Platinum(IV)-mediated coupling of dione monoximes and nitriles: a novel reactivity pattern of the classic oxime-based chelating ligands

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The reaction between dione monoximes and platinum(IV) nitrile complexes leads, instead of the conventional substitution, to metal-mediated coupling, giving iminoacylated species which, on being liberated, undergo disintegration to the nitrile and the oxime.

Introduction

It is well documented that various dione monoximes (**A** in Fig. 1),[1] including the classic 1,2-naphthoquinone 1-monoxime (⇌ nitrosonaphthol) (**B** in Fig. 1),[2,3] readily bind transition metal ions, forming strong, often deeply coloured, chelates (**C** in Fig. 1). These properties give rise to some practical applications of these reagents, *e.g.*, photometric determination of metals[4] and the use of their metal complexes as synthetic dyestuffs and pigments.[5] Special attention should be drawn to the fact that these ligands are of biological importance, and this gives a strong motivation for studies of their metal-binding properties.[6]

As far as the platinum(II) ion is concerned, it reacts with dione monoximes forming complexes of high stability and this property has been successfully used for quantitative analysis of Pt(II) species in aqueous solution[5,7] and also for chromatographic separations of platinum(II) chelates.[8] The number of studies on reactions between platinum(IV) complexes and dione monoximes is less than that with platinum(II) and, in this respect, it is worth mentioning a few works on extraction and photometric analysis of platinum(IV) species involving dione monoximes[9] and a detailed study on the reaction between butane-2,3-dione monoxime and trimethylplatinum(IV), leading to the N,O-ligation of the bidentate ligand to the Pt(IV) center.[10] The abundance of accounts on the bidentate complexation of dione monoximes to different metal centres is in dramatic contrast with the insignificant amount of works on other reactivity patterns of those species. To the best of our knowledge, the only examples of non-conventional reactions between metal complexes and dione monoximes include the oxidative addition of 4-isonitroso-3-(*R*-substituted)-isoxazol-5(4*H*)-one and 3-(*R*-substituted)-isoxazolone to a platinum(0) centre *via* O–H bond rupture[11] and the platinum(II)-[12] and nickel(II)-templated[13] condensation involving dione monoximes to give macrocyclic complexes.

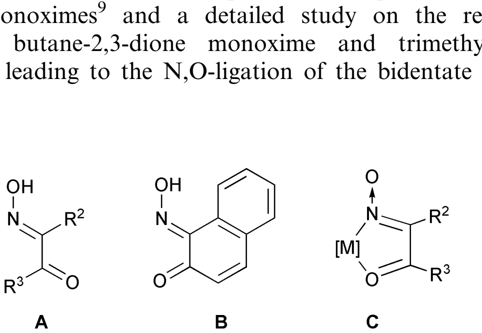

Fig. 1 The general structure of dione monoximes (**A**) and their transition metal complexes (**C**), and the structure of 1,2-naphthoquinone 1-monoxime (**B**).

In view of our general interest in ligand reactivity and catalysis,[1,14–20] we have focused our attention in recent years on reactions of metal-activated organonitriles[21–26] and this topic has been reviewed.[20] In particular, we have observed an addition of oximes, HON=CR^{1}R^2, to nitriles bound to the platinum(IV) centre in [PtCl$_4$(RCN)$_2$], to give the iminoacylated products [PtCl$_4${HN=C(R)ON=CR^{1}R^2}$_2$],[21] and this reaction was later extended to Pt(II),[22] Rh(III),[23] Re(IV)[24] and Co(II)[25] nitrile complexes; although in the case of cobalt(II), the iminoacylated species were just assumed as intermediates. As a further step in the exploration of the oxime–nitrile coupling, we attempted the reaction of [PtCl$_4$(RCN)$_2$] with *vic*-dioximes, HON=C(R′)C(R′)=NOH, and found, instead of chelation, quantitative one-end addition of these oximes to the ligated nitrile species to generate the Pt(IV)-based metallaligands [PtCl$_4${HN=C(R)ON=C(R′)C(R′)=NOH}$_2$].[27]

As a part of our ligand reactivity programme, we have now studied the addition of another type of chelating ligands, *i.e.* dione monoximes, to the platinum(IV) compounds [PtCl$_4$(RCN)$_2$] (R = Me, Et). Our reasons for wanting to extend previous work on the addition of *vic*-dioximes[27] to these compounds were at least three-fold. Firstly, we intended to show whether the addition is restricted only to *vic*-dioximes or has a more general character for other bifunctional oxime species. Secondly, if the one-end addition of bifunctional reagents was successful and liberation of the newly formed

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ligand could be performed, a route to imines inaccessible in pure organic chemistry could be found. Thirdly, by conducting the coupling, synthons with a remote uncoordinated peripheral group for further assembly might be obtained. Herein, we report on an unprecedented reactivity mode of dione monoximes, *i.e.* platinum(IV)-mediated coupling between these species and coordinated nitriles, which leads to a novel type of *O*-acylated dione monoxime that can be liberated from the binding platinum centre, thus providing a significant contribution towards the achievement of our three main aims.

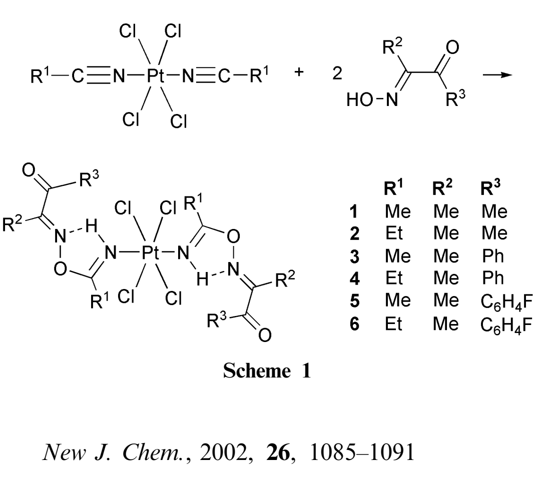
Results and discussion

Coupling of dione monoximes and Pt(IV)-bound nitriles and characterisation of products

The dione monoximes react with the platinum(IV) nitrile compounds $[\mathrm{PtCl_4(R^1CN)_2}]$ ($\mathrm{R^1}$ = Me, Et) in a non-conventional way for these classic chelating ligands, forming the products of the addition of the OH group across the C≡N bond of the platinum(IV)-bound nitrile (Scheme 1). This dione monoxime coupling is all the more surprising if one takes into account the weak donor properties of organonitriles,[28] which determine the ability of nitrile complexes to serve as useful synthons for the synthesis of different metal compounds by substitution reactions.[29]

This reaction proceeds under more drastic conditions (35–40 °C, 1 d) as compared to the nitrile–oxime couplings with simple oximes bearing *donor* groups, *e.g.* $\mathrm{(Alkyl)_2C{=}NOH}$ (70 °C, 10 min).[21,27] This observation is consistent with that from previous work[30] which describes the significant retardation of the iminoacylation rate when chloroximes containing a strong *acceptor* substituent, *i.e.* Cl, bound to the C=NOH group were involved. All isolated Pt(IV) compounds *trans*-$[\mathrm{PtCl_4\{NH{=}C(R^1)ON{=}C(R^2)C(R^3)({=}O)\}_2}]$ (**1**–**6**, Scheme 1) gave satisfactory elemental analyses and the expected molecular ion/fragmentation patterns in the FAB$^+$ mass spectra. Complexes were characterised by IR spectroscopy [the absence of C≡N stretching vibrations, the presence of ν(N–H) bands and characteristic ν(C=N) and ν(C=O) peaks were recognized] and by ^{1}H, ^{13}C{^{1}H} and ^{195}Pt NMR spectroscopy (see Experimental).

The coordinated iminoacyl species, formed from *irreversible* nitrile–oxime coupling, exhibit substantial stability towards hydrolysis. Thus, the complexes remain intact in water–acetone mixtures at 40 °C for *ca.* three weeks, and only after that incubation period werethe carboxamide complexes *trans*-$[\mathrm{PtCl_4\{HN{=}C(OH)R^1\}_2}]$[31] detected in trace amounts. We anticipate that the stabilisation, by coordination, of highly unstable—towards both hydrolysis and trimerization—imino compounds, especially those bearing donor substituents, is rather general, although still a little explored phenomenon. Indeed, such stabilisation has been observed not only in platinum(II)[22] and platinum(IV),[21,27] but also in rhodium(III) imino complexes.[23] In addition, the high stability of the imino metal compounds is presumably the main driving force for the condensation between acetone and ammonia coordinated to an Au(III) centre.[32] We hope that the increasing amount of both experimental and theoretical studies on imino metal compounds will further stimulate interest towards a better understanding of the nature of the [M]–imine bond.



	R¹	R²	R³
1	Me	Me	Me
2	Et	Me	Me
3	Me	Me	Ph
4	Et	Me	Ph
5	Me	Me	$\mathrm{C_6H_4F}$
6	Et	Me	$\mathrm{C_6H_4F}$

Scheme 1

X-Ray structure determinations of iminoacylated Pt(IV) complexes

The structures of compounds **1**, **4** and **6** were determined by X-ray single-crystal diffraction. The coordination geometries of the three complexes are slightly distorted octahedra (Fig. 2–4).

In all structures, the Pt atoms are positioned on a crystallographic inversion centre. The Pt–Cl bond distances are in the range from 2.31 to 2.32 Å, and these distances agree well with those in previously characterised platinum(IV) chloride compounds.[21,27] The two iminoacyl ligands in all complexes are mutually *trans*, which is the thermodynamically stable form for complexes having metal centres in a high oxidation state.[27,33] In the iminoacyl ligands, the two C=N bond lengths [1.270–1.277 Å] are almost identical within 3σ and correspond to the mean lengths of C=N double bonds.[34] All these ligated species are in the *E*-configuration as a result of a hydrogen bond between N(1)–H and the oxime N atom; the distances

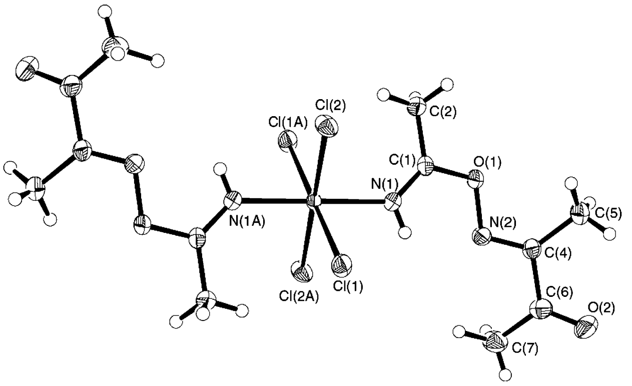


Fig. 2 ORTEP view of complex **1** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

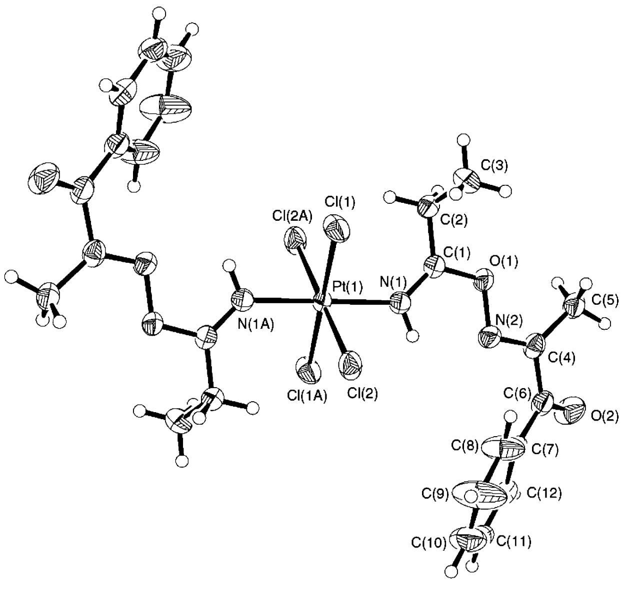


Fig. 3 ORTEP view of complex **4** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

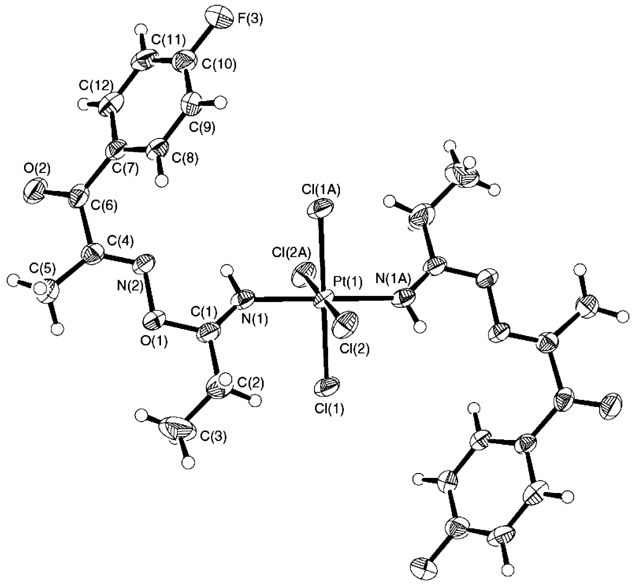


Fig. 4 ORTEP view of complex **6** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

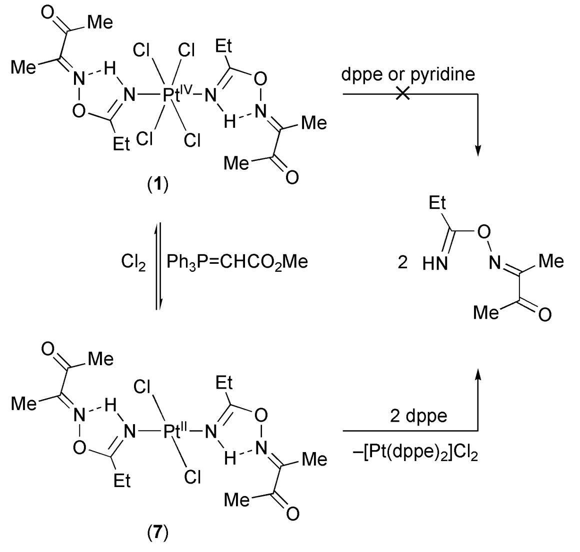
N(1)···N(2), N(1)–H and N(1)H···N(2) are 2.579(3), 0.81(2) and 2.15(2) Å for **1**, 2.585(6), 0.88 and 2.12 Å for **4**, 2.574(8), 0.88 and 2.09 Å for **6**, and 2.556(9), 0.88 and 2.08 Å for **6B**, respectively. The angle N(1)–H···N(2) is 113.3(19), 112.5, 113.6 and 113.4°, respectively. These values are less than the sum of the van der Waals radii for H and N (1.20 + 1.55 = 2.75 Å[35]) and also fall in the typical ranges reported for N···N [2.94–3.15 Å] and H···N [2.20 Å] distances in the case of NH···N bonding.[36] In addition to the *intra*molecular hydrogen-bonding interaction, there is also a weak *inter*molecular hydrogen-bonding interaction between N(1) and O(2) (at $1/2 - x$, $-1/2 + y$, $-1/2 - z$) of the neighboring molecule in **7**. In **6**, the aromatic rings of adjacent molecules are almost parallel. The angle between the ring planes C(7)–C(12) and C(7B)–C(12B) is 3.3°. The closest rings are stacked with a centroid–centroid distance of 3.843 Å. In **4**, this type of stacking is not found. The centroid–centroid distance between the closest ring planes C(7)–C(12) and C(7#)–C(12#) (C at equivalent position $-x$, $-y$, $1 - z$) is much longer, *i.e.* 4.872 Å.

Reduction of complex 1 and liberation of the iminoacylated oxime

We have recently found a useful method for the reduction of different platinum(IV) species in non-aqueous media to the corresponding platinum(II) complexes, using the commercially available phosphorus ylide $Ph_3P{=}CHCO_2Me$.[21] This method can be applied to the reduction of the above complexes and is exemplified here by the conversion of complex **1** to **7** (Scheme 2).

The reaction between **1** and one equiv. of $Ph_3P{=}CHCO_2Me$ proceeds under mild conditions to give a mixture of the platinum-containing product **7**, along with phosphorus-containing species; the latter remain on silica gel on passage of the mixture through a short column filled with this material. The general features of the IR, ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** are similar to those observed for the precursor **1**. The most significant spectroscopic difference between the two complexes is their ^{195}Pt NMR spectra, displaying an almost 2000 ppm shift on going from Pt(IV) [−235 ppm] to Pt(II) [−2044 ppm].

The X-ray crystal structure of complex **7** (Fig. 5) revealed its *trans*-configuration, with the iminoacyl ligands in the *E*-configuration, and inspection of the bond lengths and angles indicates a good agreement with those of the corresponding platinum(IV) complexes (Table 1).



Scheme 2

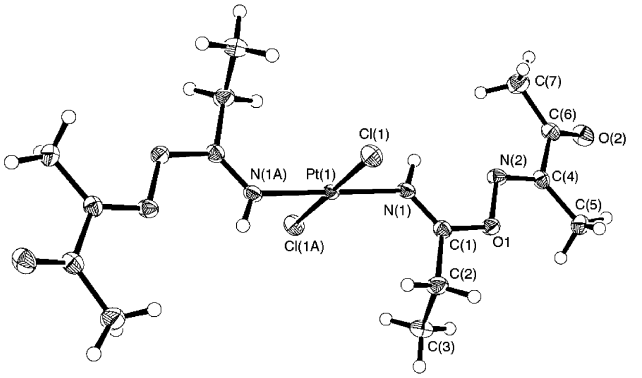


Fig. 5 ORTEP view of complex **7** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

The iminoacylated ligands in **7** were easily liberated by substitution with 2 equiv. of dppe. The reaction is fast in $CDCl_3$ and gives solid $[Pt(dppe)_2]Cl_2$;[37] the latter can be removed by filtration. NMR monitoring of the filtrate allows the identification of the imine, which is unstable and gradually decomposes at room temperature to give, after 1 day, EtCN and the parent oxime (see Experimental). Attempts to liberate the ligand starting from **1** *via* treatment with either dppe or pyridine, as previously,[26] failed and a complex mixture of compounds was detected by ^1H NMR spectroscopy.

Final remarks

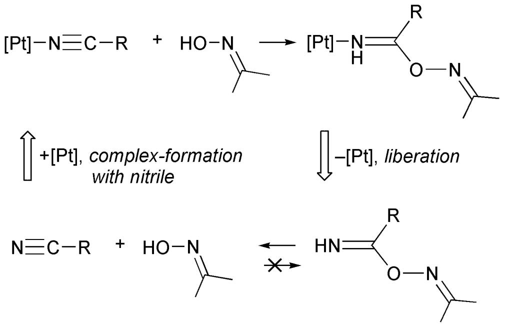
We have observed an unusual reactivity pattern for potential chelating ligands, *i.e.* the unprecedented *irreversible* metal-mediated coupling between dione monoximes and nitriles bound to a Pt(IV) centre. The obtained ligated iminoacylated species were easily liberated from the metal site by reduction with $Ph_3P{=}CHCO_2Me$ followed by displacement with dppe. The imine, having a restricted life-time, *reversibly* decomposes to the organonitrile and the oxime (Scheme 3).

This unusual finding, along with the observation of the absence of any reaction between HON=C(Me)C(Me)C=O and free EtCN, even upon prolonged heating, gives explicit evidence in favour of the metal-mediated process.

It is still worthwhile to mention that: (i) The reactions described here provide a convenient method for the synthesis of iminoacylated oxime species which, to the best of our

Table 1 Selected bond lengths (Å) and angles (°) for **1**, **4**, **6** and **7**

	(1)	**(4)**	**(6)**	**(6B)**	**(7)**
Pt(1)–Cl(1)	2.3170(6)	2.3157(12)	2.3194(18)	2.316(2)	2.3037(7)
Pt(1)–Cl(2)	2.3193(6)	2.3216(12)	2.3167(17)	2.299(2)	
Pt(1)–N(1)	2.018(2)	2.015(4)	2.019(5)	2.026(6)	2.015(2)
N(1)–C(1)	1.270(3)	1.276(6)	1.277(8)	1.270(10)	1.268(4)
C(1)–O(1)	1.356(2)	1.356(6)	1.352(8)	1.359(9)	1.368(3)
O(1)–N(2)	1.434(2)	1.436(5)	1.449(6)	1.436(7)	1.432(3)
N(2)–C(4)	1.277(3)	1.273(6)	1.262(8)	1.284(8)	1.283(4)
Cl(1)–Pt(1)–Cl(2)	89.78(2)	88.95(5)	91.70(7)	90.87(10)	
Cl(1)–Pt(1)–N(1)	86.45(6)	95.07(11)	94.6(2)	95.2(2)	91.04(6)
Cl(2)–Pt(1)–N(1)	94.18(6)	87.08(12)	92.7(2)	86.3(2)	
Pt(1)–N(1)–C(1)	134.8(2)	134.6(4)	135.6(5)	135.0(5)	126.1(2)
N(1)–C(1)–O(1)	121.6(2)	121.6(4)	120.8(6)	120.9(7)	124.7(2)
C(1)–O(1)–N(2)	112.04(15)	112.4(3)	112.3(5)	111.6(5)	113.6(2)
O(1)–N(2)–C(4)	110.6(2)	109.3(4)	109.7(5)	110.0(5)	108.8(2)



Scheme 3

knowledge, were previously unknown, although other *O*-acyl oximes are quite common and efficiently applied as photoinitiators for radical polymerisation[38] and as radical acceptors.[39] It is anticipated that, although unstable, these imino compounds can be used *in situ* when reactions are faster than the decomposition. (ii) The coupling leads to complexes with a remote uncoordinated carbonyl group and it is anticipated that they can be used for further design and assembly of Pt(IV)-containing aggregates involving reactions of the –C=O moiety, *e.g.* the Schiff condensation. Both these projects are under way in our group.

Experimental

Materials and instrumentation

Solvents were obtained from commercial sources and used as received. Melting points were determined on a Kofler table. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28 10^{15} J) Xe atoms. Mass calibration for the data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument from KBr pellets. ^1H, ^{13}C, ^{19}F and ^{195}Pt NMR spectra were measured on Varian UNITY 300 (Lisbon) and Bruker Avance DPX 400 (Vienna) spectrometers at ambient temperature. ^{19}F chemical shifts are quoted relative to $CF_3COOH = 0$ ppm, ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ (by using $K_2[PtCl_4]$, $\delta = -1630$ ppm, as a standard) and the half height line width is given in parentheses.

X-Ray crystallography

The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the Collect[40] data collection program. The Denzo-Scalepack[41] program package was used for cell refinements and data reduction. The structures **1** and **7** were solved by direct methods using the SHELXS97 program[42] and the WinGX graphical user interface.[43] Structures **4** and **6** were solved by the Patterson method using the DIRDIF-99 program.[44] A multi-scan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 5.1)[45] was applied to all data. Structural refinements were carried out with the SHELXL97 program.[46] The hydrogens in **4**, **6** and **7** were placed in idealised positions and constrained to ride on their parent atom. All hydrogens in **1** were located from the difference Fourier map and refined isotropically. The crystallographic data are summarised in Table 2, and selected bond lengths and angles are shown in Table 1. Two independent different halves of *trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(Me)C(C_6H_4F\text{-}p)({=}O)\}_2]$ were found in the asymmetric unit of **6**. The second one was labelled as molecule B in Table 1.

CCDC reference numbers 186192–186295. See http://www.rsc.org/suppdata/nj/b2/b202947b/ for crystallographic data in CIF or other electronic format.

Synthetic work and characterisation

Reaction of $[PtCl_4(RCN)_2]$ (R = Me, Et) with HON=C(Me)CC(R′)(=O) [R′=Me, Ph, C_6H_4F-*p*]. The corresponding dione monoxime (0.10 mmol) was added to a solution of $[PtCl_4(RCN)_2]$ (0.050 mmol) in MeCN (2 mL) [R = Me] or in $CHCl_3$ (2 mL) [R = Et] and the mixture was heated at 35–40 °C for 1 day. The yellow solution thus formed was concentrated to *ca.* half of the initial volume. In the case of R = Me, diethyl ether (50 mL) was added to precipitate a yellow crystalline product, which was isolated by filtration, washed twice with 3 mL portions of Et_2O and dried *in vacuo* at room temperature. The washed residue was then dissolved in chloroform (1 mL) and the complexes formed were purified by column chromatography on SiO_2 (Chemapol Silica gel L 40/100). In the case of R = Et, the concentrated solution was used directly, *i.e.* without intermediate precipitation, for the purification by column chromatography. In both cases, the first fraction from the column contained the yellow addition product $[PtCl_4\{NH{=}C(R)ON{=}C(Me)C(R')({=}O)\}_2]$.

***trans*-$[PtCl_4\{NH{=}C(Me)ON{=}C(Me)C(Me)({=}O)\}_2]$ (1).** Yield 47%. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.58$ (eluent CH_2Cl_2). Mp = 194 °C (dec.). Anal. calcd for $C_{12}H_{20}N_4Cl_4O_4Pt$: C, 23.20; H, 3.25; N, 9.02; found: C, 23.07; H, 3.18; N, 9.22%. FAB^+-MS, *m*/*z*: 585 $[M - Cl]^+$, 550 $[M - 2Cl]^+$. IR (KBr, selected bands, cm^{-1}): 3286 m–w *ν*(N–H), 1666 s and 1638 s *ν*(C=O) and *ν*(C=N), 1186 m *ν*(C–O). ^1H NMR

Table 2 Crystal data and structure refinement for **1**, **4**, **6** and **7**

	1	**4**	**6**	**7**
Empirical formula	$C_{12}H_{20}Cl_4N_4O_4Pt$	$C_{24}H_{28}Cl_4N_4O_4Pt$	$C_{24}H_{26}Cl_4F_2N_4O_4Pt$	$C_{14}H_{24}Cl_2N_4O_4Pt$
Formula weight	621.21	773.39	809.38	578.36
Temperature/K	120(2)	120(2)	120(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	6.1415(2)	7.8552(2)	7.4829(15)	6.14820(10)
b/Å	15.0031(4)	8.5681(2)	12.489(3)	9.4605(2)
c/Å	11.3715(2)	11.6142(3)	16.111(3)	17.0184(3)
α/°	90	88.8886(12)	71.07(3)	90
β/°	101.215(2)	74.9911(12)	86.40(3)	96.5058(9)
γ/°	90	73.4238(12)	86.11(3)	90
Volume/Å^3	1027.78(5)	722.39(3)	1419.6(5)	983.50(3)
Z	2	1	2	2
Density (calc.)/g cm^{-3}	2.007	1.778	1.893	1.953
Absorption coefficient/mm^{-1}	7.369	5.262	5.370	7.431
Max. and min. transmission	0.3204 and 0.2159	0.31680 and 0.23636	0.28248 and 0.19631	0.17958 and 0.11968
F(000)	596	378	788	560
θ/°	3.77–27.47	3.94–25.36	2.50–25.06	4.26–26.36
Index ranges	$-7 \le h \le 7$, $-19 \le k \le 19$, $-12 \le l \le 13$	$-9 \le h \le 9$, $-10 \le k \le 10$, $-13 \le l \le 13$	$-8 \le h \le 8$, $-14 \le k \le$, $-19 \le l \le 19$	$-7 \le h \le 7$, $-11 \le k \le 11$, $-21 \le l \le 21$
Reflections collected	13 112	9834	19 480	11 539
Independent reflections	2232	2629	4975	1984
Goodness-of-fit on F^2	1.095	1.109	1.058	1.148
$R_{\rm int}$	0.0271	0.0406	0.0486	0.0344
$R1$ [$I > 2\sigma(I)$]	0.0157	0.0287	0.0360	0.0160
$wR2$ [$I > 2\sigma(I)$]	0.0389	0.0743	0.0816	0.0386
$wR2$ (all data)	0.0398	0.0745	0.0915	0.0406
Largest diff. peak and hole/e Å^{-3}	0.684 and −0.868	1.935 and −1.059	1.470 and −1.779	0.381 and −0.788

(CDCl$_3$), δ: 2.24 (s, 3H, Me), 2.55 (s, 3H, Me), 2.91 [s + d, $^4J_{\rm PtH}$ 4.2 Hz, 3H, =C(CH_3)O], 8.84 (s, br, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 11.1 (Me), 18.3 [=C(CH$_3$)O], 26.0 (Me), 162.2 (C=N), 174.2 (C=NH), 193.6 (C=O). ^{195}Pt NMR (CDCl$_3$), δ: −235 (550 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(Me)(=O)}$_2$] (2).** Yield 52%. TLC on Silufol UV 254 SiO$_2$: $R_{\rm f} = 0.70$ (eluent Me$_2$CO–CHCl$_3$ 1:4). Mp = 140 °C (dec.). Anal. calcd for $C_{14}H_{24}N_4Cl_4O_4Pt$: C, 25.9; H, 3.73; N, 8.63; found: C, 25.82; H, 3.50; N, 8.43%. FAB$^+$-MS, m/z: 569 [M − 4Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3289 m–w ν(N–H), 1711 s and 1666 s ν(C=O) and ν(C=N), 1173 m ν(C–O). ^{1}H NMR (CDCl$_3$), δ: 1.39 (t, $^3J_{\rm HH}$ 7.3 Hz, 3H, CH$_2$CH_3), 2.25 and 2.56 (s, 3H,=CCH_3CCH$_3$=), 3.36 (q, $^3J_{\rm HH}$ 7.3 Hz, 2H, CH_2CH$_3$), 8.89 (s, br, 1H, –NH–). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 10.66 (CH$_3$), 11.0 (CH$_2$$CH_3$), 25.97 ($CH_2CH_3$), 162.19 (C=N), 176.90 (–N=C–), 193.70 (C=O). ^{195}Pt NMR (CDCl$_3$), δ: −199 (807 Hz).

***trans*-[PtCl$_4${NH=C(Me)ON=C(Me)C(Ph)(=O)}$_2$] (3).** Yield 42%. TLC on Merck 60 F$_{254}$ SiO$_2$ plates: $R_{\rm f} = 0.42$ (eluent CH$_2$Cl$_2$). Mp = 187 °C (dec.). Anal. calcd for $C_{22}H_{24}N_4Cl_4O_4Pt$: C, 35.44; H, 3.22; N, 7.52; found: C, 35.12; H, 3.01; N, 7.71%. FAB$^+$-MS, m/z: 744 [M]$^+$, 709 [M − Cl]$^+$, 674 [M − 2Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3304 m–w ν(N–H), 1663 s and 1636 s ν(C=O) and ν(C=N), 1161m ν(C–O). ^{1}H NMR (CDCl$_3$), δ: 2.43 (s, 3H, Me), 2.90 [s + d, $^4J_{\rm PtH}$ 4.2 Hz, 3H, =C(CH_3)O], 7.56 (t, 7.8 Hz, 2H, Ph), 7.66 (t, 7.5 Hz, 1H, Ph), 8.02 (d, 7.0 Hz, 2H, Ph), 8.68 (s, br, 1H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 13.6 (Me), 18.3 [=C(CH$_3$)O], 128.5, 129.1, 130.6 and 134.6 (Ph), 162.5 and 174.2 (C=N), 193.9 (C=O). ^{195}Pt NMR (CDCl$_3$), δ: −220 (600 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(Ph)(=O)}$_2$] (4).** Yield 46%. TLC on Silufol UV 254 SiO$_2$: $R_{\rm f} = 0.48$ (eluent CHCl$_3$). Anal. calcd for $C_{24}H_{26}N_4Cl_4O_4Pt$: C, 36.85; H, 3.33; N, 7.16; found: C, 36.95; H, 3.63; N, 7.15%. FAB$^+$-MS, m/z: 631 [M − 4Cl]$^+$. Mp = 154 °C (dec.). IR (KBr, selected bands, cm^{-1}): 3281 m–w ν(N–H), 1669 s and 1653 s ν(C=O) and ν(C=N), 1158 m ν(C–O). ^{1}H NMR (CDCl$_3$), δ: 1.39 (t, $^3J_{\rm HH}$ 7.4 Hz, 3H, CH$_2$CH_3), 2.43 (s, 3H, CH$_3$), 3.34 (q, $^3J_{\rm HH}$ 7.4 Hz, 2H, CH_2CH$_3$), 7.56 (t, $^3J_{\rm HH}$ 7.2 Hz, 2H, Ph-H$_{meta}$), 7.69 (t, $^3J_{\rm HH}$ 7.6, 1H, Ph-H$_{para}$), 8.02 (d, $^3J_{\rm HH}$ 6.9 Hz, 2H, Ph-H$_{ortho}$), 8.69 (s, br, 1H, –NH–). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 11.34 (CH$_3$), 14.20 (CH$_2$$CH_3$), 25.99 ($^3J_{\rm PtC}$ 9.2 Hz, CH$_2$CH$_3$), 129.82 (Ph-C$_{meta}$), 131.33 (Ph-C$_{para}$), 134.68 (–N=CMe–), 153.30 (Ph-C$_{ortho}$), 163.23 (Ph-C$_{ipso}$), 177.58 (Pt–N=C–), 188.93 (C=O). ^{195}Pt NMR (CDCl$_3$), δ: −210 (809 Hz).

***trans*-[PtCl$_4${NH=C(Me)ON=C(Me)C(C$_6$H$_4$F-*p*)(=O)}$_2$] (5).** Yield 42%. TLC on Silufol UV 254 SiO$_2$ plates: $R_{\rm f} = 0.44$ (eluent CH$_2$Cl$_2$). Anal. calcd for $C_{22}H_{22}N_4Cl_4F_2O_4Pt$: C, 33.80; H, 2.82; N, 7.17; found: C, 33.62; H, 2.91; N, 7.05%. FAB$^+$-MS, m/z: 711 [M − 2Cl]$^+$, 734 [M − 2Cl + Na]$^+$. Mp = 166 °C (dec.). IR (KBr, selected bands, cm^{-1}): 3309 m–w ν(N–H), 1672 s and 1645 s ν(C=O) and ν(C=N), 1170 m ν(C–O). ^{1}H NMR (CDCl$_3$), δ: 2.45 (s, 3H, Me), 2.86 [s, $^4J_{\rm PtH}$ 4.2 Hz, 3H, =C(CH_3)O], 7.51 (t, 2H, Ph-H$_{meta}$), 8.09 (dd, 2H, Ph-H$_{ortho}$), NH not observed. ^{19}F NMR (CDCl$_3$), δ: −25.26. ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 13.7 (Me), 18.3 [=C(CH_3)O], 128.5, 129.1, 130.6 and 134.6 (Ph), 116.7 (Ph-C$_{meta}$), 133.6 (d, Ph-C$_{ortho}$), 162.5 (C=N), 165.0 (Ph-C$_{ipso}$), 168.4 (Ph-C$_{para}$), 174.2 (C=N), 186.5 (C=O). ^{195}Pt NMR (CDCl$_3$), δ: −219 (600 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(C$_6$H$_4$F-*p*)(=O)}$_2$] (6).** Yield 48%. TLC on Silufol UV 254 SiO$_2$: $R_{\rm f} = 0.45$ (eluent CHCl$_3$). Anal. calcd for $C_{24}H_{26}N_4Cl_4F_2O_4Pt$: C, 35.61; H, 3.24; N, 6.92; found: C, 35.43; H, 3.15; N, 6.91%. FAB$^+$-MS, m/z: 666 [M – 4Cl – H]$^+$. Mp = 156 °C (dec.). IR (KBr, selected bands, cm^{-1}): 3283 m–w ν(N–H), 1671 s and 1631 s

ν(C=O) and ν(C=N), 1155 m ν(C–O). ^{1}H NMR (CDCl$_3$), δ : 1.43 (t, $^3J_{HH}$ 7.6 Hz, 3H, CH$_2$CH_3), 2.46 (s, 3H, CH$_3$), 3.38 (q, $^3J_{HH}$ 7.6 Hz, 2H, CH_2CH$_3$), 7.27 (t, J_{app} $^3J_{HH} \approx {}^3J_{HF}$ 8.7 Hz, 2H, Ph-H$_{meta}$), 8.13 (dd, $^3J_{HH}$ 8.7 Hz, $^4J_{HF}$ 5.1 Hz, 2H, Ph-H$_{ortho}$), 8.73 (s, br, 1H, –NH–). ^{19}F NMR (CDCl$_3$), δ : -101.37 [qt, br, J_{app} $1/2(^3J_{HF} + {}^4J_{HF}) = 6.9$ Hz]. ^{13}C{^{1}H} NMR (CDCl$_3$), δ : 11.33 (CH$_3$), 14.21 (CH$_2$CH$_3$), 25.96 ($^3J_{PtC}$ 10.3 Hz, CH$_2$CH$_3$), 117.23 ($^2J_{CF}$ 22.6 Hz, Ph-C$_{meta}$), 131.01 (–N=CMe–), 134.25 (d, $^3J_{PtC}$ 9.1 Hz, Ph-C$_{ortho}$), 165.70 (Ph-C$_{ipso}$), 177.63 ($^2J_{PtC}$ 48.3 Hz, –N=CEt–), 187.22 (C=O). The resonance for C$_{para}$ could not be observed, probably due to coupling to the fluorine nucleus. ^{195}Pt NMR (CDCl$_3$), δ : -210 (806 Hz).

Reduction of [PtCl$_4${NH=C(Et)ON=C(Me)C(Me)(=O)}$_2$] with the ylide Ph$_3$P=CHCO$_2$Me. Ph$_3$P=CHCO$_2$Me (45 mg, 0.070 mmol) was added to a solution of *trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(Me)(=O)}$_2$] (18 mg, 0.050 mmol) in CH$_2$Cl$_2$ (2 mL). The reaction mixture was left to stand at 40 °C for 24–36 h, whereupon the product was separated by column chromatography on SiO$_2$ (Lachema/Chemapol Silica gel L 40/100, eluent CHCl$_3$–Me$_2$CO = 5:1).

***trans*-[PtCl$_2${NH=C(Et)ON=C(Me)C(Me)(=O)}$_2$] (7).** Yield 37% after chromatographic purification. TLC on Merck 60 F$_{254}$ SiO$_2$ plates: $R_f = 0.58$ (eluent Me$_2$CO–CHCl$_3$ 1:5). Mp = 140°C (dec.). Anal. calcd for C$_{14}$H$_{24}$N$_4$Cl$_4$O$_4$Pt: C, 31.98; H, 4.02; N, 9.30; found: C, 31.98; H, 4.09; N, 9.08%. FAB$^+$-MS, m/z: 505 [M – 2Cl – H]$^+$. IR (KBr, selected bands, cm^{-1}): 3238 m–w ν(N–H), 1709 s and 1665 s ν(C=O) and ν(C=N), 1162 m ν(C–O). ^{1}H NMR (CDCl$_3$), δ : 1.45 (t, $^3J_{HH}$ 7.6 Hz, 3H, CH$_2$CH_3), 2.11 and 2.49 (s, 3H, =CCH$_3$CCH$_3$=), 3.24 (q, $^3J_{HH}$ 7.5 Hz, 2H, CH_2CH$_3$), 8.12 (s, br, 1H, –NH–). ^{13}C{^{1}H} NMR (CDCl$_3$), δ : 10.27 (CH$_3$C=N), 10.71 (CH$_2$CH$_3$), 26.03 (CH$_2$CH$_3$) 27.02 (CH$_3$C=O), 161.67 (C=N), 173.19 (–N=C–), 194.32 (C=O). ^{195}Pt NMR (CDCl$_3$), δ : -2044 (450 Hz).

Liberation of the iminoacylated oxime. Dppe (14.8 mg, 0.0371 mmol) was added to a solution of *trans*-[PtCl$_2${NH=C(Et)ONC(Me)C(Me)=O}$_2$] (10.7 mg, 0.0185 mmol) in CDCl$_3$ (1 mL; 99.8% D, H$_2$O < 0.01%), 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 and ^{13}C{^{1}H} NMR. NH=C(Et)ONC(Me)C(Me)=O: ^{1}H NMR (CDCl$_3$), δ : 1.29 (t, $^3J_{HH}$ 7.5 Hz, 3H, CH$_2$CH_3), 1.32 (t, $^3J_{HH}$ 7.5 Hz, 3H, CH$_2$CH_3), 1.98 (s, 3H, CH_3C=N), 2.10 (s, 3H, CH_3C=N), 2.371 (quart, $^3J_{HH}$ 7.5 Hz, 2H, CH_2CH$_3$), 2.373 (s, 3H, CH_3C=O), 2.45 (quart, $^3J_{HH}$ 7.5 Hz, 2H, CH_2CH$_3$) 2.50 (s, 3H, CH_3C=O), 8.23 (s, br., 1H, NH), 10.99 (s, br., OH). ^{13}C{^{1}H} NMR (CDCl$_3$), δ : 8.39 (CH$_3$), 10.73 (CH$_3$), 10.86 (CH$_2$CH$_3$), 11.29 (CH$_2$CH$_3$), 25.65 (CH$_3$C=O), C=N and C=O not detected.

The NMR spectra after two days [^{1}H NMR (CDCl$_3$), δ : 1.32 (t, 7.5 Hz, 3H, CH$_2$CH_3), 1.97 (s, 3H, CH_3C=N), 2.371 (quart, 7.5 Hz, 2H, CH_2CH$_3$), 2.373 (s, 3H, CH_3C=O), 9.88 (s, br., OH). ^{13}C{^{1}H} NMR (CDCl$_3$), δ : 8.38 (CH$_3$C=N), 10.87 (CH$_2$CH$_3$), 11.30 (CH$_2$CH$_3$) 25.46 (CH$_3$C=O), 120.94 (CH$_3$CH$_2$CN), 156.93 (C=N), 197.97 (C=O)] indicate the presence of both EtCN and the dione monoxime, whose structure was elucidated using ^{13}C, ^{1}H-HMBC spectroscopy *via* ^1J-, ^2J- and ^3J(C, H)-coupling. Furthermore, EtCN was added to the mixture, resulting in an increase in the ^{1}H (1.32 and 2.37 ppm) and ^{13}C (10.87, 11.28 and 120.94 ppm) signals, as expected from the previous experiments. Moreover, the oxime was isolated by column chromatography on SiO$_2$ and identified by TLC and IR methods.

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References

1 (*a*) V. Yu. Kukushkin, D. Tudela and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1996, **156**, 333; (*b*) V. Yu. Kukushkin and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1999, **181**, 147 and references therein

2 J. Charalambous, T. A. Thomas, O. Howarth and R. N. Whiteley, *Polyhedron*, 1996, **15**, 3851.

3 S. F. Kaplan, V. Yu. Kukushkin and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2001, 3279.

4 (*a*) B. C. Haldar, *J. Indian Chem. Soc.*, 1974, **51**, 224; (*b*) A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.

5 V. M. Peshkova, V. M. Savostina and E. K. Ivanova, *Oximes* [in Russian], Nauka, Moscow, 1977 and references therein.

6 (*a*) L. C. Sellin and J. J. McArdle, *Pharm. Toxicol.*, 1994, **74**, 305 and references therein; (*b*) H. P. M. van Helden, R. W. Busker, B. P. C. Melchers and P. L. B. Bruijnzeel, *Arch. Toxicol.*, 1996, **70**, 779; (*c*) J. V. Peter and A. M. Cherian, *Anaesthesia Intensive Care*, 2000, **28**, 11; (*d*) L. Karalliedde, *Anaesthesia*, 1999, **54**, 1073; (*e*) R. Lameka, H. Wanjek and W. Beck, *Z. Naturforsch., B: Chem. Sci.*, 1996, **51**, 574.

7 (*a*) A. Wasey, M. Katyal and M. Satake, *Analyst (London)*, 1986, **111**, 743; (*b*) S. K. Nath and R. P. Agarwal, *Chim. Anal. (Paris)*, 1966, **48**, 439; (*c*) S. K. Sindhwani and R. P. Singh, *Talanta*, 1973, **20**, 248; (*d*) V. M. Savostina, O. A. Shpigun, N. V. Klimova and V. M. Peshkova, *Zh. Anal. Khim.*, 1977, **32**, 1574.

8 (*a*) S. P. Malve, *Chem. Environ. Res.*, 1996, **5**, 313; (*b*) S. P. Malve, *Chem. Abstr.*, 1998, **128**, 135 815; (*c*) S. P. Malve, *J. Indian Chem. Soc.*, 1997, **74**, 316.

9 (*a*) P. S. More and A. D. Sawant, *J. Indian Chem. Soc.*, 1996, **73**, 377; (*b*) A. Flieger and S. Przeszlakowski, *Chem. Anal. (Warsaw)*, 1987, **32**, 85; (*c*) A. Flieger and S. Przeszlakowski, *Chem. Abstr.*, 1988, **109**, 121 478; (*d*) A. Flieger and S. Przeszlakowski, *Talanta*, 1985, **32**, 1141; (*e*) P. K. Paria and S. K. Majumdar, *Indian J. Chem., Sect. A*, 1976, **14**, 916.

10 (*a*) E. W. Abel, P. J. Heard, K. Kite, K. G. Orrell and A. F. Psaila, *J. Chem. Soc., Dalton Trans.*, 1995, 1233; (*b*) P. J. Heard and K. Kite, *J. Chem. Soc., Dalton Trans.*, 1996, 3543.

11 E. Leidl, U. Nagel and W. Beck, *Chem. Ber.*, 1983, **116**, 1370.

12 (*a*) N. N. Proskina and O. S. Konovalenko, *Bul. Acad. Stiinte Repub. Mold. Stiinte Biol. Chim.*, 1992, 62; (*b*) N. N. Proskina and O. S. Konovalenko, *Chem. Abstr.*, 1994, **121**, 72 342.

13 N. V. Gerbeleu, S. G. Baka and L. A. Nemchinova, *Zh. Neorg. Khim.*, 2000, **45**, 451.

14 (*a*) A. J. L. Pombeiro, M. F. C. Guedes da Silva and R. A. Michelin, *Coord. Chem. Rev.*, 2001, **218**, 43; (*b*) R. A. Michelin, A. J. L. Pombeiro and M. F. C. Guedes da Silva, *Coord. Chem. Rev.*, 2001, **218**, 75; (*c*) A. J. L. Pombeiro, *J. Organomet. Chem.*, 2001, **632**, 215; (*d*) A. J. L. Pombeiro, *Inorg. Chem. Commun.*, 2001, **4**, 585; (*e*) A. J. L. Pombeiro and M. F. C. Guedes da Silva, *J. Organomet. Chem.*, 2001, **617–618**, 65.

15 (*a*) A. J. L. Pombeiro, *New J. Chem.*, 1997, **21**, 649; (*b*) A. J. L. Pombeiro, *New J. Chem.*, 1994, **18**, 163; (*c*) A. J. L. Pombeiro, in *Transition Metal Carbyne Complexes*, ed. F. R. Kreissl, Kluwer, Dordrecht, 1993, pp. 105–121; (*d*) A. J. L. Pombeiro, in *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Complexes*, ed. A. J. L. Pombeiro and J. McCleverty, Kluwer, Dordrecht, 1993, pp. 331–344; (*e*) A. J. L. Pombeiro, *Inorg. Chim. Acta*, 1992, **198–200**, 179.

16 J. A. Davies, C. M. Hockensmith, V. Yu. Kukushkin and Yu. N. Kukushkin, *Synthetic Coordination Chemistry: Principles and Practice*, World Scientific, Singapore/New Jersey, 1996, pp. 492.

17 V. Yu. Kukushkin, *Coord. Chem. Rev.*, 1995, **139**, 375.

18 (*a*) L. Zhang, M. F. C. Guedes da Silva, M. L. Kuznetsov, M. P. Gamasa, J. Gimeno, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Organometallics*, 2001, **20**, 2782; (*b*) P. Sobota, K. Przybylak, J. Utko, L. B. Jerzykiewicz, A. J. L. Pombeiro, M. F. C. Guedes da Silva and K. Szczegot, *Chem. Eur. J.*, 2001, **7**, 951; (*c*) M. F. N. N. Carvalho, A. M. Galvão and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 3393; (*d*) P. M. Reis, J. A. L. Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Chem. Commun.*, 2000, 1845; (*e*) L. Zhang, M. P. Gamasa, J. Gimeno, M. F. C. Guedes da Silva, A. J. L. Pombeiro, C. Graiff, M. Lanfranchi and A. Tiripicchio, *Eur. J. Inorg. Chem.*, 2000, 1707; (*f*) M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, M. A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 2000, 373.

19 (*a*) A. J. L. Pombeiro, M. T. A. R. S. Costa, Y. Wang and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1999, 3755; (*b*) M. F. Meidine, A. J. L. Pombeiro and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1999, 3041; (*c*) S. S. P. R. Almeida, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1999, 467; (*d*) M. F. N. N. Carvalho, S. S. P. R. Almeida, A. J. L. Pombeiro and R. A. Henderson, *Organometallics*, 1997, **16**, 5441; (*e*) S. S. P. R. Almeida and A. J. L. Pombeiro, *Organometallics*, 1997, **16**, 4469.

20 (*a*) V. Yu. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771; (*b*) R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, 1996, **147**, 299.

21 (*a*) V. Yu. Kukushkin, T. B. Pakhomova, Yu. N. Kukushkin, R. Herrmann, G. Wagner and A. J. L. Pombeiro, *Inorg. Chem.*, 1998, **37**, 6511; (*b*) 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.

22 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.

23 (*a*) 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; (*b*) V. Yu. Kukushkin, I. V. Ilichev, M. A. Zhdanova, G. Wagner and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 1567.

24 G. Wagner, A. J. L. Pombeiro, N. A. Bokach and V. Yu. Kukushkin, *J. Chem. Soc., Dalton Trans.*, 1999, 4083.

25 M. N. Kopylovich, V. Yu. Kukushkin, M. F. C. Guedes da Silva, M. Haukka, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1569.

26 (*a*) G. Wagner, A. J. L. Pombeiro and V. Yu. Kukushkin, *J. Am. Chem. Soc.*, 2000, **122**, 3106; (*b*) G. Wagner, M. Haukka, J. J. R. Fraústo da Silva, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 264; (*c*) M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Inorg. Chem.*, 2002, **41**, 219.

27 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.

28 K. R. Dunbar, *Comments Inorg. Chem.*, 1992, **13**, 313.

29 (*a*) V. Yu. Kukushkin, *Platinum Met. Rev.*, 1998, **42**, 106; (*b*) V. Yu. Kukushkin, V. M. Tkachuk and N. V. Vorobiov-Desiatovsky, *Inorg. Synth.*, 1998, **32**, 144; (*c*) V. Yu. Kukushkin, Å. Oskarsson and L. I. Elding, *Inorg. Synth.*, 1997, **31**, 279.

30 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.

31 K. V. Luzyanin, M. Haukka, N. A. Bokach, M. L. Kuznetsov, V. Yu. Kukushkin and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2002, 1882.

32 (*a*) J. Vicente, M.-T. Chicote, M.-D. Abrisqueta, R. Guerrero and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1203; (*b*) J. Vicente, M. T. Chicote, R. Guerrero, I. M. Saura-Llamas, P. G. Jones and M. C. Ramírez de Arellano, *Chem. Eur. J.*, 2001, **7**, 638.

33 (*a*) V. Yu. Kukushkin, *Zh. Neorg. Khim.*, 1988, **33**, 1905; (*b*) V. Yu. Kukushkin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1988, **33**, 1085.

34 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

35 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

36 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 5th edn., 1986.

37 G. K. Anderson, J. A. Davies and D. J. Schoeck, *Inorg. Chim. Acta*, 1983, **76**, L251.

38 (*a*) For a review, see: F. Amat-Guerri, R. Mallavia and R. Sastre, *J. Photopolym. Sci. Technol.*, 1995, **8**, 205; (*b*) F. Amat-Guerri, R. Mallavia and R. Sastre, *Chem. Abstr.*, 1995, **123**, 170 225.

39 For a review, see: H. Miyabe, *J. Pharm. Soc. Jpn.*, 2000, **120**, 667.

40 Collect, Data Collection Software, Nonius B.V., Delft, The Netherlands, 1997–2000.

41 Z. Otwinowski and W. Minor, *Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307–326.

42 G. M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.

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

44 P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, The DIRDIF-99 Program System, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

45 G. M. Sheldrick, SHELXTL, version 5.1, Bruker Analytical X-ray Systems, Bruker AXS, Inc., Madison, WI, USA, 1998.

46 G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.