



Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of a ferrocene-functionalized unsymmetrical benzo[*b*]thienyl-thienylethene photoswitch with a cyclopentene core

Nathaniel B. Zuckerman, Xiongwu Kang, Shaowei Chen, Joseph P. Konopelski*

Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

ARTICLE INFO

Article history:

Received 7 December 2012

Revised 4 January 2013

Accepted 8 January 2013

Available online 17 January 2013

Keywords:

Ferrocene

Microwave Stille

Ruthenium nanoparticles

Diarylethene photoswitch

Intervalence transfer

ABSTRACT

A new and potentially general synthetic route toward unsymmetrical benzo[*b*]thienyl-thienylethene compounds is described, with specific focus on conjugation of a ferrocene to the benzo[*b*]thiophene subunit. The route proceeds in an overall yield of 17%.

© 2013 Elsevier Ltd. All rights reserved.

The desire to miniaturize electronic components and devices has led to a renewed focus on organic compounds in the development of molecular scale electronics. One such group of compounds is that of diarylethenes,¹ whose photochromic properties are amenable to use in memory applications.^{2–5} The ideal components of the photoswitch scaffold have been well documented over the past 20+ years and include the desirable qualities of: (1) induced reversible ring closure (light, acid, redox), (2) thermal irreversibility, and (3) fatigue resistance. Photochromism in the solid state is also a very desirable characteristic.

Of the large variety of photoswitches developed over the years, symmetric molecules that contain a perfluorinated cyclopentene bridge have remained superior for use in materials applications.⁶ However, if one requires an unsymmetrical perfluorocyclopentene-bridged photoswitch without the tedious separation of a mixture of compounds, there are few synthetic options. Such unsymmetrical compounds are attractive to both materials and biological applications.⁷

Within the last 15 years, there has been an expansion of research regarding the synthesis of perhydrocyclopentene-bridged photoswitches,^{8–10} largely directed toward the more desirable subunits thiophene¹¹ and benzo[*b*]thiophene.¹² Many of these compounds have the key aforementioned requirements of a desirable photoswitch. Additionally, the syntheses of these compounds are generally more amenable to scale up, lower in cost, and use

reagents that are relatively easy to attain and handle in comparison to their fluorinated counterparts.

Our desire in pursuing the unsymmetrical cyclopentene-bridged photoswitch scaffold **1** was driven by our continuing interest in organic monolayer-protected ruthenium nanoparticles.¹³ In recent publications we have demonstrated that ferrocene moieties conjugated to the metal nanoparticle via ruthenium–carbene π bonds display an intervalence transfer at mixed valence. Conversely, a single saturated carbon between the ferrocene and nanoparticle negates any communication between the ferrocenyl metal centers. Within this context, compound **1** provides an interesting test case. Appended to a ruthenium nanoparticle through olefin metathesis of the terminal alkene, photoisomerization of **1** to **2** (Fig. 1) provides for a fully conjugated pathway between the ruthenium core and the ferrocenyl substituent.¹⁴ Reversion to the open form (i.e., **1**) breaks the conjugation and any interaction between metal sites.

However, the synthesis of **1** poses certain challenges. There are few examples of unsymmetrical photoswitch molecules and, to our

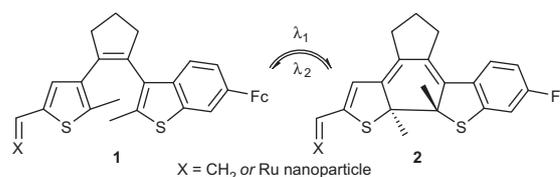


Figure 1. Open (**1**) and closed (**2**) forms of photoswitch; Fc = ferrocene.

* Corresponding author. Tel.: +1 831 459 4676; fax: +1 831 459 2935.

E-mail address: joek@ucsc.edu (J.P. Konopelski).

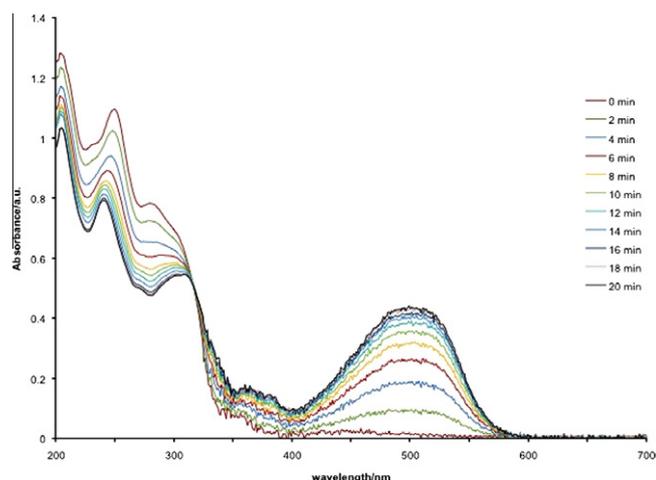


Figure 2. Open to closed. UV-vis spectra of interval irradiation of **1** in heptane (4.5×10^{-5} M) with 306 nm light.

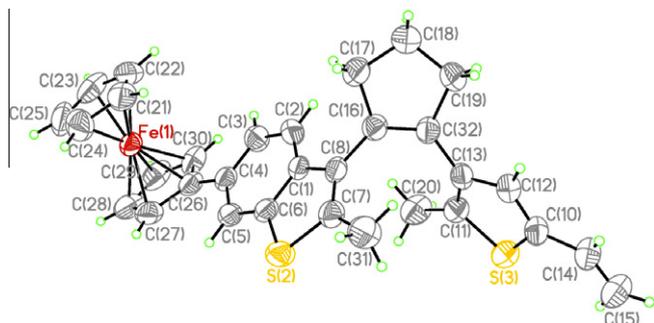


Figure 3. X-ray crystal structure of **1**.

Additionally, the previously described microwave Stille conditions gave **14** and **15** in 65% and 69% yield, respectively.

One of the main goals of our synthesis of an unsymmetrical photoswitch was to avoid the possibility of mixtures and the corresponding decreased overall yield. Methyl ester **14** or Weinreb amide **15** would allow us to pursue this goal without the need to directly protect the ketone portion of the molecule. Reduction of both carbonyl functionalities of **14** or **15** with DIBAL-H provided lactol **5**, which bore the desired masked aldehyde functionality that is revealed in the presence of excess lithium anion **4** (Scheme 3). Precedence for this type of reaction with complex anions is seen in the work toward the total synthesis of (+)-macbecin I by Martin and co-workers.²⁵ Multiple equivalents of nucleophile were necessary to give a good yield of diol **16** as a noticeable color change from red to brown above -40 °C signified possible anion decomposition. It should be noted that the dimethyl acetal was readily hydrolyzed during acidic workup to give diol **16**. The utility of this particular nucleophilic addition should be highly advantageous to the creation of a variety of mixed photoswitches.

Aldehyde **16** was treated with excess methylenetriphenylphosphorane to give alkene **17** in 85% yield. Oxidation of diol **17** did not proceed well under PCC, Swern, or Dess–Martin conditions, providing mostly decomposed product. However, Ley conditions provided a 68% yield of diketone **3**. The McMurry reaction proceeded smoothly to furnish **1** in 80% yield as orange crystals.^{12,16} The yield of **1** from commercially available **9** over nine steps, through Weinreb amide **15**, is 17%.

To investigate the degree of photocyclization, solutions of **1** were irradiated with monochromatic light from a xenon source

(306 nm). The molecule displays distinct maxima typical to dithienylethene compounds in the UV at 206 and 252 nm, as well as shoulders at 284 and 360 nm (Fig. 2). There is also a weaker intensity peak that extends from the UV into the visible region (maximum 450 nm), which can be attributed to ferrocene. Irradiation of a dilute solution of **1** with UV light turns the solution from colorless to red and gives rise to a new peak at 505 nm. Over irradiation time the intensity of the peaks below 350 nm decrease and there is a noticeable hypsochromic shift from 252 to 242 nm. Also, the shoulder at 284 nm is replaced with a more defined peak at 310 nm.

X-ray quality single crystals of **1** were formed upon slow evaporation from a mixture of hexanes and dichloromethane.²⁶ The ORTEP diagram of the structure is given in Figure 3. The distance between the reactive carbon atoms, labeled C7 and C11 in Fig. 1, is 3.67 Å, well below the determined necessary distance for solid-state cyclization (~ 4.2 Å)²⁷ upon irradiation with UV light at a suitable wavelength. However, under UV irradiation, the yellow crystals of **1** do not appear to photocyclize in the solid state. As discussed above, in the solution phase a colorless or pale yellow solution of **1** becomes pink to dark red upon irradiation with 306 nm light. The yellow crystals of **1** do not change color following irradiation with UV light.

Conclusions

A new synthetic route toward unsymmetrical benzo[*b*]thienylethene photoswitches, which allows the potential for an extensive variation of subunits, is described. Each aryl subunit is functionalized prior to the McMurry cyclization, which reduced the handling of the photoactive compound. Further study of the photoswitch properties of **1**, together with experiments to attach **1** to ruthenium nanoparticles, is underway and will be reported in due course.

Acknowledgments

This work was supported in part by the National Science Foundation (Grants CHE-0832605). Thanks to Dr. Honghan Fei (UCSC) for solving the X-ray structure. Single-crystal, X-ray diffraction data were recorded on an instrument supported by the US National Science Foundation Major Research Instrumentation (MRI) program; grant no. CHE- 0521569.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.01.033>.

References and notes

- Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
- Jakobsson, F. L. E.; Marsal, P.; Braun, S.; Fahlman, M.; Berggren, M.; Cornil, J.; Crispin, X. *J. Phys. Chem. C* **2009**, *113*, 18396–18405.
- Tsujioka, T.; Onishi, I.; Natsume, D. *Appl. Opt.* **2010**, *49*, 3894–3899.
- Wu, Y.; Chen, S.; Yang, Y.; Zhang, Q.; Xie, Y.; Tian, H.; Zhu, W. *Chem. Commun.* **2012**, *48*, 528–530.
- Zou, Q.; Li, X.; Zhang, J.; Zhou, J.; Sun, B.; Tian, H. *Chem. Commun.* **2012**, *48*, 2095–2097.
- Irie, M. *Photochem. Photobiol. Sci.* **2010**, *9*, 1535–1542.
- Singer, M.; Jäschke, A. *J. Am. Chem. Soc.* **2010**, *132*, 8372–8377.
- Huang, Z.-N.; Xu, B.-A.; Jin, S.; Fan, M.-G. *Synthesis* **1998**, *8*, 1092–1094.
- Lucas, L. N.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313–2314.
- Xu, B. A.; Huang, Z. N.; Jin, S.; Ming, Y. F.; Fan, M. G.; Yao, S. D. *J. Photochem. Photobiol., A: Chem.* **1997**, *110*, 35–40.
- Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2003**, 155–166.

12. Krayushkin, M. M.; Migulin, V. A.; Yarovenko, V. N.; Barachevskii, V. A.; Vorontsova, L. G.; Starikova, Z. A.; Zavarzin, I. V.; Bulgakova, V. N. *Mendeleev Commun.* **2007**, *17*, 125–127.
13. (a) Chen, W.; Chen, S.; Ding, F.; Wang, H.; Brown, L. E.; Konopelski, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 12156–12162; (b) Kang, X.; Zuckerman, N. B.; Konopelski, J. P.; Chen, S. *J. Am. Chem. Soc.* **2012**, *134*, 1412–1415.
14. For another ferrocene-substituted photoswitch, see Sun, L.; Tian, H. *Tetrahedron Lett.* **2006**, *47*, 9227–9231.
15. Krayushkin, M. M.; Migulin, V. A.; Russian Patent No. RU 2,421,453 C1, 2011.
16. Migulin, V. A.; Krayushkin, M. M.; Barachevsky, V. A.; Kobeleva, O. I.; Valova, T. M.; Lyssenko, K. A. *J. Org. Chem.* **2012**, *77*, 332–340.
17. Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 275–284.
18. Plaumann, D. E.; Fitzsimmons, B. J.; Ritchie, B. M.; Fraser-Reid, B. *J. Org. Chem.* **1982**, *47*, 941.
19. Gronowitz, S.; Björk, P.; Malm, J.; Hörnfeldt, A.-B. *J. Organomet. Chem.* **1993**, *460*, 127–129.
20. Mamane, V. *Mini-Rev. Org. Chem.* **2008**, *5*, 303–312.
21. Liu, C.-M.; Luo, S.-J.; Liang, Y.-M.; Ma, Y. X. *Synth. Commun.* **2000**, *30*, 2281–2285.
22. Liu, C.-M.; Chen, B.-H.; Liu, W.-Y.; Wu, X.-L.; Ma, Y.-X. *J. Organomet. Chem.* **2000**, *598*, 348–352.
23. Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502–2505.
24. Impagnatiello, N.; Heynderickx, A.; Moustrou, C.; Samat, A. *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 243–248.
25. Martin, S. F.; Dodge, J. A.; Burgess, L. E.; Hartmann, M. *J. Org. Chem.* **1992**, *57*, 1070–1072.
26. CCDC 876470.
27. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 2804–2805.