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Microwave-assisted [2 + 3] cycloaddition of nitrones to platinum-(II) and -(IV) bound organonitriles

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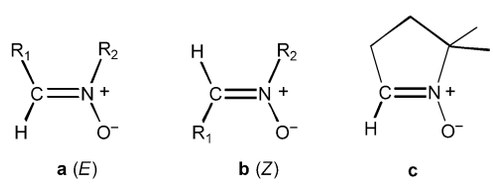
The coordinated EtCN in the anionic platinum(II) $[Ph_3PCH_2Ph][PtCl_3(EtCN)]$, the neutral platinum(II) $[PtCl_2(EtCN)_2]$ or the neutral platinum(IV) $[PtCl_4(EtCN)_2]$ complexes undergo [2 + 3] cycloadditions with cyclic non-aromatic nitrones and these reactions are greatly accelerated by microwave irradiation, to give, with a high stereoselectivity, complexes with bicyclic fused oxadiazolines as a racemic mixture in 60–90% yields, while acyclic nitrones are much less reactive and give a mixture of two diastereoisomers in the ratio 1 : 1. The new bicyclic oxadiazoline ligands can be liberated by reaction with a diphosphine. However, with a cyclic aromatic nitrone no cycloaddition is observed and only the product of the nitrile substitution is obtained. All compounds were characterised by elemental analyses, IR, ^1H, ^{13}C and ^{195}Pt NMR spectroscopies.

Introduction

The 1,3-dipolar cycloaddition reaction between nitrones and unsaturated systems is a powerful method for the organic synthesis of a wide variety of new heterocyclic derivatives structurally related to lactams, indolizidine alkaloids which have shown application to the preparation of complex molecules with useful biological activity such as antibiotics and glycosidase inhibitors.[1] Within this field, one of us[2–4] has been focusing her attention on the synthesis, by conventional organic methods, of chiral heterocycles of potential biological activity exploring the fact that addition of nucleophiles to a C=C double bond offers an attractive route for the creation of novel C–C, N–O and C–O bonds and for the generation of new heterocyclic derivatives. However, numerous examples of limitations of the so-called pure organic chemistry in this area have been recognized,[5,6] namely the insufficient activation of some dipolarophiles (resulting in the inhibition of the cycloaddition) and the need to use drastic experimental conditions such as high temperatures and long reaction times. Therefore, new methods of activation, such as microwave chemistry and coordination to a metal centre, have been attempted. In fact, it was recently observed that the microwave field decreases the activation energy of various types of reactions in particular with organonitriles.[7] Moreover, metals in coordination processes can dramatically increase the reactivity of organonitriles (a matter reviewed recently by two of us[5] and others[8]) and metal-mediated processes can lead to the formation of heterocyclic species.[5] As a relevant example, it is noteworthy to mention that, although nonactivated organonitriles (RCN) do not undergo cycloaddition with acyclic nitrones, $^-ON^+(R_2)=C(H)(R_1)$, even under harsh heating conditions, their activation by coordination to a platinum centre has made such a reaction possible, as well as many others involving nucleophilic additions to the nitriles. These behaviours occur typically in the Pt^{IV} complexes $[PtCl_4(RCN)_2]$ in which we have shown that the nitriles can add a wide variety of nucleophiles such as oximes,[9–13] hydroxamic acids,[14] imines,[15] sulfimides,[16] alcohols[17] or water.[18] Acyclic nitrones can also add[19,20] to give the first synthesis of platinum oxadiazoline complexes. These products were obtained as mixtures of diastereoisomeric forms from which the free heterocycles could be liberated as the corresponding oxadiazoline isomeric mixtures. Hence, such reactions are not satisfactory with regard to regiochemistry and stereoselectivity in part due to the possible interconversion of the configurations *E* (**a**) and *Z* (**b**) (Fig. 1) of the acyclic nitrones. Consequently, it would be highly desirable to develop new methods for higher stereoselective synthesis of optically active heterocycles.



a (*E*) **b** (*Z*) **c**

Fig. 1

Moreover, the above platinum-promoted nitrile–nitrone coupling studies[19,20] have been performed only with nitrones having an aromatic R_1 group (phenyl or substituted phenyl) and, in the case of the alkyl nitriles (which are less reactive than the aromatic ones), the reaction requires the use of the metal in the high IV oxidation state. In addition, considerable reaction times are needed for an extensive formation of the oxadiazoline complexes, *e.g.* one day for the reaction of the Pt^{II} benzonitrile complex $[PtCl_2(PhCN)_2]$ or 6 h for the Pt^{IV} acetonitrile compound $[PtCl_4(MeCN)_2]$.[19,20] Hence, the search of developments to overcome those limitations appears appropriate.

In the current work, we have addressed those aims by using, for the first time, cyclic nitrones (**c**, Fig. 1) and the combination of microwave irradiation with metal-binding activation of the organonitrile. Such nitrones, in contrast with the acyclic ones, only exhibit the *E* configuration, which can favour the selectivity. Moreover, this configuration is more stereochemically favourable to the cycloaddition than the *Z* one, and this addition could also be dependent on (eventually promoted by) the electron-donor character of the organic groups in the cyclic nitrone (note that, in the previously used acyclic nitrones, R_1 was always aromatic). In agreement with these expectations, we have now achieved a better stereoselectivity of the [2 + 3] cycloaddition of the nitrones to the organonitrile ligands, as well as the promotion of such a reaction to an extent that it can even occur for alkyl nitriles coordinated to less activating Pt^{II} centres and always at faster rates (*e.g.* in some cases the reaction can now be essentially complete in just a few minutes) than those previously observed.

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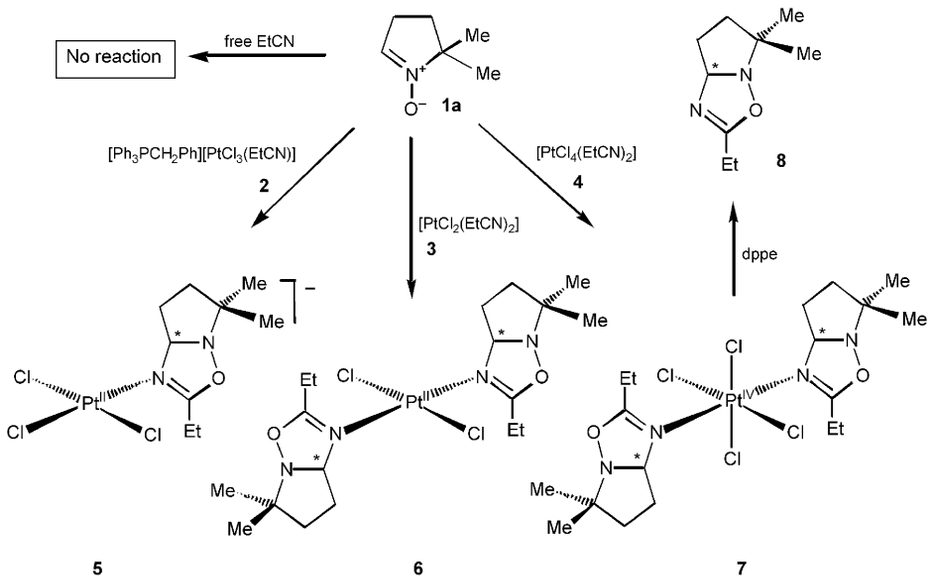


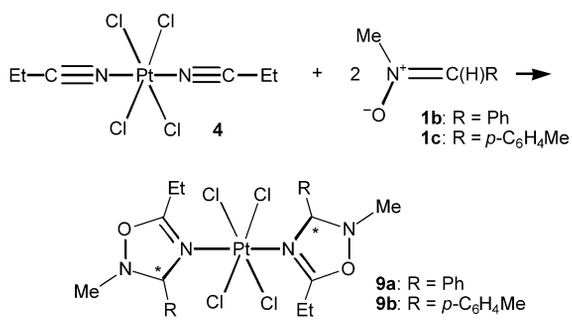
Scheme 1 [2 + 3] cycloadditions of a cyclic nitrone (**1a**) to Pt^{II}- and Pt^{IV}-ligated ethanonitriles.

Results and discussion

We have focused our attention on the cycloaddition of various platinum-(II) and -(IV) complexes with different types of nitrones, in particular cyclic ones (both non-aromatic and aromatic) and, for comparative purposes, also acyclic nitrones, thus aiming to investigate the effects of the nature of the metal centre and of the nitrone on the stereoselectivity and outcome of such reactions under conventional conditions and under microwave irradiation.

The ethanonitrile platinum compounds $[Ph_3PCH_2Ph][PtCl_3(EtCN)]$ **2** (with an anionic Pt^{II} centre), *trans*-$[PtCl_2(EtCN)_2]$ **3** (with a neutral Pt^{II} centre) and *trans*-$[PtCl_4(EtCN)_2]$ **4** (with a Pt^{IV} site), were selected, ordered according to their expected increase of reactivity towards nucleophilic addition reactions with a protic nucleophile. All of them undergo [2 + 3] cycloaddition reactions with the cyclic non-aromatic nitrone **1a** (see Scheme 1), including both the Pt^{II} complexes, in contrast to the previously recognized[20] inactivity of the related acetonitrile–Pt^{II} complex $[PtCl_2(MeCN)_2]$ towards the addition of the acyclic nitrones $^{-}ON^{+}(R_2)=C(H)(R_1)$ (R_1 = phenyl or substituted phenyl, R_2 = Me or CH_2Ph), thus indicating a higher reactivity of cyclic nitrone **1a** in comparison with the acyclic ones. Particularly interesting, from this point of view, is the addition of the cyclic nitrone **1a** to the aliphatic nitrile in the anionic Pt^{II} complex **2**, in which the alkanenitrile ligand is still sufficiently activated towards the cyclic nitrone cycloaddition. Under similar experimental conditions, no reaction was observed between the free nitrile and the nitrone, indicating that the cycloaddition is metal-mediated.

The reactions proceed smoothly at room temperature, in CH_2Cl_2, and using stoichiometric amounts of reagents, and lead to the corresponding complexes **5**, **6** and **7** (Scheme 1) containing fused bicyclic Δ^4-1,2,4-oxadiazoline ligands, which have been purified by chromatography on silica gel and isolated as yellow solids in good yields (60, 65 or 85%, correspondingly) after 2 days, 1 day or only 10 min reaction times, respectively, reflecting the expected order of reactivity, the Pt^{IV} complex being much more reactive than the Pt^{II} ones. Moreover, *trans*-$[PtCl_4(EtCN)_2]$ **4** reacts much faster with the cyclic nitrone **1a** (10 min) than with the acyclic ones, $^{-}ON^{+}(Me)=C(H)(R)$ [**1b**: R = Ph, **1c**: R = *p*-C_6H_4Me] (6 h reaction time) which lead to the Δ^4-1,2,4-oxadiazoline complexes **9a** (R = Ph) and **9b** (R = *p*-C_6H_4Me) (Scheme 2), in accord with the higher reactivity of the former nitrone. Complex **4** reacts with the acyclic nitrones similarly to the related acetonitrile compound $[PtCl_4(MeCN)_2]$.[20] Under analogous experimental conditions, no reaction was observed between *cis*-$[PtCl_4(EtCN)_2]$ and the cyclic nitrone **1a**.



Scheme 2 [2 + 3] cycloadditions of acyclic nitrones (**1b**,**c**) to Pt^{IV}-ligated ethanonitriles.

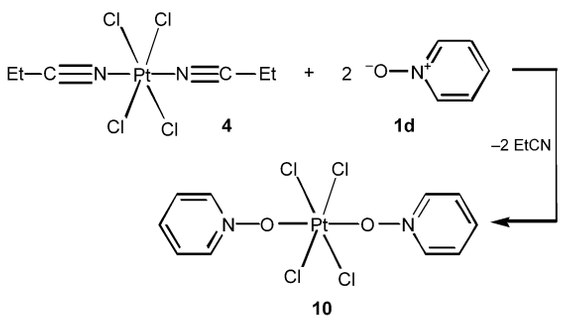
The reactions are greatly accelerated under focused microwave irradiation and similar or better isolated yields (in comparison with those for the conventional procedure) of the corresponding products **5**, **6**, **7** or **9** are obtained with only 3 h, 1 h, 5 min or 30 min reaction times at 25–30 °C in dry dichloromethane (method *i*) or in the solid state (dry silica gel, method *ii*), respectively. Hence, relatively to the conventional method, the microwave activation leads to quite a shortening of the reaction time without a change in the obtained cycloaddition products which have all been characterised by IR, ^1H, ^{13}C and ^{195}Pt NMR spectroscopies, elemental analyses and polarimetry. Moreover the reactions undertaken without any solvent, *i.e.* using dry silica gel as a solid support, are cleaner. The adsorbed reagents are placed in a vessel and subjected to microwave irradiation, whereupon the products are extracted with dichloromethane from the support. By this process, no by-products were detected by TLC, in contrast with the reaction in solution when some unidentified TLC spots were observed.

In the IR spectra of the above products, ν(C=N) of the oxadiazoline ligands is detected as a strong band in the 1663–1697 cm^{-1} range, which replaces the higher wavenumber ν(C≡N) band of the nitrile ligand in the parent complexes.

Complex **5** presents one stereocentre and appears as a racemic mixture as indicated by polarimetry measurements (specific rotation of the mixture [α] = 0) and by the single set of ^1H and ^{13}C NMR signals. Similarly, the other products of the cyclic nitrone addition, **6** and **7**, also display one set of ^1H and ^{13}C NMR signals, in contrast with the products

of the reaction with the acyclic nitrones, *i.e.* *trans*-[$PtCl_4$-{N=C(Et)O–N(Me)CHR)$_2$}] **9a** or **9b**, which exhibit two sets of signals as observed[19,20] for related products of acyclic nitrone additions which appear as [(*R*,*S*) + (*R*,*R*)/(*S*,*S*)] diastereoisomeric mixtures. These spectroscopic features are indicative that the cycloaddition of the platinum complexes **3** and **4** with the cyclic nitrone **1a** proceeds with high stereoselectivity leading to the formation of a pair of [(*R*,*R*)/(*S*,*S*)] enantiomers for the corresponding products **6** and **7**. ^{195}Pt NMR data for **7**, **9a** and **9b** are well-coherent with those for with the previously obtained Pt^{IV} oxadiazoline complexes[19] which exhibit the *trans*-configuration. The newly formed fused bicyclic oxadiazoline **8** can be easily liberated as shown by the reaction of complex **7** with $Ph_2PCH_2CH_2PPh_2$ (dppe) that also leads to the formation of [Pt(dppe)$_2$]Cl_2 which precipitates out of the $CHCl_3$ reaction solution.

We have also examined the reaction of *trans*-[$PtCl_4$(EtCN)$_2$] **4** with an aromatic cyclic nitrone, pyridine *N*-oxide (PyO) **1d**, and observed only the formation of the nitrile substitution product *trans*-[$PtCl_4$(PyO)$_2$] **10** (Scheme 3).



Scheme 3 Reaction of an aromatic nitrone (**1d**) with the Pt^{IV} ethanonitrile complex.

Conclusions

We have found that a non-aromatic cyclic nitrone readily adds to nitrile ligands at either Pt^{II} or Pt^{IV} centres to form, under mild conditions, bicyclic oxadiazoline complexes as a result of a [2 + 3] cycloaddition reaction. We also have shown that the nature of the nitrone plays a relevant role in this reaction which occurs much more favourably with such a type of nitrones than with acyclic ones. Hence, in contrast with the acyclic nitrones, the non-aromatic cyclic nitrones can add even to an alkanenitrile at a negatively charged Pt^{II} metal centre, in spite of the most stringent requirements[19,20] for the addition of acyclic nitrones *i.e.* the use of a more reactive aromatic nitrile (which nevertheless is not sufficiently activated to the reaction when ligating an anionic metal centre) or of a higher metal oxidation state, Pt^{IV}, centre with a stronger activating power [alkanenitriles are unreactive towards the addition of acyclic nitrones when binding a Pt^{II} site, either an anionic or a neutral one]. Moreover, the structure of the cyclic nitrone offers a more rigid conformation (*E*) than in the case of the acyclic ones, preventing one of the nitrone sides from the reaction, thus also promoting the stereoselectivity.

We have also demonstrated the accelerating effect on the reaction of the focused microwave irradiation which leads to the same oxadiazoline complexes as those obtained with conventional methods, but in much shorter reaction times. Hence, the dual mode of activation of the organonitriles, by combining coordination to a suitable metal centre with microwave irradiation, appears particularly effective.

It is also noteworthy to mention that some platinum complexes with *N*-heterocyclic ligands show very promising anticancer activity[21] and this study further provides novel and potential candidates to be tested. In addition, the new fused bicyclic oxadiazoline species can be liberated from the metal centre and the current method opens up new perspectives for the metal-mediated synthesis of biologically significant heterocyclic species. Its possible extension to the cycloaddition with other dipolarophiles, besides the nitrile group, also deserves to be explored and those attempts are currently under investigation in our laboratory.

Experimental

Materials and instrumentation

Solvents were purchased from Aldrich and dried by usual procedures. The complexes [Ph_3PCH_2Ph][$PtCl_3$(EtCN)] **2**, [$PtCl_2$(EtCN)$_2$] **3** and [$PtCl_4$(EtCN)$_2$] **4** and the nitrones **1b** and **1c** were prepared according to published methods.[19,20] Nitrones **1a** and **1d** were obtained from commercial sources (Aldrich) and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Leica Galen III Kofler table. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 ml cylinder with 13 mm diameter) which is fitted with a rotational system and an IR detector of temperature. For TLC, Merck UV 254 SiO_2 plates have been used. ^{1}H, ^{13}C and ^{195}Pt NMR spectra (in $CDCl_3$) were measured on a Varian Unity 300 spectrometer at ambient temperature.^{1}H, and ^{13}C chemical shifts (δ) are in ppm relative to $Si(CH_3)_4$ 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 Hertz. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets and the wavenumbers are in cm^{-1}.

Preparation of the platinum oxadiazoline complexes *via* cycloaddition

(i) By a conventional method**.** A solution of the platinum organonitrile complex (0.10 mmol) and the corresponding nitrone (0.20 mmol for the synthesis of compounds **6**, **7** and **9**, and 0.10 mmol for compound **5**) in 2.0 ml of dry CH_2Cl_2–EtCN (1 : 1) was stirred at room temperature and the progress of the reaction was monitored by TLC. After chromatography on SiO_2/CH_2Cl_2 or CH_2Cl_2–Et_2O and evaporation of the solvent, the products were obtained as yellow powders which were washed with diethyl ether and dried *in vacuo*. In the ^{1}H NMR and IR spectra we have detected, in some cases, the presence of solvents due to their retention by heterocyclic products.

(ii) By focused microwave irradiation in dry CH_2Cl_2**.** The reagents, in amounts identical to those detailed above, were added to in a cylindrical Pyrex tube which was then placed in the focused microwave at 30 °C. After the reaction, the mixture was allowed to cool down, the solvent was removed *in vacuo*, the crude residue was purified by chromatography on SiO_2/CH_2Cl_2 and the products were isolated upon evaporation of the solvent and dried *in vacuo*.

(iii) By focused microwave irradiation without solvent, on silica gel support**.** A silica gel support was impregnated with the platinum organonitrile complex (0.10 mmol) and the corresponding nitrone (0.20 mmol). After subsequent solvent removal the mixture was microwave irradiated at 30 °C as indicated in method (*ii*). Extraction of the crude product with CH_2Cl_2, acetone and evaporation of the solvent *in vacuo* led to the isolation of the crude platinum complex product which was purified by column chromatography (SiO_2/CH_2Cl_2) followed by evaporation of the solvent and drying *in vacuo*

5: The reaction time was 48 h at room temperature by method (*i*) (60% yield) and 3 h by method (*ii*) at 30 °C (62% yield). Mp: 101 °C. IR: 1663s ν(C=N). ^{1}H NMR: δ 1.09 (s, 3H, Me), 1.16 (s, 3H, Me), 1.21 (t, 3H, CH_2Me, $^3J_{HH}$ = 7.5), 1.40–1.49 (m, 2H, CH_2), 2.13–2.01 (m, 1H, CH_2), 2.88–2.93 (m, 1H,

CH_2), 2.96–3.09 (m, 2H, CH_2), 5.13–5.18 (d, 2H, CH_2Ph, $^2J_{HP}$ = 14.1), 5.35 (d, 1H, NCHN, $^3J_{HH}$ = 4.1), 7.05–7.80 (m, 20H, 4Ph). $^{13}C\{^1H\}$ NMR: δ 10.01 (Me), 20.80 (Me), 22.44 (Me), 27.41 (CH_2), 29.42 (CH_2), 33.75 (CH_2), 69.59 (C–N), 88.08 (NCHN), 169.17 (C=N). ^{195}Pt NMR: δ −1905 (152 Hz). Anal. Calc. for $C_{34}H_{38}N_2OCl_3PPt\cdot0.5Et_2O$: C, 50.27; H, 5.03; N, 3.26. Found: C, 50.70; H, 4.67; N, 3.19%.

6: The reaction time was 24 h by method (*i*) (65% yield) at room temperature, 15 min at 50 °C or 1 h at 25 °C by method (*ii*) (65% yield) and 15 min at 50 °C by method (*iii*) (70% yield). Mp: 160 °C. IR: 1663 s ν(C=N). ^{1}H NMR: δ 1.71 (s, 6H, Me), 1.23 (s, 6H, Me), 1.40 (t, 6H, CH_2Me, $^3J_{HH}$ = 7.8), 1.58–1.78 (m, 4H, CH_2), 2.28–2.40 (m, 2H, CH_2), 2.89–3.09 (m, 6H, CH_2Me), 5.44 (d, 2H, NCHN, $^3J_{HH}$ = 3.9). $^{13}C\{^1H\}$ NMR: δ 10.03 (Me), 20.98 (Me), 22.37 (Me), 27.26 (CH_2), 29.70 (CH_2), 33.71 (CH_2), 69.83 (C–N), 88.72 (NCHN), 169.93 (C=N). ^{195}Pt NMR: δ −2199 (626 Hz). Anal. Calc. for $C_{18}H_{32}N_4O_2Cl_2Pt\cdot Et_2O\cdot CH_2Cl_2$: C, 36.24; H, 5.77; N, 7.35. Found: C, 36.03; H, 6.36; N, 7.50%.

7: The reaction time was 15 min by method (*i*) (85% yield) at room temperature, 10 min at 25 °C by method (*ii*) (90% yield) and 10 min at 25 °C by method (*iii*) (90% yield). Mp: 153 °C. IR: 1663 s ν(C=N). ^{1}H NMR: δ 1.10 (s, 6H, Me), 1.25 (s, 6H, Me), 1.44 (t, 6H, CH_2Me, $^3J_{HH}$ = 7.5), 1.73–1.79 (m, 4H, CH_2), 2.28–2.37 (m, 4H, CH_2), 3.17–3.20 (m, 4H, CH_2Me), 5.94 (dd, 2H, NCHN, $^3J_{HH}$ = 4.2, $^3J_{HH}$ = 2.8, $^3J_{HPt}$ = 12.0). $^{13}C\{^1H\}$ NMR: δ 10.80 (Me), 22.89 (Me), 23.75 (Me), 25.20 (CH_2), 35.20 (CH_2), 36.88 (CH_2), 70.20 (C–N), 89.53 (NCHN), 175.71 (C=N). ^{195}Pt NMR: δ +950 (621 Hz). Anal. Calc. for $C_{18}H_{32}N_4O_2Cl_4Pt\cdot 0.75EtCN$: C, 34.03; H, 5.04; N, 9.30. Found: C, 34.29; H, 5.57; N, 8.88%.

8: The liberation of this bicyclic Δ^4-1,2,4-oxadiazoline from the corresponding platinum(IV) complex **7** was achieved upon reaction with dppe in $CHCl_3$ at room temperature. A solution (2.0 ml) of **7** (50 mg, 0.075 mmol) and dppe (64 mg, 0.16 mmol) was stirred for 24 h. During the course of the reaction, $[Pt(dppe)_2]Cl_2$ precipitated as a white powder. After filtration, the filtrate was evaporated to dryness *in vacuo* and the residue was purified by column chromatography (SiO_2/CH_2Cl_2) followed by evaporation of the solvent and drying *in vacuo*. Yield: 61%. Oil. ^{1}H NMR: δ 1.10 (s, 3H, Me), 1.27 (s, 3H, Me), 1.41 (t, 3H, CH_2Me, $^3J_{HH}$ = 7.5), 1.62–1.79 (m, 2H, CH_2), 2.18–2.28 (m, 2H, CH_2), 3.35–3.02 (m, 2H, CH_2Me), 4.81 (d, 1H, NCHN, $^3J_{HH}$ = 4.8). $^{13}C\{^1H\}$ NMR: δ 10.82 (Me), 22.21 (Me), 23.36 (Me), 27.55 (CH_2), 34.17 (CH_2), 35.24 (CH_2), 71.28 (C–N), 90.00 (NCHN), 174.76 (C=N).

trans-$[PtCl_4\{\overline{N{=}C(Et)O{-}N(Me)C}(H)Ph\}_2]$ **9a**: The reaction time was 6 h at room temperature by method (*i*) (70% yield), 30 min at 30 °C by method (*ii*) (72% yield) at room temperature and 30 min at 30 °C by method (*iii*) (80% yield). Mp: 158 °C. IR: 1697 s ν(C=N). ^{1}H NMR: δ 1.36 and 1.37 (two t, 3H each, CH_2Me, $^3J_{HH}$ = 7.8), 2.90 and 2.91 (s, 3H, NMe), 3.58–3.34 (m, 4H, CH_2 for each isomer), 6.44 and 6.45 (two s, 1H each, NCHN, $^3J_{HPt}$ = 11.6), 7.41–7.20 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR: δ 10.99 (Me), 22.98 (NMe), 46.00 (CH_2), 90.30 (NCHN), 125.92, 128.40, 128.80, 137.91 (Ph), 173.45 (C=N). ^{195}Pt: δ −178 (497 Hz). Anal. Calc. for $C_{22}H_{28}N_4O_2Cl_4Pt$: C, 36.83; H, 3.93; N, 7.81. Found: C, 36.57; H, 4.06; N, 7.49%.

trans-$[PtCl_4\{\overline{N{=}C(Et)O{-}N(Me)C}(H)(p\text{-}C_6H_4Me\}_2]$ **9b**: The reaction time was 6 h at room temperature by method (*i*) (70% yield). Mp: 164 °C. IR: 1688 s ν(C=N). ^{1}H NMR: δ 1.33 and 1.34 (two t, 3H each, CH_2Me, $^3J_{HH}$ = 7.6), 2.31 (s, 6H, *p*-C_6H_4Me), 2.87 and 2.88 (two s, 3H each, NMe), 3.58–3.29 (m, 4H, CH_2), 6.40 and 6.41 (two s, 1H each, NCHN, $^3J_{HPt}$ = 11.4), 7.15–7.08 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR: δ 10.99 (Me), 21.18 (Me), 22.95 and 23.01 (CH_2), 45.91 and 45.96 (NMe), 90.24 and 90.29 (NCHN), 125.77, 129.12, 138.60 (Ph), 176.70 (C=N). ^{195}Pt NMR: δ −175 (350 Hz). Anal. Calc. for $C_{24}H_{32}N_4O_2Cl_4Pt\cdot H_2O$: C, 37.72; H, 4.45; N, 7.33. Found: C, 37.59; H, 4.38; N, 7.01%.

Preparation of the pyridine *N*-oxide complex $[PtCl_4(PyO)_2]$ 10

The reaction was carried out similarly to those described above (method *i*) for the preparation of the oxadiazoline complexes. The product **10** was isolated after 10 min reaction time (85% yield). IR: 1608 s ν(C=N). ^{1}H NMR: δ 7.15–8.07 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR: δ 126.74, 127.18 (Ph), 144.22 (C=N). ^{195}Pt NMR: δ +610 (222 Hz). Anal. Calc. for $C_{10}H_{10}N_2O_2Cl_4Pt$: C, 22.78; H, 1.91; N, 5.31. Found: C, 22.42; H, 1.67; N, 4.98%.

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