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Reaction of $(PPh_3)_2C{\rightarrow}CO_2$ with Halogenated Hydrocarbons; Formation and Crystal Structure of a Cationic Ester with 1,2-Dichloroethane

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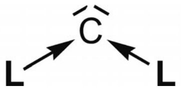
Abstract. The carbodiphosphorane CO_2 adduct (**2**) reacts slowly with 1,2-dichloroethane to give $(HC\{PPh_3\}_2)Cl$ (**5**) as result of HCl abstraction along with the ester-like salt $(ClCH_2CH_2O(O)CC\{PPh_3\}_2)Cl$ (**4**) from nucleophilic substitution of one Cl^- by **2**. Both compounds could be separated by fractional crystallization. Attempts to dissolve **2** in 1,2-difluorobenzene leads to small amounts of the hydrolysis product $(HC\{PPh_3\}_2)(HCO_3){\cdot}H_2O$ (**6**$\cdot H_2O$) caused by some humidity in the solvent. All compounds could be crystallized and the structures studied by X-ray analyses and ^{31}P NMR spectroscopy.

1 Introduction

It has recently been shown that the bonding situation in the double ylide hexaphenylcarbodiphosphorane $C(PPh_3)_2$ (**1**),[1] which has a bent equilibrium geometry[2] is best described in terms of donor-acceptor interactions between two phosphane ligands and a bare carbon(0) atom. For those compounds of the general type $\mathbf{CL}_2$ the term carbones has been suggested, in which **L** is represented by various neutral electron donor molecules.[3]



Due to the presence of two electron lone pairs (HOMO and HOMO-1) carbones have first and second proton affinities,[4] which are very large for **1**. Carbones exhibit a chemical behavior that is distinctively different from carbenes such as NHC's, which have only one lone pair at a carbon(II) atom.[5] Compound **1** reacts with the electron poor heterocumulene CO_2 to give the betain **2** as shown in Equation (1).[6] The molecular structure of **2** was established by X-ray analysis by us recently.[7]

$$1 + CO_2 \rightarrow (PPh_3)_2C{\rightarrow}CO_2\ (\mathbf{2}) \qquad (1)$$

Similar adducts are formed with CS_2 and COS. Compound **2** can act as a monodentate or as a chelating ligand towards transition metal[8] or main group Lewis acids[9] via the two oxygen atoms;[10,11] coordination of both oxygen atoms each at different beryllium atoms was also achieved.[12] During attempts to study the chemistry of **2** with several Lewis acids we found that the betain is insoluble in benzene, toluene, and other non polar hydrocarbons but is not stable in solutions of halogenated hydrocarbons. Upon reacting of **2** with Lewis acids in these solvents proton abstraction and loss of CO_2 was observed with formation of the cation $(HC\{PPh_3\}_2)^+$ either as main product or as byproduct of the desired addition compound.

Herein we report on the behavior of **2** in various halogenated hydrocarbons and the formation and the X-ray structure of a cationic ester-like compound upon reacting **2** with 1,2-dichloroethane.

2 Results and Discussion

In an earlier report the alkylation of **2** with MeI was described with result of the cationic compound $(\{PPh_3\}_2C{\rightarrow}C(O)OMe)I$ (**3**), which was characterized by IR and ^{31}P NMR spectroscopy.[13] Further ester-like compounds of the type $(\{PPh_3\}_2C{\rightarrow}C(O)OR)X$ were not reported so far.

The ^{31}P NMR spectrum of a freshly prepared solution of **2** in DCM exhibits two singlet at δ = 13.50 and 19.04 ppm in a 1:008 ratio, which were assigned to **2** and the cation $(HC\{PPh_3\}_2)^+$, respectively. On standing of the probe at room temperature under exclusion of air the ratio has changed to 1:0.24 after 6 h and to 1:3.4 after 4 h; after one day standing the signal of **2** has disappeared.

If **2** was dissolved in 1,2-dichloroethane a clear solution was obtained. The ^{31}P NMR spectrum after 1 h showed three singlet signals at δ = 20.8, 19.9, and 14.3 ppm in a 0.2:0.4:1 ratio, respectively. After 3 h the ratios changed to 0.6:0.9:1 ratio. 22 h later the initial signal of **2** at δ = 14.3 ppm has disappeared in favor of a 1:1 ratio of the signals at δ = 20.8 and 19.9 ppm.

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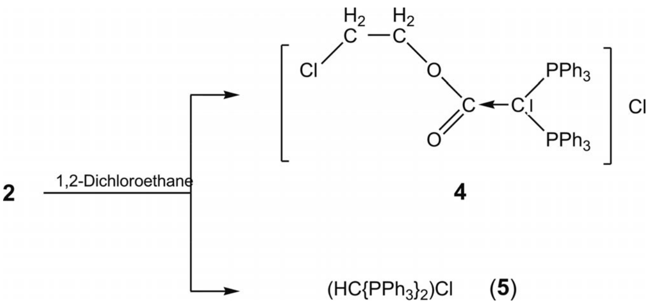
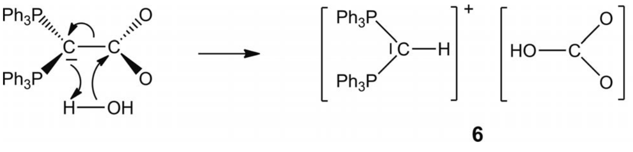
The NMR signals were assigned to $(ClCH_2CH_2O(O)CC\{PPh_3\}_2)Cl$ (**4**) and $(HC\{PPh_3\}_2)Cl$ (**5**), respectively. Layering the solution with *n*-pentane generated two sorts of crystalline materials. On fractional crystallization the first part of crystals turned out to be **5**. Further colorless crystals of **4**$\cdot 2C_2H_4Cl_2$ were obtained as the result of a nucleophilic substitution of one chlorine atom by the oxygen atom of the betain **2**. If **4** was dissolved in DCM the signal of **4** slowly disappeared in favor of the signal of **5**; no alkylation with DCM was observed (Scheme 1).



Scheme 1. Reaction of **2** in 1,2-dichloroethane to give **4** and **5**.

In the IR spectrum of **4** a strong band at 1670 cm^{-1} was found, which was assigned to the ν(CO) vibration of the free carbonyl function; a further strong band at 1230 cm^{-1} may be attributed to the vibration of the C–O–C group. A comparison with typical organic esters shows that the carbonyl vibration of **4** has shifted to lower frequencies; ester carbonyl groups absorb in a narrow range between 1735 and 1770 cm^{-1}.[14] A similar cationic ester was obtained from alkylation of the betain NHC→CO$_2$; the ν(CO) vibration of $(NHC\rightarrow C(O)OEt)^+$ amounts to 1745 cm^{-1}[15] being in the range of organic esters. The shift to lower frequency in **4** can be explained with a higher π electron density at the carboxylate carbon atom due to some π donation from the occupied p orbital of the **CL**$_2$ carbon atom.

Attempts to dissolve **2** in 1,2-difluorobenzene gave a suspension. Compound **2** is nearly insoluble in this solvent, but the ^{31}P NMR spectrum of the supernatant solution showed a singlet at δ = 20.0 ppm. Filtration after several hours stirring at room temperature and layering of the solution with *n*-pentane gave colorless crystals, which turned out to be the hydrogen carbonate $(HC\{PPh_3\}_2)(HCO_3)\cdot H_2O$ (**6**$\cdot H_2O$). The formation of the hydrogen carbonate can be explained with a not completely dried 1,2-difluorobenzene causing part of **2** to hydrolyze by traces of water to give **6**. The additional free pair of electrons at the carbon atom of **2** is basic enough to attract a proton, which weakens the C–C bond. Subsequent nucleophilic attack of OH$^-$ at the CO$_2$ carbon atom finally leads to splitting of the C–C bond and formation of the salt **6**; an intermediate protonated version of **2** could not be found (Scheme 2).



Scheme 2. Proposed mechanism of the hydrolysis of **2**.

3 Crystal Structure Determination

Crystals suitable for X-ray analyses were obtained from **4**$\cdot 2C_2H_4Cl_2$, **5**, and **6**$\cdot H_2O$. Crystallographic details were summarized in Table 1. Molecular structures of **4** and **6** are shown in Figure 1 and Figure 2, respectively; the molecular structure of **5** is presented as Supporting Information (Figure S1). In **4**$\cdot 2C_2H_4Cl_2$ the solvent molecules were strongly disordered. The residual electron density of these molecules was omitted with SQUEEZE.[16]

3.1 Molecular Structure of 4·2C$_2$H$_4$Cl$_2$

The molecular structure of **4**$\cdot 2C_2H_4Cl_2$ is depicted in Figure 1. The environments at C(1) and C(2) are exactly planar indicating sp^2 hybridization of the carbon atoms. No contacts exist to the Cl$^-$ ion or to the disordered solvent molecules. The C(1)–C(2) bond length has decreased from 1.494(3) in **2** to 1.459(4) in **4** indicating a slight increase in double bond character upon alkylation. The cation of **4** can be compared with organic esters and with the neutral compounds $[Cl_2SnO(O)CC\{PPh_3\}_2]$ (**7**)[9] and $[(CO)_5WO(O)CC\{PPh_3\}_2]$ (**8**),[8] in which $ClCH_2CH_2^+$ are replaced by SnCl$_2$ and W(CO)$_5$, respectively. The planes OCO and PCP form a dihedral angle of 29° which is larger than the related angle in **2** (10°) or even in **7** (13°) and **8** (9°). Similar as in **4** the two C–O bond lengths are different and the longer one belongs to the coordinating CO function [**7**: 1.251(7)/1.297(7), Δ = 0.046; **8**: 1.241(6)/1.290(6), Δ = 0.049; **4**: 1.221(5)/1.363(5), Δ = 0.142 Å) and the largest difference Δ of C–O bond lengths is recorded for **4**. The related pairs of bond length in typical esters are 1.202/1.333 Å; both values are slightly shorter than those in **4**. The elongated CO bond in **4** corresponds to the low ν(CO) vibration found by IR spectroscopic studies.

3.2 Molecular Structure of (HC{PPh$_3$}$_2$)(HCO$_3$)·H$_2$O (6·H$_2$O)

The molecular structure of **6**$\cdot H_2O$ is depicted in Figure 2. The unit cell of the salt contains a centrosymmetric dimer of **6**$\cdot H_2O$. Two HCO$_3^-$ anions are linked by O–H···O bridges forming a planar eight-membered ring. As expected three different C–O bond lengths are found in the dimeric anion. The unbridged C–O bond lengths amounts to 1.233(3) Å and is about 0.12 Å shorter than the C–O–H bond and about 0.04 Å shorter than the C–O····H bond. No contacts to the cation exist and its parameters are close to those of the cation of **5**. The bridged oxygen atoms are separated by 2.664(2) Å. Further OH bridges exist to water molecules with O···O separations of 2.904(2) and 2.896(2) Å. A similar dimeric structure was found in the salt $(C\{NMe_2\}_3)(HCO_3)$. The related $(HCO_3)_2^{2-}$ unit has no further contacts and the corresponding bridged C–O bond lengths are about 0.01 Å shorter than those in **6**$\cdot H_2O$ [17].

Table 1. Crystallographic data of $(ClCH_2CH_2O(O)CC\{PPh_3\}_2)Cl{\cdot}2C_2H_4Cl_2$ (**4**$\cdot 2C_2H_4Cl_2$), $(HC\{PPh_3\}_2)Cl$ (**5**), and $(HC\{PPh_3\}_2)(HCO_3){\cdot}H_2O$ (**6**$\cdot H_2O$).

	4$\cdot 2C_2H_4Cl_2$	$(HC\{PPh_3\}_2)Cl$ (**5**)	**6**$\cdot H_2O$
Formula	$C_{44}H_{42}Cl_6O_2P_2$	$C_{37}H_{31}ClP_2$	$C_{38}H_{34}O_4P_2$
Mw /g·mol^{-1})	877.48	573.05	616.63
a /Å	20.577(1)	9.470(1)	13.594(1)
b /Å	9.749(1)	19.070(2)	16.642(1)
c /Å	40.326(2)	16.942(2)	14.934(1)
a /°	90	90	90
β /°	93.04(1)	102.88(1)	112.27(1)
γ /°	90	90	90
Crystal size /mm	$0.23 \times 0.18 \times 0.08$	$0.29 \times 0.27 \times 0.07$	$0.23 \times 0.19 \times 0.18$
Volume /Å^3	8078(1)	2982.6(6)	3126.5(1)
Z	8	4	4
d_{calc} /g·cm^{-3}	1.443	1.276	1.31
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$I2/a$ (Nr. 15)	$P2_1/n$ (Nr. 14)	$P2_1/n$ (Nr. 14)
Diffractometer	IPDS II (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Temperature /K	193	193	193
μ /cm^{-1}	5.4	2.6	1.8
$2\theta_{max}$ /°	52.43	52.53	52.55
Index range	$-25 \le h \le 25$ $-12 \le k \le 12$ $-50 \le l \le 50$	$-11 \le h \le 11$ $-23 \le k \le 23$ $-19 \le l \le 20$	$-16 \le h \le 16$ $-20 \le k \le 20$ $-18 \le l \le 18$
Number of rflns collected	57093	21440	44810
Number of indep. rflns (R_{int})	8079 (0.0892)	5890 (0.0989)	6282 (0.0656)
Number of observed rflns with $F_o > 4\sigma(F_o)$	5330	3482	4094
Parameters	417	366	411
Absorption correction	numerical	numerical	numerical
Structure solution	direct methods SHELXL-97[19]	direct methods SHELXS-97[20]	direct methods SHELXL-97[19]
Refinement against F^2	SHELXL-97[19]	SHELXL-97[19]	SHELXL-97[19]
Hydrogen atoms	calculated positions with common displacement parameter	calculated positions with common displacement parameter; H(1) was refined freely	calculated positions with common displacement parameter
R_1	0.0752	0.0523	0.034
wR_2 (all data)	0.2254	0.1069	0.077
Max. electron density left / e·Å^{-3}	0.54	0.19	0.52

4 Conclusions

The ester-like salt **4** is the first alkylation product of **2**, which could be confirmed by X-ray diffraction analysis. The related NHC addition compound with NHC→CO_2 was studied by X-ray analysis[15] but to the best of our knowledge no structural details of related ester-like $[NHC{\rightarrow}C(O)OR]^+$ compounds were reported so far. Addition compounds between the carbone **1** and Lewis acidic heteroallenes such as CO_2 in **2** can act as monodentate or chelating ligands towards various Lewis acids. Attempts to alkylate **2** led either to R^+ transfer to one oxygen atom or to proton abstraction with loss of CO_2 and formation of the cation $(HC\{PPh_3\}_2)^+$. This competition reaction will be explored more intensively during further studies. With 1,2-dichloroethane nucleophilic substitution of Cl^- to **4** and HCl abstraction to give **5** take place simultaneously. However, if **2** is dissolved in CH_2Cl_2 abstraction of HCl occurs and slow formation of the $(HC\{PPh_3\}_2)^+$ and no alkylation product [e.g. $ClCH_2O(O)CC\{PPh_3\}_2$] could be found. With $OSCC(PPh_3)_2$ and CH_2Cl_2 a similar pathway occurred and we could identify the olefin ClHC=CHCl by gas chromatographic studies; the olefin formed upon dimerization of the carbene CHCl after proton abstraction from DCM.[18]. A possible double alkylation of **2** to give the dication $[(RO)_2C{\leftarrow}C(PPh_3)_2]^{2+}$ could not be observed so far; a challenge for further studies.

5 Experimental Section

General: 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 (the Nujol mull bands are omitted). For the ^{31}P NMR spectra we used the instrument Bruker AC 300. The carbodiphosphorane $C(PPh_3)_2$ (**1**) was prepared according to a modified literature procedure.[21] **2** was obtained as colorless precipitate upon admitting CO_2 to a solution of **1** in toluene at room temperature.

Reaction of 2 with 1,2-Dichloroethane: Compound **2** (0.20 g, 0.34 mmol) was dissolved in 1,2-dichloroethane (about 2 mL). The reaction was monitored by ^{31}P NMR spectroscopy. After 1 h at room temperature signals at $\delta = 20.8$, 19.9, and 14.3 ppm in a 0.2:0.4:1 ratio, respectively, were found. After 3 h the ratios changed to 0.6:0.9:1 and after 22 h the signal of **2** at $\delta = 14.3$ ppm has disappeared in favor of the signals at $\delta = 20.8$ and 19.9 ppm in a 1:1 ratio. Layering of the

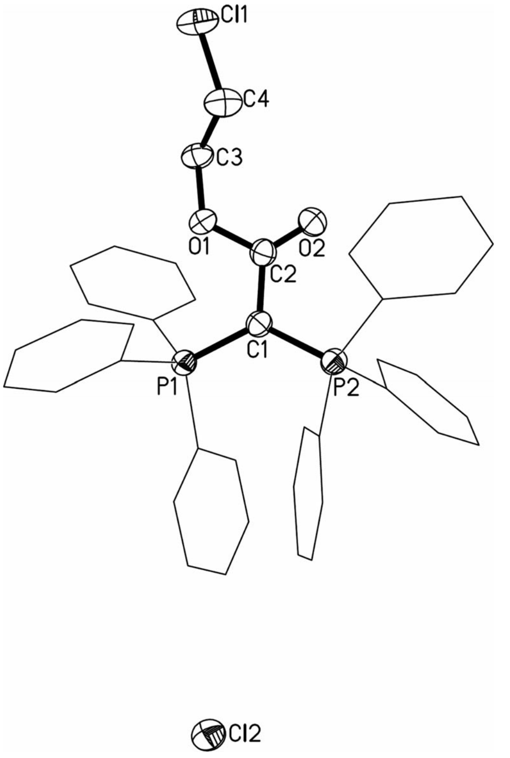


Figure 1. Molecular structure of $(ClCH_2CH_2O(O)CC\{PPh_3\}_2)Cl$ in $\mathbf{4}\cdot2C_2H_4Cl_2$ showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level and the phenyl rings are presented as thin lines. The hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: C(1)–C(2) 1.459(6), P(1)–C(1) 1.738(4), P(2)–C(1) 1.745(4), O(1)–C(2) 1.363(5), O(2)–C(2) 1.221(5), O(1)–C(3) 1.430(5), C(3)–C(4) 1.497(7), Cl(1)–C(4) 1.787 (5); P(1)–C(1)–P(2) 127.5(2), P(1)–C(1)–C(2) 116.9(3), P(2)–C(1)–C(2) 115.5(3), O(1)–C(2)–O(2) 121.6(4), O(1)–C(2)–C(1) 111.7(4), O(2)–C(2)–C(1) 126.7(4).

solution with *n*-pentane (0.5 mL) gave crystals of $(HC\{PPh_3\}_2)Cl$ (**5**). After removal of the crystals the solution showed only the signal at δ = 20.8 ppm in the ^{31}PNMR spectrum. New colorless crystals of $\mathbf{4}\cdot2C_2H_4Cl_2$ have grown after layering again with *n*-pentane. **^{31}P NMR** (in 1,2-dichloroethane): δ = 20.8 ppm. **IR** (Nujol mull): $\tilde{\nu}$ = 1671 vs, 1585 w, 1481 s, 1451 m, 1437 s, 1261 w, 1312 w, 1284 m, 1263 m, 1229 s, 1198 m, 1162 w, 1103 s. 1181 m, 1054 w, 997 m, 925 m, 879 w, 755 s, 745 s, 717 s, 699 s, 669 m, 650 m, 542 m, 526 s, 503 s, 437 w, 404 w cm^{-1}.

Formation of $\mathbf{6}\cdot\mathbf{H_2O}$: Compound **2** (0.24 g, 0.41 mmol) was suspended in *o*-difluorobenzene (about 2.5 mL) and the mixture was stirred for five days at room temperature and filtered. The IR spectrum of the residue was similar to that of **2**. The ^{31}P NMR of the solution showed a single signal at δ = 20.0 ppm. Layering of the solution with *n*-pentane caused separation of colorless crystals suitable for an X-ray analysis, which turned out to be $\mathbf{6}\cdot H_2O$. Traces of water in the solvent probably were responsible for the hydrolysis of **2**. Further experiments with more dried *o*-difluorobenzene showed that **2** is only slightly soluble in this solvent and a signal at δ = 13.4 ppm was obtained for **2**. After 4 h on standing in the NMR tube, the signal of **2** has diminished in favor of that of the cation $(HC\{PPh_3\}_2)^+$ (1:2 ratio). After three days only the signal of the cation was recorded.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-867347 ($\mathbf{4}\cdot2C_2H_4Cl_2$), CCDC-867348 (**5**), and CCDC-867349 ($\mathbf{6}\cdot H_2O$) (Fax: +44-1223-336-033; E-Mail: deposit@-ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Structural view and information on compound **5**.

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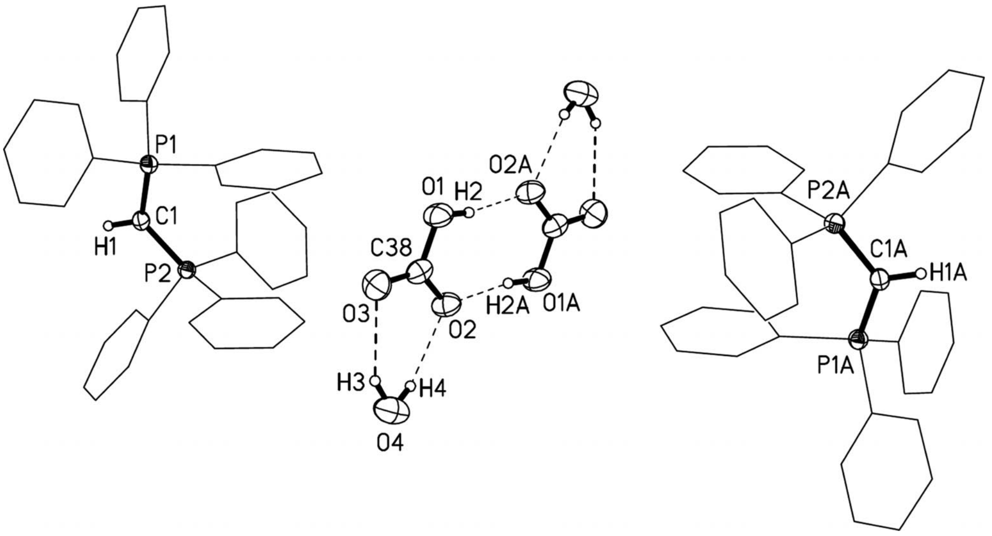

Figure 2. Molecular structure of the salt $(HC\{PPh_3\}_2)(HCO_3)\cdot H_2O$ ($\mathbf{6}\cdot H_2O$) showing the atomic numbering scheme. The ellipsoids are drawn at a 40 % probability level and the phenyl groups are represented as thin lines. Selected bond lengths /Å and angles /°: P(1)–C(1) 1.704(2), P(2)–C(1) 1.707(2), O(1)–C(38) 1.355(3), O(2)–C(38) 1.269(2), O(3)–C(38) 1.233(3), O(1)–H(2) 0.89(2); P(1)–C(1)–P(2) 128.9(1), O(1)–C(38)–O(2) 116.8(2), O(1)–C(38)–O(3) 117.1(2), O(2)–C(38)–O(3) 126.1(2).

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