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Stabilization of unstable unsaturated molecules in five-coordinate TBP complexes of Pt(II): enol, diol and dialdehyde derivatives

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Abstract

Protection and stabilization of some unstable olefins has been effectively achieved by coordination in five-coordinate [PtClMe(2,9-Me_2-1,10-phenanthroline)(olefin)] complexes. These have been characterized by ^{1}H-NMR spectroscopy and in the case of [PtClMe(2,9-Me_2-1,10-phenanthroline)(*Z*-EtCH=CHOH)] by X-ray diffractometry. Chemoselective reactions have been accomplished on the complexes, some of them involving alcoholic or aldehydic functions of the unsaturated ligand.

Keywords: Platinum; Olefin complexes; Enols

1. Introduction

The cooordination of a poorly stable molecule to a metal can afford both protection of the coordinated function and stabilization of the whole ligand molecule. The usefulness of these achievements, which can pertain e.g. olefins [1] or phosphines [2], can be substantial and this explains why the known successful results of this research area date by far [1a].

In a previous study a new approach was proposed to the protection of the double bond of unstable olefins [3]. It was considered that within the generally favorable platinum chemistry the coordinatively saturated trigonal bipyramidal species of the type [Pt(*N*,*N*-chelate)(L)(L′)(olefin)] are to date the compounds by far best suited for the coordination of a substituted olefin, due to the general stability of the complexes [4]. We succeeded in the isolation of stable vinyl alcohol complexes [3] displaying an unprecedented and fairly wide reactivity of the coordinated olefin.

Here the study is extended to higher enols RCH=CHOH and to the ethenediol HOCH=CHOH. We report the synthesis and characterization of their complexes, including the X-ray structure of [PtClMe(dmphen)(EtCH=CHOH)] (dmphen = 2,9-Me_2-1,10-phenanthroline). Chemo- and regio-selective reactions of hydroxyl groups of the metal-anchored substrates are described. In this study we conclude the test of the proposed approach by isolating also complexes of a poorly stable olefin with non-alcoholic functions, i.e. fumaraldehyde, on which some clean reactions have been performed.

2. Results and discussion

2.1. Synthesis and behavior of RCH=CHOH complexes (R = Me, Et)

Both 1-propen-1-ol and 1-buten-1-ol are more stable olefins than the previously investigated vinyl alcohol, although their ketonization is easily accelerated by catalysts inducing hydrogen abstraction, and their general stability is fairly poor [5]. On the other hand, their use as unsaturated substrates in this study allows an immediate comparison with the behavior of the lower ethenol [3]. The corresponding trimethylsilyl enol ethers

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are readily prepared from propanal and butanal, respectively, according to a known procedure [6]. The geometry of the two silylated products can be inferred from ^{1}H-NMR spectroscopy on consideration of the previous assignments and of the HC=CH coupling constants [7]. In this work Z/E mixtures of (RCH=CHOSiMe$_3$) were used in stoichiometric excess for addition to [PtClMe(dmphen)] (Eq. (1)).

$$[PtClMe(dmphen)] + RCH{=}CHOSiMe_3 = [PtClMe(dmphen)(RCH{=}CHOSiMe_3)]\ \mathbf{1a}\ (R = Me),\ \mathbf{1b}\ (R = Et) \quad (1)$$

In both cases the addition is stereoselective and only the Z-isomers were observed in the products **1** (vide infra). Subsequent hydrolysis of the adducts **1a** and **1b** afforded respectively the five-coordinate complexes **2a** and **2b** (Eq. (2)):

$$\mathbf{1} + H_2O = [PtClMe(dmphen)(Z\text{-}RCH{=}CHOH)] + \text{`}HOSiMe_3\text{'}\ \mathbf{2a}\ (R = Me),\ \mathbf{2b}\ (R = Et) \quad (2)$$

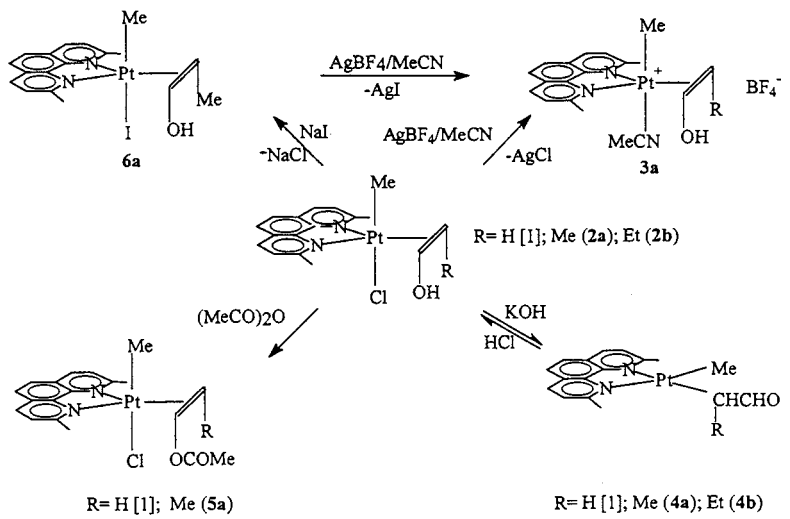
The white complexes **2** display fair solubility in common organic solvents and good general stability in solid state and in solution. The geometry of the coordinated olefin is Z according to the X-ray structure of **2b** (see below) and to the close similarity of the ^3J(H–H) coupling constants (7 Hz) of the olefin protons in the two complexes.

Although only one stereoisomer of the enol is bonded to the metal, two different isomers (each one an enantiomeric couple) can be conceived according to the orientation of R and OH relative to the axial ligands. However, the ^{1}H-NMR data indicate that also the orientation of the olefin is stereospecific, since one signal is observed for the proton adjacent to OH, and the chance of rapid rotation of the olefin is unlikely [4]. The adopted geometry seems to be in both cases that with OH near the halide, on consideration that the chemical shift of the proton RCH=C*H*OH is 4.52 δ, very near to that (4.58 δ) of the corresponding proton of CH$_2$=CHOH in the similar adduct of known stereochemistry [3]. Moreover, the same type of geometry is disclosed by the X-ray analysis of **2b** to exist in the solid state (vide infra), similarly to the finding for the corresponding vinyl alcol complex [3].

Some reactions of the complexes **2** are reported in Scheme 1, where the behavior of the corresponding vinyl alcohol complexes is recalled for comparison sake.

The similarity in behavior of the vinyl alcohol and of its homologs, that was obviously expected for the halide exchange and the attainment of cationic complexes, encompasses also the reactions of the unsaturated ligands. Particularly significant appears the attainment of square planar σ derivatives by reaction with base and the reconversion to the coordinatively saturated η^2 ethenol complex on acid treatment. The isolated complexes, as well as their reactions, can be useful models of the species involved in important reactions of C$_2$–C$_4$ oxygenated molecules on catalyst surfaces. This is, e.g., the case of aldheyde oxidation on metal oxide surface, where the role of enols and enolates has been thoroughly investigated [8].

It is also to note that the ^{1}H-NMR signal of MeCH=C*H*OAc in the acetylation product of **2a** is at $\delta = 6.2$, diagnostic (vide supra) of the acetate group facing the methyl. We also recall that for the corresponding CH$_2$=CHOAc derivative [3] the first formed stereoisomer ($\delta = 5.6$) turns to a more stable one ($\delta =$ 6.2). It seems reasonable that, since acetylation eliminates the possibility of O–H···Cl hydrogen bond, the acetylated isomers having the ester group near the axial methyl become more stable.



Scheme 1.

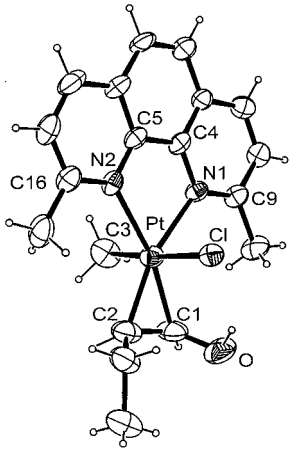


Fig. 1.

2.2. Molecular structure of [PtClMe(dmphen)(Z-EtCH=CHOH)]

The molecular structure of **2b**, together with the atom labelling scheme, is shown in Fig. 1. Selected bond lengths and angles are presented in Table 1. The structure appears to be closely similar to the analog complex of the Ref. [3]. Both complexes exhibit regular trigonal bipyramidal coordination geometry with the dmphen ligand and the olefin carbon atoms in the equatorial plane while the methyl group and the halogen atom are in axial position. The geometry features of the two structures accord very well, the only significant differences being given by the values of the Pt–Me bond length. In the title complex, where the axial opponent is Cl, its value is 2.06(2) Å, whereas in the complex of Ref. [3], where the axial opponent is Br, its value is 2.209(9) Å. The discrepancy is to be ascribed to the marked difference in the trans-influence of the two halogen atoms. On the other hand a conservative feature, which in both structures plays a stabilizing role, is given by the O–H···X hydrogen bond where X is the halogen atom. In the title compound its parameters are: O···Cl 3.16(2) Å, H···Cl 2.23(4) Å, O–H···Cl 139(2)°.

2.3. Synthesis and behavior of Z-HOCH=CHOH complexes

Z-1,2-ethenediol is an unstable molecule which polymerizes in a few minutes at 25°C [9]. The bis-trimethylsilyl derivative was prepared as previously described [10]. To obtain the five-coordinate species a procedure similar to that used for ethenols was adopted, first involving addition of the silyl derivative to give **7** (Eq. (3)).

$$[PtClMe(dmphen)] + Z\text{-}Me_3SiOCH{=}CHOSiMe_3 = [PtClMe(dmphen)(\underset{\mathbf{7}}{Z\text{-}Me_3SiOCH{=}CHOSiMe_3})] \quad (3)$$

It is noted that when the above step was performed by using a nearly equimolar mixture of the bis-trimethylsilyl derivatives of *E*- and *Z*-1,2-ethenediol [10], the selective uptake of the *Z* form by the square precursor was observed. In fact, the equivalence of the halves of both the olefin and the chelate in the NMR spectrum gives evidence of the C_s symmetry of the complex.

The five-coordinate compound **8** was obtained by hydrolysis (Eq. (4)):

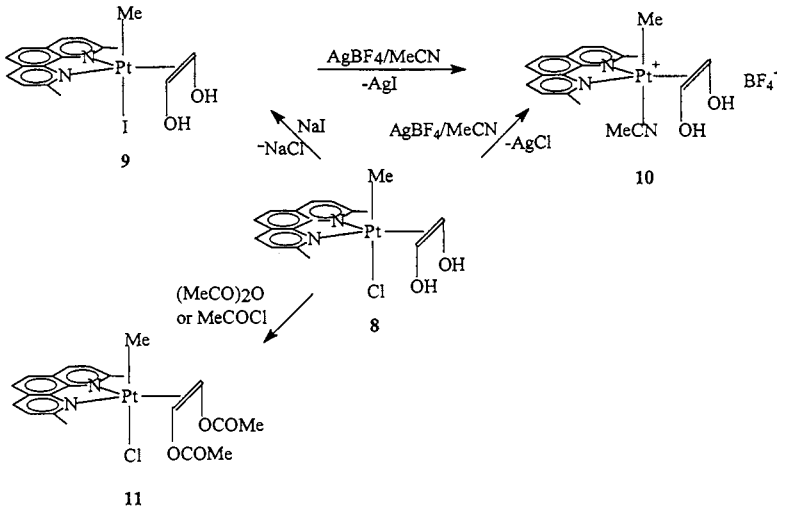
$$\mathbf{7} + 2H_2O = [PtClMe(dmphen)(\underset{\mathbf{8}}{Z\text{-}HOCH{=}CHOH})] + 2\text{`}HOSiMe_3\text{'} \quad (4)$$

The white complex is fairly soluble in common organic solvents and displays good general stability in solid state and in solution.

As expected, the above mentioned NMR features agree with a C_s symmetry also in the case of **8**. Furthermore, of the two conceivable isomers of C_s symmetry, **8** is likely to be the one bearing the OH groups on the halogen side, by analogy with the ethenol complexes (vide supra).

Table 1
Selected bond distances (Å) and angles (°) for complex **2b**

Bond distances (Å)					
Pt–Cl	2.470(4)	Pt–N1	2.22(1)	Pt–C1	2.06(1)
Pt–C3	2.06(2)	Pt–N2	2.236(9)	Pt–C2	2.06(2)
C1–C2	1.40(1)				
Bond angles					
Cl–Pt–N1	88.5(3)	Cl–Pt–N2	88.7(3)		
Cl–Pt–C1	92.8(5)	Cl–Pt–C2	94.6(5)		
Cl–Pt–C3	176.5(5)	N1–Pt–N2	74.2(3)		
N1–Pt–C1	119.7(5)	N2–Pt–C1	166.1(5)		
N1–Pt–C3	88.7(5)	N2–Pt–C3	88.5(5)		
N1–Pt–C2	159.3(5)	N2–Pt–C2	126.3(5)		
C1–Pt–C2	39.9(6)	C1–Pt–C3	90.3(7)		
C2–Pt–C3	88.8(7)				



Scheme 2.

Reactions (Scheme 2) not involving the olefin, i.e. halide exchange and attainment of a cationic species are similar to those observed for related enol compounds. We note that the diol cationic derivative **10** was observed in solution, but it decomposed when isolation was attempted.

Esterification of **8** with acetic anhydride was also successfully accomplished in high yield.

2.4. Synthesis and behavior of E-OHCCH=CHCHO complexes

Fumaraldheyde displays low stability, and it has been previously trapped [11] by reaction of its dimethyl acetal in the stable complex $[Fe(CO)_4(E$-OHCCH=CHCHO)], which undergoes thermal isomerization to a η^4 complex. To obtain the coordinatively saturated species **12** we reacted the tetraacetal, which at difference with the diacetal is commercially available, in a one pot synthesis with [PtClMe(dmphen)] in the presence of a small amount of trifluoroacetic acid, so that hydrolysis and coordination were both obtained (Eq. (8)).

$$[PtClMe(dmphen)] + E\text{-}(OMe)_2CHCH{=}CHCH(OMe)_2 + 4H_2O = [PtClMe(dmphen)(\underset{\mathbf{8}}{E\text{-}OHCCH{=}CHCHO})] + 4MeOH \quad (8)$$

The yellow complex is fairly stable and soluble in organic solvents. Its attainment was not accompanied by formation of η^4 derivatives, as observed on Fe(0) [11]. It did not show appreciable decomposition on standing 24 h at 100°C in nitromethane solution.

The tetraacetal appears to be a very favorable precursor of the coordinated dialdheyde, since in presence of a catalytic amount of CF_3CO_2H the corresponding Pt(0) complex **17** is formed from the ethylene homolog (Eq. (9)).

$$[Pt(C_2H_4)(dmphen)] + E\text{-}(OMe)_2CHCH{=}CHCH(OMe)_2 + 4H_2O = [Pt(dmphen)(\underset{\mathbf{17}}{E\text{-}OHCHC{=}CHCHO})] + 4MeOH + C_2H_4 \quad (9)$$

The three-coordinate compound is stable for several days in chloroform solution as well in solid state in air. An electrophilic attack of bromine on it generates a five-coordinate specie as showed in the following equation (Eq. (10)).

$$\mathbf{17} + Br_2 = [PtBr_2(dmphen)(\underset{\mathbf{18}}{E\text{-}OHCCH{=}CHCHO})] \quad (10)$$

Clean reactions of complex **12**, including transformations of the aldehyde functions alone, could be obtained (Scheme 3).

It is worth noting that the fumaraldehydic acid bonded in **16** finds no easy stereospecific synthesis [12]. Thus, its recovery from **16** by treatment with cyanide can be a suitable synthetic route for small amounts of *E* product.

3. Conclusions

The present study is the second and conclusive part of an investigation on the ability of the [PtClMe(*N*,*N*-chelate)] fragment to act as a protecting group for unstable olefins. The *N*,*N*-chelate is required to be rigid and in plane sterically demanding [4] such as dmphen, so the products are TBP adducts of the type [PtClMe(*N*,*N*-chelate)(olefin)].

In the case investigated, the planar precursor displayed stereoselectivity in the reaction with an isomeric mixture of the silyl derivative of the enol, a result which is not trivial, due to the difficulties presented by the separation of the isomeric silyl enol ethers [7]. The

five-coordinate complexes are generally stable, and also related cationic species can be obtained. Attempts to transform functional groups of the coordinated unsaturated substrates have been performed with good chemoselectivity. Moreover, ancillary ligands can be substituted without affecting the unsaturated substrate. The results have been accomplished on mono- and bi-functional olefins. Finally, structure analysis could be effected on a butenol complex and results compared with those concerning coordinated vinyl alcohol.

In conclusion our results strongly suggest that linking to a [PtClMe(*N*,*N*-chelate)] fragment is the method of choice in the case stabilization and/or protection of a labile olefin is required.

4. Experimental

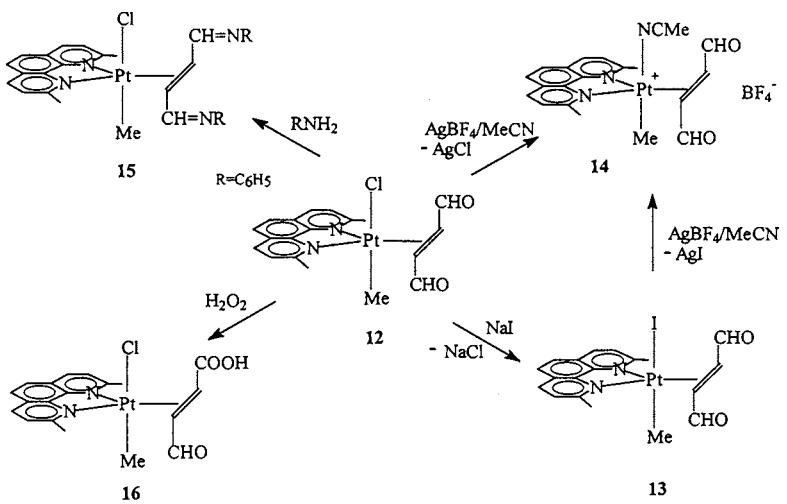
^{1}H-NMR spectra were recorded on 250-MHz Bruker model AC-250 spectrometer. $CDCl_3$ was used as solvent unless otherwise reported, and $CHCl_3$ ($\delta = 7.26$) as internal standard. The following abbrevations were used for describing NMR multiplicities: no attribute, s, singlet; d, doublet; qt, quartet; q, quintet; m, multiplet; b, broad signal. IR spectra were recorded in Nujol mulls on a Perkin–Elmer 457 IR spectrophotometer using CsI windows. Solvents were dried before use. All reactions were carried out under a nitrogen atmosphere by using Schlenk technique. 2,9-dimethyl-1,10-phenanthroline (dmphen) and 1,1,4,4-tetramethoxy-*trans*-2-butene were commercially available (Aldrich). [PtClMe(dmphen)] [13], [Pt(C_2H_4)(dmphen)] [14], *Z*-MeCH=CHOSiMe$_3$ [6], *Z*-EtCH=CHOSiMe$_3$ [6a], *Z*-Me$_3$SiOCH=CHOSiMe$_3$ [10] were prepared as previously reported.

4.1. Synthesis of [PtClMe(dmphen)(Z-RCH=CHOSiMe$_3$)] R = Me (1a); R = Et (1b)

A 0.12 g (0.25 mmol) sample of [PtClMe(dmphen)] was suspended in 0.5 ml of dry chloroform and 0.20 ml of RCH=CHOSiMe$_3$ was added. The mixture was stirred for 24 h at room temperature (r.t.). The resulting whitish suspension was filtered and the solid product was washed three times with 1 ml portions of diethyl ether. The solid (0.20 mmol, 80% yield) was dried in vacuo. ^{1}H-NMR revealed that this material was satisfactory pure. **1a** ^{1}H-NMR: δ 8.30 (d, 2H), 7.82 (s, 2H), 7.80(d, 2H), 5.45 (d, 1H, $^2J_{Pt-H} = 110$Hz), 3.43 (s, 3H), 3.40 (s, 3H), 1.5 (m, 1H, $^2J_{Pt-H}$ = no attribute), 1.15 (d, 3H, $^3J_{Pt-H} = 70$ Hz), 0.25 (s, 9H), 0.01 (s, 3H, $^2J_{Pt-H} =$ 60Hz); **1b** ^{1}H-NMR: δ 8.28 (d, 1H), 8.25 (d, 1H), 7.80 (s, 2H), 7.75 (d,1H), 7.72 (d, 1H), 5.48 (d, 1H, $^2J_{Pt-H} =$ 100 Hz), 3.43 (s, 3H), 3.40 (s, 3H), 3.30 (m, 1H, $^2J_{Pt-H} = 90$Hz), 2.00 (m, 1H), 1.65 (m, 1H); 1.15 (t, 3H), 0.15 (s, 9H), 0.03(s, 3H, $^2J_{Pt-H} = 70$ Hz).

4.2. Synthesis of [PtClMe(dmphen)(Z-RCH=CHOH)] R = Me (2a); R = Et (2b)

To a solution of [PtClMe(dmphen)(*Z*-RCH=CHOSiMe$_3$)] (0.20 mmol) in 2.5 ml of dry chloroform, 0.020 ml of H_2O and a trace of CF_3COOH were added. After stirring for 1 h at r.t. crystallization of the white product ensued by dropwise addition of diethyl ether. The solid was filtered in vacuo, washed with diethyl ether and dried in vacuo (0.12 mmol, 60% yield). **2a**: ^{1}H-NMR: δ 8.30 (d, 2H), 7.82 (s, 2H), 7.80 (d, 1H), 7.76 (d, 1H), 4.52 (d, 1H, $^2J_{Pt-H} = 75$ Hz), 3.47 (s, 3H), 3.39 (s, 3H), 2.50 (q, 1H, $^2J_{Pt-H} = 80$ Hz), 1.52 (d, 3H, $^3J_{Pt-H} = 56$Hz); -0.11 (s, 3H, $^2J_{Pt-H} = 70$ Hz);



Scheme 3.

2b: ^{1}H-NMR: δ 8.32 (d, 2H), 7.82(s, 2H), 7.80 (d, 1H), 7.78 (d, 1H), 4.52 (d, 1H, $^3J_{Pt-H} = 85$ Hz), 3.46 (s, 3H), 3.35 (s, 3H), 2.35 (m, 1H, $^3J_{Pt-H} = 80$Hz), 2.05 (m, 1H), 1.75 (m, 1H), 1.20 (t, 3H), -0.09 (s, 3H, $^2J_{Pt-H} = 75$ Hz).

4.3. Synthesis of [PtMe(dmphen)(Z-MeCH=CHOH)(MeCN)]BF_4 (**3a**)

To a stirred suspension of **2a** (0.080g, 0.16 mmol) in 1 ml of chloroform, an equimolar amount of $AgBF_4$ dissolved in 1 ml acetonitrile was added. After 0.5 h stirring at r.t. the precipitated AgI was removed by filtration. Removal of the solvent in vacuo afforded the product as a pale yellow solid in nearly quantitative yield. ^{1}H-NMR: δ 8.45 (d, 1H), 8.40 (d, 1H), 7.93 (s, 2H), 7.88 (d, 1H), 7.86 (d, 1H), 4.92 (d, 1H, $^2J_{Pt-H} =$ 82Hz), 3.37 (s, 3H), 3.25 (s, 3H), 2.56 (qt, 1H, $^2J_{Pt-H} =$ 90Hz), 1.50 (d, 3H, $^3J_{Pt-H} = 55$Hz), -0.25 (s, 3H, $^2J_{Pt-H} = 72$ Hz).

4.4. Synthesis of [PtMe(dmphen)(CHRCHO)] R = Me (**4a**); R = Et (**4b**)

To a magnetically stirred solution of **2a** (0.125 g, 0.25 mmol) in 3 ml of chloroform, 0.25 ml of 1.0 M KOH was added. After 15 min stirring the solvent was removed in vacuo.The residue was dissolved in 2 ml of dichloromethane and the solution after filtering on a 2 cm bed of Celite was concentrated in vacuo to a small volume. By addition of diethyl ether crystallization of a yellow precipitate ensued (0.110 g, 95% yield). ^{1}H-NMR: δ 9.13 (s, 1H, $^3J_{Pt-H} = 25$ Hz), 8.33 (d, 1H), 8.28 (d, 1H), 7.75 (s, 2H), 7.62 (d, 1H), 7.59 (d, 1H), 4.37 (q, 1H, $^2J_{Pt-H} = 152$ Hz), 3.06 (s, 3H), 2.91 (s, 3H), 1.04 (s, 3H, $^3J_{Pt-H} = 63$Hz), 0.94 (s, 3H, $^2J_{Pt-H} = 84$Hz).

By applying the same procedure to **2b** was obtained **4b**. ^{1}H-NMR: δ 9.22 (d, 1H, $^3J_{Pt-H} = 23$ Hz), 8.15 (d, 2H), 8.13 (d, 2H), 7.78 (s, 2H), 7.6 (m, 2H), 4.20 (d, 1H, $^2J_{Pt-H} = 154$ Hz), 3.08 (s, 3H), 2.90 (s, 3H), 1.1 (m, 2H, $^2J_{Pt-H} =$ not attribute), 0.94 (s, 3H, $^2J_{Pt-H} = 94$Hz), 0.82 (t, 3H).

4.5. Re-conversion of **4a** to **2a** and of **4b** to **2b**

To a magnetically stirred solution of the appropriate complex [PtMe(dmphen)(CHRCHO)] (0.1 mmol) in 1 ml of chloroform, 1 ml of 0.1M HCl was added. After stirring for 1 h at r.t. the organic layer was collected, washed with a minimum amount of water, and the solvent was removed in vacuo. The residue was the corresponding nearly pure complex of type **2**.

4.6. Synthesis of [PtClMe(dmphen)(Z-MeCH=CHOCOMe)] (**5a**)

A suspension of **2a** (0.050 g,0.09 mmol) in 0.3 ml of freshly distilled acetic anhydride was stirred 24 h at r.t. The precipitated white crystalline solid was separated by filtration, washed with diethyl ether and dried in vacuo. (0.050 g 95% yield). ^{1}H-NMR: δ 8.35 (d, 1H), 8.30 (d, 1H), 7.85 (s, 2H), 7.76 (d, 1H), 7.60 (d, 1H), 6.10 (d, 1H, $^2J_{Pt-H} = 95$Hz), 3.41 (s, 3H), 3.31 (s, 3H), 3.30 (m, 1H, $^2J_{Pt-H} =$ no attribute), 2.15 (s, 3H), 1.16 (d, 3H, $^2J_{Pt-H} = 28$Hz), 0.05 (s, 3H, $^2J_{Pt-H} = 80$Hz).

4.7. Halide exchange on **2a**: synthesis of **6a**

A solution of **2a** (0.080 g, 0.15 mmol) in 5 ml of chloroform was stirred 5 h at r.t. with 1 ml of 0.15 M KI. The organic layer was separated, washed with 1 ml of water, filtered on a Na_2SO_4 bed and the solvent was removed in vacuo, yielding the iodide derivative in nearly quantitative yield as pale yellow microcrystals. ^{1}H-NMR: δ 8.30 (d, 2H), 7.82 (s, 2H), 7.80 (d, 1H), 7.76 (d, 1H), 4.52 (d, 1H, $^3J_{Pt-H} = 75$ Hz), 3.37 (s, 3H), 3.28 (s, 3H), 2.38 (m, 1H, $^3J_{Pt-H} = 80$ Hz), 1,52 (d, 3H, $^4J_{Pt-H} = 56$Hz), -0.08 (s, 3H, $^2J_{Pt-H} = 70$ Hz).

4.8. Synthesis of [PtClMe(dmphen)(Z-Me_3SiOCH=CHOSiMe$_3$)] (**7**)

To a solution of [PtClMe(dmphen)] (0.25 g, 0.55 mmol) in 0.1 ml of dry chloroform, 0.25 ml of Z-Me_3SiOCH=CHOSiMe$_3$ was added. After 24 h stirring the microcrystalline precipitate was collected by filtration, washed with a few drops of chloroform and dried in vacuo (0.26 g, 72%). ^{1}H-NMR: δ 8.25 (d, 2H), 7.80 (s, 2H), 7.72 (d, 2H), 5.10 (s, 2H, $^3J_{Pt-H} = 100$Hz), 3.42 (s, 6H, $^4J_{Pt-H} = 5$Hz), 0.25 (s, 18H) 0.16 (s, 3H, Pt–Me, $^2J_{Pt-H} = 80$ Hz).

4.9. Synthesis of [PtXMe(dmphen)(Z-HOCH=CHOH)] (X = Cl (**8**); X = I (**9**))

To a solution of **7** (0.26 g, 0.40 mmol) in 2.5 ml of dry chloroform, prepared as described in the previous section, 0.020 ml of H_2O and a trace of CF_3COOH were added. After stirring for 30 min at r.t. crystallization of the pale yellow product ensued by dropwise addition of diethyl ether. After filtering the solid **8** was washed with diethyl ether and dried in vacuo (0.10 g, 48% yield). **8**: ^{1}H-NMR: δ 8.33 (d, 2H), 7.84 (s, 2H), 7.80 (d, 2H), 4.32(s, 2H, $^3J_{Pt-H} = 80$Hz), 3.42 (s, 6H), -0.12 (s, 3H, $^2J_{Pt-H} = 76$ Hz).

The corresponding iodo complex was obtained following the procedure adopted for **6a**.

9: ^{1}H-NMR: δ 8.30 (d, 2H), 7.85 (s, 2H), 7.78 (d, 2H), 3.99 (s, 2H, $^3J_{Pt-H} = 80$ Hz), 3.30 (s, 6H), -0.06 (s, 3H, $^2J_{Pt-H} = 72$ Hz)

4.10. Synthesis of [PtClMe(dmphen)(Z-MeCOOCH=CHOCOMe)] (**11**)

To a solution of **8** (0.025 g, 0.050 mmol) in 2 ml of dry dichloromethane, 0.2 ml of freshly distilled acetic anhydride was added. After stirring at r.t., addition of diethyl ether afforded crystallization of the product. This product was identical to that obtained in 85% yield by reacting the same amount of **8** with twice the amount of acetyl chloride and pyridine in similar conditions. ^{1}H-NMR: δ 8.35 (d, 2H), 7.95 (s, 2H), 7.75 (d, 2H), 5.90 (s, 2H, $^2J_{Pt-H} = 98$ Hz) 3.30 (s, 6H), 2.15 (s, 6H), 0.28 (s, 3H, $^2J_{Pt-H} = 75$ Hz).

4.11. Synthesis of [PtMe(dmphen)(Z-HOCH=CHOH)-(MeCN)]BF_4 (**10**)

To a stirred solution of **8** (0.020 g, 0.040 mmol) in 0.5 ml deuterochloroform, an equimolar amount of $AgBF_4$ dissolved in 0.10 ml of deuteroacetonitrile was added. After 0.5 h stirring at r.t. the precipitated AgCl was removed by filtration. The product was identified by ^{1}H-NMR analysis. ^{1}H-NMR: δ 8.40 (d, 2H), 7.90 (s, 2H), 7.83 (d, 2H), 4.57 (s, 2H, $^2J_{Pt-H} = 86$ Hz), 3.32 (s, 6H), -0.43 (s, 3H, $^2J_{Pt-H} = 78$ Hz).

4.12. Synthesis of [PtXMe(dmphen)(E-OHCCH=CHCHO)] (X = Cl (**12**); X = I (**13**))

To a solution of [PtClMe(dmphen)] (0.23 g, 0.50 mmol) in 5 ml chloroform, was added an excess of 1,1,4,4-tetramethoxy-*trans*-2-butene (0.12 g, 0.75 mmol), 0.020 ml of water and a catalytic amount of trifluoroacetic acid. After 24 h stirring the solution, the whitish microcrystalline product was precipitated by addition of diethyl ether, filtered and dried in vacuo (0.21 g, 80% yield). **12**: ^{1}H-NMR: δ 9.96 (d, 1H), 9.75 (d, 1H), 8.42 (d, 2H), 7.92 (s, 2H), 7.86 (d, 1H) 7.84 (d, 1H), 5.00 (dd, 1H, $^3J_{Pt-H} = 75$Hz), 4.04 (dd, 1H, $^4J_{Pt-H} = 56$Hz), 3.33 (s, 3H), 3.19 (s, 3H), 0.51 (s, 3H, $^2J_{Pt-H} = 61$ Hz). The corresponding iodo complex **13** was obtained following the procedure adopted for **6a**.

^{1}H-NMR: δ 9.84 (d, 1H), 9.74 (d, 1H), 8.37 (d, 2H), 7.93 (s, 2H), 7.84 (d, 1H), 7.82 (d, 1H), 5.23(dd, 1H, $^3J_{Pt-H} = 84$Hz), 3.82 (dd, 1H, $^4J_{Pt-H} = 53$Hz), 3.31 (s, 3H), 3.14 (s, 3H,), 0.68 (s, 3H, $^2J_{Pt-H} = 62$ Hz).

4.13. Synthesis of [Pt(dmphen)(E-OHCCH=CHCHO)] (**17**)

To a solution of [Pt(dmphen)(C_2H_4)] (0.21 g, 0.50 mmol) in 5 ml of dichloromethane, was added an equimolar amount of 1,1,4,4-tetramethoxy-*trans*-2-butene (0.83 g, 0.50 mmol), 0.020 ml of water and a catalytic amount of trifluoroacetic acid. After 15 min stirring, the solution was filtered on a Florisil bed and concentrated in vacuo to crystallize the orange product. This was filtered, washed with diethyl ether and dried in vacuo (0.17 g, 75% yield). ^{1}H-NMR: δ 8.96 (d, 2H), 8.42 (d, 2H), 7.86 (d, 1H), 7.83 (s, 2H), 7.82 (d, 1H), 3.75 (dd, 2H, $^3J_{Pt-H} = 85$ Hz), 3.11 (s, 6H, $^4J_{Pt-H} = 8$Hz).

4.14. Synthesis of [PtMe(dmphen)(E-OHCCH=CHCHO)(MeCN)]BF_4 (**14**)

To a stirred solution of the [PtIMe(dmphen)(*E*-OHCCH=CHCHO)] (0.12 g, 0.20 mmol) in 0.5 ml of deuteriochloroform, an equimolar amount of $AgBF_4$ dissolved in 0.1 ml of acetonitrile was added. After 0.5 h stirring at r.t. the precipitated AgI was removed by filtration on Celite and the solvent was removed in vacuo. The residue was recrystallized from methylene chloride/toluene to give the pale yellow product (0.11 g, 85% yields). ^{1}H-NMR (in CD_3NO_2, CHD_2NO_2, δ = 4.33, as internal standard): δ 9.88 (d, 1H), 9.55 (d, 1H), 8.78 (d, 2H), 8.20 (s, 2H), 8.15 (d, 1H), 8.08 (d, 1H), 4.73 (dd, 1H, $^3J_{PtH} = 80$ Hz), 4.21 (dd, 1H, $^3J_{Pt-H} = 68$ Hz), 3.30 (s, 3H,), 3.19 (s, 3H), 2.01 (s, 3H) 0.67 (s, 3H, $^2J_{Pt-H} = 70$ Hz)

4.15. Synthesis of [PtBr$_2$(dmphen)(E-OHCCH=CHCHO)] (**18**)

To a stirred suspension of **17** (0.10 g, 0.20 mmol) in 2 ml of dichloromethane, 0.5 ml of a 1 M solution of bromine in the same solvent was added with a syringe. An orange solution was immediately obtained and in a few seconds an orange precipitate was formed. After addition of 1 ml of diethyl ether the precipitate was collected by filtration, washed with diethyl ether and dried in vacuo (0.90 g, 70% yield). ^{1}H-NMR: δ 9.98 (d, 2H), 8.42 (d, 2H), 7.94 (s, 2H), 7.90 (d, 2H), 5.31 (m, 2H, $^3J_{Pt-H} = 70$ Hz), 3.39 (s, 3H).

4.16. Reaction of **12** with aniline: synthesis of **15**

To a stirred suspension of **12** (0.020 g, 0.040 mmol) in 2 ml of dichloromethane, aniline (0.014 ml, 0.080 mmol) was added with a syringe. After 48 h stirring at r.t. a solution was obtained. After removal of the solvent in vacuo the residue was washed with diethyl ether and dried in vacuo to give **15** (0.022 g, 85% yield).

^{1}H-NMR: δ 8.60 (d, 1H), 8.30 (d, 2H), 7.90 (d, 1H), 7.83 (s, 2H), 7.71(d, 1H), 7.69 (d, 1H), 7.2 (m, 10H), 5.15 (dd, 2H, $^3J_{Pt-H} = 85$ Hz), 4.40 (dd, 2H, $^3J_{Pt-H} = 62$ Hz), 3.41 (s, 3H) 3.25 (s, 3H), 0.46 (s, 3H, $^2J_{Pt-H} = 70$ Hz).

4.17. Reaction of **12** with hydrogen peroxide: synthesis of **16**

To a stirred suspension of **12** (0.040 g, 0.075 mmol) in 2 ml of dichloromethane, 0.005 ml of 30% aqueous

Table 2
Summary of crystallographic data

Crystal size (mm)	$0.01 \times 0.12 \times 0.12$
Formula	$PtClON_2C_{19}H_{23}$
Formula weight	525.95
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.856(2)
b (Å)	9.596(3)
c (Å)	13.140(4)
α (°)	94.29(2)
β (°)	97.07(2)
γ (°)	73.58(2)
V (Å^3)	942.1(5)
Z	2
$F(000)$	508
D_{calc} (g cm^{-3})	1.85
λ (Mo–K$_\alpha$) (Å)	0.71073
θ_{max} (°)	26
μ (cm^{-1})	76.7
Temperature (°C)	23 ± 1
No. independent reflections	3696
No. reflections above 3σ	2316
No. independent parameters	217
Goodness of fit	0.493
R	0.048
R_w	0.056

Table 3
Positional and isotropic equivalent thermal parameters of the non-H atoms for complex **2b** [a]

Atom	x	y	z	B (Å^2)
Pt	0.34415(7)	0.24731(6)	0.21351(4)	4.51(1)
Cl	0.2614(4)	0.1708(3)	0.3715(3)	4.76(8)
O	0.523(1)	−0.069(1)	0.242(1)	8.0(3)
N1	0.503(1)	0.374(1)	0.3112(8)	4.2(2)
N2	0.156(1)	0.467(1)	0.2393(8)	4.2(2)
C1	0.465(2)	0.036(2)	0.167(1)	7.0(4)
C2	0.287(2)	0.079(2)	0.123(1)	6.8(4)
C3	0.412(2)	0.323(2)	0.086(1)	6.9(4)
C4	0.414(2)	0.514(1)	0.3354(9)	4.0(3)
C5	0.228(2)	0.562(1)	0.2990(9)	4.2(3)
C6	0.497(2)	0.610(1)	0.3936(9)	4.3(3)
C7	0.680(2)	0.557(1)	0.427(1)	5.1(3)
C8	0.766(2)	0.417(1)	0.402(1)	5.0(3)
C9	0.675(2)	0.325(1)	0.346(1)	4.8(3)
C10	0.769(2)	0.170(2)	0.323(1)	6.5(4)
C11	0.132(2)	0.704(1)	0.327(1)	5.1(3)
C12	0.217(2)	0.798(1)	0.386(1)	5.9(4)
C13	0.396(2)	0.755(1)	0.420(1)	5.8(4)
C14	−0.052(2)	0.746(2)	0.289(1)	6.6(4)
C15	−0.117(2)	0.649(2)	0.228(1)	6.3(4)
C16	−0.013(2)	0.512(1)	0.203(1)	5.4(3)
C17	−0.091(2)	0.407(2)	0.135(1)	7.3(5)
C18	0.151(2)	0.004(2)	0.148(1)	7.1(4)
C19	0.190(3)	0.151(2)	0.090(1)	8.8(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a^2*β(1,1) + b^2*(2,2) + c^2*β(3,3) + ab(cosγ)*β(1,2) + ac(cosβ)*β(1,3) + bc(cosα)*β(2,3)].

solution of H_2O_2 (0.13 mmol) was added with a syringe. After 72 h stirring at r.t. removal of the solvent in vacuo afforded a white residue. This was washed with diethyl ether and dried in vacuo to give **16** (0.030 g, 75% yield). Further treatment of **16** with hydrogen peroxide did not affect the compound. ^{1}H-NMR: δ 9.60 (d, 1H), 8.40 (d, 2H), 7.92 (s, 2H), 7.73(d, 2H), 4.61 (dd, 2H, $^3J_{Pt-H} = 80$ Hz), 4.00 (d, 1H, $^3J_{Pt-H} = 50$ Hz), 3.26 (s, 6H), 0.59 (s, 3H, $^2J_{Pt-H} = 65$ Hz). IR: ν 1718 cm^{-1} COOH, 1686 cm^{-1} CHO.

4.18. Crystallographic structure determination

Details of the structure analysis are listed in Table 2. The compound was recrystallized from dichloromethane/hexane. X-ray data were collected at r.t. on an Enraf-Nonius CAD4-F automatic diffractometer using Mo–K$_\alpha$ graphite-monochromated radiation and operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 reflections in θ range $12 \leq \theta \leq 14°$. Three monitoring reflections, measured every 500, showed an intensity decay of about 15% for which a linear correction was applied. In addition to the corrections for Lorentz and polarization factors, a semiempirical correction for absorption [15] was applied (max and min values of the transmission factor were 1.0 and 0.79).

The structure was solved by routine application of the Patterson and Fourier techniques and refined by the full-matrix least-squares procedure minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = [\sigma^2(F_0) + (0.02F_0)^2 + 1]$ where σ is derived from counting statistics. All non-hydrogen atoms were refined anisotropically. The H atoms were placed in calculated positions, also taking into account the suggestion of the difference Fourier map, and included but not refined in last refinement cycles with isotropic thermal parameters equal to those of the carrier atoms. The final Fourier difference map showed no peaks greater than 1.23 e Å^{-3}. All calculations were performed by using the Enraf-Nonius SDP set of programs [16]. Final atomic parameters are presented in Table 3.

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References

[1] (a) J.K Ariyaratne, M.L.H. Green, J. Chem. Soc. (1964) 1. (b) L.R. Criegee, G. Schroder, Angew. Chem. 71 (1959) 70. (c) S.A. Godleski, K.B. Gundlach, R.S. Valpey, Organometallics 4 (1985) 296.
[2] K. Diemert, A. Hinz, W. Kuchen, D. Lorenzen, J. Organomet. Chem. 393 (1990) 379.
[3] F. Giordano, F. Ruffo, A. Saporito, A. Panunzi, Inorg. Chim. Acta 264 (1997) 231.
[4] V.G. Albano, G. Natile, A. Panunzi, Coord. Chem. Rev. 133 (1994) 67.
[5] S.H. Berger, H. Bosnich, J. Am. Chem. Soc. 113 (1991) 958.
[6] (a) H.O. House, L.J.Czuba, M.Gall, H.D.Olmstead, J. Org. Chem. 34 (1969) 2324. (b). F.Effenberger, T.Ziegler, K.H. Schoenwaelder, T. Kesmarszky, B.Bauer, Chem. Ber. 119 (1986) 3394.
[7] C.Hippeli, N.Basso, F.Dammast, H.U.Reissig, Synthesis (1990) 26.
[8] K.H. Schulz, D.F. Cox, J. Phys. Chem. 97 (1993) 3555.
[9] M.C. Lasne, J.L. Ripoll, Tetrahedron Lett. 23 (1982) 1587.
[10] H.-D. Scharf, J. Mattay, Tetraedron Lett. 39 (1976) 3509.
[11] H. Cherkaoui, J. Martelli, R. Grée, Tetrahedron Lett. 32 (1991) 7259.
[12] H.-D Scharf, J. Janus, Chem. Ber. 111 (1978) 2741.
[13] M.E. Cucciolito, V. De Felice, A. Panunzi, A. Vitagliano, Organometallics 8 (1989) 1180.
[14] V. De Felice, M. Funicello, A. Panunzi, F. Ruffo, J. Organomet. Chem. 403 (1990) 243.
[15] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A 24 (1968) 351.
[16] CAD-4 Software, Version 5.0, Enraf-Nonius, Delft, Netherlands, 1989.