Germylene Adducts

International Edition: DOI: 10.1002/anie.201601468
German Edition: DOI: 10.1002/ange.201601468

The Bis(pentafluoroethyl)germylene Trimethylphosphane Adduct $(C_2F_5)_2Ge{\cdot}PMe_3$: Characterization, Ligand Properties, and Reactivity

*Stefanie Pelzer, Beate Neumann, Hans-Georg Stammler, Nikolai Ignat'ev, and Berthold Hoge**

Dedicated to Professor Reint Eujen on the occasion of his 70th birthday

***Abstract:** The synthesis of the germylene phosphane adduct $(C_2F_5)_2Ge{\cdot}PMe_3$ is described. Starting from $(C_2F_5)_3GeH$ in an excess of PMe_3, heating was applied, whereupon reductive elimination of C_2F_5H occurred. The molecular structure was ascertained by X-ray diffraction and compared with information obtained by quantum chemical methods. The ligand properties were derived by studying the IR spectrum of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ in the CO region. $(C_2F_5)_2Ge{\cdot}PMe_3$ turned out to be a π-accepting ligand comparable to PMe_3, in terms of Tolman's electronic parameter. Furthermore a [2+4] cycloaddition reaction with 2,3-dimethyl-1,3-butadiene, and σ-bond insertion reactions were recorded. Activation of the C−Cl bond in dichloromethane gives rise to the formation of the phosphonium ylide complex $[(C_2F_5)_2Cl_2Ge\text{-}CH_2PMe_3]$, which was fully characterized by X-ray diffraction.*

The chemistry of organogermylenes, the heavier homologues of carbenes, has been studied since the 1970s, with the first stable organogermylenes ($Ge[N\textit{t}\text{-}Bu(SiMe_3)]_2$ and $Ge[N(SiMe_3)_2]_2$) isolated by Lappert et al. in 1974 showing a monomeric structure in solution and in the gasphase, but a dimeric structure motif in solid state.[1] The first stable organogermylene, showing a germylene structure even in the solid state, was isolated by Jutzi et al. in 1991.[2]

The most prominent halides of germanium are those in the oxidation states IV and II. Whereas the tetrahalides GeX_4 (X = F, Cl, Br, I) consist of a tetrahedral molecule, the divalent species consist of Ge-X-Ge-X-… chains (X = F) or crystallize in a distorted (X = Br) or a non-distorted (X = I) CdI_2-type layer lattice. The solid-state structure of $GeCl_2$ is unknown, but structural clarification in the gas phase was accomplished through milimeter-wave spectroscopy or a combined high-temperature electron diffraction/quadrupole mass spectrometry experiment.[3] However, with 1,4-dioxane, this compound forms a soluble and conveniently tractable complex consisting of infinite chains of alternating $GeCl_2$ units, and each germanium atom is coordinated by two 1,4-dioxane molecules.[4]

Exchanging the donating ligand with the stronger and sterically more demanding triphenylphosphane leads to a monomeric structure of the germanium dichloride adduct ($Cl_2Ge{\cdot}PPh_3$), with an absence of intermolecular Ge···Cl interactions.[4] Monomeric germylenes are sextet species in a singlet spin state with a pair of electrons in a mainly s-type orbital and a vacant 4p orbital. Germylenes are thus Lewis acids that frequently add donor molecules by means of this empty 4p orbital. This was confirmed by structural and theoretical investigation of the mentioned $Cl_2Ge{\cdot}PPh_3$, which shows a Cl-Ge-Cl bond angle of 97.41(2)° and Cl-Ge-P bond angles around 90°, thus indicating high p-orbital character for the Ge−P bond.[4]

In the course of our studies on main-group-element perfluoroorganyls, we synthesized bis(pentafluoroethyl)germylene as the stable and isolable trimethylphosphane adduct $(C_2F_5)_2Ge{\cdot}PMe_3$. First attempts at the synthesis of donor-stabilized bis(pentafluoroethyl)germylene included the treatment of $(C_2F_5)_2GeH_2$[5] with donor molecules, based on the synthesis of $(C_2F_5)_2Sn{\cdot}d$ (d = thf, 4-dimethylaminopyridine),[6] but these reactions did not produce the desired outcome.

In 1989, the group of Eujen succeeded in generating the adduct $(CF_3)_2Ge{\cdot}PMe_3$, which was generated by thermolysis of $(CF_3)_3GeH$ in an excess of neat PMe_3.[7] With the application of these reaction conditions, $(C_2F_5)_2Ge{\cdot}PMe_3$ is accessible [Eq. (1)].

$$(C_2F_5)_3GeH + PMe_3 \xrightarrow[-C_2F_5H]{120\,^\circ C,\ 2\ d} (C_2F_5)_2Ge \cdot PMe_3 \qquad (1)$$

According NMR monitoring of the reaction mixture, the reactants at room temperature initially form $[HPMe_3][Ge(C_2F_5)_3]$. Heating the reaction mixture in a flask equipped with a Young valve for 2 d effected quantitative conversion of the salt-like $[HPMe_3][Ge(C_2F_5)_3]$ initial product into the title compound $(C_2F_5)_2Ge{\cdot}PMe_3$. In sharp contrast to $(CF_3)_2Ge{\cdot}PMe_3$, which is only stable in an excess of PMe_3, and which frequently polymerizes upon removal of the solvent under vacuum, the prepared $(C_2F_5)_2Ge{\cdot}PMe_3$ can be isolated as an orange oily liquid that is stable at room temperature.

The ^{19}F NMR spectrum of $(C_2F_5)_2Ge{\cdot}PMe_3$ in $CDCl_3$ at 23 °C shows two singlet-like resonances at $\delta = -83.1$ ppm (CF_3) and -110.6 ppm (CF_2), with the latter showing substantial broadening. The $^{31}P\{^1H\}$ NMR spectrum is characterized by a broad singlet-like signal at $\delta = -16.9$ ppm. Upon cooling the sample to −60 °C, the signal for the CF_2 units splits

---

[*] Dr. S. Pelzer, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. B. Hoge
Centrum für Molekulare Materialien
Fakultät für Chemie, Anorganische Chemie, Universität Bielefeld
Universitätsstraße 25, 33615 Bielefeld (Germany)
E-mail: b.hoge@uni-bielefeld.de

Dr. N. Ignat'ev
Consultant, Merck KGaA
Frankfurter Str. 250, 64293 Darmstadt (Germany)

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201601468.

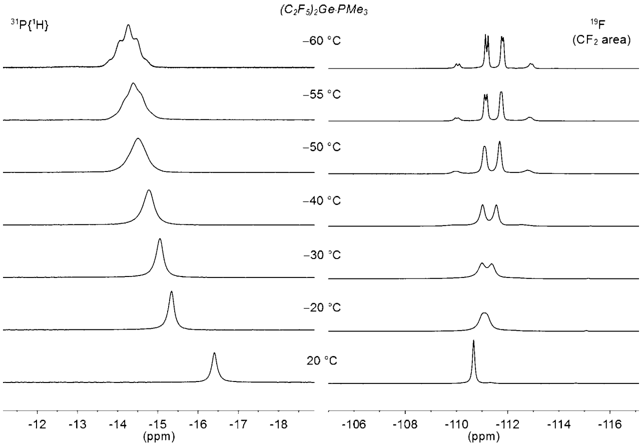


Figure 1. NMR experiments with $(C_2F_5)_2Ge{\cdot}PMe_3$ at low temperatures in $CDCl_3$.

into an AB pattern (Figure 1, top right), and this is consistent with the solid-state structure, which reveals diastereotopic fluorine atoms at each CF_2 unit (Figure 1). The $^{31}P\{^1H\}$ NMR resonance at $\delta = -14.3$ ppm may now be described as a broad quintet with a $^3J(P,F)$ coupling constant of 27 Hz (Figure 1, top left).

Single crystals suitable for X-ray investigation were grown by in situ crystallization of the orange oily product in a glass capillary. An appropriate seed crystal was manually generated slightly below the melting point of 21 °C, followed by slow cooling to −73 °C. The obtained crystal was an inversion twin (ratio 60:40). The germylene adduct $(C_2F_5)_2Ge{\cdot}PMe_3$ crystallizes in the orthorhombic space group $P2_12_12_1$, with one C_2F_5 group disordered in a ratio of 1:1. For clarity, only one conformer is displayed in Figure 2.

The molecule $(C_2F_5)_2Ge{\cdot}PMe_3$ takes the geometry of a pseudo trigonal pyramid, with the germanium atom residing in the center. PMe_3 is coordinated nearly orthogonal to the plane defined by the atoms C1, Ge, and C3A, as evidenced by the C-Ge-P bond angles ranging from 87.0(5)° to 100.3(5)°. These bond angles point to a high p-orbital character of the Ge−P bond. The lone pair of the germanium atom should thus be located in an orbital with high s character. This agrees nicely with Bent's rule[8] that electron-withdrawing substituents, such as C_2F_5 groups, induce p-orbital character, which is reflected by the C-Ge−C bond angles of 105.1(5)° (conformer A) and 87.0(5)° (conformer B). The Ge−P bond length of 239.9(2) pm is significantly shorter than in $Cl_2Ge{\cdot}PPh_3$ (250.84(7) pm),[4] which could be explained by the stronger donating properties of PMe_3 in comparison to PPh_3 and the higher Lewis acidity of the germanium atom bonded to the strong electron-withdrawing C_2F_5 groups.

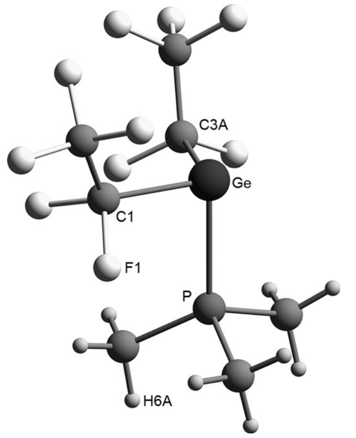
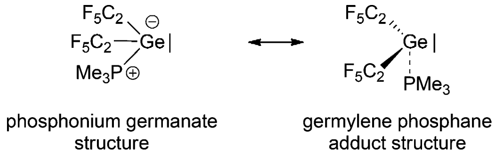


Figure 2. Molecular structure of $(C_2F_5)_2Ge{\cdot}PMe_3$, shown as a ball-and-stick model. For clarity, only conformer A is shown. All C_2F_5 groups were restrained to be same, so their bond parameters have to be regarded with suspicion. Selected bond lengths [pm] and angles [°]: Ge−P 239.9(2), Ge−C1 206.3(8), Ge−C3A 21(2), Ge−C3B 209(2); C1-Ge-C3A 105.1(5), C1-Ge-C3B 87.0(5), C1-Ge-P 91.7(2), C3A-Ge-P 88.7(4), C3B-Ge-P 100.3(5).

Formally, $(C_2F_5)_2Ge{\cdot}PMe_3$ could be regarded as a germylene phosphane adduct or as a phosphonium germanide with an ylidic structure (Scheme 1).[9] In accordance with the molecular structure in the solid state, the description of $(C_2F_5)_2Ge{\cdot}PMe_3$ as a germylene phosphane adduct seems more appropriate, but this was clarified by a theoretical study as well.

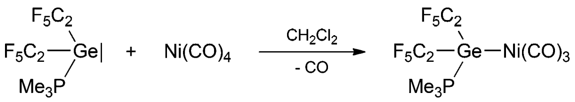


Scheme 1. Resonance structures of $(C_2F_5)_2Ge{\cdot}PMe_3$.

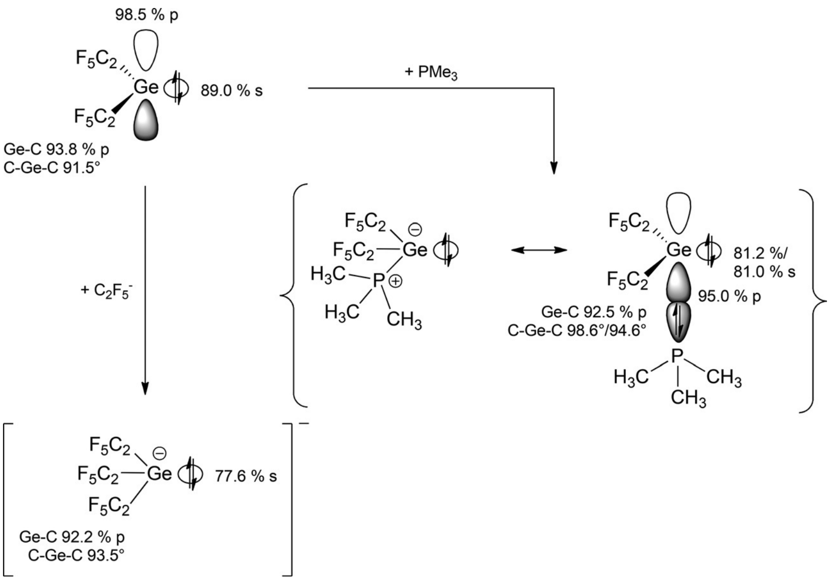
In addition to the germylene phosphane adduct, the structures of the free germylene $Ge(C_2F_5)_2$ and the germanide ion $[Ge(C_2F_5)_3]^-$ were analyzed by quantum chemical methods in the gas phase.[10] After optimization of the structure and frequency calculations, an NBO[11] analysis was performed. The results are displayed in Scheme 2.

Based on the quantum chemical calculations, no unambiguous description of the bonding situation is possible. Even if the s-orbital character of the free electron pair decreases from the free germylene (89.0% s) to the germylene phosphane adduct (81.2/81.0% s), there is even less s-orbital character in $[Ge(C_2F_5)_3]^-$ (77.6% s). Regarding the p-orbital character of the Ge−P bond in $(C_2F_5)_2Ge{\cdot}PMe_3$ (95.0% p), there is only a marginal change in comparison to the vacant p-orbital of the free germylene (98.5% p) and the p-orbital of the Ge−C bond in $[Ge(C_2F_5)_3]^-$ (92.2% p).

Phosphonium ylides are known as powerful donor ligands in the coordination chemistry of transition metals. To estimate the ligating properties of $(C_2F_5)_2Ge{\cdot}PMe_3$, a tricarbonylnickel(0) complex was synthesized according to Equation (2) in 80% yield.



$$(C_2F_5)_2(Me_3P)Ge| + Ni(CO)_4 \xrightarrow[-\,CO]{CH_2Cl_2} (C_2F_5)_2(Me_3P)Ge{-}Ni(CO)_3 \qquad (2)$$



Scheme 2. Quantum chemical results (B3LYP/6-311++G(2d,p), NBO 6.0).[10,11] The given orbital character refers to the germanium atom.

The ^{19}F NMR spectrum of the light orange crystals of $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ shows a singlet-like resonance for the CF_3 groups and an AB pattern with a pseudo-doublet splitting for the CF_2 groups (Figure 3).

The resolution of the spin system in the ^{31}P NMR spectrum of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ was also higher than that for the non-coordinated $(C_2F_5)_2Ge{\cdot}PMe_3$. This indicates a more fixed coordination in the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$. Based on an AA′BB′M$_6$X spin system (A, B = ^{19}F (CF_2), M = ^{19}F (CF_3), X = ^{31}P), the ^{31}P NMR spectrum was simulated (Figure 4). Two different ^3J(P,F) coupling constants were determined, with values of $^3J(P,F_A) = {}^3J(P,F_{A'}) = 17.39$ Hz and $^3J(P,F_B) = {}^3J(P,F_{B'}) = 16.69$ Hz. The ^4J(P,F) coupling constant is 2.60 Hz.

The molecular structure of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ was elucidated by X-ray diffraction analysis. The investigated crystal was non-merohedrically twinned by a rotation of 180° around [001], with a ratio of 95:5. $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ crystallizes in the monoclinic space group $P2_1/c$. The germanium atom is in the center of a distorted tetrahedron (Figure 5). The bond angles C-Ge-C (97.0(1)°) and C-Ge-P (94.51(7)° and 98.21(7)°) are markedly compressed in comparison to the angles C-Ge-Ni (124.52(8)° and 122.24(7)°) and P-Ge-Ni (114.11(2)°). The Ge−P bond length (238.29(6) pm) is slightly shorter than in the non-coordinated $(C_2F_5)_2Ge{\cdot}PMe_3$ (239.9(2) pm). The Ge−Ni bond length is 229.59(3) pm, making it comparable to the assumed P−Ni bond (228 pm)[12] used to determine the Tolman cone angle for phosphane ligands. Therefore, with respect to atoms H6C, F4, and F8, and the van der Waals radii for hydrogen (100 pm)[12] and fluorine (135 pm),[12] the Tolman cone angle was estimated to be 168°. The ligand $(C_2F_5)_2Ge{\cdot}PMe_3$ may thus be sterically compared to PCy_3 (Cy = cyclohexyl), which has a Tolman cone angle of 170 pm.[12]

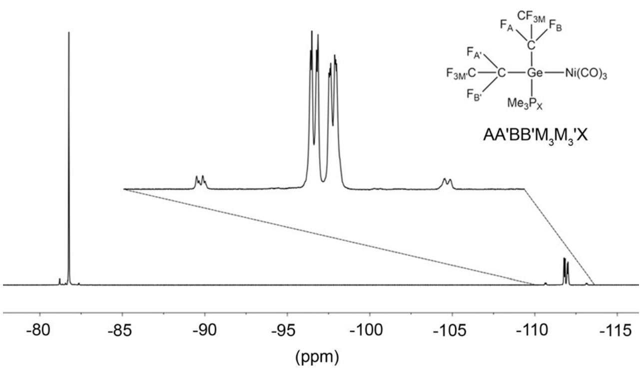


Figure 3. ^{19}F NMR spectrum, with an extension of the CF_2 area, of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$.

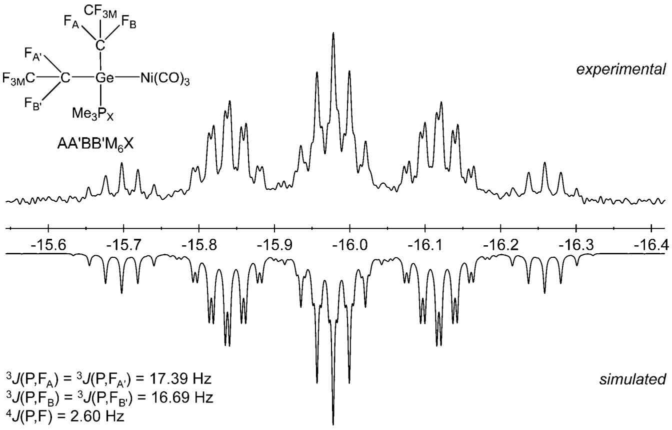


Figure 4. Experimental and simulated ^{31}P NMR spectra of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$, regarded as an AA′BB′M$_6$X spin system.

Next to steric effects, electronic effects, e.g., the π-acceptor properties of a ligand, can also be derived from a concept described by Tolman. The Tolman electronic parameter is defined as the wavenumber of the highest CO stretching vibration of a $Ni(CO)_3$ complex in CH_2Cl_2 at room temperature. Even though the IR spectrum of the nickel(0) complex $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ was not recorded in solution but in the solid state, an estimated statement about the π-acceptor properties of $(C_2F_5)_2Ge{\cdot}PMe_3$ can be given. The band for the CO stretching vibration in the IR spectrum of solid $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ at $\tilde{\nu} = 2067\ cm^{-1}$ (Figure 6) allows comparison of the $(C_2F_5)_2Ge{\cdot}PMe_3$ ligand with PMe_3 ($\tilde{\nu} = 2064\ cm^{-1}$).[12] But it may be regarded as a better π-acceptor than PCy_3 ($2056\ cm^{-1}$),[12] and clearly an inferior π-acceptor to $P(C_2F_5)_3$ in $[Ni(CO)_3P(C_2F_5)_3]$ ($\tilde{\nu} = 2114\ cm^{-1}$).[13]

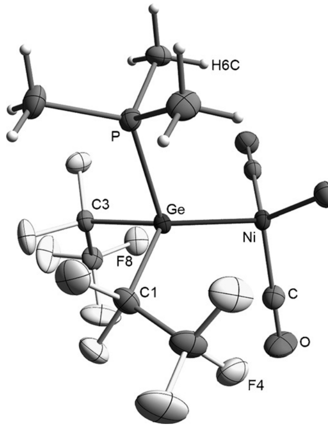


Figure 5. Molecular structure of $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$ (thermal ellipsoids are set at 50% probability). Selected bond lengths [pm] and angles [°]: Ge–Ni 229.59(3), Ge–P 238.29(6); P-Ge-C1 98.21(7), P-Ge-C3 94.51(7), P-Ge-Ni 114.11(2), C1-Ge-C3 97.0(1), C1-Ge-Ni 124.52(8), C3-Ge-Ni 122.24(7).

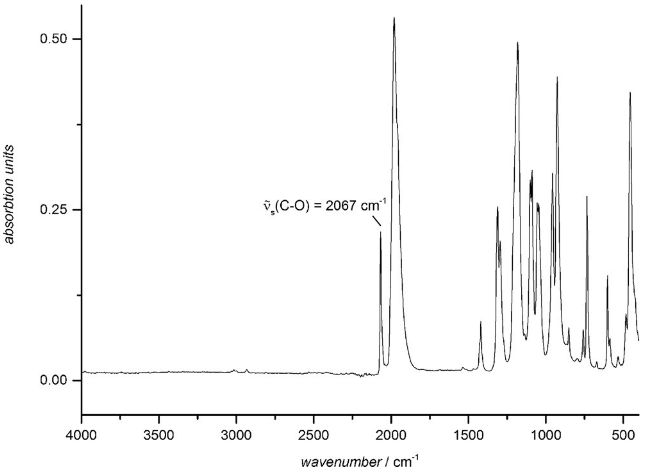
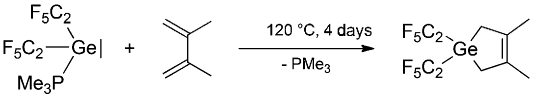


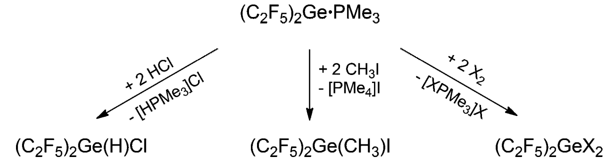
Figure 6. IR spectrum (ATR) of $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$.

By analogy to silylenes[14] and some germylenes,[7,15] which undergo oxidative 1,4-additions with unsaturated 1,3-dienes, the adduct $(C_2F_5)_2Ge{\cdot}PMe_3$ serves as a source of the germylene, as evidenced by smooth [2+4] cycloaddition to 2,3-dimethyl-1,3-butadiene to afford 1-germacyclopent-3-en [Eq. (3)] as observed by NMR spectroscopy. The ^{19}F-^{13}C HMBC NMR spectrum gave evidence for long-range couplings between the fluorine atoms of the CF_2 and CF_3 groups to the methylene carbon atoms coordinated to the germanium atom.



(3)

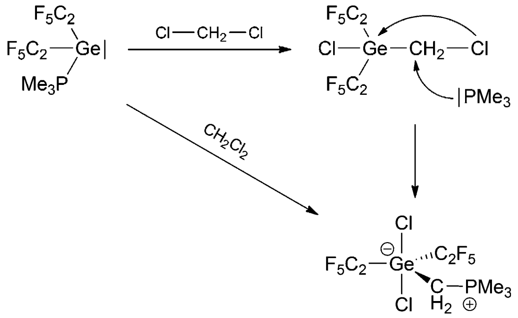
Insertion reactions with release of PMe_3 were observed for the reaction of $(C_2F_5)_2Ge{\cdot}PMe_3$ with hydrogen halides, iodomethane, and elemental halogens (Scheme 3). These reactions constitute a different approach to the previously reported bis(pentafluoroethyl)germanes $(C_2F_5)_2GeX_2$,[5] $(C_2F_5)_2Ge(CH_3)X$, and $(C_2F_5)_2Ge(H)X$ as interesting functionalizable pentafluoroethylgermanes.



Scheme 3. Insertion reactions of $(C_2F_5)_2Ge{\cdot}PMe_3$ into halogen–hydrogen, halogen–carbon, and halogen–halogen bonds (X = Br, I).

Another interesting insertion was observed when $(C_2F_5)_2Ge{\cdot}PMe_3$ was treated with CH_2Cl_2 at room temperature for 2 weeks. Obviously, the germylene adduct activates the Cl–C bond of dichloromethane to furnish the zwitterionic compound $(C_2F_5)_2GeCl_2(CH_2PMe_3)$ as a small number of isolable colorless crystals. This reaction is in a sharp contrast to the behavior of $GeCl_2{\cdot}$dioxane or $\{GeMe_2\}$ towards dichloromethane. Whereas $\{GeMe_2\}$ shows no tendency to insert into the strong Cl–C bond of the solvent,[16] harsh conditions at 180 °C in an autoclave are required to obtain $H_2C(Cl)GeCl_3$ from $GeCl_2{\cdot}$dioxane and CH_2Cl_2.[17]

For the formation of this zwitterion, which contains a chlorogermanate and a phosphonium unit, the mechanism as depicted in Scheme 4 is conceivable. This reaction is initiated by a formal insertion of the free germylene into the C–Cl bond of a dichloromethane molecule. Subsequently, nucleophilic attack of the lone pair at the phosphorus atom on the carbon atom of the methylene unit occurrs, accompanied by a chloride shift onto the germanium atom. Alternatively, the reaction of the adduct and CH_2Cl_2 could start with nucleophilic attack by PMe_3 on CH_2Cl_2, with a subsequent insertion. The product was structurally investigated by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/n$ (Figure 7). The germanium atom is in the center of a trigonal bipyramid, with the chlorides in the axial position. This geometry is due to the steric demand of the phosphonium unit and the more electronegative C_2F_5 groups coordinating in the equatorial plane. The Ge–Cl bond lengths average to 237 pm and the Cl-Ge-Cl unit is linear.



Scheme 4. Reaction of $(C_2F_5)_2Ge{\cdot}PMe_3$ with dichloromethane to form the zwitterionic compound $(C_2F_5)_2GeCl_2(CH_2PMe_3)$.

In conclusion, the germylene adduct $(C_2F_5)_2Ge{\cdot}PMe_3$ was synthesized through the reaction of $(C_2F_5)_3GeH$ with PMe_3 by

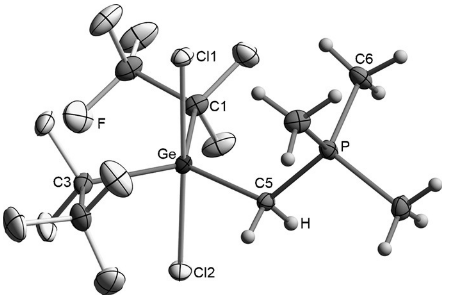


Figure 7. Molecular structure of $(C_2F_5)_2GeCl_2(CH_2PMe_3)$ (thermal ellipsoids are set at 50% probability). Selected bond lengths [pm] and angles [°]: Ge–Cl1 238.47(4), Ge–Cl2 235.41(4), Ge–C1 204.7(2), Ge–C3 205.2(2), Ge–C5 196.6(1), P–C5 179.6(1), P–C6 179.1(2); Cl1-Ge-Cl2 177.88(1), Cl1-Ge-C1 88.04(4), Cl1-Ge-C3 88.63(4), Cl1-Ge-C5 93.62(4), Cl2-Ge-C1 92.52(4), Cl2-Ge-C3 89.31(4), Cl2-Ge-C5 87.87(4), C1-Ge-C3 118.19(6), C1-Ge-C5 120.50(6), C3-Ge-C5 121.31(6).

boiling in PMe_3 for 2 days. Its molecular structure in the solid state was studied by X-ray diffraction and confirmed by DFT calculations. According to an NBO analysis, the bonding situation of $(C_2F_5)_2Ge{\cdot}PMe_3$ is better described as a germylene phosphane adduct than a phosphonium germanide. The ligating properties of $(C_2F_5)_2Ge{\cdot}PMe_3$ were studied through the preparation of $[Ni(CO)_3\{Ge(C_2F_5)_2(PMe_3)\}]$. IR spectroscopic studies make it obvious that the π-acidity of $(C_2F_5)_2Ge{\cdot}PMe_3$ is comparable to that of PMe_3. The reactivity of $(C_2F_5)_2Ge{\cdot}PMe_3$ was demonstrated by [2+4] cheletropic cycloadditions with 1,3-dienes as well as by insertion of the free germylene into halide–halide, hydrogen–halide and carbon–halide bonds. The reaction of $(C_2F_5)_2Ge{\cdot}PMe_3$ with CH_2Cl_2 revealed PMe_3 to be a non-innocent ligand, and a formal ylide complex of trimethylphosphoniummethanide ($Me_3P{=}CH_2$) and $(C_2F_5)_2GeCl_2$ was formed.

Acknowledgements

This work was supported by Merck KGaA (Darmstadt, Germany). Solvay (Hannover, Germany) is gratefully acknowledged for donation of pentafluoroethane (Solkane ® 125). We also acknowledge support by the Deutsche Forschungsgemeinschaft (Core Facility GED@BI, Mi477/21-1). We thank Prof. Dr. Lothar Weber and Dr. Julia Bader for helpful discussions and Florian Uthoff for help in the laboratory.

Keywords: fluorine · fluorinated ligands · germanium · X-ray diffraction · structure elucidation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 6088–6092
Angew. Chem. **2016**, *128*, 6192–6197

---

[1] a) D. H. Harris, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1974**, 895; b) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268; c) M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc. Dalton Trans.* **1977**, 2004.

[2] P. Jutzi, A. Becker, H. G. Stammler, B. Neumann, *Organometallics* **1991**, *10*, 1647–1648.

[3] a) A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der anorganischen Chemie*, *Vol. 102*, de Gruyter, Berlin [u.a.], **2007**; b) M. J. Tsuchiya, H. Honjou, K. Tanaka, T. Tanaka, *J. Mol. Struct.* **1995**, *352–353*, 407–415; c) G. Schultz, J. Tremmel, I. Hargittai, I. Berecz, S. Bohátka, N. D. Kagramanov, A. K. Maltsev, O. M. Nefedov, *J. Mol. Struct.* **1979**, *55*, 207–214.

[4] L. A. Leites, A. V. Zabula, S. S. Bukalov, A. A. Korlyukov, P. S. Koroteev, O. S. Maslennikova, M. P. Egorov, O. M. Nefedov, *J. Mol. Struct.* **2005**, *750*, 116–122.

[5] S. Pelzer B. Neumann, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Chem. Eur. J.* **2016**, *22*, 4758–4763.

[6] J. Klösener, Dissertation, Universität Bielefeld, Bielefeld, **2013**.

[7] M. Richter, Dissertation, Bergische Universität—Gesamthochschule Wuppertal, Wuppertal, **1989**.

[8] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275–311.

[9] a) *The Metal-Carbon Bond*, *Vol. 1* (Eds.: F. R. Hartley, S. Patai), Wiley, Chichester, **1983**; b) W. P. Neumann, *Chem. Rev.* **1991**, *91*, 311–334.

[10] M. J. Frisch et al., Gaussian09, Revision D.01, Gaussian, Inc., Wallingford CT, **2013**.

[11] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, NBO 6.0., Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2013**.

[12] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[13] A. V. Zakharov, Y. V. Vishnevskiy, N. Allefeld, J. Bader, B. Kurscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, R. J. F. Berger, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2013**, 3392–3404.

[14] a) *The Chemistry of Organic Silicon Compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**; b) N. Wiberg, W. Niedermayer, *J. Organomet. Chem.* **2001**, *628*, 57–64; c) N. Laskowski, K. Junold, C. Kupper, J. A. Baus, C. Burschka, R. Tacke, *Organometallics* **2014**, *33*, 6141–6148.

[15] a) J. Koecher, W. P. Neumann, *J. Am. Chem. Soc.* **1984**, *106*, 3861–3862; b) N. Tokitoh, K. Manmaru, R. Okazaki, *Organometallics* **1994**, *13*, 167–171; c) M. Huang, M. M. Kireenko, K. V. Zaitsev, Y. F. Oprunenko, A. V. Churakov, J. A. K. Howard, E. K. Lermontova, D. Sorokin, T. Linder, J. Sundermeyer, S. S. Karlov, G. S. Zaitseva, *Eur. J. Inorg. Chem.* **2012**, *2012*, 3712–3724.

[16] J. Koecher, M. Lehnig, W. P. Neumann, *Organometallics* **1988**, *7*, 1201–1207.

[17] N. A. Viktorov, T. K. Gar, V. F. Mironov, *J. Gen. Chem. USSR* **1985**, 1079.

Received: February 10, 2016