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Formation and Crystal Structures of Lewis Acid Adducts of $Ph_3PCHP(O)Ph_2$; New Neutral and Cationic Species

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Dedicated to Professor Bernd Harbrecht on the Occasion of His 60th Birthday

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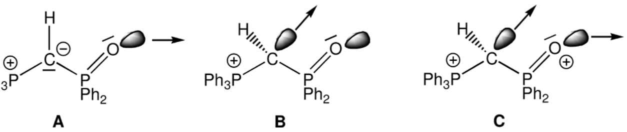
Abstract. The carbodiphosphorane $C(PPh_3)_2$ (**1**) is easily hydrolyzed from wet air to give the ylide $Ph_3PCHP(O)Ph_2$ (**2**), which forms addition compounds with various Lewis acids to give neutral or cationic compounds. According to pairs of electrons at the central carbon atom and the oxygen atom, respectively, addition compounds with coordination modes **A** (via oxygen), **B** (via carbon), and **C** (via carbon and oxygen) were isolated either as by-products from reactions of Lewis acids with **1** (contaminated with some **2**) or directly with **2**. The crystal structures and the spectroscopic properties of **2** and of the addition compounds $[Ph_3PCHP(OBF_3)Ph_2]$ (**5**), $[Ph_3PCH_2P(OBF_3)Ph_2][(\mu\text{-}OH)B_2F_6]$ (**6**), $[Ph_3PCH_2P(OBI_3)Ph_2][BI_4]$ (**7**), $[Ph_3PCHP(OSnCl_2)Ph_2]$ (**8**), and $[Ph_3PCH_2P(O)Ph_2]_2[Hg_2I_6]$ (**9**) are reported.

1. Introduction

The carbodiphosphorane $C(PPh_3)_2$ (**1**) and its hydrolysis product $Ph_3PCHP(O)Ph_2$ (**2**) were first described in 1961 by *Ramirez* et al [1]. Whereas various addition compounds of **1** have been synthesized up to now [2], the chemistry of **2** remained unexplored for many years. An earlier reported platinum complex with a side on bounded $C(PPh_3)_2$ ligand [3] was later identified as pure **2** [4]. Compound **2** can be seen as an ylide derived from the ylide CH_2PPh_3 by replacing one proton by the $P(O)Ph_2$ group or as a derivative of the phosphane oxide $OPPh_3$, in which one Ph group is replaced by the ylidic group $CHPPh_3$. To the best of our knowledge, further compounds of the type $Ph_3PCHP(E)Ph_2$ with E other than oxygen have not been reported so far.

Thus, the chemistry of **2** should be related to both, CH_2PPh_3 and $OPPh_3$. In principle, **2** is endowed with two anchor points for Lewis acids (LA), the free pair of electrons at the ylidic carbon atom between the phosphorus atoms and a pair of electrons at the oxygen atom. Therefore, 1:1 adducts with sp^2 (**A**) and sp^3 carbon atoms (**B**) or 1:2 adducts with a sp^3 carbon atom (**C**) are expected as depicted in Scheme 1. Coordination modes **A** and **B** represent hard and soft coordination sites, respectively, of the ylide. In the coordination mode **C**, the ylide **2** can also act as a chelating ligand. In principle, **2** is related to the carbonyl-stabilized ylides of the type $Ph_3PCHC(O)R$ in which the $P(O)Ph_2$ group of **2** is replaced by $C(O)R$ and which exhibits rich coordination chemistry [5].



Scheme 1. Coordination modes of **2**. The arrows indicate potential donor abilities to Lewis acids.

Reports on the chemistry of **2** are rare. The type **A** tungsten complex $[Ph_3PCHP\{OW(CO)_5\}Ph_2]$ (**3**) was described, in which **2** acts as a Lewis base coordinating with the oxygen atom at the electron deficient tungsten carbonyl fragment [6]. The salt like complex $[Ph_3PCH_2P(OAlBr_3)Ph_2][AlBr_4]$ (**4**) of type **C** was obtained by us during the preparation of the carbodiphosphorane adduct $Br_3Al\leftarrow\mathbf{1}$ [7]. Both addition compounds of **2** were formed as side-products from reactions of **1** with the appropriate Lewis acid. No type **B** compound has been reported up to now. During our studies with **1** as complex ligand, we frequently isolated further derivatives of **2** in small amounts. This prompted us to explore the chemistry of **2** more intensively in order to find out what pair of electrons is preferred upon using different kinds of Lewis acids. Herein we report on the preparation and the crystal structure of **2** and on the formation of further adducts of type **A** to **C**, which could be identified and confirmed by X-ray diffraction analyses.

2. Results and Discussion

Whereas the double ylide $C(PPh_3)_2$ (**1**) in the solid state is not very sensitive, solutions readily react with wet air to give **2**; and even if reactions with **1** were carried out in dried sol-

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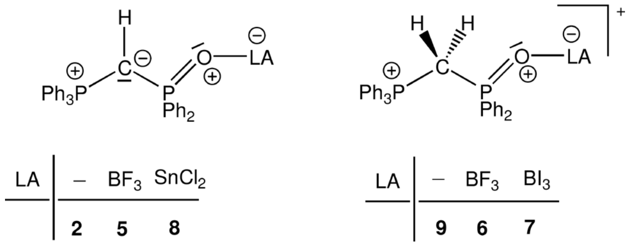
vents under argon protection, small amounts of **2** are always present as traced by ^{31}P NMR spectroscopy. Thus, **2** was obtained in quantitative yields under release of benzene according to Equation (1), if a solution of **1** in toluene was stirred in contact with wet air; the resulting **2** is soluble in toluene and can be precipitated by addition of *n*-pentane. However, direct addition of water to **1** is not successful; only decomposition products were obtained.

$$\underset{\mathbf{1}}{C(PPh_3)_2} + H_2O \rightarrow \underset{\mathbf{2}}{Ph_3PCHP(O)Ph_2} + C_6H_6 \qquad (1)$$

The ^{31}P NMR spectrum of **2** exhibits two characteristic doublets with coupling constants $^2J(P,P) = 19$ Hz indicating chemically different phosphorus atoms; the low field signal can be attributed to the PO group. A strong solvent dependency of the shifts is observed, and the shift difference Δ between the doublets range between 4.4 and 7.4 ppm, depending on the nature of the solvent. In the IR spectrum the PO stretching vibration cannot be assigned with certainty, because in the region between 1250 and 1100 cm^{-1} several strong bands were recorded. However, a very strong band at 1171 cm^{-1} seems to be reliable; the P–O vibration of Ph_3PO appears at about 1190 cm^{-1} [8, 9].

The majority of compounds based on **2** were obtained in small amounts as side-products during our efforts to prepare addition compounds LA←**1** between the double ylide and various Lewis acids LA, such as compounds of group 13 elements, and attempts to obtain crystals from the crude reaction products. In general, the reactions with **1** were carried out in toluene, because the use of halogenated hydrocarbons or even THF, DME, or DMSO led to deprotonation of the solvents with formation of the cations $(HC\{PPh_3\}_2)^+$ or $(H_2C\{PPh_3\}_2)^{2+}$. Unfortunately, the resulting adducts LA←**1** were insoluble in toluene and other nonpolar solvents, preventing sufficient characterization by NMR and X-ray analyses; however, few crystals were sporadically obtained from freshly prepared filtered toluene solutions. In most cases the precipitates from toluene are soluble in DMSO or halogenated solvents, but the ^{31}P NMR spectra show only the signal of the cation $(HC\{PPh_3\}_2)^+$, indicating reaction with the solvent with proton abstraction. This is confirmed by IR spectroscopic experiments, in which the spectra changed after the precipitates had got contact to polar solvents showing the characteristic medium intense bands of the cation at 1032, 1013, and 991 cm^{-1}. In this contribution we concentrate on the discussion of addition products of **2** either obtained as side-products by reactions of **1** with Lewis acids or upon reaction of **2** with Lewis acids, and the results are sketched in Scheme 2.



Scheme 2. Compounds of the coordination modes **A** (**5**, **8**), **B** (**9**), and **C** (**6**, **7**).

Thus, the type **A** compound $[Ph_3PCHP(OBF_3)Ph_2]$ (**5**) formed when **1**, containing small amounts of **2** (as shown by ^{31}P NMR spectroscopy), was allowed to react with gaseous BF_3 in toluene; colorless crystals of **5** separated in low yield from the toluene solution, and the desired adduct F_3B←**1** precipitated without forming crystals suitable for an X-ray analysis. Upon coordination of BF_3 at the oxygen atom of **2**, both doublets experienced a high field shift in the ^{31}P NMR spectrum of **5**. Attempts to prepare **5** directly from **2** and F_3B←OEt_2 or BF_3 in toluene gave a precipitate, which upon recrystallization from CH_2Cl_2/*n*-pentane produced the type **C** compound $[Ph_3PCH_2P(OBF_3)Ph_2][(\mu\text{-}OH)B_2F_6]$ (**6**) in good yields; source for the additional proton are the solvent or impurities in $[F_3B(OEt_2)]$.

In the ^{31}P NMR spectrum of **6** a doublet at 17.53 ppm [$^2J(P,P) = 17.80$ Hz] and a multiplet at 45.63 ppm were measured, which were assigned to PPh_3 and $P(OBF_3)Ph_2$ phosphorus atoms, respectively. Similarly, from the reaction of **1** with BI_3 in toluene the type **C** complex $[Ph_3PCH_2P(OBI_3)Ph_2][BI_4]$ (**7**) was obtained as the only crystalline product, and the desired adduct I_3B←**1** could not be identified; instead, only the salt $(H_2C\{PPh_3\}_2)[I_3]I$ [10] was isolated upon attempts to recrystallize the crude material from acetonitrile. The HI needed for protonation probably formed upon borylation and deprotonation of the appropriate solvents. The ^{31}P NMR spectrum of **7** in DCM exhibits a doublet at 16.20 ppm [$^2J(P,P) = 20.35$ Hz] and a multiplet at 54.55 Hz, according to PPh_3 and $P(OBI_3)Ph_2$ phosphorus atoms, respectively. Relative to the starting compound **2**, the low field signal has become more deshielded, whereas the high field signal has experienced a high field shift in going to the addition compounds **6** and **7**. As yet, only type **C** compounds were detected, in which the Lewis acid at the carbon atom is H^+, thus producing salt like compounds. Solvent reactions with proton abstraction of addition compounds with **1** and other Lewis acids were reported recently [11].

If **2** was allowed to react with anhydrous $SnCl_2$ in DCM the neutral type **A** addition complex $[Ph_3PCHP(OSnCl_2)Ph_2]$ (**8**) could be prepared in high yields and characterized by X-ray analysis. The ^{31}P NMR spectrum of a freshly prepared sample in DCM exhibits two doublets at 38.74 and 18.18 ppm (set **A**), which disappeared within some hours in favor of doublets at 22.96 and 21.33 ppm (set **B**). The set **B** persisted and was observed as the only signals after isolation of the product indicating the formation of only one type of compounds. The initial signals of set **A** apparently belong to an intermediate which could not be identified so far. The IR spectrum of **8** exhibits a new strong band at 1018 cm^{-1} not found in **2**, which can be assigned to the P–OSn vibration.

A quite different reaction pathway was found upon reacting **2** with HgI_2 in THF. The clear solution showed a set of two doublets at 21.58 and 20.79 ppm [$^2J(P,P) = 14.35$ Hz] along with a set of two broad signals at 27.8 and 26.0 ppm in about

1:1 ratio. Attempts to grow crystals gave colorless crystals suitable for X-ray analysis and a pale yellow micro crystalline material, which was unsuitable for X-ray analysis. The colorless crystals turned out to be the salt like compound $[Ph_3PCH_2P(O)Ph_2]_2[Hg_2I_6]$ (**9**). The salt can be considered as the first compound of the type **B** containing a “free” PO group as in **2** but a protonated ylidic carbon atom, thus being its conjugated acid. An alternative pathway, the addition of $HgCl_2$ at the carbon atom, as expected, could not be found. However, the formation of such kind of adduct as intermediate can neither be excluded nor be established; no other type of crystals was found. It could be responsible for the unusual deprotonation of the solvent. The IR spectrum of **9** exhibits a strong band at 1184 cm^{-1}, which probably can be assigned to the P–O vibration.

3. Crystal Structures

For comparison and for documentation of the changes in the parameters upon adduct formation we have also studied the crystal structure of **2**; colorless crystals separated from a toluene solution after layering with *n*-pentane. Crystals of **5** (adduct of the type **A**) were obtained as described above. The related $H[HOB_2F_6]$ adduct **6** was obtained from the reaction of **2** with $[F_3B(OEt_2)]$, and crystals of **7**$\cdot C_7H_8$ formed from a toluene solution; the adducts are of the type **C**. Additionally, we have obtained crystals of the type **A** compound **8** and the type **B** salt **9**. The structures of **2**, **5**, **6**, **7**$\cdot C_7H_8$, **8**, and **9** are shown in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6; crystallographic data are collected in Table 1; bond lengths and angles are summarized in Table 2, Table 3, Table 4, Table 5, Table 6, and Table 7.

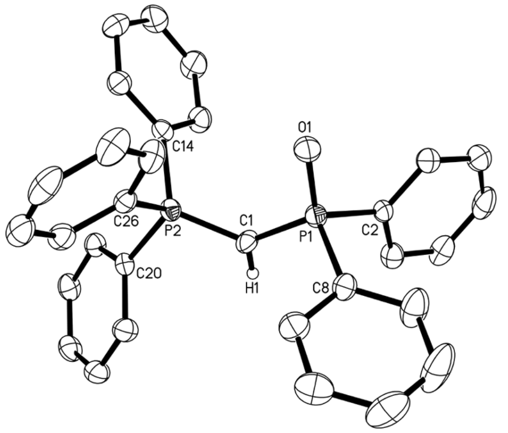


Figure 1. Molecular structure of $Ph_3PCHP(O)Ph_2$ (**2**) with thermal ellipsoids at 40 % probability, the hydrogen atoms are omitted for clarity.

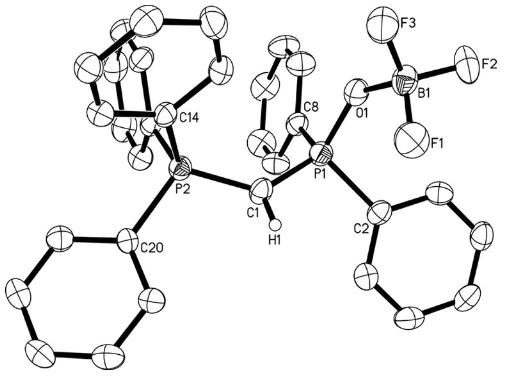


Figure 2. Molecular structure of $[Ph_3PCHP(OBF_3)Ph_2]$ (**5**) with thermal ellipsoids at 40 % probability, the hydrogen atoms are omitted for clarity.

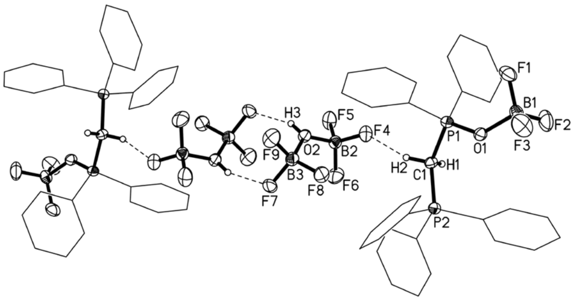


Figure 3. Molecular structure of $[Ph_3PCH_2P(OBF_3)Ph_2][(\mu\text{-}OH)B_2F_6]$ (**6**). The two cations and two anions are connected through hydrogen bonds to a centrosymmetrical dimer. The ellipsoids are drawn at a 40 % probability level; the phenyl groups are represented as thin lines omitting the hydrogen atoms for clarity.

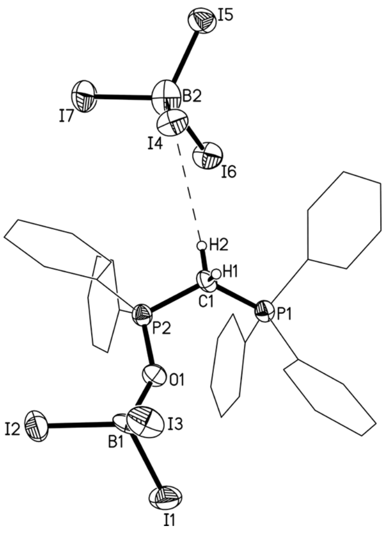


Figure 4. Molecular structure of $[Ph_3PCH_2P(OBI_3)Ph_2][BI_4]$ (**7**). The ellipsoids are drawn at a 40 % probability level; the phenyl groups are represented as thin lines omitting the hydrogen atoms for clarity.

3.1 Crystal Structure of $Ph_3PCHP(O)Ph_2$ (2)

The unit cell of **2** contains two independent molecules, the parameters of which, however, differ only slightly, and only one molecule is depicted in Figure 1. As expected, the C–P distances to the ylidic carbon atom are different. The C–PPh_3 bond length amounts to 168.8(3) pm, whereas the C–$P(O)Ph_2$ bond is longer with 171.7(3) pm. The short P–C bond is located between that of $C(PPh_3)_2$ (163.5) [12] and that of the

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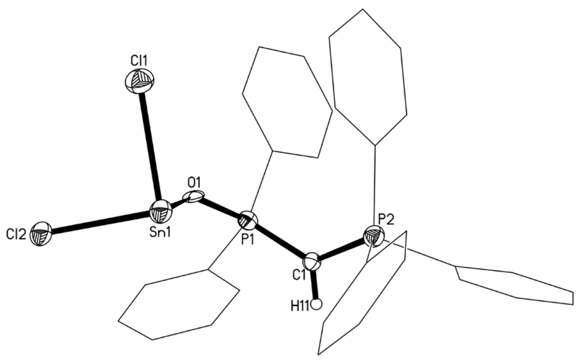

Figure 5. Molecular structure of $[Ph_3PCHP(OSnCl_2)Ph_2]$ (**8**). The ellipsoids are drawn at a 40 % probability level; the phenyl rings are refined as rigid groups and are represented as thin lines omitting the hydrogen atoms for clarity.

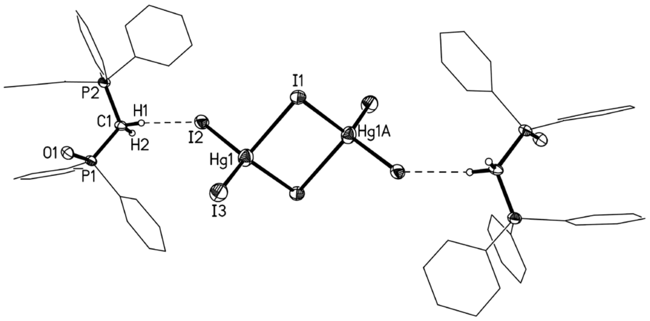

Figure 6. Molecular structure of $[Ph_3PCH_2P(O)Ph_2]_2[Hg_2I_6]$ (**9**). The ellipsoids are drawn at a 40 % probability level; the phenyl groups are represented as thin lines omitting the hydrogen atoms for clarity.

cation $(HC\{PPh_3\}_2)^+$ (mean value of 169.9 pm from about 10 compounds) [7], indicating a decreasing P–C double bond character down the row $C(PPh_3)_2$ > **2** (C–PPh_3) > $(HC\{PPh_3\}_2)^+$ > **2** [C–P(O)Ph_2] arising from variable back-bonding of the occupied p orbital at the ylidic carbon atom into P–C_{Ph} σ* orbitals [13]. The P–O distance amounts to 148.9(2) pm and is close to that in $OPPh_3$ [148.3(2) pm] [14]. With 127.5(2)° the P–C–P angle is not far away from that of an sp^2 carbon atom and more acute than the related angle in the cation $(HC\{PPh_3\}_2)^+$, probably an effect of the missing phenyl group in **2**, which is responsible for steric repulsion in the cation and related adducts of $C(PPh_3)_2$ (Table 2).

3.2 Crystal Structure of $[Ph_3PCHP(OBF_3)Ph_2]$ (5)

The molecular structure of **5** is shown in Figure 2. The coordination of a BF_3 molecule at the oxygen atom of **2** leads to an elongation of the P–O bond length by about 8 pm to 157.3(3) pm indicating a dramatic loss of π character; this is less operative in $[(Ph_3PO)BF_3]$, where the elongation amounts to 4 pm only [18]. A similar elongation is found in the compounds $[(Ph_3PO)AlX_3]$ (X = Cl, Br) [19]. As counterweight, the B–O bond length in **5** of 148.8(6) pm is appreciably shorter than that in $[(Ph_3PO)BF_3]$ [151.6(6) pm]. The P–O–B angles in both compounds are close together with 133.4(3)° in **5** and 134.5(2)° in the phosphane oxide adduct. In going from **2** to **5** the P–C–P angle opens to 131.7(3)°. The influence of the Lewis acid induces also changes in the P–C bonding situation. With the C–P(O)Ph_2 bond length of 168.1(4) pm and the C–PPh_3 bond length of 171.6(4) pm a reverse situation to **2** occurs with a shifting of the partial double bond to the other side, more directed to the PO group. The same effects on the P–O bond are observed in **3**, where a $W(CO)_5$ group is bonded to the oxygen atom instead of BF_3, however, the related P–C bond lengths are those of **2**, but according to large standard deviations in the tungsten complex, these values should be discussed with caution [6] (Table 3).

3.3 Crystal Structure of $[Ph_3PCH_2P(OBF_3)Ph_2][(\mu\text{-}OH)B_2F_6]$ (6)

In the solid state the compound forms a centrosymmetric dimer and the two units are linked by H···F bridges. A further H···F bridge exists between H(2) and F(4) of the anion with a C(1)–H(2)···F(4) distance of 326.1(4) pm. The complex can be seen as a protonation product upon addition of the hypothetical acid $H[HOB_2F_6]$ at the Lewis base **5**, and the crystal structure of the dimer unit is shown in Figure 3. The unusual and as yet unique anion $[HOB_2F_6]^-$ was described earlier with a carbenoid counter cation [20]. The bonding situation around the P–C–P group changed dramatically upon conversion of the central sp^2 carbon atom into a sp^3 carbon atom on protonation to give a type **C** salt. According to a missing back donation, the P–C bond lengths increased to 181.3(3) and 179.9(3) pm and correspond to normal single bonds. The P–O bond length amounts to 152.9(2) pm and is in between that of **2** and **5**. Relative to **5** the B–O bond length increased by about 5 pm to 154.2(4) pm, whereas the P–O–B angle remained unchanged. The P–C–P angle moved into the direction of that of an sp^3 carbon atom but with 119.9(2)° remains still large, probably according to steric repulsion between the phenyl groups. The other angles in the distorted tetrahedral environment of the carbon atom range between 100° (H–C–H) and 111° (P–C–H) (Table 4).

3.4 Crystal Structure of $[Ph_3PCH_2P(OBI_3)Ph_2][BI_4]$ ($7 \cdot C_7H_8$)

The compound crystallizes with one disordered toluene molecule without contacts to the salt-like compound and the molecular structure of **7** is shown in Figure 4. The replacement of the BF_3 group by the BI_3 group has no dramatic effect on the parameters of the cation; only the B–O bond is about 5 pm shorter and close to that of **5**, which is due to the stronger Lewis acidity of BI_3 relative to BF_3. The P–C bond lengths show the same trend as reported for the cation of **6**. Weak hydrogen bridges between H(2) of the cation and I(4) of the anion exist [C(1)–H(2)···I(4) = 399(1) pm], which leads to a long B(2)–I(4) distance of 228(1) pm relative to the three others with a mean B–I distance of 223 pm; all B–I distances are about 10 pm longer than those in the planar BI_3 molecule [21] (Table 5).

Table 1. Crystal data and structure refinement details for the compounds **2**, **5**, **6**, **7**$\cdot C_7H_8$, **8**, and **9**.

	2	5	6	7$\cdot C_7H_8$	8	9
Formula	$C_{31}H_{26}OP_2$	$C_{31}H_{26}BF_3OP_2$	$C_{31}H_{28}B_3F_9O_2P_2$	$C_{38}H_{35}B_2I_7OP_2$	$C_{31}H_{26}Cl_2OP_2Sn$	$C_{62}H_{45}Hg_2I_6O_2P_4$
Mw /g·mol^{-1}	476.49	544.30	697.92	1479.56	666.05	2117.51
a /pm	1004.8(1)	1151.7(2)	988.6(2)	1108.0(1)	1496.9(2)	1194.0(1)
b /pm	1476.5(2)	1392.1(2)	1059.4(2)	1476.5(2)	2061.0(3)	1094.2(1)
c /pm	1832.9(3)	1653.8(3)	1722.5(2)	1444.4(2)	1825.0(2)	2552.1(2)
α /°	107.93(1)	90	79.46(2)	90	90	90
β /°	98.55(1)	97.63(1)	78.46(2)	106.50(1)	90	100.36(1)
γ /°	101.09(1)	90	65.68(2)	90	90	90
Crystal size /mm	0.32 × 0.14 × 0.08	0.17 × 0.17 × 0.04	0.14 × 0.06 × 0.05	0.24 × 0.09 × 0.05	0.13 × 0.12 × 0.04	0.18 × 0.11 × 0.09
Volume / pm^3 × 10^6	2475.2(6)	2628.0(8)	1600.5(5)	2265.7(5)	5630(1)	3279.9(5)
Z	4	4	2	2	8	2
d_{calc} /g·cm^{-3}	1.279	1.376	1.448	2.169	1.571	2.144
Crystal system	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)
Diffractometer	IPDS I (Stoe)	IPDS II (Stoe)	IPDS I (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)	IPDS I (Stoe)
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Temperature /K	193	100	193	173	100	193
μ /cm^{-1}	2.1	2.1	2.2	48.9	12.35	76.36
$2\theta_{max}$/°	52.34	52.10	55.22	52.12	52.10	52.42
Index range	$-12 \le h \le 12$, $-17 \le k \le 17$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-19 \le l \le 19$	$-13 \le h \le 13$, $-17 \le k \le 18$, $-17 \le l \le 17$	$-15 \le h \le 18$, $-25 \le k \le 25$, $-21 \le l \le 22$	$-14 \le h \le 12$, $-13 \le k \le 13$, $-31 \le l \le 31$
Number of rflns collected	23300	36597	15732	16018	34625	15021
Number of indep. rflns (R_{int})	9087 (0.0739)	5138 (0.1984)	5835 (0.0863)	8017 (0.065)	5513 (0.5512)	6169 (0.0578)
Number of observed rflns with $F_o > 4\sigma(F_o)$	4091	2389	2360	5058	1579	3410
Parameters	622	348	437	438	205	350
Absorption correction	numerical	numerical	numerical	numerical	numerical	numerical
Structure solution	direct methods SHELXS-97 [15]	direct methods SIR-92 [16]	direct methods SIR-92 [16]	direct methods SHELXS-97 [15]	direct methods SIR-92 [16]	direct methods SHELXS-97 [15]
Refinement against F^2	SHELXL-97 [17]	SHELXL-97 [17]	SHELXL-97 [17]	SHELXL-97 [17]	SHELXS-97 [15]	SHELXL-97 [17]
Flack-Parameter	–	–	–	–0.05(3)	–	–
hydrogen atoms	calculated positions with common displacement parameter, H(1) was refined free	calculated positions with common displacement parameter	calculated positions with common displacement parameter, H(1), H(2), H(3) were refined free	calculated positions with common displacement parameter	calculated positions with common displacement parameter	calculated positions with common displacement parameter, H(1), H(2) were refined free
R_1	0.0361	0.0608	0.0364	0.0411	0.0872	0.0367
wR_2 (all data)	0.0651	0.1299	0.0595	0.0611	0.2199	0.0834
max. electron density °left / e·pm^{-3} × 10^{-6}	0.25	0.68	0.13	0.72	1.007	1.413

3.5 Crystal Structure of [$Ph_3PCHP(OSnCl_2)Ph_2$] (8)

Similar to the BF_3 adduct **5**, the tin derivative **8** can be considered as type **A** compound; the molecular structure is depicted in Figure 5. Thus, the relevant bond lengths P(1)–O, P(1)–C(1), and P(2)–C(1), which are influenced by the coordination of the tin atom, show the same trend in shifting of the partial double bond more directed to the PO bond relative to the starting compound **2**. The Sn–O bond length amounts to 212(1) pm, which is shorter than that in the comparable complex [$Cl_2Sn(OC(O)C\{PPh_3\}_2)$] [214.3(4) pm] described by us recently [22]. Similar Sn–O bond lengths in $SnCl_2$ addition compounds vary between 252 pm in the dioxane adduct [23] and 230 pm in the dihydrate [24]; the structures of other compounds with the simple Cl_2SnO core have not been reported so far. The two Sn–Cl bond lengths in **8** are not equal and differ by about 3 pm (Table 6). For the tin atom a typical tetrahedral environment is achieved, where one coordination site is occupied by a free pair of electrons. Together with the $(CO)_5W$ adduct **3**, the compounds **5** and **8** represent the only type **A** compounds existing as yet.

3.6 Crystal Structure of [$Ph_3PCH_2P(O)Ph_2$]$_2$[Hg_2I_6] (9)

The protonation of **2** produces the cation of **9**, its conjugated acid and a change in rehybridization of the carbon atom from planar sp^2 to tetrahedral sp^3 occurred with interruption of the

Table 2. Selected bond lengths /pm and angles /° in one of the two independent molecules of **2**.

P(1)–O(1)	148.9(2)	P(1)–C(1)	171.7(3)
P(1)–C(2)	181.2(3)	P(1)–C(8)	182.2(3)
P(2)–C(1)	168.8(3)	P(2)–C(14)	182.0(3)
P(2)–C(20)	180.7(2)	P(2)–C(26)	181.9(3)
C(1)–H(1)	0.85(3)		
O(1)–P(1)–C(1)	114.1(1)	O(1)–P(1)–C(2)	111.2(1)
O(1)–P(1)–C(8)	112.1(1)	C(1)–P(1)–C(2)	109.4(2)
C(1)–P(1)–C(8)	107.8(1)	C(2)–P(1)–C(8)	101.4(1)
C(1)–P(2)–C(14)	116.3(1)	C(1)–P(2)–C(20)	105.3(2)
C(1)–P(2)–C(26)	116.9(2)	C(14)–P(2)–C(20)	106.9(1)
C(14)–P(2)–C(26)	103.6(1)	C(20)–P(2)–C(26)	107.2(1)
P(1)–C(1)–P(2)	127.5(2)	P(1)–C(1)–H(1)	116(2)
P(2)–C(1)–H(1)	116(2)		

Table 3. Selected bond lengths /pm and angles /° in **5**.

P(1)–O(1)	157.3(3)	P(1)–C(1)	168.1(4)
P(1)–C(2)	179.7(4)	P(1)–C(8)	179.7(4)
P(2)–C(1)	171.6(4)	P(2)–C(14)	180.3(4)
P(2)–C(20)	180.7(4)	P(2)–C(26)	179.6(4)
F(1)–B(1)	137.6(6)	F(2)–B(1)	140.2(5)
F(3)–B(1)	135.9(5)	O(1)–B(1)	148.8(6)
C(1)–H(1)	93(4)		
O(1)–P(1)–C(1)	118.9(2)	O(1)–P(1)–C(2)	108.9(2)
O(1)–P(1)–C(8)	101.4(2)	C(1)–P(1)–C(2)	107.3(2)
C(1)–P(1)–C(8)	114.4(2)	C(2)–P(1)–C(8)	105.1(2)
C(1)–P(2)–C(14)	113.5(2)	C(1)–P(2)–C(20)	110.7(2)
C(1)–P(2)–C(26)	112.0(2)	C(14)–P(2)–C(20)	104.8(2)
C(14)–P(2)–C(26)	107.2(2)	C(20)–P(2)–C(26)	108.2(2)
P(1)–O(1)–B(1)	133.4(3)	P(1)–C(1)–P(2)	131.7(3)
F(1)–B(1)–F(2)	109.7(4)	F(1)–B(1)–F(3)	111.1(4)
F(1)–B(1)–O(1)	110.0(4)	F(2)–B(1)–F(3)	110.2(4)
F(2)–B(1)–O(1)	106.9(3)	F(3)–B(1)–O(1)	108.8(4)
P(1)–C(1)–H(1)	114(2)	P(2)–C(1)–H(1)	112(2)

Table 4. Selected bond lengths /pm and angles /° in **6**.

P(1)–O(1)	152.9(2)	P(1)–C(1)	179.9(3)
P(1)–C(2)	178.5(3)	P(1)–C(8)	177.3(3)
P(2)–C(1)	181.3(3)	P(2)–C(14)	178.6(3)
P(2)–C(20)	177.7(3)	P(2)–C(26)	178.2(3)
F(1)–B(1)	138.8(4)	F(2)–B(1)	134.2(4)
F(3)–B(1)	133.6(4)	O(1)–B(1)	154.2(4)
C(1)–H(1)	87(3)	C(1)–H(2)	97(3)
F(4)–B(2)	137.8(4)	F(5)–B(2)	137.8(4)
F(6)–B(2)	135.3(4)	F(7)–B(3)	141.6(4)
F(8)–B(3)	136.5(4)	F(9)–B(3)	137.1(4)
O(2)–B(2)	151.9(4)	O(2)–B(3)	147.6(4)
O(2)–H(3)	86(4)		
O(1)–P(1)–C(1)	106.7(2)	O(1)–P(1)–C(2)	111.2(1)
O(1)–P(1)–C(8)	111.6(1)	C(1)–P(1)–C(2)	108.5(2)
C(1)–P(1)–C(8)	106.5(2)	C(1)–P(2)–C(26)	106.2(2)
C(1)–P(2)–C(14)	109.6(2)	C(1)–P(2)–C(20)	113.6(2)
P(1)–O(1)–B(1)	133.4(2)	P(1)–C(1)–P(2)	119.9(2)
F(1)–B(1)–F(2)	110.4(3)	F(1)–B(1)–F(3)	110.8(4)
F(1)–B(1)–O(1)	106.9(3)	F(2)–B(1)–F(3)	114.9(4)
F(2)–B(1)–O(1)	107.4(4)	F(3)–B(1)–O(1)	105.7(3)
P(1)–C(1)–H(1)	110(2)	P(1)–C(1)–H(2)	107(2)
P(2)–C(1)–H(1)	107(2)	P(2)–C(1)–H(2)	111(2)
H(1)–C(1)–H(2)	100(3)	B(2)–O(1)–B(3)	127.6(3)
F(4)–B(2)–F(5)	111.7(3)	F(4)–B(2)–F(6)	110.8(3)
F(4)–B(2)–O(2)	107.3(3)	F(5)–B(2)–F(6)	111.4(4)
F(5)–B(2)–O(2)	105.3(3)	F(6)–B(2)–O(2)	110.1(3)
F(7)–B(3)–F(8)	109.9(3)	F(7)–B(3)–F(9)	108.0(3)
F(7)–B(3)–O(2)	108.8(3)	F(8)–B(3)–F(9)	112.2(4)
F(8)–B(3)–O(2)	109.5(3)	F(9)–B(3)–O(2)	108.2(3)
B(2)–O(2)–H(3)	102(2)	B(3)–O(2)–H(3)	124(2)

Table 5. Selected bond lengths /pm and angles /° in $\mathbf{7}\cdot C_7H_8$.

I(1)–B(1)	221(1)	I(2)–B(1)	222(1)
I(3)–B(1)	229(1)	P(1)–C(1)	180(1)
P(1)–C(2)	177.0(9)	P(1)–C(8)	179(1)
P(1)–C(14)	176(1)	P(2)–O(1)	154.5(1)
P(2)–C(1)	180.4(8)	P(2)–C(20)	175(1)
P(2)–C(26)	178(1)	O(1)–B(1)	148(1)
C(1)–H(1)	99	C(1)–H(2)	99
I(4)–B(2)	228(1)	I(5)–B(2)	222(2)
I(6)–B(2)	224(2)	I(7)–B(2)	222(1)
C(1)–P(1)–C(2)	107.1(5)	C(1)–P(1)–C(8)	110.9(5)
C(1)–P(1)–C(14)	110.3(5)	O(1)–P(2)–C(1)	104.7(4)
O(1)–P(2)–C(20)	116.3(4)	O(1)–P(2)–C(26)	111.0(5)
C(1)–P(2)–C(20)	106.8(5)	C(1)–P(2)–C(26)	108.0(4)
P(2)–O(1)–B(1)	139.0(7)	P(1)–C(1)–P(2)	120.9(6)
I(1)–B(1)–I(2)	109.6(4)	I(1)–B(1)–I(3)	109.9(5)
I(1)–B(1)–O(1)	107.3(7)	I(2)–B(1)–O(1)	112.9(7)
I(3)–B(1)–O(1)	108.1(6)	P(1)–C(1)–H(1)	107
P(1)–C(1)–H(2)	107	P(2)–C(1)–H(1)	107
P(2)–C(1)–H(2)	107	H(1)–C(1)–H(2)	106

π conjugation in the P–C–P–O spine. The molecular structure is shown in Figure 6. Upon protonation, both P–C bond lengths have increased by about 10 pm with respect to compound **2** being now in the range of a normal P–C single bond; however, the prevailing C–P(O) bond lengths in **2** and **9** are about 2 to 3 pm longer. The P–O bond length remains nearly unchanged (Table 7). The addition of a further Lewis acid at the oxygen atom as in **6** or **7** leads to an increase of the P–O bond by about 5 pm. In the crystals of **9** ion triples are present, held together by H···I bridges [C(1)···I(2) = 388.6(8) pm], which are stacked along H···H–O bridges as shown in Figure 7. The dianion is located around an inversion center causing the four-membered Hg–I–Hg–I ring to be completely planar, and both mercury atoms are in a distorted tetrahedral environment.

4. Conclusion

The majority of the compounds presented herein are side-products, which were obtained with low yields during various runs for preparing addition compounds of the type LA←**1** and not as a result of specific syntheses. Although **2** was only present in trace amounts in the starting material the adducts preferentially crystallized. It turned out that these are more soluble, less sensitive to polar solvents, and show better crystallization properties than those with **1**. In part, this was also the case during the reaction of $AlBr_3$ with **1** in toluene, where a couple of colorless crystals of the adduct Br_3Al←**1** grew from

Table 6. Selected bond lengths /pm and angles /° in **8**.

P(1)–O(1)	156(1)	P(1)–C(1)	168(2)
P(1)–C(2)	182.0(3)	P(1)–C(8)	183
P(2)–C(1)	172(2)	P(2)–C(14)	181
P(2)–C(20)	183	P(2)–C(26)	180
O(1)–Sn(1)	212(1)	Cl(1)–Sn(1)	250.0(5)
Cl(2)–Sn(1)	247.0(5)	C(1)–H(11)	95
O(1)–Sn(1)–Cl(2)	90.9(3)	O(1)–Sn(1)–Cl(1)	88.3(3)
Cl(2)–Sn(1)–Cl(1)	92.5(2)	P(1)–C(1)–P(2)	128(1)
P(1)–C(1)–H(11)	115.9	P(2)–C(1)–H(11)	115.9
P(1)–O(1)–Sn(1)	138.1(6)	O(1)–P(1)–C(1)	119.2(7)
O(1)–P(1)–C(2)	105.6(4)	C(1)–P(1)–C(2)	108.1(5)
O(1)–P(1)–C(8)	105.4(4)	C(1)–P(1)–C(8)	111.1(5)
C(2)–P(1)–C(8)	106.7	C(1)–P(2)–C(14)	115.5(5)
C(1)–P(2)–C(26)	108.8(5)	C(26)–P(2)–C(14)	105.5
C(1)–P(2)–C(20)	112.0(6)	C(26)–P(2)–C(20)	108.6
C(14)–P(2)–C(20)	106.0		

Table 7. Selected bond lengths /pm and angles /° in **9**.

Hg(1)–I(3)	267.01(8)	Hg(1)–I(2)	270.35(6)
Hg(1)–I(1)A	280.51(7)	Hg(1)–I(1)	300.77(8)
P(1)–O(1)	147.9(6)	P(1)–C(1)	182.2(8)
P(1)–C(2)	179.2(8)	P(1)–C(8)	180.6(7)
P(2)–C(1)	179.7(8)	P(2)–C(14)	178.5(7)
P(2)–C(20)	179.1(9)	P(2)–C(26)	179.5(8)
C(1)–H(1)	101(8)	C(1)–H(2)	93(9)
I(3)–Hg(1)–I(2)	120.81(2)	I(3)–Hg(1)–I(1)A	118.50(3)
I(2)–Hg(1)–I(1)A	108.32(2)	I(3)–Hg(1)–I(1)	107.94(2)
I(2)–Hg(1)–I(1)	102.01(2)	I(1)A–Hg(1)–I(1)	94.52(2)
Hg(1)A–I(1)–Hg(1)	85.48(2)	P(1)–C(1)–P(2)	118.2(4)
P(2)–C(1)–H(1)	102(6)	P(1)–C(1)–H(1)	115(5)
P(2)–C(1)–H(2)	116(6)	P(1)–C(1)–H(2)	105(6)
H(1)–C(1)–H(2)	101(7)	O(1)–P(1)–C(2)	112.3(3)
O(1)–P(1)–C(8)	113.0(3)	C(2)–P(1)–C(8)	109.6(4)
O(1)–P(1)–C(1)	112.5(4)	C(2)–P(1)–C(1)	102.3(3)
C(8)–P(1)–C(1)	106.4(4)	C(14)–P(2)–C(1)	110.1(4)
C(20)–P(2)–C(1)	108.3(4)	C(26)–P(2)–C(1)	112.0(4)

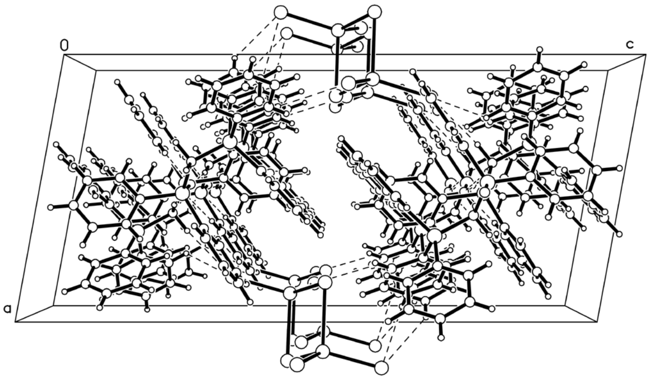

Figure 7. Crystal packing diagram of compound **9** viewed along the *b* axis; hydrogen contacts are indicated by dashed lines.

a saturated toluene solution overnight and among them were very few yellow crystals of **4** [7]. However, in the majority of reactions with $C(PPh_3)_2$ and Lewis acids in toluene or benzene no crystals of the appropriate addition compounds have been obtained from the saturated solutions as yet and attempts to get crystals have failed according to the properties mentioned above.

Herein we could show that the neutral compound $Ph_3PCHP(O)Ph_2$ (**2**) has a free pair of electrons at the carbon atom and can be protonated; the results of attempted alkylation will be reported elsewhere. Other Lewis acids such as group 13 or group 14 electron deficient compounds prefer the PO oxygen atom. Thus, adducts of the type **A**, **B**, and **C** of Scheme 1 could be realized with Lewis acids at the oxygen atom, the carbon atom, and at both atoms, respectively. In addition to the results reported, compound **2** is assumed to act as a chelating ligand with formation of a four-membered MCPO ring; however, no such compound could be isolated so far. Those compounds would have a constrained arrangement and may act as catalysts for olefin polymerization [25].

$$\underset{}{[Ph_3PCP(O)Ph_2]^-} \leftarrow \underset{\mathbf{2}}{Ph_3PCHP(O)Ph_2} \rightarrow \underset{\mathbf{9}}{[Ph_3PCH_2P(O)Ph_2]^+} \qquad (2)$$

In addition, the proton at the carbon atom of **2** may also be replaced with strong Lewis bases to produce a double ylide-like anion [Equation (2) left side] such as in complexes with the dianion $[Ph_2(E)P–C–P(E)Ph_2]^{2-}$ (E = NR, S) [26], but as yet, the acidity of this proton and the assumed amphoteric character of **2** is still unexplored. Further studies on the chemistry of **2** are currently in progress.

5. Experimental Section

All operations were carried out in an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run with a Nicolet 510 spectrometer in Nujol mull. For the ^{31}P NMR spectra we used the instrument Bruker AC 200. Elemental analyses were performed by the analytical service of the Fachbereich Chemie at the Philipps Universität Marburg, Germany. The carbodiphosphorane $C(PPh_3)_2$ (**1**) was prepared according to a modified literature procedure [27]. $[BF_3(OEt_2)]$ was commercially obtained and used without further purification. BI_3 was obtained according to the procedure described in [28].

$Ph_3PCHP(O)Ph_2$ (2): A suspension of **1** (2.3 g, 4.3 mmol) in toluene (40 mL) was stirred in a 100 mL flask. The neck was closed by glass wool to allow a slow admission of moist air. After about 2 h, the yellow color of **1** had disappeared and a colorless suspension was obtained. The solution was filtered from small amounts of an insoluble material. From the clear solution compound **1** precipitated as colorless crystals by layering with *n*-pentane. Yield 1.9 g (4.0 mmol, 95 %). **^{31}P NMR** (CH_2Cl_2, 200 MHz, 298 K): δ = 25.8 (d, PO), 19.2 [d, PPh_3), ^2J(P,P) = 19.7 Hz, Δ = 6.66 ppm]; similar values were obtained in $CHCl_3$ [25.3, 18.6 ppm, ^2J(P,P) = 19.1 Hz, Δ = 7.39 ppm], THF [26.7, 21.5 ppm, ^2J(P,P) = 19.1 Hz, Δ = 4.15 ppm], DMSO [25.2, 19.0 ppm, ^2J(P,P) = 20.4 Hz, Δ = 6.15 ppm], and toluene [25.3, 20.6 ppm, ^2J(P,P) = 19.7 Hz, Δ = 4.65 ppm] solutions. Remarkable is the shift difference Δ between the two doublets in the respective solvents. **IR** (Nujol mull): $\tilde{\nu}$ = 1479 s, 1435 vs, 1306 w, 1198 s, 1184 sh, 1171 vs, 1165 s, 1150 s, 1113 vs, 1100 vs, 1069 m, 1028m, 995 sh, 984 s, 964 s, 806 w, 789 w, 764 m, 750 s, 743 s, 714 vs, 694 vs, 569 m, 536 vs, 518 s, 500 s, 444 w cm^{-1}.

Formation of [$Ph_3PCHP(OBF_3)Ph_2$] (5): A solution of **1** (0.59 g, 1.1 mmol) containing small amounts of **2** (identified by ^{31}P NMR spectroscopy) in toluene (20 mL) was admitted to an atmosphere of gaseous BF_3 for about 1 hour and the mixture was stirred mechanically. A colorless precipitate formed immediately. After several days of standing, colorless whiskers of **5** had grown from the filtered solution. **^{31}P NMR** (CH_2Cl_2, 200 MHz, 298 K): δ = 21.02, 19.38, ^2J(P,P) = 12.71 Hz. **IR** (Nujol mull): $\tilde{\nu}$ = 1613 m, 1588 w, 1487 w, 1441 st, 1358 m, 1196 st, 1154 st, 1113 st, 997 m, 922 w, 903 w, 862 m, 883 st, 797 st, 739 st, 710 w, 685 st, 660 w, 579 m, 564 w, 507 m, 501 m, 488 m cm^{-1}. $C_{31}H_{36}BF_3OP_2$: found C 67.4, H 5.1 %; calcd. C 68.4, H 4.8 %. The main product, probably the adduct $F_3B{\leftarrow}$**1**, dissolves in DMSO, and the ^{31}P NMR shows a signal at 20.8 ppm, which indicates the formation of the cation $(HC\{PPh_3\}_2)^+$ via proton abstraction from the solvent. Similar behavior was observed with other polar solvents such as DCM, DCE, and THF, therefore the structure of the precipitate could not be identified as yet.

Formation of [$Ph_3PCH_2P(OBF_3)Ph_2$][HOB_2F_6] (6): From **2** and [$BF_3(OEt_2)$]: [$BF_3(OEt_2)$] (0.1 mL, 0.8 mmol) was layered in a Schlenk tube with toluene (2 mL). This mixture was layered with a solution of **2** (0.05 g, 0.11 mmol) in toluene (1 mL) and allowed to stand overnight. Colorless crystals of **6** separated. **^{31}P NMR** (CH_2Cl_2, 200 MHz, 298 K): δ = 45.63 (m, PO), 17.54 (d, PPh_3), ^2J(P,P) = 17.80 Hz. **IR** (Nujol mull): $\tilde{\nu}$ = 2723 m, br [ν(OH)], 1589 w, 1485, w, 1439 s, 1406 w, 1367 m, 1341 w, 1173 to 1117 vs. [ν(BF)], 1034 m, 999 m, 856 s, 847 s, 801 s, 781 s, 743 vs, 731 s, 689 s, 600 w, 579 w, 557 w, 505 m, 490 m cm^{-1}. Compound **6** was also obtained from **2** and BF_3: A solution of **2** (0.20 g, 0.42 mmol) in toluene (20 mL) was contacted with a bulb containing gaseous BF_3. After some days, crystals of **6** formed at the surface of the solution. The precipitate was filtered and dried in vacuo. **^{31}P NMR** (CD_2Cl_2, 200 MHz, 298 K): δ = 45.69 (m, PO), 17.55 (d, PPh_3), ^2J(P,P) = 17.80 Hz. Another set of two doublets at 23.54 and 18.75 ppm (^2J(P,P) = 13.99 Hz) belongs to **5**.

Formation of [$Ph_3PCH_2P(OBI_3)Ph_2$][BI_4] (7) and ($H_2C\{PPh_3\}_2$)[I_3]I: Solutions of **1** (0.24 g, 0.45 mmol) and of BI_3 (0.84 g, 2.14 mmol), in toluene (each about 10 mL), were combined at room temperature. The resulting precipitate was filtered. In the filtrate small yellow crystals had formed after several days which turned out to be **7**·C_7H_8. **^{31}P NMR** (CH_2Cl_2, 200 MHz, 298 K): δ = 54.55 (m, PO), 16.20 (d, PPh_3), ^2J(P,P) = 16.35 Hz. **IR** (Nujol mull): $\tilde{\nu}$ = 1558 m, 1480 m, 1439 s, 1339 w, 1312 w, 1213 m, 1181 s, 1161 m, 1099 w, 1074 w, 1028 w, 997 w, 963 m, 745 m, 735 m, 721 s, 710 w, 696 m, 687 m, 648 w, 536 s, 509 s cm^{-1}. Part of the precipitate was dissolved in MeCN. After five days needle-like orange red crystals separated which turned out to be the salt ($H_2C\{PPh_3\}_2$)[I_3]I. **^{31}P NMR** (MeCN): δ = 18.30.

[$Ph_3PCHP(OSnCl_2)Ph_2$] (8): To a solution of **2** (0.21 g, 0.44 mmol) in DCM (4 mL) anhydrous $SnCl_2$ (0.27 g, 0.88 mmol) was added and the mixture was treated for 30 min in an ultrasonic bath at room temperature. The resulting suspension was filtered from some insoluble material. The ^{31}P NMR spectrum of the solution showed two doublets at 38.74 and 18.18 ppm [^2J(P,P) = 19.67 Hz]. After about 24 h the signals had disappeared in favor of two new doublets at 22.96, 21.33 ppm [^2J(P,P) = 12.52 Hz]. Layering of the solution with *n*-pentane gave colorless crystals after about three days which turned out to be the addition compound **8**; the product was filtered and dried in vacuo; the yield was not determined. **^{31}P NMR**: δ = 23.01, 21.40 [d's, ^2J(P,P) = 14.3 Hz] in DCM and δ = 23.32. 21.79 [d's, ^2J(P,P) = 14.3 Hz] in DMSO. **IR** (Nujol mull): $\tilde{\nu}$ = 1481 m, 1447 s, 1194 m, 1181 m, 1157 w, 1117 s, 1107 s, 1030 s, 1018 s, 997 s, 972 s, 806 m, 758 m, 747 s, 737 s, 723 s, 718 m, 702 m, 692 s, 596 m, 527 s, 515 s, 494 m, 480 m, 467 w, 467 w, 434 w cm^{-1}. $C_{31}H_{26}Cl_2OP_2Sn$ (MW 666.07): found C 54.7, H 4.1 %; calcd. C 55.90, H 3.94 %.

[$Ph_3PCH_2P(O)Ph_2$]$_2$[Hg_2I_6] (9): To a solution of **2** (0.07 g, 0.15 mmol) in THF (3 mL) HgI_2 (0.09 g, 0.2 mmol) was added and a clear solution was obtained. The ^{31}P NMR spectrum of the solution showed two doublets at 21.79, 21.07 ppm [d's, ^2J(P,P) = 12.51 Hz] along with two broad bands at 27.1 and 26.3 ppm. Layering of the solution with *n*-pentane gave colorless crystals overnight, which turned out to be the salt **9**. **^{31}P NMR** (DMSO, 300 MHz, 298 K): δ = 23.34, 21.92 [d's, ^2J(P,P) = 14.3 Hz]. **IR** (Nujol mull): $\tilde{\nu}$ = 1588 m, 1484 m, 1437 s, 1375 m, 1334 m, 1185 s, 1118 s, 1071 m, 998 m, 799 s, 783 s, 743 m 743 s, 729 s, 712 s, 689 s, 556 m, 503 s, 484 m cm^{-1}. $C_{31}H_{27}HgI_3OP_2$ (MW 1058.77): found C 35.05, H 2.63 %; calcd. C 35.17, H 2.57 %.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depository numbers CCDC-757261 (**2**), -757262 (**5**), -757263 (**6**), -757264 (**7**·C_7H_8), -757265 (**8**), and -757266 (**9**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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