

Bi- and trinuclear cationic complexes involving bonds
between mercury and five-coordinate platinum(II).
Molecular structure of $\{[\text{Pt}(2,9\text{-dimethyl-1,10-phenanthroline})\text{-}$
 $(Z\text{-MeO}_2\text{CCH=CHCO}_2\text{Me})(\text{H}_2\text{O})\}_2\text{Hg}(\text{BF}_4)_2$

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Abstract

Three cationic five-coordinate platinum(II) complexes bearing alkylmercury fragments as "ligands" have been isolated. The complexes of general formula $[\text{Pt}(\text{HgR})(\text{H}_2\text{O})(\text{dmphen})(Z\text{-R}'\text{O}_2\text{CCH=CHCO}_2\text{R}')](\text{BF}_4)$ (dmphen = 2,9-dimethyl-1,10-phenanthroline; R, R' = Me; R = Me, R' = ^tBu; R = ^tBu, R' = Me) are stabilized by the factors operating in related neutral species. Two of the new complexes slowly demercuriate in solution, affording the mononuclear complexes $[\text{Pt}(\text{Me})(\text{H}_2\text{O})(\text{dmphen})(Z\text{-R}'\text{O}_2\text{CCH=CHCO}_2\text{R}')](\text{BF}_4)$ (R' = Me or ^tBu). When R = ^tBu, a slow redistribution reaction is observed, yielding the trinuclear cluster $\{[\text{Pt}(\text{dmphen})(Z\text{-MeO}_2\text{CCH=CHCO}_2\text{Me})(\text{H}_2\text{O})\}_2\text{Hg}(\text{BF}_4)_2$. The structure of this complex has been determined by X-ray analysis.

Keywords: Platinum; Mercury; Alkenes; Trinuclear complexes; X-ray analysis; Dinuclear complexes

1. Introduction

Recent studies [1] from this laboratory led to the isolation of the first large class of Pt(II) complexes bearing an alkylmercury fragment-HgR. The complexes (II) were prepared through the oxidative addition of RHgCl species to three-coordinate olefin platinum(0) precursors (I), according to Eq. (1).

Here, we report the synthesis of related cationic binuclear complexes, and discuss some aspects of their reactivity.

The course of the reaction (1) depends on the nature of R [1]. When R is Ph or Cl the highly insoluble product was formulated as the cluster $\{[\text{PtCl}(\text{dmphen})\text{-}(Z\text{-MeO}_2\text{CCH=CHCO}_2\text{Me})\}_2\text{Hg}(\text{IIIa})$ (dmphen = 2,9-dimethyl-1,10-phenanthroline), as suggested by the spectroscopic characterization of its related cationic species $\{[\text{Pt}(\text{dmphen})(Z\text{-MeO}_2\text{CCH=CHCO}_2\text{Me})\text{-}(\text{H}_2\text{O})\}_2\text{Hg}(\text{BF}_4)_2$ (III⁺a) (Fig. 1).

In this paper we confirm the proposed structural assignment and report the single crystal X-ray structure of III⁺a.

2. Results

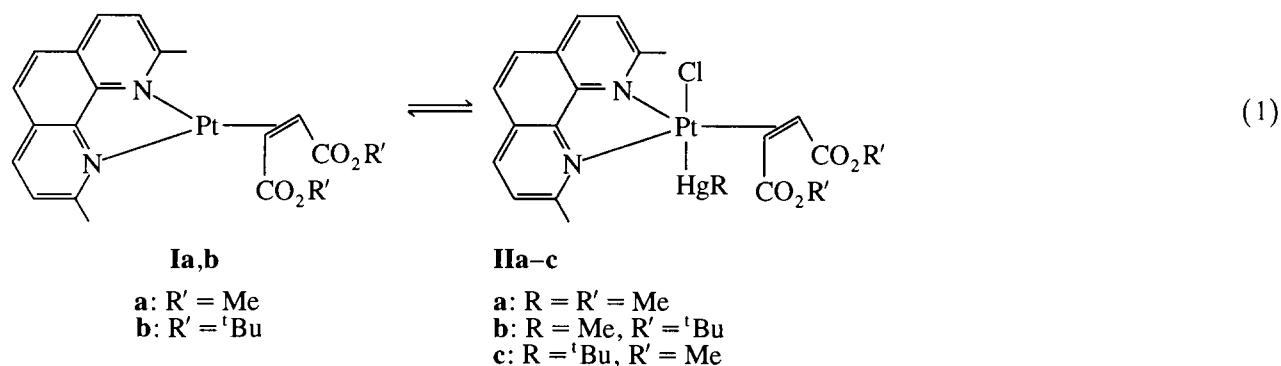
2.1. Synthesis and characterization of type II⁺ complexes

Complexes II⁺a–c (see Scheme 1) are obtained by treatment of the corresponding neutral species IIa–c with AgBF₄ in a methylene chloride-acetonitrile solution. After removal of AgCl the complexes can be crystallized by addition of diethyl ether to the reaction mixture.

The complexes are fairly soluble in chloroform, nitromethane and acetonitrile, and stable enough in solution to allow their characterization through NMR spectroscopy and conductivity measurements.

The general features of the NMR spectra are consistent with the proposed trigonal bipyramidal arrangement around the Pt atom. The two halves of dmphen and the dialkylmaleates are chemically equivalent and the chem-

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ical shifts of the olefin protons fall in the range typical of related dialkylmaleate complexes [2–4].

As already noted in the synthesis of **III**⁺**a** [1], the chloride ion is easily substituted by a molecule of water, even in the presence of the good donor MeCN. The presence of water, suggested by the observation of a strong IR band in the region between 3000 and 3200 cm⁻¹, has been confirmed through ¹H NMR spectroscopy. The intensity of the water peak in the spectra,

recorded in dry deuterated solvents, is consistent with the above formulation.

The -HgCH₃ resonances in **II**⁺**a** and **II**⁺**b** are low field compared with those of the corresponding neutral species. A shift in the same direction has already been observed for methyl groups directly bound to platinum(II) in related mononuclear cationic [PtMe(L)-(N-N)(olefin)]⁺ [5] and neutral [PtMe(X)(N-N)(olefin)] [6] species.

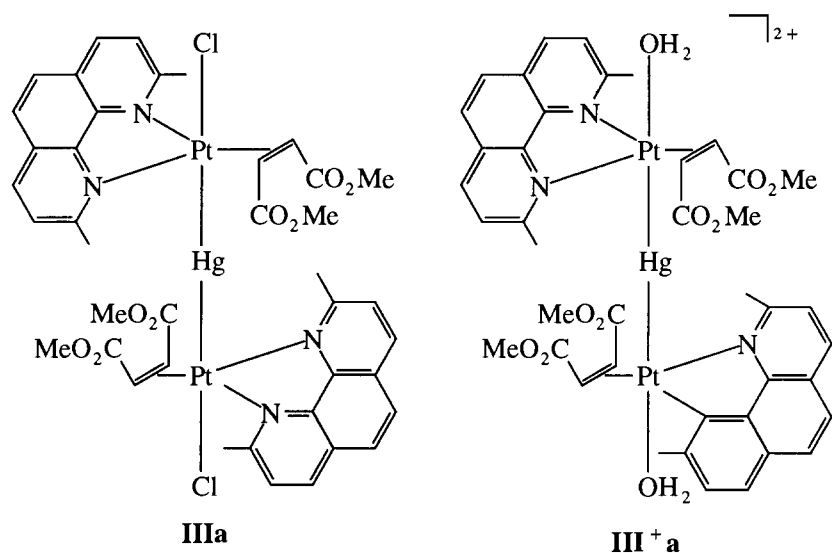
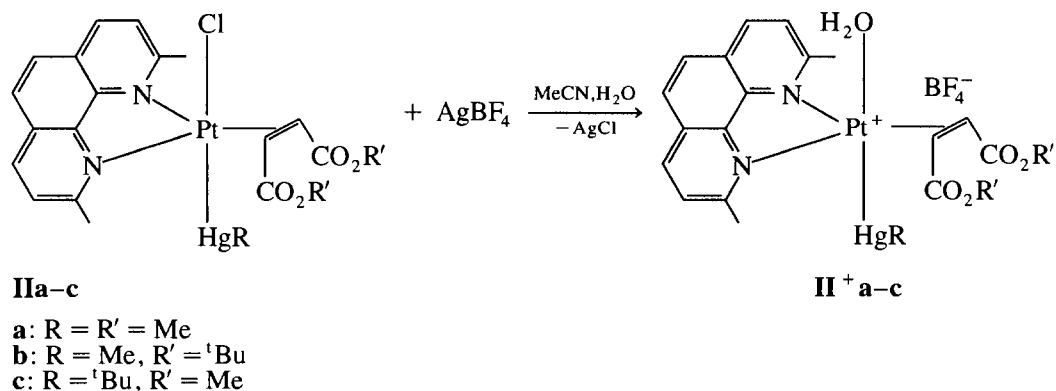


Fig. 1. The structures of **IIIa** and **III**⁺**a**.



Scheme 1.

The coupling constants $^2J_{\text{Hg-H}}$ and $^3J_{\text{Pt-H}}$ of -HgMe groups are greater than the values observed for the corresponding neutral species. As an example, the values are 140 and 16 Hz in complex **IIa** and 193 and 21 Hz in complex **II⁺a**. Conversely, the presence of a net positive charge does not affect appreciably the $^2J_{\text{Pt-H}}$ values of Pt–Me groups in mononuclear five-coordinate complexes [5,6]

Complex **II⁺a**, which can be crystallized as white needles from the reaction mixture, is rather stable in both chloroform and acetonitrile. The ^1H NMR spectra of freshly prepared samples show, in addition to the expected peaks, a signal due to free acetonitrile, which is still present even after keeping the crystals under high vacuum for several hours. In addition, the IR spectrum of **II⁺a** in a Nujol mull reveals three stretching frequencies, at 2300, 2280 and 2250 cm^{-1} . This might suggest that acetonitrile is not simply held in the lattice, but plays a structural role analogous to that of acetone in $[\text{Pt}(\text{CF}_3)(\text{HgCF}_3)(\text{PPh}_3)_2]$ [7] where the solvent was found to be coordinated to the mercury atom in a trigonal arrangement around the metal.

Early attempts to purify **II⁺a** by recrystallization from nitromethane, where five-coordinate cationic Pt(II) complexes are generally soluble [1,3,5,8], were seldom

successful, and decomposition leading to the five-coordinate mononuclear species $[\text{PtMe}(\text{H}_2\text{O})(\text{dmphen})(\text{Z-MeO}_2\text{CCH}=\text{CHCO}_2\text{Me})]^+$ (**IV⁺a**), and small amounts of the trinuclear cationic cluster **III⁺a**, occurs rapidly in MeNO_2 . However, the decomposition takes place more slowly in chloroform or acetonitrile and the former solvent can be used to obtain acetonitrile-free **II⁺a**, as a sparkling light green microcrystals.

Complex **II⁺b**, which is a light orange microcrystalline solid, behaves similarly, in that the main decomposition product in CD_3CN or CD_3NO_2 is again the demercuriation product $[\text{PtMe}(\text{H}_2\text{O})(\text{dmphen})\{\text{Z}(\text{tBu})\text{O}_2\text{CCH}=\text{CHCO}_2(\text{tBu})\}]^+$ (**IV⁺b**).

A fresh deuterioacetone solution of complex **II⁺c** is deep red, and the NMR spectrum recorded within a few minutes of dissolution reveals an already substantial amount of **III⁺a** and also aliphatic signals, while a grey solid separates. After some hours the only platinum containing product detectable in solution is cluster **III⁺a**.

Alternatively, if complex **II⁺c** is dissolved in deuteriochloroform, the decomposition process takes place more slowly, and the NMR spectrum of the fresh solution shows only resonances assigned to the binuclear species. After one week, the spectrum of the filtered solution gives rise mainly to signals in the aliphatic region, analogous to those observed in the previous experiment.

2.2. Molecular structure of **III⁺a**

The synthesis of **IIIa** and **III⁺a** has already been reported [1]. In addition we note that, owing to the low solubility of **IIIa** in the common solvents, no NMR spectra could be run. For the same reason, all attempts to obtain single crystals suitable for X-ray analysis were unsuccessful. Therefore, a preliminary investigation [1] was performed on the related cationic species **III⁺a**, whose analytical and spectroscopic data pointed to the structure proposed in Fig. 1. This has been now confirmed by the X-ray diffraction analysis of the complex discussed below.

The molecular structure of **III⁺a** is shown in Fig. 2. Final atomic parameters are listed in Table 1 and bond lengths and selected bond angles are presented in Table 2.

The mercury atom lies at an inversion centre which relates the two chemically equivalent moieties of the complex. The coordination geometry around Pt is trigonal-bipyramidal with both the dmphen and the olefin bound in the equatorial plane, while Hg and the water oxygen OW(1) are in axial positions. The Pt–Hg distance [2.5444(5) Å] compares well with the value recently measured on **IIa** [1], but is significantly shorter than that found [2.637(1) Å] in the crystal structure of $\{[(\text{PPh}_3)_2(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)\text{Pt}]_2\text{Hg}\}$ [9], where steric in-

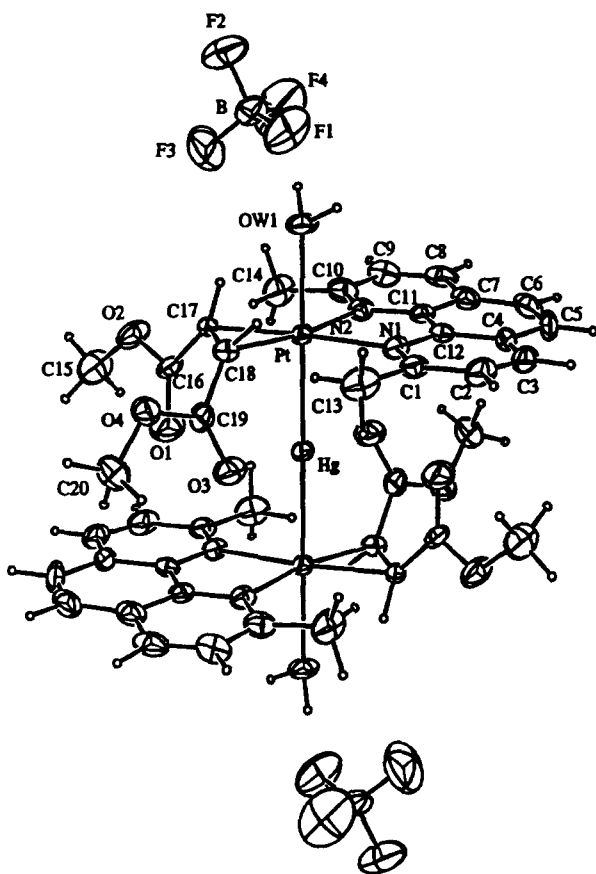


Fig. 2. ORTEP view of **III⁺a** showing the atom-labelling scheme.

Table 1

Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) of the non-hydrogen atoms of the compound $\text{III}^+ \mathbf{a}$ with their e.s.d.s in parentheses

$$B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Hg	0.5	0.5	0.5	3.72(1)
Pt	0.68068(4)	0.57307(4)	0.60950(3)	3.18(1)
O(1)	0.401(1)	0.681(1)	0.577(1)	10.4(5)
O(2)	0.485(1)	0.842(1)	0.597(1)	6.5(3)
O(3)	0.456(1)	0.463(1)	0.671(1)	7.5(3)
O(4)	0.474(1)	0.580(1)	0.777(1)	5.2(2)
N(1)	0.765(1)	0.421(1)	0.606(1)	3.6(2)
N(2)	0.747(1)	0.595(1)	0.502(1)	3.6(2)
C(1)	0.776(1)	0.337(1)	0.659(1)	4.3(3)
C(2)	0.837(1)	0.244(1)	0.648(1)	5.8(4)
C(3)	0.883(1)	0.238(1)	0.582(1)	5.7(4)
C(4)	0.875(1)	0.325(1)	0.525(1)	4.9(3)
C(5)	0.922(1)	0.325(1)	0.455(1)	6.1(4)
C(6)	0.915(1)	0.413(2)	0.405(1)	5.9(4)
C(7)	0.858(1)	0.507(1)	0.419(1)	5.0(4)
C(8)	0.848(1)	0.607(1)	0.370(1)	5.8(4)
C(9)	0.790(1)	0.690(1)	0.386(1)	5.4(4)
C(10)	0.738(1)	0.684(1)	0.452(1)	5.0(4)
C(11)	0.806(1)	0.509(1)	0.485(1)	3.8(3)
C(12)	0.816(1)	0.417(1)	0.541(1)	3.8(3)
C(13)	0.721(2)	0.342(1)	0.731(1)	6.6(5)
C(14)	0.667(2)	0.775(1)	0.465(1)	6.6(5)
C(15)	0.382(2)	0.895(2)	0.548(1)	8.2(6)
C(16)	0.488(1)	0.739(1)	0.601(1)	6.5(4)
C(17)	0.600(1)	0.691(1)	0.656(1)	5.1(3)
C(18)	0.608(1)	0.595(1)	0.705(1)	4.6(3)
C(19)	0.503(1)	0.541(1)	0.712(1)	4.9(3)
C(20)	0.373(1)	0.539(2)	0.790(1)	6.3(4)
F(1)	0.941(1)	0.822(1)	0.669(1)	12.8(5)
F(2)	0.985(1)	0.989(1)	0.712(1)	12.0(4)
F(3)	0.821(1)	0.948(2)	0.641(1)	17.7(7)
F(4)	0.940(2)	0.938(2)	0.576(1)	18.3(6)
B	0.922(2)	0.922(2)	0.646(1)	6.3(5)
OW(1)	0.848(1)	0.640(1)	0.712(1)	5.3(2)
OW(2)	0.853(5)	0.534(5)	0.901(4)	44(3)

teractions between bulky substituents on Pt are present. The Hg is perfectly colinear with Pt, and OW(1).

The dmphen and the olefin carbon atoms C(17) and C(18) bind symmetrically to Pt, defining the equatorial plane from which none of these atom is further than 0.09(2) \AA .

A water molecule occupies the apical position and forms two hydrogen bonds with two different BF_4 anions. The bond distance between OW(1) and Pt [2.36(1) \AA] is rather long consistent with the high *trans* influence of Hg [1]. A second water molecule shares the hydrogen bond network in crystal, bridging the fluorine atoms F(4) of two different anions. Hydrogen bond parameters are presented in Table 3.

Analogously with previous findings [1], Hg forms four weak Hg \cdots O interactions [2.98(1) \AA] with the carbonyl oxygens O(1) and O(3) of the carboxylate groups in an equatorial arrangement.

Table 2

Bond lengths (\AA) and relevant valence angles (deg) with their estimated standard deviations in parentheses

Hg–Pt	2.5444(5)	C(10)–C(14)	1.48(2)
Pt–C(17)	2.03(1)	C(10)–N(2)	1.34(2)
Pt–C(18)	2.02(2)	C(11)–C(12)	1.42(2)
Pt–N(1)	2.15(1)	C(11)–N(2)	1.35(2)
Pt–N(2)	2.14(1)	C(12)–N(1)	1.38(2)
Pt–OW(1)	2.36(1)	C(15)–O(2)	1.43(2)
C(1)–C(2)	1.42(2)	C(16)–C(17)	1.51(2)
C(1)–C(13)	1.51(2)	C(16)–O(1)	1.25(2)
C(1)–N(1)	1.31(2)	C(16)–O(2)	1.26(2)
C(2)–C(3)	1.34(3)	C(17)–C(18)	1.42(2)
C(3)–C(4)	1.39(3)	C(18)–C(19)	1.49(2)
C(4)–C(5)	1.42(3)	C(19)–O(3)	1.21(2)
C(4)–C(12)	1.40(2)	C(19)–O(4)	1.29(2)
C(5)–C(6)	1.32(3)	C(20)–O(4)	1.42(2)
C(6)–C(7)	1.41(3)	F(1)–B	1.29(3)
C(7)–C(8)	1.44(3)	F(2)–B	1.38(3)
C(7)–C(11)	1.41(2)	F(3)–B	1.27(3)
C(8)–C(9)	1.31(3)	F(4)–B	1.22(3)
C(9)–C(10)	1.40(2)	Hg–O(1)	2.98(1)
		Hg–O(3)	2.98(1)
Hg–Pt–C(17)	94.4(4)	Hg–Pt–C(18)	93.9(4)
Hg–Pt–N(1)	90.5(3)	Hg–Pt–N(2)	87.8(3)
Hg–Pt–OW(1)	179.5(3)	C(17)–Pt–C(18)	40.9(7)
C(17)–Pt–N(2)	123.9(7)	C(17)–Pt–OW(1)	85.6(5)
C(18)–Pt–N(1)	117.8(6)	Pt–C(17)–C(18)	69(1)
C(18)–Pt–OW(1)	85.9(5)	C(16)–C(17)–C(18)	123(1)
N(1)–Pt–N(2)	77.2(4)	Pt–C(18)–C(17)	70(1)
N(1)–Pt–OW(1)	89.3(4)	N(2)–Pt–OW(1)	92.5(4)
C(17)–C(18)–C(19)	120(1)	O(1)–Hg–O(3)	61.5(5)

2.3. Reactivity of $\text{III}^+ \mathbf{a}$

Some reactions have been performed on $\text{III}^+ \mathbf{a}$, to compare (see Section 3) the lability of the apical neutral ligand with that in the related cationic Pt(II) species [3,5,8]. The trinuclear complex was allowed to react with anionic Cl^- and neutral PhNH_2 .

The reaction with an excess LiCl regenerate complex IIIa , whereas the treatment with aniline affords the related cationic cluster $\text{III}^+ \mathbf{b}$ (Fig. 3).

Complex $\text{III}^+ \mathbf{b}$, obtained as a yellow microcrystalline powder, is soluble in nitromethane and both NMR and conductivity measurements are consistent with the proposed structure.

Table 3
Hydrogen bond parameters

Contacts	O \cdots F (\AA)	H \cdots F (\AA)	O–H \cdots F ($^\circ$)
OW(1) \cdots F(1)	2.70(2)	1.69(1)	175.0(7)
OW(1) \cdots F(2) ^a	2.77(2)	1.76(1)	174.4(8)
OW(2) \cdots F(4) ^a	2.74(6)	1.73(2)	161(3)
OW(2) \cdots F(4) ^b	2.70(6)	1.74(1)	164(3)

Atomic positions related to reference atom at x, y, z by symmetry operation: ^a 2 – x, y – 0.5, 1.5 – z; ^b x, 1.5 – y, 0.5 + z.

3. Discussion

As far as we know, the only cation containing the sequence Pt–Hg–alkyl is a methyl derivative, coordinatively saturated by a tripodal ligand [10]. Recent work [1] showed that a suitable choice of the bidentate ligand allows the attainment of a fairly wide class of neutral platinum complexes of general formula [PtCl(Hg-alkyl)(dmphen)(olefin)] (**II**). In this case the coordinative saturation is also most important for determining the stability of the complexes. Previously described square-planar complexes containing a Pt–Hg–alkyl moiety are involved in demercuration processes, which prevent their isolation [11,12].

Our results show that the effects operating in the stabilization of type **II** complexes hold for the cationic new species. Exchange of the chloride with a neutral donor in presence of a silver salt leads to the isolation of the cationic aqua-species [Pt(HgR)(H₂O)(dmphen)-(Z-R'O₂CCH=CHCO₂R')] (**III**⁺). The unusual coordination of water on Pt(II) in preference to a softer donor, such as acetonitrile, although not generally observed in related cationic species, has also been reported for another dimethyl maleate complex [3].

The lability of the neutral molecule L coordinated in the axial position of platinum(II) bipyramidal trigonal complexes is related mainly to the nature of the *trans* ligand. Whereas easy exchange of L is generally observed in cationic mononuclear hydrocarbyl species [Pt(R)(L)(dmphen)(olefin)]⁺ [5], no exchange occurs in the related chloro-derivatives [Pt(Cl)(L)(dmphen)(olefin)]⁺ [8], most probably because of the different *trans*-labilizing properties of R and Cl [13]. The results reported here concerning the easy substitution of the coordinated water in complex **III**⁺**a** by Cl[−] or PhNH₂ confirm the large *trans* influence exerted by the mercury atom. The X-ray analysis of [Pt(HgMe)(Cl)(dmphen)(Z-MeO₂CCH=CHCO₂Me)] (**IIa**) suggests

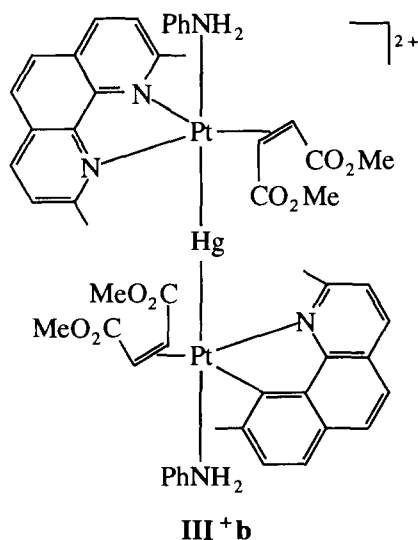


Fig. 3.

the same conclusion [1].

The olefin in type **II** and **II**⁺ species can give rise to two possible rotamers, depending whether the olefin protons face the -HgR fragment or the other axial ligand. The ¹H NMR spectra reveal only one isomer. The ²J_{Pt–H(olefin)} coupling constants of the products fall within narrow ranges, i.e. 81–84 [1] and 82–88 Hz for type **II** and type **II**⁺ compounds, respectively. In the related mononuclear complexes [Pt(R)(Cl)(dmphen)(olefin)], the value of ²J_{Pt–H(olefin)} is diagnostic of the alkene coordination stereochemistry [14], and a higher value is observed for olefin protons *trans* to facing the halogen. If analogous effects also occur for type **II** species, we might assume that in these complexes the dialkyl maleate ligands have the same orientation, and the previously reported [1] X-ray diffractometric analysis of complex **IIa** suggests that the olefin protons should face the halogen. Unfortunately, even though the NMR spectroscopic evidence imply a common stereochemistry to the three **II**⁺ species described here, we have no grounds for assessing whether the olefin protons are opposite the water molecule or the -HgR.

The alkylmercury fragments in **II**⁺ complexes are involved in decomposition processes, while the corresponding neutral type **II** species are involved in reversible dissociation in solution into the corresponding RHgCl and [Pt(dmphen)(Z-R'O₂CCH=CHCO₂R')] according to Eq. (1). The demercuration reaction involving **II**⁺**a** and **II**⁺**b** affords one of the two possible rotamers of the mononuclear cationic complexes [PtMe(H₂O)(dmphen)(Z-MeO₂CCH=CHCO₂Me)]⁺ (**IV**⁺**a**) and [PtMe(H₂O)(dmphen)-(Z-(^tBu)O₂CCH=CHCO₂(Bu'))]⁺ (**IV**⁺**b**). These compounds have been independently obtained by chlorine abstraction from the corresponding neutral species [PtMe(Cl)(dmphen)(Z-R'O₂CCH=CHCO₂R')] (R' = Me or Bu') (**IVa–b**) [15]. Apart from the rate, the demercuration process resembles that occurring in square-planar complexes containing a Pt(II)–Hg bond, and is consistent with the observation that a positive charge in five-coordinate Pt(II) complexes of the general type investigated here enhances their reactivity [16,17].

Accordingly, the formation of the trinuclear cluster **III**⁺**a** from the decomposition of **II**⁺ complexes is probably a consequence of an enhanced tendency of Pt(II)–Hg–Y bonds in the cations to undergo redistribution reactions, affording complexes containing the Pt–Hg–Pt fragment [1]. In neutral type **II** complexes this rearrangement was found to occur only when Y was Ph, whereas in the case of Y is Me, Et or ^tBu the process is inhibited.

4. Experimental details

Complex **IIc** [18] was prepared as described for **IIa** and **IIb** in Ref. [1]. ¹H NMR spectra were recorded at

270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. IR spectra were recorded on a Perkin Elmer 457 spectrophotometer in Nujol mulls. Solvents and reagents were of AnalaR grade and used without further purification.

4.1. Synthesis of $\text{II}^+ \text{a}^-$

To a stirred solution of the appropriate complex IIa-c (0.20 mmol) in 5 ml of dichloromethane AgBF_4 (0.039 g, 0.20 mmol) in 4 ml of acetonitrile at 273 K is added under dinitrogen. After 15 min stirring, AgCl is filtered off and the volume of the resulting pale yellow solution reduced to ca. 2 ml under vacuum without heating. The complex is crystallized by careful addition of diethyl ether, washed with diethyl ether and dried under vacuum (yield > 85%). $\text{II}^+ \text{a}$ can be recrystallized by dissolving 0.100 g of the complex in 6 ml of chloroform under dinitrogen and then adding 6 ml of hexane. The volume of the solution is reduced under vacuum without heating and more hexane added to complete the crystallization. The sparkling light green crystals are washed with hexane and dried under vacuum (yield: 0.080 g, 80%). Selected ^1H NMR data (298 K; s = singlet, br = broak peak) [19]: in CDCl_3 [CHCl_3 (δ 7.26 ppm) as internal standard]: $\text{II}^+ \text{a}$: 4.02 ($^2J_{\text{Pt-H}} = 84$ Hz, s, $\text{CH}=\text{CH}$); 3.78 (s, MeO, 6H); 3.25 (s, NCMe, 6H); 1.32 ($^2J_{\text{Hg-H}} = 193$ Hz, $^3J_{\text{Pt-H}} = 21$ Hz, br, MeHg) ppm; $\text{II}^+ \text{b}$: 3.96 ($^2J_{\text{Pt-H}} = 82$ Hz, s, $\text{CH}=\text{CH}$); 3.32 (s, NCMe, 6H); 1.50 (s, ^1BuO , 18H); 1.25 ($^2J_{\text{Hg-H}} = 200$ Hz, $^3J_{\text{Pt-H}} = 22$ Hz, br, MeHg) ppm; $\text{II}^+ \text{c}$: 3.95 ($^2J_{\text{Pt-H}} = 88$ Hz, s, $\text{CH}=\text{CH}$); 3.79 (s, MeO, 6H); 3.24 (s, NCMe, 6H); 0.71 ($^3J_{\text{Hg-H}} = 346$ Hz, $^4J_{\text{Pt-H}} = 18$ Hz, s, Bu^1Hg) ppm. Anal. Calc. for $\text{C}_{21}\text{H}_{25}\text{BF}_4\text{HgN}_2\text{O}_5\text{Pt}$ ($\text{II}^+ \text{a}$): C, 29.06; H, 2.90; N, 3.23%. Found: C, 29.24; H, 2.78; N, 3.19%. Calc. for $\text{C}_{27}\text{H}_{37}\text{BF}_4\text{HgN}_2\text{O}_5\text{Pt}$ ($\text{II}^+ \text{b}$): C, 34.06; H, 3.92; N, 2.94%. Found: C, 33.91; H, 4.01; N, 2.90%. Calc. for $\text{C}_{24}\text{H}_{31}\text{BF}_4\text{HgN}_2\text{O}_5\text{Pt}$ ($\text{II}^+ \text{c}$): C, 31.68; H, 3.43; N, 3.08. Found: C, 31.85; H, 3.28; N, 3.11%.

4.2. Synthesis of $\text{III}^+ \text{b}$

To a stirred solution of complex $\text{III}^+ \text{a}$ (0.050 g, 0.033 mmol) in 2 ml of nitromethane is added aniline (0.007 g, 0.076 mmol). After 16 h the volume of the solution is reduced under vacuum and the complex crystallized as a yellow microcrystalline solid by careful addition of diethyl ether. The product is then washed with diethyl ether and dried under vacuum (yield: 0.035 g, 65%). Selected ^1H NMR data (298 K; s = singlet, br = broak peak; in CD_3NO_2 [CHD_2NO_2 (δ 4.33 ppm) as internal standard]): 6.5 (br, 6H); 5.8 (br, 4H); 3.36 ($^2J_{\text{Pt-H}} = 79$ Hz, s, 2 $\text{CH}=\text{CH}$); 3.05 (s, MeO, 12H); 2.85 (s, NCMe, 12H) ppm. Anal. Calc. for $\text{C}_{52}\text{H}_{54}$ -

Table 4
Summary of crystallographic data

Crystal size/mm	0.10 × 0.18 × 0.30
formula	$1/2[(\text{HgPt}_2\text{O}_8\text{N}_4\text{C}_{40}\text{H}_{40})]^{+2} \cdot 2\text{BF}_4^- \cdot 4\text{H}_2\text{O}$
<i>f</i> w	770.6
crystal system	monoclinic
space group	$\text{P2}_1/c$
<i>a</i> /Å	12.360(4)
<i>b</i> /Å	12.296(5)
<i>c</i> /Å	16.001(9)
β	107.79(4)
<i>V</i> /Å ³	2316(3)
<i>Z</i>	4
<i>F</i> (000)	1460
<i>D</i> _c /g cm ⁻³	2.21
<i>D</i> _m /g cm ⁻³	2.21
λ (Mo K α)/Å	0.7093
θ_{max} (°)	26
μ /cm ⁻¹	94.9
no. of indep refls	4533
no. of refls above 3 σ (<i>I</i>)	3009
no. of refined params	308
goodness of fit	0.86
<i>R</i>	0.044
<i>R</i> _w	0.049

$\text{B}_2\text{F}_8\text{HgN}_6\text{O}_8\text{Pt}_2$: C, 37.73; H, 3.29; N, 5.08%. Found: C, 37.84; H, 3.36; N, 4.99%.

4.3. Crystal Structure Determination of $\text{III}^+ \text{a}$

The compound was crystallized from nitromethane. Crystal data and details of the crystal analysis are summarized in Table 4. X-ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Mo-K α graphite-monochromated radiation which was operated in the ω/θ scanning mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the θ range $12 \leq \theta \leq 15^\circ$. Three monitoring reflections, measured every 500, showed no significant crystal decay. In addition to the corrections for Lorentz and polarization factors, a semiempirical correction for absorption [20] was applied (max. and min. values of the transmission factor were 1.00 and 0.78). The structure was solved by the Patterson and Fourier techniques and refined by full-matrix least-squares procedure. The minimized quantity was $\sum w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02 F_o)^2 + 0.3]$ where σ is derived from counting statistics. Two water molecules, detected in the difference electron density map, allowed the calculated density to fit the measured (by flotation) value. The first water molecule is in the coordination polyhedron of Pt and its oxygen was refined anisotropically. The second has a high value of the thermal parameter and its oxygen was refined isotropically. Considering the specific features of the difference elec-

tron-density map, the H atoms were added at calculated positions with isotropic thermal parameters 1.2 times larger than the B of the carrier atoms and held fixed during the refinement.

The final Fourier difference map show no peaks greater than $\pm 1.9 \text{ e } \text{Å}^{-3}$.

All calculations were performed with the Enraf-Nonius (SDP) set of programs [21].

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Positional and thermal parameters of the H atoms, anisotropic thermal parameters of the non-hydrogen atoms and complete bond distances and angles have been deposited with the Cambridge Crystallographic Centre.

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