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Preliminary communication

NOVEL HETEROTRIMETALLIC COMPLEXES CONTAINING THE LINEAR CHAIN Pt—Hg—Pt: CRYSTAL STRUCTURE OF $[(PPh_3)_2(2,4,6\text{-}C_6H_2Cl_3)Pt]_2Hg$

ORIOL ROSSELL*, MIQUEL SECO, IMMACULADA TORRA,
Department of Inorganic Chemistry, University of Barcelona, Diagonal 647, Barcelona-28 (Spain)
XAVIER SOLANS* and MANUEL FONT-ALTABA
Department of Crystallography and Mineralogy, University of Barcelona, Gran Via 585, Barcelona-7 (Spain)

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Summary

Heterotrimetallic complexes with a Pt—Hg—Pt arrangement are formed by reaction of zerovalent platinum complexes with $[(PPh_3)_2RPt\text{—}HgR]$; X-ray diffraction has established the structure of $[(PPh_3)_2(2,4,6\text{-}C_6H_2Cl_3)Pt]_2Hg$.

Zerovalent platinum complexes are known to react readily with organomercury compounds RHgX or HgR_2 to give organoplatinummercury complexes having a metal—metal bond [1].

$$Pt(PPh_3)_3 + HgR_2 \rightarrow [(PPh_3)_2RPt\text{—}HgR] + PPh_3 \qquad (1)$$

Formally this reaction can be interpreted as an insertion of the $Pt(PPh_3)_2$ moiety into the Hg—R or Hg—X bonds.

We describe below a high-yield synthesis of wholly novel heterotrimetallic complexes containing the linear chain Pt—Hg—Pt by the action of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ on the substrate $[(PPh_3)_2RPt\text{—}HgR]$ (R = polychloroaryl groups)

$$[Pt(CH_2{=}CH_2)(PPh_3)_2] + [(PPh_3)_2RPt\text{—}HgR] \rightarrow$$
$$[(PPh_3)_2RPt\text{—}Hg\text{—}PtR(PPh_3)_2] + CH_2{=}CH_2 \qquad (2)$$

(I, $R = 2,4,6\text{-}C_6H_2Cl_3$;
II, $R = 2,3,5,6\text{-}C_6HCl_4$;
III, $R = C_6Cl_5$)

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The insertion of the $Pt(PPh_3)_2$ moiety into one of the Hg—R bonds (reaction 1) does not deactivate the second Hg—R bond (reaction 2). This behaviour contrasts with that of the complex $[(C_6F_5)_3Ge{-}Hg{-}Pt(PPh_3)_2Ge(C_6F_5)_3]$, where the $Pt(PPh_3)_2$ fragment completely deactivates the Hg—Ge bond, precluding the formation of the platinum complex $[(C_6F_5)_3Ge{-}Pt(PPh_3)_2]_2Hg$ [2].

The only limitation on the new method is the availability of the bimetallic compounds with Pt—Hg bonds. These are formed and stabilized when (i) R is very electronegative (e.g. CF_3 [1]) or (ii) R is an aryl group with bulky *ortho*-substituents (e.g. C_6Cl_5 [3]).

Treatment of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ or $Pt(PPh_3)_3$ with $[(PPh_3)_2RPt{-}HgR]$ in refluxing benzene under nitrogen for 2 h gave yellow crystals of the $[(PPh_3)_2RPt{-}Hg{-}PtR(PPh_3)_2]$ complexes (90% yield). The nature of the products was confirmed by analysis and IR spectroscopy. All the compounds are stable as solids and in solution, but gradual darkening is observed under strong sunlight.

An X-ray diffraction study was carried out on compound I. Suitable crystals were produced by slow addition of hexane to a benzene solution of I.

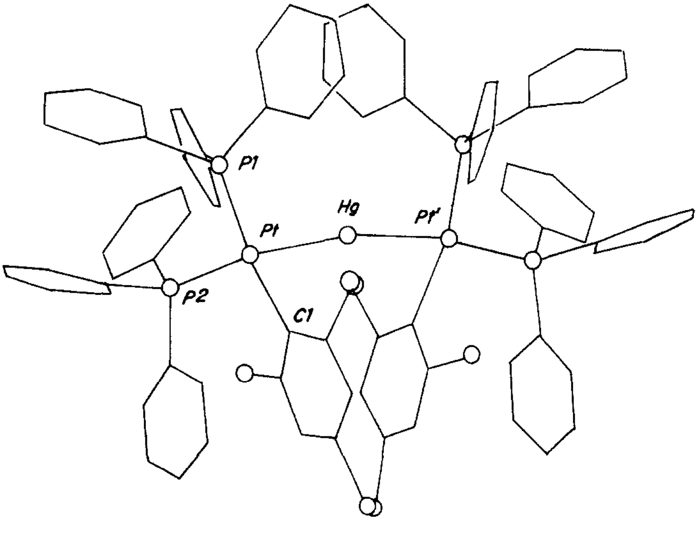

Fig. 1. Molecular structure of I with phenyl hydrogens omitted for clarity. Important internuclear distances: Pt—Hg 2.637 (1), Pt—P(1) 2.282 (4), Pt—P(2) 2.308 (3), Pt—C(1) 2.06 (1) Å; important angles: P(1)—Pt—Hg 89.3 (1), P(2)—Pt—Hg 169.0 (1), C(1)—Pt—Hg 77.6 (3), C(1)—Pt—P(1) 166.9 (4), C(1)—Pt—P(2) 91.9 (4), P(2)—Pt—P(1) 101.2 (1), Pt—Hg—Pt′ 169.57 (4)°. The angle between the coordination planes of the two Pt atoms is 41.2°.

Crystal data. I: $C_{84}H_{64}P_4Cl_6Pt_2Hg \cdot 4C_6H_6$, *M* 2313.3, monoclinic, space group *C*2/*c*, *a* 31.922(2), *b* 15.348(1), *c* 20.749(2) Å, *β* 97.91(2)°, *U* 10069.(2) Å^3, $Z = 4$, D_C 1.53 g cm^{-3}, $F(000) = 3976$, μ(Mo-K_α) 47.11 cm^{-1}. Data were collected on a Philips PW-1100 diffractometer. For the 5259 independent reflections $I \geqslant 2.5\sigma(I)$, $R = 0.052$ ($R' = 0.057$).

The most significant feature of this structure is the distorsion in the linear coordination of Hg atom due to steric interactions between the *cis* bulky phosphines attached to platinum atoms. Such interactions are also responsible for the fact that Pt—Hg bonds (2.637 Å) are the longest so far described.

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