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Journal of Organometallic Chemistry 519 (1996) 75–82

Journal of Organometallic Chemistry

Coordinatively saturated olefin platinum(II) complexes containing two η^1-C-bonded groups

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Received 20 October 1995

Abstract

Unprecedented trigonal bipyramidal Pt(II) complexes containing two η^1-C-bonded groups in axial position have been isolated. The compounds of general formula [Pt{CHR(R′)}(R″)(dmphen)(olefin)] or [Pt(CH_2NO_2)(R″)(dmphen)(olefin)] (dmphen = 2,9-dimethyl-1,10-phenanthroline; R,R′ = CO_2Me, COMe, CN; R″ = Me, CH_2Ph) are obtained by reacting the cationic precursors $[Pt(R'')L(dmphen)(olefin)]^+$ (L = MeCN, H_2O) with KCH_2NO_2 or KR(R′)CH. The β-dicarbonyl ligands are C-bonded and can be selectively removed by treatment with protic acids.

Keywords: Platinum; Olefin complexes; η'-Bonded; Alkene; Five-coordination; Alkyl complexes; Preparation

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1. Introduction

Complexes of general formula [PtX(Y)(L–L)(L′)] (**I**, Fig. 1) represent by far the widest class of five-coordinate Pt(II) species available to date [1]. A common stereochemical feature of type **I** complexes is the trigonal bipyramidal (tbp) arrangement of the ligands around the Pt atom. A chelating L–L ligand and a strong π-acceptor molecule L′ share the equatorial position of the coordination polyhedron, and two donor ligands (X, Y) occupy the axial sites.

While the choice of equatorial substituents has been limited respectively to a sterically hindered nitrogen chelate [2] and an alkene [1], or an alkyne [3] or CO [4], a larger number of axial ligands could be used. In fact, halogens [5], hydrocarbyl groups [1], hydride [6], organometal fragments [7–9], nitriles [10,11] and amines [10,11] have been placed in the axial positions, giving rise to both cationic and neutral five-coordinate platinum(II) complexes.

However, although more than two hundred type **I** complexes have been described, no report [12] of species containing two hydrocarbyl apical groups has yet appeared. Aiming to fill this gap, we investigated the feasibility of complexes of formula [PtR_2(dmphen)(olefin)] (dmphen = 2,9-Me_2-1,10-phenanthroline).

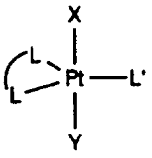

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Fig. 1. General formula for type I five-coordinate complexes.

Attempts to obtain the above species by addition of an olefin to a square-planar precursor [PtR_2(dmphen)] (R = Me, Ph or 4-MeO-Ph) were unsuccessful, despite the presence of the highly hindered nitrogen chelate. This result could be explained if we consider that both alkyl and aryl groups display good donor properties [13], and the delicate electronic balance around the metal center might not be satisfied if two very strong donor groups are placed *trans* to each other.

Attempts to enhance the stability of the five-coordinate products were made by reducing the electron-donor ability of one of the two hydrocarbyl groups. We considered both $-CH_2NO_2$ and the β-dicarbonyl carbanions [$R(R')CH^-$ (R = COMe, CO_2Me)] as suitable ligands for this purpose. In fact, although the latter commonly bind metal ions acting as O,O′-chelating ligands,

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PII S0022-328X(96)06225-0

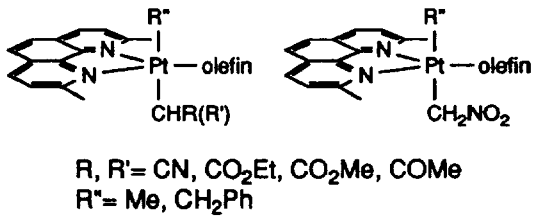


Fig. 2. Type **II** complexes.

other coordination modes are possible, e.g. through the Cγ carbon atom [14].

This choice was successful, and the first class of olefin bis-hydrocarbyl platinum(II) complexes (**II**, Fig. 2) were synthesized. Type **II** products also deserve attention because similar Ni(II) and Pd(II) derivatives are invoked as intermediates respectively in olefin hydrocyanation [15] and Stille coupling [16].

2. Results and discussion

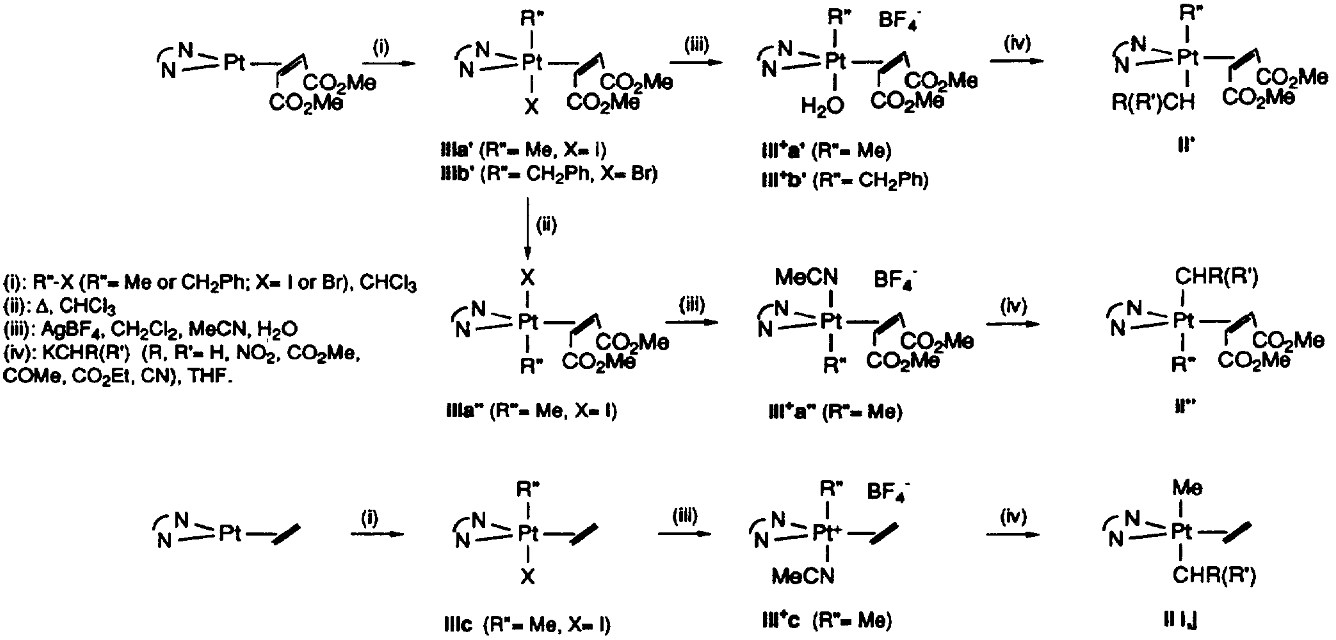
2.1. Synthetic procedure

The chemistry developed in this work is reported in Scheme 1. The oxidative addition (path (i)) of Me–I or $PhCH_2$–Br to the three-coordinate precursors [Pt(dmphen)(olefin)] (olefin = ethylene or dimethyl maleate) is immediate and affords the corresponding 18 e^- type **III** complexes [PtR(X)(dmphen)(olefin)] (R = Me or $PhCH_2$; X = Br or I). The ethylene derivative **IIIc** is known [17], while **IIIa**′ and **IIIa**″ had been previously detected in solution [6], but not isolated. The labels for type **III** and **III**$^+$ complexes are reported in Scheme 1.

The dimethyl maleate derivatives can exist in two isomeric forms and, in the case of [PtMeI(dmphen)(dimethyl maleate)], both of them have been isolated. More precisely, the oxidative addition of MeI to the three-coordinate platinum(0) complex [Pt(dmphen)(dimethyl maleate)] affords a white microcrystalline complex whose olefin protons resonate in the ^{1}H NMR spectrum at 3.38 ppm. In refluxing chloroform (path (ii)) the complex transforms within 90 min into the corresponding isomer. In this case the signal of the alkene hydrogen nuclei is at 4.71 ppm. According to previous considerations [18] it is possible to assign the configurations **IIIa**′ and **IIIa**″ to the kinetically favored isomer and to the most stable one respectively. In fact, for complexes of general formula [PtR(X)(N–N)(olefin)] (X = halide) a higher chemical shift value has been observed for the isomer whose olefin protons face the halogen.

In contrast, only one isomer (**IIIb**′) has been obtained in the case of the benzyl derivative, which presumably retains the same stereochemistry as **IIIa**′.

Type **III** complexes are converted into the corresponding cationic species by halide abstraction in the presence of silver tetrafluoroborate (path (iii)). In **III**$^+$**a**″ [10] and **III**$^+$**c** the halide ion is substituted by MeCN, while in **III**$^+$**a**′ and **III**$^+$**b**′ the coordination of H_2O in the axial position is observed. The presence of water, suggested by the presence of a strong IR band in the region between 3000 and 3500 cm^{-1}, has been confirmed through elemental analysis and by recording the



Scheme 1.

Table 1
^{1}H NMR [a] data for type **II** complexes

	Complex	Pt–Me or Pt–CH$_2$Ph [b]	Pt–CHR(R′) or Pt–CH$_2$NO$_2$ [b]	H(olefin) [b]	Me(dmphen)	Other signals
IIa′	[Pt{CH(CO$_2$Me)$_2$}Me(dmphen)(dimethyl maleate)]	−0.03(52, s, 3H)	3.92(59, s, 1H)	3.39(76, s, 2H)	3.12(s, 6H)	3.79(OMe, s, 6H) 2.90(OMe, s, 6H)
IIa″	[Pt{CH(CO$_2$Me)$_2$}Me(dmphen)(dimethyl maleate)]	0.24(59, s, 3H)	2.46(51, s, 1H)	3.94(84, s, 2H)	3.23(s, 6H)	3.72(OMe, s, 6H) 2.97(OMe, s, 6H)
IIb″	[Pt{CH(CN)(CO$_2$Et)}Me(dmphen)(dimethyl maleate)]	0.24(59, s, 3H)	1.93(49, s, 1H)	3.89(72, s, 2H)	3.32(s, 3H) 3.27(s, 3H)	3.74(OMe, s, 6H) 3.22(OCH$_2$, q, 1H) 3.02(OCH$_2$, q, 1H) 0.73(Me, t, 3H)
IIc″	[Pt{CH(COMe)(CO$_2$Me)}Me(dmphen)(dimethyl maleate)]	0.33(60, s, 3H)	2.79(51, s, 1H)	4.00(84, ABq, 2H)	3.24(s, 6H)	3.72(OMe, s, 6H) 2.93(OMe, s, 3H) 1.24(COMe, s, 3H)
IId′	[Pt{CH(CN)$_2$}Me(dmphen)(dimethyl maleate)]	0.16(53, s, 3H)	3.02(56, s, 2H)	3.44(72, s, 2H)	3.24(s, 6H)	3.79(OMe, s, 6H)
IId″	[Pt{CH(CN)$_2$}Me(dmphen)(dimethyl maleate)]	0.31(59, s, 3H)	1.59(53, s, 1H)	3.78(82, s, 2H)	3.33(s, 6H)	3.76(OMe, s, 6H)
IIe′	[Pt(CH$_2$NO$_2$)Me(dmphen)(dimethyl maleate)]	−0.18(48, s, 3H)	4.43(56, s, 2H)	3.45(76, s, 2H)	3.19(s, 6H)	3.79(OMe, s, 6H)
IIe″	[Pt(CH$_2$NO$_2$)Me(dmphen)(dimethyl maleate)]	0.00(54, s, 3H)	3.91(54, s, 2H)	3.66(81, s, 2H)	3.23(s, 6H)	3.73(OMe, s, 6H)
IIf′	[Pt{CH(CO$_2$Me)$_2$}(CH$_2$Ph)(dmphen)(dimethyl maleate)]	2.11(64, s, 2H)	4.04(64, s, 1H)	3.48(78, s, 2H)	3.12(s, 6H)	3.81(OMe, s, 6H) 2.86(OMe, s, 6H)
IIg′	[Pt{CH(CN)$_2$}(CH$_2$Ph)(dmphen)(dimethyl maleate)]	2.27(67, s, 2H)	3.23(61, s, 1H)	3.52(74, s, 2H)	3.22(s, 6H)	3.80(OMe, s, 6H)
IIh	[Pt(CH$_2$NO$_2$)(CH$_2$Ph)(dmphen)(dimethyl maleate)]	2.00(60, s, 2H)	4.57(58, s, 2H)	3.51(78, s, 2H)	3.17(s, 6H)	3.80(OMe, s, 6H)
IIi	[Pt{CH(CO$_2$Me)$_2$}Me(dmphen)(ethylene)]	−0.24(57, s, 3H)	2.42(56, s, 1H)	2.63(80, app d, 2H) 2.11(71, app d, 2H)	3.17(s, 6H)	2.97(OMe, s, 6H)
IIj	[Pt{CH(CN)$_2$}Me(dmphen)(ethylene)]	−0.15(58, s, 3H)	1.40(54, s, 1H)	2.52(77, app d, 2H) 2.27(72, app d, 2H)	3.28(s, 6H)	

[a] Recorded at 298 K, 200 or 270 MHz in CDCl$_3$ [CHCl$_3$ (δ 7.26 ppm) as internal standard]. Abbreviations: app, apparent; s, singlet; d, doublet, t, triplet; q, quartet.
[b] $^2J_{\mathrm{Pt-H}}$ (Hz) in parentheses.

Table 2
^{13}C NMR [a] data for some type **II** complexes

	Complex	Pt–Me or Pt–CH_2Ph	Pt–CHR(R′) or Pt–CH_2NO_2	C(olefin) [b]	Me(dmphen)	Other signals
IIa″	[Pt{CH(CO_2Me)$_2$}Me(dmphen)(dimethyl maleate)]	−6.8(1C)	41.1(1C)	30.7(419, 2C)	28.6(2C)	172.4(CO, 2C) 170.8(CO, 2C) 51.2(OMe, 2C) 49.3(OMe, 2C)
IId′	[Pt{CH(CN)$_2$}Me(dmphen)(dimethyl maleate)]	−8.1(1C)	−6.6(1C)	32.2(407, 2C)	28.6(2C)	171.2(CO, 2C) 120.5(CN, 2C) 52.0(OMe, 2C)
IIe′	[Pt(CH_2NO_2)Me(dmphen)(dimethyl maleate)]	−6.1(1C)	51.7(2C)	31.0(412, 2C)	28.6(2C)	171.2(CO, 2C) 66.0(OMe, 2C)
IIg′	[Pt{CH(CN)$_2$}(CH_2Ph)(dmphen)(dimethyl maleate)]	21.5(1C)	−10.4(1C)	33.0(417, 2C)	28.8(2C)	171.0(CO, 2C) 120.3(CN, 2C) 52.1(OMe, 2C)
IIi	[Pt{CH(CO_2Me)$_2$}Me(dmphen)(ethylene)]	−11.0(1C)	38.1(1C)	28.8(376, 2C)	28.2(2C)	173.0(CO, 2C) 49.0(OMe, 2C)

[a] Recorded at 298 K, 50.2 MHz in $CDCl_3$ [$^{13}CDCl_3$ (δ 77.0 ppm) as internal standard].
[b] $^1J_{Pt-C}$ (Hz) in parentheses.

^1H NMR spectra in dry deuteronitromethane. It should be noted that if the substitution reaction (path (iii)) proceeds with retention of stereochemistry, the olefin ester groups in $\mathbf{III}^+\mathbf{a}'$ and $\mathbf{III}^+\mathbf{b}'$ are oriented towards the neutral ligand. Thus, the preference for the coordination of water in these complexes could be explained if we consider that favorable hydrogen bonds might form between the $-CO_2Me$ groups and H_2O.

The neutral axial donor of type $\mathbf{III}^+$ complexes can be readily displaced by the appropriate carbon nucleophile $R(R')CH^-$ according to path (iv). The reaction is performed by adding the cationic precursor to a suspension in dry THF of the potassium salt of the carbanion. In the case of the products bearing the $-CH_2NO_2$ axial group the solvent media was a mixture of nitromethane and methanol.

After work-up of the reaction mixtures, type **II** complexes (see Table 1) are obtained in satisfactory yield as white to yellow microcrystalline solids.

In order to ascertain whether an isomerization process also occurs between type **II** dimethyl maleate derivatives, **IId′**, **IIe′** and the corresponding isomers **IId″**, **IIe″** have been separately heated in boiling chloroform for 90 min. Heating was necessary in order to quicken the isomerization which occurs very slowly at room temperature. While **IId′** was recovered unchanged after the treatment, almost complete isomerization **IId″** → **IId′** was observed. The heated solutions of **IIe″** and **IIe′** showed identical isomeric composition, the ratio **IIe″**/**IIe′** being ca. 1:6. In this case it can be inferred that an equilibrium between the two isomers is operating.

It is interesting to note that when the carbanions used in this work were reacted with a cationic square-planar ethylene complex, the course of the reaction was quite different [19]. In this case the attack involved the olefin and a neutral σ-alkyl product was obtained:

$$[\mathrm{PtCl(tmeda)(C_2H_4)}]^+ + (\mathrm{EtO_2C})_2\mathrm{CH}^- \rightarrow [\mathrm{PtCl\{(EtO_2C)_2CHCH_2CH_2\}(tmeda)}]$$

tmeda = N,N,N′,N′-tetramethylethylenediamine

Thus, the results obtained in this work confirm that, in addition to the recently assessed inhibitory effect played in migratory insertion processes [20], the coordinative saturation in platinum(II) complexes also prevent the olefin from undergoing nucleophilic attack [21,22].

2.2. Characterization

The five-coordinate type **II**, **III** and $\mathbf{III}^+$ species have been characterized through ^1H and ^{13}C NMR spectroscopy, elemental analysis and conductivity measurements (see Tables 1–3 and the Experimental section).

The NMR features agree with what is generally found for species of the same class [1]. Particularly, spectroscopic evidences which are considered diagnostic for the trigonal bipyramidal geometry are observed:

(i) equivalence of the two halves of dmphen and of the olefin;

(ii) large high-field shift of the olefin proton signals with respect to the values of the free alkenes.

The ^1H NMR spectra of type **II** species assign unequivocally the C-bonding mode to the β-dicarbonyl ligands, ruling out the O,O′-coordination. In fact, although the coupling constants between the methinic protons and ^{195}Pt are smaller (49–59 Hz) than those found in square-planar Pt(II) complexes containing C-bonded β-dicarbonyl compounds (> 100 Hz) [23–26], their values are high enough to indicate the presence of the Pt–CHR(R′) bonds.

The methinic resonances are upfield (1.59–3.92 ppm) with respect to the range generally found in square-planar Pd(II) or Pt(II) complexes [23–27]. This and the previous observation confirm that the β-dicarbonyl ligands are in the axial position of a tbp type **I** complex. In fact, in this site the Pt–CH_x resonances generally shift upfield [28] from the values observed in related square-planar complexes, and their splittings by ^{195}Pt correspondingly decrease.

Dimethyl maleate type **II** species have been isolated in some cases in both the isomeric forms. As already observed for complexes [PtX(Y)(N–N)(olefin)] [18], the

Table 3
Elemental analyses for some type **II** complexes

	Complex	Formula	Calc. (Found)		
			C	H	N
IIa″	[Pt{CH(CO_2Me)$_2$}Me(dmphen)(dimethyl maleate)]	$C_{26}H_{30}N_2O_8Pt$	45.02 (44.89)	4.36 (4.29)	4.04 (4.12)
IIc″	[Pt{CH(COMe)(CO_2Me)}Me(dmphen)(dimethyl maleate)]	$C_{26}H_{30}N_2O_7Pt$	46.09 (46.28)	4.46 (4.38)	4.13 (4.28)
IId′	[Pt{CH(CN)$_2$}Me(dmphen)(dimethyl maleate)]	$C_{24}H_{24}N_4O_4Pt$	45.93 (46.11)	3.85 (3.96)	8.93 (8.79)
IId″	[Pt{CH(CN)$_2$}Me(dmphen)(dimethyl maleate)]	$C_{24}H_{24}N_4O_4Pt$	45.93 (45.65)	3.85 (3.92)	8.93 (8.98)
IIe″	[Pt(CH_2NO_2)Me(dmphen)(dimethyl maleate)]	$C_{22}H_{25}N_3O_6Pt$	42.45 (42.49)	4.05 (3.97)	6.75 (6.84)
IIg′	[Pt{CH(CN)$_2$}(CH_2Ph)(dmphen)(dimethyl maleate)]	$C_{30}H_{28}N_4O_4Pt$	51.21 (51.60)	4.01 (4.09)	7.96 (7.89)
IIi	[Pt{CH(CO_2Me)$_2$}Me(dmphen)(ethylene)]	$C_{22}H_{26}N_2O_4Pt$	45.75 (45.91)	4.54 (4.71)	4.85 (4.74)
IIj	[Pt{CH(CN)$_2$}Me(dmphen)(ethylene)]	$C_{20}H_{20}N_4Pt$	46.96 (46.80)	3.94 (3.91)	10.95 (11.28)

stereoisomerism has a marked effect on the chemical shift values of corresponding signals. Particularly for type **II′** isomers, where the olefin substituents face the -CHR(R′) group, the following are generally observed:
(i) higher-field shift of both Pt–Me and H(olefin) resonances;
(ii) lower-field shift of the methinic -CHR(R′) protons. As an example, the chemical shift values for the -CH(CN)$_2$ protons are 3.02 and 1.59 ppm respectively in **IId′** and **IId″**. It should be noted that the latter value is very close to that observed (1.40 ppm) for the ethylene derivative **IIj**, probably because in both cases the -CH(CN)$_2$ substituent faces the olefin protons;
(iii) smaller values of both $^2J_{\mathrm{Pt-H(olefin)}}$ and $^2J_{\mathrm{Pt-H(Me)}}$ coupling constants.

2.3. Reactions of *IIa″* with protic acids

Complex **IIa″** has been reacted with some protic acids. The selective removal of the -CH(CO$_2$Me)$_2$ ligand is observed, and new five-coordinate complexes (**IVa–c**) are obtained (Scheme 2). The reactions are carried out at room temperature and are immediate but for the attack of MeCO$_2$H which requires a few hours to completion. The products **IVa–c** can be isolated as microcrystalline solids by adding diethyl ether to the reaction mixture.

While **IVc** is known [6], complexes **IVa** and **IVb** are the first example of type **I** five-coordinate platinum(II) complexes containing an anionic O-donor ligand. The very low conductivity (in chloroform) rules out the presence of cationic complexes having MeCO$_2^-$ and CF$_3$CO$_2^-$ as counterions. In addition, symmetry and chemical shifts of the ^{1}H and ^{13}C NMR spectra indicate a tbp geometry [1] for both complexes with acetate ligands in the axial position.

Finally, as one would predict taking into account the EAN rule, the acetates are monodentate. In fact, the $\nu(\mathrm{OCO})_{\mathrm{asym}}$ in the IR spectra (1685 and 1610 cm^{-1} respectively for **IVa** and **IVb**) fall in the range considered diagnostic for monodentate carboxylates (1650–1710 cm^{-1} for fluoroalkylcarboxylates and 1580–1650 cm^{-1} for alkylcarboxylates [29]).

3. Conclusions

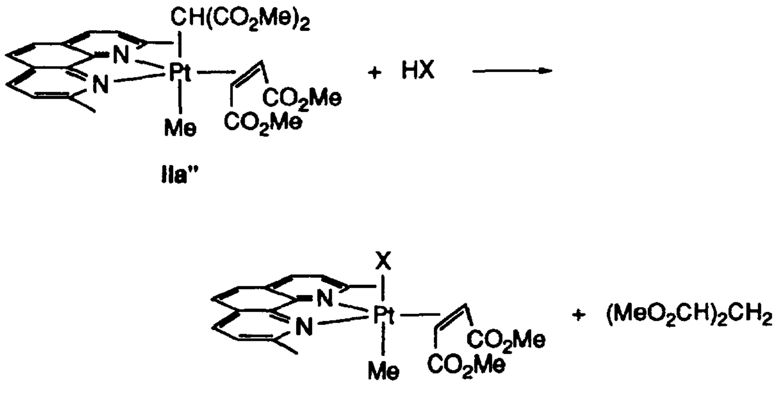
This paper deals with the synthesis and characterization of type **II** complexes of general formula [Pt(CH$_2$NO$_2$)(R″)(dmphen)(olefin)] and [Pt{CHR(R′)}(R″)(dmphen)(olefin)] (R,R′ = COMe, CO$_2$Me, CN; R″ = Me, CH$_2$Ph). The availability of the new species is of interest in the chemistry of d^8 ions of the 10th column since, as far as we know, the only alkene five-coordinate M(II) complexes containing two η^1-C-bonded groups previously isolated were the Ni(II) compounds [NiR$_2$(2,2-bipyridine)(olefin)] described by Yamamoto et al. [30].

The stability of type **II** species seems related to the careful choice of substituents on the hydrocarbyl groups, which reasonably ensures a favorable electronic balance around the Pt atom.

The selective removal of the functionalized alkyl group in the presence of protic acids has also allowed the synthesis of species bearing anionic O-donor ligands in the axial position.

4. Experimental details

^{1}H NMR spectra have been recorded at 298 K at 270 or 200 MHz on a Bruker AC-270 or Varian XL-200 spectrometer respectively. The NMR data of type **II** complexes are reported in Tables 1 and 2, while the



IIa″

IVa: X= CF$_3$CO$_2$
IVb: X= MeCO$_2$
IVc: X= Cl

Scheme 2.

NMR data for type **III** precursors and type **IV** products are in the corresponding experimental section. ^{1}H and ^{13}C NMR chemical shifts are reported in δ(ppm) relative to the solvent ($CHCl_3$, 7.26; CHD_2NO_2, 4.33; $^{13}CDCl_3$, 77.0). Abbreviation: s, singlet. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer in Nujol mulls. [Pt(Me)I(dmphen)(ethylene)] (**IIIc**) [17], [Pt(dmphen)(dimethyl maleate)] [31] and R(R′)CHK salts [32] have been prepared according to literature methods. Solvents and reagents were of Analar grade and, unless otherwise stated, were used without further purification.

4.1. Synthesis of IIIa′

To a solution of [Pt(dmphen)(dimethyl maleate)] (0.16 g, 0.30 mmol) in the minimum amount of methylene chloride was added MeI (0.43 g, 3.00 mmol). The solution became almost colorless and the yellow product was obtained in quantitative yield by removing the solvent in vacuo. Selected ^{1}H NMR (in $CDCl_3$) and analytical data are as follows: 3.78 (s, 6H, OMe), 3.39 (s, $^2J_{Pt-H} = 75$ Hz, 2H, CH=CH), 3.34 (s, 6H, Me–dmphen), 0.47 (s, $^2J_{Pt-H} = 60$ Hz, Pt–Me) ppm. Anal. Found: C, 36.52; H, 3.28; N, 4.20. $C_{21}H_{23}IN_2O_4Pt$ Calc.: C, 36.59; H, 3.36; N, 4.06%.

4.2. Synthesis of IIIa″

A stirred solution of **IIIa′** (0.21 g, 0.30 mmol) in 10 ml of chloroform was refluxed. After 90 min the solvent was removed in vacuo, affording **IIIa″** in quantitative yield. Selected ^{1}H NMR (in $CDCl_3$) are as follows: 4.71 (s, $^2J_{Pt-H} = 85$ Hz, 2H, CH=CH), 3.73 (s, 6H, OMe), 3.41 (s, 6H, Me–dmphen), 0.57 (s, $^2J_{Pt-H} = 70$ Hz, 3H, Pt–Me) ppm.

4.3. Synthesis of IIIb′

To a solution of [Pt(dmphen)(dimethyl maleate)] (0.16 g, 0.30 mmol) in the minimum amount of methylene chloride was added $PhCH_2Br$ (0.50 g, 3.00 mmol). The solution became almost colorless and the yellow product was obtained as a pale yellow microcrystalline solid by slow addition of diethyl ether. The complex was washed with diethyl ether (2 × 2 ml) and dried in vacuo (yield 85%). Selected ^{1}H NMR (in $CDCl_3$) and analytical data are as follows: 3.79 (s, 6H, OMe), 3.55 (s, $^2J_{Pt-H} = 74$ Hz, 2H, CH=CH), 3.32 (s, 6H, Me–dmphen), 2.44 (s, $^2J_{Pt-H} = 80$ Hz, 2H, Pt–CH_2Ph) ppm. Anal. Found: C, 45.38; H, 3.91; N, 4.02. $C_{27}H_{27}BrN_2O_4Pt$ Calc.: C, 45.13; H, 3.79; N, 3.90%.

4.4. Synthesis of type III$^+$ complexes

To a stirred solution of the appropriate type **III** complex (0.30 mmol) in the minimum amount of methylene chloride (ca. 10 ml) under an inert atmosphere at 273 K was added $AgBF_4$ (0.058 g, 0.30 mmol) previously dissolved in 3 ml of acetonitrile. After 15 min AgX was removed by filtration on Celite. The volume of the resulting solution was reduced in vacuo and the white product crystallized by slow addition of diethyl ether. The complex was washed with diethyl ether (2 × 2 ml) and dried in vacuo (yield > 80%). Selected ^{1}H NMR (in CD_3NO_2), IR and analytical data are as follows. **III$^+$a′**: 3.86 (s, 6H, OMe), 3.57 (s, $^2J_{Pt-H} = 59$ Hz, 2H, CH=CH), 3.26 (s, 6H, Me–dmphen), 0.75 (s, $^2J_{Pt-H} = 72$ Hz, 3H, Pt–Me) ppm. Anal. Found: C, 38.02; H, 3.68; N, 4.22. $C_{21}H_{25}BF_4N_2O_5Pt$ Calc.: C, 37.80; H, 3.78; N, 4.20% **III$^+$a″**: 4.21 (s, 2H, CH=CH), 3.75 (s, 6H, OMe), 3.37 (s, 6H, Me–dmphen), 0.49 (s, $^2J_{Pt-H} = 74$ Hz, 3H, Pt–Me) ppm. ν(MeCN): 2300 cm^{-1}. Anal. Found: C, 40.04; H, 3.85; N, 6.19. $C_{23}H_{26}BF_4N_3O_4Pt$ Calc.: C, 40.02; H, 3.80; N, 6.09%. **III$^+$b′**: 3.80 (s, 6H, OMe), 3.73 (s, $^2J_{Pt-H} = 68$ Hz, 2H, CH=CH), 3.38 (s, 6H, Me–dmphen), 2.80 (s, $^2J_{Pt-H} =$ 88 Hz, 2H, Pt–CH_2Ph) ppm. Anal. Found: C, 43.49; H, 3.88; N, 3.85. $C_{27}H_{29}BF_4N_2O_5Pt$ Calc.: C, 43.62; H, 3.93; N, 3.77%.

4.5. Synthesis of type II complexes [Pt{CHR(R′)}R″(dmphen)(olefin)]

To a solution of ^{t}BuOK (0.12 g, 1.1 mmol) in 6 ml of dry THF under an inert atmosphere was added 1.15 mmol of appropriate reagent R(R′)CH_2. To the resulting white suspension containing the salt R(R′)CHK was added the appropriate cationic precursor **III$^+$** (0.20 mmol). After 15 min stirring the solvent was removed under vacuum and the brown residue treated with 10 ml of methylene chloride. The brown suspension was filtered on Celite and the volume of the solvent reduced in vacuo. The complexes were crystallized by slow addition of diethyl ether, washed with diethyl ether (2 × 2 ml) and dried in vacuo (yield 50–70%). In some cases it was necessary to crystallize the products twice in order to obtain analytically pure complexes.

4.6. Synthesis of type II complexes [Pt(CH_2NO_2)R″(dmphen)(dimethyl maleate)] (IIe′, IIe″, IIh)

To a solution of the appropriate complex **III$^+$** (0.20 mmol) in 3 ml of nitromethane was added KOH (0.011 g, 0.20 mmol) previously dissolved in 1.5 ml of MeOH. After 2 h stirring the dark solution was filtered through Celite. The volume of the resulting solution was reduced in vacuo and the product crystallized by slow addition of diethyl ether. The complex was washed with diethyl ether (2 × 2 ml) and dried in vacuo (yield 60–70%).

4.7. Treatment of *IId′*, *IId″*, *IIe′* and *IIe″* under refluxing conditions

A solution of the appropriate type **II** complex (0.020 g) in the minimum amount of deuterochloroform (previously filtered through Alumina, Brockmann I) was refluxed for 90 min. The solution was then transferred into an NMR tube and monitored through ^{1}H NMR spectroscopy. Comparison of the spectra of the refluxed solutions with those of the pure type **II** complexes allowed an evaluation of the isomeric composition (see text).

4.8. Addition of HX ($X = CF_3CO_2$, $MeCO_2$, Cl) to *IIa″*. Synthesis of complexes *IVa–c*

To a solution of **IIa″** (0.070 g, 0.10 mmol) in the minimum amount of chloroform was added 3 to 4 equivalents of HX. After 10 min (3 h in the case of $X = MeCO_2$) the volume of the solution was reduced in vacuo and the white product crystallized by careful addition of diethyl ether. The complex was washed with diethyl ether (2 × 2 ml) and dried in vacuo (yield > 70%). Selected ^{1}H, ^{13}C NMR (in $CDCl_3$), IR and analytical data are as follows. **IVa**. ^{1}H: 4.11 (s, $^2J_{Pt-H}$ = 82 Hz, 2H, CH=CH), 3.76 (s, 6H, OMe), 3.38 (s, 6H, Me–dmphen), 0.43 (s, $^2J_{Pt-H}$ = 73 Hz, 3H, Pt–Me) ppm. ^{13}C: 170.3 (2C, CO–olefin), 51.5 (2C, OMe), 33.6 ($^1J_{Pt-C}$ = 425 Hz, 2C, C=C), 28.4 (2C, Me–dmphen), −11.7 ($^1J_{Pt-C}$ = 622 Hz, 1C, Pt–Me) ppm. ν(OCO–trifluoroacetate)$_{asym}$: 1685 cm^{-1}. Anal. Found: C, 40.69; H, 3.58; N, 4.22. $C_{23}H_{23}F_3N_2O_6Pt$ Calc.: C, 40.89; H, 3.43; N, 4.15%. **IVb**: ^{1}H: 4.14 (s, $^2J_{Pt-H}$ = 82 Hz, 2H, CH=CH), 3.74 (s, 6H, OMe), 3.41 (s, 6H, Me–dmphen), 1.56 (s, 3H, $MeCO_2$), 0.30 (s, $^2J_{Pt-H}$ = 70 Hz, 3H, Pt–Me) ppm. ^{13}C: 176.1 (1C, CO–acetate), 170.8 (2C, CO–olefin), 51.3 (2C, OMe), 33.0 ($^1J_{Pt-C}$ = 429 Hz, 2C, C=C), 28.5 (2C, Me–dmphen), 24.5 (1C, Me–acetate), −14.3 ($^1J_{Pt-C}$ = 602 Hz, 1C, Pt–Me) ppm. ν(OCO–acetate)$_{asym}$: 1610 cm^{-1}.

Acknowledgements

We thank the Consiglio Nazionale delle Ricerche and Ministero dell'Università e della Ricerca Scientifica for financial support, the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli "Federico II" for the use of the Bruker AC-270 and Varian XL-200 spectrometers, and Professor A. Panunzi for helpful suggestions.

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