## Synthesis and Characterization of the Silylated Hexaphenyl Carbodiphosphorane [Me<sub>3</sub>SiC(PPh<sub>3</sub>)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]

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**Abstract**. The addition of trimethylsilyl trifluoromethanesulfonate TMS-OTf ( $CF_3SO_3 = OTf$ , triflate) to hexaphenyl carbodiphosphorane PPh<sub>3</sub>=C=PPh<sub>3</sub> (1) in toluene yields the silylated carbodiphosphorane [Me<sub>3</sub>SiC(PPh<sub>3</sub>)<sub>2</sub>][OTf] (2). Compound 2 represents the first silylated carbodiphosphorane characterized in solution and in the solid state. 2 is an air-sensitive compound but stable in solution and in the solid state in an inert atmosphere as shown by heteronuclear NMR experi-

#### Introduction

presentation of the first carbodiphosphorane The Ph<sub>3</sub>P=C=PPh<sub>3</sub> (1) in 1961 by *Ramírez* et al. opened the door towards a new class of compounds with intriguing chemical and physical properties.<sup>[1a]</sup> The unusual topology of **1** in the solid state with a bent arrangement of the P-C-P unit<sup>[2]</sup> and the strong nucleophilic character of the central carbon atom<sup>[1b,3]</sup> were the driving forces for the investigation of the donor abilities of carbodiphosphoranes.<sup>[4,9,10]</sup> First, the bonding situation in 1 was described by resonance forms rendering the bis ylide (B) and the heterocumulene (C) character of this compound (see Scheme 1).<sup>[1]</sup> Additionally, Kaska et al. related to 1 as an "unsaturated carbon complex with a formally zerovalent central atom stabilized by phosphine groups" (which refers to resonance form A in Scheme 1) and, in this context, used the term "bis-phosphine carbon complex".<sup>[4]</sup> The concept of carbones was later introduced by Frenking and Tonner based on chemical bonding analysis for carbodiphosphoranes and carbodicarbenes<sup>[5a-5d]</sup> (see also the discussion in references<sup>[5e,5f]</sup> regarding the ylide and carbone formulation) and extended further by Frenking et al.[5g] These findings were

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 $Ph_{9}P \longrightarrow E \qquad Ph_{9}P \longrightarrow Ph_{9}P \longrightarrow Ph_{9}P \longrightarrow E$   $ph_{9}P \longrightarrow Ph_{9}P \longrightarrow Ph_{9}P \longrightarrow E$   $ph_{9}P \longrightarrow Ph_{9}P \longrightarrow E$   $ph_{9}P \longrightarrow Ph_{9}P \longrightarrow Ph_{9}P$ 

ments and also by X-ray diffraction analysis. Compound 2 crystallizes

in the monoclinic space group  $P2_1/n$  with the cell dimensions a =

1161.7(1), b = 1714.4(1), c = 1903.3(1) pm;  $\beta = 102.74(1)^{\circ}$  and

Z = 4. Structure, frontier orbitals, and dissociation energies for 2 were

determined by density functional theory-based computations high-

lighting the character of 2 as a Lewis acid adduct of a carbon(0) com-

Scheme 1. Resonance forms (A, B, and C), and bonding modes of carbodiphosphorane 1 with one (D) or two Lewis acids (E).

substantiated by experimental work by *Petz*<sup>[6]</sup> and other groups.<sup>[9,10]</sup>

Therefore, the hexaphenyl carbodiphosphorane **1** is best described as a divalent carbon(0) atom stabilized by two triphenylphosphine donor ligands. These strong donor-acceptor interactions stabilize this type of CL<sub>2</sub> compounds.<sup>[7]</sup> Additionally, two lone pairs of electrons are centred at the carbon(0) atom with  $\sigma$  and  $\pi$  symmetry and do not participate in the donor-acceptor bonds.<sup>[5a,5b,5c,6]</sup> Generally, the two lone pairs

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residing at the carbon(0) atom are capable of donating to one (**D**) or two electrophiles (**E**, see Scheme 1).<sup>[8]</sup>

Several examples of such carbodiphosphorane complexes and adducts have been presented in the literature with main group elements<sup>[9]</sup> and transition metal electrophiles.<sup>[10]</sup>

We are interested in the silvlation of carbodiphosphoranes and their application as precursors in organometallic synthesis. For example, silvlated ylides turned out to be a powerful tool in generating salt free trialkylphosphonium alkylides.[11] Therefore, we resumed work done on silicon in carbodiphosphorane chemistry. The first compound of this type, [Me<sub>3</sub>SiC(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, was described by Schmidbaur and Tronich in the course of their studies on substituted ylides.<sup>[11a]</sup> Subsequent publications of the Schmidbaur group on the reaction of the carbodiphosphoranes  $C(PPh_2Me)_2^{[12]}$  and  $C(PMe_3)_2^{[7a]}$ with trimethylsilyl chloride (TMSCl) provided a dichloride salt [(Me<sub>3</sub>Si)<sub>2</sub>C(PPh<sub>2</sub>Me)<sub>2</sub>]<sup>2+</sup> and a transylidation product  $Me_3P=C(H)-P(Me_2)=C(H)-SiMe_3$ , respectively. Uedelhoven et al. obtained [Ph<sub>3</sub>SiC(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> from the reaction of a transition metal substituted ylide with trimethylphosphane.<sup>[13]</sup> Later on, Bestmann et al. reported on a reaction of carbodiphosphorane 1 with TMSCl including  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{31}P{}^{1}H$ NMR spectroscopic data for the obtained product [Me<sub>3</sub>SiC(PPh<sub>3</sub>)<sub>2</sub>]<sup>+.[14]</sup> Recently, Alcarazo et al. obtained [EtMe<sub>2</sub>SiC(PPh<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] from an Si-H bond activation reaction of EtMe<sub>2</sub>SiH with the frustrated lewis pair (FLP)  $1/B(C_6F_5)_3$ .<sup>[15]</sup> Herein, we present our results regarding the synthesis and characteristics of silvlated carbodiphosphorane 1.

#### **Results and Discussion**

Carbodiphopsphorane 1 can be silvlated quantitatively by reacting it with trimethylsilyl triflate (TMS-OTf) in toluene. The precipitated ionic compound  $[Me_3SiC(PPh_3)_2][OTf]$  (2) can be recrystallized from CH2Cl2/n-pentane to obtain single crystals of 2. In solution, compound 2 is stable in an inert atmosphere. The  ${}^{31}P{}^{1}H$  NMR spectrum of 2 in CDCl<sub>3</sub> shows only one singlet at  $\delta_{\rm P}$  26.2 ppm, which is comparable to the value found by *Bestmann* et al. ( $\delta_P$  25.3 ppm).<sup>[14]</sup> Typically, adducts of **1** and cationic units of the type  $[EC(PPh_3)_2]^+$  fall into this region. In the corresponding <sup>1</sup>H NMR spectrum only the resonance signals of the phenyl protons ( $\delta_{\rm H}$  7.41– 7.57 ppm) and the TMS group ( $\delta_{\rm H}$  –0.24 ppm) are present. However, the resonance signal of the TMS group appears at even lower frequencies than denoted by Bestmann et al.  $(\delta_{\rm H}$  +0.1 ppm). Significant differences to the findings of Bestmann are apparent in the  ${}^{13}C{}^{1}H$  NMR spectrum of 2: for the carbon(0) atom the anticipated triplet can be found at even lower frequency at  $\delta_{\rm C}$  –0.89 ppm with a coupling constant of  ${}^{1}J_{CP}$  = 73.4 Hz<sup>[16]</sup> (cf. *Bestmann*:  $\delta_{C}$  2.2 ppm,  ${}^{1}J_{CP}$  = 119 Hz). The resonance signals of the phenyl groups are located in the aromatic region with the characteristic virtual coupling pattern of the corresponding carbon atoms to the two phosphorus atoms (AA'X spin system). The carbon atoms in ortho and meta position appear as virtual triplets, and the carbon atoms in *ipso* position give rise to an apparent doublet with N =

92.9 Hz (N =  $|{}^{1}J_{CP} + {}^{3}J_{CP}|$ ). The remaining *para* carbon atoms show a singlet only.<sup>[17]</sup> Furthermore, the silicon atom in **2** gives rise to a triplet in the  ${}^{29}\text{Si}\{{}^{1}\text{H}\}$  NMR spectrum at  $\delta_{\text{Si}}$  –1.0 ppm with a two bond coupling to the phosphorus atoms ( ${}^{2}J_{\text{SiP}} = 5.4 \text{ Hz}$ ).<sup>[18]</sup> The singlet resonance signal in the  ${}^{19}\text{F}$  NMR spectrum at  $\delta_{\text{F}}$  –77.9 ppm shows no signs of bonding interactions between the cationic unit and the triflate anion.

The precise assignment of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} resonance signals were carried out on the basis of 2D NMR experiments (HMQC, HMBC, and NOESY: see Supporting Information). In particular, the <sup>3</sup>J long range coupling of the carbon(0) atom to the protons of the TMS group yields the anticipated cross peak in the HMBC spectrum of  $2^+$  (Figure S3, Supporting Information). Additionally, unambiguous proof for the stability of cation  $2^+$  in solution is given by the NOEs between the protons of the TMS group and the aromatic protons in *ortho* and *meta* position (Figure 1).

The positive ESI mass spectrum shows the molecular peak  $(M)^+$  at m/z 609.2287, which is assigned to the cation  $2^+$ (calcd. 609.2296). The infrared and Raman spectra of 2 are rich in bands and dominated by the skeleton vibrations of the phenyl groups (see Supporting Information). Therefore, the assignment of the bands to the key vibrations is not possible.<sup>[19]</sup> But, in the Raman spectrum, a pair of new bands are present at 692 cm<sup>-1</sup> and 641 cm<sup>-1</sup>. These can be assigned to the total symmetric  $A_1$  and twofold degenerate E vibration of the Si-CH<sub>3</sub> bonds of the TMS group.<sup>[20]</sup> In the IR spectrum, the bands of the typical vibrations of the free triflate anion<sup>[21]</sup> are superimposed by the bands of the carbodiphosphorane vibrations. However, two characteristic features are apparent in the IR spectrum of **2**: (i) a medium intense band at 894 cm<sup>-1</sup>, which represents the vibration of the newly formed (CH<sub>3</sub>)<sub>3</sub>Si-C(0) bond and (ii) the vibration of the now weaker P-C(0)-P bonds resulting in a medium intense band at 994 cm<sup>-1</sup>. These experimental results are in very good agreement with the computed vibrational frequencies for compound 2 {corresponding computed wavenumbers:  $v[(CH_3)_3Si-C(0)] = 874 \text{ cm}^{-1}$ ,  $v[P-C(0)-C(0)] = 874 \text{ cm}^{-1}$  $P] = 991 \text{ cm}^{-1}$ .<sup>[22]</sup>

Single crystals of **2** suitable for X-ray diffraction studies can be obtained by layering a  $CH_2Cl_2$  solution of **2** with *n*-pentane. The molecular structure of **2** is shown in Figure 2.<sup>[23]</sup>

The molecular structure of 2 shows discrete cationic and anionic units. The cation  $2^+$  adopts a planar arrangement around the central C1 atom (sum of angles at C1: 359.8°), which points to a sp<sup>2</sup> hybridization at C1. The TMS group shows local  $C_{3\nu}$  symmetry. The C<sup>TMS</sup>–Si–C<sup>TMS</sup> bond angles are below the ideal value for tetrahedrons (103.6-107.7°) and the C(0)-Si-C<sup>TMS</sup> bond angles lie above this value (112.1-114.6°), which is due to steric repulsion between the TMS group and the phenyl rings. The Si1-C1 bond length of 190.6 pm is slightly longer than for Si-C single bonds but fits well with the value expected for single bonds of silicon atoms with sp<sup>2</sup> hybridized carbon atoms.<sup>[24]</sup> The P-C1 bond lengths (172.9 pm and 173.2 pm) are about 10 pm longer than in 1 and therefore clearly substantiate the decrease of the P-C1 bond order upon reaction of 1 with TMS-OTf. They are similar to P-C(0) bond lengths in other mono adducts of 1, e.g. the BeCl<sub>2</sub>



Figure 1. Section of <sup>1</sup>H NOESY NMR spectrum of 2 at 300 K in CDCl<sub>3</sub>; mixing time 300 ms.



**Figure 2.** Molecular structure of  $[Me_3SiC(PPh_3)_2][OTf]$  (2) with 50% probability for thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /°: C1–P1 172.9(2), C1–P2 173.2(2), C1–Si1 190.6(2), P1–C8 180.7(2), P1–C2 182.1(2), P1–C14 182.4(2), P2–C26 181.4, P2–C20 181.8(2), P2–C32 182.3(2), Si1–C38 187.6(2), Si1–C39 187.3(2), Si1–C40 187.9(2); P1–C1–P2 119.9(1), P1–C1–Si1 122.3(1), P2–C1–Si1 117.6(1), P1–C1–P2 119.9, P1–C1–P2 119.9, C1–Si1–C38 112.11(9), C1–Si1–C39 111.72(9), C1–Si1–C40 114.61(9), C38–Si1–C39 106.40(9), C38–Si1–C40 107.72(9), C39–Si1–C40 103.63(9).

adduct.<sup>[9a]</sup> The P1–C1–P2 bond angle of  $119.9^{\circ}$  lies in the range of values observed for isostructural carbodiphosphorane adducts.<sup>[25]</sup>

In order to obtain a better insight into the bonding situation and stability of compound  $2^+$ , we performed quantum chemical calculations and examined the frontier (Kohn-Sham) orbitals and dissociation energies.

Figure 3 shows the optimized structure of  $2^+$  and the corresponding values for selected bond lengths and angles, which are in good agreement with the experimental results.



**Figure 3.** Computed (BP86/def2-SVP) structure of  $2^+$  in comparison to results from X-ray structural analysis (*in italics*). Bond lengths in Å, angles in degrees. Hydrogen atoms are omitted for clarity.

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 $\Delta G_{298} = -64.3 \text{ kcal mol}^{-1}$ 

As can be seen in Figure 4, the calculated HOMO of  $2^+$ exhibits mainly lone pair character at the central carbon atom, characteristic for carbon(0) compounds. This is underlined by a strong negative partial charge (NBO) at the central carbon atom (-1.54 e).



Figure 4. HOMO (BP86/def2-SVP, -13.4 eV) for 2<sup>+</sup>. Hydrogen atoms are omitted for clarity.

Based on these data compound  $2^+$  can best be described with the resonance form shown on the left in Figure 5, including a single bond between silicon and the central carbon atom, which has a remaining lone pair of electrons with p character. The P-C(0) bonds are weakened and therefore elongated due to the newly formed Si-C bond.



Figure 5. Resonance forms of 2<sup>+</sup>.

In a further step, we computationally investigated the strength of the C-Si bond in  $2^+$ . As shown in Scheme 2, the free energy of dissociation for the SiMe3+ cation is 65.1 kcal·mol<sup>-1</sup> and thereby at the upper range for main-group adducts of 1.<sup>[5c,9]</sup> Since it is known that 1 can form adducts to two Lewis acids, we performed calculations for the attachment of a second SiMe<sub>3</sub><sup>+</sup> cation. Although this resulted in a structure, which is a minimum on the potential energy surface, the dication  $[(Me_3Si)_2C(PPh_3)_2]^{2+}$  (3<sup>2+</sup>) exhibits a negative free energy of dissociation for one TMS group (-64.3 kcal·mol<sup>-1</sup>) and is therefore not regarded as a viable target for chemical synthesis (Scheme 2).<sup>[26]</sup>

As stated above, in solution compound 2 is stable in an inert atmosphere. But, if the inert atmosphere is no longer preserved, conversion of compound 2 to the main decomposition product  $[HC(PPh_3)_2]^+$  (4<sup>+</sup>)<sup>[27]</sup> is observed. This can also be monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy by exposing a NMR sample of 2 (in  $CDCl_3$ ) to air. In the <sup>1</sup>H NMR spectrum the typical triplet of the proton attached to the carbon(0) atom



Scheme 2. Free energies of dissociation (BP86/def2-TZVPP//BP86/ def2-SVP) for compounds  $2^+$  (a) and hypothetical  $3^{2+}$  (b).

Ph<sub>2</sub>F

in 4<sup>+</sup> is present at  $\delta_{\rm H}$  1.86 ppm (<sup>2</sup>J<sub>PH</sub> = 5.3 Hz). In the corresponding <sup>31</sup>P{<sup>1</sup>H} NMR spectrum a new signal appears at  $\delta_{\rm P}$ 21.6 ppm, which is typical for protonated carbodiphosphorane  $[HC(PPh_3)_2]^+$ .<sup>[28]</sup>

Regarding this decomposition reaction of 2 in aerobic conditions, we envisaged an additional protonation of 2 in an inert atmosphere with trifluoromethanesulfonic acid (HOTf). Addition of one equivalent of HOTf to a solution of 2 in CDCl<sub>3</sub> gives rise to a new resonance signal in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta_{\rm P}$  20.0 ppm. However, the resonance signal of starting material **2** is still present at  $\delta_{\rm P}$  26.2 ppm. The corresponding <sup>1</sup>H NMR spectrum shows resonance signals of unreacted **2** and free TMS(OTf). Also, a new triplet is present at  $\delta_{\rm H}$  5.51 ppm with  ${}^{2}J({}^{1}H, {}^{3}P)$  of 15.9 Hz, which corresponds to the twofold protonated carbodiphosphorane 1.<sup>[29]</sup> This observation points to the formation of an intermediate that is not stable in solution and reacts immediately with another HOTf molecule to give the final product  $[H_2C(PPh_3)_2]^{2+}$  (5<sup>2+</sup>) with elimination of the  $(SiMe_3)^+$  group (see Scheme 3). Finally, full conversion of  $2^+$ to  $5^{2+}$  is achieved by adding another equivalent of HOTf to the reaction mixture.



Scheme 3. Presumed reaction course of protonation of compound 2+ to final decomposition product  $5^{2+}$  via hypothetical intermediate (IM, not observed); <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopic data in CDCl<sub>3</sub>, OTf anions are omitted for clarity.

#### Conclusions

We present herein the first molecular structure of the silvlated hexaphenyl carbodiphosphorane 2 alongside with detailed 2D and heteronuclear NMR spectroscopic experiments. Furthermore the molecular structure of 2 is presented together with electronic properties obtained by DFT methods. Experi-



ments concerning further reactivity of **2** and of carbodiphosphorane **1** towards different silicon reagents are in progress and will be presented in due course.

### **Experimental Section**

Synthesis of [Me<sub>3</sub>SiC(PPh<sub>3</sub>)<sub>2</sub>][OTf] (2): To a stirred solution of 1 (70 mg, 0.13 mmol) in toluene (10 mL) TMS-OTf (1 equiv., 0.13 mmol, 24 uL) was added whereupon a precipitate is formed. The suspension is filtered after 2 h and the solid residue is dried in high vacuum. Yield: quantitative. The crude product can be recrystallized from DCM/n-pentane to obtain single crystals of 2. M.p.: 249 °C. Elemental analysis for C41H39F3O3P2SSi (758.853): C 63.81 (calcd. 64.89), H 5.17 (5.18), S 4.12 (4.23)%, <sup>1</sup>H NMR (CDCl<sub>2</sub>);  $\delta = -0.24$ (s, 9 H, -SiCH<sub>3</sub>), 7.41 (m, 12 H, H-C<sup>meta</sup>), 7.51 (m, 12 H, H-C<sup>ortho</sup>), 7.57 (m, 6 H, *H*–C<sup>para</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = -0.89$  (t, <sup>1</sup>*J*<sub>PC</sub> = 73.4 Hz, PCP), 5.4 (-SiCH<sub>3</sub>), 127.5 (vd, AA'X: N = 92.9 Hz, PC<sup>ipso</sup>), 129.2 (vt, C<sup>meta</sup>), 133.3 (s, C<sup>para</sup>), 134.2 (vt, C<sup>ortho</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 26.2 (s, <sup>1</sup>J<sub>PC</sub> = 75.2 Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -1.0 (t,  ${}^{1}J_{SiP} = 5.4$  Hz).  ${}^{19}F$  NMR (CDCl<sub>3</sub>):  $\delta = -77.9$ . IR (ATR):  $\tilde{v} =$ 3066 vw, 2963 vw, 1589 vw, 1481 vw, 1436 w, 1266 m, 1222 w, 1186 vw, 1140 w, 1094 m, 1031 m, 1013 m, 994 m, 941 vw, 894 m, 839 w, 749 m, 694 m, 635 m, 571 vw, 560 sh, 517 m, 508 m, 438 w, 397 w, 370 w. 346 vw. 331 vw. 320 w. 295 vw. 286 vw. 272 w. 261 w. 236 w, 218 w, 206 w, 163 vw, 145 vw, 136 vw, 126 vw, 114 w, 94 w, 84 w, 75 w, 54 m, 38 vs cm<sup>-1</sup>. **Raman** (crystalline):  $\tilde{v} = 1193$  vw, 1101 w, 1034 s, 1005 vs, 754 vw, 712 vw, 692 w, 641 vw, 618 w, 574 vw, 349 vw. 312 vw. 280 vw. 263 w. 244 w. 235 vw. 215 w. 199 vw. 155 vw, 113 m, 100 w cm<sup>-1</sup>. HR-ESI-MS (79 eV, 150 °C): m/z = 609.2287  $(2)^+$  (calcd. 609.2296).

**Computational Details:** Geometry optimizations without symmetry constraints were carried out using the Gaussian09 optimizer<sup>[30]</sup> with Turbomole6<sup>[31]</sup> energies and gradients with the functional and basis set combination BP86<sup>[32]</sup>/def2-SVP.<sup>[33]</sup> Stationary points were characterized as minima and thermodynamic corrections derived by calculating the Hessian matrix analytically at this level of theory.<sup>[34]</sup> Improved energies were derived with the basis set def2-TZVPP<sup>[33]</sup> based on these structures. If not otherwise noted, all computed energies given are free energies ( $\Delta G$ , T = 298.15 K, p = 1 atm) on the BP86/def2-TZVPP// BP86/def2-SVP level of approximation.

Natural partial charges were calculated with the same method employing the Natural Population Analysis<sup>[35]</sup> as implemented in Turbomole.

**Supporting Information** (see footnote on the first page of this article): 2D NMR spectra (HMQC, HMBC, NOESY), IR and Raman spectra, crystallographic data, molecular structure, bond lengths and angles of compound **2**. Cartesian coordinates and SCF energy of computed  $2^+$ .

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### References

[1] a) F. Ramírez, N. B. Desai, B. Hansen, N. McKelvie, J. Am. Chem. Soc. 1961, 83, 3539; b) F. Ramírez, J. F. Pilot, N. B. Desai, C. P. Smith, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1967**, 89, 6273–6276; c) R. Appel, F. Knoll, W. Michel, W. Morbach, H.-D. Wihler, H. Veltmann, *Chem. Ber.* **1976**, *109*, 58–70; d) R. Appel, F. Knoll, H. Schöler, H.-D. Wihler, *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 702–703.

- [2] A. T. Vincent, P. J. Wheatley, J. Chem. Soc. Dalton Trans. 1972, 617.
- [3] a) J. S. Driscoll, D. W. Grisley Jr., J. V. Pustinger, J. E. Harris, C. N. Matthews, J. Org. Chem. 1964, 29, 2427–2431; b) H. J. Bestmann, W. Kloeters, Angew. Chem. 1977, 89, 55; c) H. J. Bestmann, W. Kloeters, Tetrahedron Lett. 1977, 18, 79–80; d) H. J. Bestmann, W. Kloeters, Tetrahedron Lett. 1978, 19, 3343–3344.
- [4] W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, J. Organomet. Chem. 1973, 47, 391–402.
- [5] a) G. Frenking, R. Tonner, Pure Appl. Chem. 2009, 81, 597–614;
  b) R. Tonner, G. Frenking, Chem. Eur. J. 2008, 14, 3260–3272;
  c) R. Tonner, G. Frenking, Chem. Eur. J. 2008, 14, 3273–3289;
  d) R. Tonner, G. Frenking, Angew. Chem. Int. Ed. 2007, 46, 8695–8698;
  e) H. Schmidbaur, Angew. Chem. Int. Ed. 2007, 46, 2984–2985;
  f) G. Frenking, B. Neumüller, W. Petz, R. Tonner, F. Öxler, Angew. Chem. Int. Ed. 2007, 46, 2984–2985;
  g) N. Takagi, T. Shimizu, G. Frenking, Chem. Eur. J. 2009, 15, 8593–8604.
- [6] R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, Angew. Chem. Int. Ed. 2006, 45, 8038–8042.
- For other carbodiphosphoranes of the type C(L)(L') see: L = L'[7] = PMe<sub>3</sub>: a) H. Schmidbaur, O. Gasser, M. S. Hussain, Chem. Ber. 1977, 110, 3501-3507; H. Schmidbaur, O. Gasser, Angew. Chem. Int. Ed. Engl. 1976, 15, 502–503;  $L = L' = PPh_2Me$ : b) H. Schmidbaur, G. Haßlberger, U. Deschler, U. Schubert, C. Kappenstein, A. Frank, Angew. Chem. Int. Ed. Engl. 1979, 18, 408-409; U. Schubert, C. Kappenstein, B. Milewski-Mahrla, H. Schmidbaur, Chem. Ber. 1981, 114, 3070–3078; L = L' = PPhMe<sub>2</sub>: c) H. Schmidbaur, O. Gasser, M. S. Hussain, Chem. Ber. 1977, 110, 3501-3507; H. Schmidbaur, T. Costa, Chem. Ber. 1981, 114, 3063-3069; H. Schmidbaur, T. Costa, B. Milewski-Mahrla, U. Schubert, Angew. Chem. Int. Ed. Engl. 1980, 19, 555-556; L =  $PPh_2-C(H_2)_n-PPh_2$  with n = 2-4: d) H. Schmidbaur, T. Costa, *Chem. Ber.* **1981**, *114*, 3063–3069;  $L = PPh_3$ ,  $L' = PR_3$  with R =Alkvl: e) R. Appel, G. Erbelding, Tetrahedron Lett. 1978, 19, 2689-2692; Additional recapitulation is given in: f) H. Schmidbaur, R. Herr, C. E. Zybill, Chem. Ber. 1984, 117, 3374-3390; H. Schmidbauer, A. Schier, Angew. Chem. Int. Ed. 2013, 52, 176-186
- [8] It is also possible that all four electrons participate in σ- and π-donation to the same lewis acid E simultaneously, see references<sup>[9b,10b]</sup>.
- Be: a) W. Petz, K. Dehnicke, N. Holzmann, G. Frenking, B. Ne-[9] umüller, Z. Anorg. Allg. Chem. 2011, 637, 1702-1710; W. Petz, K. Dehnicke, B. Neumüller, Z. Anorg. Allg. Chem. 2011, 637, 1761–1768; BH<sub>3</sub> and B $R_3$ : b) W. Petz, F. Öxler, B. Neumüller, R. Tonner, G. Frenking, Eur. J. Inorg. Chem. 2009, 4507-4517; B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, Angew. Chem. Int. Ed. 2011, 50, 8400-8403; J. S. Driscoll, D. W. Grisley Jr., J. V. Pustinger, J. E. Harris, C. N. Matthews, J. Org. Chem. 1964, 29, 2427-2431; CO<sub>2</sub> and CS<sub>2</sub>: c) W. Petz, C. Kutschera, M. Heitbaum, G. Frenking, R. Tonner, B. Neumüller, Inorg. Chem. 2005, 44, 1263-1274; In and Al: d) W. Petz, C. Kutschera, S. Tschan, F. Weller, B. Neumüller, Z. Anorg. Allg. Chem. 2003, 629, 1235-1244; I2: e) W. Petz, S. Heimann, F. Öxler, B. Neumüller, Z. Anorg. Allg. Chem. 2007, 633, 365-367; Ge and Sn: f) S. Khan, G. Gopakumar, W. Thiel, M. Alcarazo, Angew. Chem. Int. Ed. 2013, 52, 5644-5647; P: g) M. Q. Y. Tay, Y. Lu, R. Ganguly, D. Vidović, Angew. Chem. Int. Ed. 2013, 52, 3132-3135; S and Se: h) H. Schmidbaur, C. E. Zybill, D. Neugebauer, Angew. Chem. Int. Ed. Engl. 1982, 21, 310-311; H. Schmidbaur, C. E. Zybill, D. Neugebauer, Angew. Chem. Int. Ed. Engl. 1983, 22, 156-157.
- [10] Au: a) H. Schmidbaur, C. E. Zybill, G. Müller, C. Krüger, Angew. Chem. Int. Ed. Engl. 1983, 22, 729–730; J. Vicente, A. R. Singhal, P. G. Jones, Organometallics 2002, 21, 5887–5900; M. Alcarazo,

# ARTICLE

K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* 2013, 49, 3140–3142; ReO<sub>3</sub>: b) J. Sundermeyer, K. Weber,
K. Peters, H. G. Schnering, *Organometallics* 1994, 13, 2560–2562; Zn and Cd: c) W. Petz, B. Neumüller, *Eur. J. Inorg. Chem.* 2011, 4889–4895; Ni: d) W. Petz, F. Weller, J. Uddin, G. Frenking, *Organometallics* 1999, 18, 619–626; Pt: e) W. Petz, C. Kutschera, B. Neumüller, *Organometallics* 2005, 24, 5038–5043; W: f) W. Petz, B. Neumüller, R. Tonner, *Eur. J. Inorg. Chem.* 2010, 1872–1880; Hg: g) W. Petz, B. Neumüller, S. Klein, G. Frenking, *Organometallics* 2011, 30, 3330–3339; Cu and Ag: h) H. Schmidbaur, C. E. Zybill, G. Müller, C. Krüger, *Angew. Chem. Int. Ed. Engl.* 1983, 22, 729–730; C. Zybill, G. Müller, *Organometallics* 1987, 6, 2489–2494; Rh and Pt: i) K. Kubo, N. D. Jones, M. J. Ferguson, R. McDonald, R. G. Cavell, *J. Am. Chem. Soc.* 2005, 127, 5314–5315.

- [11] a) H. Schmidbaur, W. Tronich, *Chem. Ber.* **1968**, *101*, 3545–3555;
   b) H. Schmidbaur, *Acc. Chem. Res.* **1974**, *7*, 62–70.
- [12] M. S. Hussain, H. Schmidbaur, Z. Naturforsch. B 1976, 31, 721– 726.
- [13] W. Uedelhoven, K. Eberl, W. Sieber, F. R. Kreissl, J. Organomet. Chem. 1982, 236, 301–307.
- [14] H. J. Bestmann, H. Oechsner, Z. Naturforsch. B 1983, 38, 861– 865.
- [15] M. Alcarazo, C. Gomez, S. Holle, R. Goddard, Angew. Chem. Int. Ed. 2010, 49, 5788–5791.
- [16] A comparable coupling constant value is given by *Vidović* et al. for  $[iPr_2NP(Cl)C(PPh_3)_2]^+$ :  ${}^{1}J_{CP} = 76.7$  Hz, see reference<sup>[9g]</sup>.
- [17] The resonance signal of the TMS group is found at  $\delta_{\rm C}$  5.4 ppm, which also stands in contrast to the corresponding value given by Bestmann ( $\delta_{\rm C}$  0.1 ppm).
- [18] However, in the  ${}^{31}P{}^{1}H$  NMR spectrum the coupling to the  ${}^{29}Si$  satellites is not apparent.
- [19] However, in the raman spectrum of 2, the vibrations belonging to the monosubstituted phenyl rings are clearly to be seen: the dominant bands at 1005 cm<sup>-1</sup> (in-plane ring deformation) and 1034 cm<sup>-1</sup> (in-plane CH deformation), the weak band at 618 cm<sup>-1</sup> (ring deformation), and two very weak bands near 1170 cm<sup>-1</sup> (in-plane CH deformation); see also F. R. Dollish, W. G. Fateley, F. F. Bentley, *Characterisitc Raman Frequencies of Organic Compounds*, Wiley Interscience, New York-London-Sydney-Toronto 1974.
- [20] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen I, Hauptgruppenelemente*, G. Thieme Verlag, Stuttgart-New York 1981.
- [21]  $(CF_3SO_3)^-$  with  $C_{3\nu}$  symmetry yields two  $\nu(S-O)$  vibrations of SO<sub>3</sub> group  $(A_1 = 1280 \text{ cm}^{-1})$ ,  $E = 1035 \text{ cm}^{-1})$  and two  $\nu(C-F)$  vibrations of CF<sub>3</sub> group  $(A_1 \text{ and } E: 1280-1085 \text{ cm}^{-1})$ , see G. A. Lawrence, *Chem. Rev.* **1986**, 86, 17–33; A. R. Byington, W. E. Bull, *Inorg. Chim. Acta* **1977**, 21, 239–244.

- [22] For comparison: in the infra red spectrum of **1** the vibration of the P–C(0)–P unit gives rise to a very strong band at v[P–C(0)–P] =  $1312 \text{ cm}^{-1}$  (computed:  $1300 \text{ cm}^{-1}$ ).
- [23] Crystallographic data (excluding structure factors) for the structure 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 number CCDC-937006 for compound 2 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).
- [24] N. Kuhn, T. Kratz, D. Bläser, R. Boese, Chem. Ber. 1995, 128, 245–250.
- [25] See reference<sup>[9d]</sup> for different PCP angles and references cited therein.
- [26] Indeed, reaction of **1** with excess of TMS-OTf (3.7 equiv.) only results in the formation of compound **2** exclusively.
- [27] For 4<sup>+</sup> see reference<sup>[3a]</sup> and W. Petz, F. Weller, Z. Kristallogr. 1997, 212, 157.
- [28] For comparable NMR spectroscopic data of  $4^{\scriptscriptstyle +}$  see references  $\mathrm{es}^{\mathrm{[3a,10c]}}.$
- [29] See reference<sup>[3a]</sup> for corresponding dibromide salt [H<sub>2</sub>C(PPh<sub>3</sub>)  $_2$ ]<sup>2+</sup>:  $\delta_P$  18.4 ppm and  $\delta_H$  6.75 ppm [t, <sup>2</sup>J(<sup>1</sup>H, <sup>31</sup>P) = 16 Hz] in MeOD/D<sub>2</sub>0.
- [30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. B. G. Scalmani, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Gaussian 09, Revision A.02, Wallingford CT, 2009
- [31] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- [32] a) J. P. Perdew, *Phys. Rev. B* 1986, 33, 8822; b) A. D. Becke, *Phys. Rev. A* 1988, 38, 3098.
- [33] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297; b) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, 8, 1057.
- [34] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511.
- [35] A. E. Reed, R. B. Weinstock, F. Weinhold, J. Chem. Phys. 1985, 83, 735–746.

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