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2-Amino-2-oxazoline and trialkylisourea Pt(II) complexes derived from organocyanamides

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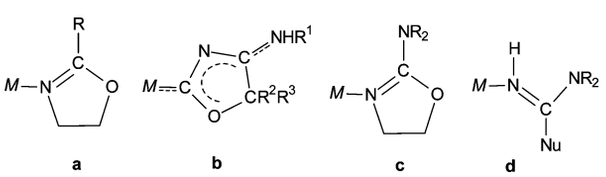
In the di(organocyanamide) complexes *trans*-$[PtCl_2(NCNR_2)_2]$ (R = Me **1a**, Et **1b**), prepared by reaction of $PtCl_2$ with the appropriate $NCNR_2$, the cyanamide ligands, activated by coordination, undergo an unprecedented nucleophilic addition, at room temperature, of an haloalcohol ($ClCH_2CH_2OH$/$LiBu^n$) or of an alcohol (MeOH) to give the corresponding 2-amino-2-oxazoline *cis*-$[PtCl_2\{\overline{N{=}C(OCH_2CH_2)}NR_2\}_2]$ (R = Me **2a**, Et **2b**) or trialkylisourea *trans*-$[PtCl_2\{NH{=}C(OMe)NR_2\}_2]$ (R = Me **3a**, Et **3b**) complexes. The X-ray crystal structure of **2b** is also reported, indicating a π-bond delocalization along the N⋯C⋯N group of the aminooxazoline ligands.

Introduction

The synthetic relevance of oxazolines is a matter of current and growing interest in both organic[1–4] and coordination[5–22] chemistries, namely in asymmetric synthesis and other metal-promoted reactions.[2,4] In particular, complexes of Pt(II) with N-metal bonded 2-oxazolines (**a**; R = alkyl, aryl) derived from organonitriles are known.[23–27]

Complexes with amino-functionalized oxazolines have been derived from a three-component cycloaddition of an isocyanide (CNR^1) and a ketone ($R^2R^3C{=}O$) to ligated hydrogen isocyanide (*M*-CNH) to form a carbenoid C2-metal coordinated 4-amino-oxazoline (**b**) in various transition metal complexes $[M\{CNC(NHR^1)C(R^2)(R^3)O\}]$.[28–32] In spite of the interest of the presence of the additional amino-group for subsequent reactivity, this route has not been explored further, conceivably on account of the difficulties normally associated with the synthesis of a well-defined CNH complex and the use of an isocyanide as the amino group source.



Organocyanamides, $N{\equiv}C{-}NR_2$, can be considered as amino-functionalized nitriles, are commercially available and easily handled compounds, and thus constitute promising starting materials for the synthesis of complexes with cyano-derived organonitrogen ligands containing the amino function, a possibility that has not been adequately explored in coordination chemistry. Therefore, we have attempted their application as convenient precursors for the preparation of amino-functionalized heterocyclic or non-heterocyclic ligands (*i.e.* the oxazoline **c** and imine **d**, repectively) by activating, upon coordination, the cyano-group towards addition of a suitable nucleophile which could either behave as the source of the CH_2CH_2O group for the oxazoline ring (in **c**) or act as a protic nucleophile (HNu, in **d**), in both cases with preservation of the amino-function.

We now report the results of these attempts by showing that organocyanamides at a Pt(II) centre react under mild conditions with 2-chloroethanol ($ClCH_2CH_2OH$) or with methanol, in the presence of $LiBu^n$ or KOH, respectively, to afford complexes with the ligated 2-amino-2-oxazoline (or *N*,*N*-dialkyl-4,5-dihydro-1,3-oxazol-2-amine) (**c**) or trialkylisourea (or *N*,*N*-dialkylimidocarbamate) (**d**, Nu = OMe). Of particular synthetic significance is the easy formation, in our study, of the 2-amino-2-oxazoline species, in view of the therapeutic interest of these compounds and the usual requirement[4] of drastic conditions (relatively high temperatures) or of elaborate multistep procedures for their synthesis in pure organic chemistry.

This work also aims to provide a contribution towards the development of the coordination chemistry of cyanamides, a field that remains little explored (in contrast with the developed chemistry of organonitriles which has been reviewed by us[33–35]) in spite of the biological and synthetic interest[36–47] of such species. The previously reported reactions of cyanamide ligands include a dimetal (Ag^I/Pt^{II} or Cu^{II}/Pt^{II}) promoted nucleophilic addition of an oxime to organocyanamides[48] and the addition of an alcohol to cyanoguanidine[49] to form a five- or six-membered azametallacycle, respectively, a β-protonation at the unsaturated C atom to yield an amidoazavinylidene species,[50] dehydrogenation of $NCNH_2$ followed by electrophilic addition,[51,52] deprotonation or deamination (of cyanoguanidine),[53] metathesis with a metal–metal triple bond[54] or insertion into a metal–carbon triple bond.[55–59]

We have now achieved the unprecedented addition of an haloalcohol (cycloaddition) and of an alcohol to organocyanamide ligands to produce oxazoline or isourea derivatives, respectively. In contrast with the above dimetal-promoted coupling with oximes[48] to produce azametallacycles, in the current study the presence of a second activating metal is not required.

Results and discussion

Synthesis and reactivity

The di(organocyanamide) complexes *trans*-$[PtCl_2(NCNR_2)_2]$ (R = Me **1a**, Et **1b**) were obtained in high yield (*ca.* 90%) by heating $PtCl_2$ in the neat liquid organocyanamide (reaction 1,

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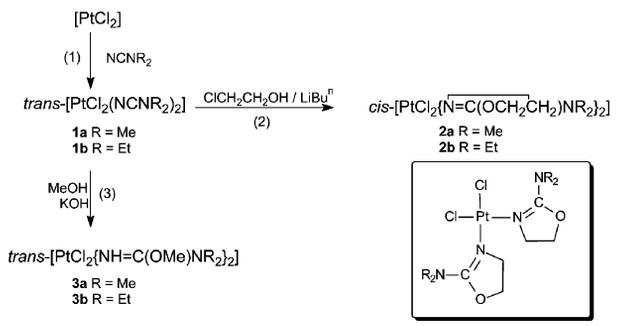
Scheme 1), following a procedure similar to that reported[60] for the related organonitrile complexes *cis*/*trans*-$[PtCl_2(NCR)_2]$ (R = Me or Ph). However, in the present case of organocyanamides, only one isomeric form was obtained (see below). The complexes were isolated as yellow solids with IR spectra (Nujol mulls) exhibiting ν(N≡C) as a very strong band at 2292 (**1a**) or 2277 (**1b**) cm^{-1} and ν(PtCl) as a medium/strong one at 347 (**1a**) or 346 (**1b**) cm^{-1}. The detection of single ν(N≡C) and ν(PtCl) bands suggests the *trans* geometry of the complexes that is also corroborated by the values of $^2J_{CPt}$ [263.3 (**1a**) or 267.4 (**1b**) Hz for the N*C*NR_2 ^{13}C NMR resonance observed at δ 115.32 (**1a**) or 114.08 (**1b**)] which are close to those reported[60] for the related organonitrile complexes *trans*-$[PtCl_2(NCR)_2]$ (R = alkyl or aryl) (273–298 Hz) and higher than those observed for the *cis* isomers (218–234 Hz range).



Scheme 1

The ν(N≡C) frequency is noticeably higher [by 92 (**1a**) or 82 (**1b**) cm^{-1}] than that observed in the free organocyanamide (liquid film, 2200 or 2195 cm^{-1}, respectively), indicating that the ligand acts as an effective electron donor with η^1-coordination *via* the cyano group.[61,62] This coordination mode has also been observed[48,49,63] in other Pt(II) complexes. The ν(NC) coordination shift is even higher than that (60–55 cm^{-1}) for *cis*-$[Pt(NCNR_2)_2(PPh_3)_2][BF_4]_2$ which can undergo[48] nucleophilic addition of oximes in the presence of Ag(I) or Cu(II) promoters.

In the complexes *trans*-$[PtCl_2(NCNR_2)_2]$ (**1a** and **1b**) the organocyanamide is activated towards nucleophilic attack by 2-chloroethanol in the presence of $LiBu^n$ or by methanol in the presence of base (KOH) to afford the corresponding 2-amino-2-oxazoline *cis*-$[PtCl_2\{\overline{N=C(OCH_2CH_2)}NR_2\}_2]$ (R = Me **2a**, Et **2b**) (reaction 2, Scheme 1) or trialkylisourea (or *N*,*N*-dialkylimidocarbamate) *trans*-$[PtCl_2\{NH=C(OMe)NR_2\}_2]$ (R = Me **3a**, Et **3b**) (reaction 3, Scheme 1) complexes. The reactions proceed smoothly at room temperature, being sufficient, for the latter, an amount of KOH (base: complex = 1 : 2.5) significantly lower than the stoichiometric one, although not so low as the catalytic amount (1 : 30) quoted[64] in the case of the organonitrile complexes *cis*- and *trans*-$[PtCl_2(NCPh)_2]$, consistent with the weaker electrophilic character of organocyanamide ligands compared with organonitriles (see below).

Although nucleophilic addition reactions are well documented[33,34] for nitrile ligands, they have not yet been explored for cyanamides which are expected to show a lower electrophilicity in view of the electron releasing character of the amido-group to the reactive cyano-centre. In particular the addition of an oxime $HON=CR^1R^2$ (R^1R^2 = Me_2 or C_4H_8) to the ligated cyanamide in *cis*-$[Pt(NCNR_2)_2(PPh_3)_2][BF_4]_2$ (R = Me or Et) to give the azametallacyclic products *cis*-$[Pt\{HN=C(ON=CR^1R^2)NR_2\}(PPh_3)_2][BF_4]_2$[48] requires the presence of a promoter Ag(I) or Cu(II) ion as an effective Lewis acid towards the amido-group of the organocyanamide with a resulting enhancement of the electrophilicity of the reactive cyano-moiety.

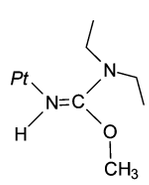
In the present study (which constitutes the first reported example of activation of cyanamides, upon coordination, towards nucleophilic addition of haloalcohols or alcohols), the remarkable activation, by the binding Pt(II) centre, undergone by the organocyanamides is sufficient to induce the nucleophilic attack by those nucleophiles, without requiring the above combined promoting effect of electron-withdrawal from the amido-end. Nevertheless, the presence of base is required for the reaction to occur, suggesting that alkoxide, rather than the alcohol, is behaving as the nucleophile.

The formation of the 2-oxazoline complexes **2** is believed to proceed *via* nucleophilic addition to the cyanamide ligand of the alkoxide $^-OCH_2CH_2Cl$ generated *in situ* by deprotonation of 2-chloroethanol with $LiBu^n$, followed by intramolecular nucleophilic attack of the imino nitrogen of the intermediate to the chlorinated methylene carbon which results in ring closure upon heterolytic C–Cl bond rupture (elimination of LiCl).

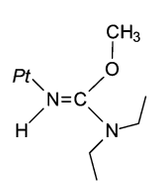
The complexes have been characterized by IR and multinuclear NMR spectroscopies, elemental analyses, FAB-MS and, in the case of **2b**, also by single crystal X-ray diffraction. Complexes **2** and **3** have been isolated as white or yellow solids, respectively, with IR spectra (KBr pellets) exhibiting a strong band at 1600–1640 cm^{-1} assigned to ν(N=C), whereas ν(Pt–Cl) is observed, for the latter complexes (*trans*), as a single and strong band at 320 (**3a**) or 305 (**3b**) cm^{-1} and, for the former compounds (**2a** and **2b**, both *cis*), as two medium intensity bands at 315 and 325 cm^{-1}. For the imidocarbamate complexes **3**, ν(NH) occurs as a strong and broad band at *ca.* 3300 cm^{-1}. Such features are comparable with those reported for some iminoester[33,34,42,65,66] or 2-oxazoline[23] platinum complexes. The strong band at *ca.* 1060 cm^{-1} exhibited by complexes **3** is tentatively assigned to ν(C–O–C) which, for some 1-amidino-*O*-alkylurea complexes of Cu(II) or Ni(II), $[ML_2]Cl_2$ [M = Cu, Ni; L = NH=C(OR)NHC(=NH)NH_2 (R = alkyl)], is reported[42] at *ca.* 1200 cm^{-1}.

The 2-oxazoline complexes **2** exist only in one isomeric form as shown by the single set of observed NMR resonances, *e.g.* for the N=*C*, O*C*H_2 and N*C*H_2 carbons in the ^{13}C–{^1H} NMR spectra (δ 160.88, 67.20 and 55.98, respectively, for **2b**), for the *C*H_3 protons [δ 3.11 (**2a**) or 1.28 (triplet, $^3J_{HH}$ = 7.1 Hz, **2b**)] in the ^1H NMR spectra, and for the metal nucleus in the ^{195}Pt NMR spectrum (δ −1879.1, **2b**).

In complexes **3** the isourea (or imidocarbamate) ligands appear to exist in the *E* and *Z* configurations, as indicated by the following evidence. Pairs of resonances are commonly observed in both the ^1H and the ^{13}C NMR spectra. Hence, *e.g.*, in the ^1H NMR spectra of **3a** and **3b** the imido-proton *H*N=C signals appear at δ *ca.* 5.7 and 4.1, whereas in the ^{13}C–{^1H} NMR spectrum of **3b** the HN=*C*(OCH_3) and HN=C(O*C*H_3) resonances are observed at δ 163.80, 163.08 and 59.20, 58.28, respectively. Moreover, both *E* and *Z* configurations in **3b** are supported by the observation of the nuclear Overhauser effect (NOE) between one of the N*H* resonances (δ 4.12) and the O*C*H_3 resonance (*E* configuration, **e**) and between the other N*H* resonance (δ 5.60) and that of the ethyl protons of the diethylamino group (*Z* configuration, **f**). Two sets of resonances assigned to the *E* and *Z* isomeric pair have been reported for iminoester[64,65,67,68] or amidine[69] complexes of platinum, derived from the addition of alcohols or amines, respectively, to nitrile complexes.



e (*E*)



f (*Z*)

The *E* isomers would be the expected kinetically favoured products of alcohol (in the protic ROH form) addition on the basis of previous mechanistic studies[70] on the nucleophilic

attack of alcohols to coordinated nitriles, indicating that the reaction proceeds *via* a four- or six-membered cyclic transition state (the latter involving two alcohol molecules) formed by *cis* O–H addition of the alcohol to the cyano group. However, the presence of base in our case, with formation of alkoxide (RO^-) from the alcohol, conceivably leads to a different mechanism (see above). The conversion of the *Z* into the *E* isomers was observed[68] for the nitrile derived iminoester complexes *cis*- and *trans*-$[PtCl_2\{N(H)=C(OR')R\}_2]$ (R = Me, Et, Ph; R′ = Me).

In the case of the amidine complexes *cis*- and *trans*-$[PtCl_2\{N(H)=C(NR^1R^2)Me\}_2]$ (R^1, R^2 = alkyl), derived from addition of a secondary aliphatic amine R^1R^2NH to *cis*- and *trans*-$[PtCl_2(NCMe)_2]$, only the *E* isomer is obtained, but the use of a primary amine, RNH_2 (R = alkyl), as the nucleophile yields exclusively the *Z* configuration which is then stabilized by a hydrogen bond between a chloride ligand and the amino proton the NHR group forming a six-membered ring.[69] In the complexes **3a** and **3b** of the present study, no such type of hydrogen bond formation is possible for either isomer.

The FAB-MS spectra of complexes **2** exhibit their molecular ions with the expected isotopic pattern, as well as the oxazoline (protonated form) peak (the most intense one), whereas in the case of compounds **3** the molecular ions were not unambiguously observed and the peak with the highest intensity corresponds to the trialkylisourea (protonated form).

In the synthesis of the 2-oxazoline complex **2b**, another product was isolated in very low yield from the mother liquor. It was tentatively formulated as the trialkylisourea complex *trans*-$[PtCl_2\{NH=C(OCH_2CH_2Cl)NEt_2\}_2]$ **4** on the basis of the similarity of properties with those of complexes **3**: IR spectroscopic bands (KBr pellet) at 3280 and 1611 cm^{-1}, assigned to ν(NH) and ν(N=C)/δ(NH), and detection, in the FAB-MS spectrum, of the molecular ion and of the protonated trialkylisourea (the latter with the most intense peak). The very small amount of isolated product prevented its further characterization.

Crystal structure of *cis*-$[PtCl_2\{\overline{N=C(OCH_2CH_2)}NRt_2\}_2]$ 2b. The single crystal X-ray diffraction analysis of complex **2b** shows the presence of two symmetrically independent molecules, **A** and **B**, in the asymmetric unit cell (Fig. 1), with the latter in a special position.

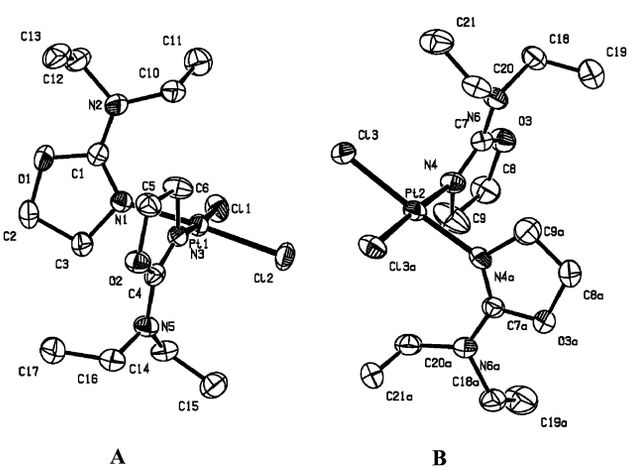


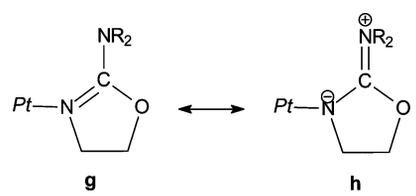
Fig. 1 Molecular structure of *cis*-$[PtCl_2\{\overline{N=C(OCH_2CH_2)}NRt_2\}_2]$ **2b** (molecules **A** and **B**). $C_{14}H_{28}C_2N_4O_2Pt$, M = 550.39, monoclinic, a = 12.192(2), b = 8.263(2), c = 29.793(6) Å, β = 97.74(3)°. U = 2974.1(11) $Å^3$, T = 933 K, space group $P2/c$ (no. 13), Z = 6, μ(Cu-Kα) = 15.828 mm^{-1}. 3551 reflections measured, 3360 unique (R_{int} = 0.0282) which were used in all calculations. The final $wR(F^2)$ was 0.0716 (all data).

Selected bond distances and angles are depicted in the Table 1. Both molecules present a *cis* square planar coordination with Pt–Cl and Pt–N distances, as well as with interligand angles, comparable with those found in related dichloro-Pt(II) complexes.[23,26] In molecule **A**, both heterocyclic rings are planar (deviation of 0.007 Å), making a torsion angle between them of 79.4°, whereas in **B** one of the rings, N(1)–C(1)–O(1)–C(2)–C(3), displays an envelope conformation with the C(2) atom deviated from planarity by 0.205 Å (the other atoms of the ring are coplanar within 0.06 Å), possibly reflecting the effect of a hydrogen bond, although weak, between one of the H atoms of the $C(2)H_2$ methylene group and one of the chloro ligands [C(2)–H(21), H(21) ··· Cl(1) and C(2)–H(21) ··· Cl(1) distances of 0.971, 2.828 and 3.620 Å, respectively; C(2)–H(21) ··· Cl(1) angle of 139.18°]. Other short contacts are displayed by the $C(6)H_2$ methylene group and another chloro ligand [C(6)–H(62), H(62) ··· Cl(3) and C(6)–H(62) ··· Cl(3) distances of 0.966, 2.836 and 3.477 Å, respectively; C(2)–H(21) ··· Cl(1) angle of 124.62°] and by the $C(21)H_3$ methyl group and an oxygen atom of the heterocycle [C(21)–H(211), H(211) ··· O(2) and C(21)–H(211) ··· O(2) distances of 0.953, 2.686 and 3.503 Å, respectively; C(2)–H(21) ··· O(2) angle of 144.22°]

Table 1 Selected bond lengths (Å) and angles (°) for *cis*-$[PtCl_2\{\overline{N=C(OCH_2CH_2)}NRt_2\}_2]$ **2b** with e.s.d.s in parentheses

Molecule **A**		Molecule **B**	
Pt1–N1	2.015(5)	Pt2–N4	2.029(6)
Pt1–N3	2.029(5)		
Pt1–Cl1	2.2996(19)	Pt2–Cl3	2.3008(19)
Pt1–Cl2	2.3042(18)		
O1–C1	1.362(8)	O3–C8	1.450(9)
O1–C2	1.441(9)	O3–C7	1.353(8)
O2–C5	1.451(8)		
O2–C4	1.344(8)		
N1–C1	1.301(8)	N4–C7	1.297(8)
N1–C3	1.453(9)	N4–C9A	1.459(16)
N2–C1	1.307(8)	N4–C9B	1.526(18)
N2–C10	1.475(9)	N6–C7	1.319(8)
N2–C12	1.486(9)	N6–C18	1.494(9)
N3–C4	1.293(8)	N6–C20	1.462(9)
N3–C6	1.471(8)		
N5–C4	1.332(8)		
C2–C3	1.513(11)	C8–C9A	1.521(18)
C5–C6	1.513(10)	C8–C9B	1.502(18)
N1–Pt1–N3	86.7(2)	N4–Pt2–N4a	87.6(3)
Cl1–Pt1–Cl2	91.58(8)	Cl3–Pt2–Cl3a	91.32(11)
Cl1–Pt1–N1	89.61(16)	Cl3–Pt2–N4a	176.95(15)
Cl1–Pt1–N3	175.96(15)	Cl3a–Pt2–N4	176.95(16)
Cl2–Pt1–N1	177.22(15)	Cl3–Pt2–N4	90.60(17)
Cl2–Pt1–N3	92.15(15)	Cl3a–Pt2–N4a	90.60(17)

The π-bond of the 2-amino-2-oxazoline ligands is delocalized along the N⋯C⋯N group comprising the exocyclic amino-N, with the average N(ring)–C(ring) and C(ring)–N(amino) distances of 1.297(8) and 1.319(8) Å, respectively, which lie between those[71] of a common single and double C–N bond. Hence, the 2-amino-2-oxazoline ligand can be represented as a hybrid of the resonance forms **g** and **h**. In agreement with the significance of the latter form, the amino group in the two 2-amino-2-oxazoline ligands in both molecules **A** and **B** approaches a trigonal planar geometry [the sum of the angles around N2, N5 and N6 being 358.2(6)°, 359.8(6)° and 360.0(6)°, respectively] which differs from the pyramidal one observed in the free cyanamide[72] and in the related dimethylcyanamide N≡C–NMe_2.[73]



g **h**

The delocalization of the unsaturated bond also contrasts with the coordinated common 2-oxazoline rings in which the N=C bond is simply localized in the planar ring, *e.g.* as observed[23] in the 2-alkyl- or 2-aryl-2-oxazoline complexes *cis*-[$PtCl_2${N=C(R)OCH$_2$CH)(Me)}$_2$] (R = Me, Ph) and *trans*-[$PtCl_2${N=C(R)OCH(Ph)CH$_2$)$_2$}$_2$].

Conclusion

This work demonstrates, for the first time, that organocyanamides, in spite of the electron releasing character of the amido group, can be readily activated towards nucleophilic attack, upon coordination of the cyano moiety to a suitable single transition metal binding centre such as {$PtCl_2$}, even without requiring the presence of a promoting agent like a Ag(I) or Cu(II) Lewis acid metal-ion[48] which would direct away from the cyano group the electron release of the amido component.

Such activation can be used in the application of organocyanamides in mild and simple syntheses of amino-functionalized organonitrogen products, either N-heterocycles or acyclic species. In particular, the study shows that the organocyanamides can behave, in metal-promoted reactions, as convenient precursors for 2-amino-2-oxazolines, compounds of therapeutic interest and whose synthesis, in pure organic chemistry, normally requires harsh operating conditions or more complicated reaction sequences. We have thus extended to such compounds the metal-mediated synthesis of heterocycles based on the activation of a cyano group. In fact, by using platinum-bound organonitriles, we have previously obtained Δ^4-1,2,4-oxadiazolines[74–76] and 1,2,4-oxadiazoles[77] upon 1,3-dipolar cycloaddition of nitrones or nitrile oxides, respectively. Further studies are in progress towards the application of organocyanamides in the synthesis of chiral 2-amino-2-oxazolines, by using chiral haloalcohols, and the extension (to other nucleophiles) of the nucleophilic additions to such bifunctionalised compounds.

Experimental

All reactions were carried out in the absence of air using standard vacuum and inert gas flow techniques. Solvents were purified by standard procedures. IR spectra were recorded on Perkin-Elmer 683 or Bio-Rad FTS 3000 MX spectrophotometers and were run in KBr pellet or Nujol mull (values in cm^{-1}; intensity of bands are referred as w = weak, m = medium, s = strong, vs = very strong, or br = broad). ^{1}H, ^{13}C{^{1}H} or ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer [δ values in ppm relative to $SiMe_4$, at ambient temperature]. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet. The fast-atom bombardment (FAB) mass spectrometric measurements were performed on a Trio 2000 instrument and the positive-ion FAB spectra were obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrixes of the samples with 8 KeV xenon atoms. Mass calibration for the data acquisition system was achieved using CsI. The reagents were purchased from Aldrich.

Synthesis of *trans*-[$PtCl_2(NCNMe_2)_2$] 1a

To solid $PtCl_2$ (0.500 g, 1.88 mmol) was added liquid $NCNMe_2$ (5.0 mL) and the reaction mixture heated in an oil bath at *ca*. 60 °C for 90 min to give a yellow-orange solution. The reaction mixture was cooled to room temperature and treated with Et_2O to give complex **1a** as an yellow precipitate which was removed by filtration, washed with warm benzene (*ca*. 40 mL) and dried *in vacuo* (0.69 g, 90% yield).

IR (Nujol mull): 2292 [vs, ν(N≡C)], 347 [s,br, ν(PtCl)]. ^{1}H NMR(CD_2Cl_2): δ 2.99 (s, Me). ^{13}C ($CDCl_3$): 115.32 (s + d, $^2J_{CPt}$ = 263.3 Hz, N*C*NMe_2), 40.47 (q, J_{CH} = 142.0 Hz, *C*H_3). Anal. Calcd.: C, 17.8; H, 3.0; N, 13.8. Found: C, 17.2; H, 3.0; N, 13.4%. FAB$^+$-MS: *m*/*z* 406 ([M]$^+$), 371 ([M − Cl]$^+$), 335 ([M − $NCNMe_2$]$^+$), 265 ([M − 2$NCNMe_2$]$^+$).

Synthesis of *trans*-[$PtCl_2(NCNEt_2)_2$] 1b

To solid $PtCl_2$ (0.235 g, 1.32 mmol) was added liquid $NCNEt_2$ (5.0 mL) and the brown reaction mixture stirred with heating in an oil bath at *ca*. 60 °C for 1 h to give an yellow-orange solution. The reaction mixture was cooled to room temperature and treated with Et_2O to give complex **1b** as an yellow precipitate which was removed by filtration, recrystallized from CH_2Cl_2/Et_2O and dried *in vacuo* (0.37 g, *ca*. 90% yield).

IR (Nujol mull): 2277 [vs, ν(N≡C)], 346 [s,br, ν(PtCl)]. ^{1}H NMR ($CDCl_3$): 3.15 (q, $^3J_{HH}$ = 7.2 Hz, 8H, CH_2CH$_3$), 1.44 (t, $^3J_{HH}$ = 7.3 Hz, 12H, CH$_2$CH_3). ^{13}C ($CDCl_3$): 114.08 [s + d, $^2J_{CPt}$ = 267.4 Hz, N*C*NEt_2], 46.47 (t, J_{CH} = 142.3 Hz, *C*H$_2$CH$_3$), 13.26 (q, J_{CH} = 128.0 Hz, CH$_2$*C*H$_3$). Anal. Calcd.: C, 26.0; H, 4.3; N, 12.2. Found: C, 25.9; H, 4.6; N, 11.8%. FAB$^+$-MS: *m*/*z* 462 ([M]$^+$), 427 ([M − Cl]$^+$), 364 ([M − $NCNEt_2$]$^+$), 265 ([M − 2$NCNEt_2$]$^+$).

Synthesis of *cis*-[$PtCl_2${N=C(OCH$_2$CH$_2$)NR_2}$_2$] (R = Me 2a, Et 2b) and *trans*-[$PtCl_2${NH=C(OCH$_2$CH$_2$Cl)NEt_2}$_2$] 4

To a thf (10 mL) solution of *trans*-[$PtCl_2(NCNR_2)_2$] [0.050 g; 0.12 mmol (R = Me **1a**), 0.11 mmol (R = Et **1b**)] was added HOCH$_2$CH$_2$Cl [83 μL, 1.10 mmol (R = Me); 73 μL, 1.20 mmol (R = Et)] and then a 1.6 M solution of ^{n}BuLi in hexane [71 μL, 0.11 mmol (R = Me); 65 μL, 0.10 mmol (R = Et)]. The reaction solution was left stirred overnight at room temperature whereafter it was concentrated *in vacuo*. Addition of Et_2O led to the precipitation of complex **2a** or **2b** as a white solid which was removed by filtration and recrystallized from CH_2Cl_2/Et_2O (*ca.* 24 mg, 40% yield). Concentration of the mother liquor *in vacuo* followed by addition of Et_2O resulted (for R = Et) in the precipitation of *trans*-[$PtCl_2${NH=C(OCH$_2$CH$_2$Cl)NEt_2}$_2$] (**4**) as a yellow solid in very low yield. Recrystallization of **2b** upon slow diffusion of Et_2O vapour into a $CDCl_3$ solution resulted in the formation of suitable crystals for X-ray diffraction analysis.

2a—IR (KBr): 1631 [m, ν(N=C)], 325 [m, ν(PtCl)], 315 [m, ν(PtCl)]. ^{1}H NMR ($CDCl_3$): δ 4.70 (s,br, 8H, OCH_2CH_2), 3.11 (s, 12H, CH_3). Anal. Calcd. (with 2CH_2Cl_2): C, 21.8; H, 3.6; N, 8.4. Found: C, 21.8; H, 3.8; N, 10.7%. FAB$^+$-MS: *m*/*z* 493 ([M]$^+$), 422 ([M − 2Cl]$^+$), 307 ([M − 2Cl − N=C(OCH$_2$CH$_2$)-NMe_2]$^+$), 115 ([N=C(OCH$_2$CH$_2$)NMe_2·H]$^+$).

2b—IR (KBr): 1640 [m, ν(N=C)], 325 [m, ν(PtCl)], 315 [m, ν(PtCl)]. ^{1}H NMR ($CDCl_3$): δ 4.35 (m,br, 8H, OCH_2CH_2), 4.02 (br, 8H, CH_2CH$_3$), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH$_2$CH_3). ^{13}C ($CDCl_3$): δ 160.88 [s,br, N=*C*], 67.20 [t, $^1J_{CH}$ = 152.0 Hz, O*C*H$_2$], 55.98 [t, $^1J_{CH}$ = 145.9 Hz, N*C*H$_2$], 43.83 [t, $^1J_{CH}$ = 138.6 Hz, N(*C*H$_2$CH$_3$)$_2$], 14.36 [q, $^1J_{CH}$ = 126.3 Hz, N(CH$_2$*C*H$_3$)$_2$]. ^{195}Pt ($CDCl_3$): δ −1879.06. Anal. Calcd. (with 2CH_2Cl_2): C, 25.1; H, 4.5; N, 7.8. Found: C, 25.7; H, 5.0; N, 8.4%. FAB$^+$-MS: *m*/*z* 551 ([M]$^+$), 516 ([M − Cl]$^+$), 481 ([M − 2Cl]$^+$), 338 ([M − 2Cl − N=C(OCH$_2$CH$_2$)NEt_2]$^+$), 143 ([N=C(OCH$_2$CH$_2$)-NEt_2·H]$^+$).

4—IR (KBr): 3280 [m,br, ν(N–H)], 1611 [s, δ(N–H)/ν(N=C)]. FAB$^+$-MS: *m*/*z* 621 ([M]$^+$), 179 ([NH=C(OCH$_2$CH$_2$Cl)NEt_2·H]$^+$).

Synthesis of *trans*-[$PtCl_2${NH=C(OMe)NR_2}$_2$] (R = Me 3a, Et 3b)

To a CH_2Cl_2 (20 mL) solution of *trans*-[$PtCl_2(NCNR_2)_2$] [0.050 g; 0.12 mmol (R = Me **1a**), 0.11 mmol (R = Et **1b**)] was slowly added dropwise a methanolic solution of KOH [0.050 mmol, 2.0 mL of a 0.025 M solution (R = Me); 0.040 mmol, 3.75 mL of a 0.011 M solution (R = Et)]. Concentration of the solution after 1 h, followed by addition of *n*-pentane resulted in the formation of an yellow oil whereafter the supernatant

solution was decanted off. Further addition of *n*-pentane to the oily residue followed by freezing in liquid nitrogen and subsequent slow warming up to room temperature (freeze–thaw technique), with vigorous stirring, resulted in the separation of complex **3a** or **3b** as an yellow solid which was removed by filtration, washed with *n*-pentane and dried *in vacuo* (*ca*. 35 mg, 60% yield).

3a—IR (KBr): 3300 [s, ν(NH)], 1630–1600 [vs,br ν(N=C)/δ(N–H)], 1060 [s, ν(C–OMe)], 320 [m, ν(PtCl)]. ^{1}H NMR ($CDCl_3$): δ 5.76 (s,br, 1H, N*H*), 4.40 (s,br, 6H, OCH_3), 4.10 (s,br, 1H, N*H*), 3.20 (s, 12H, CH_3). ^{13}C ($CDCl_3$): 163.79 [s, HN=*C*(OCH$_3$)N(CH$_3$)$_2$], 58.98 [q,br, $^1J_{CH}$ = 146.0 Hz, HN=C(O*C*H$_3$)N(CH$_3$)$_2$], 57.93 [q, $^1J_{CH}$ = 146.5 Hz, HN=C(OCH$_3$)-N(CH$_3$)$_2$], 39.38 [q,br, $^1J_{CH}$ = 141.0 Hz, HN=C(OCH$_3$)-N(*C*H$_3$)$_2$], 39.07 [q,br, $^1J_{CH}$ = 139.2 Hz, HN=C(OCH$_3$)-N(*C*H$_3$)$_2$]. Anal. Calcd. (with ¾CH$_2$Cl$_2$): C, 19.7; H, 4.0; N, 10.5. Found: C, 19.2; H, 3.9; N, 10.8%. FAB$^+$-MS: *m*/*z* 470 ([M]$^+$), 397 ([M − 2Cl]$^+$), 310 ([M − 2Cl − 2NMe$_2$]$^+$), 103 ([HN=C(OMe)NMe$_2$·H]$^+$).

3b—IR (KBr): 3280 [s, ν(NH)], 1600 [vs,br ν(N=C)/δ(N–H)], 1050 [s, ν(C–OMe)], 305 [m, ν(PtCl)]. ^{1}H NMR ($CDCl_3$): δ 5.60 (s,br, 1H, N*H*), 4.55 (s,br, 6H, OCH_3), 4.12 (s,br, 1H, N*H*), 3.49 (m, 8H, CH_2CH$_3$), 1.21 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH$_2$CH_3), 1.14 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH$_2$CH_3). ^{13}C ($CDCl_3$): 163.80 [s,br, HN=*C*(OCH$_3$)N(CH$_3$)$_2$], 163.08 [s,br, HN=*C*(OCH$_3$)N(CH$_3$)$_2$], 59.20 [q,br, $^1J_{CH}$ = 147.1 Hz, HN=C(O*C*H$_3$)N(CH$_3$)$_2$], 58.28 [q, $^1J_{CH}$ = 147.5 Hz, HN=C(O*C*H$_3$)N(CH$_3$)$_2$], 43.95 [t, $^1J_{CH}$ = 141.6 Hz, HN=C(OCH$_3$)N(*C*H$_2$CH$_3$)$_2$], 43.67 [t, $^1J_{CH}$ = 141.6 Hz, HN=C(OCH$_3$)N(*C*H$_2$CH$_3$)$_2$], 14.34 [q, $^1J_{CH}$ = 127.0 Hz, HN=C(OCH$_3$)N(CH$_2$*C*H$_3$)$_2$], 14.23 [q, $^1J_{CH}$ = 127.0 Hz, HN=C(OCH$_3$)N(CH$_2$*C*H$_3$)$_2$]. Anal. Calcd. (with ¼CH$_2$Cl$_2$): C, 26.9; H, 5.2; N, 10.3. Found: C, 26.6; H, 5.1; N, 10.2%. FAB$^+$-MS: *m*/*z* 526 ([M]$^+$), 455 ([M − 2Cl]$^+$) or ([M − 2NEt$_2$]$^+$), 310 ([M − 2Cl − 2NEt$_2$]$^+$), 131 ([HN=C(OMe)NEt$_2$·H]$^+$).

X-Ray structural analysis

Diffraction data were collected on a Syntex P-1 diffractometer (λ = 1.5418 Å). Cell parameters were obtained from centred reflections with θ between 20 and 24°. Range of *hkl*: h = 0 to 13, k = 0 to 8, l = −32 to 31. Standard reflections were measured every 100 min and showed some decay with time (4.1%). Difractometer data were processed by the program PROFIT[78] with profile analyses of reflections. The structure was solved by means of Fourier synthesis based upon the Pt- atom coordinates obtained from the Patterson syntheses using the SHELXTL package[79] and refinement was done by full-matrix least-squares based on F^2 using the SHELXS-97 package.[80] The maximum and minimum peaks in the final difference electron density map are of 1.345 and −0.981 e Å^3 located in the immediate vicinity of the platinum atoms.

CCDC reference number 199088.

See http://www.rsc.org/suppdata/dt/b3/b306690h/ for crystallographic data in CIF or other electronic format.

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