backbone); UV/Vis (CH_3CN): λ_{max}: 486, 305, 268 nm; GPC (UV): M_n = 7800, PDI = 1.08; MALDI-TOF MS: M_n = 5348 g mol^{-1}.

Received: April 22, 2002 [Z19125]

[1] a) N. Noshay, J. E. McGrath, *Block Copolymers*, Academic Press, London, **1977**; b) I. W. Hamley, *The Physics of Block Copolymers*, Oxford Science Publications, Oxford, **1998**.

[2] a) M. Szwarc, *Nature* **1956**, *178*, 1168 – 1169; b) N. Hadjichristidis, *Chem. Rev.* **2001**, *101*, 3747 – 3792.

[3] a) K. Matyjaszewski, *Chem. Rev.* **2001**, *101*, 2921 – 2990.

[4] a) J. P. Kennedy, E. G. Melby, A. Vidal, *J. Macromol. Sci. Chem.* **1975**, *A9*, 833 – 847; b) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689 – 3745.

[5] a) J. P. Kennedy, R. H. Wondraczek, *Polym. Bull.* **1981**, *4*, 445 – 450; b) T. Otsu, M. Yoshida, *Macromol. Chem. Rapid Commun.* **1982**, *3*, 127 – 132; c) O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. RajanBabu, *J. Am. Chem. Soc.* **1983**, *105*, 5706 – 5708.

[6] a) S. A. Krouse, R. R. Schrock, *Macromolecules* **1988**, *21*, 1885 – 1888; b) K. J. Ivin, J. C. Mol, *Olefin metathesis and metathesis polymerization*, Academic Press, San Diego, **1997**.

[7] a) J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, **1995**; b) J. A. Zerkowski, C. T. Seto, G. M. Whitesides, *J. Am. Chem. Soc.* **1992**, *114*, 5473 – 5475; c) J.-M. Lehn, M. Mascal, A. DeCian, J. Fischer, *J. Chem. Soc. Perkin Trans.* **1992**, *2*, 461 – 467.

[8] a) E. C. Constable, A. M. W. C. Thompson, *J. Chem. Soc. Dalton Trans.* **1992**, 3467 – 3475; b) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci.* **1993**, *90*, 5394 – 5398; c) E. He, C. N. Moorefield, G. R. Newkome, *Chem. Rev.* **1999**, *99*, 1689 – 1746; d) L. Brunsveld, B. J. B. Folmer, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2001**, *101*, 4071 – 4098.

[9] See, for example: a) E. C. Constable, *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69 – 121; b) U. S. Schubert, C. Eschbaumer, P. Andres, H. Hofmeier, C. H. Weidl, E. Herdtweck, E. Dulkeith, A. Morteani, N. E. Hecker, J. Feldmann, *Synth. Met.* **2001**, *121*, 1249 – 1252.

[10] a) G. T. Morgan, F. H. Burstall, *J. Chem. Soc.* **1937**, 1649 – 1655; b) C. M. Harris, T. N. Lockyer, N. C. Stephenson, *Aust. J. Chem.* **1966**, *19*, 1741 – 1743; c) J. Pickardt, B. Staub, K. O. Schäfer, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1217 – 1224.

[11] a) B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 1404 – 1407; b) T. Togano, N. Nagao, M. Tsuchida, H. Kumakura, K. Hisamatsu, F. S. Howell, M. Mukaida, *Inorg. Chim. Acta* **1992**, *195*, 221 – 225.

[12] a) O. Hien, C. Eschbaumer, U. S. Schubert, *Macromol. Rapid Commun.* **2000**, *21*, 1156 – 1161; b) C. Eschbaumer, U. S. Schubert, *Macromol. Symp.* **2001**, *163*, 177 – 187.

[13] B. G. G. Lohmeijer, U. S. Schubert, *Polym. Mater. Sci. Eng.* **2001**, *85*, 460 – 461.

[14] J.-F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules* **2002**, *35*, 4560 – 4563; J.-F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromol. Rapid Commun.* **2002**, *23*, 555 – 560; J.-F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, U. S. Schubert, *Macromolecules* **2002**, *35*, 7427 – 7435.

Unusual P=C Bond Cleavage by Double Dichlorosilylene Transfer from Trichlorosilyltrimethylgermane to *P*-Phosphanyl Phosphaalkenes

Wolf-Walther du Mont,* Thorsten Gust, Emma Seppälä, Cathleen Wismach, Peter G. Jones, Ludger Ernst, Jörg Grunenberg, and Heinrich C. Marsmann

Dedicated to Professor Hans Bürger on the occasion of his 65th birthday

The major breakthroughs in the chemistry of stable carbenes and Group 14 carbene analogues in the last two decades were based on the use of sterically and electronically stabilizing substituents.[1] Concerning short-lived dihalogenosilylenes, however, very little synthetic progress has been made even 30 years after the basic high-temperature and matrix studies of Timms et al.[2,3] Oligomeric silanes of the empirical formula $SiCl_2$ are synthetically available, but they do not behave as sources of monomeric $SiCl_2$;[4] the alternative use of Si_2Cl_6[5] or $HSiCl_3$[6] as precursors is very limited. Herein, we report the use of trichlorosilyltrimethylgermane ($Me_3GeSiCl_3$, **1**)[7,8] as a new reagent for the transfer of $SiCl_2$ moieties to *P*-phosphanyl phosphaalkenes under very mild reaction conditions.

Pure **1**—a monomeric molecular compound in the gas phase—[7c] is thermally stable; in the presence of tertiary amines and phosphanes, however, **1** partially decomposes to $(Me_3Ge)_2Si(SiCl_3)_2$, Me_3GeCl, and $SiCl_4$; this observation was explained by sequences of nucleophile-catalyzed transfers of Me_3Ge and $SiCl_3$.[7,8] Alternatively, for the $SiCl_3$ transfer, the formation of $(Me_3Ge)_2Si(SiCl_3)_2$ may imply insertion reactions of nucleophile-coordinated dichlorosilylene ($SiCl_2$) into Si–Cl bonds.[7,8] If nucleophiles such as Et_3N and iPr_3P can really induce the α-elimination of chlorogermanes from **1** [Eq. (1)],[9] then trichlorosilylgermanes, such as **1**, would be important reagents for $SiCl_2$ transfer reactions.

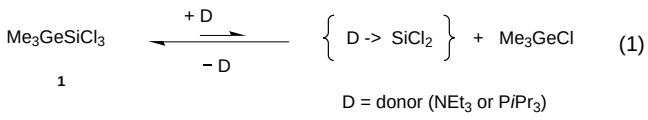
Our first choice as $SiCl_2$ trapping reagents were the *P*-phosphanyl phosphaalkenes $(Me_3Si)_2C{=}P\text{-}PRR'$(**2a**: R, R′ = *i*Pr; **2b**: R = *t*Bu, R′ = *i*Pr).[10] The dialkylphosphanyl groups within the reagent were intended to induce the desired α elimination at **1** [Eq. (1)] and coordinate intermediate $SiCl_2$, the adjacent P–P bonds may allow subsequent $SiCl_2$ insertion reactions, and the P=C bonds should be suitable for [2+1] cycloadditions with silylenes, similar to the known reactions of

[*] Prof. Dr. W.-W. du Mont, Dipl.-Chem. T. Gust, M. Sc. E. Seppälä, Dipl.-Chem. C. Wismach, Prof. Dr. P. G. Jones, Prof. Dr. L. Ernst
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Postfach 3329, 38023 Braunschweig (Germany)
Fax: (+49) 531-3915387
E-mail: w.du-mont@tu-bs.de

Dr. J. Grunenberg
Institut für Organische Chemie der Technischen Universität Braunschweig (Germany)

Prof. Dr. H. C. Marsmann
Anorganische und Analytische Chemie
Universität-Gesamthochschule Paderborn
Warburger Strasse 100, 33098 Paderborn (Germany)

  0044-8249/02/4120-3829 $ 20.00+.50/0

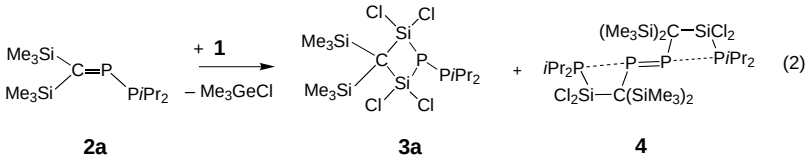


(1)

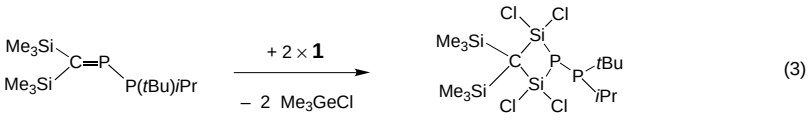
phosphaalkenes with phosphinidene precursors, to provide diphosphiranes.[11]

When equivalent amounts of **1** and **2a** are stirred at room temperature in toluene, ^{31}P NMR spectra confirm that **2a** is almost completely consumed within two hours to yield two main products **3a** and **4** (ca. 10:90) and traces of a third compound. In the ^{31}P NMR spectrum the AX pattern of **3a** indicates the presence of an iPr$_2$P group (δ^{31}P = 25.7 ppm, d, $J(^{31}P,^{31}P) \pm 183.6$ Hz) the P atom of which couples with another ^{31}P nucleus a long way upfield (δ^{31}P = −113.3 ppm).[12] The NMR spectrum of compound **4** exhibits the two pseudotriplets of an AA′XX′ spin system. One pseudotriplet can be assigned to iPr$_2$P groups (δ^{31}P = 24.2 ppm) and the other one a long way downfield (δ^{31}P = 577.5 ppm) indicates phosphorus atoms of coordination number 2.[13–15] This formulation was confirmed by a structure determination of **4** (Figure 1):[16] In the solid state **4** is a centrosymmetric diphosphene that contains two silylphosphane groups. Intramolecular P···P=P···P contacts (P···P 3.449 Å) and steric crowding result in a lengthening of the P=P and P−Si bonds of **4** by about 3 pm, compared with related diphosphenes[14,15] and silylphosphanes.[8]

The reaction of **1** with the slightly bulkier phosphaalkene **2b** furnished, in addition to Me$_3$GeCl, a new compound **3b**, which shows in its ^{31}P NMR spectrum a pattern closely related to that of **3a**. The analytical composition of pure **3b** and its spectroscopic data reveal that—surprisingly—**3b** is the product from the reaction of **2b** with *two* equivalents of SiCl$_2$. ^{13}C, ^{29}Si, and ^{31}P NMR spectra of **3b** at different magnetic field strengths lead to the conclusion that the upfield ^{31}P doublet signals of **3a** and **3b** result from Si$_2$P fragments[17] that are part of the novel 2-phospha-1,3-disiletane ring system [Eq. (2), (3)]. The NMR spectroscopic equivalence of the exocyclic SiMe$_3$ groups indicates (on the ^{1}H, ^{13}C, and ^{29}Si NMR time scales) rapid inversion of the endocyclic phosphorus atom. This result is consistent with B3LYP/G-31 + G(d) calculations,[18] which predict a barrier of 12.9 kcal mol^{-1} for the inversion of the endocyclic phosphorus atom of H$_2$C-(μ-SiH$_2$)$_2$P-PH$_2$. In the transition state of this process, the C(μ-SiH$_2$)$_2$P ring is also planar. For the ring inversion itself, only a marginal barrier is expected.



2a **3a** **4** (2)



2b **3b** (3)

Phosphasilirane intermediates with very bulky substituents on the silicon atom are known,[12] but, in various reactions of **2a** and **2b** with **1**, were not detected by NMR spectroscopy, irrespective of the experimental conditions. The complete cleavage of the P=C bonds of **2a** and **2b** by spontaneous consecutive addition of two equivalents of SiCl$_2$ furnishing 2-phospha-1,3-disiletanes **3a** and **3b** is without precedence. Consecutive addition of two equivalents of photochemically generated dimesitylsilylene to *tert*-alkylphosphaalkynes has been observed by Weidenbruch et al.;[19] these reactions, however, lead to 3-phospha-1,2-disiletenes, that is, a P=C bond of the starting material remains. Thermodynamically, H$_2$C(μ-SiH$_2$)$_2$P-PH$_2$, the simplified version of **3a** and **3b**, is 13.4 kcal mol^{-1} more stable than the isomeric 1,2-disiletane derivative (Figure 2).

Modeling the reaction paths of **2a** and **2b** with **1** will be an interesting challenge for computational methods. For the

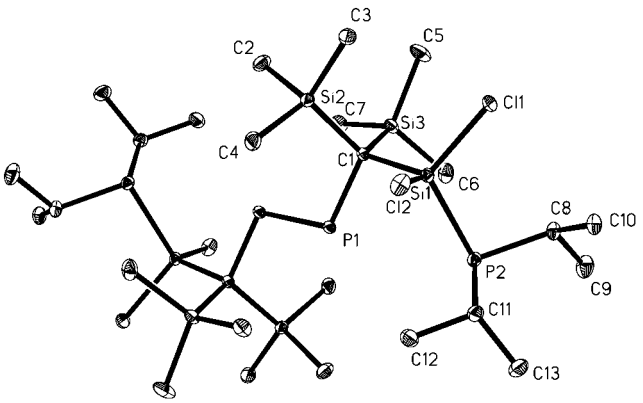


Figure 1. Molecular structure of diphosphene **4** (thermal ellipsoids set at 50% probability; H atoms omitted). Selected bond lengths [Å], angles and torsion angles [°]: P1-C1 1.8824(9), P1-P1* 2.0436(5), Si1-C1 1.8922(9), Si2-C1 1.9367(9), Si3-C1 1.9410(9), Si1-Cl1 2.0810(3), Si1-Cl2 2.0748(4), P2-Si1 2.2848(3), P2-C11 1.8780(10), P2-C8 1.8873(10), P1···P2 3.4490 (4); C1-P1-P1* 106.05(3), C11-P2-C8 105.15(4), C11-P2-Si1 103.05(3), C8-P2-Si1 99.85(3), C1-Si1-Cl2 111.15(3); P1*-P1-C1-Si1 174.83(3), C11-P2-Si1-C1 −125.21(4), C8-P2-Si1-C1 126.58(4), P2-Si1-C1-P1 42.94(4).

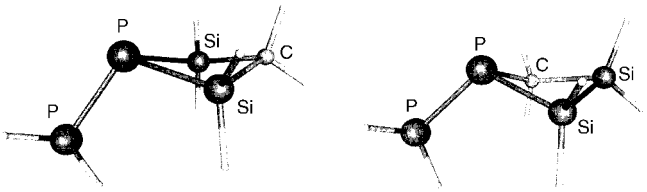


Figure 2. Geometries of calculated energy minima (B3LYP/6-31 + G(d) level) of H$_2$C(μ-SiH$_2$)$_2$P-PH$_2$ (left) and the 1,2-disiletane isomer (right) as model systems. Selected bond lengths [Å]: in H$_2$C(μ-SiH$_2$)$_2$P-PH$_2$: P-P 2.242, P-Si 2.289, Si-C 1.908; in the 1,2-disiletane isomer: P-P 2.242, P-Si 2.302, Si-C 1.917, Si-Si 2.348.

  0044-8249/02/4120-3830 $ 20.00+.50/0 *Angew. Chem. Int. Ed.* **2002**, *41*, No. 20

simultaneous formation of diphosphene **4** and **3a** [Eq. (2)] the attack of $SiCl_2$ molecules at the P=C bond of **2a** apparently competes with the $SiCl_2$ insertion into the P–P bond and the subsequent silyl-group migration.[15,20] This hypothesis is supported by the observation, that with *two* equivalents of silylgermane **1**, phosphaalkene **2a** furnishes predominantly the "2:1 product" **3a**. The formation of diphosphene **4**, however, cannot be suppressed completely. The reactive behavior of **1** towards **2a** and **2b** under very mild conditions gives rise to the expectation that finally, by using available trichlorosilylgermanes such as **1**,[7,21] silylene-based products can be prepared which contain reactive Si–Cl bonds instead of protecting organic substituents.

Experimental Section

The experiments were carried out under dry nitrogen gas. NMR spectra were recorded using Bruker spectrometers AC 200, Avance 200, Avance 400 and AMX 300, with 85% H_3PO_4 and with $SiMe_4$ as external or internal standards. Elemental analyses: Institut für Pharmazeutische Chemie der TU Braunschweig.

3b: After stirring a mixture of silylgermane **1** (0.63 g, 2.5 mmol) and phosphaalkene **2b** (0.40 g, 1.25 mmol) for 7 days at room temperature, ^{31}P NMR spectra of the orange liquid showed that 90% of **2b** was consumed. Me_3GeCl and residual **1** were removed in vacuo and further **1** (0.13 g, 0.5 mmol) was added. After 10 days, consumption of **2b** was completed. Removal of all volatiles led to an orange residue of crude **3b** (0.6 g, 92%). Crystallization from toluene furnished pale yellow crystals, m.p. 143 °C. ^{1}H NMR (400 MHz, [D$_8$]toluene, $\delta(C_6D_5CHD_2) = 2.09$): $\delta = 0.40$ (d, J(P,H) = 0.8 Hz, 18H, $Si(CH_3)_3$); 1.06 (dd, J(P,H) = 11.2 and 0.9 Hz, 9H, $C(CH_3)_3$), 1.17 (ddd, J(P,H) = 19.0 and 1.3 Hz, J(H,H) = 7.1 Hz, 3H, $CHCH_3$), 1.19 ("t"d , J(H,H) = 7.1 Hz, J(P,H) = 7.1 and 1.3 Hz, 3H, $CHCH_3$), 1.74 ppm (sept-dd, J(H,H) = 7.1 Hz, J(P,H) = 4.1 and 2.9 Hz, 1H, $CH(CH_3)_2$); ^{13}C NMR (101 MHz, [D$_8$]toluene, δ(C-1 of C_7D_8) = 137.44): $\delta = 5.6$ (d, J(P,C) = 2.5 Hz, $Si(CH_3)_3$), 23.5 (dd, J(P,C) = 14.8 and 1.4 Hz, $CHCH_3$), 24.4 (dd, J(P,C) = 34.1 and 3.0 Hz, $CHCH_3$), 24.6 (dd, J(P,C) = 33.0 and 5.6 Hz, $CH(CH_3)_2$), 29.3 (dd, J(P,C) = 14.5 and 6.1 Hz, $C(CH_3)_3$), 32.6 (dd, J(P,C) = 28.6 and 8.7 Hz, $C(CH_3)_3$), 41.7 ppm (d, J(P,C) = 3.3 Hz, CSi_2), ^{29}Si NMR (39.8 MHz, C_6D_6): $\delta = 1.1$ (d, J(P,Si) = 4.1 Hz; $Si(CH_3)_3$), 15.0 ppm (dd, J(P,Si) = 36.2 and 8.1 Hz, $SiCl_2$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = -113.5$ (d, J(P,P) = 196.1 Hz, ^{29}Si satellites J(P,Si) = 36.2 Hz, PSi_2), 44.4 ppm (d, J(P,P) = 196.1 Hz, P*t*Bu*i*Pr); CI-MS (NH_3, 150 °C): m/z 519 [$(M+1)^+$]; elemental analysis (%): calcd for $C_{14}H_{34}Cl_4P_2Si_4$: C 32.43, H 6.61, Cl 27.35; found: C 31.62, H 6.98, Cl 26.43.

4: A mixture of phosphaalkene **2a** (0.40 g, 1.31 mmol) and silylgermane **1** (0.32 g, 1.31 mmol) was stirred for 10 h at room temperature. NMR spectra of the orange solution indicated that **2a** had been consumed to 90% producing **4** and small amounts of **3a**. Removing all volatiles in vacuo gave an orange oil that was washed with small amounts of pentane. The remaining orange solid **4** (0.44 g, 83%) m.p. 112 °C is extremely sensitive towards moisture precluding satisfying analytical data. ^{1}H NMR (400 MHz, [D$_8$]toluene, $\delta(CHD_2) = 2.09$): $\delta = 0.55$ (br s, 36H, $Si(CH_3)_3$), 1.27 (dd, J(P,H) = 10.2 Hz, J(H,H) = 7.0 Hz, 12H, $CH(CH_3)$), 1.30 (dd, J(P,H) = 16.4 Hz, J(H,H) = 7.2 Hz, 12H, $CH(CH_3)$), 2.37 ppm (sept-d, J(P,H) = 1.6 Hz, J(H,H) 7.1 Hz, 4H, $CH(CH_3)$); ^{13}C NMR (101 MHz, [D$_8$]toluene, δ (C-1) = 137.44): $\delta = 5.6$ (br "d", splitting of 3.9 Hz, $Si(CH_3)_3$), 22.3 (d, J(P,C) = 6.7 Hz, $CH(CH_3)_2$), 23.9 (d, J(P,C) = 20.8 Hz, $CH(CH_3)$), 24.8 (d, J(P,C) = 20.0 Hz, $CH(CH_3)$), 43.6 ppm (br "t", $N = 42.4 \pm 0.5$ Hz, CSi_3P); assignment of isopropyl signals was by H,C-HSQC; ^{29}Si NMR (79 MHz, [D$_8$]toluene, virtual internal standard TMS): $\delta = 2.1$ (m, $Si(CH_3)_3$); 21.6 ppm (d, J(P,Si) = 101.4 Hz, $SiCl_2$); ^{31}P NMR (81 MHz, [D$_8$]toluene, virtual external standard H_3PO_4): $\delta = -23.4$ ("t" (AA′XX′), $N = 44.3$ Hz, ^{29}Si satellites: J(P,Si) = 101.4 Hz, PSi); 577.5 ppm ("t" (AA′XX′), N = 44.3 Hz, P=P).); elemental analysis (%) calcd for $C_{26}H_{64}Cl_4P_4Si_6$: C 38.61, H 7.98, Cl 17.31; found: C 33.45, H 7.68, Cl 15.86.

Received: December 11, 2001
Revised: March 18, 2002 [Z18357]

[1] A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921; D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; M. Drieß, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900–929; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828–856; N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251–272; R. West, *Acc. Chem. Res.* **2000**, *33*, 704.

[2] Stable dihalides of the heavier elements Ge, Sn, Pb are accessible as starting materials, and the chemistry of transient dihalogenocarbenes is well established: W. Kirmse, *Carbene, Carbenoide und Carbenanaloge*, Verlag Chemie, Weinheim, **1969**.

[3] P. L. Timms, *Inorg. Chem.* **1968**, *7*, 387–389; W. H. Atwell, D. R. Weyenberg, *Angew. Chem.* **1969**, *81*, 485–493; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 469; O. M. Nefedov, M. N. Manakov, *Angew. Chem.* **1966**, *78*, 1039–1056; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 1021; O. M. Nefedov, S. P. Kolesnikov, A. I. Ioffe, *Organomet. Chem. Rev.* **1977**, *5*, 181–219.

[4] E. Hengge, D. Kovar, *Z. Anorg. Allg. Chem.* **1979**, *458*, 163–167; H. Stüger, E. Hengge, *Monatsh. Chem.* **1988**, *119*, 873–887; J. R. Koe, D. R. Powell, J. J. Buffy, S. Hayase, R. West, *Angew. Chem.* **1998**, *110*, 1514–1515; *Angew. Chem. Int. Ed.* **1998**, *37*, 1441–1442.

[5] D. Kummer, H. Köster, M. Speck, *Angew. Chem.* **1969**, *81*, 574–575; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 599–600; D. Kummer, H. Köster, *Angew. Chem.* **1969**, *81*, 897–898; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 878–879.

[6] H. H. Karsch, F. Bienlein, A. Sladek, M. Heckel, K. Burger, *J. Am. Chem. Soc.* **1995**, *117*, 5160–5161.

[7] a) L. Müller, W.-W. du Mont, F. Ruthe, P. G. Jones, H. C. Marsmann, *J. Organomet. Chem.* **1999**, *579*, 156–163; b) *Main Group Metal Chemistry* **2001**, *24*, 609—612; c) D. W. H. Rankin, S. L. Hinchley, L. J. MaLachlan, H. E. Robertson, E. Seppälä, W.-W. du Mont, unpublished results

[8] W.-W. du Mont, L. Müller, R. Martens , P. M. Papathomas, B. A. Smart, H. E. Robertson, D. W. H. Rankin, *Eur. J. Inorg. Chem.* **1999**, 1381–1392.

[9] Disproportionations/α-eliminations involving alkyl(trichlorosilyl)silanes: C. J. Wilkins, *J. Chem. Soc.* **1953**, 3409–3412; D. Kummer, A. Balkir, H. Köster, *J. Organomet. Chem.* **1979**, *178*, 29–54; G. Roewer, U. Herzog, *J. Organomet. Chem.* **1997**, *544*, 217.

[10] J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe, P. G. Jones, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1447–1454.

[11] R. Streubel, E. Niecke, *Chem. Ber.* **1990**, *123*, 1245–1251; E. Niecke, R. Streubel, M. Nieger, *Angew. Chem.* **1991**, *103*, 103–105; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 90–91.

[12] M. Drieß, H. Pritzkow, *Angew. Chem.* **1992**,*104*, 775–777; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 751–753; M. J. M. Vlaar, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, A. L. Spek, M. Lutz, N. Sigal, Y. Apeloig, K. Lammertsma, *Angew. Chem.* **2000**, *112*, 4296–4299; *Angew. Chem. Int. Ed.* **2000**, *39*, 4127–4130.

[13] NMR data of **3a**: ^{1}H NMR (400 MHz, [D$_8$]toluene, lowest-field signal, $\delta = 7.09$): $\delta = 0.40$ (br s, 18H, $Si(CH_3)_3$); 1.11 (dd, J(P,H) = 13.8 Hz, J(H,H) = 7.1 Hz, 6H, $CH(CH_3)$), 1.12 (ddd, J(P,H) = 11.2 and 0.6 Hz, J(H,H) = 7.1 Hz, 6H, $CH(CH_3)$), 1.93 ppm (oct-d, J(P,H) = 7.1 and 2.1 Hz, J(H,H) = 7.1 Hz, 2H, $CH(CH_3)$), ^{13}C NMR (101 MHz, [D$_8$]toluene, δ (C-1) = 137.44): $\delta = 5.9$ (d, J(P,C) = 2.3 Hz, $Si(CH_3)_3$), 21.6 (dd, J(P,C) = 17.5 and 6.2 Hz, $CH(CH_3)$), 21.8 (dd, J(P,C) = 10.9 and 8.3 Hz, $CH(CH_3)$), 26.0 (dd, J(P,C) = 26.8 and 9.8 Hz, $CH(CH_3)_3$), 42.4 ppm (d, J(P,C) = 2.8 Hz, CSi_4), ^{29}Si NMR (79 MHz, [D$_8$]toluene, virtual internal standard TMS): $\delta = 1.0$ (d, J(P,Si) = 3.9 Hz, $Si(CH_3)_3$), 14.4 ppm (dd, J(P,Si) = 37.1 and 7.2 Hz, $SiCl_2$), ^{31}P NMR (162 MHz, [D$_8$]toluene, virtual external standard H_3PO_4): $\delta = -113.1$ ppm (d, J(P,P) = 184.3 Hz, ^{29}Si satellites: J(P,Si) = 37.1 Hz, PSi_2), 26.2 ppm (d, J(P,P) = 184.3 Hz, ^{29}Si satellites: J(P,Si) = 7.2 Hz, P*i*Pr$_2$).

[14] M. Yoshifuji in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Georg Thieme, Stuttgart, **1990**, chap. 9, pp. 321–337.

[15] A. Zanin, M. Karnop, J. Jeske, P. G. Jones, W.-W. du Mont, *J. Organometal.Chem.* **1994**, *475*, 95–98.

[16] Crystal data for **4** ($C_{26}H_{64}Cl_4P_4Si_6$): $M_r = 810.99$, monoclinic, space group $P2_1/n$, $a = 10.4428(6)$, $b = 13.6111(8)$, $c = 15.6690(10)$ Å, $\beta = 103.198(3)$, $V = 2168.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.242$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å^3), $T = 133$ K; a yellow tablet ($0.33 \times 0.33 \times 0.16$ mm^3) was mounted in inert oil on a Bruker Smart 1000 CCD

  0044-8249/02/4120-3831 $ 20.00+.50/0

area detector. Intensities were measured in the 2θ range 5–60°. Of a total of 33919 reflections, 6333 were independent ($R_{int} = 0.0468$). After absorption correction (multiple scan) the structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically against F^2 (G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen (Germany), **1997**): $R_1 = 0.0222$, $wR_2 = 0.0630$ (all data). Methyl groups were refined as rigid groups, other hydrogen atoms by using a riding model. CCDC-175445 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[17] R. T. Oakley, D. A. Stanislawski, R. West, *J. Organomet. Chem.* **1978**, *157*, 389–404; C. Couret, J. Escudie, J. Satgé, J. D. Andriamizaka, B. Saint-Roch, *J. Organomet. Chem.* **1979**, *182*, 9–15; W. Uhlig, *Z. Anorg. Allg. Chem.* **1990**, *588*, 133–138.

[18] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[19] M. Weidenbruch, S. Olthoff, K. Peters, H. G. von Schnering, *Chem. Commun.* **1997**, 1433–1434; A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, *Angew. Chem.* **1987**, *99*, 806–807; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 776–777.

[20] V. D. Romanenko, A. V. Ruban, S. V. Iksanova, L. K. Polyachenko, L. N. Markovski, *Phosphorus Sulfur Relat. Elem.* **1985**, *22*, 365–368.

[21] E. Seppälä, W.-W. du Mont, T. Gust, J. Mahnke, L. Müller, *1st Eur. Silicon Days* (München) **2001**, Abstract P27.

Fluoroformic Acid Anhydride, FC(O)OC(O)F**

Holger Pernice, Helge Willner,* Karina Bierbrauer, Maximiliano Burgos Paci, and Gustavo A. Argüello*

Dedicated to Professor Rüdiger Mews on the occasion of his 60th birthday

For many years new molecules, consisting only of fluorine, carbon, and oxygen atoms have been of fundamental interest.[1–10] The view that such species are formed in atmospheric degradation of HFCs and other CFC replacements[11,12] has motivated further work in this field.[13–16]

During our studies on radicals such as CF_3O,[17] CF_3OO,[18] $CF_3OC(O)$,[19] FCO_2[20], and FC(O)OO[18] that are important intermediates in the atmospheric degradation of CFC replacements, as well as on the catalytic oxidation of CO by CF_3O_x radicals,[21,22] we have also considered possible reaction products of these radicals, among them $CF_3OC(O)OC(O)OCF_3$.[17] Correspondingly, the formation of fluoroformic acid anhydride, FC(O)OC(O)F (**1**), by a recombination of FCO and FCO_2 radicals is considered in principle as feasible. However both radicals have to be present in sufficiently high concentrations for a satisfactory yield. We now report on the synthesis and characterization of **1**. This fundamental acid anhydride is, to our knowledge the first example of a XC(O)OC(O)Y species, with X,Y = halogen and can be viewed as halogen dicarbonate. It is at the same time the last missing member in the family of $FC(O)O_xC(O)F$ molecules ($x = 0$,[23] 1 (this work), 2,[1] 3,[24]), which had not previously been isolated in pure form.

The analogous, well known compound bis(fluoroformyl) peroxide, FC(O)OOC(O)F, is readily synthesized by the reaction of CO with a F_2/O_2 mixture; O_2, which must be present in large excess, acts as radical scavenger.[1,25–27] Accordingly, it was considered that using a 2:4:1 mixture of $F_2/CO/O_2$ may provide a suitable route for the synthesis of **1** according to reaction (1).

$$FCO + FCO_2 + M \rightarrow \mathbf{1} + M \quad (1)$$

However, since such mixtures tend to explode,[26] for the synthesis of FC(O)OOC(O)F experiments with lower concentrations of oxygen, which would lead to higher concentrations of FCO radicals, have been avoided. Our approach to synthesize **1** focuses on the thermal decomposition of FC(O)OOC(O)F in the presence of CO. Gaseous mixtures of FC(O)OOC(O)F and CO (1:5 to 1:10) are kept at 60 °C and the decay of the peroxide concentration is monitored by IR spectroscopy. We assume that the formation of **1** follows the reaction sequence given by Equations (2)–(4) then (1).

$$FC(O)OOC(O)F \xrightarrow{\Delta} 2\,FCO_2 \quad (2)$$

$$FCO_2 \xrightarrow{\Delta\Delta} F + CO_2 \quad (3)$$

$$F + CO + M \rightarrow FCO + M \quad (4)$$

The initial unimolecular decomposition of FC(O)OOC(O)F [Eq. (2)] is followed by a further unimolecular decomposition[20] [Eq. (3)] in which fluorine atoms are generated. These then react with CO to give FCO radicals [Eq. (4)]. In the final step FCO and FCO_2 radicals recombine to give the anhydride **1**, which is isolated from the reaction mixture after repeated trap-to-trap-condensation in vacuo. The gas-phase IR spectrum of **1** is depicted in Figure 1.

DFT calculations (B3LYP) with the 6-311 + G(d) basis set[28] predict the *syn–syn* conformer to be the most stable one for **1** (Figure 2). Calculated IR wavenumbers for this conformer are in good agreement with observed data (Table 1). By comparing observed and calculated band positions and

[*] Prof. Dr. H. Willner, Dipl.-Chem. H. Pernice
Fakultät 4, Anorganische Chemie
Gerhard-Mercator-Universität Duisburg
Lotharstrasse 1, 47057 Duisburg (Germany)
Fax: (+49) 203-379-2231
E-mail: willner@uni-duisburg.de
Prof. Dr. G. A. Argüello, Dr. K. Bierbrauer, Lic. Quim. M. Burgos Paci
Departemento de Físico Química
Facultad de Ciencias Químicas
Universidad Nacional de Córdoba
5000 Córdoba (Argentina)
Fax: (+54) 351-433-4188
E-mail: gaac@fcq.unc.edu.ar

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. H.P. and K.B. thank the Deutscher Akademischer Austauschdienst (DAAD) and the Agencia National de Promoción Cientifica y Tecnologica for providing traveling funds through the exchange program PROALAR.

  0044-8249/02/4120-3832 $ 20.00+.50/0