Nucleophilic Attack of Carbanions on Cationic Platinum(II) Nitrile Complexes Affording Stable η^1-Imine Enol and η^1-Enamine Coordinated Fragments

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Cationic nitrile platinum(II) complexes of formula $[PtMe(RCN)(bipy)]^+$ undergo nucleophilic addition of carbanions $^-CH(COX)(COY)$ (X, Y= Me, OMe), $^-CH(CO_2Me)CN$ and $^-CH(CN)_2$ to afford neutral products. According to the nature of the nucleophile, the organic ligand fragment displays either an imino enol or an enamine isomeric structure. The Pt–N bond can be cleaved upon reaction with acids with formation of the corresponding β-enaminodione.

Introduction

Nucleophilic attack on coordinated nitriles is an agile way for the formation of several organic functions.[1,2] For example, the addition of water,[1] alcohols,[1] amines,[1] nitrones[3] and oximes[4] to metal-bonded nitriles gives rise to the corresponding amidato, imidoester, amidine, oxadiazoline and iminoacylated oxime groups. With several metals (e.g. W, Co, Ir, Rh, Ru, Pt) stable complexes can be isolated.[1]

Within this field of research, d^8 ions exhibit a very rich chemistry. For example, Michelin[1,5] and Natile[6] have carried out extensive studies on the attack of amines and alcohols to Pd^{II} and Pt^{II} nitrile complexes, with important implications for asymmetric synthesis[7] and medicine.[8]

On the other hand, a correspondingly thorough investigation of the species involved in the addition of carbanions to d^8 metal-bound nitriles has not been developed, although this is a convenient catalytic route to β-enaminodiones.[1,2] As far as we know, only one group has investigated the attack of carbanions, for example $^-CH(COMe)_2$, on platinum(II) nitrile complexes.[9] The reaction was generally accompanied by acyl migration and the formation of neutral products containing a bidentate *N,O*-chelated moiety, such as $[Pt\{N(COMe)C(Ph)CHC(Me)O^a\}(Pt-O^a)]$. The acyl migration could be prevented with retention of the chelated fragment $[Pt\{NHC(Ph)C(COMe)C(Me)O^a\}(Pt-O^a)]$. Similar Pd^{II} and Ni^{II} complexes were also prepared[10] by an alternative method, the addition of β-enaminodiones, for example $H_2NC(Et)=C(COMe)_2$, to suitable metal precursors.

Aiming to extend the knowledge within this field, we investigated the reaction of carbanions with complexes of formula $[PtMe(RCN)(bipy)]^+$. As described below, in all cases the nucleophile easily attacks the coordinated nitrile, and different structural types are obtained according to the nature of the carbanions.

The solid-state characterisation of a representative product, as well as reactions involving the functionalised coordinated fragment, have also been carried out.

Results and Discussion

Addition of Carbanions to $[PtMe(RCN)(bipy)]BF_4$ Complexes. Characterisation of the Products

Five carbanions of general formula $^-CH(COX)(COY)$ were used, $^-CH(COMe)_2$ (**a**), $^-CH(COMe)(CO_2Me)$ (**b**), $^-CH(CO_2Me)_2$ (**c**), $^-CH(CO_2Me)(CN)$ (**d**) and $^-CH(CN)_2$ (**e**). In most cases the cationic platinum(II) precursor was $[PtMe(MeCN)(bipy)]BF_4$ (**1**, bipy = 2,2′-bipyridine), although in some experiments the related complexes $[PtMe(PhCN)(bipy)]BF_4$ (**2**), $[PtMe(MeCN)(phen)]BF_4$ (**3**, phen = 1,10-phenanthroline) and $[PtMe(MeCN)(dmphen)]BF_4$ (**4**, dmphen = 2,9-dimethyl-1,10-phenanthroline) were used. The latter was chosen in order to see the effect of the steric hindrance of the chelating ligand.

When an acetonitrile suspension of the Pt^{II} complexes was allowed to react with an excess of the appropriate nucleophile, the colour of the reaction mixture turned from yellow to orange-red within a few minutes. The metal products could be isolated in good yields as microcrystalline powders according to standard procedures. Only when the chelate was the hindered dmphen was the yield low, possibly due to the pronounced crowding in the square-planar coordination plane.

The new complexes are soluble in chlorinated solvents, although very poorly in the case of the cyano derivatives derived from **d** and **e**. Characterisation was carried out by IR and NMR spectroscopy, elemental analysis and, in one representative case, by X-ray diffractometry.

In principle, nucleophiles can react with cationic nitrile-containing platinum(II) complexes either by substitution or

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by attacking the ligand, with formation of a corresponding metal-bonded organic fragment. The following NMR spectroscopic features allow us to confirm that all the reactions involved the attack of the anion on the nitrile with formation of a square-panar product:

i) the presence of a peak for the σ-bonded Pt−Me group with ^{195}Pt satellites of the appropriate intensities ($^{2}J_{Pt-H}$ = 80−85 Hz).[11]

ii) a singlet weakly coupled to ^{195}Pt around δ = 2.3 attributable to the methyl group of a Me−C−N−Pt fragment ($^{4}J_{Pt-H}$ = 8 Hz) in the case of the acetonitrile precursor. When benzonitrile was used, the aromatic region contained the expected Ph pattern.

iii) the presence of other singlets attributable to CO_2Me and COMe groups, when present in the reacting nucleophile. In the case of symmetric carbanions, i.e. X = Y, these groups are equivalent even at 213 K.

iv) the non-equivalence of the two halves of the chelating ligand, according to the absence of a mirror plane orthogonal to the square-planar coordination plane. The $^{3}J_{Pt-H}$ coupling constants of the protons H6 (12−16 Hz) and H6′ (45−50 Hz) of bipy are significantly different. On the grounds of the higher trans influence of Me groups with respect to N atoms, these values are compatible with the presence of a Me and an N atom trans to N1 and N1′ respectively. Analogously, the H2 and H9 protons of phen split to a different extent, and the smaller coupling is attributable to the hydrogen trans to Me.

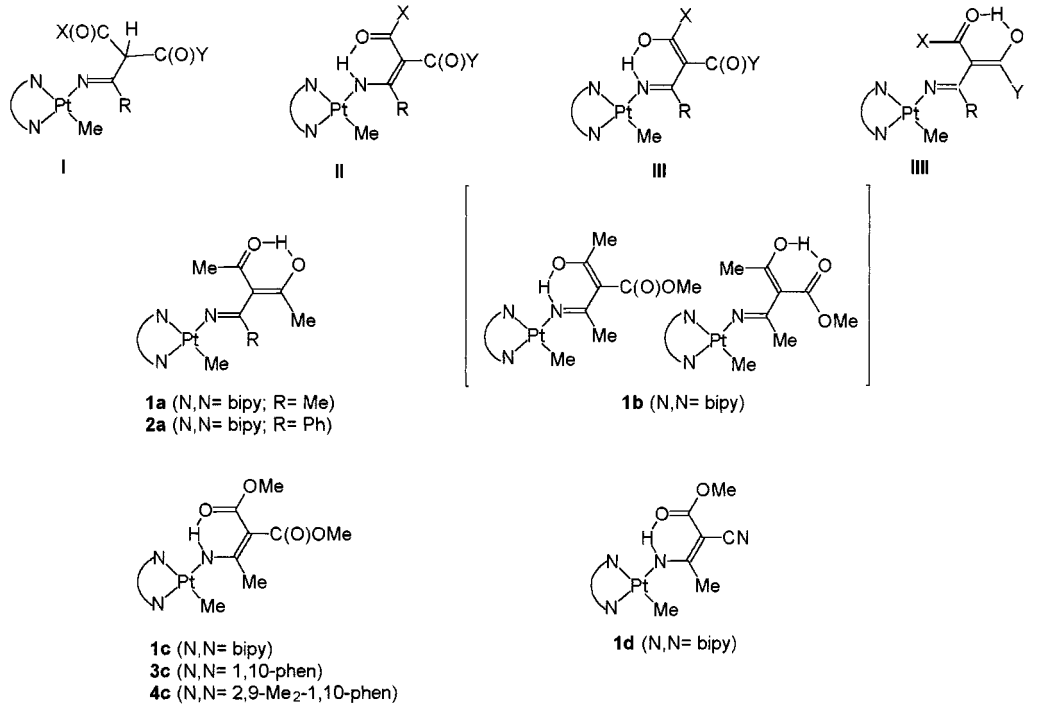
When the nucleophile contains at least one carbonyl function (**a**−**d**), the product resulting from the addition can exist in an equilibrium between the following isomers:[12] keto enamine (**I**), enamine with N−H···O hydrogen bonds (**II**) and imino enol (with either O−H···N, **III**, or O−H···O hydrogen bonds, **III′**), as depicted in Scheme 1.

Structures such as **I** seem to contribute little to our products since the ^{1}H NMR spectra lack a signal attributable to the CH proton that was originally present in the nucleophiles. Instead, a broad singlet is present at very low field (δ = 9.5−12), which disappears in a couple of hours when a few drops of CD_3OD are added to a $CDCl_3$ solution of the complexes. The position of this peak is typical of a proton involved in a hydrogen bond,[13] as is found in isomers of types **II**, **III** and **III′**.

Further structural information was obtained from the IR spectra of the complexes in chloroform solution. More precisely, in the products derived from acetylacetone (X= Y= Me, **1a** and **2a**), the COMe signals were found below 1570 cm^{-1}. A similarly significant lowering of the carbonyl frequencies suggests that an imino enol (isomer **III′**) is present, which forms an O−H···O chelating moiety. An IR band at 2500 cm^{-1} is in agreement with this linkage. The electronic delocalisation within the dicarbonyl moiety would account for the equivalence of the carbonyl functions in the NMR spectra (see point iii, above).

Analogously, the COMe stretching in **1b** (X= Me, Y= OMe) is found at 1568 cm^{-1}, while the CO_2Me signal lies at 1670 cm^{-1}. This suggests that an imino enol isomer is favoured here as well, even though a distinction between **III** and **III′** appears to be quite difficult. In fact, the lowering of the CO_2Me stretching mode at 1670 cm^{-1} can also be ascribed to the conjugation in the organic fragment, rather than to the possible formation of a hydrogen bond.[10]

It should be noted that the organic moiety present in complexes **1a, 1b** and **2a** is strongly related to the above-



Scheme 1

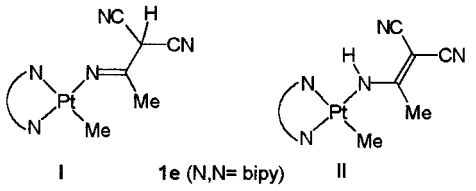
mentioned chelated fragments [M{NHC(R)C(COMe)-C(Me)O^a}(*M-O^a*)].[1,2,9,10] In the latter cases, the ligand binds the metal by forming a six-membered ring. In **1a, 1b** and **2a** the lack of an easily accessible coordination site prevents chelation through the oxygen atom, which therefore binds the mobile proton. As far as we know, these are the first examples of β-imino enols bonded to a d^8 ion in an η^1 fashion.

When the carbonyl group does not belong to a ketonic function (**c**,**d**), an enolic form of the product is no longer possible,[13] and hence the isomeric forms **III** and **III′** can be ruled out. In keeping with this hypothesis, the IR spectra of **1c**, **1d 3c**, and **4c** (Scheme 1) show N−H bands in the range 3230−3320 cm^{-1}. This band disappears upon addition of deuterium oxide to a chloroform solution of the complexes. The two carbonyl stretchings in **1c** appear at 1670 and 1610 cm^{-1}. The difference of ca. 60 cm^{-1} can be attributed to the fact that only one of them is involved in a hydrogen bond N−H···O[13] according to a type **II** structure (Scheme 1). The carbonyl groups are equivalent on the NMR time scale, as expected by site exchange through conformational rearrangements.

Analogous considerations hold true for **3c** and **4c**, which contain phen and dmphen as chelating ligands, respectively.

For complex **1d**, derived from the attack of $^-$CH(CO$_2$Me)CN, an enamine type **II** isomer seems favoured in chloroform solution. In addition to the above-mentioned N−H band (3250 cm^{-1}) and to a sharp signal at 2180 cm^{-1} (CN), the IR spectrum also displays the carbonyl stretching shifted to 1640 cm^{-1}. This frequency is in agreement with the involvement of this moiety in a N−H···O hydrogen bond.

Finally, when the nucleophile does not contain a carbonyl group, i.e. $^-$CH(CN)$_2$ (**e**), the formation of a hydrogen bond in the product **1e** (Scheme 2) is obviously not possible. In this case the absence of a methinic -CH(CN)$_2$ signal in the ^{1}H NMR spectrum rules out a keto enamine form (**I** in Scheme 2). The presence of a broad signal at δ = 6.5, which slowly disappears upon addition of CD$_3$OD, suggests the presence of an N−H bond,[5] which is confirmed by the corresponding IR stretching at 3316 cm^{-1}. Furthermore, the two non-equivalent nitriles give rise to two strong signals at 2195 and 2167 cm^{-1}, respectively. Thus, in this case the most stable structure is the enamine (type **II** in Scheme 2).



Scheme 2

Solid-State Structure of 1a

The molecular structure of **1a** is shown in Figure 1, and bond parameters of interest are listed in Table 1.

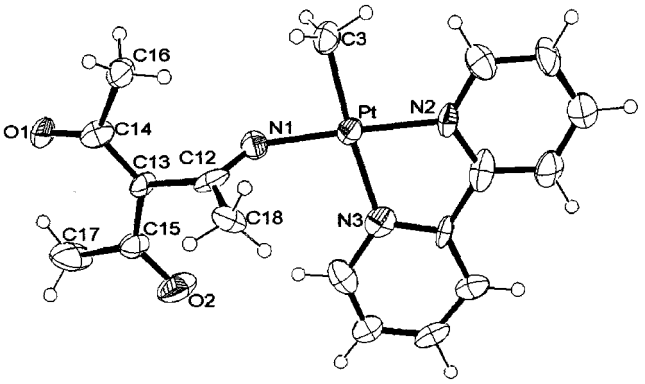


Figure 1. The molecular structure of **1a**

Table 1. Selected distances (Å) and angles(°) with their standard deviations in parentheses

Pt−N(1)	2.01(2)	C(12)−C(13)	1.53(3)
Pt−N(2)	2.01(2)	C(12)−C(18)	1.48(3)
Pt−N(3)	2.06(2)	C(13)−C(14)	1.39(3)
Pt−C(3)	2.00(2)	C(13)−C(15)	1.44(3)
O(1)−C(14)	1.24(3)	C(14)−C(16)	1.54(3)
O(2)−C(15)	1.25(3)	C(15)−C(17)	1.53(4)
N(1)−C(12)	1.29(2)		
N(1)−Pt−N(2)	173.9(6)	C(12)−C(13)−C(14)	122(2)
N(1)−Pt−N(3)	96.8(7)	C(12)−C(13)−C(15)	111(2)
N(1)−Pt−C(3)	86.6(8)	C(14)−C(13)−C(15)	127(2)
N(2)−Pt−N(3)	78.4(6)	O(1)−C(14)−C(13)	127(2)
N(2)−Pt−C(3)	98.1(8)	O(1)−C(14)−C(16)	117(2)
N(3)−Pt−C(3)	175.8(6)	C(13)−C(14)−C(16)	116(2)
Pt−N(1)−C(12)	129(2)	O(2)−C(15)−C(13)	121(2)
N(1)−C(12)−C(13)	118(2)	O(2)−C(15)−C(17)	120(2)
N(1)−C(12)−C(18)	123(2)	C(13)−C(15)−C(17)	119(2)
C(13)−C(12)−C(18)	119(1)		

The metal complex displays a square-planar geometry with the platinum lying out of the plane defined by the coordinated atoms by 0.05 Å.

The distances Pt−N(2) [2.01(2) Å] and Pt−N(3) [2.08(3) Å] are different and reflect the higher *trans* influence of Me with respect to the nitrogen function.

The most relevant feature of the structure is the electronic distribution within the ligand fragment resulting from the addition. It should be noted that: (i) atoms C(12), C(13), C(14) and C(15) are hybridised sp^2; (ii) N(1)−C(12) [1.29(3) Å] is a double bond, while C(12)−C(13) [1.53(4) Å] is a single bond; (iii) the atoms C(12), C(13), C(14), C(15), C(16), C(17), O(1) and O(2) lie in the same plane within 0.02 Å. This plane forms an angle of 76.3(5)° with the plane Pt−N(1)−C(12)−C(13)−C(18); (iv) C(13)−C(14) and C(13)−C(15) are intermediate between a single and a double bond; (v) the C(14)−O(1) and C(15)−O(2) bond lengths are characteristic of the carboxyl group.

These features, which indicate π-electron delocalisation within the planar dicarbonyl moiety, allow us to state that an imino enol isomer is also present in the solid state, al-

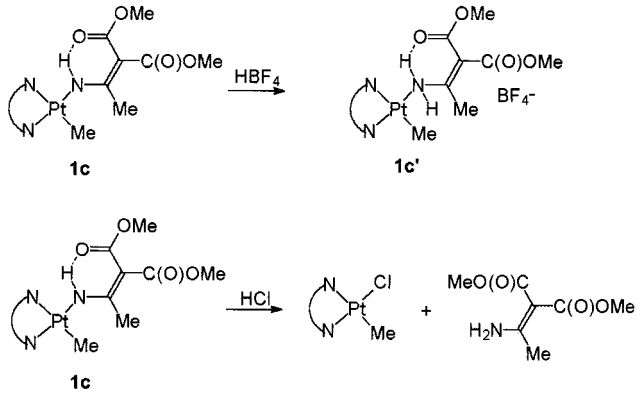
though not of type **III**, which implies the complete planarisation of the whole fragment including N(1) and C(18). This conformation seems in any case to be ruled out by the presence of a short methyl−methyl contact. The crystal structure shows a *transoid* conformation of the oxygen atoms, which makes it different also from the *cisoid* form **III′** found in solution, where an intramolecular hydrogen bond is present. In the solid state, the enolic H is statistically shared by O(1) and O(2). One of these positions is stabilised by the formation of the H bond O(2)−H···Cl [O(2)−Cl 2.86 Å] with a Cl atom of the solvent molecule CH_2Cl_2 in one of the two alternative sites of occupancy (see Exp. Sect.). On the other hand, when the hydrogen is linked to O(1), an intermolecular hydrogen bond is established with N(1) [O(1)−H···N(1), O(1)−N(1) 2.91 Å], and in this case the solvent lies far from the complex in order to minimise the steric contacts.

In conclusion, crystal forces stabilise a molecular structure in the solid state which is different from that found in solution, even though the main bonding properties are retained.

Reactions of 1c

The reaction of **1c** with protic acids were examined. Reaction with $HBF_4{\cdot}Et_2O$, which contains a non-coordinating anion, was very fast. The spectroscopic features of the product are similar to those displayed by the parent complex, except for a new signal at δ = 4.89 integrating for one proton. This evidence can be interpreted as the protonation of **1c**, with formation of a cationic product. Actually, in a type **II** structure (Scheme 3) the nitrogen atom has a lone pair, which can be protonated to form **1c′**. The large difference in chemical shift (5 ppm) between the hydrogen atoms bound to N can be ascribed to the fact that only one is involved in a hydrogen bond. It should be noted that **1c′** can be obtained independently by reacting $H_2NC(Me)=C(CO_2Me)_2$ with [PtClMe(bipy)] in the presence of one equivalent of $AgBF_4$.

The β-enaminodione can be liberated by reacting **1c** with HCl, which contains a coordinating anion. In this case, the formation of an intermediate product was followed by cleavage of the organic molecule and coordination of the chloride anion affording the stable complex [PtCl(Me)(bipy)] (Scheme 3).



Scheme 3

Conclusion

In this study we have demonstrated that nitriles (RCN) coordinated to square-planar cationic Pt^{II} complexes easily undergo nucleophilic attack by carbanions. The structure of the resulting organic ligand moiety can be controlled by varying the nature of the nucleophile. When it contains a ketonic function, imino enoles coordinated in an η^1 fashion are attained. In the other cases, an enamine structure is favoured.

It should also be noted that the same nucleophiles react with five-coordinated olefin complexes of formula $[PtMe(RCN)(N,N\text{-chelate})(olefin)]^+$ by simply substituting the axial nitrile.[14] This finding confirms once again the great influence of the coordination environment on the stability and reactivity of Pt^{II} complexes.

The reaction of a protic acid HX affords the corresponding β-enaminodione, which is either still coordinated to the metal centre or is obtained free, according to the coordinating ability of the X^- anion.

Experimental Section

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents and reagents were of AnalaR grade and were used without further purification, unless otherwise stated. THF was dried and distilled from Na/benzophenone. The carbanions,[15] [PtClMe(*N*,*N*-chelate)][16,17] and $[PtMe(MeCN)(N,N\text{-chelate})]BF_4$ [18] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer. $CDCl_3$, CD_3NO_2 and $C_2D_2Cl_4$ were used as solvents and $CHCl_3$ (δ = 7.26), CD_2HNO_2 (δ = 4.33) and C_2DHCl_4 (δ = 5.98) as internal standard. ^{13}C NMR spectra were recorded on a Varian XL-200 (^{13}C: 50.3 MHz). $^{13}CDCl_3$ (δ = 77) and $^{13}CD_3NO_2$ (δ = 62.8) were used as internal standard. The following abbreviations are used for describing NMR multiplicities: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad signal. Infrared spectra were recorded on a JASCO FT/IR 430 spectrometer.

[PtMe(PhCN)(bipy)]BF$_4$ (2): $AgBF_4$ (0.107 g, 0.550 mmol) and benzonitrile (0.100 mL, 1.00 mmol) were added to a cooled dichloromethane solution (10 mL) of [PtClMe(bipy)] (0.201 g, 0.500 mmol). After 1 h of stirring AgCl was removed by filtration and the solvent was evaporated under vacuum. The residue was washed with diethyl ether (2 × 5 mL) and dried. The yield was almost quantitative (0.270 g, 97.1%). − $C_{18}H_{16}BF_4N_3Pt$ (556.24): calcd. C 38.87, H 2.90, N 7.55; found C 39.03, H 2.95, N 7.52. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 1.11 (s, $^2J_{Pt-H}$ = 75 Hz, 3 H, Pt-Me), 7.73 (m, 3 H, PhCN), 7.90 (m, 2 H, PhCN), 8.07 (dd, 2 H, H5 and H5′-bipy), 8.40 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.98 (d, $^3J_{Pt-H}$ = 16 Hz, 1 H, H6-bipy), 8.98 (d, $^3J_{Pt-H}$ = 60 Hz, 1 H, H6′-bipy). − ^{13}C NMR (CD_3NO_2): δ = −13.1 ($^1J_{Pt-C}$ = 678 Hz, Pt-Me), 110.9 (C1-PhCN), 120.7 (C≡N), 124.8 (C3-bipy), 125.4 ($^3J_{Pt-C}$ = 33 Hz, C3′-bipy), 129.0 ($^3J_{Pt-C}$ = 55 Hz, C5′-

bipy), 130.0 (C5-bipy), 131.1 (C3 and C5-PhCN), 135.0 (C2 and C6-PhCN), 136.8 (C4-PhCN), 141.9 and 142.4 (C4 and C4′-bipy), 149.4 ($^2J_{Pt-C}$ = 25 Hz, C6-bipy), 150.8 ($^2J_{Pt-C}$ = 51 Hz, C6′-bipy), 154.8 and 159.9 (C2 and C2′-bipy).

Complexes 1a−e, 3c, 4c. − General Procedure: A THF suspension (6 mL) of the appropriate carbanion (2.0 mmol) was added to an acetonitrile solution (2 mL) of [PtMe(MeCN)(*N*,*N*-chelate)]BF_4 (0.200 mmol). The mixture was stirred for 30 min. The solvent was then removed under vacuum and the residue extracted with dichloromethane (4 × 5 mL). The extracts were filtered through Celite, then concentrated to 1−2 mL. An orange-red crystalline product was obtained by adding diethyl ether (yield: 80−90%).

1a: $C_{18}H_{21}N_3O_2Pt$ (506.38): calcd. C 42.69, H 4.18, N 8.30; found C 42.44, H 4.26, N 8.18. Yield: 0.091 g, 90%. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, $^2J_{Pt-H}$ = 84 Hz, 3 H, Pt-Me), 2.28 (s, $^4J_{Pt-H}$ = 8 Hz, 3 H, MeCN), 2.34 (s, 6 H, MeCO), 7.50 (m, 2 H, H5 and H5′-bipy), 8.15 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.62 (d, $^3J_{Pt-H}$ = 12 Hz, 1 H, H6-bipy), 8.97 (d, $^3J_{Pt-H}$ = 44 Hz, 1 H, H6′-bipy), 12.05 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = −15.1 ($^1J_{Pt-C}$ = 780 Hz, Pt-Me), 28.5 ($^3J_{Pt-C}$ = 81 Hz, *Me*CN), 31.5 (*Me*CO), 115.9 [*C*(COMe)$_2$], 122.6 and 123.5 (C3 and C3′-bipy), 127.0 and 127.6 (C5 and C5′-bipy), 138.1 (C4 and C4′-bipy), 147.8 and 148.6 (C6 and C6′-bipy), 154.1 and 157.9 (C2 and C2′-bipy), 174.4 (Me*C*N), 196.5 (Me*C*O) − IR($CHCl_3$): $\tilde{\nu}$= 2476 (O−H···O), 1557 (COMe) cm^{-1}.

1b: $C_{18}H_{21}N_3O_3Pt$ (522.38): calcd. C 41.39, H 4.05, N 8.04; found C 41.19, H 4.15, N 8.23. Yield: 0.090 g, 86%. − ^{1}H NMR ($CDCl_3$): δ = 0.84 (s, $^2J_{Pt-H}$ = 80 Hz, 3 H, Pt-Me), 2.32 (s, $^4J_{Pt-H}$ = 8 Hz, 3 H, MeCN), 2.34 (s, 3 H, MeCO), 3.72 (s, 3 H, MeOCO), 7.50 (m, 2 H, H5 and H5′-bipy), 8.15 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.58 (d, $^3J_{Pt-H}$ = 16 Hz, 1 H, H6-bipy), 8.96 (d, $^3J_{Pt-H}$ = 44 Hz, 1 H, H6′-bipy), 12.1 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = −15.1 ($^1J_{Pt-C}$ = 769 Hz, Pt-Me), 28.5 ($^3J_{Pt-C}$ = 80 Hz, *Me*CN), 29.7 (*Me*CO), 50.3 (*Me*OCO), 102.4 [*C*(COMe)(CO_2Me)], 122.8 and 123.7 (C3 and C3′-bipy), 126.9 and 127.4 (C5 and C5′-bipy), 138.1 (C4 and C4′-bipy), 147.4 and 148.5 (C6 and C6′-bipy), 154.2 and 157.9 (C2 and C2′-bipy), 172.6 (MeO*C*O), 174.5 (Me*C*N), 191.9 (Me*C*O) − IR ($CHCl_3$): $\tilde{\nu}$= 2471 (O−H···O), 1670 (CO_2Me), 1568 (COMe) cm^{-1}.

1c: $C_{18}H_{21}N_3O_4Pt$ (538.38): calcd. C 40.16, H 3.93, N 7.80; found C 40.30, H 4.04, N 7.69. Yield: 0.090 g, 84%. − ^{1}H NMR ($CDCl_3$): δ = 0.93 (s, $^2J_{Pt-H}$ = 82 Hz, 3 H, Pt-Me), 2.37 (s, $^4J_{Pt-H}$ = 8 Hz, 3 H, MeCN), 3.73 (s, 6 H, MeOCO), 7.50 (m, 2 H, H5 and H5′-bipy), 8.10 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.71 (d, $^3J_{Pt-H}$ = 16 Hz, 1 H, H6-bipy), 9.06 (d, $^3J_{Pt-H}$ = 46 Hz, 1 H, H6′-bipy), 10.1 (br, 1 H, NH). − ^{13}C NMR ($CDCl_3$): δ = −15.1 ($^1J_{Pt-C}$ = 776 Hz, Pt-Me), 28.2 ($^3J_{Pt-C}$ = 77 Hz, *Me*CN), 50.3 (*Me*OCO), 87.5 [*C*(CO_2Me)$_2$], 122.5 and 123.3 (C3 and C3′-bipy), 127.0 and 127.5 (C5 and C5′-bipy), 137.9 and 138.0 (C4 and C4′-bipy), 147.7 and 148.9 (C6 and C6′-bipy), 154.2 and 158.1 (C2 and C2′-bipy), 171.1 (MeO*C*O), 173.8 (Me*C*N) − IR ($CHCl_3$): $\tilde{\nu}$= 3227 (N−H···O), 1670 (CO_2Me), 1610 (CO_2Me) cm^{-1}.

1d: $C_{17}H_{18}N_4O_2Pt$ (505.35): calcd. C 40.40, H 3.59, N 11.09; found C 40.26, H 3.67, N 11.29. Yield: 0.081 g, 80%. − ^{1}H NMR ($C_2D_2Cl_4$): δ = 0.94 (s, $^2J_{Pt-H}$ = 80 Hz, 3 H, Pt-Me), 2.33 (s, 3 H, MeCN), 3.73 (s, 3 H, MeOCO), 7.53 (t, 1 H, H5-bipy), 7.62 (t, 1 H, H5′-bipy), 8.08 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.62 (d, $^3J_{Pt-H}$ = 16 Hz, 1 H, H6-bipy), 9.06 (d, $^3J_{Pt-H}$ = 44 Hz, 1 H, H6′-bipy), 9.65 (br, 1 H, NH) − IR ($CHCl_3$): $\tilde{\nu}$ = 3250 (N−H···O), 2180 (CN), 1640 (CO_2Me) cm^{-1}.

1e: $C_{16}H_{15}N_5Pt$ (472.33): calcd. C 40.69, H 3.20, N 14.82; found C 40.93, H 3.09, N 14.62. Yield: 0.076 g, 80%. − ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 3 H, $^2J_{Pt-H}$ = 80 Hz, Pt-Me), 2.28 (s, $^4J_{Pt-H}$ = 8 Hz, 3 H, MeCN), 6.55 (br, 1 H, NH), 7.56 (t, 1 H, H5-bipy), 7.72 (t, 1 H, H5′-bipy), 8.15 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.68 (d, $^3J_{Pt-H}$ = 12 Hz, 1 H, H6-bipy), 9.13 (d, $^3J_{Pt-H}$ = 52 Hz, 1 H, H6′-bipy) − IR ($CHCl_3$): $\tilde{\nu}$ = 3316 (N−H), 2195 (CN), 2167 (CN) cm^{-1}.

3c: $C_{20}H_{21}N_3O_4Pt$ (562.40): calcd. C 42.71, H 3.76, N 7.47; found C 42.88, H 3.61, N 7.53. Yield: 0.094 g, 84%. − ^{1}H NMR ($CDCl_3$): δ = 1.09 (s, $^2J_{Pt-H}$ = 82 Hz, 3 H, Pt-Me), 2.41 (s, 3 H, MeCN), 3.76 (s, 6 H, MeOCO), 7.80 (dd, 1 H, H3-phen), 7.85(dd, 1 H, H8-phen), 7.99 (s, 2 H, H5 and H6-phen), 8.58 (d, 1 H, H4-phen), 8.67 (d, 1 H, H7-phen), 8.98 (d, 1 H, H2-phen), 9.31 (d, $^3J_{Pt-H}$ = 44 Hz, 1 H, H9-phen), 10.2 (br, 1 H, NH). − ^{13}C NMR ($CDCl_3$): δ = −16.1 ($^1J_{Pt-C}$ = 780 Hz, Pt-Me), 28.3 ($^3J_{Pt-C}$ = 73 Hz, *Me*CN), 50.4 (*Me*OCO), 87.5 [*C*(CO_2Me)$_2$], 125.5 and 126.0 (C3 and C8-phen), 127.5 and 127.4 (C5 and C6-phen), 130.1 and 130.9 (C10 and C12-phen), 136.8 and 137.2 (C4 and C7-phen), 148.0 and 148.7 (C2 and C9-phen), 171.2 (MeO*C*O), 174.0 (Me*C*N) − IR ($CHCl_3$): $\tilde{\nu}$= 3229 (N−H···O), 1669 (CO_2Me), 1609 (CO_2Me) cm^{-1}.

4c: $C_{22}H_{25}N_3O_4Pt$ (590.46): calcd. C 44.75, H 4.27, N 7.12; found C 44.92, H 4.16, N 7.25. Yield: 0.103 g, 87.0%. − ^{1}H NMR ($CDCl_3$): δ = 1.12 (s, $^2J_{Pt-H}$ = 84 Hz, 3 H, Pt-Me), 2.40 (s, $^4J_{Pt-H}$ = 8 Hz, 3 H, MeCN), 2.74 (s, 3 H, Me-dmphen), 2.97 (s, $^4J_{Pt-H}$ = 4 Hz, 3 H, Me-dmphen), 3.69 (s, 6 H, MeOCO), 7.57 (d, 2 H, H3 and H8-dmphen), 7.78 (s, 2 H, H5 and H6-dmphen), 8.33 (d, 2 H, H4 and H7-dmphen), 10.1 (br, 1 H, NH). − ^{13}C NMR ($CDCl_3$): δ = −19.3 ($^1J_{Pt-C}$ = 755 Hz, Pt-Me), 25.8 and 27.8 (Me-dmphen), 28.5 ($^3J_{Pt-C}$ = 75 Hz, *Me*CN), 50.3 (*Me*OCO), 87.5 [*C*(CO_2Me)$_2$], 125.6 and 126.2 (C3 and C8-dmphen), 126.4 and 127.1 (C5 and C6-dmphen), 136.3 (C4 and C7-dmphen), 161.9 and 164.2 (C2 and C9-dmphen), 171.1 (MeO*C*O), 173.5 (Me*C*N) − IR ($CHCl_3$): $\tilde{\nu}$= 3228 (N−H···O), 1668 (CO_2Me), 1609 (CO_2Me) cm^{-1}.

Complex 2a: This complex was prepared as above, but with THF as solvent. Yield: 0.091 g, 80%. − $C_{23}H_{23}N_3O_2Pt$ (568.45): calcd. C 48.60, H 4.08, N 7.39; found C 48.49, H 4.15, N 7.52. − ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, $^2J_{Pt-H}$ = 81 Hz, 3 H, Pt-Me), 2.00 (s, 6 H, MeCO), 7.10 (m, 3 H, PhCN), 7.40 (m, 2 H, H5 and H5′-bipy), 7.62 (m, 2 H, PhCN), 8.10 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.43 (d, $^3J_{Pt-H}$ = 12 Hz, 1 H, H6-bipy), 8.86 (d, $^3J_{Pt-H}$ = 43 Hz, 1 H, H6′-bipy), 11.9 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = −14.4 (Pt-Me), 31.4 (*Me*CO), 116.3 [*C*(COMe)$_2$], 122.6 and 123.6 (C3 and C3′-bipy), 126.9 and 127.3 (C5 and C5′-bipy), 128.3 and 128.7 (C2, C3, C5 and C6-PhCN), 137.6 (C4 and C4′-bipy), 142.0 (C4-PhCN), 147.6 and 148.7 (C6 and C6′-bipy), 153.6 and 157.6 (C2 and C2′-bipy), 176.3 (Ph*C*=C), 197.3 (Me*C*O) − IR ($CHCl_3$): $\tilde{\nu}$= 2475 (O−H···O), 1542 (COMe) cm^{-1}.

Complex 1c′: (a) HBF_4·Et_2O (0.016 g, 0.10 mmol) was added to a chloroform solution (5 mL) of **1c** (0.054 g, 0.10 mmol). The colour of the solution turned from orange to yellow, and the solvent was removed under vacuum affording the product **A** in quantitative yield (0.062 g).

(b) A deuteronitromethane solution (1 mL) of $AgBF_4$ (0.010 g, 0.050 mmol) and $NH_2C(Me)=C(COMe)_2$ (0.010 g, 0.059 mmol) was added to solid [PtClMe(bipy)] (0.020 g, 0.050 mmol). After one hour of stirring AgCl was removed by filtration through a short column of Celite, and the filtrate transferred into an NMR tube. The spectrum was identical to that of the product **1c′** obtained as in (a) above. ^{1}H NMR (CD_3NO_2): δ = 0.82 (s, 3 H, $^2J_{Pt-H}$ =

80 Hz, Pt-Me), 2.57 (s, $^4J_{Pt-H}$ = 12 Hz, 3 H, MeCN), 3.92 (s, 6 H, MeOCO), 4.89 (s, 1 H, NH), 7.8 (m, 2 H, H5 and H5′-bipy), 8.4 (m, 4 H, H3,H3′,H4 and H4′-bipy), 8.59 (d, 1 H, H6-bipy,), 9.01 (d, $^3J_{Pt-H}$ = 52 Hz, 1 H, H6′-bipy), 11.1 (br, 1 H, NH).

X-ray Crystallographic Determination of 1a: Details of the structure analysis are listed in Table2. The compound was recrystallised from dichloromethane/toluene. X-ray data were collected at room temperature on an Enraf−Nonius CAD4-F automatic diffractometer using Mo-K_α graphite-monochromated radiation and operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 reflections in the θ range 12°≤ θ ≤14°. Three monitoring reflections, measured every 500 reflections, showed an intensity decay of about 12% for which a linear correction was applied. In addition to the corrections for Lorentz and polarisation factors, a semiempirical correction for absorption was applied[19] (max and min. values of the transmission factor were 1.3 and 1.0). The structure was solved by routine application of the Patterson and Fourier techniques and refined by a full-matrix least-squares procedure minimising the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = [\sigma^2(F_0)+(0.02F_0)^2+4]$, where σ is derived from counting statistics. A molecule of CH_2Cl_2 per molecule of complex allowed the calculated density to fit the measured value (by flotation). However, scrutiny of the Fourier difference map showed the solvent molecule to be distributed over two different sites and only the position of the four Cl atoms could be located and refined with isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. The H atoms were placed in calculated positions and included, but not refined, in the last refinement cycles with isotropic thermal parameters equal to those of the carrier atoms. The final Fourier difference map showed no peaks greater than 1.5 e·Å^{-3}. All calculations were performed with the Enraf−Nonius SDP set of programs.[20]

Table 2. Crystal and data collection details for **1a**

Crystal size	0.05 × 0.20 × 0.30 mm
Formula	$PtO_2N_3C_{18}H_{21}\cdot CH_2Cl_2$
Molecular weight	591.41
System	triclinic
Space group	$P\bar{1}$
a	8.187(2) Å
b	12.561(3) Å
c	12.743(3) Å
α	61.34(2)°
β	74.56(2)°
γ	82.26(2)°
V	1108(3) Å^3
Z	2
D_{calc}	1.77 g/cm^3
D_{obs}	1.78 g/cm^3
Radiation	Mo-K_α (0.71073 Å)
μ	66.5 cm^{-1}
Temperature	23 ±1°
Corrections	Lorentz-polarization linear decay (from 1.000 to 1.064 on *I*) reflection averaging (agreement on *I* = 4.0%) empirical absorption (from 1.000 to 1.315 on *I*)
θ_{max}	27°
Parameters refined	233
No independent reflections	4966
No reflections above 3σ	1705
Unweighted agreement factor	0.049
Weighted agreement factor	0.063
Esd of obs. of unit weight	1.06

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167118. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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