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Reactions of Bis(triphenylphosphonio)isophosphindolide Salts with Mercury(II) Compounds: Coordination Induced Addition and Oxidation Reactions and Synthesis of a Monomeric 1:1 Complex of the Type $[R_2(R'O)P]HgBr_2$

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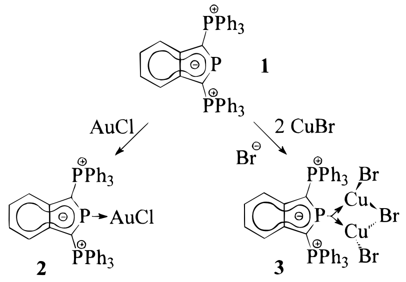
Bis(triphenylphosphonio)isophosphindolide triflate (**1**[CF_3SO_3]) reacted with $HgCl_2$ and H_2O or MeOH to give a phosphinito complex which was converted with excess $HgCl_2$ into the dimercury complex **5**. In contrast, methanolysis of **1**[X] (X = CF_3SO_3, Br) in the presence of $Hg(OAc)_2$ afforded the phosphonium cation **9**. A mercury complex **8** was isolated for X = Br as a reaction intermediate. Salts of a macrocyclic cation with a constitution similar to that of **9** were obtained by reaction of **1**[CF_3SO_3] with $Hg(OAc)_2$ and triethylene glycol. The products were characterised by ^1H, ^{13}C, and ^{31}P NMR spectroscopy; in addition, ^{199}Hg NMR data of some complexes were obtained from 2D ^{31}P,^{199}Hg shift correlations. Complexes **5** (space group $P2_12_12_1$, $Z = 4$, $a = 12.449(2)$ Å, $b = 17.583(3)$ Å, $c = 23.111(3)$ Å, $V = 5058.8(14)$ Å^3, 8917 reflections refined to $R_{w2} = 0.103$) and **8** (space group $C2/c$, $Z = 8$, $a = 20.028(2)$ Å, $b = 15.513(2)$ Å, $c = 30.247(8)$ Å, $\beta = 91.91(1)°$, $V = 9392(3)$ Å^3, 7955 reflections refined to $R_{w2} = 0.177$) were further characterized by single crystal X-ray diffractommetry. Compound **8** is the first example of a *monomeric* complex of the type $LHgX_2$ (L = phosphine donor, X = halogen); formation of a halide bridged dimer is presumably prevented by the extraordinarily sterically demanding ligand. A reaction mechanism for the formation of **5** and **8** is proposed which involves the formation of mercury complexes of **1** as the initial step.

Introduction

Bis(phosphonio)isophosphindolide cations such as **1**[1] (Scheme 1) feature a formally negatively charged heteronaphthalenic 10π-electron system[2] whose two-coordinate phosphorus exhibits ambiphilic properties[1,2] similar to those of the phosphorus in phosphenium ions.[3] As we have recently established, **1** may coordinate to coinage metals in either of two modes,[4−6] forming either mononuclear (**2**) or binuclear (**3**) complexes. While **2** essentially resembles a phosphenium complex,[4] the bonding in the Cu_2P unit of **3** was described[5] in analogy to copper aryls[7] as a dative two-electron, three-center bond which results mainly from L(σ) → M charge transfer from the phosphorus lone pair and is further stabilized by L(π) → M charge transfer from ligand π-orbitals and M(d) → L(π*) back-donation.

A similar bonding situation, albeit with increased participation by ligand−metal π-interactions which was attributed to a higher electrophilicity of the metals, was proposed for binuclear silver complexes.[6] The apparent variability in σ/π-bonding contributions raised the question of whether or not an even more pronounced increase in metal acidity might induce a further strengthening of L(π) → M bonding and thus force the ligand to behave as a genuine four-electron donor similar to a μ^2,η^1(P)-coordinated phospholide anion which forms two two-electron, two-center bonds to different metals.[8] This hypothesis prompted us to study the reactivity of **1** toward Hg^{2+} which combines a high Lewis acidity with a preference for linear coordination[9] and should therefore meet the special steric requirements of the bis(phosphonio)isophosphindolide ligand.[4]

Scheme 1



Results

Reactions. In analogy to the formation of **1**[HgI_3] from **1**[Br] and HgI_2,[1] the salt **1**[Cl] reacted with $HgCl_2$ to give $[HgCl_3]^-$ (^{199}Hg (in CH_2Cl_2): δ 1040 lit. 1058[10]), while cation **1** remained unchanged. In contrast to our experience that complexation of **1** may be promoted when more nucleofugic anions than halides are present,[4] neither $HgCl_2$ nor $Hg(OAc)_2$ reacted with a stoichiometric quantity of **1**[CF_3SO_3] in dry acetone/tetrahydrofuran (THF); in the former case, ^{31}P and ^{199}Hg NMR spectra

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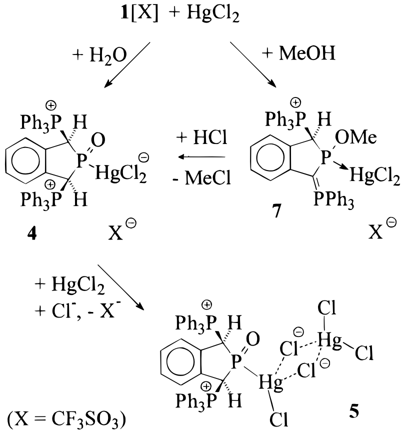
S0020-1669(96)00883-X CCC: $14.00

Scheme 2



revealed the coexistence of intact **1** and $HgCl_2$ (^{199}Hg (in THF): δ 758, lit. 703[10]). A rapid reaction between both components occurred, however, when moist solvents were employed or when a stoichiometric amount of water was deliberately added. The single product was identified by NMR spectroscopy as complex **4** (Scheme 2), which contains the same ligand as the diastereomeric gold complexes obtained by hydrolysis of **2**.[4] Storage of reaction mixtures at 0 °C afforded small quantities of the binuclear complex **5**, which was characterized by single crystal X-ray diffractometry; **5** was accessible in much better yield from reactions of **1**[CF_3SO_3] with a 2-fold excess of $HgCl_2$ under otherwise identical conditions. Crystalline **5** is colorless and, in contrast to **4**, sparingly soluble in acetone, $MeNO_2$, or MeOH. Solutions of **4** and **5** display identical ^1H and ^{31}P NMR data and are stable under anhydrous conditions but decompose in the presence of moisture to give, beside several unidentified products, mercury and the isolable phosphonium salt [$Ph_3P^+CH_2C_6H_4CH_2PPh_3^+$][$HgCl_2$] (**6**[$HgCl_2$]).

A reaction between **1** and $HgCl_2$ was also found to take place in the presence of alcohols such as methanol, even if in this case a product mixture rather than a single species was formed. ^{31}P NMR spectroscopic analysis showed that complex **4** had again formed as the main product. Of the side products only cation **6** was positively identified; furthermore, a transient intermediate was detected which was on the basis of its AMX pattern (^{31}P: δ 155.5 (A), 23.6 (M), 21.0 (X); $J_{AX} = 74.3$ Hz), tentatively formulated as the addition product **7**. A compound with analogous constitution had been obtained by methanolysis of the gold complex **2**.[4]

A different course of the alcoholysis was observed when $Hg(OAc)_2$ instead of $HgCl_2$ was used as the mercury salt. Thus, **1**[Br] reacted with $Hg(OAc)_2$ in MeOH to give as first spectroscopically detectable products acetic acid and complex **8** (Scheme 3), which precipitated as a yellow, crystalline solid. Prolonged stirring of the heterogeneous mixture resulted in conversion of **8** into mercury and the phosphonium cation **9**, which was isolated after anion exchange as a light yellow, air stable BPh_4 salt. Cation **9** was likewise formed in the reaction of **1**[CF_3SO_3] with MeOH and $Hg(OAc)_2$ or $Pd(OAc)_2$. The conversion **8** → **9** was facilitated by higher temperatures and a slight excess of $Hg(OAc)_2$ but could be inhibited by addition of KBr, and **8** could be isolated in yields of up to 90% by filtration. Complex **8** is moderately soluble in CH_2Cl_2 and dimethyl sulfoxide (DMSO); the solutions decompose slowly to give mercury and a mixture of the salts **9**[Br] and **1**[Br]. Reaction with zink resulted in cleavage of methoxide and re-formation of cation **1**.

Scheme 3

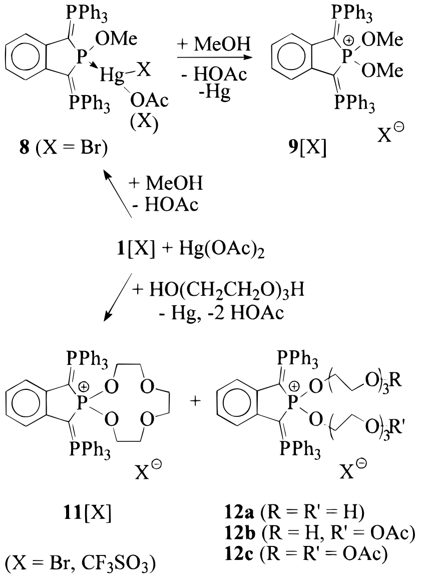


Table 1. ^{31}P and ^{199}Hg NMR Data (at 30 °C) of **4**, **5**, and **8**

	solvent	δ ^{31}P	$^2J_{PP}$, Hz	δ $^{199}Hg^a$	$^1J_{HgP}$,^{a} Hz	$^3J_{HgP}$, Hz
4	MeOH	103.7, 23.5	−7.6	1194	9864	40
5	Acetone	103.7, 23.5	7.6	1218	9719	40
8	CH_2Cl_2	113.4, 13.9	75.5	*b*	10890	32

[a] Accuracy ± 1 ppm for δ ^{199}Hg and ±5 Hz for $^1J_{HgP}$. [b] Not determined.

Further studies showed the described oxidative alcoholysis to be readily extendable to higher monoalcohols and bifunctional polyethylene glycols. For example, reaction of equimolar quantities of **1**[CF_3SO_3], $Hg(OAc)_2$, and triethylene glycol in CH_2Cl_2 afforded a product mixture whose major component (40% by integration of ^{31}P NMR spectra, the amount increased to 60% if 1 equiv of CF_3SO_3Li was present during the reaction) was isolated after chromatography and identified as the phosphorus containing crown ether **11** by spectroscopic techniques. The remaining products could not be isolated, but spectroscopic analysis (^1H, ^{31}P NMR, (+)FAB-MS) suggested the presence of coupling products between **1** and 2 equiv of the diol, which were tentatively formulated as **12**.

NMR Spectroscopic Characterization of Mercury Complexes. ^{31}P and ^{199}Hg NMR data of complexes **4**, **5**, and **8** are listed in Table 1. The given ^{199}Hg δ values were derived from ^{31}P detected ^{31}P,^{199}Hg 2D spectra whose acquisition was preferable over 1D ^{199}Hg spectroscopy because it has higher sensitivity and further allows one to obtain the sign of $^2J_{PP}$ in **5** (Figure 1).

The identical constitution of the organophosphorus ligands in **4** and **5** follows from the equivalence of both ^1H NMR spectra and ^{31}P δ and $^2J_{PP}$ values. The observed data match those of the gold complexes obtained by hydrolysis of **2**,[4] but the signal multiplicities indicate that **4** and **5** form only a single stereoisomer with *cis*-standing PPh_3 groups. The values of $^1J_{HgP}$ and ^{199}Hg δ compare to those of *n*-Bu(Ph)P(O)HgX (^{199}Hg [$^1J_{HgP}$, Hz]: δ 1231 [10 525] (X = Cl), 1132 [10 288] (X = Br)[11]). The different metal NMR data of **4** and **5** suggest that the binuclear unit of **5** is preserved in solution and the P-substituted metal is connected to one chloride and one $[HgCl_4]^{2-}$ ligand, while in **4** it carries two chlorides. Complex **8** displays significantly higher values of $^2J_{PP}$ than those of **4** and **5**, presumably due to the lower coordination number of the

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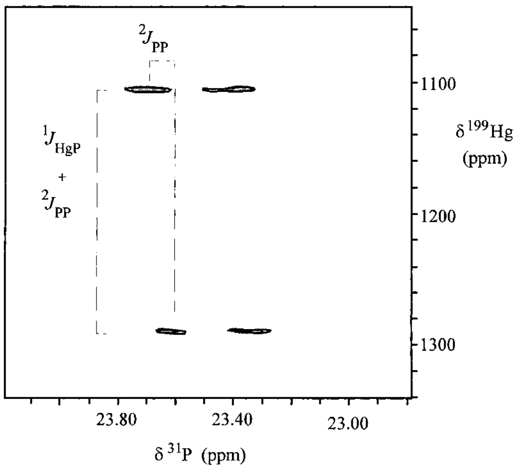


Figure 1. ^{31}P,^{199}Hg shift correlation of **4** via heteronuclear zero quantum coherence. The ^{31}P carrier frequency was placed on the center of the PPh$_3$ resonance, and a defocusing delay of 10 ms was used to achieve coherence transfer via $^3J_{HgP}$. The tilt of the cross-peak indicates that $(^2J_{PP} + {}^1J_{HgP})/{}^2J_{PP} < 0$; assuming a positive sign for $^1J_{HgP}$,[10] this gives $^2J_{PP} < 0$.

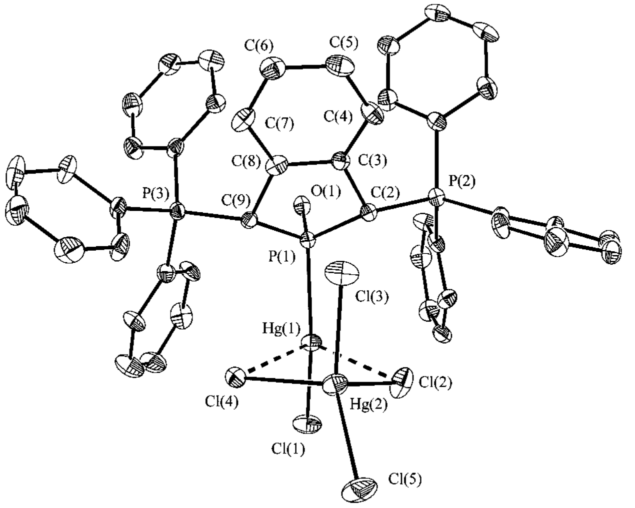


Figure 2. ORTEP representation of the molecular structure of **5** in the crystal. (Thermal ellipsoids represent a 50% probability, hydrogen atoms have been omitted for clarity.)

intermediate carbon.[12] The magnitude of $^1J_{HgP}$ is much larger than that in complexes [(R$_3$P)HgX$_2$]$_2$ (X = halogen, $^1J_{HgP}$ = 4200−7200 Hz[13]); similar couplings were reported for (Mes$_3$P)-Hg(NO$_3$)$_2$ (10 278 Hz[14]) and phosphite complexes such as [((EtO)$_3$P)$_2$HgCl$_2$]$_2$ (11 300 Hz[15]). Following common explanation patterns,[10] the large couplings may be related with a low metal coordination number and high degree of s-character in the Hg−P bond.

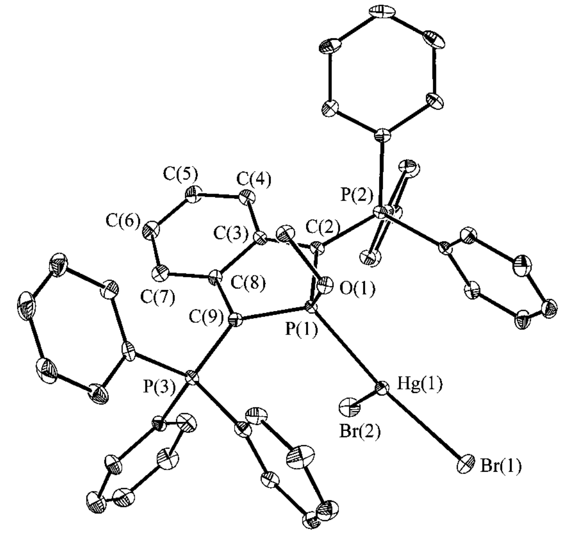
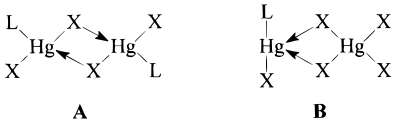


Figure 3. ORTEP representation of the molecular structure of **8** in the crystal. (Thermal ellipsoids represent a 50% probability, hydrogen atoms have been omitted for clarity.)

Chart 1



Crystal Structure Determinations. Crystalline **5** exhibits binuclear complexes whose metals are connected by two asymmetric μ-Cl bridges (Figure 2). The five membered ring in the organophosphorus ligand adopts an envelope conformation. The two PPh$_3$ groups are in a *cis*-equatorial position, and the oxygen at P(1) is in an axial "flagpole" position. The Hg(1)−P(1) (2.384(3) Å) distance corresponds to a normal coordinative bond as found in (R$_3$P)$_2$Hg$_2$X$_4$ (X = halogen, acetate; Hg−P, 2.36−2.44 Å [16]), and the P(1)−O(1) distance (1.474(8) Å) suggests considerable double bond character. Both values match corresponding bond lengths in phosphonato complexes (EtO)$_2$P(O)HgCl and [(EtO)$_2$P(O)]$_2$Hg (Hg−P, 2.31−2.41; P−O, 1.40−1.47 Å [17]).

Even if bridging of two Hg^{2+} ions by two halides is a well-known motive in the structural chemistry of mercury compounds,[9,18] **5** exhibits some peculiarities. Thus, Hg$_2$X$_2$ rings in complexes [(L)(X)Hg(μ-X)$_2$Hg(X)(L)] (**13**, L = X$^-$ or PR$_3$, X = halogen) are usually planar, and opposite Hg−X bonds have equal lengths.[17,18] In contrast, both bonds from the μ-Cl atoms to the P-substituted Hg(1) atom in **5** (Hg1−Cl2/Cl4, 2.811(3), 3.051(3) Å) are longer than those to Hg(2) (Hg(2)−C(l2)/C(l4), 2.603(3), 2.577(3) Å), and the Hg$_2$Cl$_2$ unit is folded along the C(l2)−C(l4) axis with a dihedral angle between Hg(μ-Cl)$_2$ planes of 19.3°. Regarding further that the exocyclic P(1)−Hg(1)−Cl(1) angle (155.9(1)°) is substantially larger than the corresponding angle at Hg(2) (Cl(3)−Hg(2)−Cl(5), 128.2(1)°), it is suggested that **5** should not be described like **13** as an adduct resulting from pairwise donor−acceptor interaction of two trigonal [LHgX$_2$] fragments (A, Chart 1), but rather as an aggregate between a linear [LHgCl]$^{2+}$ and a tetrahedral [HgCl$_4$]$^{2-}$ fragment (B, Chart 1).

Most remarkable in the crystal structure of **8** is the presence of monomeric (L)HgBr$_2$ units (Figure 3) instead of halide bridged dimers of type **13**, which are commonly found in structures of 1:1 adducts of mercury halides with phosphines

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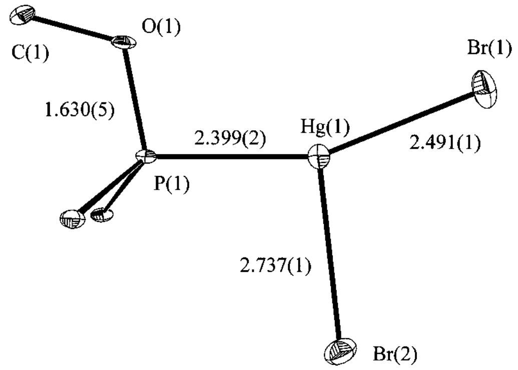

Figure 4. ORTEP representation of the coordination environment of the Hg(1) and P(1) atoms in **8** (thermal ellipsoids at the 50% probability level).

or phosphites.[9,17] The P(1) atom displays a distorted tetrahedral coordination with a P(1)−Hg(1) distance (2.399(2) Å) similar to that in **5** but a longer P(1)−O(1) distance (1.630(5) Å) indicative of a single bond. The P(1)−C(2)/C(9) bonds (1.7475(6), 1.727(8) Å) in the planar isophosphindole ring match the corresponding distances in ylides of the type $Ph_3P^+-C^-(R)PR'_2$ (→P−C, 1.62−1.73 Å [12,19]), while the exocyclic P(2)−C(2)/P(3)−C(9) bonds (1.709(7), 1.718(7) Å) are shorter than there (>P−C, 1.78−1.80 Å [12]).

The Hg(1) atom displays a planar, almost T-shaped coordination geometry (Figure 4) with considerably different Hg−Br(1)/Br(2) bond lengths (2.491(1), 2.737(1) Å) and P(1)−Hg(1)−Br(1)/Br(2) angles (157.7(1), 96.4(1)°) and a similar steric shielding by the PPh_3 moieties as in bis(phosphonio)isophosphindolide complexes.[4−6] The Hg(1)−Br(1) bond to the halide which is "*trans*" to phosphorus is similar to the "intramolecular" bond distance in $HgBr_2$ (2.48 Å [20]), while the longer Hg(1)−Br(2) distance lies between this value and that of the secondary, "intermolecular" distances in $HgBr_2$ (3.23−3.50 Å [20]). Since the closest Hg−C contacts to phenyl−carbon atoms (3.27−3.32 Å) are in the range of van der Waals distances,[21] **8** represents the rare case of a mercury complex with "characteristic" and "effective" coordination numbers[22] of 2 and 3. The marked deviation from regular trigonal coordination is precedented by the structures of some organomercury derivatives[23] and may, according to the results of a recent theoretical study,[24] be related to relativistic contraction of the 6s orbital at Hg.

Discussion

The studied reactions of the salts **1**[X] (X = Cl, Br, CF_3SO_3) with HgY_2 (Y = Cl, OAc) gave no evidence for the formation of spectroscopically detectable or even isolable mercury complexes of **1**. However, the observations that (i) reactions between **1**[X], HgY_2, and water/alcohols afforded quantitative yields of compounds with the same constitution as the hydrolysis or alcoholysis products of the gold complex **2**[4] and (ii) ROH/H_2O did not react with **1**[X] in the absence of HgY_2 strongly suggest that such complexes are involved in the three component reactions as reactive intermediates. As in the case of **2**,[4] the electron withdrawing effect of the metal ion presumably activates the π-electron system in the coordinated ligand to undergo addition of water/alcohol to give the observed products **4**, **7**, or **8** (here, the primary addition product is probably deprotonated by OAc^-). The conversion **7** → **4** via C-O bond cleavage resembles the known dealkylation of alkyl phosphites,[25] while the isolation of the dinuclear complex **5** in reactions of equimolar amounts of **1**[CF_3SO_3] and $HgCl_2$ can be explained as a result of partial decomposition of **4** which liberates $HgCl_2$.

The failure to observe the postulated mercury complexes by NMR spectroscopy suggests that only a small amount of the complex coexists in equilibrium with a large excess of free **1** and HgY_2. This implies that mercury complexes of **1** should be markedly less stable than complexes with coinage metals. If one considers that Hg^{2+} is not only a stronger Lewis-acid than univalent group 11 ions but exhibits also a much lower capability for back-donation, it appears that, as for phosphenium complexes,[26] $M \rightarrow L(\pi)$ charge transfer also plays a key role for the stability of complexes of bis-phosphonio-isophosphindolides.[27]

The metal coordination modes in complexes **5** and **8** deserve further comments. Even if compounds with three-coordinate Hg^{2+} ions in a T-shaped geometry are known,[23] complex **8** is to our knowledge the first 1:1 adduct of a mercury halide with a phosphine donor which exists as a monomer rather than as a halide bridged dimer with tetrahedrally coordinated metals, as is realized for **5**. The different aggregation behavior may be attributed to differences in stereochemical rather than electronic properties of the organophosphorus ligands. The PPh_3 groups in **5** form a large cavity around the phosphorus lone pair which may easily accommodate a tetrahedral metal fragment. In **8**, the bulky PPh_3-moieties encapsulate the phosphorus lone pair in a manner similar to that in **1** and its complexes.[4−6] As there, the available space permits coordination of a metal whose remaining ligands can be arranged in a plane between the substituents, while any marked deviations from planarity will induce strong steric interferences between metal ligands and PPh_3 groups and result in energetic destabilization of the complex.

The conversion of the bis(phosphonio)isophosphindolide **1** into the phosphonium ions **9** and **11** can be classified as 1.1-oxidative addition at the two coordinate phosphorus. This overall reaction resembles the oxidation of aromatic λ^3-phosphinines to 1.1-dialkoxy-λ^5-phosphinines by reaction with $Hg(OAc)_2$ and alcohols which was first described by Dimroth.[28] Even if there may be differences in mechanistic details, the analogy between both reactions suggests that the parallels between **1** and isoelectronic compounds such as phosphinines or naphthalene[2] are not only of a purely formal nature but extend to the chemical properties.

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Table 2. Crystallographic Data and Summary of Data Collection and Refinement

	5	**8**
formula	$C_{46}H_{42}Cl_5Hg_2N_2O_5P_3$	$C_{47}H_{41}Br_2Cl_4HgOP_3$
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No.19)	$C2/c$ (No.15)
a, Å	12.449(2)	20.028(2)
b, Å	17.583(3)	15.513(2)
c, Å	23.111(3)	30.247(8)
β, deg		91.91(1)
V, Å^3	5058.8(14)	9392(3)
Z	4	8
ρ_{calc}, g cm^{-3}	1.80	1.72
μ, cm^{-1}	64.7	112
diffractometer	Nicolet R3m	Enraf-Nonius CAD4
radiation	Mo Kα	Cu Kα
λ, Å	0.710 73	1.541 78
T, °C	20	−65
max 2θ, deg	50	130
no. of data	9447	8123
no. of unique data	8917	7955
no. of var/restraints	528/6	523
$R(F)^a$	0.045	0.057
$R_{w2}(F^2)$ for all data^b	0.103	0.177

[a] For $I > 2(I)$, $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_{w2} = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$; $w = 1/\sigma^2(F_i)$.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters U(eq) (Å^2 × 10^3) for **5**

	x	y	z	U(eq)
Hg(1)	6955(1)	−61(1)	2130(1)	46(1)
Hg(2)	7650(1)	2180(1)	1866(1)	56(1)
Cl(1)	7586(3)	−495(2)	3019(1)	70(1)
Cl(2)	8691(3)	896(2)	1855(2)	75(1)
Cl(3)	6911(3)	2325(2)	905(2)	73(1)
Cl(4)	6096(2)	1523(2)	2407(1)	55(1)
Cl(5)	8744(3)	3044(2)	2387(2)	88(1)
P(1)	6029(2)	−146(2)	1229(1)	32(1)
O(1)	5595(6)	−899(4)	1074(3)	44(2)
C(2)	6798(8)	309(5)	629(4)	32(2)
C(3)	5967(9)	684(6)	258(5)	37(3)
C(4)	6097(11)	916(6)	−303(5)	49(3)
C(5)	5286(13)	1296(8)	−588(6)	63(4)
C(6)	4324(11)	1470(8)	−310(6)	57(3)
C(7)	4228(9)	1281(6)	251(6)	49(3)
C(8)	5026(9)	872(6)	547(5)	43(3)
C(9)	4993(8)	609(6)	1182(4)	34(2)
P(2)	7753(2)	−356(2)	286(1)	37(1)
C(10)	8904(8)	201(6)	85(4)	37(2)
C(11)	8919(10)	977(6)	68(5)	50(3)
C(12)	9821(12)	1380(9)	−83(6)	74(5)
C(13)	10767(11)	987(8)	−181(6)	60(4)
C(14)	10790(11)	205(9)	−160(6)	69(4)
C(15)	9870(8)	−180(7)	−9(5)	52(3)
C(16)	8168(10)	−1060(6)	802(4)	41(3)
C(17)	8837(9)	−853(7)	1236(5)	47(3)
C(18)	9107(10)	−1367(8)	1684(5)	59(4)
C(19)	8720(10)	−2105(8)	1662(6)	62(3)
C(20)	8081(12)	−2306(7)	1205(6)	65(4)
C(21)	7828(12)	−1796(6)	772(5)	59(4)
C(22)	7122(9)	−799(6)	−329(4)	42(3)
C(23)	7664(11)	−839(7)	−847(5)	56(3)
C(24)	7171(14)	−1215(7)	−1302(5)	66(4)
C(25)	6199(12)	−1543(7)	−1234(6)	61(4)
C(26)	5658(11)	−1496(7)	−717(6)	58(3)
C(27)	6120(11)	−1126(7)	−264(6)	55(3)
P(3)	3720(2)	313(2)	1488(1)	37(1)
C(28)	3047(9)	−400(6)	1062(5)	44(3)
C(29)	3339(9)	−571(6)	500(5)	46(3)
C(30)	2800(12)	−1169(6)	218(6)	63(4)
C(31)	2015(11)	−1565(7)	501(6)	61(3)
C(32)	1736(11)	−1391(8)	1040(6)	67(4)
C(33)	2252(10)	−820(7)	1335(6)	58(3)
C(34)	2916(8)	1157(6)	1557(5)	45(3)
C(35)	1808(10)	1131(7)	1461(6)	61(4)
C(36)	1220(11)	1775(10)	1579(8)	84(5)
C(37)	1715(12)	2441(8)	1732(7)	78(5)
C(38)	2787(13)	2469(7)	1825(7)	81(4)
C(39)	3376(10)	1828(7)	1735(7)	65(4)
C(40)	3973(8)	−82(7)	2189(5)	48(3)
C(41)	3904(11)	351(7)	2680(5)	55(3)
C(42)	4132(13)	2(11)	3215(6)	87(5)
C(43)	4399(13)	−745(10)	3269(6)	81(5)
C(44)	4434(12)	−1177(8)	2781(7)	73(4)
C(45)	4239(11)	−871(7)	2234(5)	58(3)

Experimental Section

All reactions were carried out under dry argon. Solvents were dried by using standard procedures, and mercury salts were vacuum-dried prior to use. Compound **1**[Br] and **1**[CF_3SO_3] were prepared as described;[1,2] **1**[Cl] was synthesised as **1**[Br] from **6**[Cl]$_2$ and PCl_3. NMR spectra: Bruker AMX 300 spectrometer (300.13, 121.5, 75.46, and 53.63 MHz for ^{1}H, ^{31}P, ^{13}C, and ^{199}Hg). Chemical shifts are referenced to ext. TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480 747), and 0.1 M $Hg(ClO_4)_2$ (Ξ = 17.870 535 MHz). ^{31}P detected ^{31}P,^{199}Hg HMQC spectra were recorded with a 5 mm triple resonance probe head using standard pulse sequences.[29] H-atoms in the isophosphindole skeleton are denoted by 1-H to 7-H; $\sum J$ denote the sum of couplings to the exocyclic, and J_M is the coupling to the endocyclic ^{31}P nuclei. Mass spectra: Kratos Concept 1H, Xe-FAB with an m-NBA matrix; molecular masses refer to the most abundant isotopes. Melting points were determined in sealed capillaries. Elemental analyses: Heraeus CHNO-Rapid.

General Procedure for the Reaction of 1[X] (X = Cl, Br, CF_3SO_3) with $Hg(OAc)_2$ and $HgCl_2$. A mixture of 0.05−0.1 mmol of **1**[X] and an equimolar amount of mercury salt was treated with 2−5 mL of the appropriate solvent (CH_2Cl_2, $MeNO_2$, 1:1 THF/acetone, MeOH). If desired, water was added by means of a microsyringe. The mixture was stirred for 5 min, remaining solids were filtered off, and the filtrate was analyzed by ^{31}P and ^{199}Hg NMR spectroscopy. The ^{31}P NMR spectra of all solutions containing neither alcohol nor water displayed exclusively the unchanged resonances of cation **1**. ^{199}Hg NMR data: see text.

Complex 5. **Procedure A**: Compound **1**[CF_3SO_3] (255 mg, 0.37 mmol) and $HgCl_2$ (100 mg, 0.37 mmol) were suspended in a mixture of $MeNO_2$ (5 mL) and MeCN (5 mL). A 9:1 mixture (v/v) of MeCN/H_2O was added dropwise under stirring by means of a microsyringe under ^{31}P NMR control until the signals of **1** had completely disappeared. The mixture was stirred for a further 10 min and then evaporated to dryness. The residue was dissolved in dry MeOH, and the resulting clear solution was analyzed by ^{1}H, ^{31}P, and ^{199}Hg NMR (Table 1). ^{1}H NMR (MeOH, suppression of solvent signals by presaturation): δ 7.89 (m, 12H), 7.74 (m, 6 H), and 7.53 (m, 12 H), C_6H_5; 7.07 (dd, $\sum J$ = 4.4 Hz, J_M = 17.7 Hz), 1-H/3-H; 6.89 (m, 2H) and 6.71 (m, 2H), 4-H to 6-H. Prolonged storage of reaction mixtures at 0 °C produced small quantities (10−50 mg) of the dinuclear complex **5**.

Procedure B: Compound **1**[CF_3SO_3] (255 mg, 0.37 mmol) and $HgCl_2$ (200 mg, 0.74 mmol) were suspended in a mixture of $MeNO_2$ (10 mL) and MeCN (10 mL). As described above, water was added under ^{31}P NMR control until the signals of **1** had disappeared. The color of the suspension turned from light yellow to gray. The mixture was stirred for a further 10 min, warmed until most of the solids dissolved, and filtered. Storage of the filtrate at +7 °C for several days produced colorless crystals which were collected by filtration and dried in a stream of dry argon to give 135 mg (27%) of **5**·2$MeNO_2$; mp 314 °C. Anal. Calcd for $C_{44}H_{36}Cl_5Hg_2OP_3$(M_r=1252.14)·2H_3-CNO_2: C, 40.21; H, 3.08; N, 2.04. Found: C, 39.08; H, 3.69; N, 2.26. ^{1}H NMR (acetone-d_6, 30 °C): δ 7.89 (br, 12H), 7.74 (br, 6 H), and 7.53 (br, 12 H), C_6H_5; 7.07 (dd, $\sum J$ = 4 Hz, J_M = 18 Hz, 1-H/3-H); 6.89 (m, 2H), 6.70 (m, 2H), 4-H to 6-H. (+)FAB MS (m/e (%)): 909 (13) [$C_{44}H_{35}ClHgOP_3^+$].

Complex 8. A solution of $Hg(OAc)_2$ (430 mg, 1.35 mmol) in MeOH (30 mL) was added at 0 °C to a solution of **1**[Br] (1.00 g, 1.36 mmol) and KBr (160 mg, 1.36 mmol) in MeOH (30 mL). A bright yellow precipitate formed immediately. After being stirred for 30 min, the

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(29) Benn R.; Rufinška, A. *Magn. Reson. Chem.* **1988**, *26*, 895.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters *U*(eq) ($Å^2 \times 10^3$) for **8**

	x	*y*	*z*	*U*(eq)
Hg(1)	947(1)	5671(1)	1446(1)	26(1)
Br(1)	603(1)	4142(1)	1545(1)	50(1)
Br(2)	2110(1)	5618(1)	995(1)	45(1)
O(1)	205(2)	7337(3)	1775(2)	23(1)
C(1)	0(4)	8222(5)	1855(3)	28(2)
P(1)	889(1)	7211(1)	1504(1)	15(1)
C(2)	1572(3)	7725(4)	1761(2)	19(2)
C(3)	1813(3)	8414(5)	1475(2)	19(1)
C(4)	2320(3)	8992(5)	1559(3)	27(2)
C(5)	2490(4)	9606(5)	1251(3)	35(2)
C(6)	2149(4)	9657(6)	850(3)	37(2)
C(7)	1630(4)	9073(5)	748(3)	33(2)
C(8)	1449(3)	8458(5)	1060(3)	21(2)
C(9)	903(3)	7825(5)	1028(3)	21(2)
P(2)	1930(1)	7450(1)	2262(1)	19(1)
C(10)	1780(3)	8231(5)	2691(3)	23(2)
C(11)	1525(3)	9033(5)	2570(3)	27(2)
C(12)	1416(4)	9650(6)	2893(3)	39(2)
C(13)	1549(5)	9481(6)	3329(4)	44(2)
C(14)	1782(4)	8692(7)	3450(3)	44(2)
C(15)	1901(4)	8057(6)	3140(3)	35(2)
C(16)	2824(3)	7348(5)	2222(3)	24(2)
C(17)	3277(4)	7601(5)	2563(3)	31(2)
C(18)	3953(4)	7507(6)	2514(4)	42(2)
C(19)	4183(4)	7168(6)	2131(4)	42(2)
C(20)	3748(4)	6905(5)	1789(3)	34(2)
C(21)	3068(4)	7012(5)	1832(3)	28(2)
C(22)	1614(3)	6435(5)	2451(2)	21(2)
C(23)	1942(4)	5673(5)	2348(3)	28(2)
C(24)	1687(4)	4889(6)	2485(3)	38(2)
C(25)	1115(5)	4857(6)	2724(3)	40(2)
C(26)	773(5)	5614(6)	2820(4)	41(2)
C(27)	1023(4)	6403(5)	2681(3)	31(2)
P(3)	365(1)	7680(1)	580(1)	21(1)
C(28)	−229(4)	8563(5)	500(3)	29(2)
C(29)	−93(4)	9348(5)	691(3)	34(2)
C(30)	−548(5)	10034(7)	642(4)	50(3)
C(31)	−1132(5)	9898(7)	400(4)	57(3)
C(32)	−1279(5)	9115(8)	216(4)	56(3)
C(33)	−828(4)	8442(7)	253(3)	42(2)
C(34)	789(4)	7515(5)	71(3)	27(2)
C(35)	1456(4)	7208(6)	91(3)	39(2)
C(36)	1762(5)	6992(7)	−290(4)	50(3)
C(37)	1439(6)	7056(7)	−695(3)	50(3)
C(38)	780(6)	7334(7)	−716(4)	56(3)
C(39)	465(5)	7569(6)	−333(3)	37(2)
C(40)	−124(3)	6715(5)	673(3)	26(2)
C(41)	87(4)	5932(6)	516(3)	30(2)
C(42)	−279(5)	5197(6)	599(3)	40(2)
C(43)	−856(5)	5259(6)	835(3)	45(2)
C(44)	−1063(5)	6041(7)	998(4)	53(3)
C(45)	−699(4)	6780(6)	914(3)	33(2)

precipitate was filtered off, washed with MeOH (20 mL), and dried under vacuum. Recrystallization (1:1 CH_2Cl_2/MeOH) gave 1.32 (93%) of **8**·$2CH_2Cl_2$ of mp > 160 °C (dec). Anal. Calcd for $C_{45}H_{37}Br_2HgOP_3$(M_r=1047.11)·$2CH_2Cl_2$: C, 46.39; H, 3.40. Found: C, 44.12; H, 3.15. ^1H NMR (CD_3OD): δ 7.53−7.90 (m, 30H), C_6H_5; 7.07 (2H), 6.95 (2H), 4-H to 6-H; 3.31 (d, J_{PH} = 14.7 Hz, 3 H), OCH_3. (+)FAB MS (*m*/*e* (%)): 967 (21) [$C_{45}H_{37}BrHgOP_3^+$], 655 (100) [$C_{44}H_{34}P_3^+$].

Compound 9[BPh_4]. A solution of **1**[CF_3SO_3] (440 mg, 0.6 mmol) in MeOH (15 mL) was added to a stirred suspension of $Hg(OAc)_2$ (380 mg, 1.2 mmol) in MeOH (10 mL). The mixture changed color to yellow and after awhile to greyish green. After 12 h, the formed precipitate was filtered off. Dropwise addition of a methanolic solution of $NaBPh_4$ (205 mg, 0.6 mmol) to the stirred filtrate produced a white precipitate which was filtered off and dried under vacuum to give 585 mg (94%) of **9**[BPh_4] of mp > 200 °C (dec). The same product was obtained when **1**[Br] was used at the starting material. Anal. Calcd for $C_{70}H_{60}BO_2P_3$(M_r=1036.98): C, 81.08; H, 5.83. Found: C, 80.02; H, 6.09. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30 °C): 89.3 (t), 8.9 (d), J_{PP} = 43.2 Hz. ^1H NMR ($CDCl_3$): δ 7.46−7.68 (m, 30H), PC_6H_5; 7.42 (m, 8H), 6.97 (m, br, 8H), 6.83 (br, 4H), BC_6H_5; 6.53 (2H), 6.38 (2H), 4-H to 6-H; 2.80 (d, J_{PH} = 14.3 Hz, 6H), OCH_3. (+)FAB MS: (*m*/*e* (%)): 717 (100) [$C_{51}H_{46}F_3O_7P_3S^+$].

Compound 11[CF_3SO_3]. To a solution of **1**[CF_3SO_3] (620 mg, 0.77 mmol) in CH_2Cl_2 (30 mL) were added triethylene glycol (0.1 mL), $LiCF_3SO_3$ (120 mg, 0.77 mmol), and $Hg(OAc)_2$ (490 mg, 1.54 mmol). The color of the stirred suspension changed from yellow to greenish grey. After being stirred for 4 h, the grey precipitate was filtered off. ^{31}P NMR analysis of the filtrate indicated the formation of **11** (A_2X spin system, δ 80.8 (t), 9.5 (d), J = 42.4 Hz, 60% of the spectral intensity) along with several side products (I:A_2X spin system, δ 86.5 (t), 9.0 (d), J = 43.8 Hz; II: A_2X spin system, δ 79.3 (t), 9.1 (d), J = 44.5 Hz; further A_2X spin systems of very low intensity), and a (+)FAB mass spectrum displayed among others peaks attributable to **11** and **12** (*m*/*e* (%)): 1037 (0.2) [$C_{60}H_{64}O_{10}P_3^+$ (**12c**)], 995 (4) [$C_{58}H_{62}O_9P_3^+$ (**12b**)], 953 (14) [$C_{56}H_{60}O_8P_3^+$ (**12a**)], 803 (41) [$C_{50}H_{46}O_4P_3^+$ (**11**)]). The filtrate was evaporated to dryness, the residue redisolved in CH_2Cl_2/MeCN (2:1), and submitted to chromatography (silica gel, 2:1 CH_2Cl_2/MeCN). Crude **11**[CF_3SO_3] was eluated as the first yellow band. The residue obtained after evaporation of the solvents was redissolved in CH_2Cl_2 and precipitated with ether. The resulting yellow powder was filtered off and dried under vacuum to give 190 mg (26%) **11** [CF_3SO_3], mp >324 °C (dec). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 82.3 (t), 10.7 (d) (J_{PP} = 41.9 Hz). ^1H NMR ($CDCl_3$): δ 7.52−7.71 (m, 30H), C_6H_5; 6.30 (2H), 6.18 (2H), 4-H to 7-H; 3.21 (m, 4H), $POCH_2$; 3.04 (m, 4H), OCH_2; 2.89 (m, 4H), OCH_2. (+)FAB-MS (*m*/*e* (%)): 952 (5) [$C_{51}H_{46}F_3O_7P_3S^+$], 803 (100) [$C_{50}H_{46}O_4P_3^+$].

Crystallography. Crystals of **5**·$2MeNO_2$ (colorless prisms from 1:1 $MeNO_2$/MeCN) and **8**·$2CH_2Cl_2$ (yellow prisms from 1:1 CH_2Cl_2/MeOH) were mounted on thin walled Lindemann capillaries. Crystal structure determinations were performed on a Nicolet R3m diffractometer at 293(2) K with graphite monochromatized Mo Kα radiation for **5** and on an Enraf-Nonius CAD4 diffractometer at 208(2) K with Cu Kα radiation for **8**. Crystal data, data collection parameters, and results of the structure analyses are listed in Table 2. Structures were solved with the SHELXTL-PLUS and refined with the SHELXL-93[30] program packages. For **5**, a semiempirical absorption correction from ψ-scans and for **8**, an empirical absorption correction using the program DIFABS[31] were employed. Both structures were solved using direct methods and refined on F^2 (full-matrix least-squares). All non-hydrogen atoms were refined anisotropically, hydrogen atoms with a "riding" model. Atomic position and isotropic displacement parameters are listed in Tables 3 and 4; important bond distances and angles are discussed in the text. The absolute structure in **5** was determined by Flack's *x*-parameter (x = −0.009(8)).

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Supporting Information Available: Listings of ^{13}C NMR data for compounds **8** and **11**[CF_3SO_3] and crystal data anisotropic thermal factors, complete positional parameters, bond distances and angles for complexes **5** and **8** (14 pages). Ordering information is given on any current masthead page.

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