DOI: 10.1002/ejic.201100646

Reaction of $C(PPh_3)_2$ with MI_2 Compounds (M = Zn, Cd) – Formation and Crystal Structures of $[I_2Zn\{C(PPh_3)_2\}]$, $[(I_2Cd\{C(PPh_3)_2\})_2]$ and the Salt-Like Compounds $(HC\{PPh_3\}_2)[MI_3(THF)]$ and $(HC\{PPh_3\}_2)_2[ZnI_4]$

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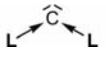
Keywords: Ylides / Zinc / Cadmium / Addition compounds / Carbodiphosphorane

The reaction of the carbodiphosphorane $C(PPh_3)_2$ (**1**) with group 12 MI_2 compounds in THF leads to the salts $(HC\{PPh_3\}_2)[MI_3(THF)]$ (M = Zn^{2+}, **2**; Cd^{2+}, **3**) in good yields upon proton abstraction from the solvent. The salt-like complex $(HC\{PPh_3\}_2)_2[ZnI_4]$ (**4**) formed upon reaction of ZnI_2 with **1** in toluene and subsequent heating of the resulting powder in 2-bromofluorobenzene. When this reaction was carried out in 2-bromofluorobenzene as the solvent, no proton transfer occurred, and the colorless addition compounds $[I_2Zn{\leftarrow}\mathbf{1}]$ (**5**) and $[I_2Cd{\leftarrow}\mathbf{1}]_2$ (**6**) were isolated. Compound **5** is monomeric, whereas in **6** the monomeric units are linked by bridging iodine ligands to produce a dimer. All compounds were characterized by X-ray analyses and ^{31}P NMR and IR spectroscopy.

1. Introduction

The double ylide $C(PPh_3)_2$ (**1**) can be considered as a carbon atom stabilized by two phosphane ligands. Compound **1** has a bent structure and belongs to a series of CL_2 compounds, in which a carbon(0) atom attains eight valence electrons by the coordination of two neutral donor molecules, L. L stands for various donors such as PR_3, N-heterocyclic carbenes (NHCs), and others with a free pair of electrons. This newly recognized class of compounds,[1] for which the name carbones has been proposed,[2] possesses one σ- and one π-type lone pair orbital [highest occupied molecular orbital (HOMO) and HOMO–1] at the carbon atom. We have recently reported a compilation of transition metal complexes of carbones accompanied by theoretical calculations.[3]



Transition metal complexes with **1** are rare and concentrate on a few examples. Thus, addition compounds are described and confirmed by X-ray analyses, in which a molecule of **1** coordinates with the carbon atom at the electron deficient transition metal fragments $Ni(CO)_n$ (n = 2, 3),[4] ReO_3^+,[5] CuCl,[6] and CuCp*.[7] A Au complex has also been described, in which **1** bridges a Au–Au bond.[8] Coordination to Pt is accompanied by orthometallation of one or two phenyl rings of **1** with the formation of a *C,C,C* pincer ligand;[9] similar results have been found with Rh[10] and Pd compounds.[11] Further addition compounds of the type $M{\leftarrow}\mathbf{1}$ have been prepared and characterized for main-group Lewis acids with M = S, Se,[12] I^+,[13,14] H^+, Cl^+, and the molecules $InMe_3$ and $AlBr_3$.[15] We have recently reported the coordination of **1** to two boron atoms.[16] The coordination chemistry of ylides has been summarized in several reviews.[17,18,19] We have recently isolated the first complex with two molecules of **1** in a linear arrangement in the cationic complex $[\mathbf{1}{\rightarrow}Ag{\leftarrow}\mathbf{1}]^+$.[20] We found that CuI and HgI_2 react similarly to produce the related cationic compounds $[\mathbf{1}{\rightarrow}Cu{\leftarrow}\mathbf{1}]^+$ and $[\mathbf{1}{\rightarrow}Hg{\leftarrow}\mathbf{1}]^{2+}$, respectively.[21] These results prompted us to extend our studies to homologues with group 12 elements. Here we report the outcome of reactions of **1** with ZnI_2 and CdI_2 in various solvents.

2. Results and Discussion

Although the reaction of **1** with HgI_2 in tetrahydrofuran (THF) generates the cationic complex $[\mathbf{1}{\rightarrow}Hg{\leftarrow}\mathbf{1}]^{2+}$, under the same conditions the homologous MI_2 compounds (M = Zn, Cd) prefer a reaction pathway that we have frequently observed with main-group Lewis acids,[15] $[Co_2(CO)_8]$,[22] and $[Mn_2(CO)_{10}]$[23] in THF, which leads to proton abstraction from the solvent forming the salts $(HC\{PPh_3\}_2)[MI_3(THF)]$ (M = Zn **2**, M = Cd, **3**). Both compounds were obtained from THF as large colorless crystals as the only crystalline products. The reaction with ZnI_2 was also performed in dimethoxyethane (DME) with nearly the same results; the insoluble colorless powder indicates the formation of $(HC\{PPh_3\}_2)^+$, which was identified by IR and ^{31}P

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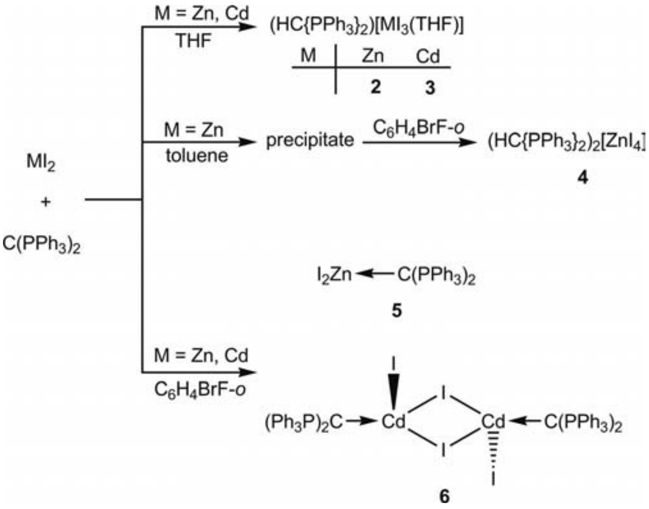
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100646.

NMR spectroscopy. Although the cation bears a free pair of electrons, the nucleophilicity is apparently too weak to replace the coordinated THF molecule in the anions of **2** and **3**. However, in the absence of coordinating anions the cation can act as a ligand as shown in the complex $[(PPh_3)_2\text{-}HC{\rightarrow}Ag{\leftarrow}HC(PPh_3)_2]^{3+}$.[1] We have also reacted ZnI_2 with **1** in toluene. A pale yellow insoluble precipitate formed whose IR spectrum does not indicate the presence of $(HC\{PPh_3\}_2)^+$. The insoluble material dissolves in dimethylsulfoxide (DMSO) and the ^{31}P NMR spectrum exhibits a singlet at 19.6 ppm, which was identified as that of $(HC\{PPh_3\}_2)^+$; addition of small amounts of $(HC\{PPh_3\}_2)I$ to this solution gave no new signal. Thus, the initially formed adduct between **1** and ZnI_2 deprotonates in DMSO as well as THF. The precipitate from the reaction of ZnI_2 in toluene was heated in 2-bromofluorobenzene. Upon cooling, colorless crystals separated, which were the salt-like complex $(HC\{PPh_3\}_2)_2[ZnI_4]$ (**4**). The different pathways within the group 12 iodides shown in Scheme 1 may be explained by the less covalent nature of these compounds relative to HgI_2 and their proximity to main-group Lewis acids.



Scheme 1. Reaction pathways of **1** with MI_2 (M = Zn, Cd) in THF, toluene, and 2-bromofluorobenzene.

Alternatively, **1** was allowed to react with ZnI_2 and CdI_2 directly in 2-bromofluorobenzene. With ZnI_2, a colorless precipitate formed, which dissolved upon heating to give a brownish solution. On cooling, large colorless crystals separated in high yield, which were the addition compound **5**. 2-Bromofluorobenzene is more polar than toluene but the proton abstraction that occurs in THF is suppressed. Complex **5** is the first addition compound of a carbone and a Zn^{2+} compound; even Zn^{2+} complexes with NHCs are rare.[24] However, to the best of our knowledge, no carbene complexes with ZnI_2 have been reported to date. The reaction of CdI_2 under the same conditions led to a clear, pale beige solution and, on cooling to room temperature, all material remained in solution. Layering with *n*-pentane gave colorless crystals of **6**. In contrast with **5**, **6** is dimeric and the monomeric units are connected by two bridging I atoms. It is interesting to note that cadmium complexes with NHCs or other carbenes have not been reported to date.

The ^{31}P NMR spectrum of **5** exhibits singlets at 17.8 ppm in 2-bromofluorobenzene and 19.0 ppm in DMSO. However, after several hours in DMSO the signal disappears and is replaced by that of $(HC\{PPh_3\}_2)^+$ at 20.6 ppm. The crystals dissolve slightly in THF but only the signal of the cation was detected in the ^{31}P NMR spectrum. The spectrum of **6** shows a ^{31}P NMR signal at 18.5 ppm in 2-bromofluorobenzene and only that of $(HC\{PPh_3\}_2)^+$ in DMSO. Thus, both compounds easily abstract protons similar to many main group addition compounds of **1**.

3. Crystal Structures

To gain an insight into the nature of the complexes and the bonding situation, X-ray analyses of **2**–**6** were performed. The structures of **2**, **4**, **5**, and **6** are shown in Figures 1–4; crystallographic data are collected in Table 5, and selected distances and angles are presented in Tables 1–4.

3.1 Crystal Structures of $(HC\{PPh_3\}_2)[MI_3(THF)]$ (M = Zn, 2; Cd, 3)

The structural parameters of the cations are close to those found in related salts based on the data from about 30 examples of $(HC\{PPh_3\}_2)X$ salts.[15,25] The molecular

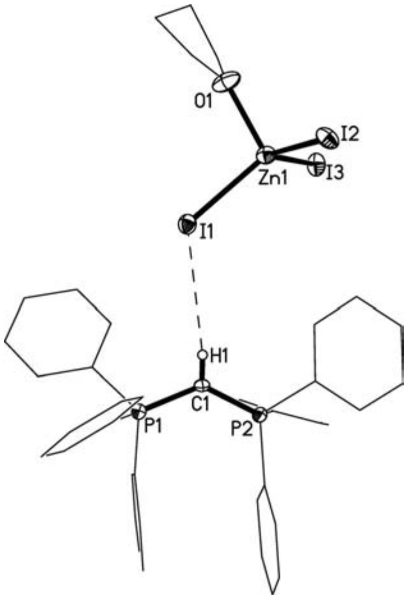


Figure 1. Molecular structure of **2** showing the atomic numbering scheme. Compound **3** is isostructural (Supporting Information). The ellipsoids are drawn at 40% probability. The phenyl groups and THF are represented as thin lines, and the H atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] of **2** and **3**.

M = Zn/Cd			
M(1)–O(1)	2.071(2)/2.314(2)	M(1)–I(3)	2.5589(4)/2.7247(3)
M(1)–I(2)	2.5649(5)/2.7263(3)	M(1)–I(1)	2.5830(4)/2.7384(3)
C(1)–P(2)	1.692(3)/1.699(2)	C(1)–P(1)	1.706(3)/1.703(3)
C(1)–H(1)	0.077(4)/0.081(3)	P(1)–C(2)	1.796(3)/1.801(2)
P(1)–C(8)	1.811(3)/1.807(2)	P(1)–C(14)	1.814(3)/1.817(2)
P(2)–C(20)	1.805(3)/1.807(2)	P(2)–C(26)	1.803(3)/1.804(2)
P(2)–C(32)	1.813(3)/1.817(2)		
O(1)–M(1)–I(3)	102.37(6)/99.17(4)	O(1)–M(1)–I(2)	103.73(8)/107.28(5)
I(3)–M(1)–I(2)	115.59(2)/115.341(9)	O(1)–M(1)–I(1)	103.04(8)/99.08(5)
I(3)–M(1)–I(1)	114.81(2)/119.890(9)	I(2)–M(1)–I(1)	114.78(2)/112.625(9)
P(1)–C(1)–P(2)	130.2(2)/128.0(2)		

structure of **2** is depicted in Figure 1. The cations and anions are connected by hydrogen bridges with C(1)–I(1) distances of 4.087(2) Å in **2** and 4.149(3) Å in **3**, which cause the related M–I(1) bond lengths to be slightly elongated relative to the two other M–I bonds (Table 1). No uncoordinated solvent molecules are incorporated in the unit cell. The central transition metals of the anions are in a distorted tetrahedral environment with small O–M–I and large I–M–I angles. To the best of our knowledge, only two other compounds with the anions $[MI_3(THF)]^-$ (M = Zn, Cd) have been reported to date in $[(THF)_5NdI_2][MI_3(THF)]$; here, the anions have no contacts to the cations leading to more balanced M–I distances.[26] The molecular structure of **3** can be found in the Supporting Information.

3.2 Crystal Structure of $(HC\{PPh_3\}_2)_2[ZnI_4]$ (4)

The molecular structure of **4** is shown in Figure 2. There are no remarkable contacts between the ions. The anions are stacked along [001] and the gaps are filled by the cations; the unit cell is shown in Figure 3. The mean Zn–I bond length is 2.6356(9) Å, which is appreciably longer than that in **2** (Table 2). Only one of the six I–Zn–I angles corresponds to the ideal tetrahedral angle of 109.5°; the angles range between 107° and 112°.

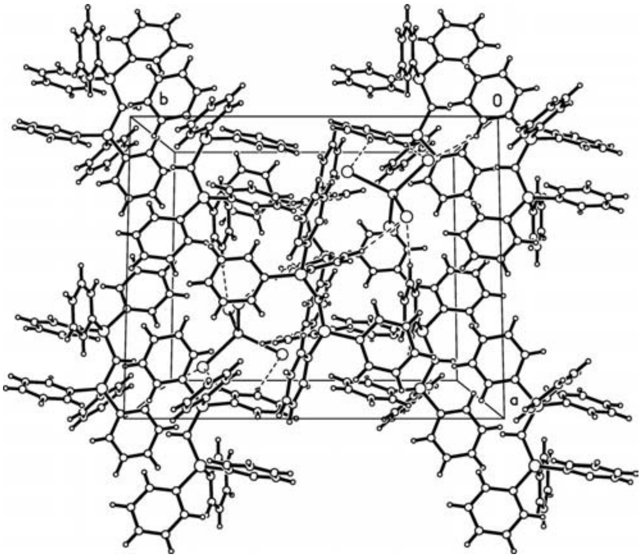


Figure 3. Unit cell of **4** viewed down [001].

3.3 Crystal Structure of $[I_2Zn\{C(PPh_3)_2\}]$ (5)

Complex **5** crystallizes with two independent molecules in the unit cell, not including solvent molecules, and the structure of one molecule is shown in Figure 4. Compound **5** represents a rare example of three-coordination at the Zn

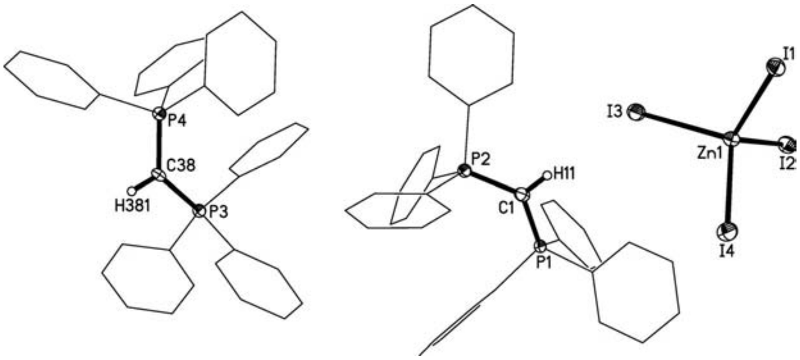


Figure 2. Molecular structure of **4** showing the atomic numbering scheme. The ellipsoids are drawn at 40% probability. The phenyl groups are represented as thin lines, and the H atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of **4**.

Zn(1)–I(4)	2.6278(9)	Zn(1)–I(3)	2.6365(8)
Zn(1)–I(2)	2.6328(9)	Zn(1)–I(1)	2.6452(8)
C(1)–P(2)/C(38)–P(4)	1.716(6)/1.701(7)	C(1)–P(1)/C(38)–P(3)	1.700(6)/1.709(7)
C(1)–H(11)/C(38)–H(381)	0.95/ 0.95	P(1)–C(2)/P(3)–C(39)	1.809(6)/1.807(6)
P(1)–C(8)/P(3)–C(45)	1.811(8)/1.808(7)	P(1)–C(14)/P(3)–C(51)	1.792(6)/1.807(6)
P(2)–C(20)/P(4)–C(57)	1.815(6)/1.826(7)	P(2)–C(26)/P(4)–C(63)	1.812(7)/1.811(7)
P(2)–C(32)/P(4)–C(69)	1.804(7)/1.809(7)		
I(4)–Zn(1)–I(2)	112.14(3)	I(4)–Zn(1)–I(3)	109.56(3)
I(2)–Zn(1)–I(3)	106.87(3)	I(4)–Zn(1)–I(1)	106.62(3)
I(2)–Zn(1)–I(1)	110.30(3)	I(3)–Zn(1)–I(1)	111.40(3)
P(1)–C(1)–P(2)/P(3)–C(38)–P(4)	128.9(4)/127.7(5)		

atom; the bulky phenyl groups of the ligand and the small ionic radius of Zn^{2+} (0.74 Å) prevent dimerization. The Zn atom and the coordinating C(1) atom are in planar environments, which indicates *sp*^{2} hybridization; the I_2Zn and P_2C planes form a dihedral angle of 67°. The large angle is probably caused by steric repulsion between the iodine atoms and the phenyl rings. The Zn–C(1) bond length (Table 3) is appreciably shorter than that in most of the addition compounds between Zn^{2+} species and various NHCs[24] and slightly longer than that in the dimeric ArZnI complex [Ar = 2,6-bis(2,6-diisopropylphenyl)phenyl].[27]

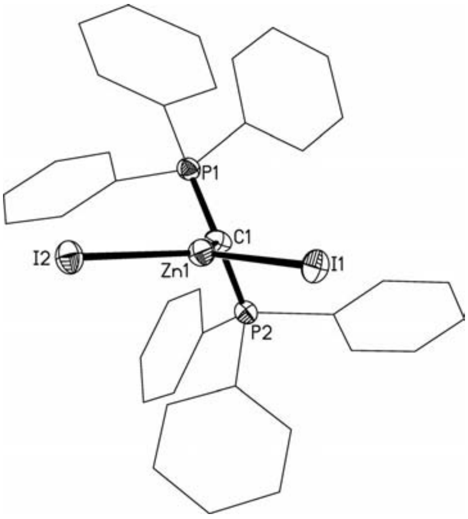


Figure 4. Molecular structure of **5** showing the atomic numbering scheme. The ellipsoids are drawn at 40% probability. The phenyl groups are represented as thin lines, and the H atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] of one independent molecule of **5**.

Zn(1)–C(1)	2.000(9)	Zn(1)–I(1)	2.577(1)
Zn(1)–I(2)	2.556(1)	C(1)–P(1)	1.691(9)
C(1)–P(2)	1.703(8)		
P(1)–C(1)–P(2)	128.3(6)	C(1)–Zn(1)–I(1)	121.0(2)
C(1)–Zn(1)–I(2)	123.9(2)	I(2)–Zn(1)–I(1)	115.16(5)
P(1)–C(1)–Zn(1)	116.7(4)	P(2)–C(1)–Zn(1)	113.9(4)

3.4 Crystal Structure of [({Ph_3P}$_2$C)CdI(μ-I)$_2$ICd(C{PPh_3}$_2$)]·2(1-Br-2-F-C_6H_4) (6)

The molecular structure of **6** is depicted in Figure 5. In contrast to **5**, **6** consists of two $I_2Cd \leftarrow$**1** units linked by two bridging iodine atoms. Two molecules of the solvent are included in the unit cell but have no near contacts to the centrosymmetric dimer. The larger ionic radius of cadmium (0.92 Å) allows a dimeric arrangement, such that the favored coordination number of four is achieved with 18 electrons for the Cd ion. The plane of the four membered Cd_2I_2 ring forms an angle of 95° with the P(1)–C(1)–P(2) plane. A distorted tetrahedral environment with angles ranging between 91° and 120° for the Cd ion is recorded; the smallest being the I–Cd–I angle in the four membered ring.

For C(1), *sp*^{2} hybridization is achieved but the sum of the angles amounts to 357.6(6), indicating slight pyramidalization; the C atom is located about 0.16 Å out of the P(1)–Cd–P(2) plane. The Cd(1)–C(1) bond length is larger [2.25(1) Å, Table 4] than that in the dimeric ArCdI complex [2.15 Å; Ar = 2,6-bis(2,6-diisopropylphenyl)phenyl].[27]

4. Conclusion and Outlook

Linearly dicoordinated complexes with carbones are represented by a few examples based on Cu^+, Ag^+, and Hg^{2+} exclusively with **1** as a ligand to date. Extending the series to include Zn^{2+} and Cd^{2+} could not be realized. During our experiments with Lewis acid adducts of **1**, we have frequently observed that reactions with solvents such as THF, DME, DMSO, and halogenated hydrocarbons occur with transformation of H^+ to **1** to produce $(HC\{PPh_3\}_2)^+$ or $(H_2C\{PPh_3\}_2)^{2+}$ especially with main-group Lewis acids. The first and second group 12 iodides follow this route in THF and DMSO solution. The use of 2-bromofluorobenzene as the solvent apparently combines some polarity with the lack of proton abstraction ability, which enables the isolation of **5** and **6**. However, dissolution of **5** and **6** in DMSO generates $(HC\{PPh_3\}_2)^+$ as shown by ^{31}P NMR spectroscopy.

As an alternative to the *sp*^{2}-hybridized carbon atom shown in **A** (Scheme 2) and an electron pair of π symmetry, pyramidalization to give a σ-type electron pair may occur as shown in **B** (Scheme 2); this means that the occupied *p* orbital gains some *sp* contribution. The resulting **B** form is probably more basic and able to abstract a proton from an appropriate solvent such as THF. A bent array as shown in **B** apparently plays a role in compounds where **M** represents group 12 (Hg) and group 13 (BH_3) Lewis acids, and slight pyramidalization at the related carbon atoms was recorded, similar to **6**. It is interesting to note that the pyramidalized

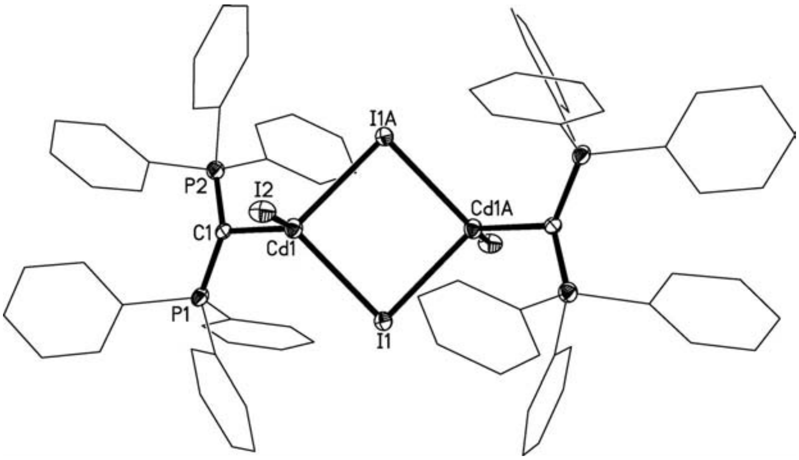


Figure 5. Molecular structure of **6** showing the atomic numbering scheme. The ellipsoids are drawn at 40 % probability. The phenyl groups are represented as thin lines, and the H atoms are omitted for clarity.

Table 4. Selected bond lengths [Å] and angles [°] of **6**.

Cd(1)–C(1)	2.25(1)	Cd(1)–I(1)	2.886(1)
Cd(1)–I(1A)	2.924(1)	Cd(1)–I(2)	2.782(1)
C(1)–P(1)	1.700(9)	C(1)–P(2)	1.68(1)
P(1)–C(1)–P(2)	124.8(7)	C(1)–Cd(1)–I(1)	117.1(2)
C(1)–Cd(1)–I(2)	120.7(2)	I(2)–Cd(1)–I(1)	106.26(4)
C(1)–Cd(1)–I(1A)	116.0(3)	I(2)–Cd(1)–I(1A)	100.80(3)
I(1)–Cd(1)–I(1A)	91.11(3)	Cd(1)–I(1)–Cd(1A)	88.89(3)
P(2)–C(1)–P(1)	124.8(7)	P(2)–C(1)–Cd(1)	115.1(5)
P(1)–C(1)–Cd(1)	117.7(6)		

HOMO *p* orbital in **6** is in the plane with the terminal Cd–I(2) bond, which the P atoms are bent away from. For the addition compound $\mathbf{1}\leftarrow BH_3$, pyramidalization has been predicted theoretically,[28] which means that this phenomenon is electronic rather than steric in origin.

Scheme 2. Possible coordination modes of carbones with Lewis acids (**M**).

One reason for the different behavior of group 12 ions may be that the Hg–C bond is more covalent, which prevents proton abstraction from the solvent. The shape of **5** is of the $X_2E\leftarrow\mathbf{1}$-type and resembles that of the addition compounds $[(CO)_2Ni\leftarrow\mathbf{1}]$,[4] $[S_2C\leftarrow\mathbf{1}]$, and $[O_2C\leftarrow\mathbf{1}]$.[29] To date, Lewis acids **M** have been found to be of the types XE, X_2E, and X_3E. For the following $X_2E\leftarrow\mathbf{1}$ compounds the bonding parameters, mean P–C bond length and dihedral angles [Å/°] have been recorded: ZnI_2, 1.697(8)/67; $Ni(CO)_2$, 1.677(3)/9; CS_2, 1.751(2)/20; CO_2, 1.723(3)/10.

For electron deficient $X_2E\leftarrow\mathbf{1}$ compounds with X = halogen, dimerization is optional to attain electron saturation. In going from Zn^{2+} in **5** to Cd^{2+} in **6**, this step is achieved by the increase of the ionic radius by 0.18 Å (and increase of the M–C bond length by 0.25 Å), which allows the steric repulsion to be minimized.

Does a partial double bond between Zn and the carbon atom in **5** exist? In this arrangement the three-coordinate Zn atom has only 16 valence electrons as in $[(CO)_2Ni\leftarrow\mathbf{1}]$. However, the relatively short P–C bond length of about 1.700 Å is indicative of a single bond, and the doubly occupied *p* orbital at the carbon atom is mainly involved in some $P–C_{Ph}$ σ^* negative hyperconjugation. Long P–C bonds and additionally increased C–C double bond character were found in the related CS_2 and CO_2 addition compounds, where π donation into the vacant *p* orbital at the carbon atoms seems reliable. A C–Re double bond is proposed in the cation $[O_3Re\leftarrow\mathbf{1}]^+$ where the mean P–C bond length is 1.771 Å;[5] for comparison, the mean P–C bond lengths in other $X_3E\leftarrow\mathbf{1}$ adducts are in the range between 1.685 and 1.718 Å, similar to those in **5** and **6**, indicating single bonds.

Experimental Section

General: All operations were carried out under an argon atmosphere in dry 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. Elemental analyses were performed by the analytical service of our department. ^{31}P NMR spectra were measured with a Bruker AC 300 instrument. Compound **1** was prepared according to a modified literature procedure.[30] Commercially available ZnI_2 and CdI_2 were dried in vacuo prior to use. 2-Bromofluorobenzene from ACROS was dried with P_2O_5.

$(HC\{PPh_3\}_2)[MI_3(THF)]$ (M = Zn, 2; Cd, 3): A mixture of **1** (0.27 g, 0.50 mmol) and CdI_2 (0.27 g, 0.75 mol) in THF (4 mL) was treated for 10 min in an ultrasonic bath. The clear solution was separated from small amounts of precipitate by filtration. The ^{31}P NMR spectrum of the solution showed two signals at 20.6 and 17.0 ppm in a 1:0.3 ratio. The signal at 20.6 ppm was assigned to $[H\leftarrow\mathbf{1}]^+$. Layering with *n*-pentane produced large colorless crystals of **3**. IR (Nujol mull): ṽ = 1586 (w), 1480 (m), 1435 (s), 1337 (w), 1312 (w), 1213 (s), 1181 (s), 1161 (w), 1099 (s), 1074 (m), 1036 (m), 1028 (m), 1007 (m), 988 (s), 877 (m), 808 (m), 760 (m), 747 (s), 719 (s), 692 (s), 557 (s), 529 (s), 515 (s), 500 (s), 488 (m) cm^{-1}.

A similar procedure with **1** (0.30 g, 0.56 mmol) and ZnI_2 (0.27 g, 0.84 mmol) in THF (ca. 4 mL) gave a pale yellow solution. The ^{31}P

NMR spectrum of the solution showed a singlet at 20.6 ppm due to the formation of $[\mathrm{H}\leftarrow\mathbf{1}]^+$. The work up procedure gave colorless crystals of **2** in high yield. IR (Nujol mull): ṽ = 1586 (w), 1480 (m), 1435 (s), 1339 (w), 1314 (w), 1213 (s), 1181 (s), 1161 (w), 1099 (s), 1074 (m), 1028 (m), 1007 (m), 986 (s), 874 (m), 808 (m), 760 (m), 747 (s), 720 (s), 696 (s), 557 (s), 530 (s), 515 (s), 498 (s), 488 (m) $\mathrm{cm^{-1}}$.

When the reaction was carried out in DME, a colorless precipitate formed. The supernatant solution showed two signals at 21.2 and 20.8 ppm in a 1:0.4 ratio. The IR spectrum of the precipitate is identical to that of **3** from THF.

$(\mathrm{HC\{PPh_3\}_2})_2[\mathrm{ZnI_4}]$ (4): The reaction described above was also carried out in toluene resulting in the formation of insoluble material. IR (Nujol mull): ṽ = 1588 (w), 1481 (m), 1437 (s), 1333 (w), 1310 (w), 1233 (w), 1184 (w), 1159 (w), 1123 (vs), 1099 (vs), 1090 (m), 1071 (w), 1026 (w), 1010 (w), 997 (m), 990 (m), 812 (s), 799 (s), 741 (vs), 714 (vs), 692 (vs), 530 (vs), 522 (s), 517 (s), 500 (s) $\mathrm{cm^{-1}}$.

$[\mathrm{I_2Zn\{C(PPh_3)_2\}}]$ (5): A mixture of **1** (0.20 g, 0.34 mmol) and $\mathrm{ZnI_2}$ (0.12 g, 0.37 mmol) in 2-bromofluorobenzene (2 mL) was treated in an ultrasonic bath for about 5 min. The resulting suspension was heated for about 2 min, and a clear tan solution was obtained from which colorless crystals of **5** separated upon cooling to room temperature in about 70% yield. ^{31}P NMR (2-bromofluorobenzene): δ = 17.8 (s) ppm. IR (Nujol mull): ṽ = 1481 (s), 1135 (s), 1310 (m), 1261 (w), 1237 (w), 1184 (m), 1122 (s), 1026 (m), 997 (m), 812 (s), 798 (s), 741 (s), 714 (s), 693 (s), 576 (w), 530 (s), 500 (s), 450 (w) $\mathrm{cm^{-1}}$. $\mathrm{C_{37}H_{30}I_2P_2Zn}$ (855.73): calcd. C 51.93, H 3.53; found C 51.88, H 3.54.

$[(\{\mathrm{Ph_3P}\}_2\mathrm{C})\mathrm{CdI}(\mu\text{-}\mathrm{I})_2\mathrm{ICd}(\mathrm{C}\{\mathrm{PPh_3}\}_2)]\cdot2(1\text{-Br-}2\text{-F-}\mathrm{C_6H_4})$ (6): In a similar procedure to that described for **5**, a mixture of **1** (0.17 g, 0.32 mmol) and $\mathrm{CdI_2}$ (0.13 g, 0.37 mmol) was reacted in 2-bromofluorobenzene (2 mL). No crystals formed upon cooling the clear tan-colored solution to room temperature. Layering the solution with *n*-pentane gave colorless crystals of **6** in about 80% yield. ^{31}P NMR (2-bromofluorobenzene): δ = 18.5 (s) ppm. IR (Nujol mull): ṽ = 1478 (s), 1136 (s), 1310 (w), 1262 (w), 1236 (w), 1104 (vs), 1081 (s), 1026 (m), 997 (m), 793 (s), 750 (s), 713 (s), 694 (s), 654 (w), 564 (w), 526 (s), 501 (s) $\mathrm{cm^{-1}}$. $\mathrm{C_{86}H_{68}Br_2Cd_2F_2I_4P_4}$ (2155.50): calcd. C 47.92, H 3.18; found C 47.02, H 3.21%.

For details on the X-ray crystal structure determinations see Table 5.

CCDC-793477 (for **2**), -793478 (for **3**), -827706 (for **4**), -827707 (for **5**), and -827708 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from

Table 5. Crystal data for **2**–**6**.

	2	**3**	**4**	**5**	**6**
Formula	$\mathrm{C_{41}H_{39}I_3OP_2Zn}$	$\mathrm{C_{41}H_{39}CdI_3OP_2}$	$\mathrm{C_{74}H_{62}I_4P_4Zn}$	$\mathrm{C_{37}H_{30}I_2P_2Zn}$	$\mathrm{C_{86}H_{68}Br_2Cd_2F_2I_4P_4}$
MW	1055.73	1102.76	1648.09	855.72	2155.5
Crystal system	monoclinic				
Space group	*I*2/*a* (No. 15)	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*n* (No. 14)	*Cc* (No. 9)	*P*2$_1$/*n* (No. 14)
a [Å]	31.825(1)	17.138(1)	14.077(1)	11.013(1)	11.051(1)
b [Å]	10.221(1)	14.526(1)	16.945(1)	18.077(1)	17.221(1)
c [Å]	25.157(1)	18.064(1)	28.707(1)	34.213(2)	21.031(1)
α [°]	90	90	90	90	90
β [°]	94.05(1)	116.98(1)	102.34(1)	97.78(1)	100.21(1)
γ [°]	90	90	90	90	90
Volume [Å^3]	8162.7(9)	4007.5(4)	6689.4(7)	6748.5(8)	3939.0(5)
Z	8	4	4	8	2
$d_{\mathrm{calcd.}}$ [g cm^{-3}]	1.718	1.828	1.636	1.684	1.817
Temperature [K]	100	100	100	100	100
μ [cm^{-1}]	29.79	29.66	23.51	26.77	32.52
$2\theta_{\max}$ [°]	51.90	51.84	56.84	51.82	51.92
Radiation	Mo-K_α				
Diffractometer	IPDS II (Stoe)				
Crystal size [mm]	0.17 × 0.16 × 0.07	0.25 × 0.21 × 0.16	0.11 × 0.11 × 0.06	0.14 × 0.11 × 0.05	0.17 × 0.04 × 0.03
Index range	$-39 \geq h \geq 39$ $-12 \geq k \geq 12$ $-30 \geq l \geq 30$	$-14 \geq h \geq 14$ $-17 \geq k \geq 17$ $-25 \geq l \geq 25$	$-18 \geq h \geq 18$ $-19 \geq k \geq 22$ $-25 \geq l \geq 28$	$-10 \geq h \geq 13$ $-22 \geq k \geq 19$ $-41 \geq l \geq 41$	$-13 \geq h \geq 13$ $-19 \geq k \geq 21$ $-20 \geq l \geq 25$
Reflections collected	56241	55737	35348	13549	16077
Independent reflections (R_{int})	7941 (0.0559)	7798 (0.0411)	16625 (0.1132)	10624 (0.0412)	7569 (0.095)
Observed reflections [$F_o > 4\sigma(F_o)$]	5782	6059	6839	6541	3018
Refinement against F^2	SHELXL-97[31]				
Parameters	438	438	749	758	452
Structure solution	Patterson method, SHELXTL-Plus [32]	direct methods, SHELXS-97[33]	direct methods, Sir-92 [34]	direct methods, SHELXS-97[33]	direct methods, Sir-92[34]
H atoms	calculated positions with common displacement parameter; H(1) was refined freely			calculated positions with common displacement parameter	
Flack parameter	–	–	–	0.09(2)	–
R_1	0.0234	0.0176	0.0444	0.0285	0.0477
wR_2 (all data)	0.0425	0.0329	0.0724	0.0443	0.0896
Max. resid. electron density [e Å^{-3}]	0.665	0.698	0.94	0.392	1.066

The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Molecular structure of $(HC\{PPh_3\}_2)[CdI_3(THF)]$ (**3**).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. W. P. is also grateful to the Max Planck Society, Munich, Germany for supporting this research project.

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Received: June 24, 2011