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Authors: Nils Spang, Matthias Müller, and Magnus Richard Buchner

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The phosphonium ion $[Cy_3PCHCl_2]^+$: synthesis and properties

Nils Spang,[a] Matthias Müller,[a] and Magnus R. Buchner*[a]

Abstract: The synthetic pathway to the functional phosphonium cation $[Cy_3PCHCl_2]^+$ (**3**) has been evaluated *via in situ* ^{31}P NMR spectroscopy and mass spectrometry. The synthesis is only successful if $CCl_4/CHCl_3$ mixtures are used. A mechanism for the varying reactivity in different solvents is given as well as a for the observed equilibrium between ions $[Cy_3PCHCl_2]^+$ and $[Cy_3PCH_2Cl]^+$ (**12**). Through the anticipated hydrogen bonding interaction between $[Cy_3PCHCl_2]^+$ and the corresponding anion, crystal structures of the compounds $[Cy_3PCHCl_2]Cl \cdot 2CHCl_3$ (**3a**) and $[Cy_3PCHCl_2]_3[H_3O][H_5O_2]Cl_5 \cdot C_6D_6$ (**3b**) could be obtained and evaluated.

Introduction

Tetraphenyl phosphonium (**1**) (figure 1) is widely employed as a weakly coordinating cation.[1] Even though the weak interaction between the phosphonium ion and the investigated anion is generally desirable this has the drawback, that the anions are frequently disordered in the crystal lattice.[2] This problem is more severe with small anions. To facilitate ordered crystallization some interaction between cation and anion is necessary.[3] This has been achieved for example in pyridinium hexafluorotitanates,[4] imidazolium hexafluorophosphates,[5] diamidopyridinium phosphates[6] and cyclam salts[7] which all form cation-anion hydrogen bonds.[8] However most of these systems have the drawback, that they are only soluble in water or at least highly protic solvents. Therefore phosphonium cations are of interest, which bear three bulky organic groups to still facilitate solubility in organic solvents, but also have a group which is able to coordinate to the anion. Thus C-H-acidic groups like (di)chloro methylene, which can form hydrogen bonds with anions would be ideal. However there are only very little examples of such cations with $[Ph_3PCHCl_2]^+$ (**2**) being by far the most prominent.[9] Though this phosphonium salt is extremely C-H-acidic, which results in easy deprotonation with the subsequent formation of the phosphorus ylide. Hence cation **2** is exclusively used as substrate for *Wittig* reactions.[10] To reduce the C-H-acidity of the methylene group more electron donating substituents like tricyclohexyl are necessary at the phosphorus atom. However there are only two examples of tricyclohexylphosphonium ions.[11, 12] We therefore decided to establish a synthetic route to tricyclohexyl dichloromethyl phosphonium cation **3**. This cation would not only be an ideal cation to facilitate the ordered crystallization of small anions from organic media but should also be promising in phosphonium ion catalyzed reactions.[13]

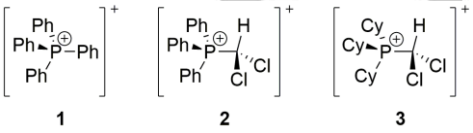

Figure 1. Tetraphenylphosphonium (**1**), triphenyl dichloromethyl phosphonium (**2**) and tricyclohexyl dichloromethyl phosphonium (**3**) cations.

Results and Discussion

Appel and *Huppertz* reported the synthesis of alkyl diphenyl dichloromethyl phosphonium salts from alkyl diphenylphosphines (**4**) in non-polar aprotic solvents. They describe, that the phosphine is converted to alkyl diphenyl trichloromethyl phosphonium chloride (**5**) by reaction with CCl_4. The salt **5** is subsequently attacked by free phosphine **4** to yield alkyl diphenyl dichloromethylene phosphoranes **6** and alkyl diphenyl chloro phosphonium chlorides **7**. Ylide **6** then deprotonates phosphonium salt **7** to produce the desired alkyl diphenyl dichloromethyl phosphonium salts **8** and diphenyl chloro ylides **9** and the latter rearranges to α-chloroalkyl diphenyl phosphine **10**.[14] This reaction cascade is summarized in scheme 1. In analogy to this synthesis we reacted tricyclohexylphosphine with CCl_4 in toluene following the conditions described by *Appel* and *Huppertz*. However we were neither able to isolate pure tricyclohexyl dichloromethyl phosphonium chloride (**3a**) nor an α-chloro tricyclohexylphosphine. Instead we observed the formation of salt **3a** together with tricyclohexyl dichloro phosphorane (**11**)[15] in the ^{31}P NMR spectrum of the reaction product.

Two column scheme, please see penultimate page of the document

Scheme 1. Reaction of *n*-propyl diphenylphosphine with CCl_4 in non-polar aprotic solvents described by *Appel* and *Huppertz*.[14]

It was unclear whether the different reactivities observed for PCy_3 and alkyl diphenylphosphines **4** were caused by the higher electron density at the phosphorus atom in the prior phosphine or through different solubilities. Therefore we reacted PCy_3 with CCl_4 in benzene (aprotic solvent without dipole moment), dichloromethane (aprotic solvent with dipole moment) and chloroform (protic). Additionally we also investigated the reactivity of PCy_3 with chloroform in the absence of CCl_4. Upon addition of CCl_4 to a dichloromethane solution of PCy_3 the reaction mixtures turned intensely yellow. Also the benzene/CCl_4 solution with PCy_3 turned yellow overnight, while the reaction solutions containing chloroform stayed colorless. *In situ* reaction monitoring *via* ^{31}P NMR spectroscopy revealed, that PCy_3 was

[a] N. Spang, M. Müller, Dr. M. R. Buchner
Anorganische Chemie, Nachwuchsgruppe Berylliumchemie
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse 4, 35032 Marburg (Germany)
E-mail: magnus.buchner@chemie.uni-marburg.de
http://www.uni-marburg.de/fb15/ag-buchner [a] Initial(s),

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completely converted to two different species in the chloroform/CCl_4 mixture overnight. The ^{31}P NMR signals of these two species were observed at 40.8 and 34.2 ppm with an integral ratio of ca. 6.6:1 and are assigned to the phosphonium cations **3** and $[Cy_3PCH_2Cl]^+$ (**12**) respectively. In dichloromethane/CCl_4 and benzene/CCl_4 mixtures four different species were observed after 12 h. The most intense signal was again observed at 40.8 ppm while additional signals at 64.8, 98.7 and 107.7 ppm were observed. The signal at 98.7 ppm is assigned to known phosphorane **11**[16] while the one at 107.7 ppm belongs to $[Cy_3PCl]^+$, the corresponding phosphonium form.[17] In benzene/CCl_4 the signal at 64.8 ppm disappears after 36 h while this takes several days in CH_2Cl_2/CCl_4. In the absence of CCl_4 no conversion of PCy_3 in chloroform was observed at ambient temperature. However after heating this solution to 80 °C for 12 h in a closed vessel two more signals besides the one for PCy_3 could be observed in the ^{31}P NMR spectrum. The major one at 34.2 ppm being phosphonium salt **12** and one at 21.2 ppm which we assign to $[Cy_3PCH_3]^+$. The final ^{31}P NMR spectra of these four reaction mixtures are depicted in figure 2.

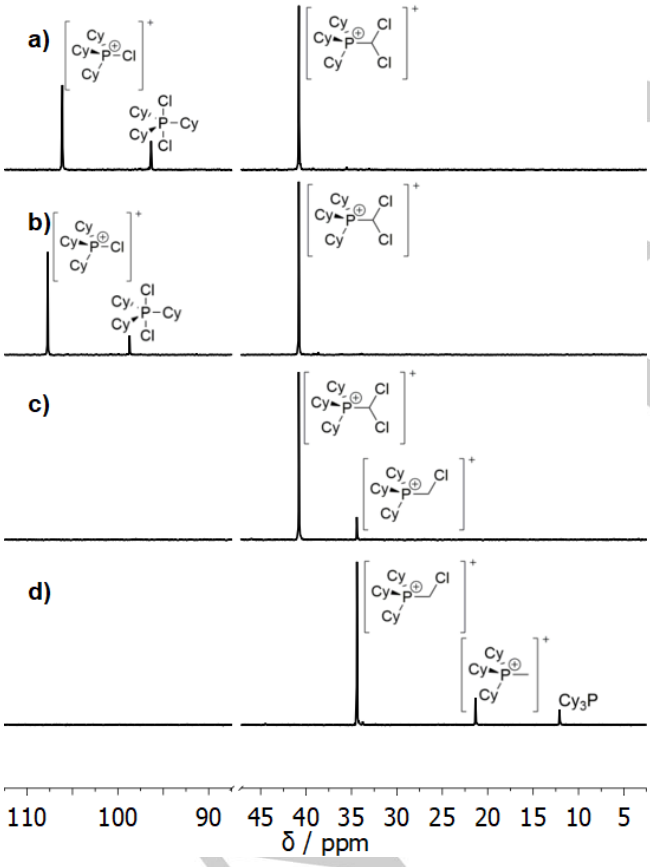

Figure 2. ^{31}P NMR spectra of Cy_3P in a) benzene / CCl_4, b) dichloromethane / CCl_4, c) chloroform / CCl_4 mixtures and d) neat chloroform after a)-c) two weeks at rt and d) 13 days at rt and 12 h at 80 °C. Relative signal integrals: a) $[Cy_3PCl]^+$: Cy_3PCl_2 : $[Cy_3PCHCl_2]^+$ = 2.8 : 1 : 6.3 , b) $[Cy_3PCl]^+$: Cy_3PCl_2 : $[Cy_3PCHCl_2]^+$ = 5.1 : 1 : 9.3, c) $[Cy_3PCHCl_2]^+$: $[Cy_3PCH_2Cl]^+$ = 5.9 : 1 and d) $[Cy_3PCH_2Cl]^+$: $[Cy_3PCH_3]^+$: Cy_3P = 6.9 : 1.5 : 1.

To confirm our assignments of the phosphonium salts high resolution LIFDI mass spectrometry was performed on the reaction solutions. Table 1 summarizes the observed cations and gives the relative signal intensities. In all solutions containing CCl_4 the phosphonium ions **3** and **12** were observed together with the tricyclohexyl trichloromethyl phosphonium cation **13** and $[Cy_3PCH_3]^+$. Additionally aggregates of two phosphonium cations with one chloride anion could be detected, which are similar to known $\{[Ph_3PCl]Cl[ClPPh_3]\}^+$.[18] This shows that these phosphonium cation can indeed interact with anions through hydrogen bonds as anticipated. In contrast to the CCl_4 containing solutions only signals for cations **12** and $[Cy_3PCH_3]^+$ together with the corresponding aggregate $\{[Cy_3PCH_2Cl]Cl[Cy_3PCH_3]\}^+$ could be detected in the chloroform solution.

To gain insights into the nature of the intermediate species accountable for the ^{31}P NMR signal at 64.8 ppm LIFDI mass spectrometry was performed on PCy_3 solutions in dichloromethane / CCl_4 mixtures after different reaction times (SI Table S1). Only the cations **13** and **3** were observed, with the prior initially being the dominant species. The intensity of this signal diminished rapidly over time while the one for ion **3** increased and after 115 h only species **3** could be detected. We therefore assign the signal at 64.8 ppm to $[Cy_3PCCl_3]^+$.

Table 1. Summary of observed cations in LIFDI mass spectrometry (FD+ ionization mode) and their relative signal intensities in the reaction solutions of PCy_3 with benzene / CCl_4, dichloromethane / CCl_4, chloroform / CCl_4 mixtures and with neat chloroform after two weeks reaction time.

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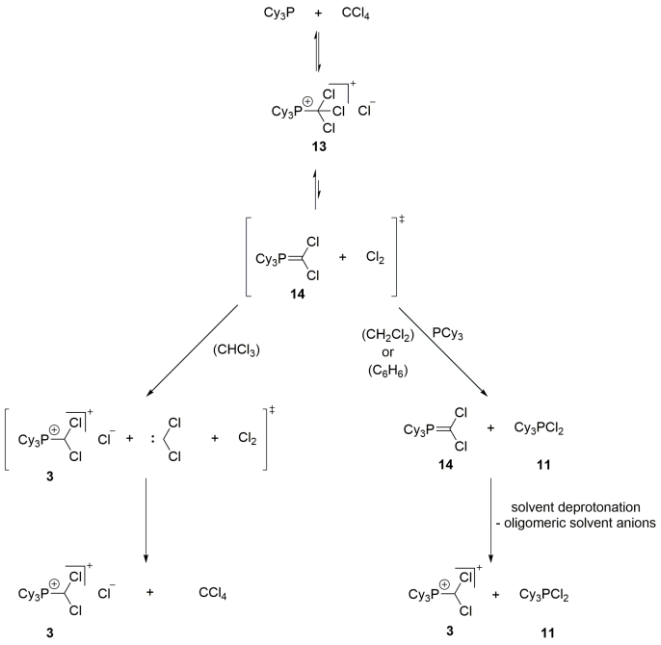
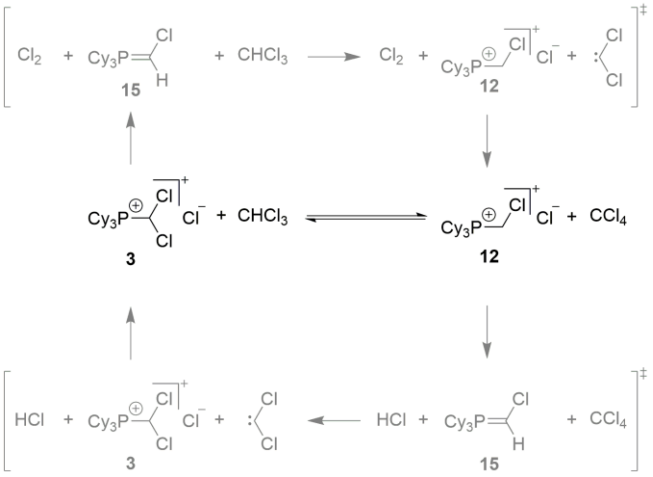
In accordance with our findings from NMR spectroscopy and mass spectrometry we therefore propose the following reaction mechanism in the presence of CCl_4. Tricyclohexylphosphine reacts instantaneously with CCl_4 to give $[Cy_3PCCl_3]^+$ (**13**), which is in agreement with the analogous reaction of triphenylphosphine that yields $[Ph_3PCCl_3]^+$.[9] Cation **13** then reacts with chloride to the ylide $Cy_3P{=}CCl_2$ (**14**) and chlorine, even though the equilibrium should be far on the side of cation **13**. In chloroform ylide **14** is instantaneously protonated by the solvent due to the relatively high C-H-acidity, generating cation **3** and dichlorocarbene. The latter then traps the chlorine in solution and forms CCl_4. In the case of the less C-H-acidic solvents, benzene and dichloromethane, ylide **14** is more stable. Therefore the formed chlorine is trapped faster by excess phosphine than solvent deprotonation occurs, so phosphorane **11** is formed.[19] Ylide **14** subsequently deprotonates the solvent giving cation **3**. However due to the lack of chlorine the deprotonated solvent can react with further solvent molecules to form oligomeric species which account for the yellow color of the reaction solutions. The described mechanism is depicted in scheme 2.



Scheme 2. Proposed reaction cascade for the formation of phosphonium ion **3** and phosphorane **11**.

In accordance with this reaction mechanism in chloroform we tested if catalytic amounts of CCl_4 are sufficient to convert PCy_3 to phophonium cation **3**. However we observed the formation of phosphonium cations **3** and **12** in a ratio of 1:1.2 *via* ^{31}P NMR spectroscopy. This is presumable caused by an equilibrium between these two phosphonium ions. Due to the steric bulk of the cyclohexyl groups cation **3** may react with chloride under the formation of chlorine and $Cy_3P{=}CHCl$ (**15**), which then deprotonates chloroform to give species **12** and dichlorocarbene which react with chlorine to CCl_4. In the same manor cation **12** may react with chloride to form ylide **15** and hydrogen chloride. Through reaction with CCl_4 ion **3** is then reformed and dichlorocarbene is generated which now reacts with HCl to chloroform. This is summarized in scheme 3. Therefore excess CCl_4 is needed to shift the equilibrium to the side of phosphonium ion **3**. This also explains why in the absence of CCl_4 only cations **12** and $[Cy_3PCH_3]^+$ were observed. Direct reaction of PCy_3 with chloroform gives cation **3**. However since this reaction needs heating to progress at reasonable reaction rates also the equilibrium is established faster and is shifted completely onto the side of cation **12** due to the lack of CCl_4 in solution. *Via* an analogue mechanism also the completely dechlorinated phosphonium salt $[Cy_3PCH_3]^+$ can be formed.



Scheme 3. Proposed equilibrium between the tricyclohexyl dichloromethyl phosphonium (**3**) and tricyclohexyl chloromethyl phosphonium (**12**) cations (black) and suggested exchange mechanism (grey).

Therefore tricyclohexyl dichloromethyl phosphonium chloride was prepared by stirring Cy_3P for three days in a 1:2 mixture of $CHCl_3$ and CCl_4. Layering of the reaction mixture with *n*-pentane gave colorless crystals of the chloride salt $[Cy_3PCHCl_2]Cl \cdot 2CHCl_3$ (**3a**) in 36 % isolated yield. Crystallographic details are given in table 2. Compound **3a** crystallizes in the monoclinic space group $P2_1/c$ (14). The structure of cation **3** is shown in figure 3.

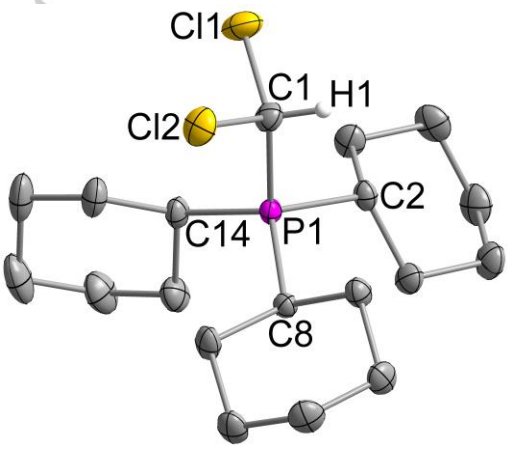


Figure 3. Molecular structure of cation **3** in the crystal structure of compound **3a**. Displacement ellipsoids are shown at the 70 % probability level at 100 K, hydrogen atom isotropic with arbitrary radii and cyclohexyl hydrogen atoms are omitted for clarity.

The phosphorus atom is bound to the four carbon atoms C1, C2, C8 and C14, which results in tetrahedral coordination around the phosphorus atom. The cyclohexyl substituents and the substituents at the C1 atom adopt a staggered conformation. The P-C distances to the three cyclohexyl carbon atoms (C2, C8

and C14) directly bound to the phosphorus atom are with 1.8163(15)-1.8433(15) Å slightly shorter than the corresponding distances in PCy_3 (1.865(5)-1.871(7) Å)[20] and comparable to the ones found in $[Cy_3P(C_6H_4F)]^+$ (1.815(5)-1.822(4) Å)[12] and $[Cy_3PH]^+$ (1.817(2)-1.823(2) Å).[11] The reduction in bond length by approximately 0.02 Å is in accordance with the smaller P-C distances observed in $[Ph_4P]Cl$ (1.781(2)-1.793(2) Å)[21] $[Ph_4P]Br$ (1.768(5)-1.792(4) Å) and $[Ph_4P]I$ (1.799(4) Å)[22] compared to PPh_3 (1.822(5)-1.831(5) Å).[23] The distance of the phosphorus atom to the methylene carbon atom (C1) is with 1.8467(17) Å comparable to the other P-C distances in salt **3a**. The C-C distances in the cyclohexyl rings are with 1.518(3)-1.545(2) Å comparable to the ones found in PCy_3,[20] $[Cy_3P(C_6H_4F)]^+$[12] and $[Cy_3PH]^+$.[11] The C-Cl distances in the methylene subunit are with 1.7756(16) and 1.7783(17) Å similar to the ones found in CH_2Cl_2 (1.7684(14) Å)[24] and $CHCl_3$ (1.7587(12)-1.7613(7) Å).[25] Due to the sterics the Cl1-C1-Cl2 bond angle is with 109.53(9)° smaller than in CH_2Cl_2 (112.009(4)°)[24] and comparable to $CHCl_3$ (109.65(6)-111.16(4)°).[25] The C2-P1-C14 and C8-P1-C14 angles are with 110.61(7)° and 114.58(7)° respectively larger than the C2-P1-C8 angle of 108.24(7)°, which is due to carbon atom C14 standing into the sterically most crowded quadrant where the two chloride atoms at the methylene carbon atom C1 are situated. In accordance to this the C1-P1-C14 angle is with 109.99(8)° larger than the C1-P1-C8 (109.41(7)°) and C1-P1-C2 (103.41(7)°) angles.

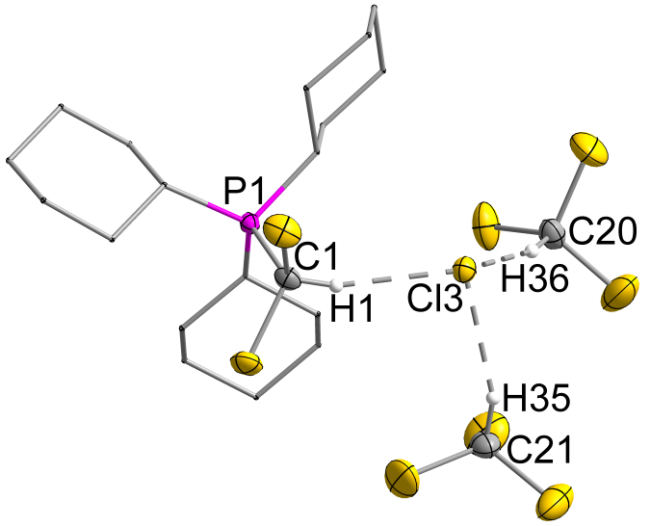


Figure 4. Hydrogen bonding of cation **3** and chloroform to chloride in the crystal structure of compounds **3a**. Displacement ellipsoids are shown at the 70 % probability level at 100 K, hydrogen atoms isotropic with arbitrary radii and the cyclohexyl groups as wireframe image for clarity.

Hydrogen bonds between the hydrogen atom of the methylene group (H1) as well as the hydrogen atoms at the two chloroform molecules (H35 & H36) to the chloride anion are present, resulting in a distorted T-shaped coordination mode at chloride atom Cl3, with D···A distances of 3.359(2) Å (C1···Cl3), 3.338(2) Å (C20···Cl3) and 3.382(2) Å (C21···Cl3), which is in the typical range of H-bonding interactions. (figure 4).[26]

Table 2. Selected crystallographic data for compound **3a** and **3b**.

	3a	**3b**
Empirical formula	$C_{21}H_{36}Cl_9P$	$C_{60}H_{113}Cl_{11}O_3P_3$
Color and appearance	colorless needle	colorless block
Molecular mass / g·mol^{-1}	638.52	1365.36
Crystal system	monoclinic	monoclinic
Space group type (No.)	$P2_1/c$ (14)	$C2/c$ (15)
a / Å	10.9200(4)	27.235(6)
b / Å	13.9926(6)	15.953(3)
c / Å	19.8402(8)	33.640(7)
β / °	101.640(1)	106.17(3)
V / Å^3	2969.2(2)	14038(5)
Z	4	8
λ / Å	0.71073 (Mo-K$_\alpha$)	1.54186 (Cu-K$_\alpha$)
T / K	100(2)	100(2)
μ / mm^{-1}	0.913	4.939
θ_{max}	28.229	65.080
hkl_{max}	$-14 \le h \le 13$	$-26 \le h \le 32$
	$-18 \le k \le 18$	$-10 \le k \le 18$
	$-26 \le l \le 26$	$-39 \le l \le 34$
Size / mm^3	0.2 · 0.07 · 0.07	0.055 · 0.050 · 0.040
R_{int}, R_σ	0.050, 0.021	0.117, 0.122
$R(F)$ ($I \ge 2\sigma(I)$, all data)	0.032, 0.043	0.054, 0.130
$wR(F^2)$ ($I \ge 2\sigma(I)$, all data)	0.074, 0.079	0.109, 0.127
S (all data)	0.98	1.02
Data, parameter, restraints	7320, 424, 0	11415, 726, 0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å^{-3}	0.72 / −0.52	0.50 / −0.78

Attempts to synthesize cation **3** *via* the route of *Appel* and *Huppertz*[14] as described above resulted in the serendipitous formation of a complex salt with the composition $[Cy_3PCHCl_2]_3[H_3O][H_5O_2]Cl_5 \cdot C_6D_6$ (**3b**) in which three cations **3** co-crystallized with one hydronium (H_3O^+) and one *Zundel* ion ($H_5O_2^+$). This compound presumably formed when the precipitate of the reaction of PCy_3 with CCl_4 in toluene was dissolved in non-dried benzene-d_6 and layered with non-dried *n*-pentane under air. Likely phosphorane **11** reacted with traces of water to give HCl and phosphine oxide. The HCl subsequently reacted with further water molecules to the hydronium and *Zundel* ions. Compound **3b** crystallizes in the monoclinic space group *C*2/*c* (15) (figure 5).

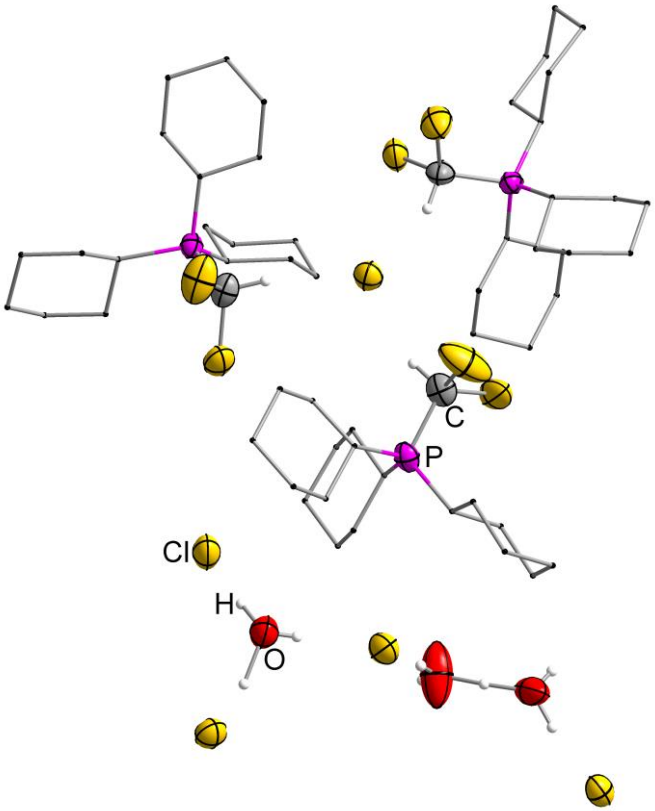


Figure 5. A section of the crystal structure of compound **3b**. Displacement ellipsoids are shown at the 70 % probability level at 100 K. For clarity hydrogen atoms are displayed isotropic with arbitrary radii, the cyclohexyl groups as wireframe image and crystal benzene is omitted.

The phosphorus atoms in compound **3b** show the same coordination geometry and comparable atom distances and bond angles found in compound **3a**. Again the cyclohexyl substituents and the substituents at the C1 atom adopt a staggered conformation, however the difference in the C-P-C angles is more pronounced with the $C_{methylene}$-P-$C_{cyclohexyl}$ angle in the chloride quadrant (*vide supra*) being in the range of 113.57(18)-114.85(19)°, therefore larger than the other $C_{methylene}$-P-$C_{cyclohexyl}$ angles with 104.50(18)-105.43(17)° and the $C_{cyclohexyl}$-P-$C_{cyclohexyl}$ angle opposite to the chlorine quadrant ranging from 107.24(18)° to 109.68(17)° while the other $C_{cyclohexyl}$-P-$C_{cyclohexyl}$ angles are with 115.85(17)-117.8(2)° sufficiently larger.

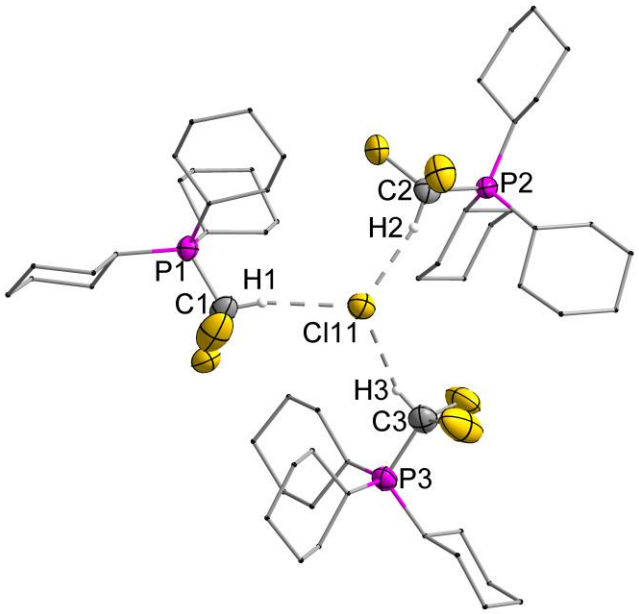


Figure 6. Hydrogen bonding of three phosphonium cations **3** towards one chloride in the crystal structure of compound **3b**. Displacement ellipsoids are shown at the 70 % probability level at 100 K, hydrogen atoms isotropic with arbitrary radii and the cyclohexyl groups as wireframe image for clarity.

One chloride ion is coordinated *via* three hydrogen bonds to the methylene groups of the three phosphonium cations. This results in a trigonal planar coordination of the chlorine atom Cl11 by the hydrogen atoms H1, H2 and H3 (figure 6). The D···A distances of 3.505(5) Å (C1···Cl3), 3.442(5) Å (C2···Cl3) and 3.405(5) Å (C3···Cl3) are slightly longer than the ones found in salt **3a** but still in the typical range for H-bonding interactions.[26] The remaining chloride ions bridge hydronium and *Zundel* ions to infinite chains (figure 7). The structural parameters of the $[H_3O]^+$ and $[H_5O_2]^+$ cations compare well with reference compounds.[27] Two *Zundel* ions are bridged by chlorine atom Cl10 directly on the side of the O3 oxygen atom, while they are bridged on the side of the O2 oxygen atom *via* chlorine atoms Cl7 and Cl9 to the hydronium ion. The free hydrogen-bonding site at the hydronium ion is saturated by coordination to chlorine atom Cl8.

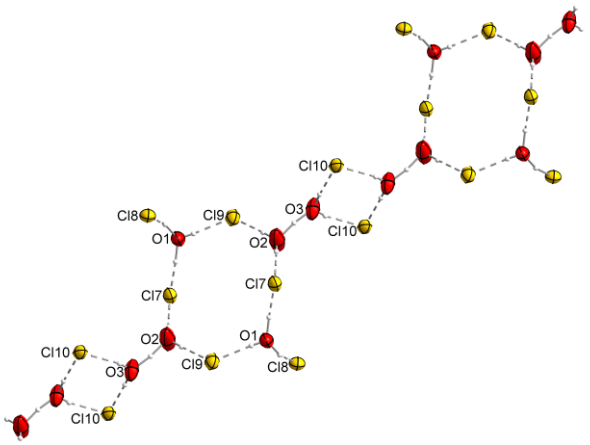


Figure 7. Hydrogen bond network between chloride, hydronium and *Zundel* ions in the crystal structure of compound **3b**. Displacement ellipsoids are shown at the 70 % probability level at 100 K, hydrogen atoms isotropic with arbitrary radii.

Conclusions

We were able to synthesize the $[Cy_3PCHCl_2]^+$ cation **3** which is able to form hydrogen bonds to anions as anticipated. This is evident from the species observed in mass spectrometry. Through this cation anion interaction the salts $[Cy_3PCHCl_2]Cl \cdot 2CHCl_3$ (**3a**) and $[Cy_3PCHCl_2]_3[H_3O][H_5O_2]Cl_5 \cdot C_6D_6$ (**3b**) could be crystallized. It is also evident that the solvent system is crucial to synthesize the dichloromethylene phosphonium ion **3**. Only in the presence of CCl_4 and a protic solvent like chloroform cation **3** is produced without side reactions. However due to an equilibrium between ions $[Cy_3PCHCl_2]^+$ (**3**) and $[Cy_3PCH_2Cl]^+$ (**12**) traces of the latter cation are always present. Also rather high ratios of CCl_4 to $CHCl_3$ are necessary to drive the equilibrium onto the side of the desired compound **3**.

Experimental Section

General experimental techniques

All manipulations were performed either under solvent vapor pressure or dry argon using glovebox and *Schlenk* techniques if not stated otherwise. Glassware was flame-dried prior to use. Chlorinated solvents were dried over CaH_2, benzene and toluene over sodium and C_6D_6 over Na/K-alloy and distilled prior to use. Tricyclohexylphosphine was purchased from *ABCR* and used as received.

NMR spectroscopy

^1H, ^{13}C and ^{31}P NMR spectra were recorded on *Bruker* Avance III HD 250, *Bruker* Avance III HD 300 and Avance III 500 NMR spectrometers. The latter was equipped with a *Prodigy* Cryo-Probe. ^1H NMR (300 / 500 MHz) and ^{13}C NMR (76 / 126 MHz) chemical shifts are given relative to the solvent signal for $CDCl_3$ (7.26 and 77.2 ppm) and CD_2Cl_2 (5.32 and 53.8 ppm) while ^{31}P (101 / 122 / 202 MHz) used 85% H_3PO_4 as an external standard. NMR spectra were processed with the MestReNova software.[28]

IR spectroscopy

IR spectra were recorded on a *Bruker* alpha FTIR spectrometer equipped with a diamond ATR unit in an argon filled glovebox. Processing of the spectra was performed with the OPUS software package.[29]

Single crystal X-ray diffraction

Single crystals of **3a** were grown from CCl_4 / $CHCl_3$ solution by layering with *n*-pentane and of **3b** by layering a C_6D_6 solution with *n*-pentane. Crystals were selected under exclusion of air in cooled perfluorinated polyether (Galden, *Solvay* Solexis) and mounted using the *MiTeGen* MicroLoop system. X-ray diffraction data were collected using the graphite monochromated Mo-K_α radiation of a *Bruker* D8 Quest diffractometer equipped with an *Incoatec* Microfocus Source and a *CMOS* Photon 100 detector and the monochromated Cu-K_α radiation of a *Stoe* StadiVari diffractometer equipped with a *Xenocs* Microfocus Source and a *Dectris* Pilatus 300K detector. The diffraction data were reduced with the X-Area and APEX software package and corrected for absorption numerically using X-Red.[30] The structure was solved using Direct Methods (SHELXS-2013/1) and refined against F^2 (SHELXL-2016/4) using the ShelXle software package.[31] All atoms were located by Difference Fourier synthesis and non-hydrogen atoms refined anisotropically. Hydrogen atoms were refined isotropically. CCDC 1840433 and CCDC 1840436 contain the supplementary crystallographic data for compounds **3a** and **3b** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Mass spectrometry

Mass spectrometry was performed on a *Jeol* AccuTOF GCv equipped with a combined FD / FI / LIFDI source using liquid field desorption ionization (LIFDI) as ionization technique.

Synthesis and characterization

$[Cy_3PCHCl_2]Cl \cdot 2\,CHCl_3$ (3a): 500 mg (1.78 mmol) tricyclohexyl phosphine were weighed into a *Schlenk* tube, 8.30 ml chloroforme and 15.0 ml CCl_4 were added and the reaction mixture stirred for three days at ambient temperature. The obtained colorless solution was layered with *n*-pentane. After 8 days colorless needles had formed, which were isolated by filtration and dried in *vacuo* to receive 413 mg (0.647 mmol, 36 %) of product as colorless needles.
^1H NMR (500 MHz, CD_2Cl_2) δ = 1.27 – 1.53 (m, 9H, H_{Cy}), 1.71 – 1.86 (m, 9H, H_{Cy}), 1.94 – 2.03 (m, 6H, H_{Cy}), 2.17 – 2.26 (m, 6H, H_{Cy}), 2.93 (dtt, 3H, $^2J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 2.7 Hz, PC*H*$(CH_2)_2$), 7.36 (s, 2H, C*H*Cl_3), 8.28 (d, 1H, $^2J_{PH}$ = 1.9 Hz, PC*H*Cl_2). ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 25.8 (d, $^4J_{PC}$ = 1.6 Hz, C_{Cy}), 27.3 (d, $^2J_{PC}$ = 12.1 Hz, C_{Cy}), 27.8 (d, $^3J_{PC}$ = 4.2 Hz, C_{Cy}), 32.7 (d, $^1J_{PC}$ = 33.5 Hz, P*C*$(CH_2)_2$), 60.8 (d, $^1J_{PC}$ = 41.2 Hz, P*C*HCl_2), 78.1 (s, *C*H_3Cl). ^{31}P NMR (202 MHz, CD_2Cl_2) δ = 40.8. FT-IR (cm^{-1}): 2925 (m), 2851 (m), 2804 (w), 2435 (w), 1445 (m), 1252 (m), 1177 (w), 1108 (w), 1085 (w), 1039 (w), 1002 (w), 918 (w), 891 (w), 849 (w), 828 (w), 742 (vs), 701 (w), 659 (m), 622 (w), 531 (m), 523 (m), 502 (w), 474 (w), 449 (w), 425 (w). MS (FD^+): m/z (%) 295.27 $[(Cy_3PCH_3)^+]$ (25), 329.23 $[(Cy_3PCH_2Cl)^+]$ (100), 363.19 $[(Cy_3PCHCl_2)^+]$ (45), 659.45 $[\{(Cy_3PCH_3)Cl(Cy_3PCH_2Cl)\}^+]$ (17), 693.41 $[\{(Cy_3PCH_2Cl)Cl(Cy_3PCH_2Cl)\}^+]$ (65), 729.38 $[\{(Cy_3PCHCl_2)Cl(Cy_3PCH_2Cl)\}^+]$ (63), 763.33 $[\{(Cy_3PCHCl_2)Cl(Cy_3PCHCl_2)\}^+]$ (50). HR-MS (FD^+): m/z calcd. for $[(Cy_3PCHCl_2)^+]$: 363.17697; found: 363.18914. Anal. calcd. for $[Cy_3PCHCl_2]Cl \cdot 2\,CHCl_3$: C, 39.50; H 5.68. Found: C, 39.64; H, 5.59.

$[Cy_3PCHCl_2]_3[H_3O][H_5O_2]Cl_5 \cdot C_6D_6$ (3b): 700 mg (2.50 mmol) tricyclohexyl phosphine in 2.5 ml of toluene was added to a mixture of 5.0 ml of toluene and 2.5 ml of CCl_4 at 0 °C. The solution turns orange and the reaction mixture is warmed to ambient temperature and stirred for one hour. The formed voluminous white precipitate was isolated by filtration and dried in *vacuo* to receive a colorless oil which was triturated with *n*-pentane. The obtained off-white solid was dried in *vacuo* and a sample dissolved under air in non-dried benzene-d_6. This sample was subsequently layered with *n*-pentane to yield the product as colorless blocks.
^1H NMR (500 MHz, $CDCl_3$) δ = 1.22 – 1.38 (m, 27H, H_{Cy}), 1.67 – 1.84 (m, 27H, H_{Cy}), 1.93 – 2.06 (m, 18H, H_{Cy}), 2.20 – 2.34 (m, 18H, H_{Cy}), 3.04 (dt, 9H, $^2J_{PH}$ = 12.7 Hz, $^3J_{HH}$ = 12.7 Hz, PC*H*$(CH_2)_2$), 7.18 (bs, 8 H, H_3O, H_5O_2), 8.79 (d, 3H, $^2J_{PH}$ = 1.9 Hz, PC*H*Cl_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 25.4 (d, $^4J_{PC}$ = 1.7 Hz, C_{Cy}), 26.8 (d, $^2J_{PC}$ = 12.1 Hz, C_{Cy}), 27.5 (d, $^3J_{PC}$ = 4.2 Hz, C_{Cy}), 32.2 (d, $^1J_{PC}$ = 33.6 Hz, P*C*$(CH_2)_2$), 60.9 (d, $^1J_{PC}$ = 40.3 Hz, P*C*HCl_2). ^{31}P NMR (202 MHz, $CDCl_3$) δ = 40.6.

[Cy_3PCH_2Cl]Cl (12a): 97.7 mg (0.35 mmol) tricyclohexyl phosphine was dissolved in 1.50 ml of chloroform, three drops CCl_4 were added and the solution was stirred at ambient temperature for 12 days. Removal of the volatiles in *vacuo* yielded 130 mg of a colorless oil which consisted of a 1:1.2 mixture of [Cy_3PCHCl_2]Cl and [Cy_3PCH_2Cl]Cl respectively according to the NMR spectra.
^{1}H NMR (500 MHz, CD_2Cl_2) δ = 1.18 – 1.51 (m, 9H, H_{Cy}), 1.59 – 2.01 (m, 15H, H_{Cy}), 2.08 (d, 6H, $^3J_{PH}$ = 11.6 Hz, H_{Cy}), 2.84 (dtt, 3H, $^2J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 2.5 Hz, PC*H*$(CH_2)_2$), 5.11 (d, 2H, $^2J_{PH}$ = 5.6 Hz, PCH_2Cl). ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 25.91 (d, $^4J_{PC}$ = 1.5 Hz, C_{Cy}), 26.69 (s, C_{Cy}), 26.80 (d$^3J_{PC}$ = 2.9 Hz, C_{Cy}), 27.10 (d, $^2J_{PC}$ = 12.2 Hz, C_{Cy}), 27.41 (d, $^2J_{PC}$ = 11.7 Hz, C_{Cy}), 27.55 (d, $^3J_{PC}$ = 3.9 Hz, C_{Cy}), 30.56 (d, $^1J_{PC}$ = 38.5 Hz, P*C*$(CH_2)_2$), 35.56 (d, $^1J_{PC}$ = 60.2 Hz, PCH_2Cl). ^{31}P NMR (202 MHz, CD_2Cl_2) δ = 34.2. FT-IR (cm^{-1}): 2925 (m), 2851 (m), 1579 (w), 1442 (m), 1302 (w), 1260 (m), 1215 (w), 1179 (w), 1159 (s), 1109 (m), 1081 (m), 1040 (m), 1007 (m), 979 (w), 918 (w), 891 (m), 853 (m), 821 (m), 799 (m), 742 (vs), 691 (m), 669 (w), 657 (m), 563 (w), 546 (m), 532 (s), 502 (w), 780 (m), 471 (m), 442 (m), 435 (m). MS (FD^+): m/z (%) 295.26 [(Cy_3PCH_3)$^+$] (27), 329.22 [(Cy_3PCH_2Cl)$^+$] (100), 659.42 [{(Cy_3PCH_3)Cl(Cy_3PCH_2Cl)}$^+$] (13), 693.37 [{(Cy_3PCH_2Cl)Cl(Cy_3PCH_2Cl)}$^+$] (44), 729.34 [{(Cy_3PCHCl_2)Cl(Cy_3PCH_2Cl)}$^+$] (6). HR-MS (FD^+): m/z calcd. for [(Cy_3PCH_2Cl)$^+$]: 329.21594; found: 329.21528.

NMR scale reactions: 30 mg (0.10 mmol) tricyclohexyl phosphine was weighed into a NMR tube, 0.50 ml of a 1:1 solvent mixture (CCl_4 / C_6H_6, CCl_4 / CH_2Cl_2, CCl_4 / $CHCl_3$) or neat chloroform respectively were added and the tube was flame sealed subsequently.

MS reaction monitoring: 30 mg (0.10 mmol) tricyclohexyl phosphine was weighed into a vessel and 0.50 ml of CH_2Cl_2 and 0.25 ml of CCl_4 were added. The reaction mixture was kept at ambient temperature for the stated amount of time, subsequently diluted with CH_2Cl_2 and analyzed *via* LIFDI mass spectrometry.

Acknowledgements

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Keywords: phosphonium • hydrogen bonds • C-H-acidity • hydronium ion • *Zundel* ion

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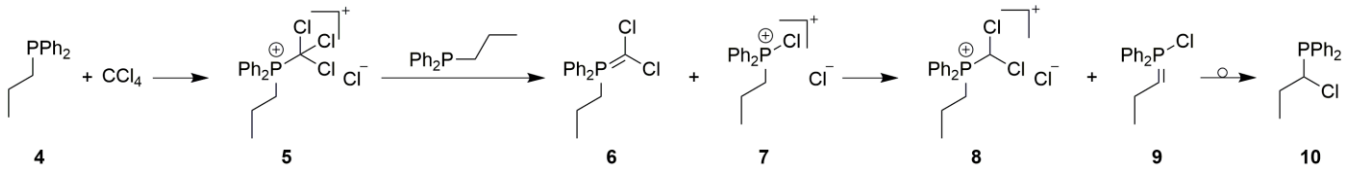

Scheme 1. Reaction of *n*-propyl diphenylphosphine with CCl_4 in non-polar aprotic solvents described by *Appel* and *Huppertz*.[14]

Table 1. Summary of observed cations in LIFDI mass spectrometry (FD+ ionization mode) and their relative signal intensities in the reaction solutions of PCy_3 with benzene / CCl_4, dichloromethane / CCl_4, chloroform / CCl_4 mixtures and with neat chloroform after two weeks reaction time.

		Relative signal intensities / %			
Ion	m / z	C_6H_6 / CCl_4	CH_2Cl_2 / CCl_4	$CHCl_3$ / CCl_4	$CHCl_3$
$[Cy_3PCH_3]^+$	295.25	51	10	25	100
$[Cy_3PCH_2Cl]^+$	329.22	100	100	100	5
$[Cy_3PCHCl_2]^+$	363.18	81	48	45	0
$[Cy_3PCCl_3]^+$	397.14	8	2	2	0
$\{[Cy_3PCH_3]Cl[Cy_3PCH_2Cl]\}^+$	659.42	15	3	17	2
$\{[Cy_3PCH_2Cl]Cl[Cy_3PCH_2Cl]\}^+$	693.41	37	32	65	0
$\{[Cy_3PCH_2Cl]Cl[Cy_3PCHCl_2]\}^+$	729.38	66	51	63	0
$\{[Cy_3PCHCl_2]Cl[Cy_3PCHCl_2]\}^+$	763.33	70	43	50	0

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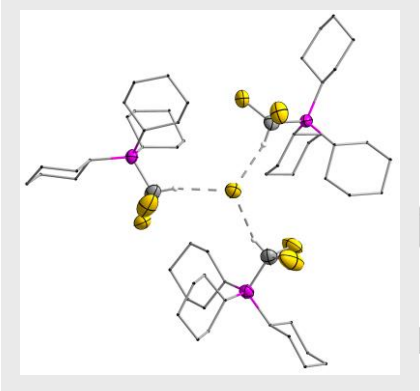
Layout 1:

COMMUNICATION

The functional phosphonium ion $[Cy_3PCHCl_2]^+$ could be synthesized which is able to form hydrogen bonds to the corresponding anion. Through these interactions salts $[Cy_3PCHCl_2]Cl \cdot 2CHCl_3$ (**3a**) and $[Cy_3PCHCl_2]_3[H_3O][H_5O_2]Cl_5 \cdot C_6D_6$ could be stabilized. Also the mechanism for the formation of cation $[Cy_3PCHCl_2]^+$ has been investigated.



Crystallization assistance*

*Nils Spang, Matthias Müller, Magnus R. Buchner**

Page No. – Page No.

The phosphonium ion $[Cy_3PCHCl_2]^+$: synthesis and properties

*one or two words that highlight the emphasis of the paper or the field of the study