Five-co-ordinate Methylmercury and Trimethyltin Palladium and Platinum Complexes. *X*-Ray Crystal Structure of $[N(CH_2CH_2PPh_2)_3Pt(HgMe)]BPh_4$

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The Pd^0 three-co-ordinate $(np_3)Pd$, $[np_3 = N(CH_2CH_2PPh_2)_3]$, and the Pt^0 pseudotetrahedral $(np_3)Pt(PPh_3)$ complexes react with MeHgI and Me_3SnCl to give $[(np_3)M(HgMe)]^+$ and $[(np_3)M(SnMe_3)]^+$ complexes; the molecular structure of $[(np_3)Pt(HgMe)]BPh_4$ has been established by single crystal diffraction methods.

The reactions of organomercury(II) salts with platinum(0) complexes provide an efficient route to σ-organoplatinum compounds. Such a process, which has been extensively studied, occurs by oxidative addition of the HgR group and rapid elimination of mercury.[1] Intermediate metal–organomercury compounds have been so far isolated only when either R has high electron-withdrawing capacity (*e.g.* R = CF_3) or (and) relevant steric hindrance (*e.g.* R = variously substituted phenyl).[1,2]

Now we have prepared stable platinum(II) and palladium(II) derivatives of formula $[(np_3)M(HgMe)]^+$ by reaction of MeHgI with $(np_3)Pd$ or $(np_3)Pt(PPh_3)$ (Scheme 1) $[np_3 = N(CH_2CH_2PPh_2)_3]$. These metal substrates react analogously with Me_3SnCl to give the $[(np_3)MSnMe_3]^+$ derivatives. Triorganotin chlorides have previously been found to react by oxidative addition of the tin–carbon rather than the tin–chloride bond to platinum(0) complexes.[3]

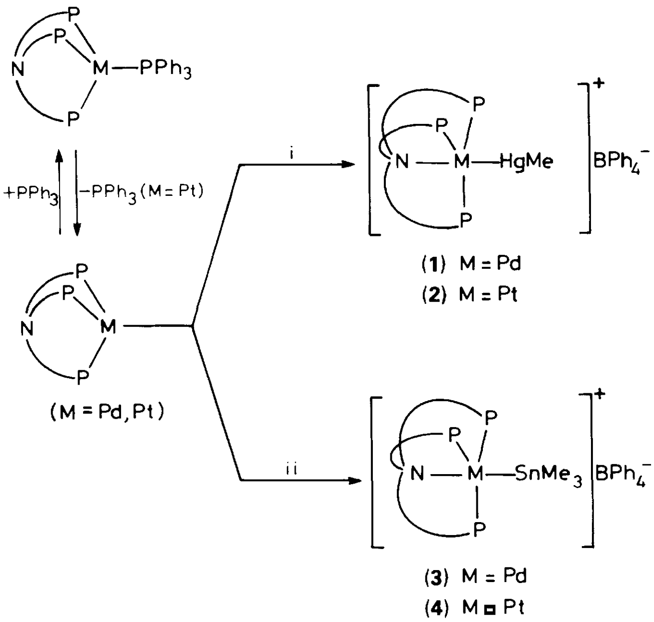
The oxidative additions of alkyl halides and methylene chloride to the above np_3 Pd^0 and Pt^0 complexes have recently been found to give five-co-ordinate alkyl and methyl chloride derivatives.[4]

The complexes $[(np_3)MHgMe]BPh_4$ [(**1**) M = Pd; (**2**) M = Pt] were prepared by the reaction of $(np_3)Pd$ [or $(np_3)Pt(PPh_3)$] (1 mmol) with MeHgI (1 mmol) in tetrahydrofuran (THF) at room temperature, under an inert atmosphere, followed by the addition of $NaBPh_4$ (1 mmol) in ethanol (av. yield 90%). The trimethyltin derivatives $[(np_3)MSnMe_3]BPh_4$ [(**3**) M = Pd; (**4**) M = Pt] were prepared analogously, by using Me_3SnCl (av. yield 70%). The solutions of the products slowly decompose in air (hours). The MeHg

Table 1. N.m.r. data[a] for the complexes (**1**)—(**4**).

Compound		$\delta(^1H)^b$	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$\delta(^{199}Hg)$	$\delta(^{119}Sn)$	$^2J_{HgH}$	$^2J_{SnH}$	$^3J_{PtH}$	$^1J_{PtP}$	$^2J_{HgP}$	$^2J_{SnP}$	$^1J_{HgPt}$	$^1J_{PtSn}$
$[(np_3)PdHgMe]BPh_4$	(**1**)	1.10(s)	31.2(s)		830(q)		130				160			
$[(np_3)PtHgMe]BPh_4$	(**2**)	0.8(s)	25.7(s)	−4005(q)	760(q)		119.7		14.5	3208	156		5087	
$[(np_3)PdSnMe_3]BPh_4$	(**3**)	0.12(s)	16.3(s)			143(q)		47				82		
$[(np_3)PtSnMe_3]BPh_4$	(**4**)	0.01(s)	17.3(s)	−4563(q)		−50(q)		46	3.5	3126		102		6200

[a] CD_2Cl_2, room temp.; ^1H and $^{31}P\{^1H\}$ spectra were measured with a Varian VXR 300 spectrometer operating at 299.944 and 121.421 MHz respectively, and the $^{195}Pt\{^1H\}$, $^{199}Hg\{^1H\}$, and $^{119}Sn\{^1H\}$ spectra with a Jeol GX 270 MHz instrument operating at 57.82, 48.25, and 100.76 MHz respectively. Chemical shifts (in p.p.m.) are relative to internal $SiMe_4$ (^1H); and external H_3PO_4 (^{31}P), H_2PtCl_6 (1.0 M) in HCl (10 M) (^{195}Pt); Me_4Sn (^{119}Sn), PhHg(OAc)(Me_2SO) (1.0 M) solution (^{199}Hg); coupling constants are in Hz; s = singlet, q = quartet. [b] Me groups.



Scheme 1. *Reagents and conditions:* i, MeHgI/$NaBPh_4$, −NaI; ii, $Me_3SnCl/NaBPh_4$, −NaCl.

derivatives are light-sensitive, decomposing to give Hg metal.

The results of multinuclear n.m.r. measurements (Table 1) agree well with the above formulation of the complexes (**1**)—(**4**) (Scheme 1). The three phosphorus atoms of the np_3 ligand are equivalent in all the complexes. The ^1H chemical shifts of the Me groups and the $^2J_{HgH}$ or $^2J_{SnH}$ coupling constants for the mercury and tin derivatives are comparable with those reported for MeHg compounds[5] and $PtSnMe_2Cl$ complexes,[3] respectively. The values for $^3J_{PtH}$ [14.5 Hz for (**2**) and 3.5 Hz for (**4**)] are much smaller than that found for $^2J_{PtH}$ in $[(np_3)PtMe]BPh_4$ (66 Hz).[6] The ^{195}Pt chemical shift for the tin derivative is similar to values observed for other compounds containing Pt–Sn (or Pt–Pb) linkages.[7] However for the Pt–Hg compound the ^{195}Pt chemical shift is some 500 p.p.m. to higher frequency. Such a difference may be attributed to the different number of substituents on the metal attached to platinum. The ^{119}Sn and ^{199}Hg chemical shifts are in the normal range for four-co-ordinate tin and two-co-ordinate mercury, respectively. The $^1J_{PtSn}$ and $^1J_{HgPt}$ are very similar (6200 and 5087 Hz) but, interestingly, the value for $^1J_{PtSn}$ is somewhat smaller than those found in analogous systems[8] (where they are usually about 12 000 Hz).†

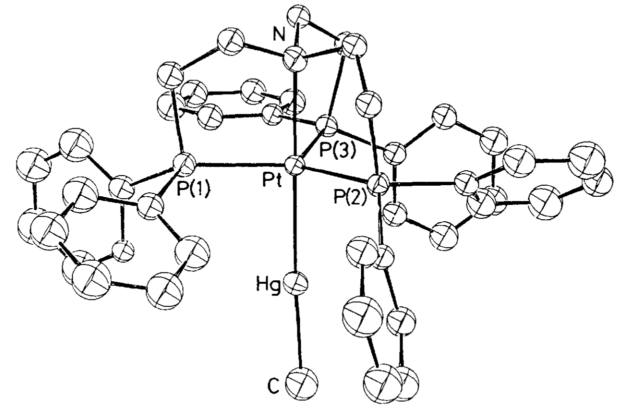


Figure 1. Perspective view of the complex cation $[(np_3)Pt(HgMe)]^+$. ORTEP drawing with 30% probability ellipsoids. Important bond distances and angles: Pt–Hg 2.531(1), Pt–N 2.235(15), Pt–P (av.) 2.309(5), Hg–C 2.20(3) Å; N–Pt–Hg 176.6(4), Pt–Hg–C 175.7(7), P–Pt–P (av.) 119.4(14)°.

The molecular structure‡ of (**2**) consists of $[(np_3)Pt(HgMe)]^+$ complex cations, tetraphenylborate anions, and ethanol solvent molecules interspersed in the lattice. A perspective view of the cation is given in Figure 1. The platinum centre displays trigonal bipyramidal co-ordination, being surrounded by the three phosphorus atoms of the np_3 ligand in the equatorial plane and by the np_3 nitrogen and a mercury atom in the axial sites. The mercury atom completes its linear two-co-ordinate geometry with a methyl group.

The interesting feature of this structure is the presence of the platinum–mercury linkage, which has rarely been reported. In particular, as far as we know, no crystallographically characterized complex containing the Pt–Hg–Me fragment has hitherto been reported. The Pt–Hg distance [2.531(1) Å],

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† The lack of reports for $^1J_{HgPt}$ prevents a reliable comparison.

‡ *Crystal data* for $[(np_3)Pt(HgMe)]BPh_4{\cdot}C_2H_5OH$: M = 1413.75, monoclinic, space group $P2_1/n$, a = 34.872(9), b = 17.340(6), c = 10.781(4) Å, β = 96.1(1)°, U = 6481.2 Å^3, Z = 4, D_c = 1.448 g cm^{-3}, monochromatic Cu-K_α radiation, λ = 1.5418 Å, μ(Cu-K_α) = 95.1 cm^{-1}. The intensity data were collected within 2θ = 130° on a Philips PW 1100 diffractometer, using the ω–2θ scan technique at 295 K. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedures. The phenyl rings were treated as rigid groups and the hydrogen atoms were introduced in calculated positions, but not refined. The R and R_w factors are 0.062 and 0.063 respectively for 4764 absorption corrected observed reflections with $I \geqslant 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice Authors, Issue No. 1.

indicative of a single Pt–Hg bond, corresponds well to the sum of the radii of Pt and Hg (2.532 Å), as obtained from the covalent linkages Pt–Pt [2.557(1) Å][9] and Hg–Hg (2.507 Å).[10] It is also in good agreement with the values reported for the distorted octahedral [$(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}MeCO_2)PtHg(O_2CMe)$ [2.513(1) Å][11] and for the square planar *cis* [$(Ph_3P)_2(F_3C)PtHg(CF_3)$] [2.569(2) Å],[12] the latter two compounds pointing to high covalent character of the metal–metal bond.

The unprecedented stabilization of the M–Hg–Me fragment in (**1**) and (**2**) may be attributed to the particular conformation of the np_3 ligand with the phenyl groups leading to marked steric hindrance in the vicinity of the metal–metal bond. However this cannot be considered a conclusive factor. In fact we have found that Ni(np_3) undergoes oxidative addition with [MeHg]NO_3 with rapid elimination of Hg metal. In this case the complex [(np_3)NiMe]$^+$, previously prepared by a different method,[13] was obtained.

The unusual nature of the reaction of Me_3SnCl with (np_3)Pd [or (np_3)Pt(PPh_3)] in comparison with the corresponding reactions with platinum(0) monophosphine complexes[3] may be attributed either to a different mechanism or a different steric control of the same mechanism.

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