This would then be related to what we have found [6, 21, 22] for the 'Pt---H–C' moiety.

In an attempt to characterize a possible 'Pt---H–N' interaction we have monitored the reaction of $[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ with **5** via ^1H NMR immediately after mixing. At room temperature the proton lines are broad; however, at 243 K, one observes two new complexes in *c.* 10:1 ratio. The major component, presumably **9**, reveals NH signals at 7.44 and 8.14 ppm, thereby confirming that both NH_2 protons are still present. These signals are relatively broad and have not been



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*Crystals of **8a** are monoclinic with space group $P2_1/c$ (No. 14) with $a = 16.677(6)$, $b = 9.491(1)$, $c = 15.936(1)$ Å, $\beta = 73.14(2)$°; $V = 2414(1)$ Å^3, $Z = 4$. A total of 4726 independent reflections was collected of which 3736 were considered as observed having ($|F_o|^2 > 3.0\sigma(F_o)$). The structure was refined by full matrix least-squares using anisotropic displacement parameters for all atoms. The final agreement factor was $R = 0.032$.

assigned; however, we note that these are, on average, downfield from the uncoordinated ligand NH resonances at 6.67 and 7.89 ppm*. There is no observable coupling to ^{195}Pt; although if this latter were $\leqslant 10$ Hz it would go unobserved. A 2-D ^{15}N,^{1}H NMR correlation spectrum, see Fig. 2, reveals $^{1}J(^{15}N,^{1}H)$ values of *c.* 90.5 and 92.2 Hz, i.e relatively unchanged from the *c.* 90 Hz found in ligand **5**. Consequently, a *strong* interaction of an N–H with the platinum can be ruled out [12], since the $^{1}J(^{15}N,^{1}H)$ should drop by at least 10–20%; however, a weak interaction is still possible. The amide ^{15}N chemical shift for **9** moves to lower field by *c.* 18 ppm relative to that of the free ligand. This suggests some change in the local electronic structure of the amide group (and is too large to be attributed to anisotropic effects). Further, a ^{1}H 2-D NOESY measurement shows that both NHs have contacts with the CH_3s of the PEt_3, with the low field NH NOE somewhat stronger than the corresponding high field NOE. Thus the NHs spend some time above the platinum(II) roughly as in **9**.

In summary, there is *no* compelling evidence for a strong Pt---H–N bond in **9**. A weaker one cannot be excluded and it is equally likely that a Cl---H–N interaction develops. These structural possibilities, as well as the chemistry associated with the minor isomer (which we think has a structure similar to **7**) are being pursued further.

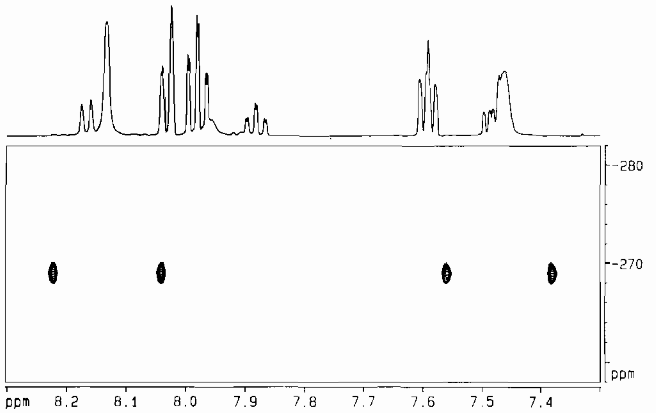

Fig. 2. ^{15}N,^{1}H correlation for **9** showing the connectivity to the two low field NH signals. The vertical axis with the ^{15}N signal is referenced to CH_3NO_2.

Acknowledgments

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*The assignment of the ligand NH protons is not straightforward. We have carried out temperature, solvent and concentration studies to be certain of our assignment and will report on these in the full paper; nevertheless, since the ligand NH chemical shifts are sensitive, they are not a good reference for the complex NH line positions.