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# Trigonal-bipyramidal Co-ordinatively Saturated Platinum(II) Olefin Complexes bearing an Organomercury Fragment in Axial Position†

**Maria Elena Cucciolito,[a] Federico Giordano,[a] Achille Panunzi,[a] Francesco Ruffo *,[a] and Vincenzo De Felice[b]**
[a] *Dipartimento di Chimica, Università di Napoli 'Federico II', via Mezzocannone 4, I-80134, Napoli, Italy*
[b] *DISTAAM, Università del Molise, Via Tiberio 21/A, I-86100, Campobasso, Italy*

The reactions of organomercury halides HgR′(Cl) (R′ = Me, Et, Bu$^t$ or Ph) with complexes of the type [Pt(dmphen){(*Z*)-RO$_2$CCH=CHCO$_2$R}] (dmphen = 2,9-dimethyl-1,10-phenanthroline; R = Me, Et or Bu$^t$) have been studied. The dmphen ligand with suitable 'in-plane' steric hindrance stabilizes five-co-ordinate adducts of general formula [PtCl(HgR′)(dmphen){(*Z*)-RO$_2$CCH=CHCO$_2$R}] when R′ = alkyl. An influence of the nature of the Hg-bound hydrocarbyl group on the reaction course is observed. Thus, a cluster containing the Pt–Hg–Pt sequence was obtained when R′ = Ph or Cl. The molecular structure of [PtCl(HgMe)(dmphen){(*Z*)-MeO$_2$CCH=CHCO$_2$Me}] [space group $P2_1/c$; $a$ = 13.079(2), $b$ = 13.167(2), $c$ = 15.495(3) Å and β = 94.18(2)°] reveals a large *trans* influence of the organomercury fragment.

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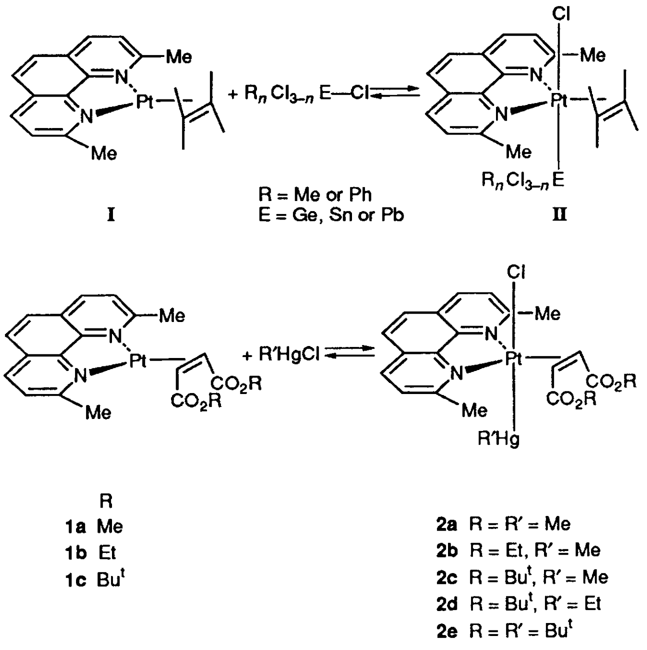
Recent studies have led to the isolation of co-ordinatively saturated platinum(II) complexes containing a Group 14 organometallic fragment. A variety of bimetallic species **II** was obtained by oxidative addition of organic halides of Sn,[1] Ge[2] and Pb[2] to trigonal species **I** (Scheme 1). The steric features of the chelate play an essential role in the stabilization of the products, as established[3] also for related halogeno and hydrocarbyl complexes. Spectroscopic[1,2] and crystallographic[1] results indicated that the organometallic ligand in all cases occupies an axial position in an uncommon trigonal-bipyramidal (*TBPY*) arrangement around platinum.

Owing to the interesting reactivities displayed by some of the complexes **II**[4] and the general and synthetic interest in organomercurials,[5] we have extended our investigation to the products of reaction of organomercury derivatives HgR′(Cl) with type **I** species. Thus, we report here on the synthesis and characterization of type **II** mercury derivatives, and of two related clusters. The single-crystal structure of a mononuclear five-co-ordinate compound, [PtCl(HgMe)(dmphen){(*Z*)-MeO$_2$CCH=CHCO$_2$Me}] (dmphen = 2,9-dimethyl-1,10-phenanthroline) has also been determined.

## Results

*Synthesis and Characterization of the Complexes.*—The three-co-ordinate type **I** complexes employed are shown in Scheme 1. Complex **1c** was used as the three-co-ordinate substrate in most of the addition reactions. In all cases the reactions outlined in Scheme 1 are equilibrium processes in chloroform solution. The five-co-ordinate products were accompanied by some unreacted starting materials. However, the products could be isolated in all cases by adding hexane to the reaction solution, and the elemental analyses confirmed their compositions.

The geometry of type **II** complexes was generally determined on the basis of their $^1$H NMR spectra, taking into account previous observations concerning related species.[1–3] Tables 1 and 2 give the analytical and relevant $^1$H NMR data. In the case of the products derived from **1c** (*i.e.* **2c**–**2e**), the $^1$H NMR spectra recorded at 298 K show broad signals, suggesting rapid equilibria between the five-co-ordinate adduct and some platinum(0) and HgR′(Cl) species. The equilibria were more evident for complexes **2a** and **2b**. In this case different broad signals could be observed for all species involved.



**Scheme 1**

In order to obtain more detailed information about the new complexes the spectra were also recorded at 243 K (see below). The main spectral features are as follows. (*i*) The two methyl groups on the chelate, the two olefin protons and the two R groups on CO$_2$R are equivalent. These features are consistent with the presence of a mirror plane including the centre of the C=C bond and the midpoint of the N ··· N segment. (*ii*) The chemical shift of the olefin protons in the type **II** complexes

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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**Table 1** Elemental analysis for the five-co-ordinate complexes [PtCl(HgR′)(dmphen)(olefin)]

| Complex | Analysis (%)* C | H | N |
|---|---|---|---|
| **2a** [PtCl(HgMe)(dmphen){(*Z*)-$MeO_2CCH{=}CHCO_2Me$}] | 31.75 (31.60) | 2.75 (2.90) | 3.60 (3.50) |
| **2b** [PtCl(HgMe)(dmphen){(*Z*)-$EtO_2CCH{=}CHCO_2Et$}] | 33.50 (33.40) | 3.25 (3.30) | 3.30 (3.40) |
| **2c** [PtCl(HgMe)(dmphen){(*Z*)-$Bu^tO_2CCH{=}CHCO_2Bu^t$}] | 36.65 (36.75) | 4.00 (4.00) | 3.20 (3.15) |
| **2d** [PtCl(HgEt)(dmphen){(*Z*)-$Bu^tO_2CCH{=}CHCO_2Bu^t$}] | 37.40 (37.50) | 4.25 (4.15) | 3.00 (3.10) |
| **2e** [PtCl($HgBu^t$)(dmphen){(*Z*)-$Bu^tO_2CCH{=}CHCO_2Bu^t$}] | 39.00 (38.95) | 4.60 (4.45) | 2.95 (3.05) |

* Calculated values in parentheses.

**Table 2** Selected $^1$H NMR[a] (δ, *J*/Hz) for the five-co-ordinate complexes [PtCl(HgR′)(dmphen)(olefin)]

| Complex | Hg–$CH_x$[b] | olefin H[c] | Me of dmphen | Others |
|---|---|---|---|---|
| **2a** | 0.69 (140, 16, 3 H) | 3.99 (81, 2 H) | 3.32 (6 H) | 3.76 (MeO, 6 H) |
| | [0.69 (130, br, 3 H)] | [4.04 (81, br, 2 H)] | [3.36 (br, 6 H)] | [3.76 (br, MeO, 6 H)] |
| **2b** | 0.67 (138, 16, 3 H) | 4.00 (81, 2 H) | 3.34 (6 H) | 4.20 (m, Me$CH_2$O, 4 H) |
| | [0.67 (127, br, 3 H)] | [4.05 (81, br, 2 H)] | [3.38 (br, 6 H)] | [4.20 (br, Me$CH_2$O, 4 H)] |
| **2c** | 0.62 (138, 15, 3 H) | 3.93 (81, 2 H) | 3.38 (6 H) | 1.48 ($Bu^tO$, 18 H) |
| | [0.62 (135, br, 3 H)] | [3.97 (81, br, 2 H)] | [3.40 (br, 6 H)] | [1.50 (br, $Bu^tO$, 18 H)] |
| **2d** | 1.41 ([d], q, 2 H) | 3.91 (81, 2 H) | 3.38 (6 H) | 1.43 ($Bu^tO$, 18 H), 0.66 (t, *Me*$CH_2$Hg, 3 H) |
| | [2 H[e]] | [3.87 ([f], br, 2 H)] | [3.39 (br, 6 H)] | [1.49 (br, $Bu^tO$, 18 H)] |
| **2e**[g] | | 3.68 (84, 2 H) | 3.28 (6 H) | 1.42 ($Bu^tO$, 18 H), 0.57 ($Bu^tHg$, 9 H) |
| | | [3.77 (86, br, 2 H)] | [3.37 (br, 6 H)] | [1.50 (br, $Bu^tO$, 18 H), 0.96 (br, $Bu^tHg$, 9 H)] |

[a] The spectra were recorded at 270 MHz at 243 and 298 K (in square brackets), respectively. The samples were obtained by dissolving 0.010 mmol of the appropriate complex in $CDCl_3$ (0.6 $cm^3$); $CHCl_3$ (δ 7.26) was used as internal standard. Spectra of **2a** and **2b** contain also resonances due to the type **I** complex and alkylmercury halide formed upon dissociation of **II**. In this case only the resonances of the type **II** complexes have been reported. Abbreviations: t = triplet; q = quartet; m = multiplet; br = broad; no attribute, singlet. [b] $^2J$(Hg–H) and $^3J$(Pt–H) (if measurable) in parentheses. [c] $^2J$(Pt–H) in parentheses. [d] $^2J$(Hg–H) not measurable. [e] Broad peak, overlapped by other signals. [f] $^2J$(Pt–H) not measurable. [g] Spectrum recorded in $CD_2Cl_2$ at 213 K ($CHDCl_2$, δ 5.31).

shows a low-field shift with respect to the related type **I** species (Δδ *ca.* 0.5). This trend had been observed for the similar Group 14 derivatives,[1,2] and can be attributed to the different extents of π-back donation that exists in five- and three-co-ordinate complexes. (*iii*) The protons of the alkyl groups bound to Hg resonate at higher field [as for the other known Pt(HgMe) derivative[6]] than in the starting organomercury chlorides. For instance, the MeHg resonances at 243 K are at δ 0.69, 0.67, 0.62 and 1.12, respectively, for **2a**, **2b**, **2c** and HgMe(Cl). (*iv*) Upon co-ordination to platinum, the coupling constant $^2J$(Hg–H) between the methyl protons and mercury, in the MeHg fragments, is lowered with respect to the value measured for HgMe(Cl) (*ca.* 140 *vs.* 200 Hz). (*v*) In the $^1$H NMR spectra recorded at 243 K all signals become sharp, revealing the quartet and the triplet of EtHg group in **2d**, and the presence of coupling [$^3J$(Pt–H)= 15–16 Hz] in the Me–Hg–Pt fragments of complexes **2a**–**2c**. The latter values agree with the one previously measured.[6] In the case of **2e**, lowering the temperature to 213 K was required to obtain similar results.

The five-co-ordinate type **II** complexes are white-yellow microcrystalline solids which were stored at 253 K. They can be handled in air and very slowly decompose in chloroform. The organometal group can be removed by treatment with an equimolar amount of hydrochloric acid, and a known[7] five-co-ordinate hydride is formed in quantitative yield [equation (1)].

$$[\mathrm{PtCl(HgMe)(dmphen)}\{(Z)\text{-}\mathrm{MeO_2CCH{=}CHCO_2Me}\}] + \mathrm{HCl} \longrightarrow [\mathrm{PtCl(H)(dmphen)}\{(Z)\text{-}\mathrm{MeO_2CCH{=}CHCO_2Me}\}] + \mathrm{HgMe(Cl)} \quad (1)$$

The reaction most probably involves addition to the type **I** species in equilibrium.

The reaction of an arylmercury(II) halide HgPh(Cl) was also examined. Treatment of complex **1a** with an equimolar quantity of HgPh(Cl) in solution afforded an orange crystalline solid, almost insoluble in organic solvents, while 0.5 equivalent of $HgPh_2$ was formed. The analysis of the product rules out a type **II** formulation and is in accord with the structure **3a** (Scheme 2). We also obtained **3a** by treatment of **1a** with half of the equimolar amount of $HgCl_2$. The structure assignment is also suggested by the easy conversion of **3a** into **3b**. When **3a** is treated with $AgBF_4$ in MeCN a microcrystalline orange compound is obtained, the elemental analyses and $^1$H NMR data of which are in accord with structure **3b**. This transformation is easily reversed by adding LiCl to a solution of **3b**. The most significant feature of the spectrum of **3b** is the equivalence of the two halves of both the olefin and the dmphen ligands. The presence of $H_2O$ in **3b**, suggested by the IR spectrum, was confirmed by recording the $^1$H NMR spectrum in dry $CD_3NO_2$. The water content of the sample, as evaluated through integration of the appropriate peaks, was equivalent to that of dmphen and dimethyl maleate. Furthermore, according to conductivity data,[8] **3b** is a 1 : 2 electrolyte in nitromethane.

*Crystal Structure of Complex* **2a**.—The molecular structure of complex **2a**, together with the atom-labelling scheme, is shown in Fig. 1. Final atomic parameters are listed in Table 3 and selected bond lengths and angles in Table 4. If the olefinic bond is taken as a monodentate ligand the complex can be described as having trigonal-bipyramidal co-ordination with the dmphen ligand and the olefinic bond in the equatorial plane and with Hg and Cl(1) in axial positions. The methyl group at C(21) completes the linear co-ordination of the mercury atom.

The dmphen ligand, Pt and the olefinic atoms C(17) and C(18) are coplanar within 0.08(2) Å. The Pt–N distances are equal within experimental error and fall in the expected range, as do the Pt–C(olefinic) distances. The bite angles N(1)–Pt–N(2) and C(17)–Pt–C(18) are 76.3(6) and 41.4(9)° respectively.

According to the high value of the density (2.29 g $cm^{-3}$), the crystal packing is very tight and is responsible for the departure of the structure from potential $C_s$ symmetry: (*a*) the axis

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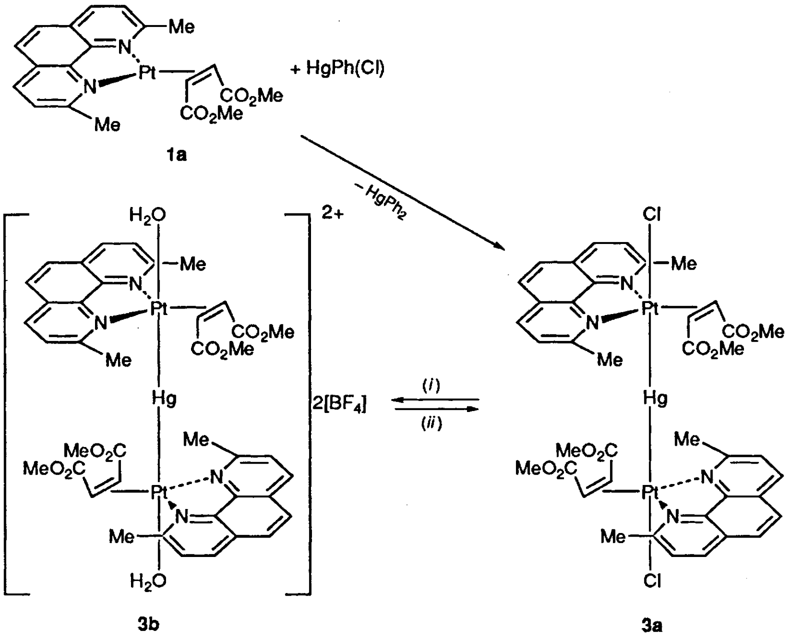

**Scheme 2** (*i*) AgBF$_4$, MeCN, water; (*ii*) LiCl

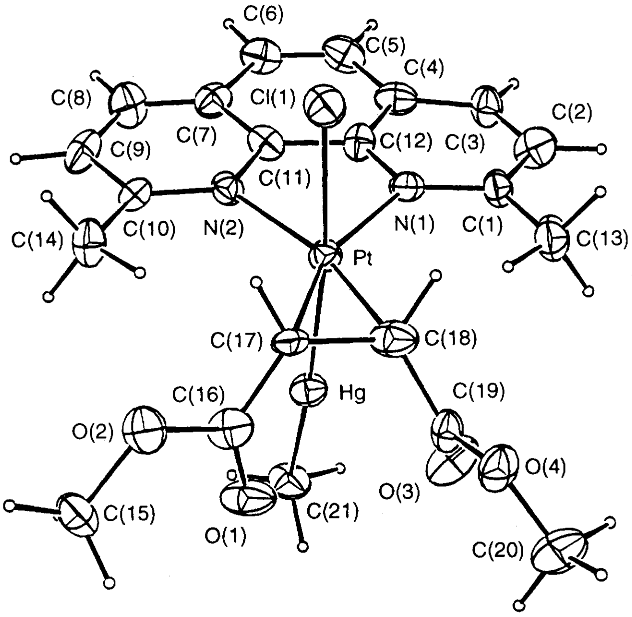

**Fig. 1** An ORTEP[9] view of the molecule with the atom-labelling scheme. Thermal ellipsoids are drawn at the 25% probability level

Cl(1)–Pt–Hg–C(21) is tilted with a value of 173.9° for both the valence angles Cl(1)–Pt–Hg and Pt–Hg–C(21); (*b*) the Cl(1)–Pt axis of the olefinic ligand is rotated by 3° in such a way as to approach N(1); (*c*) the two moieties of the dimethyl maleate ligand have different conformations, the values of the torsion angles C(18)–C(17)–C(16)–O(2) and C(17)–C(18)–C(19)–O(4) being 155(2) and 103(2)° respectively.

The most interesting feature of the structure is the presence of the Pt–Hg–Me fragment, for which scarce data are available in the literature. The Pt–Hg distance [2.558(1) Å] compares well with the value of 2.531 Å found in the structure of [Pt(HgMe){N(CH$_2$CH$_2$PPh$_2$)$_3$}]BPh$_4$.[6] The Hg–C(21) distance [2.06(2) Å] is normal for a mercury–carbon linkage, whereas Pt–Cl(1) [2.590(6) Å] is anomalously long (see below).

There are two short contacts less than the sum of van der Waals radii between Hg and the carboxylate oxygens O(1) and O(3). These distances, 2.90(2) and 2.79(2) Å, fall in the class of weak Hg • • • O bonds.[10,11]

**Table 3** Fractional atomic coordinates of the non-hydrogen atoms with their estimated standard deviations (e.s.d.s) in parentheses for complex **2a**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Hg | 0.9161(1) | 0.0716(1) | 0.1539(1) |
| Pt | 0.7511(1) | 0.0064(1) | 0.2138(1) |
| Cl(1) | 0.5912(4) | −0.0790(4) | 0.2714(3) |
| O(1) | 0.995(1) | 0.049(1) | 0.333(1) |
| O(2) | 0.954(1) | −0.087(1) | 0.406(1) |
| O(3) | 0.871(1) | 0.232(1) | 0.262(1) |
| O(4) | 0.811(1) | 0.251(1) | 0.392(1) |
| N(1) | 0.665(1) | 0.061(1) | 0.097(1) |
| N(2) | 0.762(1) | −0.117(1) | 0.123(1) |
| C(1) | 0.618(1) | 0.153(1) | 0.088(1) |
| C(2) | 0.571(2) | 0.179(2) | 0.008(1) |
| C(3) | 0.570(2) | 0.116(2) | −0.059(1) |
| C(4) | 0.613(2) | 0.017(2) | −0.052(1) |
| C(5) | 0.610(2) | −0.058(2) | −0.117(1) |
| C(6) | 0.660(2) | −0.145(2) | −0.108(1) |
| C(7) | 0.716(1) | −0.173(2) | −0.023(1) |
| C(8) | 0.767(2) | −0.257(2) | −0.012(1) |
| C(9) | 0.820(2) | −0.278(2) | 0.070(1) |
| C(10) | 0.816(2) | −0.204(1) | 0.135(1) |
| C(11) | 0.713(1) | −0.099(1) | 0.043(1) |
| C(12) | 0.662(1) | −0.004(1) | 0.030(1) |
| C(13) | 0.622(2) | 0.220(2) | 0.164(1) |
| C(14) | 0.863(2) | −0.225(2) | 0.224(1) |
| C(15) | 1.063(2) | −0.107(2) | 0.427(2) |
| C(16) | 0.926(2) | −0.007(2) | 0.357(1) |
| C(17) | 0.817(1) | 0.005(1) | 0.340(1) |
| C(18) | 0.765(2) | 0.101(2) | 0.319(1) |
| C(19) | 0.826(2) | 0.200(1) | 0.319(1) |
| C(20) | 0.856(2) | 0.348(2) | 0.399(2) |
| C(21) | 1.046(2) | 0.113(2) | 0.095(1) |
| Cl(2) | 0.2770(6) | 0.5047(6) | 0.8130(5) |
| Cl(3) | 0.4207(5) | 0.3454(6) | 0.8486(4) |
| Cl(4) | 0.3695(6) | 0.4845(8) | 0.9848(5) |
| C(22) | 0.385(2) | 0.473(2) | 0.875(1) |

## Discussion

Square-planar platinum complexes involving Pt–Hg bonds are known.[12] It was found that the steric and electronic features of the R′ group dramatically influence the stability of the Pt–Hg–R′ sequence. Only CF$_3$ or *ortho*-substituted aryl groups allow the attainment of stable compounds,[13,14] while

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**Table 4** Bond lengths (Å) and selected valence angles (°) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Hg–Pt | 2.558(1) | Hg–C(21) | 2.06(2) |
| Pt–N(1) | 2.19(2) | Pt–N(2) | 2.16(2) |
| Pt–C(17) | 2.07(2) | Pt–C(18) | 2.05(2) |
| Pt–Cl(1) | 2.590(6) | C(17)–C(18) | 1.46(3) |
| C(16)–C(17) | 1.45(3) | C(18)–C(19) | 1.52(3) |
| O(1)–C(16) | 1.23(2) | O(3)–C(19) | 1.18(2) |
| O(2)–C(16) | 1.34(3) | O(4)–C(19) | 1.34(2) |
| O(2)–C(15) | 1.47(3) | O(4)–C(20) | 1.41(3) |
| N(1)–C(1) | 1.36(3) | N(2)–C(10) | 1.35(2) |
| N(1)–C(12) | 1.34(2) | N(2)–C(11) | 1.38(2) |
| C(1)–C(2) | 1.39(3) | C(9)–C(10) | 1.41(3) |
| C(1)–C(13) | 1.47(3) | C(10)–C(14) | 1.49(3) |
| C(2)–C(3) | 1.34(3) | C(8)–C(9) | 1.43(3) |
| C(3)–C(4) | 1.42(3) | C(8)–C(7) | 1.30(3) |
| C(12)–C(4) | 1.41(3) | C(7)–C(11) | 1.42(3) |
| C(5)–C(4) | 1.41(3) | C(6)–C(7) | 1.50(3) |
| C(12)–C(11) | 1.42(3) | C(5)–C(6) | 1.31(3) |
| C(22)–Cl(2) | 1.70(3) | C(22)–Cl(3) | 1.80(3) |
| C(22)–Cl(4) | 1.74(3) | | |
| Pt–Hg–C(21) | 173.9(8) | Hg–Pt–Cl(1) | 173.9(2) |
| Hg–Pt–N(1) | 89.1(4) | Hg–Pt–N(2) | 85.5(4) |
| Hg–Pt–C(17) | 92.3(6) | Hg–Pt–C(18) | 93.2(6) |
| Cl(1)–Pt–N(1) | 92.8(4) | Cl(1)–Pt–N(2) | 89.3(4) |
| Cl(1)–Pt–C(17) | 87.9(6) | Cl(1)–Pt–C(18) | 91.0(7) |
| N(1)–Pt–N(2) | 76.3(6) | N(1)–Pt–C(18) | 118.0(8) |
| N(2)–Pt–C(17) | 124.4(8) | C(17)–Pt–C(18) | 41.4(9) |
| Pt–C(17)–C(18) | 69(1) | C(16)–C(17)–C(18) | 125(2) |
| Pt–C(18)–C(17) | 70(1) | C(17)–C(18)–C(19) | 121(2) |

demercuriation was observed in other cases. The only known compound containing the Pt–Hg–Me sequence is that recently reported by Midollini and co-workers.[6] As far as we know this is also a unique example of five-co-ordination in bimetallic platinum organomercury derivatives. In this case stabilization of the unusual co-ordination number is related to the presence of a tripodal phosphine ligand.

Our results demonstrate, also for the platinum organomercurials, the peculiar ability of the N–N chelates having suitable steric properties[3] to stabilize co-ordinatively saturated compounds with *TBPY* geometry. Thus, for the first time it has been possible to isolate compounds including the sequence R–Hg–Pt, with alkyl groups R other than methyl.

The X-ray crystallographic study on complex **2a** indicates a strong *trans* influence of the MeHg fragment. This is inferred by the lengthening of the Pt–Cl bond distance with respect to the values observed in related five-co-ordinate complexes: 2.590(6) *vs.* 2.304(1) Å in [PtCl(py)(dmphen)($C_2H_4$)] (py = pyridine),[15] 2.311(3) Å in [$PtCl_2$(dmphen)($C_2H_4$)][16] and 2.478(3) Å in [PtCl($SnPh_2Cl$)(dmphen)($C_2H_4$)].[1] This result can be compared with a previous observation[17] of a high *trans* influence exerted by a mercury-containing fragment in a platinum(IV) complex.

Concerning the type **III** clusters, the ability of mercury to connect directly two transition-metal centres surrounded by various co-ordination environments has been illustrated previously.[18–20] However, to our knowledge, this is the first well assessed example of connection of $d^8$ co-ordinatively saturated platinum ions by Hg in a simple trimetallic cluster; examples involving square-planar $Pt^{II}$[20] or five-co-ordinate $Pt^{IV}$[21] are known. In the formation of **3b** from **3a** it is also worth noting the unprecedented[15,22] preference for water in the axial co-ordination sites. The formation of the cluster is very fast when the aromatic derivative HgPh(Cl) is used, while in the case of the alkyl derivatives essentially only the mononuclear product is obtained. Monitoring of the very slow decomposition of **2b** in solution suggested the presence of only a small amount of a type **III** product after several days. This different behaviour of the alkyl and aryl organomercurials is consistent with the known higher lability[23] of aryl groups bound to Hg. It is reasonable that also in the addition of HgPh(Cl) a type **II** species is first formed. Thereafter, exchange of Ph from it [possibly with the halide in the still unreacted HgPh(Cl)] would account for the formation of the cluster, through a second addition to $Pt^0$.*

## Conclusion

The present study has provided evidence for the ability of suitable N,N-chelate and olefin ligands to stabilize five-co-ordinate *TBPY* organomercury platinum derivatives. While this could be reasonably[24] anticipated, it is not a trivial finding, considering that the balance of electronic and steric effects required to get type **II** stable species can be very delicate. For example, in the case of the hydride derivatives only one N–N ligand and one type of R group in RCH=CHR (*i.e.* $CO_2R'$) allow the formation of stable compounds.[7]

Furthermore, the new complexes constitute a homogeneous extension of the sole class of *TBPY* complexes represented with fair variety[25] in platinum chemistry.

Some properties of the new complexes deserve attention. (*i*) The long Pt–Cl bond distance in **2a** points to a large *trans* effect of the HgMe fragment. We are not aware of a generalization concerning HgR′ fragments, while at least one result[17] is in accord with our finding. (*ii*) A reversible oxidative addition/reductive elimination equilibrium involves the five-co-ordinate complexes, the trigonal starting materials, and the HgR′(Cl) electrophiles. This type of equilibrium, rarely observed[4] for co-ordinatively saturated adducts of the Group 10 divalent ions, is worthy of further study. (*iii*) The ligand environment in the type **II** complexes has allowed the isolation of organomercury platinum complexes bearing alkyl groups other than methyl on Hg. These are quite rare.[26,27] It appears that the co-ordinative saturation of platinum hinders the decomposition pathway(s) accessible to 16 $e^-$ species.

Finally, the ability of the ligand environment in structure **II** to stabilize *TBPY* five-co-ordination is maintained when two platinum atoms are linked by mercury. Some examples of clusters including the sequence M–Hg–M are known,[18–20] but no case in which M is a co-ordinatively saturated $d^8$ ion, as far as we know.

## Experimental

Proton NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. The compounds HgMe(Cl), HgPh(Cl), $HgCl_2$, (*Z*)-$MeO_2CCH=CHCO_2Me$ and (*Z*)-$EtO_2CCH=CHCO_2Et$ were commercially available; HgEt(Cl) and $HgBu^t$(Cl) were prepared according to the method described for $HgPr^i$(Cl)[28] [but with the use of tetrahydrofuran as solvent in the synthesis of $HgBu^t$(Cl)]. The compound (*Z*)-$Bu^tO_2CCH=CHCO_2Bu^t$ was obtained from isobutylene and maleic acid according to the method described for the synthesis of di-*tert*-butyl malonate.[29] Solvents and reagents were of AnalaR grade used without further purification.

*Syntheses.—Type* **I** *complexes*. The synthesis of complex **1a** has already been described.[1] We give here the general method of synthesis of type **I** complexes, which was used to prepare **1b** and **1c**.

To [Pt(dmphen)($C_2H_4$)][30] (0.100 g, 0.232 mmol) was added

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* A referee has suggested that the trinuclear species form in different ways, depending on whether **1a** reacts with $HgCl_2$ or HgPh(Cl). Presumably, **1a** acts as a nucleophile attacking Hg in $HgCl_2$ to form [PtCl(HgCl)(dmphen)(olefin)], which then undergoes a second nucleophilic attack by **1a** at Hg to form the product **3a**. Similarly, nucleophilic attack by **1a** at Hg in HgPh(Cl) initially forms [PtCl(HgPh)(dmphen)(olefin)], which then likely undergoes a redistribution reaction involving a four-centre transition state to form the products $HgPh_2$ and **3a**.

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the stoichiometric amount of the olefin, dissolved in methylene chloride (2 $cm^3$), with stirring. The resulting solution was filtered through a thin layer of Florisil and the Florisil extracted with chloroform (5 $cm^3$). The combined extracts were evaporated under vacuum and the resulting reddish oil crystallized by adding methanol. Yield: 70–80%. Selected $^1H$ NMR data [$CDCl_3$, $CHCl_3$ (δ 7.26) as internal standard, $^2J$(Pt–H)/Hz in parentheses]: **1b**, δ 4.14 (q, MeC$H_2$O, 2 H), 4.13 (q, MeC$H_2$O, 2 H), 3.46 (80, =CH, 2 H), 3.23 (NCMe, 6 H) and 1.25 (t, *Me*$CH_2O$, 6 H); **1c**, δ 3.37 (79, =CH, 2 H), 3.29 (NCMe, 6 H) and 1.49 ($Bu^tO$, 18 H).

*Type* **II** *complexes*. To 0.10 mmol of the appropriate three-co-ordinate complex dissolved in the minimum amount of chloroform (0.5–1 $cm^3$), were added 1.2 equivalents of HgR(Cl) in one portion with stirring. After dissolution of the organomercurial, hexane (2.0 $cm^3$) was added dropwise to produce microcrystals of the five-co-ordinate product. When the olefin was di-*tert*-butyl maleate, complete precipitation was achieved by reducing the volume of the solution under vacuum. The complexes were filtered off, washed with hexane and dried. Yields > 80%.

*Complex* **3a**. To complex **1a** (0.055 g, 0.10 mmol) in chloroform (1.5 $cm^3$) was added a solution of the stoichiometric amount of HgPh(Cl) (0.031 g) in the minimum amount of the same solvent. In a few minutes sparkling orange crystals separated. After 1 h they were filtered off, washed with chloroform and dried (yield: 90%).

The complex can also be obtained by addition of a solution of $HgCl_2$ (0.014 g, 0.05 mmol) in the minimum amount of diethyl ether to **1a** (0.055 g, 0.10 mmol) in chloroform (1.5 $cm^3$) (Found: C, 35.00; H, 2.85; Hg, 14.90; N, 4.05. Calc. for $C_{40}H_{40}Cl_2HgN_4O_8Pt_2$: C, 35.15; H, 2.95; Hg, 14.70; N, 4.10%).

*Complex* **3b**. Complex **3a** (0.137 g, 0.10 mmol) was suspended in dichloromethane (5 $cm^3$) under nitrogen. Two equivalents of $AgBF_4$ (0.039 g) in acetonitrile (4 $cm^3$) were added at 0 °C with stirring. After 15 min AgCl was filtered off and the cationic complex precipitated by addition of diethyl ether. The complex was washed with diethyl ether, dried and redissolved in the minimum amount of nitromethane. Evaporation of the solvent under reduced pressure afforded pure **3b** as an orange microcrystalline precipitate (yield: 70%). Selected $^1H$ NMR data [$CD_3NO_2$, $CHD_2NO_2$ (δ 4.33) as internal standard, $^2J$(Pt–H)/Hz in parentheses]: δ 3.68 (80, =CH, 2 H), 3.11 (MeO, 6 H) and 3.05 (NCMe, 6 H) (Found: C, 32.10; H, 2.85; Hg, 12.90; N, 3.65. Calc. for $C_{40}H_{44}B_2F_8HgN_4O_{10}Pt_2$: C, 31.90; H, 2.95; Hg, 13.35; N, 3.70%).

*Addition of* HCl *to Complex* **2a**.—To a stirred suspension of complex **2a** (0.030 g, 0.038 mmol) in $CDCl_3$ (1.5 $cm^3$) was added 1 equivalent of gaseous HCl. After 10 min the clear resulting solution contained only HgMe(Cl) and [PtCl(H)(dmphen)-{(*Z*)-$MeO_2CCH$=$CHCO_2Me$}],[7] as shown by $^1H$ NMR spectroscopy.

*Crystal Structure Determination of Complex* **2a**.—The compound was crystallized from $CHCl_3$. Crystal data and details of the analysis are summarized in Table 5. X-Ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Cu-Kα graphite-monochromated radiation, in the ω–θ scanning mode. The unit-cell parameters were obtained by a least-squares fitting of the setting values of 24 strong reflections in the range $14 \leqslant \theta \leqslant 28°$. Three reflections measured every 500 showed a slight crystal decay (about 7%), which was taken as negligible. In addition to the usual corrections for Lorentz and polarization factors, the data were corrected for absorption through a double procedure. During the data reduction the semiempirical correction of North *et al.*[31] was applied (maximum and minimum transmission factors 0.96 and 0.49). A second absorption correction was applied at the end of the isotropic refinement according to the method of Walker and Stuart[32] (maximum and minimum transmission factors 1.55 and 0.83). The structure was solved by the heavy-atom method and refined by full-matrix least squares. The quantity minimized was $\Sigma w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 0.2]$ where σ was derived from counting statistics. A molecule of solvent was detected in the difference electron-density map and refined like the complex molecule. All non-hydrogen atoms were refined anisotropically. The H atoms were added at calculated positions ($d_{C-H}$ = 1.0 Å) with isotropic thermal parameters 1.2 times larger than those of the carrier atoms and held fixed during the refinement.

**Table 5** Summary of crystallographic data

| | |
|---|---|
| Crystal size/mm | 0.06 × 0.10 × 0.20 |
| Formula | $C_{21}H_{23}ClHgN_2O_4Pt{\cdot}CHCl_3$ |
| *M* | 917.9 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$/Å | 13.079(2) |
| $b$/Å | 13.167(2) |
| $c$/Å | 15.495(3) |
| β/° | 94.18(2) |
| $U$/Å$^3$ | 2661(2) |
| $Z$ | 4 |
| $F$(000) | 1712 |
| $D_c$/g $cm^{-3}$ | 2.29 |
| λ(Cu-Kα)/Å | 1.5418 |
| $\theta_{max}$/° | 70 |
| μ/$cm^{-1}$ | 248.5 |
| No. of independent reflections | 5023 |
| No. of reflections above 3σ($I$) | 2837 |
| No. of refined parameters | 307 |
| $R^a$ | 0.052 |
| $R'^b$ | 0.059 |
| Goodness of fit[c] | 0.87 |

[a] $R = \Sigma(|F_o - K|F_c||)/\Sigma F_o$. [b] $R' = [\Sigma w(F_o - K|F_c|)^2/\Sigma wF_o^2]$. [c] Goodness of fit = $[\Sigma w(F_o - K|F_c|)^2/(N_o - N_v)]$ where $N_o$ and $N_v$ are the number of observations and refined parameters, respectively.

The final Fourier difference map was within ± 1.1 e Å$^{-3}$. Neutral atomic scattering factors were taken from ref. 33. All calculations, carried out on a Vax 750 computer at the Centro Interdipartimentale di Metodologie Chimico-fisiche of the University of Naples, were performed with the Enraf-Nonius (SDP) set of programs.[34]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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