Inorg. Chem. **2005**, *44*, 5960–5962

Inorganic Chemistry

Communication

Synthesis and Coordination Chemistry of a Photoswitchable Bis(phosphine) Ligand

David Sud, Robert McDonald,[†] and Neil R. Branda*

Department of Chemistry, Simon Fraser University, 8888 University Drive,
Burnaby, British Columbia, Canada V5A 1S6

Received March 22, 2005

A 1,2-dithienylethene compound bearing bis(phosphine) groups (**1o**) represents a new class of photoresponsive ligands where there are steric and electronic differences between two photogenerated isomers. The coordination chemistry of this ligand class is demonstrated by preparing a gold(I) complex (**2o**) and a phosphine selenide (**3o**).

Compounds that interconvert between two thermally stable forms when irradiated with appropriate wavelengths of light provide a practical means to regulate the chemical and physical properties of molecular devices.[1] This is due to the fact that the two isomers possess unique physical properties such as the way they absorb and emit light, their refractive indices, and their redox potentials. Photoresponsive 1,2-dithienylethenes (DTEs) are especially useful and undergo ring-closing and ring-opening reactions, often with a high degree of photostability.[2] Because metal-coordination complexes provide their own diverse assortment of photophysical and electrochemical characteristics and because the metal centers' properties are highly sensitive to the steric and electronic nature of their associated ligands, developing tunable coordination complexes by combining a switching ligand with a metal ion will advance the use of coordination compounds in optoelectronics as well as in chemical reactivity and metal catalysis. In this regard, the DTE backbone is particularly attractive because it exhibits dramatic steric and electronic differences between its two interconverting isomers and metals bound to ligands made from this architecture will experience significant variations.

Several reports have described the use of DTE derivatives where nitrogen ligands (pyridine, bipyridine, and phenanthroline) are used to construct closed-shell structures and coordination polymers.[3,4] Other ligand choices have been less fruitful. For example, the coordination complexes formed using a cyano-functionalized DTE and ruthenium proved to be photochemically unstable.[4] Similar complexes using rhenium could not be isolated, and only the starting material was recovered.

It is surprising that there are no examples of photoresponsive DTE derivatives decorated with the ligand family most ubiquitous in coordination chemistry, the tertiary phosphorus family of ligands. This is particularly surprising because these are the ligands that boast the most dramatic and versatile changes in properties based on the fine-tuning of the electronic and steric framework of the groups attached to the phosphorus atom.[5] In this Communication, we describe the first example of a photoresponsive bis(triarylphosphine) based on the DTE backbone (**1o**) and demonstrate how it binds and affects metal centers. Specifically, gold(I) and selenium compounds are used as illustrative examples.

The photoresponsive bis(phosphine) ligand is prepared as its ring-open form (**1o**) in one step from the known 1,2-bis(5′-chloro-2′-methylthien-3′-yl)perfluorocyclopentene[6] as shown in Scheme 1. The bis(phosphine) is isolated as air-stable colorless crystals and is freely soluble in a wide range of common organic solvents such as CH_2Cl_2, THF, CH_3CN, and alcohols. Irradiation of a colorless CH_2Cl_2 or CH_3CN solution of **1o** with 313-nm light[6] results in the immediate appearance of a deep purple color ($\lambda_{max} = 570$ nm) because of the generation of the ring-closed isomer **1c**. In CH_2Cl_2, the photostationary state (PSS) contains 80% of **1c** as

---

* To whom correspondence should be addressed. E-mail: nbranda@sfu.ca.

[†] Present address: X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

(1) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.

(2) Irie, M. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Gugliemetti, J. R., Eds.; Plenum: New York, 1999; Vol. 1, p 207. Irie, M. *Chem. Rev.* **2000**, *100*, 1685. Irie, M. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001, p 37. Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85.

(3) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734. Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779. Qin, B. Q.; Yao, R.; Tian, H. *Inorg. Chim. Acta* **2004**, 3382. Matsuda, K.; Shinkai, Y.; Irie, M. *Inorg. Chem.* **2004**, *43*, 3774. Matsuda, K.; Takayama, K.; Irie, M. *Inorg. Chem.* **2004**, *43*, 482. Takayama, K.; Matsuda, K.; Irie, M. *Chem. Eur. J.* **2003**, *9*, 5605. Tian, H.; Qin, B.; Yao, R.; Zhao, X.; Yang, S. *Adv. Mater.* **2003**, *15*, 2104. Qin, B. Q.; Yao, R.; Zhao, X.; Tian, H. *Org. Biomol. Chem.* **2003**, *1*, 2187. Fraysse, S.; Coudret, C.; Launay, J.-P. *Eur. J. Inorg. Chem.* **2000**, 1581.

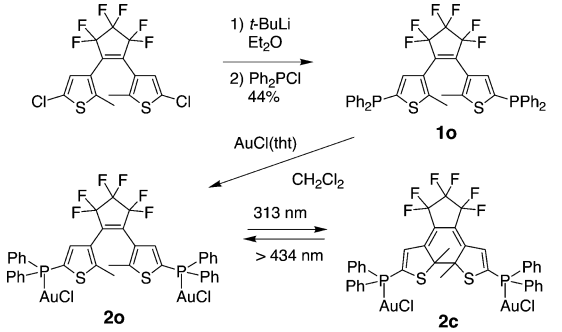
(4) Fernández-Acebes, A.; Lehn, J.-M. *Chem. Eur. J.* **1999**, *5*, 3285.

(5) Dias, P. B.; Minas de Piedade, M. E.; Martinho Simões, J. A. *Coord. Chem. Rev.* **1994**, 737.

(6) See the Supporting Information for details.

10.1021/ic050429x CCC: $30.25

Scheme 1



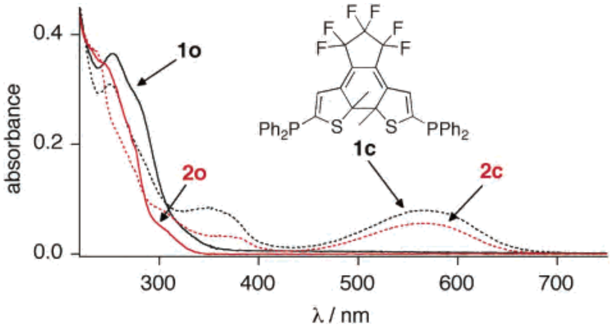
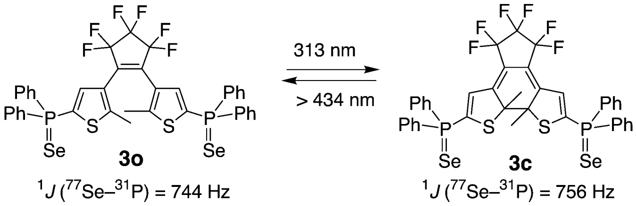


Figure 1. UV−vis absorption spectra of CH_3CN solutions of ring-open isomers **1o** and **2o** (solid lines) and the PSSs generated when the solutions are irradiated with 313-nm light (broken lines).

measured by ^1H NMR spectroscopy, where changes in chemical shifts typical for the ring-closing reaction are observed. The remaining 20% is the ring-open isomer. The UV−vis absorption spectra of both states are illustrated in Figure 1. The photocyclization reaction is highly solvent-dependent, and the photoconversion drops to 50% when CH_3CN is used. The original absorption spectrum corresponding to **1o** can be regenerated by irradiating the solution of the PSS with light of wavelengths greater than 434 nm, which triggers the reverse reaction and produces the ring-open isomer. This ring-closing/ring-opening cycle can be performed numerous times with no significant degradation. The signals in the ^{31}P NMR spectrum appear at −18.7 and −8.3 ppm for the ring-open and ring-closed isomers, respectively, illustrating the electronic differences between the two DTE isomers.

The coordination chemistry of ligand **1o** is typified by the preparation and isolation of the air-stable gold complex **2o** (Scheme 1). This is best done by treating the ring-open form of the ligand with AuCl(tht) in CH_2Cl_2 at 25 °C.[6,7] The coordination complex can be purified by column chromatography (silica, hexanes/CH_2Cl_2, 3:1). The ^1H NMR spectrum is consistent with the structure shown in Scheme 2, as is the ^{31}P NMR spectrum, which has a single signal appearing at 19.8 ppm.[6] Confirmation of the structure of **2o** is provided by X-ray crystallography. Single crystals suitable for X-ray analysis can be grown by slowly evaporating a solution of the complex in a mixture of CH_2Cl_2 and hexanes.

Scheme 2



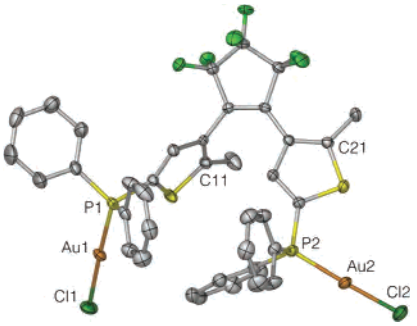


Figure 2. Molecular structure of **2o** in the crystal. Ellipsoids are shown at the 20% probability level.

The structure of the complex in the single crystal is shown in Figure 2.[6,7] In the crystal, the gold complex is locked into an unproductive conformation. It exists in a distorted parallel conformation, and the distance between the reactive carbons is too large for the photocyclization to occur in the single crystal (4.78 Å). This is verified by the fact that irradiating a single crystal of **2o** with 313-nm light for 30 min results in no observable change in the color of the crystal. The coordination geometry around the gold atom is linear with bond angles of 178°. The inter- and intramolecular distance between gold atoms indicates that there is no gold−gold bond, as shown for other (diphenylphosphino)thiophenegold(I) complexes.[8]

The photochemistry of complex **2o** is well behaved in solution. Irradiation of CH_2Cl_2 or CH_3CN solutions of **2o** with 313-nm light induces an immediate color change (colorless to purple) and the appearance of an absorption peak at 565 nm in the UV−vis spectrum (Figure 1). In the case of CH_2Cl_2, a PSS consisting of 60% of the ring-closed isomer **2c** is reached using our light sources. Cycling can be performed with minimal changes in the spectra (313 and >434 nm). A solvent that can coordinate to the gold (CH_3CN), should Au−P bond rupture be a part of the photochemical process, causes a slight decrease in the PSS to 50%, the same value that was observed for the free ligand in this solvent. However, other factors may lead to this observation.

The electron-withdrawing ability of the phosphine ligands in both forms of the photoresponsive compound is compared by direct measurement of the $^1J(^{77}Se-^{31}P)$ spin−spin coupling constants of the derived phosphine selenides.[9] The bis(selenide) compound **3o** is prepared quantitatively by heating

---

(7) X-ray data were collected at 193 K on a Bruker PLATFORM/SMART 1000 CCD with Mo Kα radiation. The crystal structure was solved using direct methods (SHELXS-86) and refined by full-matrix least squares on F^2 (SHELXL-93). Crystal data for $C_{39}H_{28}Au_2Cl_2F_6P_2S_2$: fw = 1201.51, triclinic $P\bar{1}$ (No. 2), $a = 9.7100(6)$ Å, $b = 10.2317(6)$ Å, $c = 20.4590(12)$ Å, $\alpha = 83.1693(9)°$, $\beta = 76.9049(8)°$, $\gamma = 84.1473(9)°$, $V = 1959.8(2)$ Å^3, $\rho_c = 2.036$ g cm^{-3}, $Z = 2$, $\mu = 7.860$ mm^{-1}, R1 $[F_0^2 \geq 2\sigma(F_0^2)] = 0.0214$, wR2 $[F_0^2 \geq -3\sigma(F_0^2)] = 0.0542$, and $4.32° < 2\theta < 52.76°$.

(8) Clot, O.; Akahori, Y.; Moorlag, C.; Leznoff, D. B.; Wolf, M. O.; Batchelor, R. J.; Patrick, B. O.; Ishii, M. *Inorg. Chem.* **2003**, *42*, 2704.

a mixture of the bis(phosphine) **1o**, selenium powder, and $CHCl_3$ at reflux.[6] The excess selenium is removed by filtering through a short silica plug. The photoactivity of this compound is demonstrated by the change in color of $CHCl_3$ solutions of **3o** from colorless to purple when irradiated with 313-nm light and by the changes in the ^{31}P NMR spectra. In this case, the PSS contains 55% of the ring-closed isomer **3c**. The signals in the ^{31}P NMR spectra are different for the two isomers and appear at 22.4 and 27.0 ppm for **3o** and **3c**, respectively. What is more indicative of the electronic differences affecting the nucleophilicity of the lone pair on the phosphorus atoms are the coupling constants $^1J(^{77}Se-^{31}P)$, which are 744 and 756 Hz for **3o** and **3c** respectively. This indicates that the ring-closed isomer of the parent bis(phosphine), **1c**, is a weaker nucleophile than the ring-open isomer **1o**. This difference can be attributed to the increased electron-withdrawing properties of the molecular backbone in **1c**. The difference in the $^{77}Se-^{31}P$ coupling constants for **3o** and **3c** is comparable in magnitude to that obtained when a phenyl group in triphenylphosphine is replaced by an alkyl group, which is a change that is well accepted to lead to significant differences in reactivity.

Further research efforts will focus on illustrating that the steric and electronic differences between the two interconverting isomers (**1o** and **1c**) can be harnessed in practical applications such as chemical reactivity and catalysis. These results will be reported in due course.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chairs Program, and Simon Fraser University (SFU) for financial support of this research. We thank Nippon Zeon Corp. for supplying the octafluorocyclopentene needed to prepare the photochromic compounds and Prof. Daniel Leznoff (SFU) for AuCl(tht) and helpful advice.

Supporting Information Available: Synthetic details and photochemical reactions for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050429X

---

(9) Chevykalova, M. N.; Manzhukova, L. F.; Artemova, N. V.; Luzikov, Y. N.; Nifant'ev, I. E.; Nifant'ev, E. E. *Russ. Chem. Bull.* **2003**, *52*, 78. Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, 51.