Mixed unsymmetric oxadiazoline and/or imine platinum(II) complexes†‡§

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Received 21st March 2007, Accepted 4th May 2007
First published as an Advance Article on the web 1st June 2007
DOI: 10.1039/b704329e

Iminoacylation of acetone oxime $Me_2C{=}NOH$ **2** upon reaction with *trans*-$[PtCl_2(NCCH_2CO_2Me)_2]$ **1** and [2 + 3] cycloaddition of acyclic nitrone $^-O^+N(Me){=}C(H)(C_6H_4Me\text{-}4)$ **3** to a nitrile ligand in **1** lead to the formation of mono-imine *trans*-$[PtCl_2(imine\text{-}a)(NCCH_2CO_2Me)]$ **4** [imine-a = $NH{=}C(CH_2CO_2Me)ON{=}CMe_2$] and mono-oxadiazoline *trans*-$[PtCl_2(oxadiazoline\text{-}a)(NCCH_2CO_2Me)]$ **6** [oxadiazoline-a = $\overline{N{=}C(CH_2CO_2Me)ON(Me)C}(H)(C_6H_4Me\text{-}4)$] unsymmetric mixed ligand complexes, respectively, as the main products. Reactions of **6** or **4** with acetone oxime **2**, cyclic nitrone $^-O^+\overline{N{=}CHCH_2CH_2CMe_2}$ **8** or *N*,*N*-diethylhydroxylamine **11** give access, in moderate to good yields, to the unsymmetric mixed ligand oxadiazoline and/or imine complexes *trans*-$[PtCl_2(oxadiazoline\text{-}a)(imine\text{-}a)]$ **9**, *trans*-$[PtCl_2(oxadiazoline\text{-}a)(oxadiazoline\text{-}b)]$ **10** [oxadiazoline-b = $\overline{N{=}C(CH_2CO_2Me)ONC(H)CH_2CH_2CMe_2}$], *trans*-$[PtCl_2(imine\text{-}a)(imine\text{-}b)]$ **12** [imine-b = $NH{=}C(CH_2CO_2Me)ONEt_2$] or *trans*-$[PtCl_2(imine\text{-}a)(oxadiazoline\text{-}b)]$ **13**. The *cis* mono-imine mixed ligand complex *cis*-$[PtCl_2(imine\text{-}a)(NCCH_2CO_2Me)]$ **4a** is the major product from the reaction of *cis*-$[PtCl_2(NCCH_2CO_2Me)_2]$ **1a** with the oxime **2**, while the di-imine compound *cis*-$[PtCl_2(imine\text{-}a)_2]$ **5a** is a minor product. Reaction of *cis*-$[PtCl_2(imine\text{-}a)(NCCH_2CO_2Me)]$ **4a** with *N*,*N*-diethylhydroxylamine **11** or the cyclic nitrone **8** affords, in good yields, the unsymmetric mixed ligand complexes *cis*-$[PtCl_2(imine\text{-}a)(imine\text{-}b)]$ **12a** or *cis*-$[PtCl_2(imine\text{-}a)(oxadiazoline\text{-}b)]$ **13a**, respectively. All these complexes were characterized by elemental analyses, IR and ^1H, ^{13}C and ^{195}Pt NMR spectroscopies, and FAB^+-MS. The X-ray structural analysis of *trans*-$[PtCl_2\{NH{=}C(CH_2CO_2Me)ON{=}CMe_2\}(NCCH_2CO_2Me)]$ **4** is also reported.

Introduction

Apart from the relevance of platinum compounds with N-ligands in pharmaceutical chemistry due to their antitumor activity,[1,2] the synthetic use of organonitrile–Pt complexes as precursors for a wide variety of N-containing Pt compounds is also a matter of current interest.[3–7] It has been shown that, when coordinated to a suitable Pt^{II} or Pt^{IV} center, nitrile ligands can undergo coupling with different types of nucleophiles[8,9] or 1,3-dipole reagents.[10] For instance, in our earlier work we have shown that nitriles of the type $NCCH_2R$ (R = CO_2Me, Cl) in $[PtCl_2(NCCH_2R)_2]$ compounds undergo [2 + 3] cycloaddition with cyclic or acyclic nitrones to afford di(oxadiazoline) complexes[11,12] while iminoacylation of ketoximes leads to the formation of di(imine)platinum(II) complexes,[13] under mild conditions. In such reactions, both ligated nitriles were transformed into the derived ligands. The major resulting achiral and symmetrical products were generally stable and obtained as mixtures of 1 : 1 diastereoisomers, unsuitable for application in asymmetric chemistry.

Compared to its common application, ligand exchange reactions, much less use has been made of selective differentiation between initially equivalent ligands,[8h,14,15,16] although such behaviour has been observed in some cases, for example in the reactions of *cis*- or *trans*-$[PtCl_2(NCPh)_2]$ with the secondary aliphatic amines RR′NH (R = Me; R′ = Et, Bu^t) to produce the mono-amidine complexes *cis*- or *trans*-$[PtCl_2\{N(H){=}C(NRR')Ph\}(NCPh)]$,[8h] and in the [2 + 3] cycloaddition of nitrones to afford mono and mixed oxadiazoline complexes.[16] In this last case, a geometrical dependence is observed, since the *cis*-mono(oxadiazoline)(nitrile) complexes do not undergo further cycloaddition with a second equivalent of acyclic nitrone, in contrast to the corresponding *trans*-complexes.[16]

Aiming to contribute to the development of the synthesis of unsymmetric mixed ligand Pt^{II} complexes, and to study some electronic factors of their selectivity, we have now focused our attention on the preparation of novel polyfunctional *cis* and *trans* unsymmetric complexes, such as $[PtCl_2(oxadiazoline\text{-}a)(imine\text{-}a)]$, $[PtCl_2(oxadiazoline\text{-}a)(oxadiazoline\text{-}b)]$, $[PtCl_2(imine\text{-}a)(oxadiazoline\text{-}b)]$ and $[PtCl_2(imine\text{-}a)(imine\text{-}b)]$, each bearing two different ligands. Recently, it has been shown that a *cis*-mono(oxadiazoline)(nitrile) complex does not react further with an acyclic nitrone;[16] we attempted the addition of a different 1,3-dipolar reagent or nucleophile *i.e.* a cyclic nitrone or *N*,*N*-diethylhydroxylamine to the nitrile group in a *cis*-mono(imine)(nitrile) complex. Interestingly, *cis*-$[PtCl_2(imine\text{-}a)(nitrile)]$ is converted to mixed ligand unsymmetric complexes *cis*-$[PtCl_2(imine\text{-}a)(oxadiazoline\text{-}b)]$ or *cis*-$[PtCl_2(imine\text{-}a)(imine\text{-}b)]$ by reaction with a second equivalent of this reagent, giving the first examples of

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† The HTML version of this article has been enhanced with colour images.

‡ CCDC reference number 641242. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704329e

§ Electronic supplementary information (ESI) available: Crystallographic details. See DOI: 10.1039/b704329e

these types of compounds. This may eventually offer an interesting application in the synthesis of biologically relevant molecules, and further studies are in progress.

Results and discussion

In this study, we report the synthesis of new *trans*- and *cis*-mixed unsymmetric oxadiazoline and/or imine complexes by using the bis(methylcyanoacetate) complexes *trans*- and *cis*-[$PtCl_2(NCCH_2CO_2Me)_2$] as starting dinitrile Pt^{II} complexes, and acetone oxime $Me_2C{=}NOH$ **2**, the acyclic nitrone $^{-}O^{+}N(Me){=}C(H)(C_6H_4Me\text{-}4)$ **3**, the cyclic nitrone $^{-}O^{+}\overline{N{=}CHCH_2CH_2}CMe_2$ **8** or *N*,*N*-diethylhydroxylamine **11**, as the reacting nucleophiles.

All the complexes obtained, whose formation was monitored by TLC, were purified by column chromatography on silica gel and characterized by IR, ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopy, FAB^{+}-MS and elemental analyses (in one case also by single-crystal X-ray diffraction).

Reactions of *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] 1

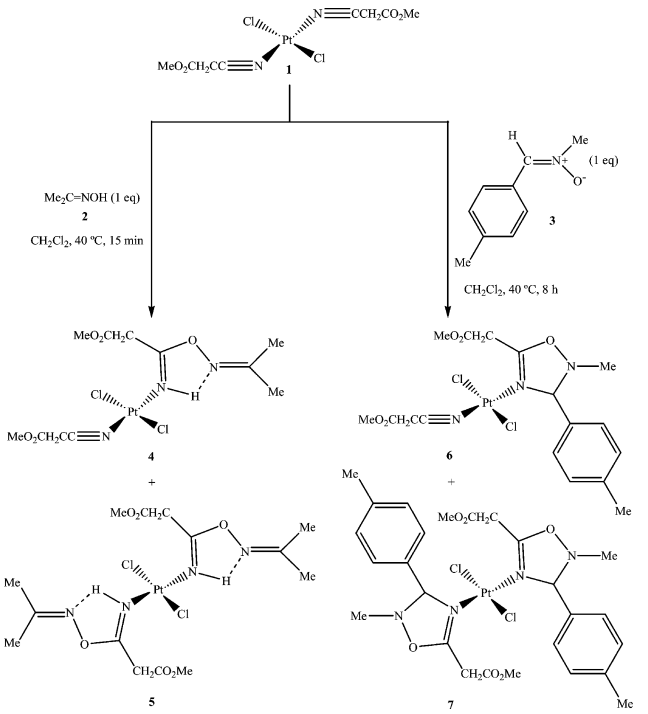
Trans-[$PtCl_2(NCCH_2CO_2Me)_2$] **1** is fully soluble in CH_2Cl_2 and thus the reactions of this complex with acetone oxime **2** and the acyclic nitrone **3**, the former leading to imine complexes *via* iminoacylation of the oxime and the latter affording oxadiazoline species upon [2 + 3] cycloaddition to a nitrile ligand, occur in homogenous media with favourable 1 : 1 stoichiometric conditions. The reactions were carried out in a 0.1 mmol scale with equimolar amounts of *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] **1** and the nucleophile.

The iminoacylation of acetone oxime **2** proceeds under mild conditions (40 °C, 15 min), in dry CH_2Cl_2, to give the mono-imine *trans*-[$PtCl_2$(imine-a)$(NCCH_2CO_2Me)$] **4** [imine-a = $NH{=}C(CH_2CO_2Me)ON{=}CMe_2$] as the major product (51% yield), together with the known[13] bis-imine *trans*-[$PtCl_2$(imine-a)$_2$] **5** (17%) (Scheme 1). In the case of the reaction of *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] **1** with the acyclic nitrone **3**, the system was stirred, in dry CH_2Cl_2, at 40 °C for 8 h to give the mono-oxadiazoline *trans*-[$PtCl_2$(oxadiazoline-a)$(NCCH_2CO_2Me)$] **6** [oxadiazoline-a = $\overline{N{=}C(CH_2CO_2Me)ON(Me)C(H)(C_6H_4Me\text{-}4)}$] as the main product (52% yield), along with the known[12] bis-(oxadiazoline) *trans*-[$PtCl_2$(oxadiazoline-a)$_2$] **7** (25%) (Scheme 1).

The complexes **5** and **7** derived from nucleophilic additions to both nitrile ligands are formed in much lower yields; thus the reactions show a considerable selectivity towards the mixed ligand products derived from a single addition, *i.e.* **4** and **6** (major products).

Once the first iminoacylation or cycloaddition has taken place, the second nitrile ligand exhibits a lower reactivity due to the different electronic properties of the imine or the oxadiazoline now in the *trans*-position, in comparison with the nitrile in **1**. Steric effects are not expected to play an important role because the ligands concerned are in *trans* positions.

Complexes **4** and **6** were derived from a single iminoacylation or a single cycloaddition, respectively, and their IR spectra exhibit quite similar $\nu(N{\equiv}C)$ values (2338 or 2336 cm^{-1}, respectively) which are also identical to that of the starting material **1** (2337 cm^{-1}). The N=C vibrations (1647 and 1666 cm^{-1} for **4**, or 1660 cm^{-1} for **6**) are also comparable with those of the corresponding bis-imine **5** (1646 and 1666 cm^{-1}) or bis-oxadiazoline **7**



Scheme 1 (The mixed ligands complexes **4** and **6** are the major products.)

(1657 cm^{-1}) complexes. In the ^{1}H NMR spectrum of **4**, the chemical shift of the N*H* proton is detected at 8.17 ppm, which indicates the existence of a hydrogen bond between the imine hydrogen and oxime nitrogen atoms which stabilizes the *E*-conformation of the iminoacyl ligands. The ^{13}C NMR spectrum of **4** shows the expected signals of the iminoester and nitrile ligands.

The single crystal X-ray diffraction structural analysis of the mono-iminoacylated Pt^{II} complex *trans*-[$PtCl_2\{NH{=}C(CH_2CO_2Me)ON{=}CMe_2\}(NCCH_2CO_2Me)$] **4** confirms the formulation and *trans* configuration (the molecular structure is depicted in Fig. 1, crystal data and selected bond lengths and angles are given in Tables 1 and 2, respectively). The values of bond lengths Pt–N(1) [1.991(4) Å], Pt–N(2) [1.980(5) Å], Pt–Cl(1) [2.293(14) Å], Pt–Cl(2) [2.299(13) Å], N(1)–C(10) [1.282(7) Å], N(2)–C(20) [1.128(7) Å] and N(1)–H(1) [0.87(5) Å], and angles

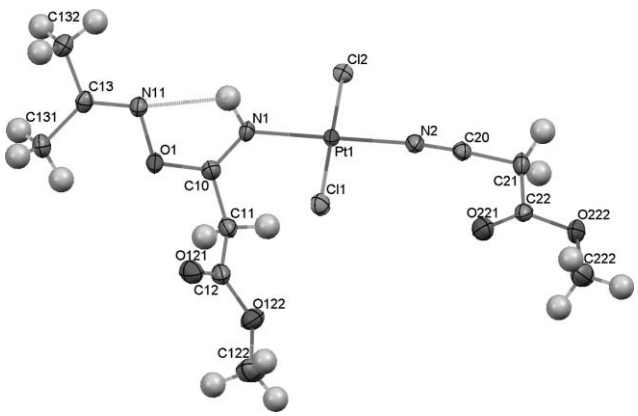


Fig. 1 Molecular structure of the mono-iminoacylated Pt^{II} complex *trans*-[$PtCl_2\{NH{=}C(CH_2CO_2Me)ON{=}CMe_2\}(NCCH_2CO_2Me)$] **4** with atomic numbering scheme (ellipsoids are drawn at 30% probability).

Table 1 Crystal data for *trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=CMe_2}-($NCCH_2CO_2Me$)] **4**

	4
Empirical formula	$C_{11}H_{17}Cl_2N_3O_5Pt$
Fw	537.27
Temp/K	150(2)
λ/Å	0.71069
Cryst. syst.	Orthorhombic
Space group	*Pccn*
a/Å	15.1631(4)
b/Å	29.3035(7)
c/Å	7.5829(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	3369.32(15)
Z	8
ρ_{calc}/mg m^{-3}	2.118
μ(Mo-Kα)/mm^{-1}	8.670
No. of collected rflns	18 444
No. of unique rflns	3069
$R_{Int.}$	0.0322
$R1^a$ ($I \geq 2\sigma$)	0.0283
$wR2^b$ ($I \geq 2\sigma$)	0.0684

^{a} $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond lengths [Å] and angles [°] for **4**

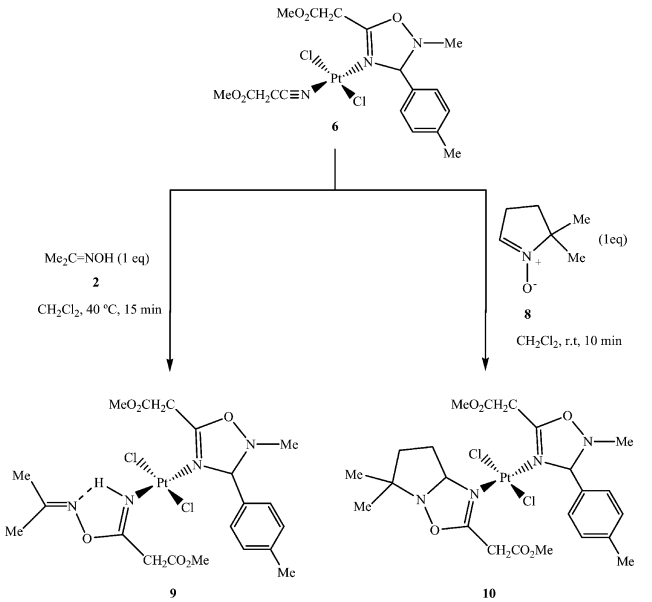
Pt(1)–Cl(1)	2.293(14)	O(1)–N(11)	1.457(6)
Pt(1)–N(1)	1.991(4)	N(2)–C(20)	1.128(7)
Pt(1)–N(2)	1.980(5)	N(1)–C(10)	1.282(7)
O(1)–C(10)	1.330(7)	N(1)–H(1)	0.87(5)
O(221)–(C22)	1.202(6)	O(222)–(C22)	1.314(6)
Cl(1)–Pt(1)–N(1)	90.14(14)	N(1)–Pt(1)–N(2)	178.16(19)
Cl(2)–Pt(1)–N(2)	91.05(14)	N(11)–O(1)–C(10)	111.6(4)
O(221)–C(22)–O(222)	125.4(5)	O(221)–C(22)–C(21)	123.6(5)
Pt(1)–N(1)–H(1)	121(3)	N(1)–H(1)···N(11)	114

Cl(1)–Pt(1)–N(1) [90.14(14)°], Pt(1)–N(1)–H(1) [121(3)°] and Cl(1)–Pt(1)–N(2) [88.69(14)°], as well as the N(1)–H(1)···N(11) hydrogen bond between the imine hydrogen and oxime nitrogen atoms [H(1)···N(11) is 2.14 Å; N(1)–H(1)···N(11) is 114°] which stabilizes the *E*-conformation of the iminoacyl ligands, agree with those reported for other bis-iminoacylated platinum(II) complexes.[8i,13]

The ^{1}H and ^{13}C NMR spectra of **6** show that the compound contains both an oxadiazoline and a nitrile ligand. In the ^{1}H NMR spectrum, the N–C*H*–N resonance is detected at 5.90 ppm, and, in the ^{13}C NMR spectrum, the N–*C*H–N resonance appears at 92.5 ppm, while the N≡*C* signal occurs at 112.8 ppm.

The *trans* mono-oxadiazoline complex *trans*-[$PtCl_2$(oxadiazoline-a)($NCCH_2CO_2Me$)] **6** reacts with a second equivalent of acetone oxime **2** (40 °C, 15 min) or cyclic nitrone $^-O^+N$=$CHCH_2CH_2CMe_2$ **8** (rt, 10 min), in dry CH_2Cl_2, to form the new mixed unsymmetric oxadiazoline-imine or bis-oxadiazoline complexes *trans*-[$PtCl_2$(oxadiazoline-a)(imine-a)] **9** (58% yield) or *trans*-[$PtCl_2$(oxadiazoline-a)(oxadiazoline-b)] **10** [oxadiazoline-b = N=$C(CH_2CO_2Me)ONC(H)CH_2CH_2CMe_2$] (82% yield), respectively (Scheme 2).

Their IR spectra do not exhibit any band which can be assigned to ν(N≡C), while ν(N=C) is observed at 1649 cm^{-1} for **9** and 1660 cm^{-1} for **10**.



Scheme 2

In the ^{1}H NMR spectrum of **10** the two expected signals of the N–C*H*–N protons are detected at 5.88 (singlet) and 5.47 (multiplet) ppm, whereas in the ^{13}C NMR spectrum, the N–*C*H–N resonances appear at 92.5 and 90.0 ppm, assigned to the groups at the oxadiazoline-a and oxadiazoline-b, respectively. The NMR results show that complex **10** was isolated without undergoing ring opening by N–O bond rupture of the oxadiazoline-b ligand. This contrasts with what we have previously observed in the synthesis of a symmetric bis(ketoimine) complex by reaction of **1** with 2 eq. of a cyclic nitrone (CH_2Cl_2, rt, 24 h);[11] the formation of the ketoimine compound is believed to proceed *via* an unstable 1,2,4-oxadiazoline complex which spontaneously rearranges to the ketoimine product.[11]

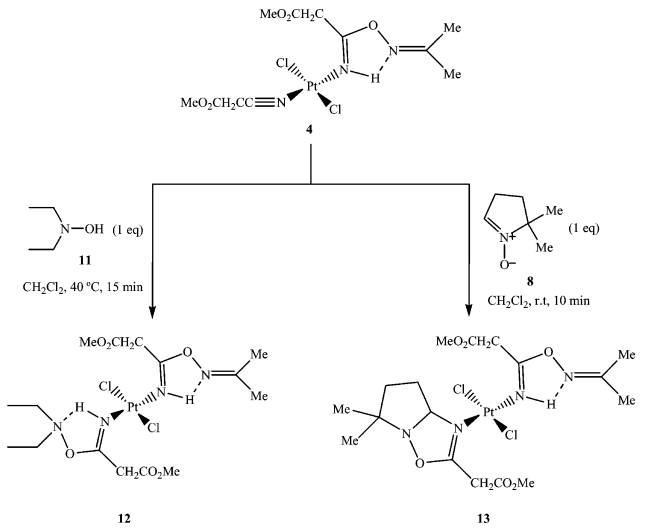
In order to obtain the desired mixed unsymmetric bis-oxadioazoline complex **10** without undergoing ring opening by N–O bond rupture, a close control of the time is required, *i.e.* the reaction should not be allowed to proceed longer than 10 min.

The *trans* mono-imine complex [$PtCl_2$(imine-a)($NCCH_2CO_2$-Me)] **4** is converted to the mixed unsymmetric complexes *trans*-[$PtCl_2$(imine-a)(imine-b)] **12** [imine-b = NH=$C(CH_2CO_2Me)$-$ONEt_2$] (77% yield) or *trans*-[$PtCl_2$(imine-a)(oxadiazoline-b)] **13** (81% yield) by reaction with a second equivalent of *N*,*N*-diethylhydroxylamine **11** or cyclic nitrone **8**, respectively (Scheme 3).

The IR spectra of these products do not exhibit any band which can be assigned to ν(N≡C), while ν(N=C) is observed in the usual range. Both ^{1}H and ^{13}C NMR spectra of complex **12** show that it contains two different iminoester ligands. The IR and NMR data of complex **13** also prove that the compound can be isolated without undergoing ring opening by N–O bond rupture (see Experimental).

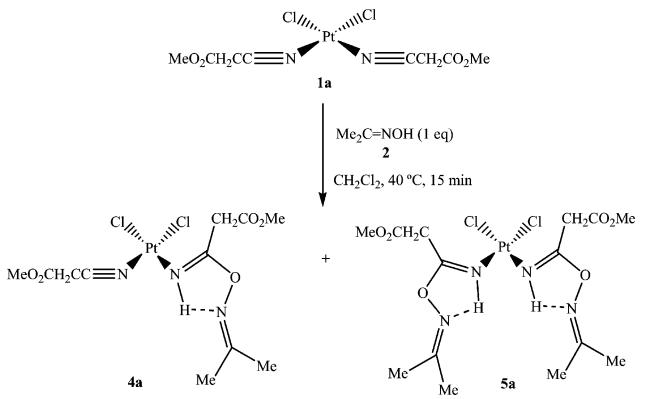
Reactions of *cis*-[$PtCl_2(NCCH_2CO_2Me)_2$] 1a

The complex *cis*-[$PtCl_2(NCCH_2CO_2Me)_2$] **1a** was obtained by replacement of the ligated EtCN in *cis*-[$PtCl_2(EtCN)_2$] by $NCCH_2CO_2Me$ under microwave irradiation (30 min, 110 °C). The complex **1a** has a lower solubility than its *trans*-isomer **1**



Scheme 3

in common solvents, and therefore its reaction mixture with the oxime $Me_2C{=}NOH$ **2** is a suspension with an excess of the latter reagent in solution. Nevertheless, the reaction affords the monoacylated complex *cis*-[$PtCl_2$(imine-a)($NCCH_2CO_2Me$)] **4a** as the major product (50% yield), the diacylated compound *cis*-[$PtCl_2$(imine-a)$_2$] **5a** being formed only in 15% yield (Scheme 4).

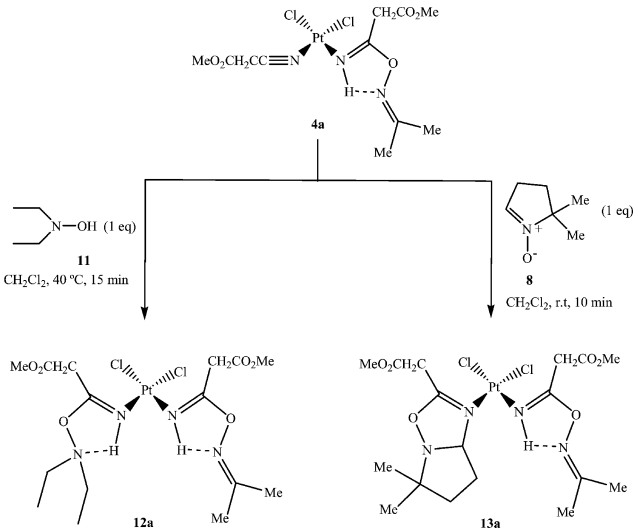


Scheme 4 (The mixed ligand complex **4a** is the major product.)

In the IR spectrum of compound **4a**, ν(N≡C) and ν(N=C) are identical to the corresponding values of the parent complex **1a** and the *cis* bis-imine complex **5a**, while the ^{13}C NMR spectrum shows the expected resonances. In the ^{195}Pt NMR spectrum, the signals of the *cis*-complexes **4a** and **5a** are shifted downfield with respect to those of the *trans*-complexes **4** and **5**. The shift is rather small ($\Delta\delta \sim 16$ ppm), as previously observed for other *cis*/*trans*-isomeric Pt^{II} complexes.[13,16,17]

Recently, it was reported that the benzonitrile complex *cis*-[$PtCl_2$(oxadiazoline)(PhCN)] does not lead to *cis*-[$PtCl_2$(oxadiazoline)$_2$] upon addition of a second equivalent of an acyclic nitrone to the ligated PhCN.[16] By repeating this experiment with a second equivalent of the more reactive cyclic nitrone **8** or *N*,*N*-diethylhydroxylamine **11**, we also observed that the starting material was recovered quantitatively, conceivably due to the weaker electrophilic character of the cyano-carbon of the aromatic nitrile in comparison with that of the ester-substituted $N{\equiv}CCH_2CO_2Me$ ligand in our complex **1a**. Prolonged reflux of the reaction mixture of the benzonitrile complex (40 °C, 10 d), in dry CH_2Cl_2, with an excess of cyclic nitrone or *N*,*N*-diethylhydroxylamine, led to decomposition of the starting material to form uncharacterised products.

Interestingly, the nitrile ligand in the *cis* mono-imine complex **4a** can undergo further nucleophilic addition by reaction with a second equivalent of *N*,*N*-diethylhydroxylamine **11** or cyclic nitrone **8**, to give the mixed unsymmetric *cis*-[$PtCl_2$(imine-a)(imine-b)] **12a** or *cis*-[$PtCl_2$(imine-a)(oxadiazoline-b)] **13a** complexes, respectively (Scheme 5). The IR spectra show ν(N=C) in the range 1644–1666 cm^{-1} and do not exhibit any band corresponding to ν(N≡C).

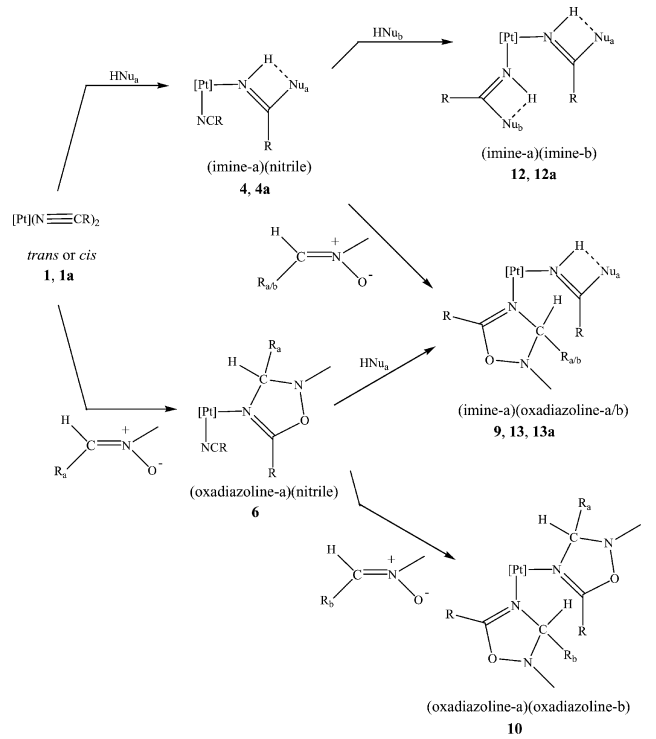


Scheme 5

In the ^{1}H NMR spectrum of **12a**, the two distinct resonances of the N*H* protons, detected at 8.20 and 8.55 ppm, are consistent with the two hydrogen bonds (one for each imine ligand) between the imine hydrogen and the oxime or the amine nitrogen atom, which stabilize the *E*-conformation of the iminoacyl ligands.

Concluding remarks

The results of this work show that a di(nitrile)-Pt^{II} complex of the type *trans*- or *cis*-[$PtCl_2(NCR)_2$] (R = electron-acceptor group) can act as a convenient starting material for the syntheses of a variety of mixed ligand complexes formed upon sequential addition of protic nucleophiles (such as an oxime or an hydroxylamine) and/or 1,3-dipoles (an acyclic or a cyclic nitrone) (see the overall Scheme 6). Thus, we can conclude that, in the mixed-ligand complexes [$PtCl_2$(imine-a)(NCR)] **4** or [$PtCl_2$(oxadiazoline-a)(NCR)] **6**, the nitrile ligand is less reactive towards the nucleophile or the 1,3-dipole than the nitrile ligands in the starting di(nitrile) complexes which imparts selectivity to the process, the di(imine) or the bis(oxadiazoline) complexes being formed in minor amounts. This is suggestive of stronger electron-donor character in the imine and oxadiazoline ligands in comparison with the nitrile, resulting in the ligated nitrile in complexes **4** or **6** having a weaker activation towards nucleophiles, than in the starting di(nitrile) complexes.



Scheme 6

Such behaviour results from a delicate balance of electronic effects. For instance, when the organic group of the nitrile ligand at Pt^{II} was an electron-donor (typically ethyl, in propionitrile), the lower electrophilic character of the nitrile prevented it from undergoing coupling with the oxime[8i] or the acyclic nitrone[10e] and the Pt^{II} products of addition or [2 + 3] cycloaddition were obtained indirectly, *via* reduction of the corresponding Pt^{IV} complexes.

The isolation of the mixed (imine)(nitrile) **4** or (oxadiazoline)(nitrile) **6** complexes allowed us to perform a further reaction, in a controlled way, with a second equivalent of the protic nucleophile or the 1,3-dipole (Scheme 6), providing easy and selective access to mixed unsymmetric complexes which can display heterocyclic ligands. As a final comment, the new mixed unsymmetric *cis*- and *trans*-platinum(II) complexes which possess an ester substituent are expected to be precursors for the synthesis of amino acids and lactams,[18] and eventually may also exhibit anticancer activity (akin to other platinum complexes with *N*-heterocyclic ligands);[19] these applications are currently being investigated by our group.

Experimental

Materials and instrumentation

Solvents were purchased from Aldrich and dried by usual procedures. The complexes *trans*-$[PtCl_2(NCCH_2CO_2Me)_2]$ **1**[11] and *cis*-$[PtCl_2(EtCN)_2]$[20] were prepared according to published methods, the latter by reaction of EtCN with aqueous tetrachloroplatinate and subsequent chromatographic purification of the product. The acyclic nitrone **3** was synthesized by condensation of 4-methylbenzaldehyde and *N*-methylhydroxylamine, according to the published method.[21] Methyl cyanoacetate, cyclic nitrone, *N*,*N*-diethylhydroxylamine and acetone oxime were obtained from commercial sources (Aldrich). C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H, ^{13}C and ^{195}Pt NMR spectra (in $CDCl_3$) were measured on a Varian Unity 300 spectrometer at ambient temperature. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. ^1H, ^{13}C chemical shifts (δ) are expressed in ppm relative to $Si(Me)_4$ and ^{195}Pt chemical shifts are relative to $Na_2[PtCl_6]$ (by using aqueous $K_2[PtCl_4]$, $\delta = -1630$ ppm, as a standard) with half-height line width in parentheses. *J* values are in Hz. Infrared spectra (4000–400 cm^{-1}) were recorded on Bio-Rad FTS 3000MX and Jasco FT/IR-430 instruments in KBr pellets and the wavenumbers are given in cm^{-1}. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W) which is fitted with a rotational system and IR temperature detector.

Preparation of the organonitrile platinum(II) complex *cis*-$[PtCl_2(NCCH_2CO_2Me)_2]$ 1a by focused microwave irradiation. Complex **1a** was obtained by replacement of the ligated EtCN in *cis*-$[PtCl_2(EtCN)_2]$ by $NCCH_2CO_2Me$, under focused microwave irradiation. A solution of the ethanonitrile complex *cis*-$[PtCl_2(EtCN)_2]$ (40 mg, 0.10 mmol) in dry CH_2Cl_2 (1 mL) and $NCCH_2CO_2Me$ (2 mL) was added to a cylindrical Pyrex tube which was then placed in a focused microwave reactor. After reaction (110 °C, 30 min), the mixture was allowed to cool down. The crude precipitated residue was filtered off, washed with diethyl ether and dried *in vacuo*.

Yield: 80%. IR (cm^{-1}): 2336 and 2339 (N≡C), 1738 (CO_2Me). FAB^+-MS, *m*/*z*: 464 $[M]^+$. The insolubility or instability of the complex in normal solvents did not allow NMR spectra to be obtained. Anal. Calcd for $C_8H_{10}N_2Cl_2O_4Pt$: C, 20.70; H, 2.17; N, 6.04. Found: C, 20.95; H, 2.34; N, 6.16.

Reaction of *trans*-$[PtCl_2(NCCH_2CO_2Me)_2]$ 1 or *cis*-$[PtCl_2(NCCH_2CO_2Me)_2]$ 1a with $Me_2C{=}NOH$ 2. A solution of **1** or **1a** (50.0 mg, 0.107 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the acetone oxime **2** (7.8 mg, 0.107 mmol) and the mixture was heated with stirring at 40 °C for 15 min, to form a bright yellow solution in the case of the *trans* isomer. However, the *cis* isomer was less soluble and the reaction mixture remained as a suspension. The progress of the reaction was monitored by TLC. After evaporation of the solvent *in vacuo* to dryness, the residue was washed with diethyl ether (5 × 3 mL portions) and then purified by column chromatography (SiO_2–CH_2Cl_2, Et_2O) followed by evaporation of the solvent *in vacuo* to give the corresponding *mono*- and *bis*-iminoacylated products **4** and **5** or **4a** and **5a**, respectively.

***trans*-$[PtCl_2\{NH{=}C(CH_2CO_2Me)ON{=}CMe_2\}(NCCH_2CO_2Me)]$ 4.** Yield: 51%. TLC on SiO_2: $R_f = 0.69$ (eluent CH_2Cl_2–Et_2O (2 : 1)). IR (cm^{-1}): 3496 (NH), 2338 (N≡C), 1748 (CO_2Me), 1647 and 1666 (C=N), 1179 (C–O). ^1H NMR, δ: 2.03 and 2.05 (two s, 3H each, $=CMe_2$), 3.79 and 3.86 (two s, 3H each, MeO), 3.90 and 4.18 (two s, 2H each, CH_2), 8.17 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ: 18.1 and 22.4 (Me groups), 26.8 and 40.2 (CH_2), 53.5 and 54.9 (MeO), 112.4 (N≡C), 161.8 and 166.6 (CO_2Me), 167.0 ($=CMe_2$), 168.8 (C(O)=N). ^{195}Pt NMR, δ: −2250 (806 Hz).

FAB$^+$-MS, *m/z*: 537 [M]$^+$. Anal. Calcd for $C_{11}H_{17}N_3Cl_2O_5Pt$: C, 24.59; H, 3.19; N, 7.82. Found: C, 24.81; H, 3.04; N, 8.04.

***trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}$_2$] 5.** Yield: 17%. TLC on SiO_2: $R_f = 0.55$ (eluent CH_2Cl_2–Et_2O (10 : 1)). All the spectroscopic, FAB-MS and elemental analytical data are in agreement with those reported previously.[13]

***cis*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}(NCCH$_2$CO$_2$Me)] 4a.** Yield: 50%. TLC on SiO_2: $R_f = 0.58$ (eluent CH_2Cl_2–Et_2O (2 : 1)). IR (cm^{-1}): 3448 (NH), 2339 (N≡C), 1748 (CO_2Me), 1647 and 1667 (C=N), 1179 (C–O). ^{1}H NMR, δ: 2.04 and 2.06 (two s, 3H each, =CMe_2), 3.79 and 3.86 (two s, 3H each, MeO), 3.95 and 4.18 (two s, 2H each, CH_2), 8.15 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ: 18.0 and 22.4 (Me groups), 26.8 and 40.2 (CH_2), 53.5 and 54.9 (MeO), 112.4 (N≡C), 161.9 and 166.6 (CO_2Me), 167.0 (=CMe_2), 168.7 (C(O)=N). ^{195}Pt NMR, δ: −2234 (901 Hz). FAB$^+$-MS, *m/z*: 537 [M]$^+$. Anal. Calcd for $C_{11}H_{17}N_3Cl_2O_5Pt$: C, 24.59; H, 3.19; N, 7.82. Found: C, 24.62; H, 3.04; N, 8.01.

***cis*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}$_2$] 5a.** Yield: 15%. TLC on SiO_2: $R_f = 0.77$ (eluent CH_2Cl_2–Et_2O (2 : 1)). IR (cm^{-1}): 3436 (NH), 1746 (CO_2Me), 1646 and 1667 (C=N). ^{1}H NMR, δ: 2.03 and 2.05 (two s, 3H each, =CMe_2), 3.80 (s, 3H, MeO), 4.20 (s, 2H, CH_2), 8.18 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ: 17.9 and 22.4 (Me groups), 40.0 (CH_2), 53.4 (MeO), 166.3 (CO_2Me), 167.1 (=CMe_2), 167.8 (C(O)=N). ^{195}Pt NMR, δ: −2064 (868 Hz). FAB$^+$-MS, *m/z*: 611 [M + 1]$^+$. Anal. Calcd for $C_{14}H_{24}N_4Cl_2O_6Pt$: C, 27.55; H, 3.96; N, 9.18. Found: C, 27.73; H, 4.02; N, 8.97.

Reaction of *trans*-[PtCl$_2$(NCCH$_2$CO$_2$Me)$_2$] 1 with acyclic nitrone $^-$O$^+$N(Me)=C(H)(C$_6$H$_4$Me-4) 3. A solution of **1** (50.0 mg, 0.107 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the acyclic nitrone **3** (15.9 mg, 0.107 mmol). The mixture was heated with stirring at 40 °C for 8 h and a bright yellow solution was formed. The progress of the reaction was monitored by TLC. After evaporation of the solvent to dryness *in vacuo*, the residue was purified by column chromatography (SiO_2–CH_2Cl_2, Et_2O) followed by evaporation of the solvent *in vacuo* to give the final yellow powders of the **6** and **7** products.

***trans*-[PtCl$_2${N=C(CH$_2$CO$_2$Me)ON(Me)C(H)(C$_6$H$_4$Me-4)}(NCCH$_2$CO$_2$Me)] 6.** Yield: 52%. TLC on SiO_2: $R_f = 0.58$ (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 3474 (NH), 2336 (N≡C), 1750 (CO_2Me), 1660 (C=N), 1176 (C–O). ^{1}H NMR, δ: 2.36 (s, 3H, CH_3Ph), 2.95 (s, 3H, CH_3N), 3.81 and 3.83 (two s, 3H each, MeO), 3.88 (s, 2H, CH_2), 3.98 (d, J_{HH} 17.1 Hz, 1H, CH_2), 4.44 (d, J_{HH} 17.1 Hz, 1H, CH_2), 5.90 (s, 1H, N–C*H*–N), 7.24 (d, J_{HH} 7.8 Hz, 2H, C$H_{aromatic}$), 7.49 (d, J_{HH} 7.8 Hz, 2H, C$H_{aromatic}$). ^{13}C{^{1}H} NMR, δ: 22.0 (CH_3Ph), 26.7 (CH_2), 34.2 (CH_3N), 47.3 (CH_2), 53.7 and 54.7 (MeO), 92.5 (N–*C*H–N), 112.8 (N≡C), 128.4, 130.1, 132.9 and 140.3 ($C_{aromatic}$), 161.9 and 165.3 (CO_2Me), 165.8 (C(O)=N). ^{195}Pt NMR, δ: −2329 (886 Hz). FAB$^+$-MS, *m/z*: 613 [M]$^+$. Anal. Calcd for $C_{17}H_{21}N_3Cl_2O_5Pt$: C, 33.29; H, 3.45; N, 6.85. Found: C, 33.24; H, 3.22; N, 6.76.

***trans*-[PtCl$_2${N=C(CH$_2$CO$_2$Me)ON(Me)C(H)(C$_6$H$_4$Me-4)}$_2$] 7.** (two diastereoisomers 1 : 1). Yield: 25%. TLC on SiO_2: $R_f = 0.64$ (eluent CH_2Cl_2–Et_2O (20 : 1)). All the spectroscopic, FAB-MS and elemental analytical data are in agreement with those reported previously.[12]

Reaction of *trans*-[PtCl$_2${N=C(CH$_2$CO$_2$Me)ON(Me)C(H)(C$_6$H$_4$Me-4)}(NCCH$_2$CO$_2$Me)] 6, *trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}(NCCH$_2$CO$_2$Me)] 4 or *cis*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}(NCCH$_2$CO$_2$Me)] 4a with acetone oxime 2 or *N*,*N*-diethylhydroxylamine 11. A solution of **6** (50.0 mg, 0.081 mmol), **4** or **4a** (50.0 mg, 0.093 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the acetone oxime **2** (1 eq.), or *N*,*N*-diethylhydroxylamine **11** (1 eq.). The mixture was stirred at 40 °C for 15 min and a bright yellow solution formed. The progress of the reaction was monitored by TLC. After evaporation of the solvent *in vacuo* to dryness, the residue was washed with diethyl ether (5 × 3 mL portions) and then purified by column chromatography (SiO_2–CH_2Cl_2, Et_2O) followed by evaporation of the solvent *in vacuo* to give the final yellow powders of the **9**, **12** or **12a** products, respectively.

***trans*-[PtCl$_2${N=C(CH$_2$CO$_2$Me)ON(Me)C(H)(C$_6$H$_4$Me-4)}$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}] 9.** Yield: 58%. TLC on SiO_2: $R_f = 0.55$ (eluent CH_2Cl_2–Et_2O (20 : 1)). IR (cm^{-1}): 3284 (NH), 1749 (CO_2Me), 1649 (C=N), 1176 (C–O). ^{1}H NMR, δ: 1.99 and 2.01 (two s, 3H each, =CMe_2), 2.37 (s, 3H, CH_3Ph), 2.95 (s, 3H, CH_3N), 3.74 and 3.85 (two s, 3H each, MeO), 3.97–4.51 (m, 4H, CH_2), 5.91 (s, 1H, N–C*H*–N), 7.24 (d, J_{HH} 8.1 Hz, 2H, C$H_{aromatic}$), 7.54 (d, J_{HH} 8.1 Hz, 2H, C$H_{aromatic}$), 8.05 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ: 17.9 and 22.3 (Me groups), 22.0 (CH_3Ph), 34.0 (CH_3N), 40.0 and 47.3 (CH_2), 53.3 and 53.6 (MeO), 92.6 (N–*C*H–N), 128.4, 129.9, 133.6 and 139.9 ($C_{aromatic}$), 164.4 and 166.2 (CO_2Me), 166.4 (=CMe_2), 166.9 and 167.8 (C(O)=N). ^{195}Pt NMR, δ: −2164 (806 Hz). FAB$^+$-MS, *m/z*: 686 [M]$^+$. Anal. Calcd for $C_{20}H_{28}N_4O_6Cl_2Pt$: C, 34.99; H, 4.11; N, 8.16. Found: C, 34.87; H, 4.29; N, 8.28.

***trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}{NH=C(CH$_2$CO$_2$Me)ONEt$_2$}] 12.** Yield: 77%. TLC on SiO_2: $R_f = 0.57$ (eluent CH_2Cl_2–Et_2O (20 : 1)). IR (cm^{-1}): 3213 (NH), 1747 (CO_2Me), 1666 (C=N), 1175 (C–O). ^{1}H NMR, δ: 1.10 (t, J_{HH} 7.5 Hz, 3H each, CH_3CH_2), 1.98 and 2.01 (two s, 3H each, =CMe_2), 2.92 (q, J_{HH} 7.5 Hz, 2H each, CH_3CH_2), 3.75 and 3.76 (two s, 3H each, MeO), 4.06 and 4.15 (two s, 2H each, CH_2), 8.16 and 8.5 (two s, br, 1H each, NH). ^{13}C{^{1}H} NMR, δ: 12.2 (CH_3CH_2), 17.9 and 22.4 (Me groups), 39.2 and 39.9 (CH_2), 53.2 and 53.3 (MeO), 53.6 (CH_3CH_2), 166.2 and 167.0 (CO_2Me), 167.2 (=CMe_2), 167.7 and 169.7 (C(O)=N). ^{195}Pt NMR, δ: −2069 (806 Hz). FAB$^+$-MS, *m/z*: 626 [M]$^+$. Anal. Calcd for $C_{15}H_{28}N_4Cl_2O_6Pt$: C, 28.76; H, 4.50; N, 8.94. Found: C, 28.81; H, 4.42; N, 8.87.

***cis*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}{NH=C(CH$_2$CO$_2$Me)ONEt$_2$}] 12a.** Yield: 70%. TLC on SiO_2: $R_f = 0.30$ (eluent CH_2Cl_2–Et_2O (20 : 1)). IR (cm^{-1}): 3437 (NH), 1745 (CO_2Me), 1665 and 1644 (C=N), 1175 (C–O). ^{1}H NMR, δ: 1.15 (t, J_{HH} 7.2 Hz, 3H each, CH_3CH_2), 2.02 and 2.05 (two s, 3H each, =CMe_2), 2.96 (q, J_{HH} 7.2 Hz, 2H each, CH_3CH_2), 3.78 and 3.80 (two s, 3H each, MeO), 4.10 and 4.20 (two s, 2H each, CH_2), 8.20 and 8.55 (two s, br, 1H each, NH). ^{13}C{^{1}H} NMR, δ: 12.2 (CH_3CH_2), 17.9 and 22.5 (Me groups), 39.3 and 40.0 (CH_2), 53.3 (MeO), 53.7 (CH_3CH_2), 166.2 (CO_2Me), 167.2 (=CMe_2), 167.8 and 169.6 (C(O)=N). ^{195}Pt NMR, δ: −2052 (874 Hz). FAB$^+$-MS, *m/z*: 626 [M]$^+$. Anal. Calcd for $C_{15}H_{28}N_4Cl_2O_6Pt$: C, 28.76; H, 4.50; N, 8.94. Found: C, 28.91; H, 4.22; N, 8.75.

Reaction of *trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}-(NCCH$_2$CO$_2$Me)] 4, *cis*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}-(NCCH$_2$CO$_2$Me)] 4a or *trans*-[PtCl$_2${N=C(CH$_2$CO$_2$Me)ON-(Me)C(H)(C$_6$H$_4$Me-4)}(NCCH$_2$CO$_2$Me)] 6 with cyclic nitrone $^-$O$^+$N=CHCH$_2$CH$_2$CMe$_2$ 8. A solution of **4** or **4a** (50.0 mg, 0.093 mmol) or **6** (50.0 mg, 0.081 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the cyclic nitrone **8** (1 eq). The mixture was stirred at room temperature for 10 min and a bright yellow solution formed. The progress of the reaction was monitored by TLC. After evaporation of the solvent to dryness *in vacuo*, the residue was purified by column chromatography (SiO_2–CH_2Cl_2, Et_2O) followed by evaporation of the solvent *in vacuo* to give the final yellow products **13**, **13a** or **10**, respectively.

***trans*-PtCl$_2${N=C(CH$_2$CO$_2$Me)ONC(H)(CH$_2$CH$_2$CMe$_2$)} {N=C(CH$_2$CO$_2$Me)ON(Me)C(H)(C$_6$H$_4$Me-4)} 10. (two diastereoisomers 1 : 1).** Yield: 82%. TLC on SiO_2: $R_f = 0.50$ (eluent CH_2Cl_2–Et_2O (20 : 1)). IR (cm^{-1}): 1750 (CO_2Me), 1660 (C=N), 1171 (C–O). ^{1}H NMR, δ: 1.11 and 1.28 (two s, 3H each, Me), 1.58–1.77 (m, 2H, CH_2), 2.18–2.25 (m, 1H, CH_2), 2.38 (s, 3H, CH_3Ph), 2.68–2.73 (m, 1H, CH_2), 2.96 (s, 3H, CH_3N), 3.74 and 3.85 (two s, 3H each, MeO), 3.79–4.04 (m, 3H, CH_2CO$_2$Me), 4.33–4.43 (m, 1H, CH_2CO$_2$Me), 5.47 (m, 1H, N–CH–N, oxadiazoline-b), 5.88 (s, 1H, N–CH-N, oxadiazoline-a), 7.25 (d, J_{HH} 8.4 Hz, 2H, C$H_{aromatic}$), 7.56 (d, J_{HH} 8.4 Hz, 2H, C$H_{aromatic}$). ^{13}C{^{1}H} NMR, δ: 22.0 (CH_3Ph), 23.3 and 27.6 (Me groups), 30.8, 30.9 and 34.0 (CH_2), 34.2 (CH_3N), 47.1 (CH_2), 53.5 and 53.7 (MeO), 71.5 (Me$_2$C-N), 90.0 (N–CH–N, oxadiazoline-b), 92.5 (N–CH-N, oxadiazoline-a), 128.6, 129.9, 133.7 and 140.1 (C$_{aromatic}$), 163.8 and 164.0 (CO_2Me), 165.8 and 166.1 (C(O)=N). ^{195}Pt NMR, δ: −2247 (806 Hz). FAB$^+$-MS, m/z: 726 [M]$^+$. Anal. Calcd for $C_{23}H_{32}N_4O_6Cl_2Pt$: C, 38.02; H, 4.44; N, 7.71. Found: C, 38.25; H, 4.51; N, 7.79.

***trans*-PtCl$_2${N=C(CH$_2$CO$_2$Me)ONC(H)(CH$_2$CH$_2$CMe$_2$)} {NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}] 13.** Yield: 81%. TLC on SiO_2: $R_f = 0.54$ (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 1749 (CO_2Me), 1657 and 1665 (C=N), 1170 (C–O). ^{1}H NMR, δ: 1.13 and 1.31 (two s, 3H each, Me), 1.61–1.83 (m, 2H, CH_2), 2.02 and 2.04 (two s, 3H each, =CMe$_2$), 2.28–2.36 (m, 1H, CH_2), 2.89–2.94 (m, 1H, CH_2), 3.78 and 3.80 (two s, 3H each, MeO), 3.93 (d, J_{HH} 16.5 Hz, 1H, CH_2), 4.12 (s, 2H, CH_2), 4.25 (d, J_{HH} 16.5 Hz, 1H, CH_2), 5.56 (m, 1H, N–CH–N), 8.15 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ: 17.9 and 22.4 (=CMe_2), 23.4 and 27.6 (Me groups), 31.1, 34.1, 40.0 and 40.1 (CH_2), 53.4 and 53.5 (MeO), 71.5 (Me$_2$C-N), 90.2 (N–CH–N), 163.9 and 166.1 (CO_2Me), 166.4 (=CMe_2), 167.0 and 167.9 (C(O)=N). ^{195}Pt NMR, δ: −2166 (765 Hz). FAB$^+$-MS, m/z: 650 [M]$^+$. Anal. Calcd for $C_{17}H_{28}N_4O_6Cl_2Pt$: C, 31.39; H, 4.34; N, 8.61. Found: C, 31.17; H, 4.23; N, 8.59.

***cis*-PtCl$_2${N=C(CH$_2$CO$_2$Me)ONC(H)(CH$_2$CH$_2$CMe$_2$)} {NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}] 13a.** Yield: 80%. TLC on SiO_2: $R_f = 0.73$ (eluent CH_2Cl_2–Et_2O (5 : 1)). IR (cm^{-1}): 1746 (CO_2Me), 1647 and 1666 (C=N). ^{1}H NMR, δ: 1.13 and 1.30 (two s, 3H each, Me), 1.60–1.84 (m, 2H, CH_2), 2.01 and 2.03 (two s, 3H each, =CMe$_2$), 2.29–2.36 (m, 1H, CH_2), 2.90–2.94 (m, 1H, CH_2), 3.78 and 3.79 (two s, 3H each, MeO), 3.92 (d, J_{HH} 17.1 Hz, 1H, CH_2), 4.11 (s, 2H, CH_2), 4.24 (d, J_{HH} 17.1 Hz, 1H, CH_2), 5.55 (m, 1H, N–CH–N), 8.13 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ: 17.9 and 22.3 (=CMe_2), 23.3 and 27.5 (Me groups), 31.1, 34.2, 39.9 and 40.0 (CH_2), 53.4 and 53.5 (MeO), 71.5 (Me$_2$C-N), 90.0 (N–CH–N), 163.8 and 166.1 (CO_2Me), 166.5 (=CMe_2), 167.0 and 167.8 (C(O)=N). ^{195}Pt NMR, δ: −2151 (785 Hz). FAB$^+$-MS, m/z: 650 [M]$^+$. Anal. Calcd for $C_{17}H_{28}N_4O_6Cl_2Pt$: C, 31.39; H, 4.34; N, 8.61. Found: C, 31.42; H, 4.03; N, 8.85.

X-Ray crystallographic data for 4

Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation. Data was collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structure was solved by direct methods by using the SHELXS-97 package[22] and refined with SHELXL-97[23] with the WinGX graphical user interface.[24] All hydrogens were inserted in calculated positions except H1, H21A and H21B which were located. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave $R_1 = 0.0283$ [$I > 2\sigma(I)$; $R_1 = 0.0345$ (all data)]. The maximum and minimum peaks in the final difference electron density map are of 1.449 and −1.452 e Å^{-3}, located around the platinum atom.‡

Acknowledgements

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT) and its POCI 2010 program (FEDER funded) (Portugal). J. L. expresses gratitude to FCT for a post-doc fellowship (grant SFRH/BPD/20927/2004).

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