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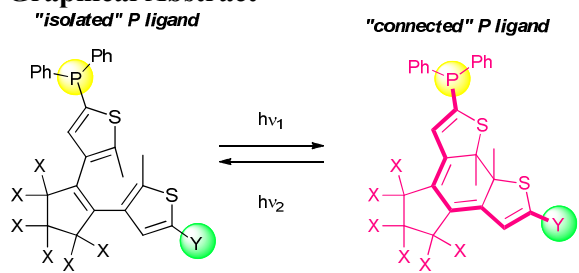
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## Graphical Abstract



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## ARTICLE TYPE

## Photomodulable Phosphines Incorporating Diarylethene Moieties

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**Incorporation of the dithienylethene moiety as a substituent provides new ‘switchable’ phosphine ligands whose electronic properties are reversibly modulated by light. The presence of electron-withdrawing substituents in the photochromic unit increases the  $\sigma$ -donation gap between the photo-modulated open and closed phosphine isomers.**

Regulation of enzymes activity is of crucial importance in the living system and this feature is mainly achieved by supramolecular recognition of chemical *stimuli* as allosteric effectors. Chemical regulation of artificial catalysts has been elegantly performed by using the same strategy<sup>1</sup> and more recently photo-switchable catalysis is emerging as the latest frontier in reversible homogeneous catalyst control. Considerable efforts have been made in the development of catalytic devices endowed with efficient light modulated structure leading to high catalytic differences between the photoisomers.<sup>2</sup>

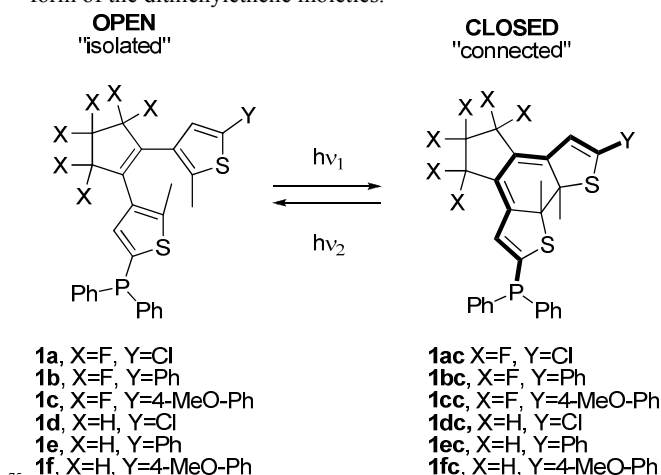
Among several possible chromophoric units, significant structural changes have been achieved by exploiting the photochemical properties of the azobenzene unit.<sup>3</sup> From the pioneering work of Ueno and co-workers in the 1980's,<sup>4</sup> to the more recent pyridine based catalyst of Stoll,<sup>5</sup> the reversible interconversion of the azobenzene unit provided an efficient tool to sterically regulate the access of reagents to the true catalytic site. Among 1,3,5-hexatrienes as photochromic units, 1,2-di(3-thienyl)ethenes have been pre-eminent in the construction of several molecular devices with reversible electronic properties, such as photochromic complexes,<sup>6</sup> photomodulable mixed valence systems,<sup>7</sup> data storage systems,<sup>8</sup> bioactive compounds,<sup>9</sup> synthetic materials and many others.<sup>10</sup> The most relevant features of these compounds are the fast and efficient photo-interconversion, the markedly different electronic properties between the photoisomeric forms as function of the structure and substitutions of the 1,2-di(3-thienyl)ethenes substituents.<sup>11</sup> The acyclic open form shows no electronic connection between the two thiophene rings, while the cyclic isomer, obtained upon irradiation usually in the UV range, is characterised by an extended  $\pi$ -system where the thiophene rings are electronically connected (Scheme 1). Irradiation of the latter species in the visible region leads to ring opening of the structure, yielding back the original open isomer.

Very recently Hecht showed reversible Diels Alder reaction between a diene containing dithienylethene moiety and a maleimide dienophile controlled exclusively by illumination with different wavelength light.<sup>12</sup> Branda and co-workers described

efficient and reversible systems based on the dithienylethenes unit to introduce light control in chemical reactivity on aldehydes and pyridine units.<sup>13</sup> They also showed that the photochemical ring-closure of dithienylethenes affects the electronic properties of the central backbone unit<sup>14</sup> and a carbene mounted on the backbone was used as photomodulable catalysts in a transesterification reaction.<sup>15</sup>

Phosphines remain the most widely used class of ligands for transition metal catalysis. As a consequence, the implementation of photomodulable units to this class of ligands would open the way to the control of several well-established catalytic systems; reactions including Rh(I) mediated hydroformylations or Pd(II) mediated carbonylations where the electron density of the P ligands greatly affects the catalytic activity of the transformation, would benefit of this allowing their control by light. To the best of our knowledge, only one example of a symmetric diphosphine bearing a central dithienylethene unit is known.<sup>16</sup>

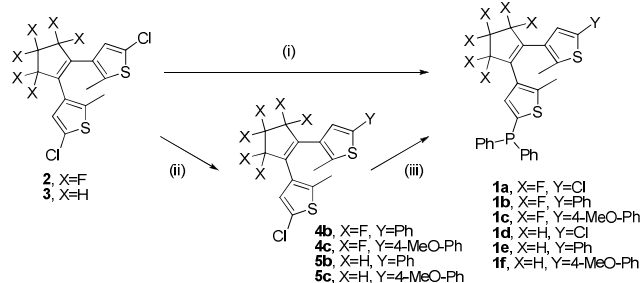
In this work we present a series of six new monophosphines (Scheme 1) directly connected to one thiophene ring of the dithienylethene moieties and characterized by i) different substituents and electronic properties on the other thiophene ring and ii) fluorinated or non-fluorinated five membered bridging unit. Their photochromic behavior is presented in order to correlate the  $\sigma$ -donation ability of the P atom with the electronic properties of the open *isolated* form and the closed *connected* form of the dithienylethene moieties.



**Scheme 1.** Structure of the open dithienylethene phosphines **1a-1f** and the corresponding closed isomers **1ac-1fc**.

In all the prepared photomodulable phosphines, one thiophene ring was functionalized with a diphenylphosphinic group whilst the second ring was equipped with substituents characterized by different electronic properties, ranging from the electron donating 4-MeO-phenyl substituent (**1c** and **1f**), to the electronically intermediate phenyl moiety (**1b** and **1e**), to the weakly electron withdrawing chlorine atom (**1a** and **1d**). Furthermore, comparison between the phosphines bearing a perfluorinated cyclopentene bridging unit (**1a-1c**) and those with the regular cyclopentene unit (**1d-1f**), allowed us to evaluate the effects of different bridging units.

The new ligands were synthesized following a divergent strategy (Scheme 2) starting from precursors **2** and **3**.<sup>17</sup>



**Scheme 2.** Synthetic pathway for the incorporation of the dithienylethene moiety within a monophosphinic ligand; *i*) *n*BuLi (1.0 eq.), PPh<sub>2</sub>Cl (2.0 eq.); *ii*) *n*BuLi (1.0 eq.), B(O*n*Bu)<sub>3</sub> (2.0 eq.) then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 eq.), K<sub>2</sub>CO<sub>3</sub> (4.5 eq.), ArBr (2.0 eq.); *iii*) *n*BuLi (1.2 eq.), PPh<sub>2</sub>Cl (2.2 eq.).

Phosphines **1b-1c** and **1e-1f** were obtained by reacting chlorodiphenylphosphine (2.2 eq.) with the reactive species obtained by the halogen-metal exchange on compounds **4b-4c** and **5b-5c** respectively, with yields ranging from 60-64% after flash chromatography. The latter intermediates were obtained following the protocol for the synthesis of non-symmetric dithienylethenes developed by Feringa and co-workers, which consists in a Suzuki cross-coupling between specific aryl halide and dithienylethene borate species in the presence of a Pd(0) catalyst.<sup>18</sup> Borates were synthesized by tri-*n*-butylborate quench (2 eq.) of the intermediates obtained by reacting compounds **2** and **3** with organolithium species (1.0 eq.). Intermediates **4b** and **4c**, as well as **5b** and **5c**, were obtained with yields around 55% after flash chromatography. Similarly, phosphines **1a** and **1d** were easily obtained reacting chlorodiphenylphosphine (2 eq.) with the reactive species obtained by treating compounds **2** and **3**, respectively, with organolithium reagents (1 eq.).

All the phosphines were characterized by <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C-NMR spectroscopy techniques together with <sup>19</sup>F NMR and HRMS (ESI) for **1a-1c**. In the <sup>1</sup>H NMR, particularly relevant are the signals of the residual thiophene protons separated into two different sets. In the different phosphines, the proton of the thiophene ring equipped with the phosphinic moiety provided a doublet in the range 7.29-6.97 ppm with typical <sup>3</sup>J<sub>H-P</sub> of 7.1-6.0 Hz, while the other thiophene proton appeared at lower field (7.21-6.59 ppm as singlet). Phosphines **1a-c** showed <sup>31</sup>P resonances as singlets around -19 ppm, close to the value reported in the literature for a similar compound,<sup>16</sup> whereas

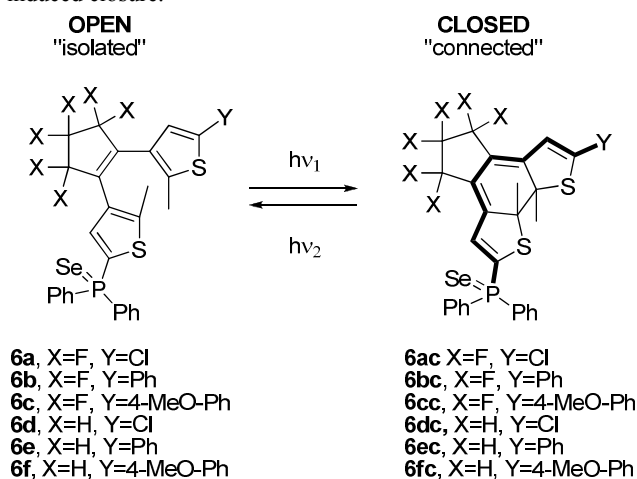
phosphines **1d-1f** led to singlets at higher field, around -21 ppm. UV-Vis analysis revealed absorption of light up to 370 nm for all compounds **1**, excepting **1d** that adsorbed light up to 320 nm. On this basis, UV irradiation at 365 nm for ligands **1b**, **1c**, **1e**, **1f** and at 310 nm or 254 nm for ligands **1a** and **1d** was used to induce the formation of the corresponding connected forms (see Electronic Supplementary Information). Upon proper irradiation, the closed phosphines **1b** and **1c** showed deep blue colour with new absorption maxima at 577 and 572 nm, respectively, while phosphine **1a** turned crimson with a new maximum at 535 nm. Phosphines **1e** and **1f** turned red-crimson and new maxima at 529 and 500 nm were observed, respectively. Phosphine **1d** did not show any new maximum but only an increased light adsorption in the range 450-300 nm, providing a yellow-orange solution. Since all phosphines showed to be oxygen sensitive especially in solution, we were not able to completely discard the absorption contributes from the phosphine oxides and always minor amounts of the oxidized phosphine were present. As long as the closed forms are considered, compounds from **1ac** to **1cc** showed <sup>31</sup>P-NMR signals around -9 ppm, close to the value already reported for a diphosphine bearing fluorinated five membered ring central backbone.<sup>16</sup> Conversely, the phosphines equipped with the perhydrogenated bridging unit showed <sup>31</sup>P NMR spectroscopy resonances at higher field around -13 ppm. As proof of reversibility of the photochemical isomerization, all the phosphines provided complete decolouration when irradiated with visible light (λ > 600 nm).

The σ-donation ability of phosphines could be evaluated by the magnitude of P-Se coupling constants (*J*<sub>P-Se</sub>) of the corresponding phosphine selenides.<sup>19</sup> Since the Se-P bond has low Pπ-3d-Seπ-4d character, the effects of the substituent present on phosphorous on the coupling constants values can be referred to the *s* character of the lone pair of the phosphorous. Electron withdrawing groups cause an increase in *s* character of the lone pair, whereas electron donating groups provide a decrease of the *s* character. As a consequence, selenides of phosphines bearing electron donating substituents are characterized by lower values of <sup>1</sup>J(<sup>31</sup>P-<sup>77</sup>Se) compared to analogous phosphines bearing electron-withdrawing substituents.

The corresponding selenides **6a-6f** were prepared in quantitative yield refluxing phosphines **1a-1f** in chloroform in the presence of elemental Se and were characterised by <sup>1</sup>H and <sup>31</sup>P-NMR techniques.

The selenides **6a-6f** retained the photochemical activity of the corresponding free phosphines **1a-1f**, showing coloration after UV irradiation (Scheme 3). The chemical shifts and coupling constants for both the open isolated and closed connected forms of selenides **6a-6f** are reported in Table 1. First of all we observed that phosphine-selenides **6a-6c** bearing the hexafluorocyclopentene backbone showed similar resonances and coupling constants with respect to the photomodulable *bis*-phosphine reported in the literature.<sup>16</sup> This clearly means that there are not substantial differences due to the substitution pattern present on the thiophene rings. As long as selenides **6d-6f** equipped with the regular cyclopentene moiety are concerned, both the open and closed forms showed resonances at higher field

with respect to the fluorinated counterparts. In, all cases the  $^1J_{\text{P-Se}}$  Se values for the closed isomers resulted greater than that observed for the corresponding open isomers indicative of a reduction of the  $\sigma$ -donation ability of phosphines upon photo-induced closure.



**Scheme 3.** Structure of the open dithienylethene phosphine selenides **6a-6f** and the corresponding closed isomers **6ac-6fc**.

The  $\Delta^1J_{\text{P-Se}}$  values observed between closed and open forms resulted uniformly larger for the corresponding fluorinated selenides with respect to non-fluorinated ones. This implies that larger variations of the  $\sigma$ -donation properties of the P atom are possible with the fluorinated dithienylethene backbone. A decrease in the  $\sigma$ -donation ability observed between the closed and the open forms of **6a** ( $\Delta^1J_{\text{P-Se}}$  of about 15 Hz) is comparable to changing  $\text{PPh}_3$  with the less coordinating  $\text{Ph}_2\text{PNEt}_2$  or (*t*-Bu) $\text{PPh}_2$  with  $\text{PPh}_3$ .<sup>20</sup>

| P=Se      | OPEN<br>Isolated               |                             | CLOSED<br>Connected            |                             | $\Delta^1J_{\text{P-Se}}$<br>(Hz) |    |
|-----------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|-----------------------------------|----|
|           | $^31\text{P } \delta$<br>(ppm) | $^1J_{\text{P-Se}}$<br>(Hz) | $^31\text{P } \delta$<br>(ppm) | $^1J_{\text{P-Se}}$<br>(Hz) |                                   |    |
| <b>6a</b> | 22.05                          | 742                         | <b>6ac</b>                     | 26.76                       | 757                               | 15 |
| <b>6b</b> | 22.05                          | 744                         | <b>6bc</b>                     | 26.72                       | 756                               | 12 |
| <b>6c</b> | 21.97                          | 744                         | <b>6cc</b>                     | 26.60                       | 756                               | 12 |
| <b>6d</b> | 20.31                          | 737                         | <b>6dc</b>                     | 24.35                       | 747                               | 10 |
| <b>6e</b> | 20.18                          | 740                         | <b>6ec</b>                     | 24.20                       | 746                               | 6  |
| <b>6f</b> | 20.14                          | 737                         | <b>6fc</b>                     | 24.15                       | 742                               | 5  |

**Table 1.**  $^31\text{P}$  NMR chemical shift and  $^1J_{\text{P-Se}}$  for the isolated and connected selenides **6a-6f** and the corresponding closed selenides **6ac-6fc**.

A trend between  $\Delta^1J_{\text{P-Se}}$  and the electronic effects imparted by the Y substituents was observed. In particular it was found that  $\Delta^1J_{\text{P-Se}}$  decreased moving from electron-withdrawing Y moieties

to electron-donating Y moieties, especially when non-fluorinated dithienylethene phosphines are considered, indicating that the presence of electron-withdrawing Y groups favor larger variation of the  $\sigma$ -donation properties of the P upon irradiation. All these observations clearly speak for the great importance played by the central backbone in determining the electronic properties of the closed isomers.

In conclusion, we demonstrated that the electronic properties of phosphine moieties can be photo-modulated by installation of a dithienylethene residue as a substituent on the P atom. In the closed connected forms, the effect of the electronic properties of the Y moieties installed on the opposite side with respect to the P atom was found to be significant. In particular larger variations of  $\sigma$ -donation ability of the P atom upon irradiation were observed for ligands endowed with the perfluorinated cyclopentene scaffold. This opens the way to the implementation of similar classes of P ligands in homogeneous catalysis to achieve reversible photo-control of the catalytic activity. Some preliminary experiments were carried out concerning the implementation of the described photomodulable ligands for the synthesis of catalytically active Pt(II) complexes bearing two coordinated ligands. Unfortunately, the presence of the metal center hampered the efficient photo-conversion of the dithienylethene moieties. Experiments on the use of the ligands for the preparation of Rh(I) complexes to be used in catalysis are currently underway in our laboratories and will be reported in due course.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: experimental procedures, characterization data and spectroscopic properties. See DOI: 10.1039/b000000x/

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