1 paper) in pyridine/butanol/acetic acid/water (1:1:1:1), with alkaline silver nitrate detection. Compounds **1**–**3** were eluted from paper with water.

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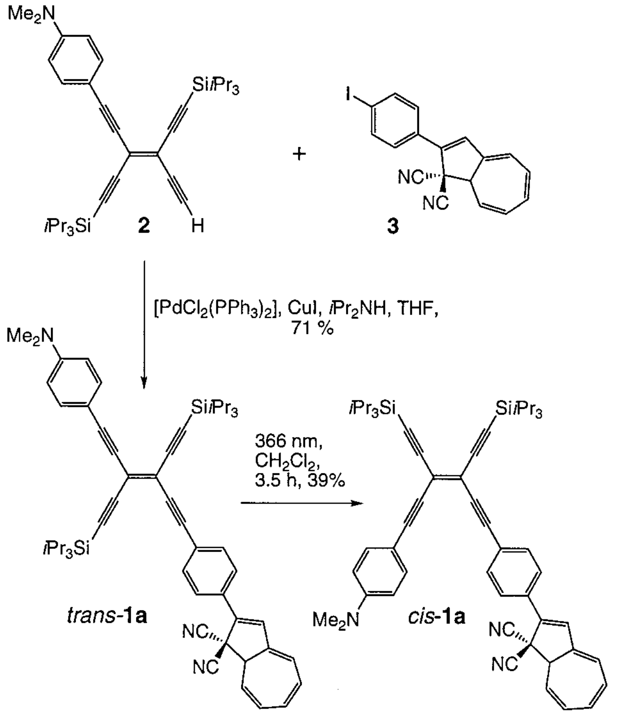
A Novel Three-Way Chromophoric Molecular Switch: pH and Light Controllable Switching Cycles[**]

Luca Gobbi, Paul Seiler, and François Diederich*

Dedicated to Professor Fritz Vögtle on the occasion of his 60th birthday

The field of molecular switches has received much attention in recent years.[1] Of particular interest are photoresponsive systems since the use of light as an external stimulus for the interconversion of two states allows for rapid and clean processes.[2] Herein we report a molecule with three addressable subunits that can undergo individual, reversible switching cycles.[3] Compound **1a** (Scheme 1) consists of a) a tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne)[4] core, which can be reversibly photoisomerized between its *cis* and *trans* forms,[5] b) a dihydroazulene (DHA) unit, which can be transformed into a vinylheptafulvene (VHF) moiety upon irradiation,[6] and c) a proton sensitive *N*,*N*-dimethylanilino (DMA) group.

The target compound *trans*-**1a** (Scheme 1) was prepared by Sonogashira cross-coupling[7] of TEE **2**[8] with the aryl iodide **3**.[9] The X-ray crystal structure analysis of *trans*-**1a**[10] (Figure 1) shows only minor deviations (ca. 0.1 Å) from planarity in the diarylated TEE core. The dihydroazulene moiety is slightly turned out of this plane, with the dihedral angle C14-C10-C7-C8 amounting to 13°. The diastereoisomeric *cis*-**1a** was obtained in 39% yield upon photolysis of *trans*-**1a** in CH_2Cl_2 at $\lambda = 366$ nm.



Scheme 1. Synthesis of *trans*-**1a** and *cis*-**1a**.

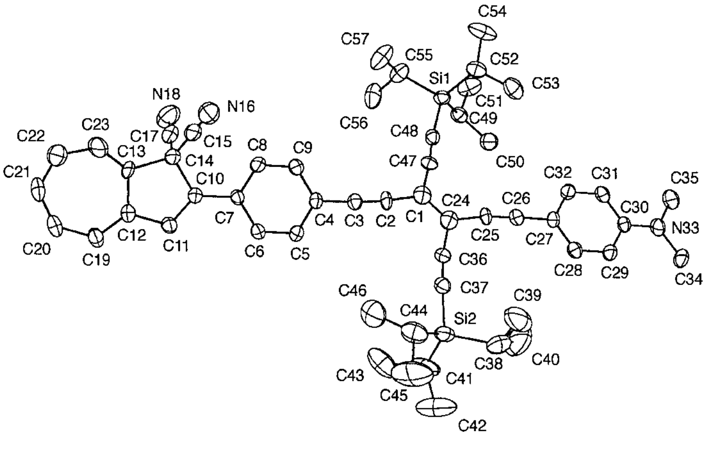


Figure 1. ORTEP plot of *trans*-**1a** in the crystal. The vibrational ellipsoids shown are at the 30% level.

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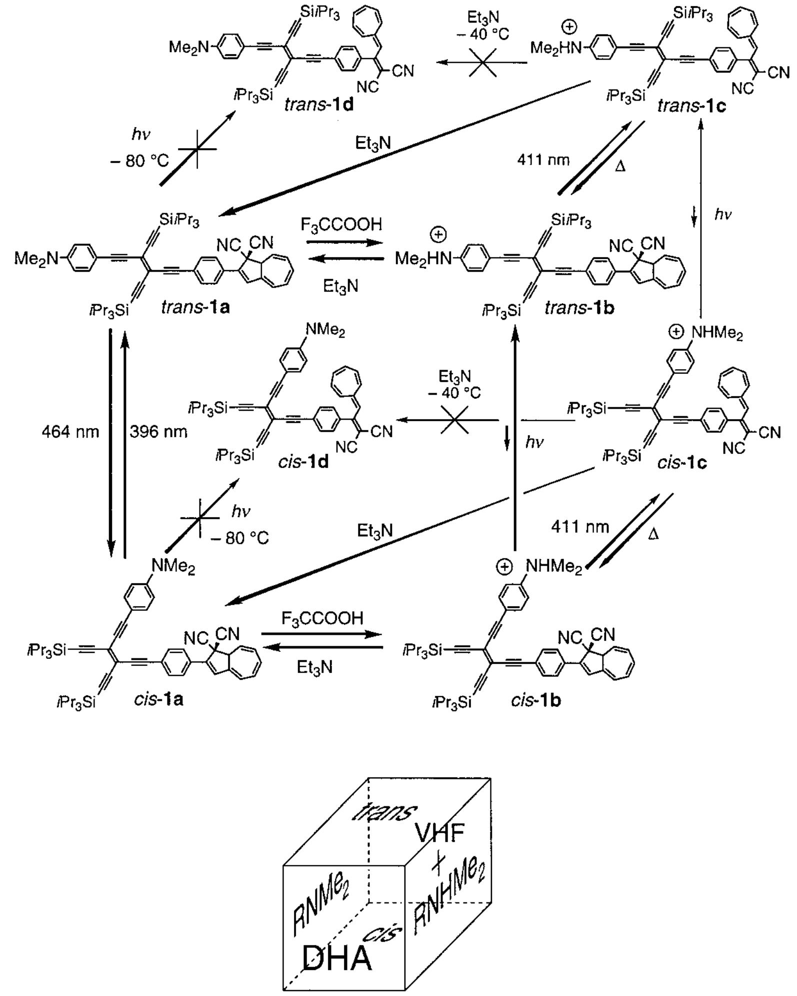
With three possible switching processes, **1** can adopt eight interconvertible states. Such a complex system is best visualized in a three-dimensional representation by a cube with each corner describing one distinct state (*trans*- and *cis*-**1a**–**d**, Scheme 2). Individual interconversion processes could be cleanly addressed despite this functional complexity, and six of the eight states were detected.

The photochemical, reversible *trans*–*cis* isomerization of arylated TEEs has recently been investigated.[5] Irradiation at the longest wavelength absorption maximum ($\lambda_{max} = 464$ nm, $\varepsilon = 44000$ L mol^{-1} cm^{-1}) of *trans*-**1a** induces rapid conversion into *cis*-**1a**, while irradiation at the wavelength corresponding to the most intense absorption band of the latter ($\lambda_{max} = 396$ nm, $\varepsilon = 55000$ L mol^{-1} cm^{-1}) allows the reverse reaction to take place (Figure 2). The ratio of *trans* and *cis* isomers at the photostationary states and the quantum yields for the photoisomerization processes are summarized in Table 1.[11]

Both *cis*-**1a** and *trans*-**1a** display a strong fluorescence with a maximum at $\lambda = 606$ nm. This emission was monitored during several switching cycles to study the resistance of the *cis*–*trans* isomerization process to photofatigue (Figure 3). The intensity of the fluorescence at 606 nm decreases to about 90% of the initial value after 15 cycles.



Scheme 2. Three-dimensional switching diagram of compound **1**. The eight possible states are shown as the corners of a cube.

Table 1. Physical data for the photochemical *cis*–*trans* isomerization of **1a** in CH_2Cl_2 at 25 °C.

λ[a] [nm]	*cis*[b] [%]	*trans*[b] [%]	$\Phi_{c\to t}$[c]	$\Phi_{t\to c}$[c]	K_{eq}[d]	ε_{cis}[e] [L mol^{-1} cm^{-1}]	ε_{trans}[e] [L mol^{-1} cm^{-1}]
396	35	65	0.19	0.17	1.83	55000	33000
464	68	32	0.51	0.37	2.15	26000	44000

[a] Irradiation wavelength. [b] Percentile of *cis*- and *trans*-**1a**, respectively, in the photostationary state. [c] Partial quantum yields for the *cis*→*trans* and *trans*→*cis* interconversions, respectively. [d] Photoequilibrium constant, that is, the ratio between the isomers at the photostationary state. [e] Molar extinction coefficients of *cis*-**1a** and *trans*-**1a** at the irradiation wavelength.

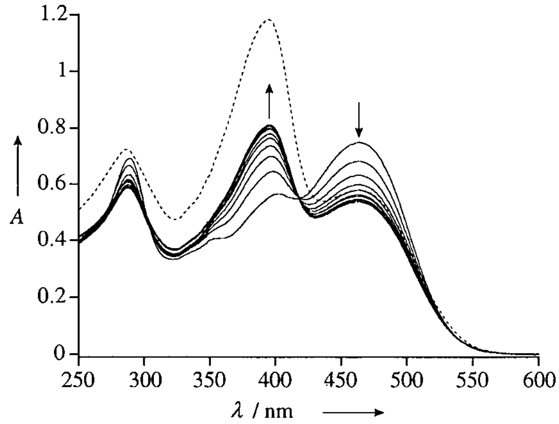


Figure 2. Electronic absorption spectrum in CH_2Cl_2 of pure *cis*-**1a** (----, $c = 2.09 \times 10^{-5}$ M) and spectra recorded at 10 s intervals during the *trans*→*cis* isomerization process ($\lambda_{irr} = 464$ nm) starting from pure *trans*-**1** ($c = 1.70 \times 10^{-5}$ M) (—).

Molecular switches that rely on light-triggered electrocyclization and retroelectrocyclization steps have been studied successfully in the past.[3, 6, 14] The thermally reversible 10-electron photo-retrocyclization of 1,1-dicyano-1,8a-dihydroazulenes (DHA) to 8-(2,2-dicyanovinyl)heptafulvenes (VHF) was first reported by Daub and co-workers.[6] Compound **1a** bears such a DHA group, but the photoinduced retrocyclization to the VHF form could not be accomplished. However, when the DMA moiety in **1a** was protonated with trifluoroacidic acid—to give **1b** (Scheme 2)—the photochemical ring-opening to the VHF-containing TEE **1c** took place. Protonation of **1a** to give **1b** is clearly indicated by the downfield shifts of the aromatic signals of the DMA group in the ^{1}H NMR spectrum (from 6.65 and 7.39 ppm to 7.51 and 7.65 ppm for the *trans* isomer and from 6.67 and 7.38 ppm to 7.51 and 7.62 ppm for the *cis* isomer). Yellow solutions of protonated DHA derivatives *cis*-**1b** and *trans*-**1b** in CH_2Cl_2 both showed an absorption maximum of similar intensity at 411 nm and displayed only a weak yellow fluorescence. The VHF-containing compounds *cis*-**1c** and *trans*-**1c** featured a new absorption band at $\lambda_{max} = 500$ nm in the same solvent, which renders the solution orange-brown. The conversion of *trans*-**1b** into *trans*-

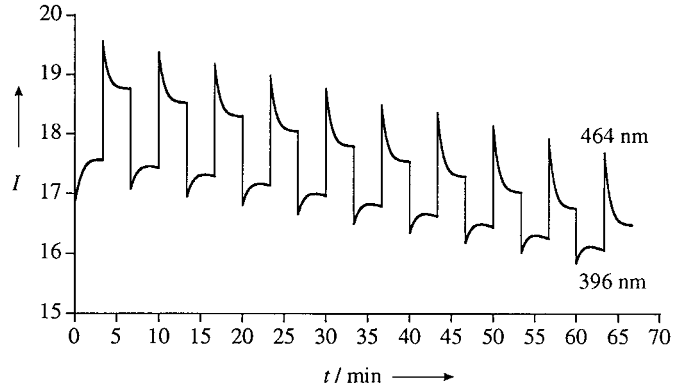


Figure 3. Fluorescence intensity of **1a** ($c = 2.09 \times 10^{-5}$ M in CH_2Cl_2) measured at 606 nm at 25 °C for ten switching cycles, starting from *cis*-**1a**. The sample was irradiated at 396 nm (*cis*-**1a** → *trans*-**1a**) and at 464 nm (*trans*-**1a** → *cis*-**1a**).

1c, upon irradiation at $\lambda = 411$ nm, was monitored by both ^1H NMR and UV/Vis spectroscopy (Figure 4). Standard ^1H NMR solutions ($c \approx 10$ mM) of *trans*-**1b** are too concentrated to be irradiated and successfully switched. However, when a dilute solution ($c \approx 0.3$ mM) of *trans*-**1b** in $CDCl_3$ was irradiated at 411 nm at −50 °C, conversion of the DHA-containing starting compound into VHF-containing *trans*-**1c** was observed by ^1H NMR spectroscopy. The VHF-containing compounds **1c** (*trans* or *cis*) readily undergo thermal electrocyclization back to **1b** ($k_{25^\circ C} = 7.37 \pm 0.02 \times 10^{-4}\,s^{-1}$, $t_{1/2} = 15.7$ min);[15] therefore, mixtures of **1b** and **1c** were always observed even after long irradiation times at room temperature. The ratio of the DHA and VHF isomers at equilibrium proved to be strongly dependent on the experimental conditions; in the NMR experiment the final ratio of *trans*-**1c** to *trans*-**1b** was approximately 90:10.

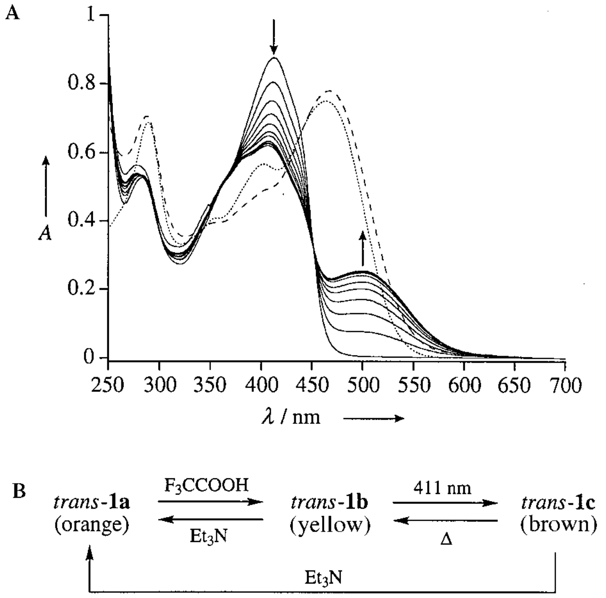
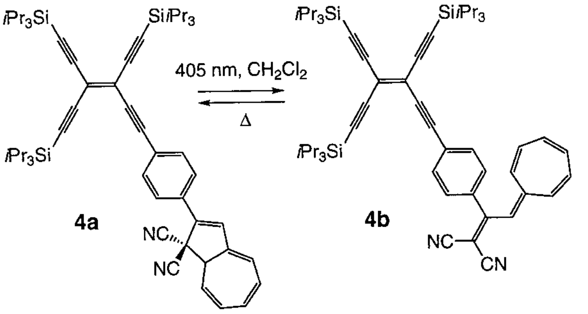


Figure 4. A) Electronic absorption spectra for the *trans*-**1a** → *trans*-**1b** → *trans*-**1c** → *trans*-**1a** switching cycle (B) in CH_2Cl_2 ($c = 1.70 \times 10^{-5}$ M) at 25 °C. The dotted line corresponds to the initial starting material *trans*-**1a**. The solid lines show the conversion of *trans*-**1b** to *trans*-**1c**, recorded at 1 min intervals during irradiation at $\lambda = 411$ nm. The dashed line shows the spectrum of *trans*-**1a** recovered after deprotonation with Et_3N.

The clean interconversion of *trans*-**1b** and *trans*-**1c** during irradiation at 411 nm, without any isomerization to the *cis* forms, was also evidenced by several isosbestic points in the UV/Vis spectrum (Figure 4). At other wavelengths *trans* → *cis* isomerization also occurred.

The switching process of a TEE-linked DHA group into a VHF group was also studied for compound **4** [Equation (1)], in which *trans*–*cis* isomerization leads to the same compound. The UV/Vis spectra are very similar and show an absorption maximum at 405 nm for the DHA-containing **4a** and at 481 nm for the VHF derivative **4b**. However, the thermal electrocyclization back to **4a** is much slower than in the case of the reaction **1c** → **1b** ($k_{25^\circ C} = 3.917 \pm 0.007 \times 10^{-5}\,s^{-1}$, $t_{1/2} = 4.9$ h).[15]



(1)

Treatment of **1c** (a mixture of *cis* and *trans* isomers) with Et_3N causes deprotonation of the amino group and leads directly to the formation of the DHA-containing compound **1a**, as observed by UV/Vis, ^1H and ^{13}C NMR spectroscopy. The VHF-containing donor–acceptor system[16] **1d** could not be obtained either by deprotonation of **1c**—even at −40 °C—or by irradiation of the DMA derivative **1a** at −80 °C. These results are attributed to a very fast thermal electrocyclization of **1d** to **1a**. This seems to indicate that photoinduced electron transfer (PET) or electronic energy transfer (EET) processes that involve the unprotonated DMA group are not responsible for the quenching of the photo-retrocyclization from **1a** to **1b**. These kind of processes have been widely used to construct photoionically-driven fluorescent sensors and switches.[17]

When a solution of pure *trans*-**1a** in CH_2Cl_2 was treated with CF_3COOH, then irradiated at 411 nm, and finally treated with Et_3N in the dark, only *trans*-**1a** was recovered as shown by UV/Vis (Figure 4) and ^{13}C NMR spectral analysis; no trace of diastereoisomeric *cis*-**1a** could be detected. The reversible conversion of *trans*-**1a** into *trans*-**1b** and then into *trans*-**1c** can be described as an AND logic gate.[18] The *trans*-**1c** state can only be obtained when both protons and light are present; that is two "inputs" are necessary to generate one "output". Nondestructive readout of this AND logic gate is ensured by monitoring the appearance of the absorption band of *trans*-**1c** at $\lambda_{max} = 500$ nm (Figure 4). In contrast, the same cycle, which starts from pure *cis*-**1a**, leads to the recovery of an isomeric mixture that contains mainly the *trans* form. Thus the conversion *cis*-**1a** → *cis*-**1b** → *cis*-**1c** is not suited for an AND logic gate, as *cis* → *trans* isomerization also occurs.

In addition to the described AND logic gate three write/erase processes are present in system **1**, which are not affected by side reactions to other states on the cubic switching diagram if appropriate conditions are used: the reversible *cis*–*trans* photoisomerization between *trans*-**1a** and *cis*-**1a**, and the reversible protonations/deprotonations of the couples *trans*-**1a**/*cis*-**1a** and *trans*-**1b**/*cis*-**1b**. Since the fluorescence enhancement after deprotonation of **1b** amounts to a factor of about 300,[19] a very efficient nondestructive readout of information for the *cis*-**1a/b** and *trans*-**1a/b** couples is available by using excitation light of 396 nm for the *cis* and of 464 nm for the *trans* isomer.

The switching system discussed here represents a first step towards multifunctional molecular devices where the performed operation is dependent upon the stimulus that is chosen. The challenge now lies in further development of this system so that it can perform logic operations at a macroscopic level, and thus possess real-life applications.

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Keywords: fluorescence spectroscopy · molecular devices · optical memory · photochromism · tetraethynylethenes

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[9] The photoresponsive dihydroazulene **3** was synthesized according to published methods.[6c] All new compounds were fully characterized by UV/Vis, fluorescence, IR, ^{1}H, and ^{13}C NMR spectroscopy, FAB-MS, and elemental analysis.

[10] X-ray crystal structure of *trans*-**1a**; $C_{54}H_{63}N_3Si_2$ $M_r = 810.25$; triclinic, space group $P\bar{1}$ (no. 2), $\rho_{calcd} = 1.095$ g cm^{-3}, $Z = 2$, $a = 8.661(4)$, $b = 13.259(6)$, $c = 22.456(7)$ Å, $\alpha = 94.31(3)$, $\beta = 93.48(4)$, $\gamma = 106.36(3)°$, $V = 2458(2)$ Å^3, $T = 200$ K, Nonius CAD4 diffractometer, $\lambda(\mathrm{Cu}_{K\alpha}) = 1.5418$ Å. Single crystals were obtained by slow evaporation of a MeOH solution. The structure was solved by direct methods (*SHELXS-86*) and refined by full-matrix least-squares analysis (*SHELXL-93*), by using an isotropic extinction correction and $w = 1/[\sigma^2(F_o^2) + (0.0999\,P)^2 + 3.2032\,P]$, where $P = (F_o^2 + 2\,F_c^2)/3$. The $i\mathrm{Pr}_3\mathrm{Si}$ groups at Si2 as well as the five- and the seven-membered rings are statically disordered. The disorder within these rings could be resolved for the atoms C13, C22, and C23, that is, two peaks could be located in a difference map and refined isotropically with population parameters of ca. 0.63 and 0.37, respectively. All other heavy atoms were refined anisotropically (H-atoms isotropic, whereby H positions are based on stereochemical considerations). Final $R(\mathrm{F}) = 0.058$, $wR(F^2) = 0.16$ for 566 parameters and 3377 reflections with $I > 2\sigma(I)$ and $\theta < 50°$. The disordered seven-membered ring, based on one set of atomic positions, is nearly planar. However, by refining partial atoms as mentioned above, two different conformations are obtained. The one shown in Figure 1 (based on a population parameter of 0.63) is approximately boat shaped, whereas the other (based on a population parameter of 0.37) is less clear. Crystallographic data (without structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-102924. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The quantum yields for both photochemical *cis* → *trans* and *trans* → *cis* isomerization reactions have been determined as described in the literature[5, 12] from data obtained by following the emission and absorption spectra as a function of the irradiation time. For the isomerization (a) the rate constants $k_{c\to t}$ and $k_{t\to c}$ were calculated from the overall rate constant k [Eq. (b)] and the photoequilibrium constant K_{eq} [Eq. (c)]

$$\textit{cis}\text{-isomer} \underset{k_{t\to c}}{\overset{k_{c\to t}}{\rightleftharpoons}} \textit{trans}\text{-isomer} \tag{a}$$

$$k = k_{t\to c} + k_{c\to t} \tag{b}$$

$$K_{\text{äq}} = \frac{k_{c\to t}}{k_{t\to c}} = \frac{C_t^{\mathrm{eq}}}{C_c^{\mathrm{eq}}} \tag{c}$$

K_{eq} was determined starting from the UV/Vis spectra. k for the reaction from *trans* to *cis* was calculated from the electronic absorption spectra from an exponential fit[12] at the wavelengths of 375, 396, 450, 464 nm [Eq. (d)] where l is the length of the cell. k for the reaction from *cis* to *trans* was determined from a simple exponential fit of the data of the electronic emission spectra at $\lambda_{em} = 606$ nm [Eq. (e); the first three curves in Figure 3 for the reaction *cis*-**1a** → *trans*-**1a** were used]. The emission quantum yields are given by Equations (f) and (g).

$$\frac{A_\lambda(t)}{l} = \varepsilon_t C_t^{\mathrm{eq}} + \varepsilon_c C_c^{\mathrm{eq}} + (\varepsilon_t - \varepsilon_c) C_c^{\mathrm{eq}} \mathrm{e}^{-kt} \tag{d}$$

$$I_\lambda(t) = I_\infty + (I_0 - I_\infty)\mathrm{e}^{[k(t_0 - t)]} \tag{e}$$

$$\Phi_{c\to t} = \frac{k_{c\to t}}{1000\,I_0[(1 - 10^{-A_\lambda^{\mathrm{eq}}})/A_\lambda^{\mathrm{eq}}]\varepsilon_c} \tag{f}$$

$$\Phi_{t\to c} = \frac{k_{t\to c}}{1000\,I_0[(1 - 10^{-A_\lambda^{\mathrm{eq}}})/A_\lambda^{\mathrm{eq}}]\varepsilon_t} \tag{g}$$

The light intensity I_0 was determined by the actinometric ferrioxalate method.[13] An absolute error of about 10% is claimed for the quantum yields.

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Synthetic Utility of Stable Phosphanylcarbenes: Synthesis and Crystal Structure of an α-(Lithiomethylene)phosphorane**

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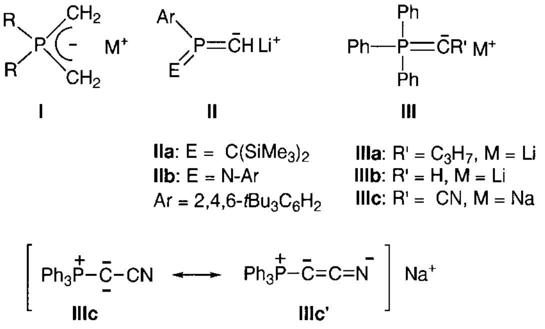
Antoine Baceiredo, and Guy Bertrand*

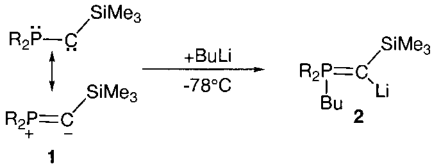
Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday

Alkali metal phosphonium diylides **I** are well-characterized compounds and their properties and molecular structures have been thoroughly investigated.[1] In contrast, the phosphonium yldiides **II** and **III**, which formally feature a dicarbanion center, have been poorly studied (Scheme 1). Niecke et al.[2] concluded that the stability of the lithium phosphoranylidene ylides **IIa, b** was due to the incorporation of the metalated carbon atom into the heteroallylic π-electron system. The first synthesis of an α-(lithiomethylene)phosphorane (**IIIa**) was proposed by Schlosser et al.[3] and was based on the reaction of pentaphenylphosphorane with excess *n*-butyllithium. Later, Corey et al.[4] showed that the phosphonium yldiide **IIIb** can be prepared at low temperature by direct lithiation of the corresponding ylide, and underwent Wittig reactions even with sterically hindered ketones. The (sodiocyanomethylene)phosphorane **IIIc**[5] is the only α-(metallomethylene)phosphorane, which has been isolated so far. However, from IR and NMR data, Bestmann et al.[5] showed that the resonance structure **IIIc′** strongly contributed to the electron distribution in **IIIc** and, therefore, this compound can hardly be considered as a phosphonium yldiide. The instability of derivatives **III** and the difficulties associated with the metalation of the starting phosphonium ylides hampered their promising synthetic application.[6] Here, we propose a new strategy for the one-step synthesis of α-(lithiomethylene)phosphoranes of type **III**, as well as the first single-crystal X-ray diffraction study of such a highly reactive compound.



Scheme 1.

We have already shown that the stable phosphanyl(silyl)carbene **1** undergoes formal 1,2-addition reactions with protic reagents (MeOH, Me_2NH, etc.)[7] as well as with Lewis acids ($MeOB(OMe)_2$, $MeGaMe_2$, etc.)[8] giving rise to the corresponding phosphorus ylides. Thus, we investigated the reaction of **1** with alkyllithium reagents, in the hope of obtaining the corresponding 1,2-adduct, namely the lithium phosphonium yldiide **2** (Scheme 2). Indeed, according to ^{31}P NMR spectroscopic results, addition of one equivalent of *n*BuLi (1.6 M in hexane) to a solution of carbene **1**[8b] in pentane at $-78\,°C$ instantaneously and quantitatively led to the desired adduct **2**. On warming to room temperature and partial evaporation of the solvent, two equivalents of THF were added. From this solution single crystals, suitable for an X-ray diffraction study,[9] were obtained at $-20\,°C$. The molecular structure of **2** is shown in Figure 1. In the solid state, **2** is monomeric and features a trigonal-planar coordinated lithium atom (sum of the angles: 359.9°), which is complexed by two molecules of THF. The geometry around the ylidic carbon atom is also planar (sum of the angles: 359.8°), whereas in nonstabilized ylides it is slightly pyramidalized.[10] The P–C bond length (1.636 Å) is one of the shortest known for a P–C(ylide) bond;[10a] the Si–C1 bond length is also very short (1.775 Å compared to 1.87–1.91 Å for Si–CH_3), which emphasizes the stabilizing effect of the negative charge by the silyl group.[11] Significantly, the C–Li bond almost eclipses the P–C(Bu) bond (Li-C1-P-C29 dihedral angle: 17.4(1.0)°). All structural data are in agreement with the results of ab initio calculations[12] which also predicted that the deprotonation of $H_3P{=}CH_2$ to give $H_3P{=}CHLi$ would induce a rotation about the P–C bond, causing the C–Li bond to eclipse one of the P–H bonds.



Scheme 2. R = *c*Hex_2N.

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