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Mechanism of Oxidative Addition of Mercury(II) Compounds to Platinum(II)

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Electron-rich platinum(II) complexes can react with mercury(II) compounds HgX_2 (X = halide or carboxylate) to give adducts containing $Pt \rightarrow HgX_2$ donor−acceptor bonds (**A**, Chart 1)[1] or products of oxidative addition containing PtX(HgX) groups (**B** or **C**, Chart 1),[2] which can be important as reaction intermediates.[1−3] Some of the most interesting compounds are those containing Pt_nHg groups ($n = 2−4$) formed by reaction of HgX_2 with 2 equiv or more of $[PtMe_2(NN)]$, with NN = 2,2′-bipyridine or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline,[4] characterized by NMR to have the chain structures shown in Chart 1, formed by insertion of platinum(II) into either the Hg−O bond of **C** (**D**, Chart 1) or the Pt−O bond (**E** and **F**, Chart 1), which are of interest as molecular wires.[4] This article reports that the Pt_2Hg complexes are unsymmetrical, containing *both* covalent and donor−acceptor bonds within the same molecule, and that their unprecedented structures can be considered to lie on a transition state path leading to oxidative addition.

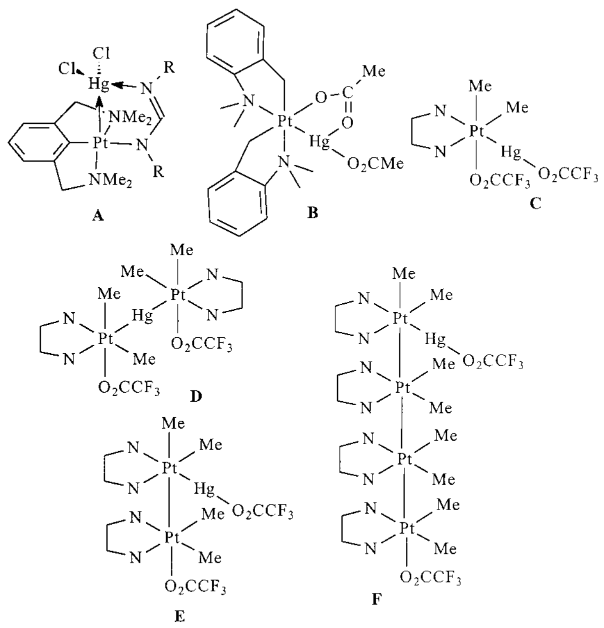
Reaction of $[PtMe_2(^tbu_2bpy)]$, **1**,[5] with HgX_2 in a 1:1 ratio gave products of the oxidative addition with trans or cis stereochemistry when X = Br or CF_3CO_2 to give **2a** and **3**, respectively, as shown in Scheme 1.[6] The formation of complexes with different stereochemistries for different X groups is new[4] and was readily deduced from the ^1H NMR spectra and confirmed by structure determinations (Figure 1).[6] The ^{195}Pt NMR spectra of **2a** and **3** contain single resonances with satellites due to the coupling $^1J(PtHg)$ [**2a**, $\delta(Pt) = -2250$, $^1J(PtHg) = 34\,520$ Hz; **3**, $\delta(Pt) = -1981$, $^1J(PtHg) = 37\,610$ Hz], thus confirming the presence of a Pt−Hg bond. The Pt−Hg distances in **2a** and **3** of 2.52665(5) and 2.5131(4) Å indicate strong single bonds.[1]

No intermediates were observed during formation of **2a**, but the initial reaction of **1** with $Hg(O_2CCF_3)_2$ at −80 °C gave the product **2b** of trans addition, which then isomerized at about −30 °C to give the isolated complex **3**. The ^1H NMR spectrum of **2b** at −50 °C showed a single Pt−Me resonance [$\delta = 1.62$ ppm] with coupling constants $^2J(PtMe) = 56$ Hz and $^3J(HgMe) = 24$ Hz in the range expected for platinum(IV) complexes.[4] The kinetic product **2** is formed by trans addition in both cases and suggests an ionic mechanism of oxidative addition via an intermediate $[Pt(HgX)Me_2(^tbu_2bpy)]^+X^-$.

Addition of a second equivalent of **1** to **2a** or **3** immediately gave the corresponding product **4a** or **4b**, respectively (Scheme 1), which were isolated as dark-red solids and characterized by NMR spectroscopy and by X-ray structure determinations (Figure 2).[6] The structures of **4a** and **4b** are similar, each containing both an octahedral and a square pyramidal platinum center, and may be considered to be formed by addition of **1** to the trans isomer **2a** or **2b** by formation of a donor−acceptor platinum−mercury bond (Scheme 1). Formation of **4b** probably occurs by easy isomerization of **3** back to **2b** followed by addition of **1** (Scheme 1).

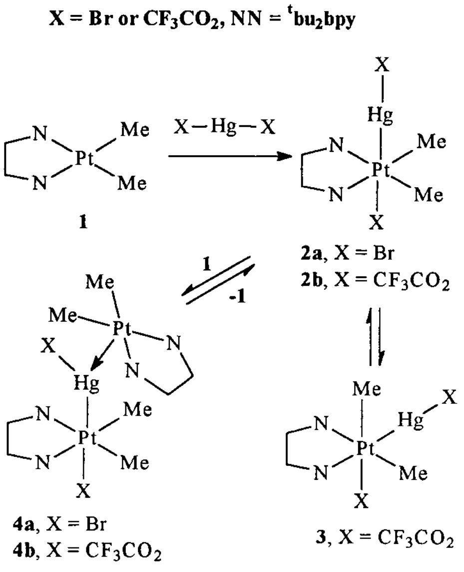
In **4a** and **4b**, the covalent Pt−Hg bond distances [2.5767(7) and 2.5425(3) Å] are only slightly longer than in **2a** and **3**, but the donor−acceptor bonds [2.6973(4) and 2.6283(3) Å] are longer.[2] The mercury atoms are three-coordinate, and the HgX

Chart 1



A B C D E F

Scheme 1



1

2a, X = Br
2b, X = CF_3CO_2

4a, X = Br
4b, X = CF_3CO_2

3, X = CF_3CO_2

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(1) (a) Ara, I.; Falvello, L. R.; Fornies, J.; Sicilia, V.; Villarroya, P. *Organometallics* **2000**, *19*, 3091. (b) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1982**, *1*, 1066.

(2) (a) Fornies, J.; Martin, A.; Sicilia, V.; Villarroya, P. *Organometallics* **2000**, *19*, 1107. (b) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. (c) Jawad, J. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1978**, *31*, L391.

(3) (a) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155. (b) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892.

(4) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 1458.

(5) Achar, S.; Scott, J. D.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4592.

(6) See Supporting Information.

10.1021/ic001145+ CCC: $20.00

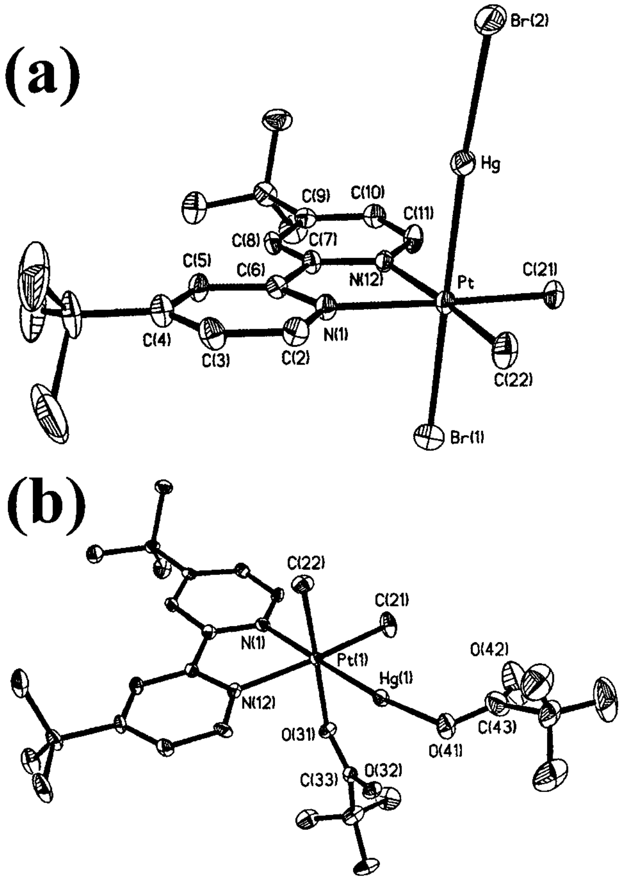


Figure 1. Structures of (a) [PtMe$_2$Br(HgBr)(^{t}bu$_2$bpy)], **2a**, and (b) [PtMe$_2$(O$_2$CCF$_3$)(HgO$_2$CCF$_3$)(^{t}bu$_2$bpy)], **3**, illustrating the trans and cis stereochemistries, respectively.

bonds are significantly longer than in **2a** and **3** [*d*(HgBr) = 2.659(1) and 2.481(1) Å in **4a** and **2a**, respectively; *d*(HgO) = 2.499(5) and 2.123(6) Å in **4b** and **3**, respectively]. The angle Pt(IV)HgPt(II) is 138.33(2)° in **4a** and 150.96(1)° in **4b**.

Addition of excess **1** to complexes **4a** or **4b** did not give complexes analogous to **F** (Chart 1). Crystallization gave starting materials only, though in solution all PtMe$_2$(^{t}bu$_2$bpy) groups were equivalent. We suggest that rapid exchange gives the appearance of formation of **F** and hence that the system is unlikely to give such 1-D chain compounds. This work thus gives new insights into the platinum-rich complexes of Chart 1 and shows that the new Pt$_2$Hg complexes have structure **4** rather than structure **D**, **E**, or **F**.

The trans stereochemistry of the primary oxidative addition to give **2** supports a mechanism in which formation of a PtHg donor acceptor bond is followed by displacement of X$^-$ followed by coordination of X$^-$ to platinum (Scheme 2, R = X). Evidently complex **2** is not sufficiently electrophilic to give further oxidative addition to form **D** (Chart 1) or **J** (Scheme 2), but the mercury center is still electrophilic enough to allow a PtHg donor acceptor bond to form. Complexes **4a** and **4b** may then represent examples of an “arrested” oxidative addition, with structures that can be described as **G** or **H** [Scheme 2, R = PtXMe$_2$(^{t}bu$_2$bpy)]. Further, since the donor−acceptor PtHg bond is shorter in **4b** than in **4a** [2.6283(3) vs 2.6973(4) Å] and the PtHgPt angle is larger in **4b** compared to **4a** [150.96(1)° vs 138.33(2)°], it seems that **4a** is closer to **G** and **4b** is closer to **H** (Scheme 2). Hence, it may be considered that **4a** is trapped earlier and **4b** is trapped later on the reaction coordinate leading to oxidative addition (Scheme 2), the difference clearly reflecting the greater ease of dissociation of trifluoroacetate over bromide.

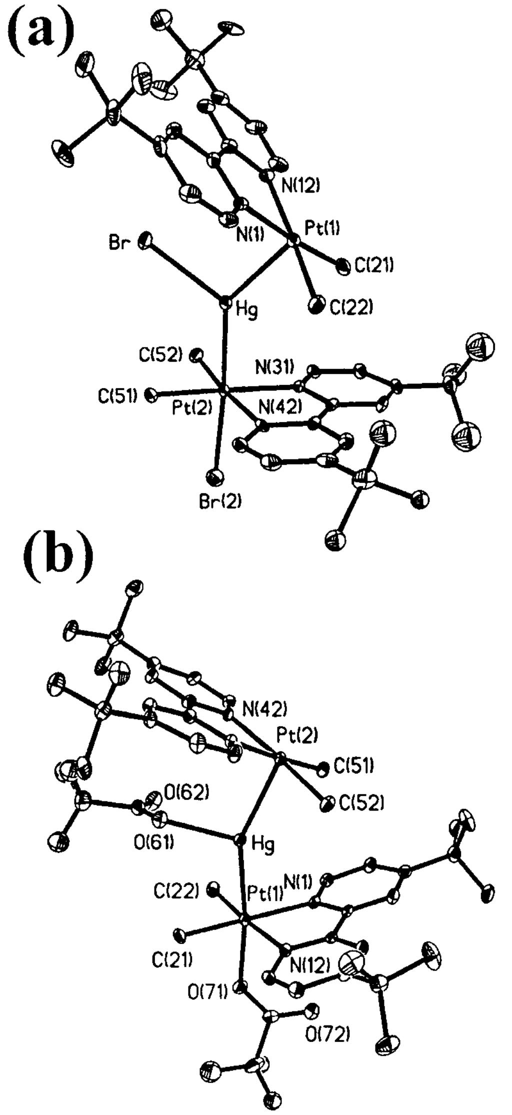
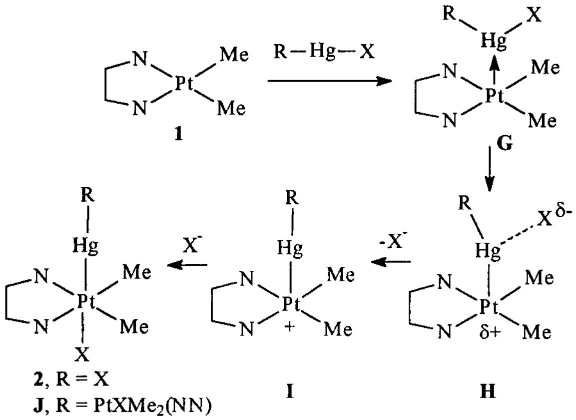


Figure 2. Structures of (a) [PtMe$_2$Br(HgBr)(^{t}bu$_2$bpy){PtMe$_2$(^{t}bu$_2$bpy)}], **4a**, and (b) [PtMe$_2$(O$_2$CCF$_3$)(HgO$_2$CCF$_3$)(^{t}bu$_2$bpy){PtMe$_2$(^{t}bu$_2$bpy)}], **4b**.

Scheme 2

R = X or PtXMe$_2$(NN), X = Br or CF$_3$CO$_2$, NN = ^{t}bu$_2$bpy



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Supporting Information Available: Experimental details and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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