3.838 gcm⁻³, space group P_{2_1}/m (no. 11), $\mu(Mo_{ks}) = 198.70 \text{ cm}^{-1}$, $1.65 \le \theta \le 25.40^{\circ}$, index ranges: $-13 \le h \le 13$, $0 \le k \le 8$, $0 \le l \le 14$; 8462 measured reflections; 1966 unique reflections ($R_{int} = 0.044$); 1575 reflections with $F_o^2 > 3\sigma(F_o^2)$. No. of variables: 104. Final R = 0.034 Rw = 0.036 (refined on |F|), GOF = 1.87; largest Difference peak and hole: $1.04/ - 1.10 \ e \ A^{-3}$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406200. b) R. H. Blessing, *Acta Crystallogr. A* **1995**, 51, 33–38. c) G. M. Sheldrick, in *Crystallographic Computing* 3; (Eds.: G. M. Sheldrick, C. Kruger, R. Doddard), Oxford University Press, Oxford, England, **1985**, p. 175–189. d) TEXSAN: Single Crystal Structure Analysis Software (**1981 & 1992**). Molecular Structure Corporation, The Woodlands, TX 77381 (USA). e) R: $\bar{v} = 515, 453, 441, 401$, and 360 cm⁻¹ ($\frac{1}{x}[P_3Se_4^{-1}]$ unit), as well as 486 and 313 cm⁻¹ ($[P_2Se_6]^{4-1}$ group).

- [13] W. Hönle, R. Kremer, H. G. von Schnering, Z. Kristallogr. 1987, 179, 443-453.
- [14] V. D. J. Braun, W. Jeitschko, Z. Anorg. Allg. Chem. 1978, 445, 157-166.
- [15] E. A. Seddon, K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, New York, 1984, pp. 503-511.

R₂Si=P-SiR₂F: 1,3-Sigmatropic Migration of Fluorine in a 2-Phospha-1,3-disilaallyl Derivative Capable of Conjugation and Its Conversion to Phosphadisilacyclopropanes**

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Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday

Although stable compounds with isolated Si=E bonds (E = C, Si, N, P, As, S), which have an enormous synthetic potential at their disposal, have been prepared and even structurally characterized over the last few years,^[1, 2] only very little is known about heteronuclear conjugated Si-E π systems, and nothing is known about corresponding homonuclear Si-Si π systems. Until now, only the 1,3-diphospha- and 1,3-diaza-2-silaallyl anionic derivatives $A^{[3]}$ and $B^{(4)}$ have been experimentally studied. We have been investigating the synthesis of stable conjugated Si-P π systems C (allyl, butadiene, and benzene analogues), whose stepwise formation can be achieved with salt-condensation reactions, as, for example, in the preparation of phosphasilenes (Si=P compounds).^[2]



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[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie. We thank Messer Griesheim GmbH for donation of chemicals. Here we report the first 2-phospha-1,3-disilaallyl fluoride derivative 1, which undergoes a 1,3-sigmatropic shift (fluctional behavior) of the fluorine atom above 40 °C. Ab initio calculations on $H_2Si=P-SiH_2F$ are in agreement with this. Reduction of 1 with lithium leads to the elimination of LiF and, surprisingly, formation of the *P*-lithium phosphadisilacyclopropanide 2. Compound 2, which is most likely formed as a reactive intermediate via its valence isomer 5, readily reacts to form neutral 3.



The synthesis of 1 was carried out in a stepwise manner starting from the bulkily substituted bis(fluorosilyl)phosphane 6,^[5] which was converted to the lithium phosphanide 7 (a precursor of 1) by reaction with lithium. The lithium center in 7 is coordinated by two THF molecules and is, as expected, dissociated in toluene at 25 °C (Table 1). The compound crystallized as a monomer and, surprisingly, enantiomerically pure in the space group $P2_12_12_1$ (Figure 1).^[6]

The Li center is fourfold coordinated by two THF molecules, the phosphorus atom, and the fluorine atom. In contrast, the

Table 1. Selected NMR and MS data of 1, 3, 4, 7, and 8. Is = $2,4,6-iPr_3C_6H_2$.

1: ¹H NMR (300 MHz, C_6D_6 , 298 K): $\delta = 1.18$ (d, 12 H, J(H,H) = 6.8 Hz, p-CHMe₂), 1.26 (s, 9 H, tBu), 1.32 (s, 9 H, tBu), 1.33–1.60 (m, 24 H, o-CHMe₂), 2.72 (sept, 2 H, J(H,H) = 6.8 Hz, p-CHMe₂), 3.35 (m, 2 H, o-CHMe₂), 3.62 (sept, 1 H, J(H,H) = 6.9 Hz, o-CHMe₂), 3.78 (sept, 1 H, J(H,H) = 6.9 Hz, o-CHMe₂), 6.92 (s, 2 H, arom. H), 7.14 (s, 2 H, arom. H); ¹⁹F-NMR (84.7 MHz, C_6D_6 , 298 K, CFCl₃ ext. standard): $\delta = -140.7$ (d, ²J(F,P) = 44 Hz); ³¹P NMR (81 MHz, C_6D_6 , 298 K): $\delta = -33.0$ (d, ²J(P,F) = 44 Hz); MS (EI): m/z = 626 [M^+ , 8%], 569 [$(M - tBu)^+$, 15%], 307 [(tBulsSiF)⁺, 90%], 288 [(tBulsSi)⁺, 100%]; correct C,H analysis

3: ¹H NMR (200 MHz, C_6D_6 , 298 K): $\delta = 1.05$ (s, 18 H, *t*Bu), 1.25 (d, 12 H, J(H,H) = 6.9 Hz, *p*-CHMe₂), 1.30–1.80 (m, 24 H, *o*-CHMe₂), 2.78 (sept, 2 H, J(H,H) = 6.9 Hz, *p*-CHMe₂), 4.10 (sept, 2 H, J(H,H) = 6.9 Hz, *o*-CHMe₂), 4.00 (sept, 1 H, J(H,H) = 6.9 Hz, *o*-CHMe₂), 7.21 (s, 4 H, arom. H); ³¹P NMR (81 MHz, C_6D_6 , 298 K): $\delta = -325.0$ (d, ¹J(P,H) = 161 Hz); ²⁹Si NMR (36 MHz, C_6D_6 , 298 K): $\delta = -43.6$ (d, ¹J(Si,P) = 36 Hz), -44.5 (d, ¹J(Si,P) = 36 Hz); MS (E1): m/z = 608 [M^* , 85%], 551 [$(M - tBu)^+$, 93%], 288 [(tBulsSi)⁺, 85%], 231 [(lsSi)⁺, 100%]

4: ¹⁹F NMR (84.7 MHz, THF, CFCl₃ ext. standard): $\delta = -132.5$ (d, ²*J*(F,P) = 38 Hz); ³¹P NMR (36 MHz, THF): $\delta = -306.0$ (d, ²*J*(P,F) = 38 Hz)

7: ¹H NMR (300 MHz, C_6D_6 , 298 K): $\delta = 1.24$ (d, 12 H, J(H,H) = 6.8 Hz, p-CHMe_2), 1.26 (m, 8H, THF), 1.31 (d, 6H, J(H,H) = 6.8 Hz, o-CHMe_2), 1.37 (d, 6H, J(H,H) = 6.8 Hz, o-CHMe_2), 1.41 (d, 6H, J(H,H) = 6.8 Hz, o-CHMe_2), 1.49 (s, 18H, *t*Bu), 1.59 (d, 6H, J(H,H) = 6.8 Hz, o-CHMe_2), 2.79 (sept, 2H, J(H,H) = 6.8 Hz, p-CHMe_2), 3.33 (m, 8H, THF), 3.85 (sept, 2H, J(H,H) = 6.8 Hz, o-CHMe_2), 4.33 (sept, 2H, J(H,H) = 6.8 Hz, o-CHMe_2), 7.15 (s, 4H, arom. H); ¹⁵F NMR (84.7 MHz, C_6D_6 , 298 K): $\delta = -288.8$ (s)

8: ³¹P NMR (81 MHz, C₆D₆, 298 K): $\delta = -221.6$ (d, ¹*J*(P,H) =170.2 Hz); ²⁹Si NMR (36 MHz, C₆D₆, 298 K): $\delta = 23.5$ (d, ¹*J*(Si,P) =15 Hz), 24.2 (d, ¹*J*(Si,P) = 15 Hz); MS (E1): *m*/*z* = 624 [*M*⁺, 9%], 567 [(*M* - *t*Bu)⁺, 64%], 510 [(*M* - 2*t*Bu)⁺, 17%], 247 [(IsSiO)⁺, 60%]



Figure 1. Crystal structure of 7. Selected distances [Å] and angles [°]: P1-Si1 2.199(2), P1-Si2 2.195(2), Si1-F1 1.619(3), Si2-F2 1.666(3), Li1-P1 2.538(9), Li1-F2 1.998(9), Li1-O1 1.955(10), Li1-O2 1.895(10), Si1-C1 1.914(4), Si2-C20 1.920(4). Si1-C16 1.918(5), Si2-C35 1.915(4); Si1-P1-Si2 113.56(7), Si1-P1-Li1 118.5(2), Si2-P1-Li1 74.5(2), F2-Li1-P1 81.1(3), P1-Si2-F2 99.9(1), P1-Si1-F1 110.4(1).

Li center in the analogous bis(di-*tert*-butylfluorosilyl)phosphanide^[7] is not coordinated by the phosphorous atom, but by the two fluorine atoms in a chelating fashion. The substituents in 7 are apparently bulkier, and the observed arrangement provides efficient space filling. The Li1–F2 distance is 1.998(9) Å, and the Si2–F2 bond length (1.666(3) Å) is, as expected, longer than that of Si1–F1 (1.619(3) Å). However, this has no effect on the Si–P bond lengths (2.195 and 2.199(2) Å), which are in the range observed in related fluorosilylphosphanides.^[8]

Heating a solution of 7 to 70 °C results in loss of LiF and formation of the desired 2-phospha-1,3-disilaallyl fluoride 1, which crystallizes from hot toluene(!) as pale yellow cubes. The ³¹P NMR spectrum of 1 (Table 1) shows a doublet ($\delta = -33.0$, $^{2}J(P,F) = 44$ Hz), which is at relatively high field for phosphasilenes. This indicates greater σ -donor character of the fluorodiorganosilyl group with respect to the triorganosilyl group.^[2] All of the structures calculated by ab initio methods and the "thermally corrected" relative free energies were determined at the MP2/6-31G* level.^[9] The calculated Si=P bond length in the parent compound **D** is 2.070 Å (Scheme 1), and the Si-P bond length in D is 2.235 Å. The crystal structure analysis of 1,^[6] which is unfortunately disordered in the crystal, gave similar distances. In addition, it showed that the fluorine atom is located in a position trans to the tert-butyl group. An isolated Si=P bond is present, and there are no intramolecular or intermolecular Si-F-Si contacts (Figure 2).



Relative free energy (298 K) ΔG [kcal mol⁻¹]

	D (<i>C</i> _s , min.)	E (C ₁ , TS)	F (C _s , min.)
X = P X = CH	0.0	14.7	12.5
	0.0	24.2	23.9
distances [Å	Ŋ		
Si=P/Si-F Si=C/Si-F	2.070/1.628	2.100/1.725[a]	2.147/1.852
	1.719/1.626	1.747/1.804[b]	1.759/1.871

[a] Si---F 2.193 Å; [b] Si---F 1.980 Å

Scheme 1. Ab initio calculated migration of fluorine in **D** with the transition states **E** and **F**; X = P, CH. ΔG is the difference in the Gibbs free energy [kcalmol⁻¹] at 298.15 K, min = minimum, TS = transition state.



Figure 2. Crystal structure of 1, which is disordered (two sites for both the P and F atoms). Selected distances [Å] and angles [°]: P1-Si1A 2.053(2), P1-Si1 2.207(2), Si1-F1 1.764(3), Si1-C16 1.895(4), Si1-C1 1.879(4); Si1A-P1-Si1 104.60(9), P1-Si1-F1 74.1(1), P1-Si1A-C16 105.4(1), P1-Si1A-C1 139.7(1), C1-Si1A-C16 114.1(2).

The ¹H NMR spectrum of **1** shows two types of anisochronic tert-butyl groups and aryl protons, and confirms that the isolated Si=P bond is retained in solution at 25 °C. Equilibration of the tert-butyl groups and thus fluctuation of the fluorine atom (suprafacial [1,3]-sigmatropic shift) is first observed at about 40 °C in [D₈]toluene. Therefore, this process has a Gibbs activation energy of about 16 kcalmol⁻¹. Until now, such fluctional behavior had only been observed in the silaethene $Me_2Si = C(SiMe_3)_2$.^[10] We studied the reaction pathway of the [1,3]-fluorine shift in **D** with the fragments X = P (2-phospha-1,3-disilaallylfluoride) and X = CH (1,3-disilaallylfluoride) with ab initio calculations.^[9] The transition state approximately corresponds to the expected structure F, with a symmetrically bridging fluorine atom between the silicon centers, only in the case of X = CH, whereas the transition state for X = P is described by E (Scheme 1). The experimentally verified migration of the methyl group of Me₂Si=C(SiMe₃)₂ occurs via a transition state with a structure analogous to that of F (as for D when X = CH.^[10] For X = P, the calculated barrier of 14.7 kcalmol⁻¹ agrees well with the experimental value of 16 kcalmol⁻¹ for 1. The barrier for $H_2Si = CH(SiH_2F)$, which is approximately 10 kcal mol⁻¹ higher and results from the relatively high ring strain of F, is noteworthy.

We then carried out studies to investigate whether 1 could be converted to 4 by addition of lithium to the Si=P bond, and whether the lithium 1,3-disila-2-phosphaallyl anion 5 could be obtained by subsequent elimination of LiF. Addition of lithium to 1 does indeed occur at room temperature in THF, and 4 is formed as an extremely reactive intermediate.



We were only recently able to prepare compounds of the type 4 from other phosphasilenes.[11] Because of its very high reactivity, it was only possible to characterize 4 by means of ³¹P NMR spectroscopy, which shows a doublet at very high field ($\delta =$ -306, ${}^{2}J(P,F) = 38$ Hz) at 25 °C (Table 1). However, gentle warming of 4 to 40 °C in THF or hexane initially leads to strongly basic 2 by elimination of LiF. This in turn is protonated (partially under the reaction conditions and completely upon work-up in anhydrous hexane) to form 3. The hydrogen atom on the phosphorus atom in 3 originates from the THF ligands that initially solvate the lithium center in 2 and are then partially cleaved due to the strong basicity of the phosphanide (ether cleavage). The conversion of 4 into the ring compound 2 with elimination of LiF most likely occurs via 5. The shift from 5 to 2 would be a particularly interesting parallel to the isomerization of bis(methylene)phosphoranes to phosphacyclopropanes.^[12] Since the electrons in the HOMO of allyl anions are localized at the 1,3 positions and this structure is very unfavorable for the electropositive Si centers, the formation of a Si-Si bond proves very effective. In contrast, and as expected, no cyclization is observed for the "inverse" 1,3-diphospha-2silaallyl anions A with more electronegative phosphorus atoms at the 1,3 positions.^[3]

The composition of 3 was confirmed by mass spectrometry, and its structure determined by NMR spectroscopy (Table 1) and crystallography.^[6] The ³¹P NMR spectrum shows a doublet with ²⁹Si satellites at high field ($\delta = -325$), as expected for phosphasilacyclopropanes,^[14] with a relatively small coupling constant of ¹J(P,H) = 161 Hz. Furthermore, the ¹J(P,Si) coupling constant of 36 Hz is much smaller than that for other phosphacyclopropanes (¹J(P,Si) = 72.5-121.7 Hz).^[13] The high degree of p character of the P–Si bonds apparently lowers ring strain. Geometry optimization of the derivative **3*** was carried out with the density-function method by Becke (B3LYP/ 6-31G*), and the ³¹P and ²⁹Si NMR chemical shifts were calculated at the GIAO/6-311 + +G(2d,2p) level.^[9] The δ (³¹P) and δ (²⁹Si) values for **3*** (-344 and -48.4, respectively) agree well with the experimental values for **3** (-325 and -43.6/-44.5).



The *two* doublet signals at high field ($\delta = -43.6$ and -44.5, ¹J(Si,P) = 36 Hz) in the ²⁹Si NMR spectrum of **3** are characteristic for silacyclopropanes^[14] and show unequivocally that the two silicon atoms are not chemically equivalent. These data are only consistent with the *trans* configuration of the *tert*-butyl groups on silicon and pyramidal coordination of the phosphorus atom, as confirmed by crystal-structure analysis (Figure 3).^[6]

Until now, single crystals were only obtained of a mixture of **3** and the novel four-membered PSi_2O heterocycle **8** (ratio about 7:1). As a result of this "disorder", a discussion of the geometrical parameters is not meaningful. Surprisingly, **8** is formed as a side product (about 10 %, ³¹P NMR) in the reaction of **1** with lithium in THF. The oxygen atom in **8** most likely originates from THF. We can exclude both unintentional entry of air and the presence of surface oxide/hydroxide on the lithium powder as possible sources of oxygen from control experiments. These



Figure 3. Overlap of the crystal structures of **3** and **8** (ratio about 7:1). Selected distances [Å] and angles [Å]: Si1-Si2 2.357(3), Si1-P1 2.292(3), Si2-P1 2.282(2), Si1-O1 1.56(2), Si2-O1 1.57(2); Si1-P1-Si2 62.04(8), P1-Si1-Si2 58.76(8), P1-Si2-Si1 59.20(7), C1-Si1-C16 114.7(2), C35-Si2-C20 115.0(2).

showed that 1 is inert to suspensions of Li₂O/LiOH in THF and that solutions of 3 and 8 do not react with oxygen in the air at room temperature.

The calculated Si–P (2.318 Å) and Si–Si (2.285 Å) distances as well as the endocyclic angles on phosphorus (59.06°) and silicon (60.47°) in **3*** show no principle differences to the corresponding experimental values of other heterodisilacyclopropanes with a Si₂X framework (X = O, S, Te, C, Ge, N, W).^[14] In contrast, the calculated Si–Si distance in *P*-metallated phosphadisilacyclopropane derivatives of **3*** varies considerably depending on the nature of the metal center (s-, p-, and d-block metals), because the Si–Si bond can act as a σ and/or a π donor towards the metal centers. We are currently attempting to synthesize a heteroallyl π complex with the Si₂P framework.

Experimental Section

7: 6 (5.0 g, 7.74 mmol) in THF (50 mL) was allowed to react with *n*-BuLi (0.49 g, 7.74 mmol, 2.5 m solution in hexane) at -78 °C. The clear yellow solution was warmed slowly to 25 °C, and the solvent removed under vacuum (10⁻² Torr). The residue was dissolved in a little hexane, and colorless, air-sensitive 7 crystallized at 25 °C. Yield: 5.3 g (6.6 mmol, 86 %).

1: 7 (5.3 g, 6.6 mmol) was stirred in toluene (50 mL) for 8 h at 70 °C. On cooling, poorly soluble 1 was obtained as extremely air-sensitive, pale yellow crystals. Yield: 3.7 g (5.9 mmol, 88 %).

3: 1 (2.0 g, 3.2 mmol) was stirred with Li powder (about 100 mg) in THF (30 mL) at 25 °C. Compound 4 was formed within 2–4 h (³¹P NMR). The solvent was removed, and the yellow residue dissolved in hexane. Excess lithium powder was filtered off. The colorless solution was concentrated under reduced pressure (10^{-2} Torr) at 25 °C, and colorless crystals were formed (about 90% 3 and 10% 8; ³¹P NMR). Yield: 1.5 g (2.5 mmol, 78 %).

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- [2] Recent review on Si=P and Si=As: M. Driess, Adv. Organomet. Chem. 1996, 39, 193, and references therein; Coord. Chem. Rev. 1995, 145, 1; M. Driess, H. Pritzkow, S. Rell, U. Winkler, Organometallics 1996, 39, 193.
- [3] E. Niecke, E. Klein, M. Nieger, Angew. Chem. 1989, 101, 792; Angew. Chem. Int. Ed. Engl. 1989, 28, 751.
- [4] G. E. Underiner, R. P. Tan, D. R. Powell, R. West, J. Am. Chem. Soc. 1991, 113, 8437.

^[1] Recent review on Si=C: A. G. Brook, M. A. Brook, Adv. Organomet. Chem. 1996, 39, 71; Si=Si: R. Okazaki, R. West, *ibid.*, 232; Si=N: I. Hemme, U. Klingebiel, *ibid.*, 159; Si=S: H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, J. Am. Chem. Soc. 1994, 116, 11578.

- [5] M. Driess, H. Pritzkow, S. Rell, unpublished results. Compound 6 is formed by salt condensation from Is(tBu)Si(F)-PHLi with Is(tBu)SiFCl. $Is = 2.4.6 iPr_3C_6H_2$.
- [6] Crystal structure analyses: All intensity measurements were carried out on a Siemens-Stoe AED2 diffractometer at -70 °C. The H atoms were placed in calculated positions, and the other atoms refined anisotropically [15]. 7: rhombic, space group $P2_12_12_1$, a = 15.392(8), b = 17.995(9), c = 18.026(9) Å, V = 4993 Å³, Z = 4, 4880 independent reflections (Mo_{K2} radiation, ω scans, $2\theta_{\text{max}} = 50$), R1 = 0.047 (observed reflections, $I > 2\sigma(I)$), wR2 = 0.126 (all reflections) [15b]. The THF molecules are disordered. 1: monoclinic, space group C2/c, a = 27.94(2), b = 9.905(6), c = 21.443(14) Å, $\beta = 138.34(3)^{\circ}$, $V = 3945 \text{ Å}^3$, Z = 4, 3883 independent reflections (Mo_{Ka} radiation, ω scans, $2\theta_{\text{max}} = 54$). $R_1 = 0.063$ (observed reflections, $I > 2\sigma(I)$), $wR_2 = 0.169$ (all reflections) [15b]. The molecule is disordered; two sites are half occupied by a phosphorus and fluorine atom, respectively. Moreover, the tert-butyl groups and the aryl substituents show rotational disorder. 3: triclinic, space group P1, $a = 9.312(8), \quad b = 10.300(8), \quad c = 11.673(9) \text{ Å}, \quad \alpha = 74.35(6), \quad \beta \approx 78.38(6),$ $\gamma = 65.63(6)$, V = 976.8 Å³, Z = 1,5591 independent reflections (Mo_{Ka} radiation, ω scans. $2\theta_{\text{max}} = 60^{\circ}$), R1 = 0.056 (observed reflections, $I > 2\sigma(I)$), wR2 = 0.137 (all reflections) [15b]. The crystals contain about 14 % of 8 as an impurity. The observed structure is an overlap of both structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100141. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@ chemcrys.cam.ac.uk).
- [7] U. Klingebiel, M. Meyer, U. Pieper, D. Stalke, J. Organomet. Chem. 1991, 408, 19.
- [8] M. Driess, U. Winkler, W. Imhof, L. Zsolnai, G. Huttner, Chem. Ber. 1994, 127, 1031, and references therein.
- [9] GAUSSIAN 94. Revision B. 3., M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Oritz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
- [10] N. Wiberg, H. Köpf, Chem. Ber. 1987, 120, 653.
- [11] M. Driess, H. Pritzkow, Z. Anorg. Allg. Chem. 1996, 622, 858.
- [12] W. W. Schoeller, T. Busch, J. Chem. Soc. Chem. Commun. 1989, 234.
- [13] M. Baudler, H. Jongebloed, Z. Anorg. Allg. Chem. 1979, 458, 9; M. Weidenbruch, M. Herrndorf, A. Schaefer, K. Peters, H. G. von Schnering, J. Organomet. Chem. 1985, 295, 7; M. Baudler, T. Pontzen, Z. Anorg. Allg. Chem. 1982, 491, 27, M. Driess, H. Pritzkow, Angew. Chem. 1992, 104, 775; Angew. Chem. Int. Ed. Engl. 1992, 31, 751; M. Driess, H. Pritzkow, M. Reisgys, Chem. Ber. 1991, 124, 1923.
- [14] Recent review on Si_2X three-membered rings: M. Weidenbruch, *Chem. Rev.* 1995, 95, 1489, and references therein.
- [15] a) G. M. Sheldrick. SHELXS86, Universität Göttingen (Germany), 1986;
 b) G. M. Sheldrick, SHELXL93, Universität Göttingen, 1993.

Hexaphenylethane Derivatives Exhibiting Novel Electrochromic Behavior**

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9,9,10,10-Tetraphenyl-9,10-dihydrophenanthrene (3) is a stable molecule^[1] whose central C-C bond is predicted to be the longest among "clamped" hexaphenylethane derivatives.^[2] Although this weakened bond is resistant to homolytic rupture,

the activation energy for its scission can be lowered by electron transfer,^[3] especially when suitable substituents are introduced. Bearing this in mind, we have now designed a new redox system in which reversible C-C bond breaking and bond making occur upon two-electron transfer (Scheme 1). This system has the fol-



a: Ar = p-Me₂NC₆H₄; **b**: Ar = p-MeOC₆H₄

Scheme 1. Dynamic redox behavior of 1 and 2^{2+} .

lowing interesting features: 1) the four dimethylamino and methoxy substituents in **1a** and **1b**, respectively, should facilitate the removal of electrons from these molecules, thereby activating the scissile bond; 2) the central bond in **1** like that in **3** is still expected to be sufficiently stable against homolysis taking into consideration that the aromatic substituents have little effect on the Gibbs activation energy of the homolytic cleavage $\Delta G_{\text{homolysis}}^*$ in 1,2-diarylethanes;^{(3, 4]} 3) the dications 2^{2+} formed by the oxidation of **1** should be stabilized by delocalization of each positive charge over half of the molecule and due to the presence of the triarylmethylenium chromophores these cations are intensely colored; 4) the interconversions between **1** and 2^{2+} should proceed very cleanly because they are intramolecular processes. Here we report the preparation, properties, and structures of these novel redox couples.



The dication salts $2a^{2+}(BF_4^-)_2$ and $2b^{2+}(BF_4^-)_2$ were obtained in 98 and 93% yield by treating the diols $4a^{151}$ and 4b, respectively, with HBF₄. Reduction of these salts with Mg in MeCN gave ethanes 1a and 1b as stable solids in 86 and 93% yield, respectively. On the other hand, oxidation of 1a and 1b with two equivalents of $(p-BrC_6H_4)_3N^+SbCl_6^-$ in CH₂Cl₂ led to the regeneration of the dications $2a^{2+}$ and $2b^{2+}$, which were isolated as $SbCl_6^-$ salts in 85 and 97% yield, respectively. The high-yield interconversions between 1 and 2^{2+} indicate that they constitute "reversible" redox couples, although the bond breaking and making are induced by electron transfer.

The sharp contrast in the UV/Vis spectra of these couples is noteworthy. Ethanes 1 show absorption only in the UV region, whereas intense absorption bands in the visible region occur for the dications $2a^{2+}$ [λ_{max} (MeCN): 661 (lge 4.92), 604 nm (5.05)] and $2b^{2+}$ [539 sh (4.72), 514 (4.87)]. Thus, electrochromic systems with color changes from colorless to deep blue and colorless to deep red could be constructed by using *p*-dimethylamino

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