Oxidative Addition Reactions of Bis-aryl Cyclometallated Platinum(II) Compounds with Mercury(II) Carboxylates. *X*-Ray Crystal and Molecular Structure of the Binuclear Platinum–Mercury Compound *rac-a*-(μ-acetato-*O,O′*)-*b*-(*O*-acetatomercurio)-*cf,de*-bis[2-(dimethylaminomethyl)-phenyl-*N,C*]platinum

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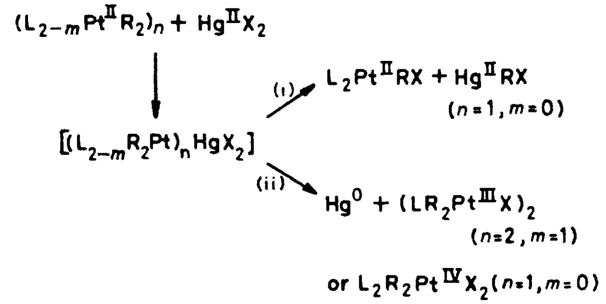
Summary Oxidative addition reactions of $Hg^{II}(O_2CR)_2$ with *cis*-$[(o\text{-}Me_2NCH_2C_6H_4)_2Pt^{II}]$ as well as of $[\{oo'\text{-}(Me_2NCH_2)_2C_6H_3\}Pt^{II}Br]$ resulted in the formation of a novel type of stable aryl Pt–Hg compounds of which $[(o\text{-}Me_2NCH_2C_6H_4)_2Pt(\mu\text{-}MeCO_2)Hg(O_2CMe)]$ was the subject of an *X*-ray diffraction study [Pt–Hg 2·513(1) Å]; in contrast reaction of *trans*-$[(o\text{-}Me_2NCH_2C_6H_4)_2Pt^{II}]$ with $Hg^{II}(O_2CMe)_2$ proceeded *via* unstable Pt–Hg intermediates with the elimination of Hg^0 and formation of the isomers of $[(o\text{-}Me_2NCH_2C_6H_4)_2Pt^{IV}(O_2CMe)_2]$ (*cis* C, *trans* N and *trans* C, *cis* N).

THERE is much interest in the reactions of organoplatinum(II) compounds (L_2PtR_2) with mercury(II) salts. Transmetallation is the preferred reaction route when the donor ligands are soft (L = phosphine).[1] In the case of hard donor ligands either transmetallation (i)[2,3] or sequential oxidative addition and elimination of metallic mercury (ii) leading to dinuclear organoplatinum(III)[4] or mononuclear platinum(IV)[3] compounds has been observed (Scheme).



SCHEME

Evidence has been presented that binuclear Pt–Hg compounds are key intermediates in these reactions, but little information is available concerning the structure of the Pt–Hg intermediates and the factors governing product formation *via* either reactions (i) or (ii).

In order to study these aspects, we have employed organoplatinum compounds in which the organo-group contains hard nitrogen donor atoms. From the reactions of these compounds with mercury(II) salts we have isolated binuclear Pt–Hg complexes and for the first time obtained detailed structural information about intermediates of the type $[L_2R_2PtHgX_2]$.

Reactions of the complex (**1**)[5] with $Hg(O_2CR)_2$ (R = Me or Pr^i) in $CHCl_3$ or toluene afforded quantitatively the yellow, monomeric complexes (**2a**) and (**2b**). Reactions

$[(o\text{-}Me_2NCH_2C_6H_4)_2Pt]$
(**1**) *cis*
(**5**) *trans*

$[(o\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}RCO_2)PtHg(O_2CR)]$
(**2**) **a**; R = Me
b; R = Pr^i

$[\{oo'\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$
(**3**)

$[\{oo'\text{-}(Me_2NCH_2)_2C_6H_3\}(RCO_2)(\mu\text{-}RCO_2)PtHgBr]$
(**4**) **a**; R = Me
b; R = Pr^i

$[(o\text{-}Me_2NCH_2C_6H_4)_2PtHg(O_2CMe)_2]$
(**6**)

of the bromo-complex (**3**)[6] and $Hg(O_2CR)_2$ in $CHCl_3$ afforded the yellow, monomeric complexes (**4a**) and (**4b**).

Insoluble compounds were obtained from similar reactions of (**1**) and (**3**) using $HgCl_2$ instead of $Hg(O_2CR)_2$. Crystals of (**2a**) suitable for an *X*-ray diffraction study were obtained from chloroform–hexane.

Crystal data: (**2a**), $C_{22}H_{30}HgN_2O_4Pt$, orthorhombic, space group *Pccn*, $Z = 8$, $a = 14{\cdot}811(6)$, $b = 17{\cdot}318(6)$, $c = 18{\cdot}578(6)$ Å, $U = 4764{\cdot}9$ Å^3, $D_c = 2{\cdot}174$ g/cm^3. The structure determination was carried out with 3743 independent reflexions with $I \geqslant 2{\cdot}5\sigma(I)$. Data were collected on an ENRAFNONIUS CAD 4 diffractometer using Zr-filtered Mo-K_α radiation and corrected for absorption [μ(Mo-K_α) = 118·3 cm^{-1}]. The structure was solved by standard Patterson and Fourier techniques and refined by anisotropic blocked fullmatrix least-squares techniques with the program ILIAS[7] to a final $R_F = 0{\cdot}043$ ($R_w = 0{\cdot}040$), $w^{-1} = [\sigma^2(F) + 0{\cdot}0001\ F^2]/2{\cdot}8$.† Hydrogen atoms were refined in the 'riding mode' on their neighbouring carbon atoms.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

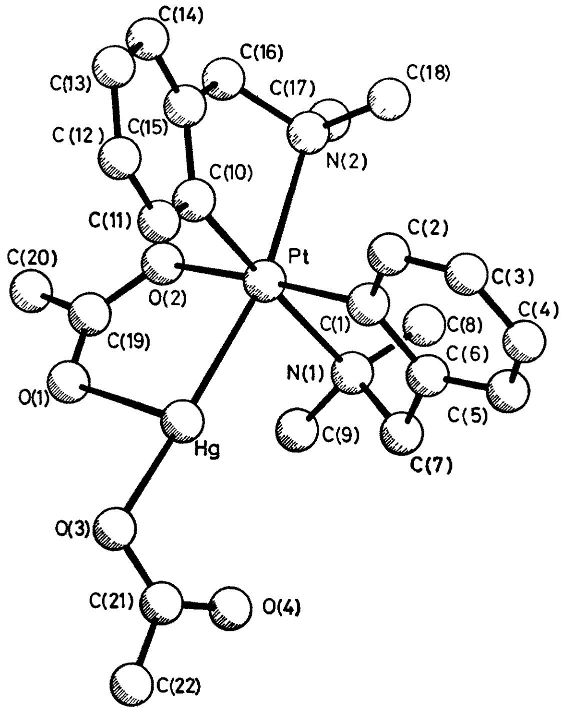
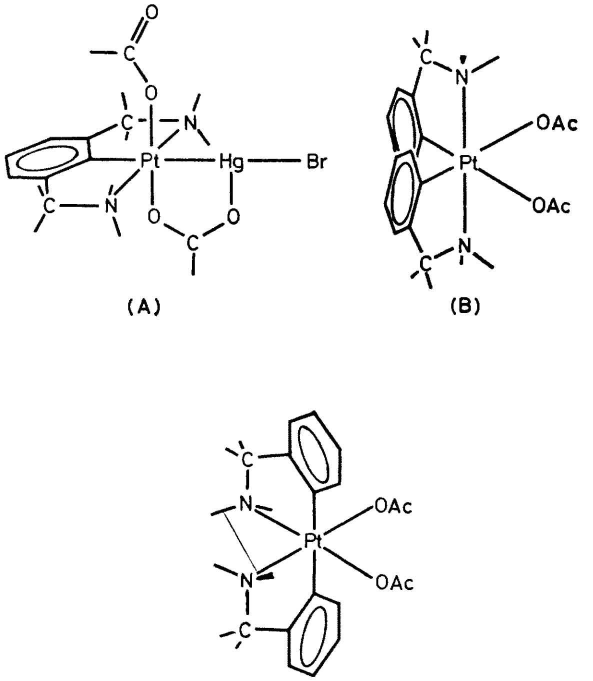


FIGURE 1. PLUTO drawing of the molecular structure of (**2a**). Hydrogen atoms are omitted for clarity. Relevant bond distances (Å) and bond angles (°) are: Pt–C(1), 2·02(1); Pt–N(1), 2·22(1); Pt–C(10), 2·02(1); Pt–N(2), 2·32(1); Pt–O(2), 2·15(1); Pt–Hg, 2·513(1); Hg–O(1), 2·62(1); Hg–O(3), 2·10(1); N(2)–Pt–C(10), 80·0(3); N(2)–Pt–C(1), 99·4(3); N(2)–Pt–N(1) 102·2(3); N(2)–Pt–O(2), 81·2(3); C(1)–Pt–N(1), 81·2(2); N(1)–Pt–O(2), 92·5(3); O(2)–Pt–C(10), 93·3(3), C(1)–Pt–C(10), 93·0(4), Hg–Pt–C(1), 87·4(3); Hg–Pt–N(1), 90·1(2); Hg–Pt–O(2), 93·3(2);Hg–Pt–C(10), 88·5(3); Pt–Hg–O(1), 80·5(2); Pt–Hg–O(3),172·3(2); O(1)–Hg–O(3), 103·9(3).

The structure of (**2a**) (Figure 1) shows that the Pt atom in the discrete monomeric unit has a distorted octahedral co-ordination. This distortion arises from the small bite of the *o*-$Me_2NCH_2C_6H_4$ ligands of 80·0(2) and 81·2(2)°; these values are comparable with that observed for [(*o*-$Me_2NCH_2C_6H_4$)(CO)$_4$Mn] (80·2°)[8] but are greater than those observed for other compounds such as [(*o*-$Me_2NCH_2C_6H_4$)Ph_2SnBr] (75·3°).[9] The octahedral unit comprises two chelate bonded *o*-$Me_2NCH_2C_6H_4$ ligands, a Pt–Hg bond, and a Pt–O bond to the acetato group bridging Pt and Hg. The Hg atom and the co-ordinated C atoms of the *o*-$Me_2NCH_2C_6H_4$ ligands are mutually *cis*. The Pt–Hg distance [2·513(1) Å] is as expected for a single Pt–Hg bond. {The Pt–Hg distance in [$(PPh_3)_2(F_3C)Pt^IHg^I(CF_3)$] is 2·569(2) Å,[10] while the sum of the radii for Pt and Hg derived from [{(*p*-Me-C_5H_4N)(Me)$_2$(μ-CF_3CO_2)Pt}$_2$] [Pt–Pt = 2·557(1) Å][11] and Hg_2Cl_2(Hg–Hg = 2·507 Å)[12] amounts to 2·532 Å}. The bridging acetato group is asymmetrically bonded with a Pt–O(2) bond of 2·15(1) Å {*cf.* Pt–O of 2·19(1) Å in [{(*p*-Me-C_5H_4N)Me_2(μ-CF_3CO_2)Pt}$_2$][11]} and an Hg–O(1) bond of 2·62(1) Å. It is noteworthy that the Pt, Hg, O(1), O(2), C(19), and C(20) atoms are coplanar (max. deviation from least-squares plane 0·02 Å). Similar structures with triazenido or acetato bridged Rh–Hg[13] and Pt–Pt[11] bonds all show distortions from planarity. The second acetato group is monodentate bonded to Hg[Hg–O(3) 2·10(1) Å] with a Pt–Hg–O(3) angle of 172·5(2)°.

^{13}C N.m.r. spectroscopy showed that in solution at room temperature the complexes (**2a**) and (**2b**) retain the same structural features and it is important to note that the terminal and bridging carboxylato groups do not exchange on this timescale; for the carboxylato α-C atoms two singlets are observed [(**2a**): δ ($CDCl_3$; internal Me_4Si) 21·4 and 23·7 (*Me*CO_2), 47·7, 49·1, 49·9, and 54·8 (J_{Pt-C} 18 Hz, NMe), 70·0 (J_{Pt-C} 26, J_{Hg-C} 55 Hz, NCH_2), and 73·1 (J_{Pt-C} 50, J_{Hg-C} 27 Hz, NCH_2) p.p.m.].



(A)

(B)

(C)

FIGURE 2. Proposed structures (A) for compound (**4**) and (B) and (C) for isomers (**7a**) and (**7b**), respectively.

The products (**4a**) and (**4b**), on the basis of microanalytical and ^{1}H and ^{13}C n m.r. data [δ (^{1}H; $CDCl_3$; internal Me_4Si; 30 °C): (**4a**), 1·93 ($MeCO_2$), 3·10 (J_{Pt-H} 34 Hz, NMe), and 4·25 (J_{Pt-H} 46 Hz, NCH_2); (**4b**), 1·25 (*Me*$_2CHCO_2$), 3·30 (J_{Pt-H} 31 Hz, NMe), and 4·53 (J_{Pt-H} 44 Hz, NCH_2)] have the structures proposed in Figure 2(A), in which, as in (**2a**) and (**2b**), a Pt–Hg bond is bridged by a single carboxylato-group. The structure implies that exchange of a bromide atom and a carboxylato-group has occurred between the platinum and mercury centres during complex formation. A similar exchange was observed in reactions of rhodium and iridium halogen complexes with mercury triazenido or formamidino compounds which afforded triazenido or formamidino bridged Rh(Ir)–Hg bonds.[13,14] The structural assignment of Hg and Br *trans* with respect to carbon is supported by the dynamic behaviour of the compounds.

The meridional spanning of the *oo*′-$(Me_2NCH_2)_2C_6H_3$ ligand is imposed by its fixed geometry and the two Me_2NCH_2 units are co-ordinated to platinum [J(Pt-CH_3) 34 Hz] over the whole temperature range studied (−50 to 40 °C). At low temperature the carboxylato-groups are dissimilar as shown by two singlets for both the carboxylato CH_3 protons (δ 1·87 and 2·01) and carbon atoms and, moreover, at this point broadened ^{1}H and ^{13}C resonances were observed for the Me_2NCH_2 unit. (A further contribution to this broadening can be expected from a wagging of the phenyl ring of the ligand which will affect the environment of the benzylic protons as is reported for [*oo'*-$(Me_2NCH_2)_2C_6H_3SnR_2$]X.[15]) At higher temperatures the Me_2NCH_2 resonances became sharp and the carboxylato CH_3 proton resonances coalesced (δ 1·93, T_c 10 °C) providing evidence for an intramolecular exchange of the co-ordination mode of the carboxylato ligands. A likely process is attack of the non-co-ordinated O-atom of the monodentate bonded carboxylato group on the Hg atom with concomitant dissociation of the Hg–O bond of the bridging carboxylato group. By this process the molecule effectively obtains a molecular mirror plane (on the n.m.r. time-scale) containing the *oo'*-$(Me_2NCH_2)_2C_6H_3$ skeleton. This renders the diastereotopic NMe_2 groups enantiotopic.

The stability of the organoplatinum–mercury compounds depends on the mutual arrangement of the ligands. The reaction of the *trans*-complex (**5**) and $Hg(O_2CMe)_2$ in $CHCl_3$ or toluene affords an unstable intermediate which most probably is (**6**). In contrast to the relative high stability of (**2**) and (**4**) in solution this intermediate decomposes even at low temperature (*e.g.* complete decomposition at −50 °C takes about 15 min) into metallic mercury and two cream diorganoplatinum(IV) compounds (**7a**) and (**7b**) with molecular formula [(*o*-$Me_2NCH_2C_6H_4)_2Pt(O_2CMe)_2$] in a 1:8 molar ratio, which were separated by fractional crystallisation; they are monomeric in $CHCl_3$.

The structures of the two isomers could be deduced from the Me_2NCH_2 n.m.r. resonances [δ (^{1}H; $CDCl_3$; internal Me_4Si): (**7a**), 1·53 ($MeCO_2$), 2·30 ($J_{Pt\text{-}H}$ 32 Hz, NMe), 2·97 (NCH_2), and 4·68 ($J_{Pt\text{-}H}$ 6, J_{AB} 13 Hz, NCH_2); (**7b**) 2·05 ($MeCO_2$), 3·01 ($J_{Pt\text{-}H}$ 24 Hz, NMe), 3·06 ($J_{Pt\text{-}H}$ 37 Hz, NMe), 3·25 ($J_{Pt\text{-}H}$ 50 Hz, NCH_2) and 4·88 ($J_{Pt\text{-}H}$ *ca.* 4, J_{AB} 13 Hz, NCH_2)]. Both compounds contain two equivalent *o*-$Me_2NCH_2C_6H_4$ ligands, equivalent (accordingly monodentate bonded) acetato groups and diastereotopic NCH_2 protons. Hence, the possible isomer structures are limited to those shown in Figure 2(B) and (C). Inert (in the sense that dissociation of the N–Pt bond does not occur on the n.m.r. time-scale, but may occur on the laboratory time-scale) N–Pt coordination will also render the NMe groups diastereotopic, though for the isomer (**7a**) only one singlet is observed which implies a very small chemical shift difference. Based on this observation we assign the structure (B), in which all four NMe groups reside above and near the two acetato groups, to isomer (**7a**) and accordingly the isomer (**7b**) corresponds to structure (C).

From the present results some preliminary conclusions can be drawn. For the first time it is shown that the stability of the diorganoplatinum(III)–mercury(I) compounds depends on the geometry of the C–Pt–C entity, the *cis*-compound being more stable than the *trans*. In this respect it is interesting that in the reaction of [(2,2'-bipyridyl)$(Me)_2Pt$] and $Hg(O_2CMe)_2$ it is *cis*-[$(Me)_2$(2,2'-bipyridyl)$(MeCO_2)PtHg(O_2CMe)$] which is the stable product.[3] In the cyclometallated-Pt-$Hg(O_2CR)_2$ system transmetallation obviously does not occur. Instead, selective oxidation of Pt^{II} to Pt^{III}–Hg^{I} [(**1**) → (**2**)] or, when the Pt–Hg intermediate is not stable, to Pt^{IV} and Hg^{0} [(**5**) → (**7a,b**)] occurs.

We are now investigating whether we can direct these oxidations to the selective formation of dinuclear platinum compounds by changing the geometry of the cyclometallated ligands as well as the nature of the anion of the mercury salts (*e.g.* triazenido and formamidino).

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