New chemistry of olefin complexes of platinum(II) unravelled by basic conditions: synthesis and properties of elusive cationic species

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The evolution in basic medium ([RO^-] = 1 M in methanol, R = H or Me) of five-coordinate platinum(II) compounds, [$PtCl_2(\eta^2\text{-}C_2H_4)$(N–N)], **2a–c**, (N–N = *N,N,N′,N′*-tetramethyl-1,2-ethanediamine, **a**; 2,2′-bipyridyl, **b**; 1,10-phenanthroline, **c**) leads to the formation of [$PtCl(\eta^1\text{-}CH_2CH_2\text{-}OCH_3)$(N–N)], **5a–c**. The analogous compound **5d** (N–N = 2,9-dimethyl-1,10-phenanthroline, **d**) can also be prepared, but not *via* transformation of the five-coordinate species **2d** in basic medium where it is quite stable. **5d** can instead be prepared by reaction of **d** with a strongly basic methanol solution of Zeise's anion [$PtCl_3(\eta^2\text{-}C_2H_4)]^-$, **1**. In such a medium the di-anionic *trans*-[$PtCl_2(OR)(\eta^1\text{-}CH_2CH_2\text{-}OCH_3)]^{2-}$ species (**1″**) reacts with **d** to form exclusively **5d**. Hydrolysis of **5a–c** with acids bearing weakly coordinating anions leads to [$PtCl(\eta^2\text{-}C_2H_4)$(N–N)]$^+$, **3a–c**, as stable cations; upon the same treatment **5d** does not generate **3d**, but it reacts with HCl to give **2d** in almost quantitative yield. Cationic complexes **3b**, **3c**, here reported for the first time, were reacted with some nucleophiles and their behaviour compared with that of the already known **3a**. In **3b**, **3c** the metal centre competes with the coordinated ethene for binding to nucleophiles; therefore the acetylacetonate anion can either add to the olefin (affording compounds **6b**, **6c**) or to the metal ion replacing the ethene ligand (yielding compounds **7b**, **7c**). Under similar conditions, **3a** gives exclusively **6a**. Secondary amines readily add to ethene in **3b**, **3c**, affording the addition products **8b**, **8c**, which undergo a ready cyclization to an azaplatinacyclobutane ring (**9b**, **9c**). The remarkable ease of the four-membered ring formation has been related to the high electrophilic character of the metal core in **3b**, **3c**.

Introduction

Olefin complexes of late transition metals are of great importance in organometallic chemistry especially when they bear a net positive charge, which enhances the electrophilic character of the unsaturated ligand.[1,2] The metal–olefin bond can still be understood in terms of the Chatt, Dewar, and Duncanson model[3] where the presence of a positive charge on the metal core reduces the π-back donation from the metal to the olefin, which assumes a partial carbocationic character.[4] The electrophilicity of the coordinated olefin, however, is not only governed by the charge of the complex but also by the nature of the ancillary ligands which can influence the energy level of the outer metal orbitals. For instance the ease of nucleophilic addition goes along with the lowering of the LUMO in which olefin π* and metal dp orbitals are mixed.[2] Cationic species, bearing unsaturated ligands, are frequently encountered as reactive intermediates in catalytic cycles,[5] however in some instances they have enough stability to be isolated[6] and characterized. Apart from nucleophilic attack,[6b,e,j,l,q,r] the unsaturated ligand can exhibit Brønsted acidity,[7] and also give insertion reactions when adjacent to a metal–carbon or metal–hydrogen bond.[8]

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As far as the chemistry of platinum(II) is concerned, a number of cationic olefin complexes have been reported over the years.[6a,g–p,r,8] The preparative procedures generally fall into three categories: (i) substitution of an olefin for a solvent molecule in a cationic solvento species, (ii) oxidative addition to a platinum(0) complex containing a coordinated olefin, and (iii) spontaneous dissociation of a chlorido ligand from a five-coordinate complex of formula [$PtCl_2(\eta^2\text{-}C_2H_4)$(N–N)].

In particular, using the last procedure, we have isolated some [$PtCl(\eta^2\text{-}C_2H_4)$(N–N)]$^+$ complexes. This method, however, has a limited scope and good yields of cationic species can be achieved only when the nitrogen ligand is an aliphatic diamine, *e. g.* N–N = *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (tmeda)[6g,j,7o] or *N,N′*-dimethyl-2,3-diaminobutane. Starting from [$PtCl(\eta^2\text{-}C_2H_4)$(tmeda)]$^+$ several other analogues have been prepared by metathetical olefin exchange reactions[6g,i–l]

We have now found a quite general new procedure for the preparation of cationic olefin complexes of platinum(II) starting from Zeise's anion but using a strong basic medium. The synthesis of new compounds, their characterization, and a deeper insight in the ligand substitution processes will be described. Part of this work has been previously communicated.[9]

Results

Reactivity of Zeise's anion in basic solution

The already reported behaviour of Zeise's anion towards chelating ligands [such as *N,N,N′,N′*-tetramethyl-1,2-ethanediamine

(tmeda, **a**), 2,2′-bipyridyl (bpy, **b**), 1,10-phenanthroline (phen, **c**), and 2,9-dimethyl-1,10-phenanthroline (Me_2phen, **d**)] in methanol and in the absence of added base, is depicted in the upper row of Scheme 1. The initially formed five-coordinate complex (**2**) eventually evolves to the four-coordinate dichlorido species **4**. In the process **2** → **4** the cationic complex **3** is only a transient species.

If the five-coordinate species, **2a–c**, are treated with basic methanol, a quantitative transformation into **5a–c** is observed. Such a transformation is believed to occur through formation of the cationic species **3a–c** followed by addition of methoxide to the η^2-bonded olefin. **2d** is very stable also in basic medium and the evolution to the alkyl–chlorido complex **5d** is not observed.

Compounds **5** can be obtained also in a one pot reaction by adding the nitrogen ligand to a basic solution of the Zeise's anion (the reaction temperature must be carefully controlled).[10] The latter procedure differs from the previous one for the order in which the reactants are mixed (first the chelate dinitrogen ligand and then the base in the former case; first the base and then the chelate ligand in the latter one). Following the latter procedure **5d** can also be prepared.[11] In particular, the two reaction pathways sketched in Scheme 1 (upper and lower row, respectively) are in competition and conducting the reaction at increasing concentration of base, it was possible to monitor by ^{1}H NMR the increasing yield of **5d** with respect to **2d**. At very high base concentration (1 M KOH and KOH/Zeise's anion ratio ≥ 4) the formation of the five-coordinate species **2d** was totally inhibited. Since **2d** cannot be converted to **5d** even under strong basic conditions, it is possible to conclude, beyond any reasonable doubt, that the formation of the methoxide addition product **5d** takes place through the reaction pathway depicted in the lower row of Scheme 1 and not by transformation of the five-coordinate species (**2d**).

We have found (^{1}H NMR in CD_3OD) that in strong basic conditions the Zeise's anion, besides chlorido substitution, undergoes also methoxide addition to the η^2-ethene.[9] Hence, dissolution of **1** in such a medium produces instantaneously species **1′** and **1″** in comparable yield (on standing both species undergo further chlorido substitution which, however, will not be discussed in the present context).[12,13] We could monitor, after addition of Me_2phen (**d**), the immediate disappearance of **1″** and the slower, progressive consumption of **1′**, compound **5d** being the only reaction product. This indicates that Me_2phen (**d**) can rapidly react with **1″**, but not with **1′** (since the reaction with **1′** would have lead to formation of **2**).

All new compounds of type **5** have been isolated and fully characterized (elemental analysis, ESI MS, and NMR). The ^{1}H NMR ($CDCl_3$) spectrum is particularly diagnostic for the presence of the Pt–$C_\alpha H_2C_\beta H_2$–OCH_3 moiety (see Fig. 1 and Tables 1 and 2).[14]

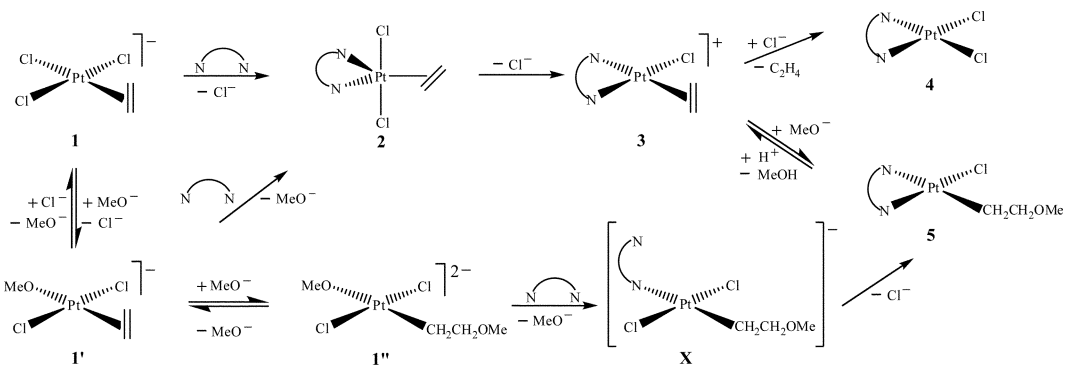
Table 1 ^{1}H chemical shifts (ppm, downfield from $Si(CH_3)_4$) of the Pt–$C_\alpha H_2$–$C_\beta H_2$–X moiety of some synthesized complexes (X = OCH_3, **5a–d**; $CH(COCH_3)_2$, **6a–c**; $NHEt_2$, **8a–c**; NEt_3, **8′a–c**; NEt_2, **9a–c**)

	Pt-$C_\alpha H_2$–$C_\beta H_2$–X or Pt–$\overline{C_\alpha H_2–C_\beta H_2–X}$ only for **9a–c**	
Compound	$C_\alpha H_2$	$C_\beta H_2$
5a[a]	1.64 ($^2J_{Pt-H}$ = 92 Hz)	3.48
5b	2.22 ($^2J_{Pt-H}$ = 90 Hz)	3.61
5c	2.41 ($^2J_{Pt-H}$ = 90 Hz)	3.70
5d	2.33 ($^2J_{Pt-H}$ = 95 Hz)	3.71
6a[b]	1.17 ($^2J_{Pt-H}$ = 88 Hz)	1.80
6b	1.85	2.12
6c	2.07	2.20
8a[c]	1.62 ($^2J_{Pt-H}$ = 94 Hz)	3.13
8b	2.08 ($^2J_{Pt-H}$ = 90 Hz)	3.24
8c	2.36 ($^2J_{Pt-H}$ = 90 Hz)	3.44
8′a	1.46	3.38
8′b	2.09 ($^2J_{Pt-H}$ = 89 Hz)	3.52
8′c	2.19 ($^2J_{Pt-H}$ = 89 Hz)	3.54
9a[c]	0.98 ($^2J_{Pt-H}$ = 91 Hz)	4.46 ($^3J_{Pt-H}$ = 58 Hz)
9b	1.65 ($^2J_{Pt-H}$ = 89 Hz)	4.83 ($^3J_{Pt-H}$ = 58 Hz)
9c	1.72 ($^2J_{Pt-H}$ = 90 Hz)	4.75 ($^3J_{Pt-H}$ = 45 Hz)

[a] Ref. 14. [b] Ref. 16. [c] Ref. 18.

Table 2 ^{13}C chemical shifts (ppm, downfield from $Si(CH_3)_4$) of the Pt–C_α–C_β– moiety of some synthesized complexes

Compound	C_α	C_β
5b	6.3 ($^1J_{Pt-C}$ = 753 Hz)	76.2
5c	5.5 ($^1J_{Pt-C}$ = 745 Hz)	76.4
5d	−1.2 ($^1J_{Pt-C}$ = 700 Hz)	76.1
6b	2.82	30.8
6c	2.12	31.4
7b	37.7 ($^1J_{Pt-C}$ = 601 Hz)	—
7c	37.9 ($^1J_{Pt-C}$ = 605 Hz)	—
8b	−2.7 ($^1J_{Pt-C}$ = 717 Hz)	57.1
8c	−3.4 ($^1J_{Pt-C}$ = 750 Hz)	57.8
8′b	−6.6	62.8
8′c	n.d.	n.d.
9b	−26.7	67.4
9c	−26.4	68.4



Scheme 1

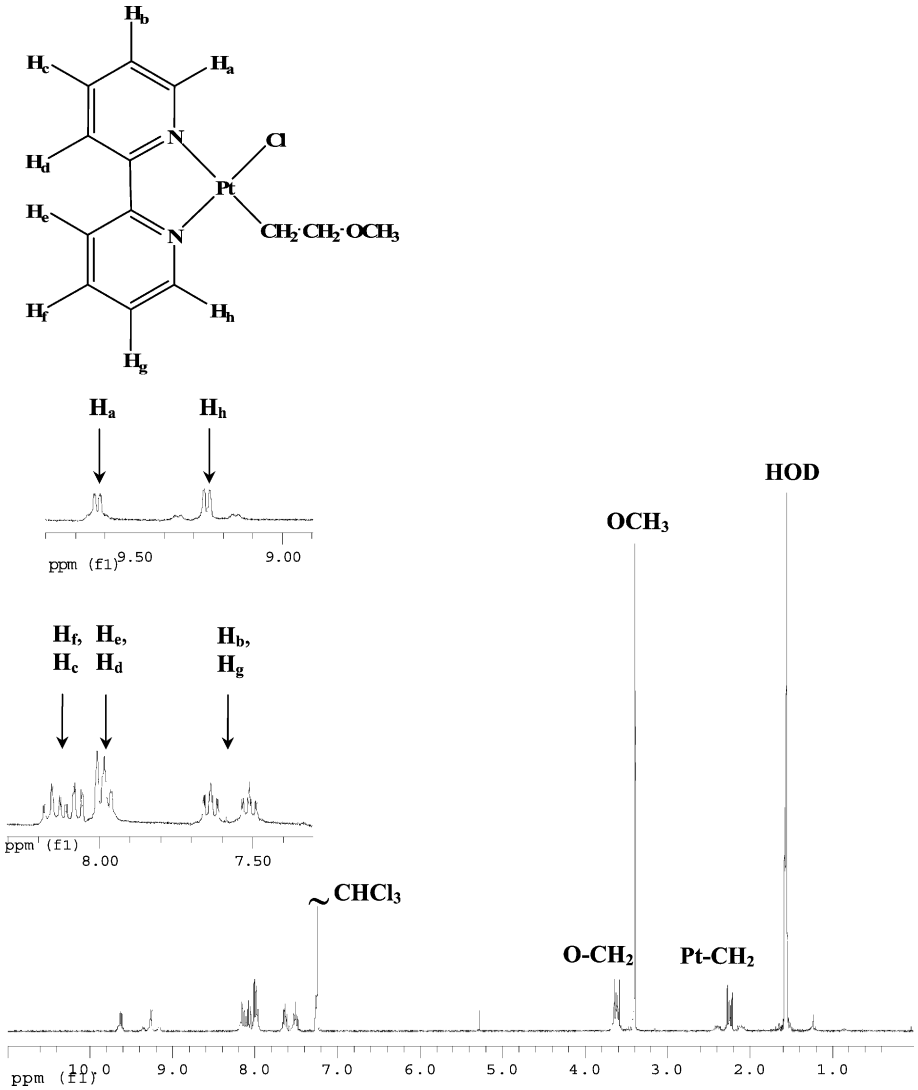


Fig. 1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 294 K) of complex [PtCl(η^1-CH_2CH_2–OCH_3)(bpy)], **5b**.

Synthesis of new cationic complexes

Reaction of species **5a–c** with acids bearing weakly coordinating anions (*e.g.* HBF_4 or $HClO_4$) results in the quantitative formation of cationic complexes **3a–c**.

3a has been previously obtained through controlled decomposition, in methanol, of **2a** in the presence of free tmeda and $LiClO_4$ (eqn (1)).[6g]

$$2\ \mathbf{2a} + \text{tmeda} + 2\ LiClO_4 \rightarrow [(\text{tmeda})ClPt–CH_2CH_2(\text{tmeda})CH_2CH_2–PtCl(\text{tmeda})](ClO_4)_2\downarrow + 2\ LiCl \quad (1)$$

The dimeric complex of eqn (1) could be quantitatively precipitated from the reaction solution as a diperchlorate salt and its subsequent hydrolysis with $HClO_4$ led to **3a**(ClO_4) (eqn (2)). The just quoted dimer has no equivalent in the case of ligands **b** and **c** and the cationic species **3b**, **3c** have so far eluded capture.

$$[(\text{tmeda})ClPt–CH_2CH_2(\text{tmeda})CH_2CH_2–PtCl(\text{tmeda})](ClO_4)_2 + 2\ HClO_4 \rightarrow 2\ \mathbf{3a}(ClO_4) + \text{tmeda}\cdot 2HClO_4 \quad (2)$$

3b, **3c** have been characterized *via* elemental analysis, IR, ESI-MS and NMR. The ^{1}H NMR (acetone-d_6) spectrum of **3c** is reported in Fig. 2. The resonance frequency of the ethene protons (5.3 and 5.4 ppm in **3b** and **3c**, respectively) is placed at the lower end of the range exhibited by platinum complexes having the olefin *trans* to a pyridine-like nitrogen.[15]

The reaction of **5d** with acids having weakly coordinating anions did not give **3d** but a number of ill defined products. In contrast the reaction with hydrochloric acid gave **2d** in high yield (a solution of **5d** in $CDCl_3$ treated with aqueous DCl yields nearly pure **2d**).

Reactivity of the new cationic complexes (3b, 3c) towards nucleophiles

The electrophilic character of the ethene molecule in **3b**, **3c** has been tested *via* reaction with a carbanion (acetylacetonate), and a secondary and a tertiary alkylamine (diethyl and triethylamine). In the case of **3a** all these nucleophiles gave stable products of addition to ethene.

The reaction of **3b**, **3c** with acetylacetonate (Scheme 2), leads to a mixture of two products: [PtCl{$CH_2CH_2CH(COCH_3)_2$}(N–N)] (**6b**, **6c**), formed by addition of the nucleophile to the

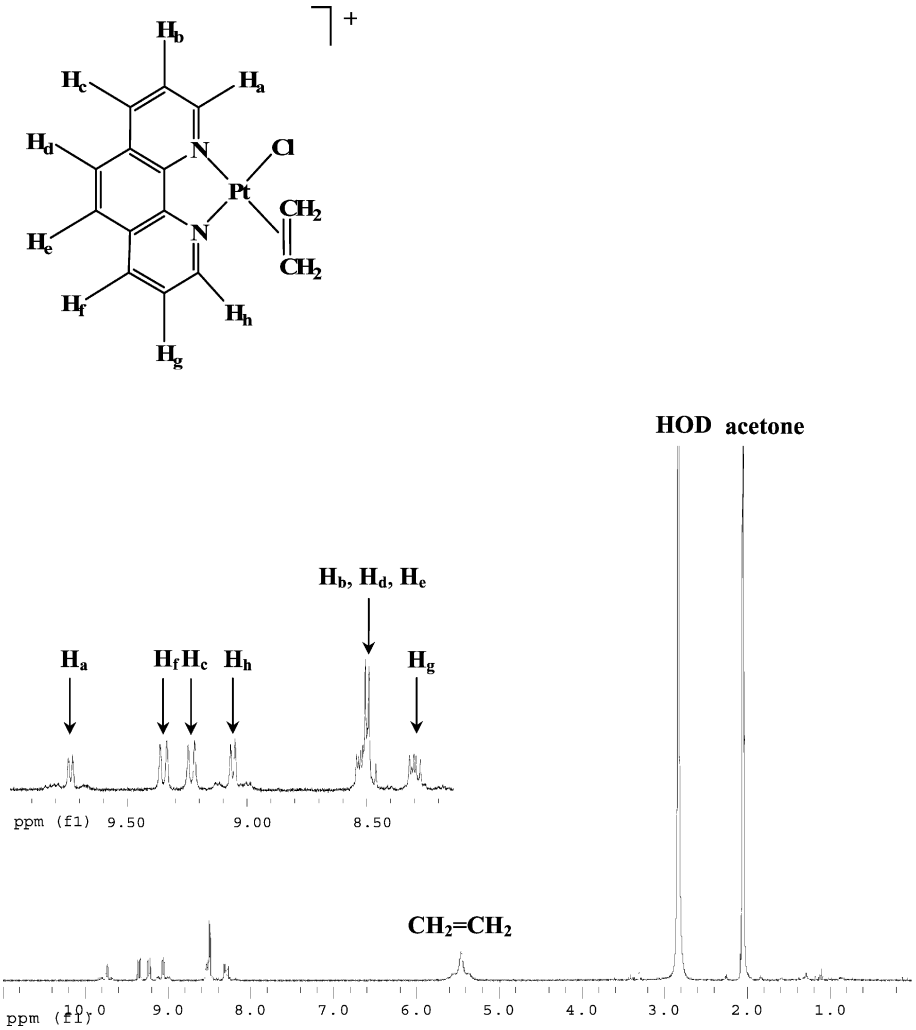
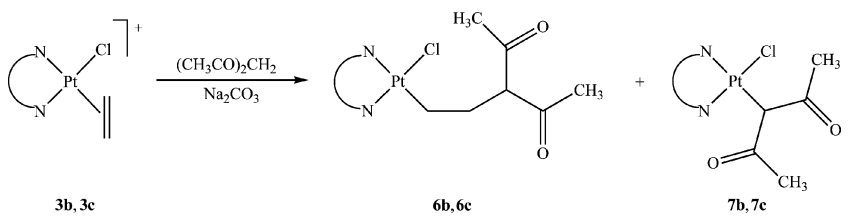


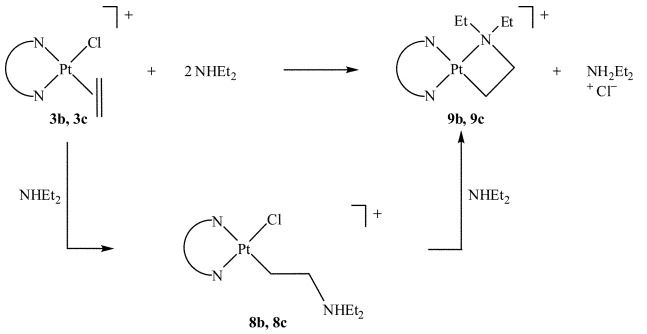
Fig. 2 ^{1}H NMR spectrum (300 MHz, acetone-d_6, 294 K) of complex [PtCl(η^2-CH_2=CH_2)(phen)]$^+$, **3c**.

coordinated olefin, and [PtCl{$CH(COCH_3)_2$}(N–N)] (**7b**, **7c**), formed by substitution of acetylacetonate for ethene. The ratio between the two compounds is somewhat influenced by the nature of the chelating ligand and by the reaction temperature (0 or 25 °C). The addition product **6** was slightly favoured in both cases (ligand **b**: **6b**/**7b** = 60 : 40 both at 0 and 25 °C; ligand **c**: **6c**/**7c** = 65 : 35 and 50 : 50 at 0 and 25 °C, respectively). In contrast, by performing an analogous reaction in the case of **3a**, only the addition product **6a** was obtained.[16] **6b**, **6c** and **7b**, **7c** were separated by conventional column chromatography over silica gel and characterized by elemental analysis and NMR. In the NMR spectrum ($CDCl_3$) the spin system assignable to the $C_\alpha H_2C_\beta H_2$–$CH(COCH_3)_2$ moiety is diagnostic for a structure of type **6** (see Tables 1 and 2). A difference between **6b**, **6c** and the already reported **6a** is that in the former compounds the acetylacetonate moiety is present only in the keto form, while in the latter one there is an equilibrium between keto and enol tautomers.[16] Compounds **7b**, **7c** have no equivalent in the case of the tmeda ligand (**a**). The most significant feature of their NMR spectra ($CDCl_3$) is the signal of the platinum bound methyne (δ(^{1}H) ~ 6.0 ppm, $^2J_{Pt-H}$ = 120 Hz; δ(^{13}C) ~ 38 ppm); also in **7b**, **7c**, the acetylacetonate ligand is present only in the keto form.

The reaction of **3b**, **3c** with diethylamine is depicted in Scheme 3. The amine adds rapidly to the ethene moiety and the addition



Scheme 2



Scheme 3

products (**8b**, **8c**) undergo nitrogen deprotonation by excess free amine and intramolecular substitution of the chlorido ligand, to form **9b**, **9c** which contain an azaplatinacyclobutane ring. Isolation of pure **8b**, **8c** (which were characterized *via* ESI-MS and NMR) required a $NHEt_2/Pt$ ratio ≤ 1 (see Tables 1 and 2 and Experimental). In contrast, the use of excess amine led to the rapid and complete production of compounds **9b**, **9c**.[17] The structure of cations **9b**, **9c** has been elucidated by IR (absence of Pt–Cl stretching vibration), ESI-MS (base peak at $m/z = 451.0$ and 474.0 for **9b** and **9c**, respectively), and NMR spectra. The 2D COSY ($^1H,^1H$) (acetone-d_6) spectrum of **9b** is reported in Fig. 3. As far as the NMR spectra are concerned, in the case

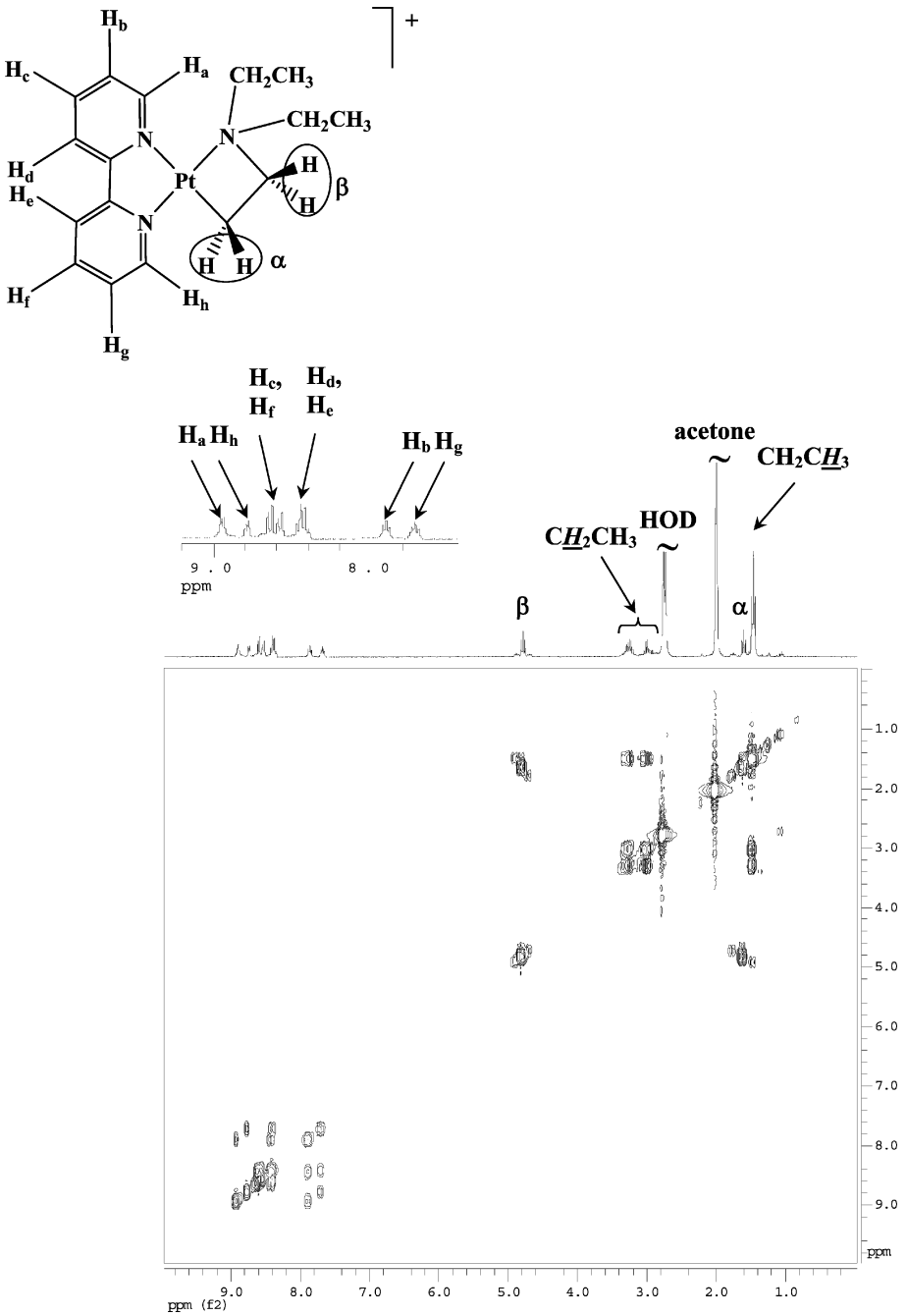
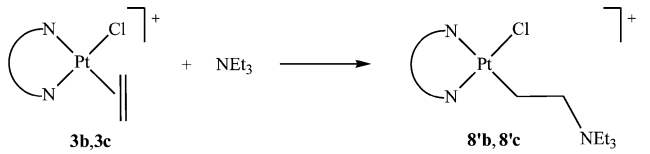


Fig. 3 2D COSY ($^1H,^1H$) NMR spectrum (300 MHz, acetone-d_6, 294 K) of complex $[Pt(\eta^1\text{-}CH_2CH_2\text{–}NEt_2\text{-}\kappa C,\kappa N)(bpy)]^+$, **9b**.

of **9** a number of features, typical of the ring closed structure Pt–$C_\alpha H_2 C_\beta H_2$–NEt_2-κ*C*,κ*N* are observed. In particular, with respect to the open arm complexes of type **8**, the ^1H and ^{13}C resonance frequencies move upfield for the α methylene and downfield for the β one, moreover the methylene protons of the amine ethyl groups become diastereotopic (see Tables 1 and 2).[18]

By reaction with tertiary amines (triethylamine) compounds **3b**, **3c** are converted to the corresponding addition products **8′b**, **8′c** (analogous to **8b**, **8c**), which cannot be transformed any further having no protons on the quaternized nitrogen atom (Scheme 4).



Scheme 4

Discussion

It is well established that in the reaction of Zeise's anion with a bidentate nitrogen ligand (see Scheme 1, upper row), after substitution of the chlorido *trans* to the olefin, the second end of the bidentate ligand binds to platinum increasing the metal coordination number from four to five. The five-coordinate species has trigonal bipyramidal geometry with the two ends of the chelating ligand and the olefin sharing the trigonal plane and the two chlorido ligands in axial positions (*x*-axis).[19] One can view the five-coordinate complex as a species in which both ends of the N–N ligand share the single coordination position previously occupied by the released chlorido ligand. The factors ruling the thermodynamic stability of the five-coordinate species reside in the strong π-acidic character of the olefin which can successfully remove the electric charge built up in the trigonal plane.[20] In this plane two pairs of non-bonding metal d^8 electrons (d_{z^2} and d_{yz} orbitals) are also confined. Ligand bite and bulk of substituents on the nitrogen atoms also play a crucial role for the stability of the five-coordinated species. A limited bite reduces the repulsion with the metal d electrons and large substituents on the nitrogen atoms can be better accommodated in the trigonal plane of a five-coordinate species than in the tetragonal plane of a $[PtCl_2(N–N)]$ molecule.

On some occasions, like in the case of Me_2phen (ligand **d**), the five-coordinate species, $[PtCl_2(\eta^2\text{-}C_2H_4)(N–N)]$ (**2**), is exceptionally stable and represents the final product of the reaction.[21] More frequently the five-coordinate species undergoes a transformation consisting in the release of a chlorido ligand and formation of the cationic complex $[PtCl(\eta^2\text{-}C_2H_4)(N–N)]^+$ (**3**), which, in turn, can further react with the released Cl^- to form the neutral $[PtCl_2(N–N)]$ (**4**) complex.[22] The rate of transformation varies as a function of the nature of the bidentate nitrogen ligand and the type of solvent. In solvents of low polarity, like chloroform, the transformation occurs in one step. Most likely the cationic species reacts immediately with the released chlorido ligand substituting the olefin and forming the neutral end product.[23a] In contrast, in polar solvents, like methanol, the cationic complex $[PtCl(\eta^2\text{-}C_2H_4)(N–N)]^+$ is formed first and then it undergoes substitution of the olefin by a chlorido ligand with a 2nd order kinetic law (dependence upon the Cl^- concentration).[23b] We have now found that the presence of CH_3O^- in the reaction medium warrants the quantitative production of species **5**.

The *trans* effect of the η^2-olefin in **1** (Zeise's anion) and **1′** (a Zeise's anion analogue with a CH_3O^- ligand *trans* to ethene) stems from its ability to remove electron charge from the metal centre stabilizing the five-coordinate transition state occurring upon ligand substitution at four-coordinate square planar substrates (entering and leaving groups and the ligand *trans* to the leaving group in the trigonal plane and the ligands *cis* to the leaving group in the axial sites). In the case of compound **1″** (formed by nucleophilic addition of CH_3O^- to the olefin of **1′**) the *trans* effect stems from the strong σ-donor ability of the alkyl ligand which labilizes the *trans* CH_3O^- group and favours its dissociation while the entering nucleophile is approaching.

The different reactivity of Me_2phen (**d**) towards **1′** and **1″**, both having a strong *trans*-labilizing ligand, can be explained in the following way. Me_2phen is a sterically hindered ligand, therefore the reaction with **1″** (Scheme 1, lower row), taking place through a *quasi* dissociative mechanism, can be favoured over the reaction with **1′** which takes place through an associative mechanism. In contrast the less hindered ligands **a–c** can react also with **1′** (associative path) and give the corresponding five-coordinate species **2a–c** which then can evolve to **5a–c** through **3a–c** (upper row of Scheme 1).

As previously pointed out, stable cationic species of type **3** are obtainable only in the presence of strongly chelating N–N ligands which can successfully counterbalance the *trans*-labilizing effect of the olefin.[24] In the case of ligand **d**, the repulsion between the *ortho* methyl groups and the *cis* ligands tend to destabilize the chelation in a square-planar geometry (while the same ligand confers high stability to a trigonal bipyramidal structure of type **2**).[21] In such a situation, **3d** becomes a transient species which rapidly takes up a chlorido affording **2d**.

Comparing the reactivity of **3b**, **3c** with that of **3a** previously investigated,[6j,l,7m–o,14–16,18,25] it can be concluded that in the former complexes the electrophilicity of the coordinated ethene is fully retained (as confirmed by the ability to add tertiary amines[25]). The platinum atom, however, competes more efficiently with the olefin for addition of soft nuceophiles (such as carbanions). Therefore formation of **7b**, **7c** takes place right from the beginning and no evolution of the addition product **6** into **7** is observed.

Finally we wish to comment on the formation of compounds **9b**, **9c**. Azaplatinacyclobutane rings were first reported over twenty years ago;[25,26] in particular they were formed after addition of a secondary amine to the coordinated olefin in *cis*-$[PtCl_2(\eta^2\text{-}C_2H_4)L]$ complexes when the L ligand had a P or S donor atom; the *trans*-labilizing effect of L, favouring the release of a chlorido ligand, was considered an important aiding factor for the ring closing reaction.[26,27a] The presence of a *trans*-labilizing ligand was not necessary when the olefin did bear bulky substituents,[27b,c] the ring-closing process being favoured by the so called Thorpe–Ingold effect.[28] In the previous examples (ref. 26 and 27), the intramolecular nucleophilic substitution occurred at a platinum(II) centre formally bearing a net negative charge (only two of the three negative charges brought in by the alkyl and the two chlorido ligands are neutralized by the +2 charge of the metal core). In a recent study some of us have shown how the ring closing step (the **8** → **9** step in Scheme 3) can occur in the absence either of a

trans-labilizing ligand L or of bulky substituents on the ethanide chain,[18] if the precursor (deprotonated **8**) has no formal negative charge localized on the platinum centre. The cyclization reaction appears to be further favoured for **8b**, **8c** as compared to **8a**. *N,N,N′,N′*-Tetramethyl-1,2-ethanediamine (**a**) is a better donor than 2,2′-bipyridyl (**b**) or 1,10-phenanthroline (**c**), therefore in **8a** the metal atom has a higher electron charge than in **8b**, **8c** and is less susceptible to nucleophilic attack by the nitrogen of the 2-aminoethanide ligand.

Conclusions

A quite general method for preparing cationic complexes of formula $[PtCl(\eta^2\text{-ethene})(N–N)]^+$ (**3**) has been found. It goes through the intermediate species $[PtCl(\eta^1\text{-}CH_2CH_2–OCH_3)(N–N)]$ (**5**) (Scheme 1) which are formed in basic conditions.

The reactivity of the cationic species is modulated by the nature of the bidentate nitrogen ligand. In particular the decreased basicity of 2,2′-bipyridyl and 1,10-phenanthroline, as compared to *N,N,N′,N′*-tetramethyl-1,2-ethanediamine, renders the platinum atom more electrophilic in **3b**, **3c** than in **3a**. This difference has two main consequences: i) In compounds **3b**, **3c** the metal centre successfully competes with the olefin for reaction with soft nucleophiles such as carbanions. ii) The products of addition of diethylamine (**8b**, **8c**) are converted to the cyclometallated species (**9b**, **9c**) more easily.

Thanks to the unique character of the sterically hindered 2,9-dimethyl-1,10-phenanthroline, it has been possible to disclose a new substitution pattern at a platinum centre and unravel an unexpected reactivity of Zeise's anion in basic solutions.

Experimental section

Reagents and methods

Reagents and solvents were commercially available and used as received. Elemental analyses were performed with a CHN Eurovector EA 3011. ^{1}H and ^{13}C NMR spectra were recorded with a 300 MHz Mercury Varian and DPX-WB 300 and DPX 400 Avance Bruker instruments equipped with probes for inverse detection and with *z* gradient for gradient-accelerated spectroscopy. ^{1}H and ^{13}C NMR spectra were referenced to TMS; the residual proton signal of the solvent was used as internal standard. ^{1}H/^{13}C inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR spectra for normal coupling (INVIEAGSSI) were acquired using standard Bruker automation programs and pulse sequences. Each block of data was preceded by eight dummy scans. The data were processed in the phase-sensitive mode. The ESI-MS spectra were recorded with an Agilent 1100 Series LC-MSD Trap System VL. IR spectra were recorded as KBr or high density polyethylene pellets on a Perkin-Elmer Spectrum One.

Chemicals

All solvents and reagents, except otherwise stated, were purchased from Aldrich Chemical Company and used as received. Zeise's salt was prepared from potassium tetrachloroplatinate and ethene through a modification of the method proposed by Chock *et al.*.[29] In our case the reaction was performed under an ethene atmosphere (P = 1 atm) rather than bubbling the gas through the aqueous hydrochloric acid solution of the platinum salt. The yield of isolated product was similar to that reported in the quoted reference, but the set up of the preparation was much easier, the consumption of gas minimal, and the dispersion in the environment of un-reacted olefin practically none.

Syntheses

CAUTION: the use of perchlorates may be extremly dangerous (explosive), and should be avoided when possible.

$[PtCl(\eta^1\text{-}C_\alpha H_2C_\beta H_2–OCH_3)(bpy)]$, 5b[30]. In a typical experiment Zeise's salt, $K[PtCl_3(\eta^2\text{-}CH_2{=}CH_2)]\cdot H_2O$, (387 mg, 1 mmol) was dissolved in methanol (1 mL) and the solution placed in an ice bath. The stoichiometric amount of bipyridyl (157 mg, 1 mmol) was then added and the instantaneous formation of the five-coordinate species **2b**, as a yellow precipitate, was observed. An excess of KOH, up to 20 times the stoichiometric amount (~1 g KOH dissolved in ~3 mL of MeOH), was then added. The mixture was kept stirring for 3 h, meanwhile the colour of the precipitate became orange-yellow. 10 mL of water were then added to the mixture and this induced further precipitation of product. The solid was separated by filtration of the solution through a sintered glass filter, washed with water until the filtrate reached pH = 7 and dried *in vacuo*. It turned out to be the desidered compound **5b** (>95% yield referred to platinum). Anal. calcd for $C_{13}H_{15}N_2ClOPt$: C, 35.02; H, 3.39; N, 6.28%. Found: C, 35.30; H, 3.70; N, 5.90%. Molecular peak in ESI-MS: m/z = 468.8 = [M + Na]$^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 2.22 (m, 2H, Pt-$C_\alpha H_2$, $^2J_{Pt–H}$ = 90 Hz), 3.39 (s, 3H, OCH_3), 3.61 (m, 2H, $C_\beta H_2$-O), 7.62, 7.99, 8.12, 8.28, 8.32, 9.23 ($^3J_{Pt–H}$ = 60 Hz), and 9.59 (8H, bpy); δ_C 6.3 (C_α, $^1J_{Pt–C}$ = 753 Hz), 57.9 (OCH_3), 76.2 (C_β), 122.1, 123.5, 127.2, 127.6, 137.5, 138.4, 148.3, and 149.0 (8*C*H, bpy).

$[PtCl(\eta^1\text{-}C_\alpha H_2C_\beta H_2–OCH_3)(phen)]$, 5c[30]. Compound **5c** was prepared in a way completely analogous to that for **5b**, starting from Zeise's salt (387 mg, 1 mmol) and 1,10-phenanthroline (202 mg, 1 mmol). The yield (referred to platinum) was nearly quantitative. Anal. calcd for $C_{15}H_{15}N_2ClOPt$: C, 38.35; H, 3.22; N, 5.96%. Found: C, 37.95; H, 3.0; N, 6.20%. Molecular peak in ESI-MS: m/z = 492.9 = [M + Na]$^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 2.41 (m, 2H, Pt-$C_\alpha H_2$, $^2J_{Pt–H}$ = 90 Hz), 3.42 (s, 3H, OCH_3), 3.70 (m, 2H, $C_\beta H_2$-O), 7.81, 7.95, 8.55, 8.65, 9.53 ($^3J_{Pt–H}$ = 57 Hz), and 9.81 (8H, phen); δ_C 5.5 (C_α, $^1J_{Pt–C}$ = 745 Hz), 58.0 (OCH_3), 76.4 (C_β), 122.7, 125.2–125.3, 127.0, 136.2–136.8, and 148.0–148.1 (8*C*H, phen).

$[PtCl(\eta^1\text{-}C_\alpha H_2C_\beta H_2–OCH_3)(Me_2\text{-phen})]$, 5d. In this case all manipulations prior to isolation of the product were carried out under nitrogen. Zeise's salt and Me_2phen were pumped under vacuum at about 10 mmHg for 15 min at 60 °C to remove adsorbed moisture. MeOH was dried over molecular sieves of type 4Å (activated by heating at 120 °C for 48 h). Na (81 mg, 3.5 mmol) was dissolved in 3.5 mL of MeOH (–20 °C, ice–NaCl bath). After evolution of H_2 the temperature was increased to 0 °C, then the Zeise's salt (100 mg, 0.26 mmol) was added under magnetic stirring. A white precipitate of KCl immediately formed and the colour of the solution changed from bright to pale yellow. After 2 min Me_2phen (54 mg, 0.26 mmol) was added to the reaction mixture. The final product **5d**, which has a limited solubility in the reaction medium, precipitated from the solution

as a yellow powder. After 2 h stirring, the reaction mixture was filtered on a sintered glass filter, the solid was washed with water to eliminate residual base and KCl, and dried under vacuum. **5d** was obtained in 74% yield (referred to platinum). Anal. calcd for $C_{17}H_{19}N_2ClOPt$: C, 41.01; H, 3.85; N, 5.63%. Found: C, 41.10; H, 3.80; N, 5.50%. Molecular peak in ESI-MS: $m/z = 520.9 = [M + Na]^+$. NMR (400 MHz, $CDCl_3$, 294 K): δ_H 2.33 (m, 2H, Pt-$C_\alpha H_2$, $^2J_{Pt-H} = 95$ Hz), 2.98 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 3.33 (s, 3H, OCH_3), 3.71 (m, 2H, $C_\beta H_2$-O), 7.56, 7.59, 7.74, 7.75, 8.27, 8.33 (6H, Me_2-phen); δ_C −1.2 (C_α, $^1J_{Pt-C} = 700$ Hz), 57.8 (OCH_3), 76.1 (C_β), 26.7 and 27.8 ($2CH_3$, Me_2-phen), 125.2, 126.4, 126.6, 127.4, 136.2, and 136.3 (6*C*H, Me_2-phen).

[PtCl(η²-CH_2=CH_2)(bpy)](ClO_4), 3b(ClO_4). Compound **3b**, previously isolated as its tetrafluoroborate salt,[9] has now been prepared as a perchlorate salt. In a typical experiment **5b** (223 mg, 0.5 mmol) was suspended in dichloromethane and the stoichiometric amount of $HClO_4$ (0.5 mL of a 1.0 M aqueous solution) was then added. The mixture was kept stirring for 30 min at room temperature and then the overlying aqueous phase was removed. The solid **3b**(ClO_4) was separated by filtration of the chlorinated solution through a sintered glass filter, washed twice with dichloromethane, and dried *in vacuo*. The yield, referred to platinum, was >95%. Anal. calcd for $C_{12}H_{12}N_2Cl_2O_4Pt$: C, 28.03; H, 2.35; N, 5.45%. Found: C, 28.30; H, 2.57; N, 5.60%. Molecular peak in ESI-MS: $m/z = 413.9 = [M - ClO_4]^+$. NMR (300 MHz, acetone-$d_6$, 294 K, ppm): δ_H 5.29 (s, 4H, CH_2=CH_2, $^3J_{Pt-H} = 54$ Hz), 7.84, 7.98, 8.19, 8.60, 8.78, 8.85, 9.47 ($^3J_{Pt-H} = 36$ Hz), and 9.72 ($^3J_{Pt-H} = 36$ Hz) (8H, bpy).

[PtCl(η²-CH_2=CH_2)(phen)](ClO_4), 3c(ClO_4). Compound **3c**(ClO_4) was prepared from **5c** (235 mg, 0.5 mmol) in a way completely analogous to that for **3b**(ClO_4). The yield, referred to platinum, was >95%. Anal. calcd for $C_{14}H_{12}N_2Cl_2O_4Pt$: C, 31.24; H, 2.25; N, 5.20%. Found: C, 31.08; H, 2.51; N, 5.42%. Molecular peak in ESI-MS: $m/z = 438.8 = [M - ClO_4]^+$. NMR (300 MHz, acetone-$d_6$, 294 K, ppm): δ_H 5.45 (s, 4H, CH_2=CH_2, $^3J_{Pt-H} = 60$ Hz), 8.28, 8.50, 9.04 ($^3J_{Pt-H} = 38$ Hz), 9.21, 9.33, and 9.71 ($^3J_{Pt-H} = 36$ Hz) (8H, phen).

[PtCl{η¹-$C_\alpha H_2C_\beta H_2$–$CH(COCH_3)_2$}(bpy)], 6b and [PtCl{$CH(COCH_3)_2$}(bpy)], 7b. Compound **3b**(ClO_4) (257 mg, 0.5 mmol) was suspended in CH_2Cl_2 (5 mL) in the presence of Na_2CO_3 (159 mg, 1.5 mmol) and treated with acetylacetone (154 μL, 1.5 mmol). The mixture was stirred for 24 h. The mother liquor was filtered and evaporation of the solvent *in vacuo* left a sticky solid which, after trituration with diethyl ether, afforded a yellow solid of the two species **6b** and **7b**. The reaction was performed at two different temperatures, 0 and 25 °C, and a similar ratio of the two complexes (^{1}H NMR) was obtained (**6b**/**7b** = 60 : 40). The crude reaction product was chromatographed over a silica gel column using as eluent a mixture of CH_2Cl_2 and acetone (4 : 1 v/v). The addition product **6b** was eluted first. The isolated yield of **6b** was 40% referred to platinum. Anal. calcd for $C_{17}H_{19}N_2ClO_2Pt$: C, 39.73; H, 3.73; N, 5.45%. Found: C, 39.45; H, 3.61; N, 5.69%. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 1.85 (m, 2H, Pt-$C_\alpha H_2$), 2.12 (m, 2H, $C_\beta H_2$), 2.24 (s, 6H, $CH(COCH_3)_2$), 3.92 (t, 1H, $CH(COCH_3)_2$, $^3J_{H-H} = 6$ Hz), 7.6–8.2, 9.31 ($^3J_{Pt-H} = 60$ Hz), and 9.53 (8H, bpy); δ_C 2.82 (C_α), 30.5 ($CH(COCH_3)_2$), 30.8 (C_β), 69.9 ($CH(COCH_3)_2$), 126–127, 136–138, 148–149 (8*C*H, bpy). The isolated yield of **7b** was 25% referred to platinum. Anal. calcd for $C_{15}H_{15}N_2ClO_2Pt$: C, 37.08; H, 3.11; N, 5.77%. Found: C, 36.85; H, 3.36; N, 5.58%. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 2.47 (s, 6H, $CH(COCH_3)_2$), 5.88 (s, 1H, Pt-$CH(COCH_3)_2$, $^2J_{Pt-H} = 120$ Hz), 7.6–8.2, 9.71, and 10.09 ($^3J_{Pt-H} = 47$ Hz) (8H, bpy); δ_C 31.0 ($CH(COCH_3)_2$), 37.7 (Pt-$CH(COCH_3)_2$, $^1J_{Pt-C} = 601$ Hz), 126–127, 136–138, 148–149 (8*C*H, bpy).

[PtCl{η¹-$C_\alpha H_2C_\beta H_2$–$CH(COCH_3)_2$}(phen)], 6c and [PtCl{η¹-$CH(COCH_3)_2$}(phen)], 7c. Compounds **6c** and **7c** were prepared in a way completely analogous to that of **6b** and **7b**, starting from **3c**(ClO_4) (269 mg, 0.5 mmol). The ratio **6c**/**7c** (^{1}H NMR) was 50 : 50 at 0 °C and 35 : 65 at 25 °C. The isolated yield of **6c**, after chromatography of the crude reaction product obtained at 0 °C was 35% referred to platinum. Anal. calcd for $C_{19}H_{19}N_2ClO_2Pt$: C 42.43; H 3.56; N 5.21%. Found: C, 42.70; H, 3.66; N, 4.95%. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 2.07 (m, 2H, Pt-$C_\alpha H_2$), 2.20 (m, 2H, $C_\beta H_2$), 2.35 (s, 6H, $CH(COCH_3)_2$), 4.0 (t, 1H, $CH(COCH_3)_2$), 7.95, 8.5, 8.7, 9.65 ($^3J_{Pt-H} = 62$ Hz), and 9.80 (8H, phen); δ_C 2.12 (C_α), 30.4 ($CH(COCH_3)_2$), 31.4 (C_β), 70.6 ($CH(COCH_3)_2$), 126–127, 136.3, 137.2, 148.7, and 149.3 (8*C*H, phen). The isolated yield of **7c**, after chromatography of the crude reaction product obtained at 25 °C was 45% referred to platinum. Anal. calcd for $C_{17}H_{15}N_2ClO_2Pt$: C 40.05; H 2.97; N 5.49%. Found: C 40.33; H, 3.16; N, 5.26%. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 2.30 (s, 6H, $CH(COCH_3)_2$), 6.05 (s, 1H, Pt-$CH(COCH_3)_2$, $^2J_{Pt-H} = 120$ Hz), 7.95, 8.55, 9.9 ($^3J_{Pt-H} = 56$ Hz), and 10.5 (8H, phen); δ_C 31.4 ($CH(COCH_3)_2$), 37.9 (C_α, $^1J_{Pt-C} = 605$ Hz), 125–126, 127–128, 137.5, 138.5, 149.2, and 154.4 (8*C*H, phen).

[PtCl{η¹-$C_\alpha H_2C_\beta H_2$–$NH(CH_2CH_3)_2$}(bpy)](ClO_4), 8b(ClO_4). In a typical experiment **3b**(ClO_4) (275 mg, 0.5 mmol) was added to a solution of diethylamine (52 μL, 0.5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 3 h and the obtained solution was taken to dryness under vacuum. Trituration with diethyl ether of the sticky residue left an orange powder corresponding to compound **8b**(ClO_4). The yield, referred to platinum, was above 90%. Anal. calcd for $C_{16}H_{23}N_3Cl_2O_4Pt$: C, 32.72; H, 3.95; N, 7.15%. Found: C, 32.51; H, 3.83; N, 7.35%. Molecular peak in ESI-MS: $m/z = 487.9 = [M - ClO_4]^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 1.36 (t, 6H, $NH(CH_2CH_3)_2$, $^3J_{H-H} = 7$ Hz), 2.08 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H} = 8$ Hz, $^2J_{Pt-H} = 90$ Hz), 3.22–3.28 (m, 6H, $C_\beta H_2$ and $NH(CH_2CH_3)_2$), 7.25 (bs, 1H, N*H*), 7.59, 7.65, 8.0–8.15, 9.20 ($^3J_{Pt-H} = 60$ Hz), and 9.47 (8H, bpy); δ_C −2.7 (C_α, $^1J_{Pt-C} = 717$ Hz), 8.12 ($NH(CH_2CH_3)_2$), 44.5 ($NH(CH_2CH_3)_2$), 57.1 (C_β), 121.5, 122.7,126.5, 128.4, 137.6–138.7, 147.7, and 149.5 (8*C*H, bpy).

[PtClη¹-$C_\alpha H_2C_\beta H_2$–$NH(CH_2CH_3)_2$}(phen)](ClO_4), 8c(ClO_4). Compound **8c**(ClO_4) was prepared starting from **3c**(ClO_4) (269 mg, 0.5 mmol) in a way completely analogous to that of **8b**(ClO_4),. The yield, referred to platinum, was above 90%. Anal. calcd for $C_{18}H_{23}N_3Cl_2O_4Pt$: C, 35.36; H, 3.79; N, 6,87%. Found: C, 37.42; H, 3.96; N, 6.73%. Molecular peak in ESI-MS: $m/z = 511.7 = [M - ClO_4]^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 1.39 (t, 6H, $NH(CH_2CH_3)_2$, $^3J_{H-H} = 7$ Hz), 2.36 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H} = 8$ Hz, $^2J_{Pt-H} = 90$ Hz), 3.30 (m, 4H, $NH(CH_2CH_3)_2$), 3.44 (t, 2H, $C_\beta H_2$), 7.90–7.98, 8.08, 8.61, 9.80, and 9.71 ($^3J_{Pt-H} = 60$ Hz) (8H, phen); δ_C −3.4 (C_α, $^1J_{Pt-C} = 750$ Hz), 8.2 ($NH(CH_2CH_3)_2$),

45.1 (NH(CH_2CH_3)$_2$), 57.8 (C_β), 124.9, 127.0, 136.0–137.8, 147.6, and 150.2 (8*C*H, phen).

[PtCl{η¹-$C_\alpha H_2C_\beta H_2$–N(CH_2CH_3)$_3$}(bpy)](ClO$_4$), 8′b(ClO$_4$). In a typical experiment **3b**(ClO$_4$) (257 mg, 0.5 mmol) was added to a solution of triethylamine (209 μL, 1.5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 3 h and the obtained solution was taken to dryness under vacuum. Trituration with diethyl ether of the sticky residue removed the excess of amine and left a yellow powder corresponding to compound **8′b**(ClO$_4$). The yield, referred to platinum, was above 90%. Anal. calcd for $C_{18}H_{27}N_3Cl_2O_4Pt$: C, 35.13; H, 4.42; N, 6.83%. Found: C, 35.35; H, 4.61; N, 6.67%. Molecular peak in ESI-MS: m/z = 515.9 = [M – ClO$_4$]$^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 1.37 (t, 9H, N(CH_2CH_3)$_3$, $^3J_{H-H}$ = 7 Hz), 2.09 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 89 Hz), 3.34 (q, 6H, N(CH_2CH_3)$_3$), 3.52 (t, 2H, $C_\beta H_2$), 7.63, 7.9–8.2, 9.19 ($^1J_{Pt-H}$ = 60 Hz), and 9.51 (8H, bpy); δ_C –6.6 (C_α), 7.6 (NH(CH_2CH_3)$_2$), 51.5 (NH(CH_2CH_3)$_2$), 62.8 (C_β), 121.9–123.1, 126.7, 129.4, 138.5–139.5, and 148.0–149.9 (8*C*H, bpy).

[PtCl{η¹-$C_\alpha H_2C_\beta H_2$–N(CH_2CH_3)$_3$}(phen)](ClO$_4$), 8′c(ClO$_4$). Compound **8′c**(ClO$_4$) was prepared starting from **3c**(ClO$_4$) (269 mg, 0.5 mmol) in a way completely analogous to that of **8′b**(ClO$_4$). The yield, referred to platinum, was above 90%. Anal. calcd for $C_{20}H_{27}N_3Cl_2O_4Pt$: C, 37.57; H, 4.26; N, 6.57%. Found: C, 37.85; H, 4.46; N, 6.73%. Molecular peak in ESI-MS: m/z = 539.8 = [M – ClO$_4$]$^+$. NMR (300 MHz, $CDCl_3$, 294 K, ppm): δ_H 1.39 (t, 9H, N(CH_2CH_3)$_3$, $^3J_{H-H}$ = 7 Hz), 2.19 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 89 Hz), 3.37 (q, 6H, N(CH_2CH_3)$_3$), 3.54 (t, 2H, $C_\beta H_2$), 7.9, 8.19, 8.57, 9.42 ($^1J_{Pt-H}$ = 59 Hz), and 9.57 (8H, phen); δ_C n.d.

[Pt{η¹-$C_\alpha H_2C_\beta H_2$–N(CH_2CH_3)$_2$-κ*C*,κ*N*}(bpy)](ClO$_4$), 9b(ClO$_4$). In a typical experiment **3b**(ClO$_4$) (257 mg, 0.5 mmol) was added to a solution of diethylamine (520 μL, 5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 3 h, meanwhile a progressive disappearance of solid **3b**(ClO$_4$) was observed. The resulting solution was repeatedly extracted with water (6 × 1 mL) to remove the formed ammonium salt, diluted with CH_2Cl_2 up to 20 mL and kept over anhydrous Na_2SO_4 for some hours. The solution was filtered, and finally taken to dryness under vacuum. Trituration with diethyl ether of the sticky residue afforded a yellow powder corresponding to compound **9b**(ClO$_4$). The yield, referred to platinum, was 85%.

9b(ClO$_4$) can also be obtained by an alternative procedure. **8b**(ClO$_4$) (293.7 mg, 0.5 mmol) was added to a suspension of sodium carbonate, Na_2CO_3, in CH_2Cl_2 (5 mL). After 12 h stirring, the reaction mixture was filtered and the solution was taken to dryness under vacuum. Trituration with diethyl ether of the sticky residue afforded a yellow powder corresponding to compound **9b**(ClO$_4$). The yield, referred to platinum, was 90%.

Anal. calcd for $C_{16}H_{22}N_3ClO_4Pt$: C, 34.88; H, 4.03; N, 7.63%. Found: C, 34.65; H, 4.30; N, 7.82%. Molecular peak in ESI-MS: m/z = 451.0 = [M – ClO$_4$]$^+$. NMR (300 MHz, acetone-d$_6$, 294 K, ppm): δ_H 1.51 (m, 6H, N(CH_2CH_3)$_2$), 1.65 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 89 Hz), 3.03 (m, 2H, N(CH_2CH_3)$_2$), 3.30 (m, 2H, N(CH_2CH_3)), 4.83 (t, 2H, $C_\beta H_2$, $^3J_{H-H}$ = 8 Hz, $^3J_{Pt-H}$ = 58 Hz), 7.73, 7.91, 8.44, 8.58, 8.64, 8.79 ($^3J_{Pt-H}$ = 55 Hz), and 8.95 (8H, bpy); δ_C –26.7 (C_α), 12.0 (N(CH_2CH_3)$_2$), 55.3 (N(CH_2CH_3)$_2$), 67.4 (C_β), 122.4–124.0, 127.5–128.5, 139.0–141.0, 150.0, and 151.3 (8*C*H, bpy).

[Pt{η¹-$C_\alpha H_2C_\beta H_2$–N(CH_2CH_3)$_2$-κ*C*,κ*N*}(phen)](ClO$_4$), 9c(ClO$_4$). Compound **9c**(ClO$_4$) was prepared in a way completely analogous to that of **9b**(ClO$_4$), starting from **3c**(ClO$_4$) (269 mg, 0.5 mmol). The yield, referred to platinum, was 85%. Anal. calcd for $C_{18}H_{22}N_3ClO_4Pt$: C, 37.60; H, 3.86; N, 7.31%. Found: C, 37.83; H, 3.65; N, 7.56%. Molecular peak in ESI-MS: m/z = 474.0 = [M – ClO$_4$]$^+$. NMR (300 MHz, acetone-d$_6$, 294 K, ppm): δ_H 1.4 (m, 6H, N(CH_2CH_3)$_2$), 1.72 (t, 2H, Pt-$C_\alpha H_2$, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 90 Hz), 3.05 (m, 2H, N(CH_2CH_3)$_2$), 3.3 (m, 2H, N(CH_2CH_3)), 4.75 (m, 2H, $C_\beta H_2$, $^3J_{Pt-H}$ = 45 Hz), 7.8, 8.0, 8.2, 8.65, 8.85 ($^3J_{Pt-H}$ = 57 Hz), and 9.15 (8H, phen); δ_C –26.4 (C_α), 12.5 (2 N(CH_2CH_3)$_2$), 55.7 (2 N(CH_2CH_3)$_2$), 68.4 (C_β), 125.8, 127.6–128.1, 138.4–138.8, 150.3, and 151.3 (8*C*H, phen).

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