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The metalla-Pinner reaction between Pt(IV)-bound nitriles and alkylated oxamic and oximic forms of hydroxamic acids

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The nitrile ligands in the platinum(IV) complexes *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et, CH_2Ph) and *cis*/*trans*-$[PtCl_4(MeCN)(Me_2SO)]$ are involved in a metalla-Pinner reaction with *N*-methylbenzohydroxamic acid (*N*-alkylated form of hydroxamic acid, *hydroxamic* form; **F1**), PhC(=O)N(Me)OH, to achieve the imino species $[PtCl_4\{NH{=}C(R)ON(Me)C(=O)Ph\}_2]$ (**1**–**3**) and $[PtCl_4\{NH{=}C(Me)ON(Me)C(=O)Ph\}(Me_2SO)]$ (**7**), respectively. Treatment of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et) and *cis*/*trans*-$[PtCl_4(MeCN)(Me_2SO)]$ with the *O*-alkylated form of a hydroxamic acid (*hydroximic* form), *i.e.* methyl 2,4,6-trimethylbenzohydroximate, 2,4,6-$(Me_3C_6H_2)C(OMe){=}NOH$ (**F2A**), allows the isolation of $[PtCl_4\{NH{=}C(R)ON{=}C(OMe)(2,4,6\text{-}Me_3C_6H_2)\}_2]$ (**5**, **6**) and $[PtCl_4\{NH{=}C(Me)ON{=}C(OMe)(2,4,6\text{-}Me_3C_6H_2)\}(Me_2SO)]$ (**8**), correspondingly. In accord with the latter reaction, the coupling of nitriles in *trans*-$[PtCl_4(EtCN)_2]$ with methyl benzohydroximate, PhC(OMe)=NOH (**F2B**), gives $[PtCl_4\{NH{=}C(Et)ON{=}C(OMe)Ph\}_2]$ (**4**). The addition proceeds faster with the *hydroximic* **F2**, rather than with the *hydroxamic* form **F1**. The complexes **1**–**8** were characterized by C, H, N elemental analyses, FAB^+ mass-spectrometry, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies. The X-ray structure determinations have been performed for both hydroxamic and hydroximic complexes, *i.e.* **2** and **6**, indicating that the imino ligands are mutually *trans* and they are in the *E*-configuration.

Introduction

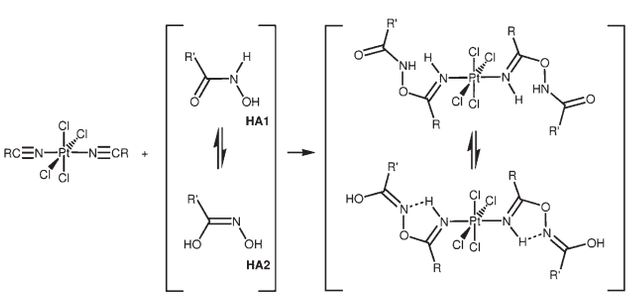
In general, the metal-mediated interaction between two organic molecules and/or ligands to give a more complex molecular fragment is of basic scientific interest and also has potential industrial applications.[1] In particular, transformations of organonitriles involving metal centres play an important role in both laboratory and industry due to the well-recognized chemical versatility of the RCN species.

Nitrile ligands usually do not behave either as strong σ-donors or effective π-electron acceptors and this imparts them with a labile character and, consequently, their complexes have been widely applied as convenient starting materials in coordination chemistry.[2] However, in spite of their limited coordination ability, RCN species can be effectively activated by ligation to a metal centre, which often results in an enhancement of the electrophilicity of the unsaturated nitrile carbon atom, thus promoting addition of a nucleophile which results in a great variety of compounds with C–O, C–S and C–N bonds of various types. The application of organonitrile transition metal complexes in synthetic chemistry has been surveyed in a number of reviews[2–7] including the ones written by two of us.[2,6,7]

One of the recent themes in the reactions of RCN ligands is the application of nucleophiles with NOH moieties.[6] Thus, our group has observed a coupling between platinum(IV) complexes of the type $[PtCl_4(RCN)_2]$ and both 'simple' and functionalized oximes ($R^1R^2C{=}NOH$[8]), *vic*-dioximes [HON=(spacer)=NOH[9]] or dialkylhydroxylamines (R^1R^2NOH[10]) which led to the formation of $[PtCl_4\{NH{=}C(R)ON{=}CR^1R^2\}_2]$, $[PtCl_4\{NH{=}C(R)ON{=}(spacer){=}NOH\})_2]$ and $[PtCl_4\{NH{=}C(R)ONR^1R^2\}_2]$, respectively. This RCN–'NOH' coupling has also been extended to Re(IV)[11] and Rh(III)[12] organonitrile complexes. We also found that Ag^+ or Cu^{2+} ions catalyze the coupling of dialkylcyanamides with oximes at a Pt(II) centre.[13]

It is worthwhile to mention that in the initial stage of our studies, the reactions between nitriles and oximes observed at *inert* metal centres had purely a basic character, whereas later—being performed at kinetically *labile* metal centres, *e.g.* Co(III),[14] Ni(II)[15] and Zn(II)[16,17]—these systems became of a more applied character insofar as they opened up attractive routes to synthesis of amidines,[14] acyl amides,[15] imidoylamidines[15] and to efficient catalytic conversion of RCN to the corresponding carboxamides.[16,17] The latter findings gave a new strong motivation for further exploration of the reactions with NOH-type nucleophiles.

Recently, as a continuation of our studies on oxime and hydroxylamine reactions with (RCN)[M] complexes, we attempted to employ another type of nucleophile, *i.e.* hydroxamic acids (where the N *amide* atom in the sp^2 hybridization[18] is different to the sp^3 *amine* nitrogen in oximes and hydroxylamines) (**HA1** ⇌ **HA2**, Scheme 1), and observed a coupling resulting in the imino complexes $[PtCl_4\{NH{=}C(Et)ON{=}C(OH)(C_6H_4R)\}_2]$, which derived from a novel metalla-Pinner[18] reaction. The results obtained[18] give *collateral* evidence in favor of a concurrent formation of the two coordinated tautomers (which correspond to oxamic **HA1** and oximic **HA2** forms of the nucleophile, Scheme 1), in a ratio depending on both experimental conditions and type of hydroxamic acid employed. For a better understanding of the nitrile–hydroxamic acid coupling we decided to perform a further study and to investigate reactions between the two tautomeric forms (**F1** *vs.* **F2**, Scheme 2) of hydroxamic acids 'frozen' by *N*- or *O*-alkylation, respectively.



Scheme 1

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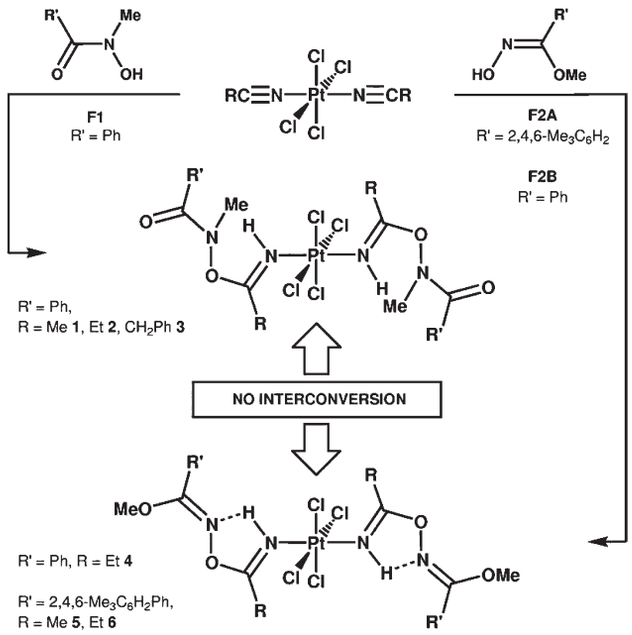

Scheme 2

The essential goals of this work were two-fold: (i) to shed light on the mechanism of the nitrile–hydroxamic acid coupling and (ii) to study the coupling between ligated nitriles and a novel type of nucleophile such as OMe-functionalized oxime (**F2**, Scheme 2). All obtained results are reported in this article.

Results and discussion

Platinum(IV)-mediated nucleophilic additions

The coupling between the nitriles ligated to a Pt(IV) centre and *hydroxamic* (*N*-methylbenzohydroxamic acid **F1**) and *hydroximic* (methyl 2,4,6-trimethylbenzohydroximate **F2A** and methyl benzohydroximate **F2B**) tautomeric forms of hydroxamic acids, 'frozen' by alkylation, readily occurs in CH_2Cl_2 to accomplish complexes **1**–**6** (Scheme 2) and $[PtCl_4\{NH{=}C(Me)ON(Me)C(=O)Ph\}(Me_2\underline{S}O)]$ (**7**) and $[PtCl_4\{NH{=}C(Me)ON{=}C(OMe)(2,4,6\text{-}Me_3C_6H_2)\}(Me_2\underline{S}O)]$ (**8**) (see Experimental).

The propionitrile complex *trans*-$[PtCl_4(EtCN)_2]$ is well soluble in dichloromethane and the reactions can be conducted in homogeneous liquid phase thus allowing the qualitative comparison of reaction rates of the two forms. Hence, *trans*-$[PtCl_4(EtCN)_2]$ reacts with **F2A** or **F2B** for *ca.* 15 min at 20–25 °C to give $[PtCl_4\{NH{=}C(Et)ON{=}C(OMe)(2,4,6\text{-}Me_3C_6H_2)\}_2]$ (**6**) and $[PtCl_4\{NH{=}C(Et)ON{=}C(OMe)Ph\}_2]$ (**4**), respectively, while treatment of *trans*-$[PtCl_4(EtCN)_2]$ with **F1**, to furnish $[PtCl_4\{NH{=}C(Et)ON(Me)C(=O)Ph\}_2]$ (**2**), proceeds under heating at 45–47 °C for *ca.* 2–3 h. These observations illustrate a considerable difference in the reactivity for both types of reagents indicating that the addition proceeds easily with the hydroximic **F2**, rather than with the hydroxamic form **F1**.

For all other cases (*i.e.* in *trans*-$[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph) with **F1** to give **1** and **3**, respectively; in *trans*-$[PtCl_4(MeCN)_2]$ with **F2A** to yield **5**; and in *cis*/*trans*-$[PtCl_4(MeCN)(Me_2\underline{S}O)]$ with **F1** and **F2A** to achieve **7** and **8**, correspondingly) the reactions are heterogeneous owing to the rather poor solubility of the Pt(IV) starting materials and they all proceed under heating (45–47 °C) for *ca.* 2–3 h. We anticipate that the rate determining step of the overall process is then the dissolution of the starting nitrile complexes. It is important that the heterogeneous reactions can be drastically accelerated by microwave irradiation (100 W) and good yields of **1**, **3**, **5**, **7** and **8** can be achieved for 20 min at 45–47 °C.

Neither **F1** nor **F2** react with RCN in the absence of Pt(IV) centre and this indicates that the coupling is Pt(IV)-mediated.

Characterization of the complexes

Complexes **1**–**8** were isolated in 75–90% yields in both conventional thermal and microwave syntheses. Elemental analyses (C, H, N), FAB-MS, IR and ^1H and $^{13}C\{^1H\}$ NMR spectra, and X-ray data for **2** and **6** (see below) are in a good agreement with the proposed structure of Pt(IV) complexes with the newly formed imino ligands.

In the IR spectra, **1**–**8** show no bands of ν(C≡N) in the range of 2270–2400 cm^{-1} [for *trans*-$[PtCl_4(EtCN)_2]$[19] ν(C≡N) at 2340 cm^{-1}] but display one intense band in the range between 1640 and 1670 cm^{-1} due to ν(C=N) stretching vibrations from the imino ligands NH=C(R)ON(Me)C(=O)R′ (**1**–**3**, **7**) or two intense bands in the ranges of 1640–1670 and 1610–1630 cm^{-1} (**4**–**6**, **8**) assigned, in the latter case, to two different ν(C=N) stretches in the imino species. All these observations are in a good agreement with those for related addition products of oxime (*e.g. trans*-$[PtCl_4\{NH{=}C(Me)ON{=}CMe_2\}_2]$[8]) and hydroxamic acids (*e.g. trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(OH)(Ph)\}_2]$[18]) to nitriles bound to Pt(IV) centres.

In the ^1H NMR spectra, **1**–**3** and **7** exhibit a signal from the alkyl group of [N(*Me*)C(=O)Ph] in the range of 3.25–3.40 ppm, whereas **4**–**6** and **8** display the signal of the methoxy group from [N=C(*OMe*)R′] which emerges in the range of 3.50–3.60 ppm. In addition, **1**–**8** display a broad peak in the range of 8.20–8.80 ppm from the imine hydrogen of the imino ligand and these data correspond well to those found for the imino-complexes $[PtCl_4\{NH{=}C(R)R'\}_2]$ (R′ = ONR$_2$″,[10] ON=CR$_2$″,[8] ONHC(=O)R″[18]). This low field position of the N*H* signal in the spectra is coherent with the position of the C=N*H* proton involved in hydrogen bond in solution,[8] which is also detected in the crystal structure of **6**.

The $^{13}C\{^1H\}$ NMR spectra of **1**–**8** display no signal of the carbon from the C≡N group (usually appears at 115–125 ppm, *e.g.* at 119 ppm for *trans*-$[PtCl_4(EtCN)_2]$[19]) of the starting material, whereas a new signal from the C=N group emerges in the typical[8–10] range of 160–170 ppm. Complexes **1**–**3** and **7** display the signal of the methyl group from [N(*Me*)C(=O)] in the range of 37–47 ppm, while **4**–**6** and **8** exhibit the peak from the methoxy group [N=C(*OMe*)R′] at a lower field (57–61 ppm).

X-ray structure determinations

The X-ray structure determinations have been performed for both hydroxamic and hydroximic complexes, *i.e.*, *trans*-$[PtCl_4\{NH{=}C(Et)ON(Me)C(=O)Ph\}_2]$ (**2**) and *trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(OMe)\{C_6H_2(2,4,6\text{-}Me_3)\}_2]$ (**6**) (Figs. 1, 2).

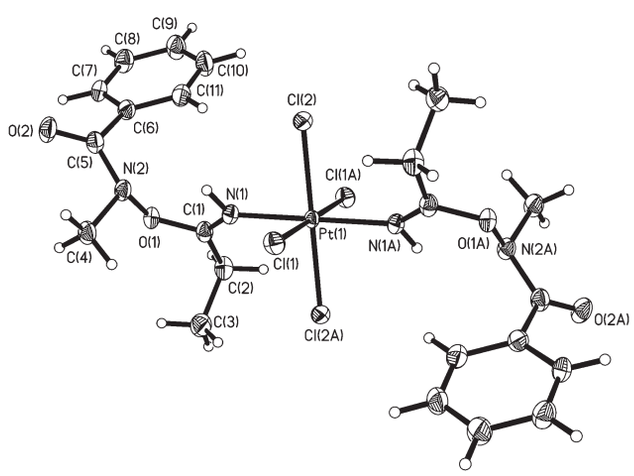

Fig. 1 Molecular structure of **2**. The thermal ellipsoids are drawn at the 50% probability level.

The coordination polyhedra of both compounds are slightly distorted octahedra; the iminoacyl ligands are mutually *trans* and both of them are in the *E*-configuration. The Pt–Cl [2.3151(10)–2.3191(10) Å for **2** and 2.3272(9)–2.3086(8) Å for **6**] and Pt–N

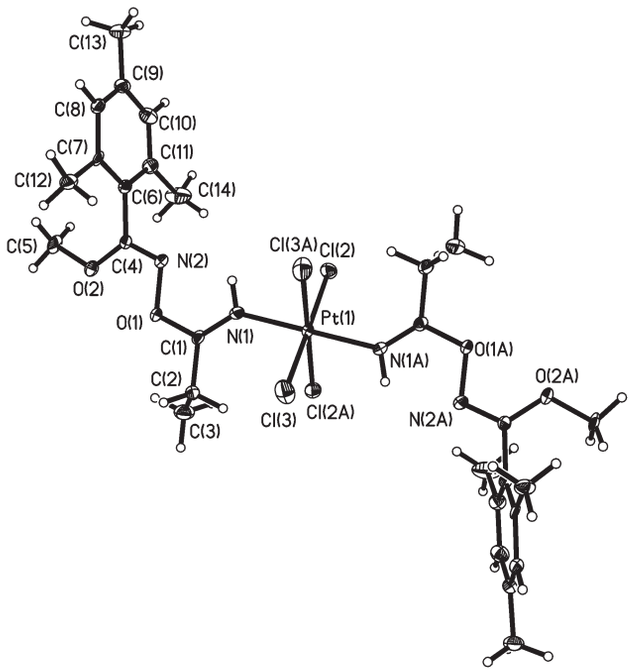

Fig. 2 Molecular structure of **6**. The thermal ellipsoids are drawn at the 50% probability level.

[2.016(3) Å for **2** and 2.012(3) Å for **6**] bond lengths and also all bond angles around the Pt centre are normal, and they agree with those observed in the majority of the previously characterized platinum(IV) complexes with iminoligands, *i.e.* *trans*-[$PtCl_4${NH=C(Me)ON=CR_2}$_2$][8] or *trans*-[$PtCl_4${NH=C(Me)ONR_2}$_2$].[10] The two C=NH bonds in both compounds are equal within 3σ [1.283(6) Å for **2** and 1.265(3) Å for **6**] and these distances are very close to the typical values (1.26–1.29 Å)[20] for the C=N double bonds.

In **6**, the CN–H and NH···H distances in the imine ligand and the C–N–H, C–O–N and N–H···H angles clearly indicate that the *E*-configuration of the ligands is stabilized by the N–H···H hydrogen bond between the imine C=N*H* atom and the hydroximic nitrogen [N(1)–H(1) 0.8800(5), N(1)–H(1)···N(2) 2.07(3), and N(1)–H(1)–N(2) 113(8)°] and this agrees with the *E*-configuration supported by H-bonding in similar systems, *i.e.* *trans*-[$PtCl_4${NH=C(Me)ON=CR_2}$_2$].[8] The H-bond was not found in **2** insofar as the hydroxamic nitrogen is blocked by the methyl group.

Concluding remarks

The results from this work can be considered from the following perspectives. First, by reacting the (nitrile)Pt(IV) complexes with the oxamic form **F1** (Scheme 2), we proved that the coupling might occur with NOH-type nucleophiles where the N atom has the sp^2 hybridization, whereas all other NOH nucleophiles previously studied were of (sp^3-N)OH-type. Second, we observed that both oxamic (**F1**) and oximic (**F2**) forms of hydroxamic acid, 'frozen' by alkylation, can act as a nucleophile towards a metal-activated nitrile and be involved in the metalla-Pinner reaction. Although the reactivity of both forms is different and the oximic form reacts faster than the oxamic one, conclusions on preferences in nucleophilic attack by one or another tautomeric form of hydroxamic acid should be taken with great care and only after a quantitative kinetic study. Third, the current study confirms our assumption[18] on concurrent formation of the two coordinated tautomers (Scheme 1). Fourth, we found that the OMe-functionalized oxime effectively couples with the (nitrile)Pt species to give imino complexes and this reaction is an extension of the previously observed addition of other oximes RR′C=NOH (R′ = alkyl, aryl, NH_2, Cl)[8–12] to another type of oxime, *i.e.* with R′ = OMe.

Experimental

Materials and instrumentation

N-methylbenzohydroxamic acid (**F1**, Scheme 2),[21] methyl benzohydroximate (methyl *N*-hydroxybenzimidate) (**F2B**)[22] and methyl 2,4,6-trimethylbenzohydroximate [methyl *N*-hydroxy-(2,4,6-trimethyl)benzimidate] (**F2A**)[23] were synthesized using published procedures. Solvents were obtained from commercial sources and used as received but methanol and dichloromethane were dried by conventional methods. The complexes *trans*-[$PtCl_4(RCN)_2$] (R = Me, Et, CH_2Ph)[8,19] and *cis*/*trans*-[$PtCl_4$(MeCN)(Me_2SO)][24] were prepared as previously described. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (≈1.28 × 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a JASCO FTS 3000MX instrument in KBr pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (max power 300 W) which is fitted with a rotational system and an IR detector of temperature.

A. Addition of *N*-methylbenzohydroxamic acid to nitriles in *trans*-[$PtCl_4(RCN)_2$]

In a typical experiment, *trans*-[$PtCl_4(RCN)_2$] (0.11 mmol) was suspended in dichloromethane (5 mL) at 20–25 °C, *N*-methylbenzohydroxamic acid (0.033 g, 0.22 mmol) was added, and the reaction mixture was treated with 100 W focused microwave irradiation in a sealed tube at 45–47 °C for *ca.* 20 min (the reaction also proceeds without microwave irradiation under heating at 45–47 °C for *ca.* 2–3 h) until the starting material was dissolved and the mixture was homogenized. The solution was evaporated to dryness and the bright yellow residue was washed with diethyl ether (two 10 mL portions) and dried in air at room temperature. Yield is 75–90%, based on Pt.

[$PtCl_4${NH=C(Me)ON(Me)C(=O)Ph}$_2$] (1)

Anal. Calcd for $C_{20}H_{22}N_4Cl_4O_4Pt$: C, 33.30; H, 3.35; N, 7.77. Found: C, 33.53; H, 3.40; N, 7.60%. FAB$^+$-MS, *m*/*z*: 748 [M]$^+$, 678 [M − 2Cl]$^+$, 643 [M − 3Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3216 mw *ν*(N–H), 1657 s *ν*(C=N), 1438 s *ν*(C=C), 830 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.24 (s, 3*H*, Me), 3.38 (s, 3*H*, NMe), 7.47–7.61 (m, 5*H*, Ph), 8.67 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in $CDCl_3$, *δ*: 20.2 (Me), 38.2 (NMe), 127.5–134.2 (Ph), 164.8 and 178.5 (C=O and HN=C).

[$PtCl_4${NH=C(Et)ON(Me)C(=O)Ph}$_2$] (2)

Anal. Calcd for $C_{22}H_{26}N_4Cl_4O_4Pt$: C, 35.26; H, 3.77; N, 7.48. Found: C, 35.53; H, 3.68; N, 7.50%. FAB$^+$-MS, *m*/*z*: 720 [M]$^+$, 685 [M − Cl]$^+$, 650 [M − 2Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3210 mw *ν*(N–H), 1655 s *ν*(C=N), 810 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.63 (t, *J* 7.5 Hz, 3*H*, Me), 3.36 (s, 3*H*, NMe), 7.47–7.61 (m, 5*H*, Ph), 8.65 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in $CDCl_3$, *δ*: 10.2 (CH_3) and 25.3 (CH_2)(Et), 37.5 (NMe), 127.0–133.0 (Ph), 164.8 and 178.5 (C=O and HN=C).

[$PtCl_4${NH=C(CH_2Ph)ON(Me)C(=O)Ph}$_2$] (3)

Anal. Calcd for $C_{32}H_{32}N_4Cl_4O_4Pt$: C, 44.08; H, 3.70; N, 6.43. Found: C, 42.50; H, 3.68; N, 6.50%. FAB$^+$-MS, *m*/*z*: 837 [M − Cl]$^+$, 802 [M − 2Cl]$^+$, 731 [M − 4Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3228 mw *ν*(N–H), 1665 s *ν*(C=N), 840 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 3.29 (s, 3*H*, NMe), 4.53 (s, 2*H*, CH_2Ph), 7.10–8.14 (m, 10*H*, Ph), 8.85 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in $CDCl_3$, *δ*: 37.5 (NMe), 64.5 (*C*H_2Ph), 127.0, 128.1, 129.9 and 133.0 (Ph), 164.8 and 178.5 (C=O and HN=C).

Table 1 Crystallographic data for **2** and **6**

	2	**6**
Empirical formula	$C_{22}H_{28}N_4Cl_4O_4Pt$	$C_{28}H_{40}N_4Cl_4O_4Pt$
FW	749.37	833.53
T/K	100(2)	100(2)
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	F d d 2
a/Å	21.8355(7)	18.5176(12)
b/Å	8.6425(4)	28.9131(15)
c/Å	15.8421(6)	12.3169(12)
β/°	112.260(3)	90
Z	4	8
μ(Mo Kα)/mm^{-1}	5.492	4.618
Collected reflections	15484	12006
Unique reflections	3119	3481
R_{Int}	0.0432	0.0192
$R_1{}^a$ ($I \geq 2\sigma$)	0.0359	0.0169
$wR_2{}^b$ ($I \geq 2\sigma$)	0.0912	0.0447

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond lengths and angles for **2** and **6**

	2	**6**
Pt(1)–Cl(1)	2.316(1)	
Pt(1)–Cl(2)	2.319(1)	2.3286(8)
Pt(1)–Cl(3)		2.3072(9)
Pt(1)–N(1)	2.016(3)	2.012(2)
N(1)–C(1)	1.283(6)	1.265(3)
C(1)–O(1)	1.358(5)	1.354(3)
O(1)–N(2)	1.442(5)	1.459(3)
Cl(1)–Pt(1)–Cl(2)	90.51(4)	
Cl(2)–Pt(1)–Cl(3)		178.48(4)
N(1)–Pt(1)–Cl(1)	85.25(10)	
N(1)–Pt(1)–Cl(2)	85.19(11)	85.24(8)
N(1)–Pt(1)–Cl(3)		94.25(8)
Pt(1)–N(1)–C(1)	134.9(3)	135.3(2)
N(1)–C(1)–O(1)	120.7(4)	122.1(2)
C(1)–O(1)–N(2)	114.0(3)	110.7(2)

B. Addition of methyl benzohydroximate and methyl 2,4,6-trimethylbenzohydroximate to nitriles in *trans*-[$PtCl_4(RCN)_2$]

In a typical experiment, *trans*-[$PtCl_4(RCN)_2$] (0.11 mmol) was suspended in dichloromethane (5 mL) at 20–25 °C, and the corresponding oxime (0.22 mmol) was added. The reaction mixture was stirred for 15 min (in the case of *trans*-[$PtCl_4(MeCN)_2$] heated at 45–47 °C for *ca.* 1 h) until the homogenization of the mixture was completed. The slight yellow solution was evaporated to dryness and the bright yellow residue was washed with diethyl ether (two 10 mL portions) and dried in air at room temperature. Yield is 85–90%, based on Pt.

[$PtCl_4${NH=C(Et)ON=C(OMe)Ph}$_2$] (4)

Anal. Calcd for $C_{22}H_{26}N_4Cl_4O_4Pt$: C, 35.26; H, 3.77; N, 7.48. Found: C, 35.53; H, 3.68; N, 7.50%. FAB$^+$-MS, *m*/*z*: 748 [M]$^+$, 678 [M − 2Cl]$^+$, 643 [M − Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3220 mw *ν*(N–H), 1655 s *ν*(C=N), 1610 s *ν*(C=N), 1448 s *ν*(C=C), 854 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 1.33 (t, *J* 7.5 Hz, 3*H*, CH_2*Me*), 2.20 (s, 3*H*, OMe), 3.18 (quart, *J* 7.5 Hz, 2*H*, CH_2Me), 7.47–7.61 (m, 5*H*, Ph), 8.65 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in $CDCl_3$, *δ*: 11.0 (CH_3) and 24.3 (CH_2)(Et), 57.5 (OMe), 127.2–133.5 (Ph), 164.8 and 178.5 [N=*C*(OMe) and HN=C].

[$PtCl_4${NH=C(Me)ON=C(OMe)(2,4,6-$Me_3C_6H_2$)}$_2$] (5)

Anal. Calcd for $C_{26}H_{36}N_4Cl_4O_4Pt$: C, 38.77; H, 4.50; N, 6.96. Found: C, 38.87; H, 4.55; N, 6.80%. FAB$^+$-MS, *m*/*z*: 769 [M − Cl]$^+$, 734 [M − 2Cl]$^+$, 699 [M − 3Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3210 mw *ν*(N–H), 1666 s *ν*(C=N), 1616 s *ν*(C=N), 1448 s *ν*(C=C), 854 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.75 (s, 3*H*, Me), 2.26 (s, 6H, *o*-Me) and 2.35 (s, 3H, *p*-MeC_6H_2), 3.59 (s, 3*H*, OMe), 6.96–6.98 (d, 2*H*, Ph), 8.64 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in DMSO-d_6, *δ*: 10.8 (CH_3), 19.7 and 21.0 (C_6H_2*Me*$_3$), 57.2 (OMe), 123.5, 129.6, 138.3 and 142.3 (Ph), 163.2 and 176.6 [N=*C*(OMe) and HN=C].

[$PtCl_4${NH=C(Et)ON=C(OMe)(2,4,6-$Me_3C_6H_2$)}$_2$] (6)

Anal. Calcd for $C_{28}H_{40}N_4Cl_4O_4Pt$: C, 40.35; H, 4.84; N, 6.72. Found: C, 38.73; H, 4.88; N, 6.30%. FAB$^+$-MS, *m*/*z*: 797 [M − Cl]$^+$, 762 [M − 2Cl + H]$^+$. IR spectrum (selected bands), cm^{-1}: 3225 mw *ν*(N–H), 1655 s *ν*(C=N), 1618 s *ν*(C=N), 1448 s *ν*(C=C), 854 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 1.68 (t, *J* 7.5 Hz, 3*H*, CH_2*Me*), 2.27 (s, 6H, *o*-Me) and 2.34 (s, 3H, *p*-MeC_6H_2), 3.26 (s, *J* 7.5 Hz, 2*H*, *CH*$_2$Me), 3.58 (s, 3*H*, OMe), 6.95 (s, 2*H*, Ph), 8.51 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in DMSO-d_6, *δ*: 10.7 (CH_3) and 25.2 (CH_2)(Et), 19.6 and 21.2 (C_6H_2*Me*$_3$), 60.6 (OMe), 127.3, 128.3, 128.6, 128.8, 128.9, 131.9 and 132.1 (Ph), 162.4 and 176.5 [N=*C*(OMe) and HN=C].

Complexes **7** and **8** were prepared by methods **A** and **B**, respectively, in accord with the procedures described above for synthesis of the corresponding complexes starting from *trans*-[$PtCl_4(MeCN)_2$].

[$PtCl_4${NH=C(Me)ON(Me)C(=O)Ph}(Me_2SO)] (7)

Anal. Calcd for $C_{20}H_{22}N_4Cl_4O_4Pt$: C, 23.74; H, 2.99; N, 4.61. Found: C, 23.94; H, 3.07; N, 4.50%. FAB$^+$-MS, *m*/*z*: 572 [M − Cl + H]$^+$, 536 [M − 2Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3274 mw *ν*(N–H), 1657 s *ν*(C=N), 1444 s *ν*(C=C), 855 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.75 (s, 3H, Me), 3.38 (s, 3*H*, NMe), 7.34–7.64 (m, 5*H*, Ph), 8.13 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR spectrum in DMSO-d_6, δ: 11.5 (Me), 41.0 (Me_2SO), 113.7–130.2 (Ph), 164.8 and 178.5 (C=O and HN=C).

[$PtCl_4${NH=C(Me)ON=C(OMe)(2,4,6-$Me_3C_6H_2$)}(Me_2SO)] (8)

Anal. Calcd for $C_{22}H_{26}N_4Cl_4O_4Pt$: C, 27.75; H, 3.73; N, 4.31. Found: C, 28.87; H, 3.31; N, 4.29%. FAB$^+$-MS, *m*/*z*: 613 [M − Cl]$^+$, 578 [M − 2Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3216 mw *ν*(N–H), 1660 s *ν*(C=N), 1614 s *ν*(C=N), 1448 s *ν*(C=C), 854 s *δ*(C–H). ^{1}H NMR spectrum in $CDCl_3$, *δ*: 2.18 (s, 3*H*, Me), 2.27 (s, 6*H*, *o*-Me) and 2.35 (s, 3*H*, *p*-MeC_6H_2), 2.80 (s, 6*H*, Me_2SO), 3.59 (s, 3*H*, OMe), 6.97 (s, 2*H*, Ph), 8.25 (br, 1*H*, C=NH). ^{13}C{^{1}H} NMR in DMSO-d_6, *δ*: 10.7 (CH_3), 19.6 and 21.2 (C_6H_2*Me*$_3$), 41.2 (Me_2SO), 57.1 (OMe), 123.2, 128.6, 137.3 and 141.1 (Ph), 163.2 and 176.7 [N=*C*(OMe) and HN=C].

X-ray structure determinations

The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Single crystals of **2** and **6** were mounted in inert oil within the cold gas stream of the diffractometer. The Denzo-Scalepack[25] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SIR-97 or SIR-2002 programs.[26,27] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.14 or SADABS v.2.10)[28,29] was applied to all data (T_{min}/T_{max} values were 0.38061/0.47286 and 0.4204/0.5894 respectively for **2** and **6**). All structures were refined with SHELXL-97[30] and WinGX graphical user interface.[31] In **2**, NH hydrogens were located from the difference Fourier map but not refined. All other hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

CCDC reference numbers 237749 and 237750.

See http://www.rsc.org/suppdata/dt/b4/b406600f/ for crystallographic data in CIF or other electronic format.

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