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[11] **2**: ^{1}H NMR (CDCl$_3$): $\delta = 1.08$ (s, 9H; CMe$_3$), 1.10 (s, 9H; CMe$_3$), 1.12 (s, 9H; CMe$_3$), 1.32 (s, 9H; CMe$_3$), 5.61 (d, $^3J = 15.9$ Hz, 1H; CH), 5.85 (d, $^3J = 15.9$ Hz, 1H; CH), 6.57 (d, $^3J = 10.8$ Hz, 1H; CH), 6.62 (d, $^3J = 10.8$ Hz, 1H; CH); ^{13}C NMR (CDCl$_3$): $\delta = 28.3$ (*C*Me$_3$), 29.4 (C*Me*$_3$), 29.5 (C*Me*$_3$), 29.6 (C*Me*$_3$), 31.3 (C*Me*$_3$), 33.6 (*C*Me$_3$), 35.7 (*C*Me$_3$), 36.1 (*C*Me$_3$), 77.1 (*C*≡C), 106.4 (*C*≡C), 121.1 (=*C*H), 121.3 (=*C*H), 129.0 (=*C*H), 132.6 (=*C*tBu), 147.6 (=*C*H), 151.1 (=*C*tBu); EI-MS: *m*/*z*: 328.3 [M^+], 271.3 [$M^+ - \mathrm{CMe_3}$], 215.2 [$M^+ - 2\,\mathrm{CMe_3}$].

[12] Crystal structure analysis of **2**, $C_{24}H_{40}$: $M_r = 328.56$, monoclinic, space group $P2_1/c$, $a = 10.001(3)$, $b = 12.231(3)$, $c = 10.237(3)$ Å, $\beta = 113.55(2)°$, $V = 1147.9(6)$ Å^3, $Z = 2$, $\mu = 0.052$ mm^{-1}, crystal dimensions $0.25 \times 0.25 \times 0.2$ mm. $2\theta_{max} = 50°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $T = 170(2)$ K, 2181 measured reflections, of which 2016 were unique and 1058 observed with $F_o > 4\sigma(F_o)$. Lorentz and polarization corrections were applied and the structure solved by direct methods (SHELX86) with full-matrix least-squares (SHELXL93) refinement based on F^2. 115 parameters. $R1 = 0.1111$, $wR2 = 0.3159$.[20] The asymmetric unit consists of one half of the triene-yne with the remainder generated by an inversion center, hence there is disorder between the terminal double and triple bonds.

[13] It is also possible that the vinylidene complex **B** is formed via the hydridoacetylide complex **C**.

[14] A. M. La Pointe, M. Brookhart, *Organometallics* **1998**, *17*, 1530–1537. In this study of the reactions of alkynes with the cationic complexes [Pd(CH$_3$)(N–N)L][BAr$^1_4$] (N–N = phenanthroline or diimine, L = Et$_2$O or MeCN, Ar^1 = 3,5-(CF$_3$)$_2$C$_6$H$_3$) the regiochemistry of the "insertion" step has been related to the steric demands of both the metal center and the alkyne. It is also reported in this paper that an excess of alkyne results in the formation of a palladium–trienyl species that can then undergo an intramolecular cyclization reaction to form a 5-ethylidene-2-cyclopentene-1-yl complex. Although a related intramolecular cyclization reaction with the rhodium–trienyl intermediate **F** (shown in Scheme 1) can be envisaged, such a process does not provide a pathway to the fulvene complex **1**.

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[16] In the case of the cobalt system studied by Klein and co-workers[5] a shut down of the oligomerization process is also observed on reversal of the regiochemistry of the insertion of a monosubstituted alkyne (PhC$_2$H). However, in contrast with the rhodium system this occurs earlier in the oligomerization process.

[17] The ^{1}H NMR data for **3** indicated the presence of three compounds in the approximate ratio 8:2:1. The fact that all three species possessed near-identical NMR spectra led us to conclude that they were all stereoisomers. In contrast, the ^{1}H NMR spectrum of the crystals of **4** showed evidence for the presence of only one stereoisomer. NMR data for the major steroisomer of **3**: ^{1}H NMR (CDCl$_3$): $\delta = 0.85$ (s, 9H; CMe$_3$), 0.89 (s, 3H; CMe$_2$), 1.01 (s, 3H; CMe$_2$), 1.19 (s, 9H; CMe$_3$), 1.21 (s, 9H; CMe$_3$), 1.45 (dd, $^2J = 11.7$, $^3J = 8.8$ Hz, 1H), 1.67 (dd, $^2J = 11.7$, $^3J = 6.3$ Hz, 1H), 1.73 (m, 2H; cod CH$_2$), 1.98 (m, 2H; cod CH$_2$), 2.08 (m, 2H; cod CH$_2$), 2.18 (m, 2H; cod CH$_2$), 2.54 (ddd, $^3J = 8.8$, $^3J = 6.3$, $^3J = 1.5$ Hz, 1H), 3.58 (m, 2H; cod CH), 3.83 (m, 2H; cod CH), 4.28 (d, $^4J = 2.4$ Hz, 1H; Cp), 4.50 (d, $^4J = 2.4$ Hz, 1H; Cp), 5.80 (d, 1.5 Hz, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 27.2$ (s; C*Me*$_2$), 27.9 (s; C*Me*$_3$), 28.5 (s; C*Me*$_2$), 31.6 (s; cod *C*H$_2$), 32.3 (s; *C*Me$_3$), 33.4 (s; C*Me*$_3$), 33.5 (s; cod *C*H$_2$), 44.5 (s; *C*H$_2$), 47.4 (s; *C*Me$_2$), 53.8 (s; *C*H*t*Bu), 63.5 (d, $^1J_{RhC} = 14.4$ Hz; cod *C*H), 66.8 (d, $^1J_{RhC} = 14.4$ Hz; cod *C*H), 80.6 (d, $^1J_{RhC} = 3.3$ Hz; Cp *C*H), 81.9 (d, $^1J_{RhC} = 4.4$ Hz; Cp *C*H), 101.6 (d, $^1J_{RhC} = 4.4$ Hz; Cp *C*C), 116.1 (d, $^1J_{RhC} = 4.4$ Hz; Cp *C*C), 117.7 (d, $^1J_{RhC} = 3.3$ Hz; Cp *C*C), 133.8 (s; *C*H=C), 146.8 (s; CH=*C*); FAB MS of **3**: *m*/*z*: 538.2 [M^+], 481.1 [$M^+ - \mathrm{CMe_3}$].

[18] Crystal structure analysis of **4**, $C_{32}H_{50}BF_4Rh$: $M_r = 624.44$, triclinic, space group $P\bar{1}$, $a = 8.931(2)$, $b = 9.389(2)$, $c = 20.404(9)$ Å, $\alpha = 103.12(3)$, $\beta = 90.14(3)$, $\gamma = 110.72(2)°$ $V = 1552.1(8)$ Å^3, $Z = 2$, $\mu = 0.593$ mm^{-1}, crystal dimensions $0.40 \times 0.20 \times 0.05$ mm. $2\theta_{max} = 55°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 16005 measured reflections, of which 7020 were unique ($R_{int} = 0.0332$) and observed. Full-matrix least-squares refinement based on F^2. 382 parameters.[20] $R1 = 0.0361$, $wR2 = 0.0807$. NMR data for **4**: ^{1}H NMR (CDCl$_3$): $\delta = 0.91$ (s, 9H; CMe$_3$), 1.05 (s, 3H; CMe$_2$), 1.26 (s, 3H; CMe$_2$), 1.33 (s, 9H; CMe$_3$), 1.34 (s, 9H; CMe$_3$), 1.59 (dd, $^2J = 11.8$, $^3J = 10.8$ Hz, 1H), 1.80 (dd, $^2J = 11.8$, $^3J = 6.5$ Hz, 1H), 2.29 (m), 2.55 (m), 2.74 (dd, $^3J = 10.8$, $^3J = 6.5$ Hz, 1H), 2.88 (m), 3.32 (m), 3.83 (m), 4.59 (m), 4.71 (m), 5.04 (m), 5.23 (d, $^4J = 1.7$ Hz, 1H; Cp), 5.46 (d, $^4J = 1.7$ Hz, 1H; Cp), 5.85 (m), 6.01 (d, $^3J < 1$ Hz, 1H).

[19] A similar reaction has been observed on treatment of [Rh(cod)Cp] with one-electron oxidants: M. D. Kitchen, PhD thesis, University of Bristol (UK), **1978**; N. G. Connelly, personal communication.

[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118903 (**2**) and -118904 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

An Atmospherically Driven Optical Switch

James J. La Clair*

An effective switch translates an external force through components of minimal complexity into a signal that regulates a desired output. A series of macromolecular switches have now been constructed that can be initiated by chemical, electrochemical, photochemical, or thermal stimuli.[1] Recent attention now focuses on adapting these materials into machines or electronic components.[2] A new device is presented that translates a change in the atmosphere into an electrical output though a photophysical change within a small group of molecules.

Here, a change is defined in units of molecules and measured by monitoring the viability of twisted intramolec-

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ular charge transfer (TICT) state formation.[3–4] Materials that contain a large dielectric constant, such as **1**, undergo facile rotation about unrestricted sp^3 bonds to form TICT states upon being excited to the singlet state (Figure 1). The orthogonal alignment of these states restricts their relaxation back to the ground state by nonemissive processes. Overall, the presence of a TICT state acts as a funnel that removes the potential for individual molecules to fluoresce.

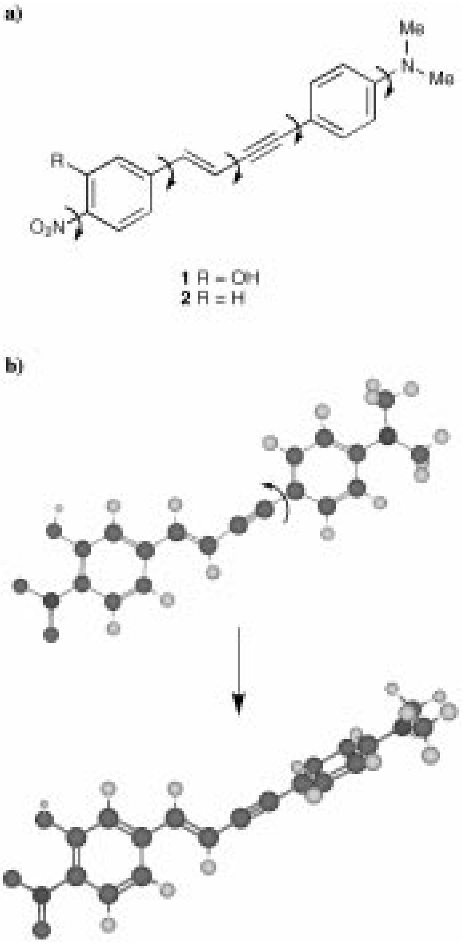

Figure 1. a) Compounds **1** and **2** contain five bonds (shown with arrows), which rotate in the excited state to provide a series of TICT states. b) Schematic representation depicting the formation of an orthogonal TICT state (bottom) from a planar conformation (top).

The formation of a TICT state is encouraged in polar media as a consequence of the relative increase in charge separation.[4] For **1**, changing the solvent from *n*-heptane to methanol red-shifted the fluorescence maxima[5] and decreased the relative quantum yield, as indicated by a change of $\lambda_F = 527$ nm ($\Phi_F = 0.10$) and $\lambda_F = 541$ ($\Phi_F = 0.0049$) in *n*-heptane to $\lambda_F = 483$ nm ($\Phi_F \sim 10^{-6}$) in methanol. This solvent effect was so pronounced that the addition of 0.005 % methanol provided only 10 % of the fluorescence normally obtained from a 1 µM solution of **1** in *n*-heptane.

The switching process was monitored using confocal single molecule spectroscopy. This technique was chosen as it is applicable to a small volume and provides a signal that requires a minimum number of molecules. Fluorescence from **1** was examined as individual molecules diffused through a 2.8 fL (2.8×10^{-15} L) conical fluorescent element. An illuminated cavity was generated by imaging the fluorescence, which arises from excitation with a 488 nm line (10 mW) of an argon ion laser through a 1 µM diameter pinhole and a 545 nm cutoff filter, onto a photoavalanche detector (Figure 2). Single molecules of **1** were readily detected in 0.1–1 nM solutions of *n*-heptane, benzene, or toluene in an argon or nitrogen atmosphere.[6, 7] In contrast, comparable detection was not possible in a variety of polar solvents, including methanol, ethanol, DMSO, DMF, 1,4-dioxane, and THF. This solvent sensitivity served as an effective switching element.

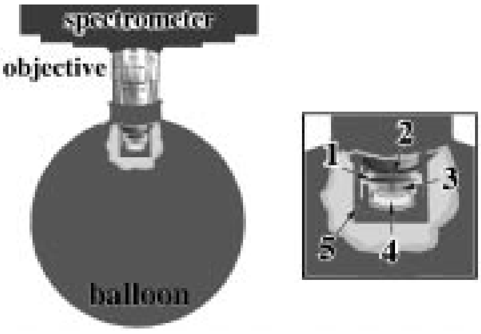

Figure 2. Schematic representation of the optical switch.[8] Left: An 80 ± 10 µL droplet of a 100 pM solution of **1** in benzene or toluene, enclosed within a balloon, is placed in contact with the objective of a confocal fluorescence spectrometer. Right: enlarged view of the probe. A laser beam (2) passes from the objective into the sample (3). The sample is held in a 50 µL gold well housed within a silver case (4). The sample holder is fixed to the objective using small strips of wood and tape (5). A small cover slip (1) is held between the objective and sample by a 20 µL drop of water to prevent contamination. Fluorescence is collected back through the objective, passed through a 1.0 µm diameter pinhole, and focused on the tip of the photoavalanche detector. The final probe volume is 2.8 fL (10^{-15} L). The chamber can be filled with argon, carbon dioxide, or nitrogen without altering the temperature of the probe.

When the atmosphere surrounding a 100 pM solution of **1** in benzene or toluene was changed from nitrogen to carbon dioxide, single molecules were no longer detected (Figure 3). Interestingly, the solubility of carbon dioxide in benzene or toluene was sufficient to decrease the net fluorescence from **1**. Single molecules were again detected after removal of the carbon dioxide and re-filling the chamber with argon or nitrogen.[9] This switching was limited only by the evaporation of the solvent. The presence of fluorescent molecules could be determined with a 99.1 ± 0.7 % certainty over 900 runs after 1.5 s. The speed of switching was not restricted by the detection element but rather by the ability to de-gas and refill the chamber.

A two-stage switch was constructed on the basis of the ability to detect single molecules of **1** as they diffused through a 2.8 fL cylinder.[7] The positions of the switch were defined as ON in an argon or nitrogen atmosphere and OFF in the presence of carbon dioxide. The lack of fluorescence in the OFF position likely arose from a combination of solvent-induced alteration in the access to the TICT state as well as carbonylation of the free phenol. Evidence for both factors come from a comparison of the results obtained with **1** with

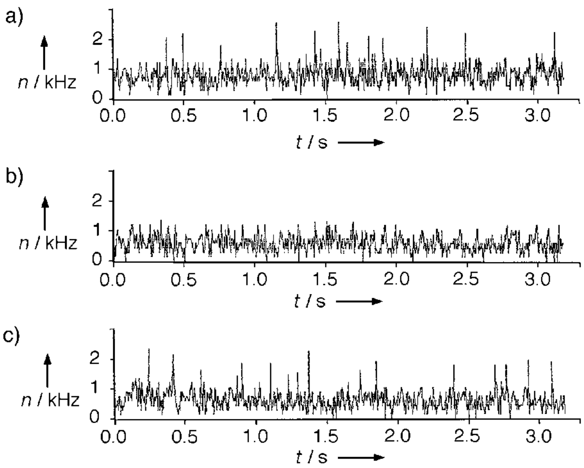

Figure 3. Traces of single molecules of **1** diffusing through a 2.8 fL (10^{-15} L) fluorescence element. a) Single molecules are readily detected in *n*-heptane solution in an argon or nitrogen atmosphere. b) Transients from these molecules disappear as the atmosphere is changed to carbon dioxide and c) reappear upon returning to an argon or nitrogen atmosphere.

those from **2**. While both materials share comparable spectroscopic properties and solvent sensitivity, the number of single molecule events was decreased but not eliminated when **2** was subjected to the same conditions as those used in Figures 2 and 3.

The fluorescence observed from the switching of **1** was translated into a graphical display (Figure 3) by conversion of the fluorescent photons into an electrical signal by means of a single-photon counting photoavalanche detector. The relay of the interaction between atmosphere and molecular photophysics to an electrical signal provides a novel approach for the design of future optical mechanical and electronic devices.

Experimental Section

Measurements were conducted on a conventional confocal single molecule spectrometer.[6, 7] A 20 μL drop of water was placed on the upper side of a circular cover-slip (Fischer) and attached to the head of a microscope objective (Zeiss Plan-neofluar Multi-immersion 40X). A 50 μL gold well encased in a silver holder (2 × 2 × 0.6 cm) and loaded with 80 ± 10 μL of a 100 pM solution of **1** in benzene or toluene was slowly brought into contact with the cover-slip. The assembly was held in place by mounting the sample holder on to the objective with four beams (see Figure 2). The droplet of **1** was open to the atmosphere. A balloon was placed over the entire sample housing and filled with gas. Confocal single molecule examinations were made repetitively on solutions of **1** in argon, nitrogen, and carbon dioxide atmospheres.

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[7] Single molecules were detected using a confocal fluorescence spectrometer as designed by Eigen–Rigler.[6a,b] Fluorescent photons were harvested by passing the filtered fluorescent beam through a 1 μm diameter pinhole and focusing this light on to a single photon counting silicon avalanche detector (EG&G SPCM-100).

[8] The switch was flipped by changing the atmosphere within the balloon between argon or nitrogen and carbon dioxide. This was conveniently accomplished by slowly purging and filling with the appropriate gas.

[9] The fact that the regenerated signal (Figure 3, bottom trace) originated from **1** was verified by two observations. Firstly, the detected transients displayed an identical diffusion time ($t_d = 55+5$ ms) with that of **1**, as given by their auto-correlated function (not shown). Secondly, the reaction of **1** with carbon dioxide was reversible as indicated by independent ^{1}H NMR characterization of a scaled-up version of this process.

Novel Catalytic Hydrogenolysis of Trimethylsilyl Enol Ethers by the Use of an Acidic Ruthenium Dihydrogen Complex[**]

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Since the first report on a tungsten complex with an η^2-bound H_2 ligand, $W(\eta^2\text{-}H_2)$, by Kubas and co-workers in 1984,[1] a great number of this unique class of complexes have

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