Direct synthesis of (imine)platinum(II) complexes by iminoacylation of ketoximes with activated organonitrile ligands

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The metal-mediated iminoacylation of ketoximes R_1R_2C=NOH (**1a** $R_1 = R_2 =$ Me; **1b** $R_1 =$ Me, $R_2 =$ Et; **1c** $R_1R_2 = C_4H_8$; **1d** $R_1R_2 = C_5H_{10}$) upon treatment with the platinum(II) complex *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] **2a** with an organonitrile bearing an acceptor group proceeds under mild conditions in dry CH_2Cl_2 to give the *trans*-[$PtCl_2\{NH$=$C(CH_2CO_2Me)ON$=$CR_1R_2\}_2$] **3a–d** isomers in moderate yield. The reaction of those ketoximes with *trans*-[$PtCl_2(NCCH_2Cl)_2$] **2b** under the same experimental conditions gives a 1 : 1 mixture of the isomers *trans*/*cis*-[$PtCl_2\{NH$=$C(CH_2Cl)ON$=$CR_1R_2\}_2$] **3e–h** and **4e–h** in moderate to good yield. These reactions are greatly accelerated by microwave irradiation to give, with higher yields (*ca.* 75%), the same products which were characterized by IR and ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopies, FAB-MS, elemental analysis for the stable *trans* isomers, and X-ray diffraction analysis (**3f**). The diiminoester ligand in **3a** was liberated upon reaction of the complex with a diphosphine.

Introduction

Organonitriles can be activated by ligation to a metal centre, what can provide a simple method for the synthesis of a large number of organonitrogen compounds.[1–3] Oximes are reagents with a rich coordination chemistry[4–6] and, in spite of their relatively weak nucleophilic character, they can act as nucleophiles towards organonitriles, NCR, when the latter are coordinated to Pt^{IV},[7] Re^{IV},[8] Rh^{III},[9] or Pd^{II},[10] and on deprotonation yield interesting substituted iminoacylated species.

The metal oxidation state exhibits a key role and, in contrast to the above reactions with oximes or other types of nucleophiles,[11–13] at electron-rich Re^{I} or Mo^{0} centres[14,15] the nitrile group is activated towards electrophilic attack. In the case of an oxime, the coupling reaction with NCR proceeds at Pt^{IV},[7,16] but not at Pt^{II}, and in order to obtain Pt^{II} products one has to reduce the previously synthesized corresponding Pt^{IV} complexes.[17] To our knowledge, only one example of extension of the nitrile–oxime coupling to Pt^{II} is known, but it concerns organocyanamides $NCNR_2$ and requires the presence of a catalytic amount of Ag^{I} or Cu^{II} as a Lewis acid[18] to bind the amino moiety and thus further activate the cyano group. Similarly, the electrophilicity of nitriles is promoted by an electron-acceptor R, such as an ester or Cl atom, and can be enhanced by coordination to Pt^{II} to undergo [2 + 3]-cycloadditions.[19] These observations stimulated our interest to extend to *trans*-Pt^{II} complexes the metal-mediated nitrile–oxime reaction, by using ester- and chloro-substituted nitriles, what would allow the direct (single pot) synthesis of iminoacylated Pt^{II} complexes without requiring the involvement of intermediate Pt^{IV} species.

Further aims of the current study are as follows. Firstly, we could prepare the difficultly accessible novel iminoacylated Pt^{II} products with those functional groups. Secondly, the study would provide an opportunity to apply unconventional methods of activation, *i.e.* focused microwave irradiation[20] to reduce the reaction time, to increase the purity and the selectivity and/or yield in comparison with traditional methods.[10] Thirdly, at a later stage, these (imine)Pt complexes with a reactive group could be used for further synthesis of derivatives structurally related to aminoesters, precursors of lactam heterocycles, with potential bioactivity or catalytic interest.[21]

Hence, we have succeeded to extend to (nitrile)Pt^{II} the iminoacylation reaction of oximes (not feasible in pure organic chemistry and previously requiring a higher metal oxidation state) and now report a direct method for generation of (imine)Pt^{II} compounds without any Lewis acid catalyst and using either traditional heating or microwave irradiation.

Results and discussion

We have addressed the above aims by treating the oximes R_1R_2C=NOH **1** (**1a** $R_1 = R_2 =$ Me; **1b** $R_1 =$ Me, $R_2 =$ Et; **1c** $R_1R_2 = C_4H_8$; **1** $R_1R_2 = C_5H_{10}$) with the platinum(II) compounds *trans*-[$PtCl_2(NCR)_2$] (**2a** R = CH_2CO_2Me, **2b** R = CH_2Cl) in dry CH_2Cl_2 for 15 min with heating at 50 °C by the conventional way. Compounds *trans*- and/or *cis*-[$PtCl_2\{NH$=$C(R)ON$=$CR_1R_2\}_2$] (**3** and/or **4**, respectively) were isolated in moderate to good yields (47–62%) (Scheme 1). The reactions are greatly accelerated by focused microwave irradiation which, at the same temperature and in a shorter time, without a decrease of selectivity, leads to higher isolated yields (*ca.* 75%, in only 1–2 min).

In order to obtain the desired imino-complexes with a maximum yield, a close control of the time and temperature is required. For example, the reaction of acetone oxime **1a** and *trans*-[$PtCl_2(NCCH_2Cl)_2$] **2b** with heating for 2 h at 50 °C

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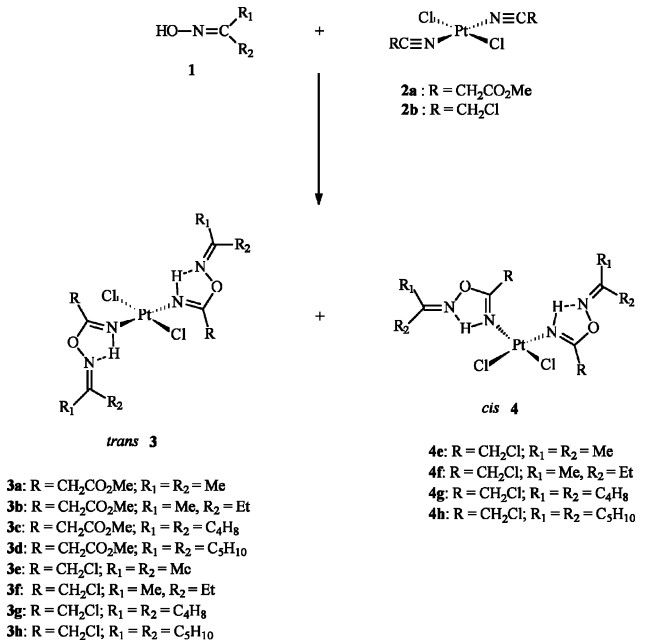
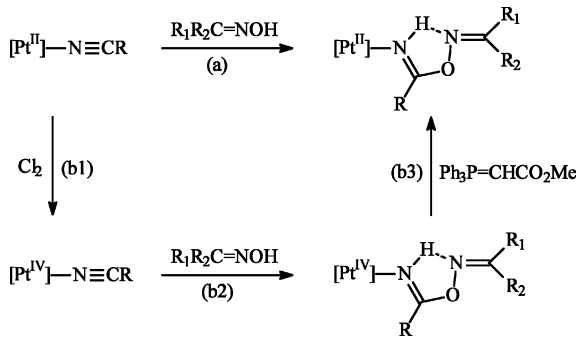


Scheme 1

gives only the *trans*-[$PtCl_2${NH=C(CH_2Cl)ON=CMe_2}$_2$] isomer in lower yield (16%) in comparison with the above mentioned conditions (15 min, 50 °C, 56–62% yield). Moreover, the reaction of *trans*-[$PtCl_2(NCCH_2Cl)_2$] **2b** with cyclohexanone oxime (C_5H_{10})C=NOH **1d** with heating for 2 h at 50 °C or heating for 10 min at 120 °C by microwave irradiation leads only to products of degradation. The *cis* isomers are less stable than the *trans* ones and undergo decomposition in solution at room temperature.

The formation of the two isomeric products is detected by TLC on silica gel (spots with different R_f values) and they have been separated by column chromatography on silica gel and isolated as yellow solids. Curiously, the reaction is more selective with the stronger electron-attractor CO_2Me group giving only the *trans* imino-complexes, whereas in the case of the chloro substituent a 1 : 1 mixture of *cis* and *trans*-[$PtCl_2${NH=C(CH_2Cl)ON=CR_1R_2}$_2$] (**4e–h** and **3e–h**, respectively) is obtained (Scheme 1).

These reactions allow the direct synthesis of iminoacylated Pt^{II} complexes from nitrile Pt^{II} precursors upon nitrile/oxime coupling (route a, Scheme 2), what constitutes a more convenient route than the alternative one (route b, Scheme 2) involving the coupling reaction at Pt^{IV}. The latter method would require the initial oxidation, by Cl_2, of Pt^{II} to Pt^{IV} (reaction b1) followed by the



Scheme 2

coupling reaction (b2) and further reduction (b3) to Pt^{II}, typically by using the phosphorus ylide Ph_3P=$CHCO_2Me$.[17]

The new complexes were characterised by elemental analyses, IR and ^1H, ^{13}C and ^{195}Pt NMR spectroscopies, and FAB-MS. In the IR spectra, no ν(N≡C) band is detected, the ν(N–H) bands appear at 3299–3195 cm^{-1} and the characteristic strong ν(C=N) bands of the imine ligands occur in the 1666–1639 cm^{-1} range, in agreement with literature results,[7h,22] thus confirming the formation of the imino–platinum complexes.

In the ^1H and ^{13}C NMR spectra, the resonances of the *cis* isomers appear at lower fields (by *ca.* 0.02 to 0.5 ppm) than the corresponding ones for the *trans* compounds. In the ^{195}Pt NMR spectra, the resonances of both isomers (from −2046 to −2080 ppm) lie within the range previously observed for complexes derived from nitrile–oxime coupling.[10,17] All *trans* isolated compounds gave satisfactory elemental analyses and the expected molecular ion/fragmentation patterns in the FAB^+ mass spectra.

The single-crystal X-ray diffraction structural analysis of *trans*-[$PtCl_2${NH=C(CH_2Cl)ON=C(Me)(Et)}$_2$] **3f** confirms the formulation and its *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). Half of the molecule was found in the asymmetric unit and the central Pt atom lies on a twofold axis. The values of bond lengths distances Pt1–N1

Table 1 Crystal data for *trans*-[$PtCl_2${NH=C(CH_2Cl)ON=C(Me)(Et)}$_2$] **3f**

	3f
Empirical formula	$C_{12}H_{22}Cl_4N_4O_2Pt$
M_r	591.23
T/K	130(2) K
λ/Å	0.71069
Crystal system	Tetragonal
Space group	$I4_1/a$
a/Å	10.9223
b/Å	10.9223
c/Å	34.2519(39)
V/Å^3	4086.1(5)
Z	8
D_c/Mg m^{-3}	1.922
μ(Mo-Kα)/mm^{-1}	7.402
No. collected reflns	18448
No. unique rflns	4617
R_{int}	0.0389
$R1^a$ ($I \geq 2\sigma$)	0.0342
$wR2^b$ ($I \geq 2\sigma$)	0.0819

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

Table 2 Selected bond lengths (Å) and angles (°) for **3f**

Pt1–Cl1	2.3098(10)	O11–N11	1.461(5)
Pt1–N1	2.002(3)	C1–C2	1.472(6)
N1–C1	1.268(5)	Cl2–C2	1.740(5)
O11–C1	1.358(5)	N1–H1	0.88(4)
N11–C11	1.255(6)		
Cl1–Pt1–N1	90.01(10)	Pt1–N1–C1	125.9(3)
Cl1–Pt1–Cl1a	178.49(4)	N11–O11–C1	110.4(3)
N1–Pt1–N1a	179.47(12)	O11–C1–N1	125.1(3)
Pt1–N1–H1	115(3)	N1–H1···N11	103(3)

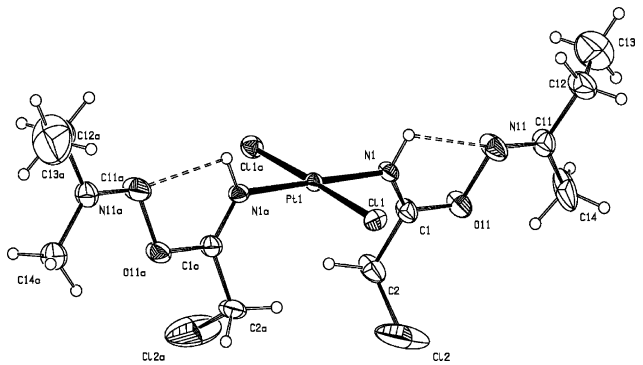
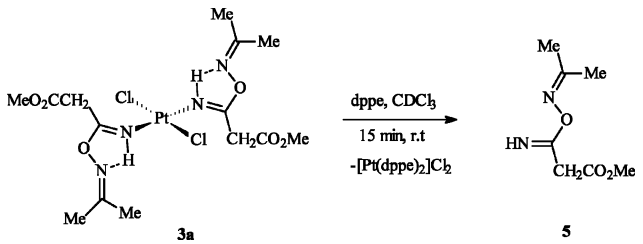


Fig. 1 ORTEP view of the iminoacylated Pt^{II} complex *trans*-$[PtCl_2\{NH{=}C(CH_2Cl)ON{=}C(Me)(Et)\}_2]$ **3f** with atomic numbering scheme (ellipsoids are drawn at 30% probability), the dotted line indicating the intramolecular H-bond. Symmetry transformations used to generate equivalent atoms: (a) $2 - x, 3/2 - y, z$.

[2.002(3) Å], Pt1–Cl1 [2.3098(10) Å], N1–C1 [1.268(5) Å)] and N1–H1 [0.88(4) Å], and angles Cl1–Pt1–N1 [90.01(10)°], Pt1–N1–H1 [115(3)°], as well as the N1–H1 ··· N11 hydrogen bond between the imine hydrogen and oxime nitrogen atoms [H1 ··· N11, 2.27(4); N1 ··· N11, 2.619(6) Å; N1–H1 ··· N11, 103(3)°] which stabilizes the *E*-conformation of the iminoacyl ligands, agree with those reported for other iminoacylated platinum complexes.[7i]

Liberation of the diiminoester **5** was achieved by adding the diphosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) to a $CDCl_3$ solution of **3a** (Scheme 3), but unfortunately the compound is not stable enough to be isolated and could be characterized only by ^1H NMR spectroscopy. Its resonances appear at higher field than the corresponding ones for the complex precursor **3a**. For example, the methylene CH_2CO_2Me protons singlet is observed at δ 3.77 in **5** and at 4.19 ppm in **3a**. According to the type of reaction of Scheme 3, we are able to obtain new substituted iminoesters that are expected to find further use for the synthesis of novel heterocyclic compounds.

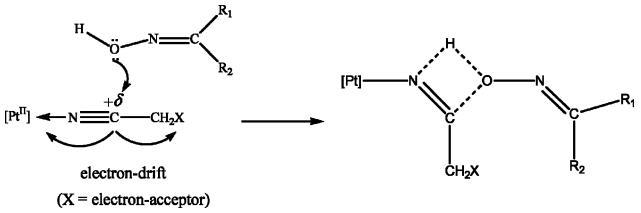


3a **5**

Scheme 3

Concluding remarks

A great enhancement of the electrophilicity of the cyano-carbon of a nitrile was achieved in this study by the combined effects of a metal and of an electron-acceptor substituent at the nitrile itself. In particular, by bearing an ester or a chloro substituent and upon coordination to a Pt^{II} centre, the cyano-carbon atom of the $NCCH_2X$ (X = CO_2Me, Cl) nitriles is doubly activated to such an extend that it can undergo ready nucleophilic addition by a weak nucleophile such as an oxime which is expected[16c] to proceed *via* a transition state with a four membered NCOH ring (Scheme 4). For normal unfunctionalized nitriles NCR (R = alkyl, aryl), their coordination to a stronger Pt^{IV} activator was required[7,16c] for such a type of reaction to occur.



Scheme 4

As a result of the combined double mode of nitrile activation, we have prepared directly, by simple coupling of an oxime to a Pt^{II}-bound nitrile, the derived iminoacyl–platinum(II) complexes. This type of compounds was previously reached only indirectly, *via* reduction (typically with a phosphorus-ylide)[17] of the corresponding Pt^{IV} complexes derived from the oxime addition to a Pt^{IV}-bound nitrile. By using the above nitriles we have also achieved novel functionalized imino compounds, *i.e.* diiminoesters and chlorodiimino species, inaccessible directly by pure organic chemistry. They can be liberated from the metal by displacement with a phosphine and, although unstable in the free state, they can be generated and further used *in situ* when required, a type of strategy that has been applied[22] for other imines. Hence, they are expected to provide a new route for the synthesis *e.g.* of heterocyclic compounds by further reactions which are under study in our laboratory.

Experimental

Materials and instrumentation

Solvents were purchased from Aldrich and dried by usual procedures. The organonitrile complexes *trans*-$[PtCl_2(NCR)_2]$ (**2a** R = CH_2CO_2Me, **2b** R = CH_2Cl) were prepared according to published methods.[19] The oximes 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) matrixes of samples with 8 keV (*ca* 1.28×10^{15} J) Xe atoms. ^1H and ^{13}C chemical shifts (δ) were 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 a Bio-Rad FTS 3000MX and a Jasco FT/IR-430 instruments in KBr pellets and the wavenumbers are 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 an IR detector of temperature.

Reactions of the organonitrile platinum(II) complexes *trans*-[$PtCl_2(NCR)_2$] (2a R = CH_2CO_2Me, 2b R = CH_2Cl) with Me_2C=NOH (1a), (Me)(Et)C=NOH (1b), (C_4H_8)C=NOH (1c), (C_5H_{10})C=NOH (1d)

(i) By conventional method. A solution of **2a** (50.0 mg, 0.107 mmol) or **2b** (50.0 mg, 0.119 mmol) in dry CH_2Cl_2 (3 mL) is added at room temperature to the appropriate oxime (3 eq) and the mixture is heated with stirring at 55–60 °C for 15 min to form a bright yellow solution. After evaporation of the solvent *under vacuum* to dryness, the residue is washed with diethyl ether (five 3 mL portions) to remove the excess of oxime, and then purified by column chromatography (SiO_2/CH_2Cl_2, Et_2O) followed by evaporation of the solvent *in vacuo* to give yellow powders of the corresponding iminoacylated products *trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=CR_1R_2}$_2$] (**3a–d**) or the 1 : 1 isomeric mixtures of *trans*/*cis*-[$PtCl_2${NH=C(CH_2Cl)ON=CR_1R_2}$_2$] (**3e–h** and **4e–h**). The *trans* isomers can be recrystallised in air from CH_2Cl_2–Et_2O.

(ii) By focused microwave irradiation. The reagents, in amounts identical to those detailed above, were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. After reaction (*ca.* 50 °C, 1–2 min), the mixture was allowed to cool down, the solvent was evaporated *under vacuum* to dryness. The residue was washed with diethyl ether (five 3 mL portions), to remove the excess of oxime, and then purified by column chromatography (SiO_2/CH_2Cl_2, Et_2O) followed by evaporation of the solvent *under vacuum* to give the final yellow powders of the **3** or **4** products (*ca.* 75% yield). The *trans* isomers can be recrystallised in air from CH_2Cl_2–Et_2O.

***trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=CMe_2}$_2$] (3a).** Method (i), 50% yield. TLC on SiO_2: R_f = 0.55 (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 3216 (NH), 1747 (CO_2Me), 1646 and 1666 (C=N), 1176 (C–O). ^1H NMR, δ 2.01 and 2.03 (two s, 3H each, =CMe_2), 3.79 (s, 3H, MeO), 4.19 (s, 2H, CH_2), 8.2 (s, br, 1H, NH). $^{13}C\{^1H\}$ 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 −2080 (774 Hz). FAB$^+$-MS, *m*/*z* 611 [M]$^+$. Anal. Calc. for $C_{14}H_{24}N_4Cl_2O_6Pt$: C, 27.55; H, 3.96; N, 9.18. Found: C, 28.05; H, 4.07; N, 8.99%.

***trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=C(Me)(Et)}$_2$] (3b).** Method (i), 48% yield. TLC on SiO_2: R_f = 0.62 (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 3221 (NH), 1747 (CO_2Me), 1643 and 1666 (C=N), 1176 (C–O). ^1H NMR, δ 1.14 (m, 3H), 1.99 and 2.01 (two s, 3H each, =CMe), 2.35 (m, 2H), 3.79 (s, 3H, MeO), 4.20 (s, 2H, CH_2), 8.2 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 10.6 and 10.9 (two s, CH_3CH_2), 16.4 and 20.1 (two s, =C*Me*), 24.9 and 30.0 (two s, CH_2CH_3), 40.1 (CH_2), 53.4 (MeO), 167.1 and 167.9 (CO_2Me), 169.9 (=*C*(Me)(Et)), 170.6 (C(O)=N). ^{195}Pt, δ −2078 (737 Hz). FAB$^+$-MS, *m*/*z* 638 [M]$^+$. Anal. Calc. for $C_{16}H_{28}N_4Cl_2O_6Pt{\cdot}H_2O$: C, 29.27; H, 4.61; N, 8.53. Found: C, 29.31; H, 4.48; N, 8.59. H_2O has been detected in the IR and ^1H NMR spectra.

***trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=C(C_4H_8)}$_2$] (3c).** Method (i), 47% yield. TLC on SiO_2: R_f = 0.7 (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 3217 (NH), 1753 (CO_2Me), 1655 (C=N), 1124 (C–O). ^1H NMR, δ 1.82 (m, 4H), 2.52 (m, 4H) (=C{C_4H_8}), 3.79 (s, 3H, MeO), 4.17 (s, 2H, CH_2), 8.2 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 24.4, 25.0, 29.7, 31.4 (C_4H_8), 39.3 (CH_2CO), 52.7 (MeO), 166.5 (CO_2Me), 167.2 (=*C*{C_4H_8}), 177.1 (C(O)=N). ^{195}Pt NMR, δ −2076 (645 Hz). FAB$^+$-MS, *m*/*z* 663 [M]$^+$, 626 [M − HCl]$^+$, 590 [M − 2HCl]$^+$. Anal. Calc. for $C_{18}H_{28}N_4Cl_2O_6Pt$: C, 32.64; H, 4.26; N, 8.46. Found: C, 32.72; H, 4.46; N, 8.14%.

***trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=C(C_5H_{10})}$_2$] (3d).** Method (i), 48% yield. TLC on SiO_2: R_f = 0.5 (eluent CH_2Cl_2–Et_2O (8 : 1)). IR (cm^{-1}): 3299 (NH), 1747 (CO_2Me), 1660 and 1639 (C=N), 1166 (C–O). ^1H NMR, δ 1.65 (m, 2H), 1.75 (m, 4H), 2.32 (t, J_{HH} 5.4 Hz, 2H), 2.51 (t, J_{HH} 5.4 Hz, 2H) (=C{C_5H_{10}}), 3.79 (s, 3H, MeO), 4.18 (s, 2H, CH_2), 8.2 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 25.8, 26.3, 27.3, 27.9, 32.5 (C_5H_{10}), 40.1 (CH_2CO), 53.4 (MeO), 167.2 (CO_2Me), 168.0 (=*C*{C_5H_{10}}), 170.9 (C(O)=N). ^{195}Pt NMR, δ −2075 (687 Hz). FAB$^+$-MS, *m*/*z* 690 [M], 653 [M − HCl]. Anal. Calc. for $C_{20}H_{32}N_4Cl_2O_6$ Pt: C, 34.79; H, 4.67; N, 8.11. Found: C, 34.50; H, 4.26; N, 7.95%.

***trans*-[$PtCl_2${NH=C(CH_2Cl)ON=CMe_2}$_2$] (3e).** Method (i), 31% yield. TLC on SiO_2: R_f = 0.5 (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 3210 (NH), 1666 and 1644 (C=N), 1278 (CH_2Cl), 1197 (C–O). ^1H NMR, δ 2.06 and 2.08 (two s, 3H each, =CMe_2), 4.93 (s, 2H, CH_2Cl), 8.32 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 18.0 and 22.4 (Me groups), 39.8 (CH_2Cl), 167.1 (=*C*Me_2), 168.6 (C(O)=N). ^{195}Pt NMR, δ −2067 (752 Hz). FAB$^+$-MS, *m*/*z* 563 [M]$^+$, 529 [M − HCl]$^+$. Anal. Calc. for $C_{10}H_{18}N_4Cl_4O_2Pt{\cdot}1/4CH_2Cl_2$: C, 21.07; H, 3.19; N, 9.58. Found: C, 21.50; H, 3.17; N, 9.34%. The solvent of crystallization CH_2Cl_2 has been detected in the NMR spectra.

***cis*-[$PtCl_2${NH=C(CH_2Cl)ON=CMe_2}$_2$] (4e).** Method (i), 31% yield. TLC on SiO_2: R_f = 0.5 (eluent CH_2Cl_2/Et_2O (6 : 1)). IR (cm^{-1}): 3176 (NH), 1670 and 1643 (C=N). ^1H NMR, δ 2.07 and 2.09 (two s, 3H each, =CMe_2), 4.95 (s, 2H, CH_2Cl), 8.6 (s, br, 1H, NH). FAB$^+$-MS, *m*/*z* 563 [M]$^+$, 529 [M − HCl]$^+$. The complex is too unstable in $CDCl_3$ to measure the $^{13}C\{^1H\}$ NMR and ^{195}Pt NMR spectra.

***trans*-[$PtCl_2${NH=C(CH_2Cl)ON=C(Me)(Et)}$_2$] (3f).** Method (i), 28% yield. TLC on SiO_2: R_f = 0.53 (eluent CH_2Cl_2). IR (cm^{-1}): 3213 (NH), 1666 and 1643 (C=N), 1269 (CH_2Cl), 1194 (C–O). ^1H NMR, δ 1.12–1.20 (dt, J_{HH} 7.8 Hz, J_{HH} 7.2 Hz, 3H, CH_3CH_2), 2.04 and 2.06 (two s, 3H, =CMe), 2.35–2.53 (dq, J_{HH} 7.8 Hz, J_{HH} 7.2 Hz, 2H, CH_3CH_2), 4.94 (s, 2H, CH_2Cl), 8.3 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 10.7 and 11.0 (CH_3CH_2), 16.5 and 20.1 (=C*Me*), 25.0 and 30.1 (CH_3CH_2), 39.9 (CH_2Cl), 168.7 and 171.5 (=*C*(Me)(Et)), 170.9 (C(O)=N). ^{195}Pt NMR, δ −2065 (806 Hz). FAB$^+$-MS, *m*/*z* 591 [M]$^+$, 557 [M − HCl]$^+$. Anal. Calc. for $C_{12}H_{22}N_4O_2Cl_4Pt$: C, 24.34; H, 3.75; N, 7.48. Found: C, 24.28; H, 3.55; N, 7.94%. Suitable crystals for X-ray analysis were obtained upon recrystallization from CH_2Cl_2–Et_2O.

***cis*-[$PtCl_2${NH=C(CH_2Cl)ON=C(Me)(Et)}$_2$] (4f).** Method (i), 28% yield. TLC on SiO_2: R_f = 0.75 (eluent CH_2Cl_2/Et_2O (6 : 1)). IR (cm^{-1}): 3195 (NH), 1666 and 1641 (C=N), 1265 (CH_2Cl), 1194 (C–O). ^1H NMR, δ 1.11–1.19 (m, 3H, CH_3CH_2), 2.03–2.07 (m, 3H, =CMe), 2.36–2.48 (m, 2H, CH_3CH_2), 4.97 (s, 2H, CH_2Cl), 8.6 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR, δ 10.6 and 11.0 (CH_3CH_2), 16.4 and 20.2 (=C*Me*), 24.9 and 30.1 (CH_3CH_2), 40.4 (CH_2Cl), 168.7 (=*C*(Me)(Et)), 170.9 (C(O)=N). ^{195}Pt NMR, δ −2046 (806 Hz). FAB$^+$-MS, *m*/*z* 591 [M]$^+$, 557 [M − HCl]$^+$.

***trans*-[PtCl$_2${NH=C(CH$_2$Cl)ON=C(C$_4$H$_8$)}$_2$] (3g).** Method (i), 29% yield. TLC on SiO_2: $R_f = 0.5$ (eluent CH_2Cl_2). IR (cm^{-1}): 3286 (NH), 1647 (C=N), 1263 (CH_2Cl), 1144 (C–O). ^{1}H NMR, δ 1.85 (m, 4H), 2.53 (m, 2H), 2.62 (m, 2H) (=C{C_4H_8}), 4.90 (s, 2H, CH_2Cl), 8.2 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ 25.1, 25.7, 30.5, 32.2 (C_4H_8), 39.8 (CH_2Cl), 168.8 (=*C*{C_4H_8}), 178.6 (C(O)=N). ^{195}Pt NMR, δ −2064 (816 Hz). FAB$^+$-MS, *m*/*z* 615 [M]$^+$, 581 [M − HCl]$^+$. Anal. Calc. for $C_{14}H_{22}N_4O_2Cl_4Pt$: C, 27.33; H, 3.60; N, 9.11. Found: C, 27.35; H, 3.16; N, 8.72%.

***cis*-[PtCl$_2${NH=C(CH$_2$Cl)ON=C(C$_4$H$_8$)}$_2$] (4g).** Method (i), 29% yield. TLC on SiO_2: $R_f = 0.57$ (eluent CH_2Cl_2–Et_2O (10 : 1)). IR (cm^{-1}): 1647 (C=N), 1227 (CH_2Cl), 1132 (C–O). ^{1}H NMR, δ 1.84 (m, 4H), 2.56 (m, 2H), 2.60 (m, 2H) (=C{C_4H_8}), 4.92 (s, 2H, CH_2Cl), 8.4 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ 25.1, 25.8, 30.6, 32.3 (C_4H_8), 40.3 (CH_2Cl), 169.3 (=*C*{C_4H_8}), 179.0 (C(O)=N). FAB$^+$-MS, *m*/*z* 615 [M]$^+$, 581 [M − HCl]$^+$. The complex is too unstable in $CDCl_3$ to measure the ^{195}Pt NMR.

***trans*-[PtCl$_2${NH=C(CH$_2$Cl)ON=C(C$_5$H$_{10}$)}$_2$] (3h).** Method (i), 29% yield. TLC on SiO_2: $R_f = 0.8$ (eluent CH_2Cl_2). IR (cm^{-1}): 3263 (NH), 1639 and 1664 (C=N), 1263 (CH_2Cl), 1147 (C–O). ^{1}H NMR, δ 1.75 (m, 6H), 2.34 (t, J_{HH} 6.3 Hz, 2H), 2.58 (t, J_{HH} 6.3 Hz, 2H) (=C{C_5H_{10}}), 4.93 (s, 2H, CH_2Cl), 8.2 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ 25.8, 26.4, 27.4, 27.9, 32.6 (C_5H_{10}), 39.9 (CH_2Cl), 168.8 (= *C*{C_5H_{10}}), 171.7 (C(O)=N). ^{195}Pt NMR, δ −2064 (780 Hz). FAB$^+$-MS, *m*/*z* 643 [M]$^+$, 609 [M − HCl]$^+$. Anal. Calc. for $C_{16}H_{26}N_4O_2Cl_4Pt$: C, 29.87; H, 4.07; N, 8.71. Found: C, 29.99; H, 4.32; N, 8.30%.

***cis*-[PtCl$_2${NH=C(CH$_2$Cl)ON=C(C$_5$H$_{10}$)}$_2$] (4h).** Method (i), 29% yield. TLC on SiO_2: $R_f = 0.6$ (eluent CH_2Cl_2/Et_2O (10 : 1)). IR (cm^{-1}): 3195 (NH), 1660 (C=N), 1223 (CH_2Cl), 1134 (C–O). ^{1}H NMR, δ 1.63 (m, 6H), 2.34 (m, 2H), 2.55 (m, 2H) (=C{C_5H_{10}}), 4.93 (s, 2H, CH_2Cl), 8.4 (s, br, 1H, NH). FAB$^+$-MS, *m*/*z* 643 [M]$^+$, 609 [M − HCl]$^+$. The complex is too unstable in $CDCl_3$ to measure the ^{13}C{^{1}H} and ^{195}Pt NMR.

Crystal structure determination of 3f

trans-[PtCl$_2${N(H)=C(CH$_2$Cl)ON=C(Me)(Et)}$_2$]. $C_{12}H_{22}N_4O_2Cl_4Pt$, $M = 591.23$, tetragonal, space group, $I4_1/a$ (no. 88), $a = b = 10.9223$, $c = 34.2519(39)$ Å, $U = 4086.1(5)$ Å^3, $Z = 8$ μ(Mo-Kα) = 7.402 mm^{-1}. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation. Data was collected at 130 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[23] and refined with SHELXL-97[24] with the WinGX graphical user interface.[25] All hydrogens were inserted in calculated positions except H1 which was located. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave $R_1 = 0.0342$ [$I > 2\sigma(I)$]; $R_1 = 0.0681$ (all data)]. The maximum and minimum peaks in the final difference electron density map are of 1.242 and −1.109 e Å^{-3}, located around the Cl2 atom.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611341a

Liberation of the iminoacylated oxime. dppe (11.7 mg, 0.029 mmol) was added to a solution of *trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}$_2$] (**3a**) (9.0 mg, 0.015 mmol) in $CDCl_3$ (1 mL, 99.8% D), the mixture was left to stand for 10 min until a colourless precipitate of [Pt(dppe)$_2$]Cl$_2$ was released. The complex was removed by filtration and the filtrate was characterised by ^{1}H NMR.

NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$:^{1}H NMR, δ 1.88 and 1.89 (two s, 3H each, =CMe$_2$), 3.66 (s, 3H, MeO), 3.77 (s, 2H, CH_2), 7.69 (s, br, 1H, NH). ^{13}C{^{1}H} NMR, δ not reliable due to decomposition of the compound.

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References

1 V. Yu. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771.
2 A. J. L. Pombeiro and V. Yu. Kukushkin, Reactivity of Coordinated Nitriles, in *Comprehensive Coordination Chemistry II*, Elsevier, Amsterdam, 2nd edn, 2003, vol. 1 (ed. A. B. P. Lever), ch. 1.34, pp. 639–660, and references therein.
3 R. A. Michelin, M. Mozzon and R. Beitani, *Coord. Chem. Rev.*, 1996, **147**, 299.
4 A. J. L. Pombeiro and V. Yu. Kukushkin, Reactivity of Coordinated Oximes, in *Comprehensive Coordination Chemistry II*, Elsevier, Amsterdam, 2nd edn, 2003, vol. 1 (ed. A. B. P. Lever), ch. 1.33, pp. 631–638, and references therein.
5 V. Yu. Kukushkin and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1999, **181**, 147.
6 V. Yu. Kukushkin, D. Tudela and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1996, **156**, 333.
7 (*a*) D. A. Garnovskii, A. J. L. Pombeiro, M. Haukka, P. Sobota and V. Yu. Kukushkin, *Dalton Trans.*, 2004, 1097; (*b*) K. V. Luzyanin, V. Yu. Kukushkin, M. Haukka, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2004, 2728; (*c*) S. S. P. R. Almeida, M. F. C. Guedes da Silva, L. B. Jerzykiewicz, P. Sobota and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2003, **356**, 259; (*d*) A. V. Makarycheva-Mikhailova, M. Haukka, N. A. Bokach, D. A. Garnovskii, M. Galanski, B. K. Keppler, A. J. L. Pombeiro and V. Yu. Kukushkin, *New J. Chem.*, 2002, **26**, 1085; (*e*) N. A. Bokach, M. Haukka, A. J. L. Pombeiro, S. N. Morozkina and V. Yu Kukushkin, *Inorg. Chim. Acta*, 2002, **336**, 95; (*f*) V. Yu. Kukushkin, T. B. Pakhomova, N. A. Bokach, G. Wagner, M. L. Kuznetsov, M. Galanski and A. J. L Pombeiro, *Inorg. Chem.*, 2000, **39**, 216; (*g*) D. A. Garnovskii, M. F. C. Guedes da Silva, T. B. Pakhomova, G. Wagner, M. T. Duarte, J. J. R. Fraústo, da Silva, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chim. Acta*, 2000, **300–302**, 499; (*h*) V. Yu. Kukushkin, T. B. Pakhomova, Y. N. Kukushkin, H. Herrmann, G. Wagner and A. J. L. Pombeiro, *Inorg. Chem.*, 1998, **37**, 6511; (*i*) G. Wagner, T. B. Pakhomova, N. A. Bokach, J. J. R. Fraústo da Silva, J. Vicente, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 1683.
8 G. Wagner, A. J. L. Pombeiro, N. A. Bokach and V. Yu Kukushkin, *J. Chem. Soc., Dalton Trans.*, 1999, 4083.
9 V. Yu. Kukushkin, I. V. Ilichev, G. Wagner, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1999, 3047.
10 D. A. Garnovskii, N. A. Bokach, A. J. L. Pombeiro, M. Haukka, J. J. R. Fraústo da Silva and V. Yu. Kukushkin, *Eur. J. Inorg. Chem.*, 2005, 3467.

11 (*a*) N. A. Bokach, T. V. Kuznetsova, S. A. Simanova, M. Haukka, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2005, **44**, 5152; (*b*) N. A. Bokach, V. Yu. Kukushkin, P. F. Kelly, M. Haukka and A. J. L. Pombeiro, *Dalton Trans.*, 2005, 1354.

12 K. V. Luzyanin, V. Yu. Kukushkin, A. D. Ryabov, M. Haukka and A. J. L. Pombeiro, *Inorg. Chem.*, 2005, **44**, 2944.

13 (*a*) J. Vicente, M. T. Chicote, M. A. Beswick and M. C. Ramírez de Arellano, *Inorg. Chem.*, 1996, **35**, 6592; (*b*) J. Vicente, M. T. Chicote, J. Fernández-Baeza, F. J. Lahoz and J. A. Lopez, *Inorg. Chem.*, 1991, **30**, 3617; (*c*) E. Ciganek, *J. Org. Chem.*, 1970, **35**, 3631.

14 M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Inorg. Chem.*, 2002, **41**, 219.

15 S. M. P. R. Cunha, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Inorg. Chem.*, 2003, **42**, 2157.

16 (*a*) M. L. Kuznetsov, V. Yu. Kukushkin, A. I. Dement'ev and A. J. L. Pombeiro, *J. Phys. Chem. A*, 2003, **107**, 6108; (*b*) M. L. Kuznetsov, V. Yu. Kukushkin, M. Haukka and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2003, **356**, 85; (*c*) M. L. Kuznetsov, N. A. Bokach, V. Yu. Kukushkin, T. Pakkanen, G. Wagner and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 4683.

17 G. Wagner, T. B. Pakhomova, N. A. Bokach, J. J. R. Fraústo da Silva, J. Vicente, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 1683.

18 C. M. P. Ferreira, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, V. Yu. Kukushkin and R. A. Michelin, *Inorg. Chem.*, 2001, **40**, 1134.

19 M. A. Charmier-Januário, M. Haukka and A. J. L. Pombeiro, *Dalton Trans.*, 2004, 2741.

20 (*a*) *Microwaves in Organic Synthesis*, ed. A. Loupy, Wiley/VCH, Weinheim, 2002; (*b*) *Microwave Assisted Organic Synthesis*, ed. J. P. Tierney and P. Lidström, Blackwell Publishing/CRC Press, Oxford, 2005.

21 (*a*) A. K. Mukerjee and R. C. Srivastava, *Synthesis*, 1973, 327; (*b*) *Chemistry and Biology of* β-*Lactam Antibiotics*, ed. R. B. Morin and M. Gorman,Academic Press, New York, 1982, vol. 1–3; (*c*) *The Chemistry of* β-*Lactam*, ed. M. I. Page, Chapman and Hall, London, 1997; (*d*) *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, Berlin, 1999.

22 N. A. Bokach, V. Yu. Kukushkin, M. Haukka, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Inorg. Chem.*, 2003, **42**, 3602.

23 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

24 G. M. Sheldrick, *SHELXL-97*, University of Gottingen, Germany, 1997.

25 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.