Dithienylethene-based photoswitchable phosphines for light-controlled palladium-catalyzed Stille coupling reaction

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^c Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Bellaterra, 08193 Barcelona, Spain ABSTRACT Homogeneous transition metal catalysis is a constantly developing field of the chemical sciences. A growing interest in this area is photoswitchable catalysis, which pursues *insitu* modulation of catalyst activity through non-invasive light irradiation. Phosphorus ligands are excellent targets to accomplish this goal by introducing photoswitchable moieties; however, only a limited number of examples has been reported so far. In this work we have developed a series of palladium complexes capable of catalyzing the Stille coupling reaction that contain photoisomerizable phosphine ligands based on dithienylethene switches. Incorporation of electron-withdrawing substituents into these dithienylethene moieties allows to vary the electron density on the phosphorus atom of the ligands upon light irradiation, which in turn leads to a modulation of the catalytic properties of the formed complexes and their activity in a model Stille coupling reaction. These results are supported by theoretical computations, which show that the energy barriers for the rate-determining steps of the catalytic cycle decrease when the photoswitchable phosphine ligands are converted to their closed state.

Introduction

Inspired by the dynamic behavior of enzymes in nature, controlling the operation of artificial molecular catalysts with external stimuli has become an active area of research with potential application in a variety of fields^{1–3} (e.g., polymer synthesis,^{4,5} bioorthogonal chemistry,^{6,7} and additive manufacturing⁸). The use of light to achieve this goal holds great promise, as it opens the way to non-invasive catalyst regulation on-demand with high selectivity and spatiotemporal precision.^{9–11} A major strategy toward this purpose is the design of photoswitchable catalysts, whose activity and selectivity can be reversibly modulated with light by installing photochromic units into their structure – i.e., light-responsive moieties such as azobenzenes,^{12,13}

dithienylethenes¹⁴ and stilbenes¹² that alter the reactivity of nearby catalytic sites by photoisomerizing between two different states.

Because of their fundamental role in modern synthetic chemistry, transition metal complexes are amongst the principal targets of photoswitchable catalysis.^{15–17} Reversible light-control of the catalytic activity of these compounds is generally accomplished by introducing photochromic ligands (e.g., photoswitchable phosphines¹⁸). In most of the cases, the geometrical changes that these ligands undergo upon photoisomerization cause catalyst reactivity modulation;^{15–17} for instance, by distorting the structure around the catalytic site^{19–21} or varying the separation distance between two cooperative active metal centers.^{22,23} However, the actual impact of these effects on catalytic activity and selectivity can be detrimentally affected by catalyst conformational flexibility²⁴ and be dependent on substrate size and geometry. An alternative, less exploited approach to light-control the performance of transition metal catalysts is to capitalize on the electronic changes that occur upon ligand photoisomerization.^{15–17} For this strategy, dithienylethenes (DTE) are the photochromic units of choice¹⁴ because, in contrast to azobenzenes and stilbenes, they undergo a large modification in electronic structure when reversibly toggling between their ring-open (**0**) and ring-closed (**c**) isomers.²⁵

To date, only a reduced number of DTE-based complexes have been described where photomodulation of catalysis is accomplished via electronic effects.^{26–29} All these systems share a common design principle: they contain DTE ligands that bind to the metal center through the groups installed in their central ethylene bridging moiety (e.g., carbene,^{26,27} phosphines²⁸), which are either removed²⁹ or lose electron density^{26–28} upon ring-closing (Scheme 1a). In contrast, other electronic features that accompany DTE photoisomerization are yet to be exploited in metal-based photoswitchable catalysis. In this work we propose to explore one of these

additional features: the variation in electronic communication between the external thiophene substituents upon photoconversion, which has already been utilized to control chemical reactivity with light-responsive organocatalysts^{30,31} and organic substrates.^{32,33} In particular, herein we devised the synthesis of asymmetric DTE derivatives as photoswitchable ligands bearing (i) a metal-binding phosphine group at one thiophene ring, and (ii) an electron-withdrawing substituent at the other (Scheme 1b). As these two groups must be electronically insulated in the open state of the system and become selectively conjugated upon ring-closing, our molecular design should allow modulating the electron density of the phosphine ligand with light and, eventually, the catalytic activity of metal centers upon coordination. To validate this hypothesis, we prepared palladium(II) complexes of our DTE ligands and tested them as pre-catalysts in Stille coupling reaction, a widely employed Pd-catalyzed transformation that is sensitive to electronic effects³⁴⁻³⁶ and has not been tested yet in photoswitchable catalysis.

Scheme 1. a) Previously reported transition metal complexes incorporating DTE-based photoswitchable units as ligands. b) DTE-based photoswitchable complexes studied in this work.



Results and discussion

Synthesis of photoswitchable ligands and monometallic complexes

To explore our approach towards photoswitchable catalysts, two different electronwithdrawing groups (EWG) were introduced in DTE-based phosphine ligands: (i) a trifluoroacetyl group in **DTE-COCF**₃, which is a strong EWG according to its Hammett σ -*meta* and σ -*para* substituent constants ($\sigma_m = 0.63$, $\sigma_p = 0.80$),³⁷ and (ii) a pentafluorophenyl group in **DTE-C**₆**F**₅, which presents a less pronounced electron-withdrawing power ($\sigma_m = 0.26$, $\sigma_p =$ 0.27).³⁷ As a reference, we also considered the preparation of a DTE-based phosphine ligand bearing a phenyl substituent (**DTE-Ph**), which should impart very minor electronic effects ($\sigma_m = 0.06$, $\sigma_p = -0.01$).³⁷

The ring-open isomer of the DTE-based ligands were synthesized through asymmetrical stepwise functionalization of 1,2-bis(2-chloro-5-methylthien-4-yl)cyclopentene (**DTE1**, Scheme 2), which is a common precursor for the preparation of dithienvlethene derivatives via lithiation-mediated processes.³⁸ For DTE^o-COCF₃ and DTE^o-C₆F₅, the sequence to introduce the phosphine and EWG groups in **DTE1** was governed by their sensitivity towards lithium reagents. For this reason, we first conducted lithiation of **DTE1** with *t*-butyllithium (*t*BuLi) followed by quenching with chlorodiphenylphosphine to obtain phosphanyl compound DTE2 (67% yield); next, additional lithiation with tBuLi followed by reaction with ethyl trifluoroacetate (69% yield) or hexafluorobenzene (70% yield) furnished DTE°-COCF₃ and $DTE^{\circ}-C_{6}F_{5}$, respectively. As for $DTE^{\circ}-Ph$, we inverted the order in which the external thiophene substituents were introduced to the DTE core according to a previously reported procedure.³⁹ In particular, its phenyl side group was first installed through consecutive lithiation, borylation and Suzuki coupling steps to produce compound DTE3 (83% yield), which was then subjected to further lithiation with n-butyllithium (nBuLi) and subsequent treatment with chlorodiphenylphosphine (68% yield) to introduce the phosphanyl moiety of DTE°-Ph. All synthesized phosphines presented a singlet in the ³¹P{¹H} NMR spectra at around $\delta \approx -19.6$ ppm, a chemical shift value that is similar to those reported for (2-methyl-5-thienyl)diphenylphosphine $(\delta = -21.9 \text{ ppm})^{40}$ and symmetric bis(phosphine) DTE ($\delta \approx -20.0 \text{ ppm}$).^{41,42} As expected, this result corroborates that the phosphanyl and electron-modulating groups in the non-planar structure of DTE°-COCF₃, DTE°-C₆F₅ and DTE°-Ph are not conjugated and, therefore, do not significantly affect each other.

Scheme 2. Synthetic route towards phosphanyl-substituted DTEs.



When two equivalents of the phosphine ligands were used to react with *trans*-[PdCl₂(PhCN)₂], monometallic palladium(II) 1:2 type complexes were formed (Figure 1a). For all these compounds, an isolated singlet was registered in their ³¹P{¹H} NMR spectra that shifted downfield to $\delta \approx 12$ ppm, thereby corroborating metal complexation and the formation of exclusively one isomer (*cis* or *trans*). In addition, negligible differences were found in the chemical shift of this ³¹P{¹H} NMR signal for the three Pd complexes prepared, which again demonstrates the lack of electronic communication between the external thiophene substituents in the open isomer of the ligands. Furthermore, complexation to the Pd centre could also be

verified by the downfield shift of the ¹H NMR resonance of the thiophene ring proton next to the phosphanyl group. Single crystals suitable for X-ray structure determination were obtained for the three complexes, which revealed that formed Pd complexes have a square-planar geometry with *trans* orientation of the phosphine ligands (Figure 1b, Figures S1-S3 and Table S1). The main difference observed between the crystal structures of these compounds was the conformation of their DTE ligands. In [PdCl₂(DTE^o-Ph)₂] and [PdCl₂(DTE^o-COCF₃)₂], the ligands are locked in a distorted parallel open state conformation with a distance of 4.31 Å and 5.19 Å, respectively, between the carbon atoms that should react upon ring-closing photoisomerization ($C_{16} - C_{26}$). As previously described in the literature,²⁵ this type of conformation cannot undergo the light-induced conrotatory electrocyclization reaction to produce the corresponding closed isomer and, consequently, no photochromism was observed in the solid state for [PdCl₂(DTE^o-Ph)₂] and [PdCl₂(DTE^o-COCF₃)₂]. Contrarily, in the case of $[PdCl_2(DTE^{\circ}-C_6F_5)_2]$, the DTE ligands are present in an antiparallel open state conformation with a shorter distance between the reactive carbons ($C_{16} - C_{26}$, 3.69 Å), two structural features that are compatible with the photoinduced ring-closing reaction.⁴³ Indeed, irradiation at 312 nm yielded a color change from yellow to red and the process was reversed with irradiation at 520 nm, thus demonstrating solid state photoswitching for $[PdCl_2(DTE^{\circ}-C_6F_5)_2]$ (Figure S4).



Figure 1. a) Synthesis of $[PdCl_2(DTE^{\circ}-COCF_3)_2]$, $[PdCl_2(DTE^{\circ}-C_6F_5)_2]$ and $[PdCl_2(DTE^{\circ}-Ph)_2]$. Ph)₂]. b) Molecular structures of $[PdCl_2(DTE^{\circ}-Ph)_2]$, $[PdCl_2(DTE^{\circ}-COCF_3)_2]$ and $[PdCl_2(DTE^{\circ}-C_6F_5)_2]$. Thermal ellipsoids set at 50% probability level. For clarity, P-bound phenyl rings are depicted in wireframe style, and co-crystallized solvent and hydrogen atoms are omitted. Distances between the reactive carbon atoms in DTE photoisomerization are marked with a dashed red line.

Photochemical behavior of ligands and complexes

Irrespective of their behavior in the solid state, all DTE-based ligands and complexes prepared should photoisomerize in solution upon irradiation. However, while DTE-COCF₃, DTE-C₆F₅ and DTE-Ph should just photoconvert between their ring-open and ring-closed isomers, a more complex situation is expected for their complexes (Scheme 3). Because of their 2:1 phosphine:metal stoichiometry, these compounds must toggle between three different states where DTE-based ligands are both ring-open (**oo**), one of them ring-open and the other ring-closed (**oc**), or both ring-closed (**cc**).

Scheme 3. Photoisomerization processes for DTE-based free ligands and their palladium(II) complexes.



To study these photoinduced processes, the UV-vis absorption spectra of the initial ring-open isomer of the synthesized DTE-based ligands and their palladium(II) complexes were first recorded in cyclohexane (Figure 2a-b and Figure S5). In addition, TD-DFT calculations at the CAM-B3LYP-D3/6,31G(d,p) level were performed to further investigate the electronic excitations of these compounds (Tables S2-S5), for which ground state geometries were first computed. For ligands and complexes bearing open state DTE units, we only considered their photocyclizable antiparallel conformation in our calculations. All open state phosphine ligands were characterized by a strong absorption in the UV region with maxima around $\lambda_{abs} \approx 290$ nm, which was reproduced in computations and could be attributed to π - π * transitions (HOMO -LUMO+1 or HOMO - LUMO) of their core (Tables S3 and S5, Figures S23-S25). In the case of **DTE-COCF**₃, a shallower absorption band ranging up to $\lambda_{abs} \approx 400$ nm was detected due to the lowering of the energy of the LUMO caused by the introduction of a strong EWG (Table S2).44 As for the UV-vis absorption of the open state Pd^{II} complexes, they did not only preserve all the spectral features of their constituting DTE° ligands, but also exhibited a new red-shifted band with a maximum at $\lambda_{abs}\approx$ 350 nm (Table 1). According to our TD-DFT calculations, this additional absorption band can be mainly assigned to a ligand-to-metal charge transfer (LMCT) transition, as the LUMO of all the open state complexes is located on the palladium center (Tables S4, S5 and Figures S26-S28).



Figure 2. a) Variation of the absorption spectrum of free ligands $DTE^{\circ}-COCF_3$ ($c = 3.0 \cdot 10^{-5}$ M) and $DTE^{\circ}-C_6F_5$ ($c = 1.0 \cdot 10^{-5}$ M) in cyclohexane upon sequential irradiation with UV ($\lambda_{exc} = 355$ or 312 nm) and green light ($\lambda_{exc} = 520$ nm) until the corresponding ring-closing and ring-opening photostationary states (PSSs) are obtained, respectively. The variation of the absorbance at the spectral maximum of the ring-closed isomer of these compounds ($\lambda_{det} = 598$ or 519 nm) upon 10 consecutive photoswitching cycles is also given ($DTE^{\circ}-COCF_3$ ($c = 6.0 \cdot 10^{-6}$ M) and $DTE^{\circ}-C_6F_5$ ($c = 9.0 \cdot 10^{-6}$ M)). Excitation wavelengths used are: $\lambda_{exc} = 365/312$ nm for the ring-closing and $\lambda_{exc} = 520$ nm for the ring-opening reactions. b) Variation of the absorption spectrum of the open state complexes [PdCl₂($DTE^{\circ}-COCF_3$)₂] ($c = 1.2 \cdot 10^{-5}$ M) and [PdCl₂($DTE^{\circ}-C_6F_5$)₂] ($c = 9.6 \cdot 10^{-6}$ M) in cyclohexane upon sequential irradiation with UV ($\lambda_{exc} = 355$ nm) and green light ($\lambda_{exc} = 520$ nm) until the corresponding ring-closing and ring-opening PSSs are obtained, respectively. The variation of the absorbance at the spectral maximum of the ring-closed isomer of these compounds ($\lambda_{det} = 604$ or 532 nm) upon 10 consecutive photoswitching cycles is also given

([PdCl₂(**DTE^o-COCF**₃)₂] ($c = 1.2 \cdot 10^{-5}$ M) and [PdCl₂(**DTE^o-C**₆**F**₅)₂] ($c = 4.2 \cdot 10^{-5}$ M)). Excitation wavelengths used are: $\lambda_{exc} = 365$ nm for the ring-closing and $\lambda_{exc} = 520$ nm for the ring-opening reactions.

Based on the electronic absorption properties of the open state ligands and complexes, their ring-closing photoisomerization was assayed upon irradiation with UV light. For open state ligands, a broad, red-shifted absorption band emerged in the visible part of the spectrum upon UV illumination of their cyclohexane solutions, which changed from colorless to deep blue (λ_{abs} = 598 nm for DTE^c-COCF₃) or deep pink ($\lambda_{abs} \approx 518$ nm for DTE^c-C₆F₅ and DTE^c-Ph) (Figure 2a, Table 1 and Figure S5). This behavior is characteristic of closed state DTEs,⁴⁵ as confirmed by TD-DFT calculations (Table S5, Figures S23-S25) and additional NMR spectroscopic measurements. In particular, we observed the appearance of a new set of signals for the closed isomer in the ¹H, ³¹P (proton-coupled and decoupled) and, when applicable, ¹⁹F NMR spectra of the UV-irradiated ligands in toluene- d_8 , which were upfield (¹H NMR) or downfield shifted (³¹P, ³¹P{¹H} and ¹⁹F NMR) relative to the NMR resonances of the open state (Figures S6-S13). Analysis of this NMR data also revealed that the photocyclization reaction of DTE-based ligands was not quantitative. Instead, a photostationary state (PSS) composed of an equilibrium mixture of the ligands' o and c states was obtained in all the cases, since both isomers absorb at the UV excitation wavelength used and, therefore, should simultaneously undergo ring-closing and ringopening reactions. Under our illumination conditions in toluene- d_8 , better photocyclization conversions were observed for DTE^{0} -COCF₃ (91% at $\lambda_{exc} = 365$ nm) and DTE^{0} -C₆F₅ (81% at $\lambda_{\text{exc}} = 312 \text{ nm}$) relative to **DTE^o-Ph** (39% at $\lambda_{\text{exc}} = 312 \text{ nm}$) (Table 1). This can be ascribed to the lower ring-closing quantum yield and high photodegradation tendency of **DTE-Ph**, which

limited the UV exposure time for photocyclization and led to a lower percentage of closed isomer.

	λ_{abs}^{o} [nm]	λ_{abs}^{c} [nm]	PSS _{o-c} composition	$\Phi_{ ext{o-c}}{}^d$	Φ_{c-o}^{e}
	$(\varepsilon [M^{-1} cm^{-1}])^a$	$(\varepsilon [M^{-1} cm^{-1}])^{\nu}$	[%] ^c		
DTE-COCF ₃	268 (35 673), 339 (6 431)	598 (12 261)	91:9	0.480	0.012
[PdCl ₂ (DTE-COCF ₃) ₂]	271 (34 149),	604 (18 870)	45:45:10	0.148/	0.013/
	355 (19 065)			0.048	0.014
DTE-C ₆ F ₅	272 (28 303)	519 (11 379)	81:19	0.530	0.015
$[PdCl_2(DTE-C_6F_5)_2]$	268 (40 394),	532 (19 391)	25:45:30	0.047/	0.015/
	357 (14 367)			0.019	0.018
DTE-Ph	273 (28 117)	518 (13 673)	39:61	0.485	0.011
$[PdCl_2(\mathbf{DTE-Ph})_2]$	270 (42 700),	538 (16 310)	27:44:29	0.060/	0.015/
	359 (15 400)			0.023	0.014

Table 1. Photochemical properties of DTE-based ligands and complexes.

^{*a*} Wavelength and molar absorptivity coefficient of the absorption band maxima of the open isomer (for complexes, **oo** state) in cyclohexane. ^{*b*} Wavelength and molar absorptivity coefficient of the maximum of the visible absorption band of the closed isomer (for complexes, **cc** state) in cyclohexane. ^{*c*} Composition of the PSS reached for the photocyclization process in toluene-*d*₈ upon irradiation at $\lambda_{exc} = 365$ nm (**DTE-COCF**₃ and all the complexes) or 312 nm (**DTE-C**₆**F**₅ and **DTE-Ph**). DTE^{*c*}:DTE^{*o*} and DTE^{*cc*}:DTE^{*oc*}:DTE^{*oo*} concentration ratios are given for free ligands and complexes, respectively. ^{*d*} Photocyclization quantum yields measured in cyclohexane at $\lambda_{exc} = 355$ nm (**DTE-COCF**₃ and all the complexes) or 312 nm (**DTE-C**₆**F**₅ and **DTE-Ph**). For the complexes, separate Φ_{o-c} values are given for the **oo** \rightarrow **oc** and **oc** \rightarrow **cc** ring-closing processes. ^{*e*} Photocycloreversion quantum yields measured in cyclohexane at $\lambda_{exc} = 532$ nm. For the complexes, separate Φ_{c-o} values are given for the **cc** \rightarrow **oc** and **oc** \rightarrow **oo** ring-opening processes.

Similar to free DTE ligands, irradiation of the Pd^{II} complexes in cyclohexane with UV light also caused the appearance of an absorption band in the visible part of the spectrum and a

concomitant color change (Figure 2b, Table 1 and Figure S5). In combination with NMR spectroscopic measurements in toluene- d_8 and TD-DFT calculations, it was demonstrated that DTE photocyclization takes place in the complexes, in contrast to some previously reported DTE-based phosphine-metal compounds.^{39,46} However, palladium(II) complexation did have a relevant effect on the UV-induced ring-closing process of the phosphine ligands. First, we could use less energetic UV radiation to promote the photocyclization of [PdCl₂(DTE^o-C₆F₅)₂] and $[PdCl_2(DTE^{\circ}-Ph)_2]$ ($\lambda_{exc} = 365 \text{ nm}$) compared to $DTE^{\circ}-C_6F_5$ and $DTE^{\circ}-Ph$ ($\lambda_{exc} = 312 \text{ nm}$). Second, a bathochromic shift of the absorption band of the closed isomer in the visible range was registered relative to the free ligands ($\lambda_{abs} = 604$, 532 and 538 nm for [PdCl₂(**DTE^c-COCF₃**)₂], $[PdCl_2(DTE^{c}-C_6F_5)_2]$ and $[PdCl_2(DTE^{c}-Ph)_2]$ (Figure 2a-b, Table 1 and Figures S26-S28). According to TD-DFT calculations, this effect is due to the decrease of the HOMO-LUMO gap of DTE-based phosphines upon Pd^{II} complexation, which should be especially important for **DTE-C**₆ F_5 and **DTE-Ph**, as experimentally observed (Table S2). On the other hand, the spectral features of the closed DTE absorption band were not influenced by the state of the nearby DTE ligand in the same complex (open or closed) - i.e., it did not evolve when photoconverting from the oc species with one open and one closed DTE unit to the fully closed cc complex, which was substantiated by TD-DFT calculations (Figures S26-S28). As a result, these two different photocyclization products could only be discriminated by NMR spectroscopic experiments, which proved that they were sequentially formed upon UV irradiation and allowed determining the composition of the equilibrium PSS generated in toluene- d_8 (Table 1 and Figures S14-S22). From this analysis we could conclude that metal complexation detrimentally affected the photocyclization conversion of DTE°-COCF₃ and DTE°-C₆F₅, as only 66% and 48% of the DTE units in $[PdCl_2(DTE^\circ-COCF_3)_2]$ and $[PdCl_2(DTE^\circ-C_6F_5)_2]$ could be ring-cycled. This

result is consistent with the lower photocyclization quantum yields (Φ_{o-c}) measured for both the **oo** and **oc** states of the complexes relative to the free ligands (Table 1), which can be attributed to two main effects: (i) the competition between photoisomerization and ligand-to-metal charge transfer, which, as previously mentioned, gives rise to additional absorption bands in the UV region of the complexes at which they are excited to promote photocyclization; and (ii) the further reduction of Φ_{o-c} for the second ring-closing step in the complexes, a behavior already reported for other DTE dimers,⁴⁷ which can be ascribed to intramolecular energy transfer between the open and closed DTE units in the **oc** state upon photoexcitation - i.e., the photocyclization of one of these units severely hinders the ring-closing reaction for the second DTE group.

Once photocyclized with UV light, the closed states of the DTE-based ligands and their palladium(II) complexes were found to be thermally stable in solution and no spontaneous backisomerization was detected in the dark at room temperature. Accordingly, visible irradiation $(\lambda_{exc} = 520 \text{ nm})$ was applied to promote photoinduced ring-opening of these compounds and to demonstrate the reversibility of their photoswitching behavior in solution. For all of them, complete disappearance of the visible absorption band associated with the closed isomer was registered, which demonstrates quantitative photochemical cycloreversion regardless of metal complexation (Figure 2a-b and Figures S5, S14, S17-S19 and S21). This is due to the selective photoexcitation of closed-state DTEs with visible light that counterbalances their commonly low ring-opening quantum yields,²⁵ as we also measured herein for the ligands and the **cc** and **oc** states of the complexes ($\Phi_{c-0} < 0.02$, Table 1). In spite of this, some residual visible absorption was registered for some of these compounds upon light-induced photocyclization reversion (**DTE-C**₆**F**₅ in Figure 2a; **DTE-Ph** and [PdCl₂(**DTE-Ph**)₂] in Figure S5), which could not be attributed to unreacted closed state species. Instead, it arose from DTE photodegradation, which is normally associated with the UV irradiation of the closed isomer during photocyclization and leads to a characteristic product that absorbs at $\lambda_{abs} \approx 500$ nm.⁴⁸ This effect was further proven by an examination of the fatigue resistance of ligands and complexes upon repetitive photoinduced ring-closing and ring-opening cycles in cyclohexane (Figure 2a-b and Figure S5). Although some deterioration of their photoswitching behavior was eventually observed for all these compounds, the highest photodegradation effects were registered for **DTE-Ph**, **DTE-C**₆**F**₅ and [PdCl₂(**DTE-Ph**)₂]. We ascribe these results to two main factors that increase the photostability of the remaining ligands and complexes: (i) the presence of the strong trifluoroacetyl EWG at the external position of the thiophene ring which is known to slow down DTE photodegradation;⁴⁸ and (ii) the use of less energetic UV light to photoisomerize the palladium(II) complexes relative to the free ligands. Consequently, the target compounds [PdCl₂(**DTE-CoCF**₃)₂] and [PdCl₂(**DTE-C**₆**F**₅)₂] showed the highest resistance to photodegradation.

Photomodulation of the properties of the phosphine ligands

As anticipated by molecular design and demonstrated by ³¹P (proton-coupled and decoupled) NMR spectroscopic measurements discussed above, the phosphanyl and electron-modulating groups of the synthesized DTE-based ligands are electronically decoupled in their open state. As a result, these ligands should present similar binding properties to metals, a behavior that we aimed to modulate upon photoisomerization. In fact, UV-induced ligand ring-closing caused a measurable downfield shift of the ³¹P and ³¹P{¹H} NMR signal of these compounds ($\Delta \delta = 9.4$, 8.2 and 8.3 ppm for **DTE-COCF₃**, **DTE-C₆F₅** and **DTE-Ph**, respectively), thus suggesting a change in the electronic properties of their phosphine groups that might be dependent on the nature of the external substituent present in the other thiophene of the DTE core. In particular, introduction of electron-withdrawing substituents such as trifluoroacetyl and pentafluorophenyl to phosphines is expected to: (i) increase the *s* character of the lone pair of electrons at the phosphorus atom involved in σ bonding to metals, while (ii) stabilizing and enlarging the size of the phosphine's σ^* antibonding orbital participating in metal π backbonding.

A well-established method to assess such an effect for phosphines is to measure the spin-spin coupling constant between ${}^{31}P$ and ${}^{77}Se$ (${}^{1}J_{P,Se}$) for the corresponding selenide derivatives (Scheme 4),^{39,41} which were prepared by heating the ligands and grey selenium in CDCl₃. In these compounds, ${}^{1}J_{P,Se}$ values depend on the s character of the P=Se bond, which is related to the electronic character and size of the substituents on the phosphorus atom.^{49–51} Consequently, they provide an estimate on the σ -donating ability of phosphines, which is lower for higher values of ${}^{1}J_{P,Se}$. For the open state selenides of DTE-COCF₃, DTE-C₆F₅ and DTE-Ph, measured ${}^{1}J_{P.Se}$ values are almost identical and match the reported coupling constant for the selenide of (2-methyl-5-thienyl)diphenylphosphine $({}^{1}J_{P,Se} = 733 \text{ Hz})^{40}$ (Scheme 3). Again, this result corroborates that the two thiophenes in DTE structures are electronically isolated and, for that reason, their phosphanyl groups have similar electronic properties. In contrast, as ringclosing extends the conjugation throughout the DTE moiety, the electron density on the phosphorus atom should decrease and can be affected by the external substituent in the other thiophene ring with which it communicates. This behavior was indeed proven by NMR measurements of the closed selenide isomers: higher ${}^{1}J_{P,Se}$ values were detected relative to the open isomers with increments ($\Delta^{c-o}({}^{1}J_{P,Se})$) that scaled up with the electron-withdrawing nature of the electron-modulating substituents (Scheme 3, Table 2) - i.e., the studied phosphines became electron-poorer upon photocyclization and introduction of a stronger EWG in the opposite

thiophene ring. Thus, the highest value of $\Delta^{c-o}({}^{1}J_{P,Se})$ was registered for the selenide of **DTE-COCF3** ($\Delta^{c-o}({}^{1}J_{P,Se}) = 14$ Hz), which equals the best results reported for the DTE-based phosphine ligands^{39,41} and mimics the electronic effects caused by substituting one phenyl ring in triphenylphosphine for a *tert*-butyl group.

Scheme 4. Variation of ${}^{1}J_{P,Se}$ in the open and closed isomers of the selenides of DTE-COCF₃, DTE-C₆F₅ and DTE-Ph.



To further investigate the photomodulation of the electronic features for the prepared DTEbased phosphines, we analyzed a set of properties derived from the DFT calculations of their ground state structures. As a first step, we considered the variation of the Mulliken charges on the phosphorus atom ($\Delta^{c-o}(q_p^{Mulliken})$) and the percentage of *s* character of the lone pair of electrons at phosphorus ($\Delta^{c-o}(\% s_p)$) for open anti-parallel and closed conformations of **DTE-COCF3**, **DTE-C6F5** and **DTE-Ph** (Table 2). According to the Mulliken charges, photocyclization decreases electron density on phosphorus, while through NBO analysis⁵² we can anticipate an increase in *s* orbital participation in the phosphorus lone pair of electrons. More importantly, the variation of these parameters was found to increase with the electronwithdrawing power of the introduced electron-modulating group, thus again validating that $DTE-COCF_3$ and, to a lesser extent, $DTE-C_6F_5$ suffer the largest change in phosphine's electronic properties upon photoisomerization.

As a second step, the effect of the light-induced modulation of the DTE-based phosphine ligands on the bond energy in their Pd^{II} complexes was investigated computationally. For this, we analyzed the difference in phosphine-Pd^{II} binding energy ($\Delta^{c-o}(BE_{P-Pd})$) between the **oo** and **cc** isomers of their 2:1 *trans*-phosphine palladium(II) complexes (Table 2). As expected, due to the loss of the phosphine's σ -donating ability, a varying decrease in BE_{P-Pd} for the complexes bearing ring-closed DTE ligands is observed, depending on the nature of the introduced electronmodulating group. Thus, weakening of the phosphine-palladium(II) binding upon photocyclization was observed for the ligands bearing the electron-withdrawing pentafluorophenyl and, especially, trifluoroacetyl substituents, as we initially devised.

Table 2. Experimental and computed parameters to estimate the photomodulation of the properties of the phosphine ligands DTE-COCF₃, DTE-C₆F₅ and DTE-Ph.

		Pd ^{II} complexes ^{<i>a</i>}		
	$\Delta^{\text{c-o}}(^{l}J_{\text{P,Se}}) [\text{Hz}]^{b}$	$\Delta^{\text{c-o}}(q_{\text{P}}^{\text{Mulliken}})^{c,d}$	$\Delta^{c-o}(\%s_{\rm P})^{c,e}$	$\Delta^{c\text{-}o}(\mathrm{BE}_{\mathrm{P}\text{-}\mathrm{Pd}}) [\mathrm{kcal} \cdot \mathrm{mol}^{-1}]^{c,f}$
DTE-COCF ₃	14	0.014	0.79	-1.98
DTE-C ₆ F ₅	7	0.004	0.42	-0.92
DTE-Ph	5	< 0.001	0.34	-0.64

^{*a*} trans-[PdCl₂(**DTE-COCF**₃)₂], trans-[PdCl₂(**DTE-C**₆**F**₅)₂] and trans-[PdCl₂(**DTE-Ph**)₂]. ^{*b*} Difference in ¹J_{P,Se} for the corresponding selenides measured in CDCl₃. ^{*c*} Computed at the B3LYP-D3 level in THF (see Experimental Section for further details). ^{*d*} Difference in Mulliken charges in electronic units on the phosphorus atom. ^{*d*} Difference in percentage of *s* character of the phosphorus lone pair of electrons. ^{*f*} Difference in phosphine-Pd^{II} bond energy (per one bond) between the **oo** and **cc** isomers.

Catalytic studies

Among the vast range of Pd-catalyzed reactions, Stille coupling was chosen to evaluate the activity of the open and closed state of the prepared metal complexes. For this reaction, previous mechanistic studies have established that bulky phosphines accelerate the rate of the oxidative addition while electron-poor phosphines are advantageous for the transmetallation step.^{36,53,54,55} This makes Stille coupling a suitable benchmark process to validate our model towards photoswitchable catalysis, as we have proven above that the electron density on the DTE-based phosphines developed herein can be modulated upon photoisomerization. With this aim, the palladium(II) complexes were tested as pre-catalysts for the Stille reaction between iodobenzene and tributylvinyltin in THF- d_8 at two different temperatures (room temperature and 50 °C) (Table 3). In all the cases, catalytic experiments were conducted in the dark and separately for the pure oo complexes and for cc-enriched mixtures of isomers. Because of the moderate efficiency of **oo**-to-**cc** photocyclization in the complexes (see Table 1), we maximized the relative amount of cc species in such mixtures by first ring-closing the corresponding free ligand and then conducting metal complexation (see the Supporting Information for further details). In this way, cc-enriched pre-catalyst mixtures contained 52, 38 and 49% of the cc isomers for [PdCl₂(**DTE-COCF**₃)₂], [PdCl₂(**DTE-C**₆**F**₅)₂] and [PdCl₂(**DTE-Ph**)₂], respectively (Figures S29-S31). To compare the catalytic efficiency of these mixtures with those of their **oo** samples, we monitored the kinetics of the Stille reaction for 6 h and measured the difference in product formation after this time (entries 1-6 and 8-13 in Table 3; Figure S32). In addition, equivalent measurements were performed using [PdCl₂(PPh₃)₂] (entries 7 and 14 in Table 3) as a non-light responsive reference pre-catalyst, which in most of the cases turned out to be less efficient than our DTE-based complexes.

	+ 1.0 equiv	Si 1.1 e	nBu 1 nBu - nBu equiv	I.5 mol% [Pd] THF (1 ml) rt or reflux			
Entry	Pre-catalyst [Pd]	State ^{<i>a</i>}	T (°C)	Yield $(\%)^b$	Entry	T (°C)	Yield $(\%)^b$
1	[PdCl ₂ (DTE-COCF ₃) ₂]	00	25	4.5	8	50	36.4
2		сс		8.8	9		48.9
3	$[PdCl_2(\mathbf{DTE-C_6F_5})_2]$	00		21.2	10		42.5
4		сс		29.5	11		59.6
5	$[PdCl_2(\mathbf{DTE-Ph})_2]$	00		13.4	12		53.8
6		сс		14.2	13		43.4
7	[PdCl ₂ (PPh ₃) ₂]			9.8	14		28.0

 Table 3. Comparison of the investigated complexes as pre-catalysts in the Stille coupling reaction.

^a **cc** state here is a closed state enriched pre-catalyst complex as specified above. ^b The average yields of two repetitions were determined by ¹H NMR spectroscopy using 1,3,5,- trimethoxybenzene as a standard.

As shown in Table 3, two different behaviors were observed in the catalytic tests. For complexes bearing DTE units with external electron-withdrawing substituents, large increments in yields for the Stille coupling at 6 h were registered for the **cc**-enriched mixtures compared to the **oo** complexes: 94% (relative increment from entry 1 to entry 2) and 34% (relative increment from entry 8 to entry 9) for [PdCl₂(**DTE-COCF**₃)₂] at room temperature and 50 °C, respectively; and ~ 40% for [PdCl₂(**DTE-C**₆**F**₅)₂] (relative increments from entries 3 to 4 and 10 to 11) both at room temperature and 50 °C. By contrast, DTE photocyclization did not enhance the Stille

coupling efficiency for $[PdCl_2(DTE-Ph)_2]$ which is lacking the electron-withdrawing substituent on the DTE core. In this case, similar reaction conversions were measured for the **oo** complex and **cc**-enriched mixture at room temperature (entries 5 and 6), while we observed a decrease in reactivity upon ring-closing at 50 °C (entries 12 and 13). Importantly, these results are in agreement with the prediction made to accomplish photoswitchable catalysis by installing external EWGs in DTE-based phosphines. Upon photocyclization, the electron-withdrawing and phosphanyl substituents become selectively conjugated in these compounds, thus varying the electronic properties of the phosphine ligand and affecting the catalytic behavior of its metal complexes. Unfortunately, the catalytic modulation accomplished in this way is limited by the non-quantitative nature of DTE photocyclization, which prevented us from conducting experiments with pure **cc** pre-catalysts.

To rationalize the modulation of Stille coupling reactivity determined for the open and closed states of $[PdCl_2(DTE-COCF_3)_2]$ and $[PdCl_2(DTE-C_6F_5)_2]$, we conducted additional DFT calculations. For this, we considered the Stille reaction mechanism,^{36,56} which requires previous reduction of the palladium(II) pre-catalyst used to palladium(0) before the catalytic cycle begins. Similar to other palladium-catalyzed couplings, the catalytic cycle consists of three major steps: oxidative addition, transmetallation and reductive elimination,⁵⁷ among which the first two are typically the rate-determining steps when aryl halides are used as substrates (Figure 3).^{35,58}. Over the years, various pathways have been proposed for each of these steps. On the one hand, the oxidative addition of the organic electrophile to Pd⁰ can occur through a monophosphine pathway, an associative displacement pathway, and a bisphosphine pathway.^{59,60} Principally, the presence of bulky ligands should favor oxidative addition via a monoligated transition state owing to steric repulsion.⁶¹ Nevertheless, it was recently established that intramolecular

dispersion forces can serve to stabilize a bisligated transition state for bulky ligands such as $PtBu_3$,⁶² thus demonstrating the importance of incorporating dispersion effects into the analysis. Accordingly, we explored both types of pathways in our computations. As for the transmetallation step, it can also proceed through three different mechanisms: cyclic, open and ionic.⁵⁸ In our calculations we only considered the first of these cases, as halides are considered to be good bridging ligands that facilitate the formation of cyclic transitions states; in contrast, open and ionic mechanisms are preferred in the case of poorly coordinating anionic ligands and highly polar solvents. Finally, the reductive elimination step can also proceed through bisligated and monoligated transition states.⁵⁸ For simplicity, herein we only explored the second of these options and did not compute the bisligated pathway.



Figure 3. General catalytic cycle for the palladium-catalyzed Stille coupling reaction.

Based on these mechanistic assumptions, we computed the catalytic cycle of the Stille coupling reaction investigated experimentally. Calculations were carried out for complexes formed with the ligand DTE-COCF₃, as it should impart the strongest electronic effects upon

photoisomerization. Three possible states of the DTE-COCF₃-based Pd⁰ catalyst were considered in these calculations: [Pd(DTE°-COCF₃)₂], [Pd(DTE°-COCF₃)(DTE^c-COCF₃)], and [Pd(DTE^c-COCF₃)₂] (Figure 4, Figures S33-S35 and Table S6). Reaction intermediates and transition states were computed at the B3LYP-D3 level of theory (see Experimental Section for additional details). The Gibbs free energies of the species at 298 K are presented relative to the zero point consisting of the corresponding bisligated palladium(0) complex (0, Figure 4), phenyl iodide and tributylvinyltin. For the oxidative addition step, the monophosphine pathway was found to be disfavored, as phosphine ligand dissociation was computed to have a high energy requirement (> 20 kcal/mol, Figures S34-S35). It is worth noting, however, that the energy barrier for the dissociation of the closed-state ligand from the cc (23.1 kcal/mol) and oc (26.8 kcal/mol) species is lower than for the dissociation of the open ligand from the oo (25.8 kcal/mol) and oc (27.3 kcal/mol) states of the catalyst, thus corroborating our predictions on the effect of the DTE-COCF₃ isomerization state on the stability of the phosphine-palladium bond. The bisphosphine oxidative addition pathway was found to be preferred as it proceeds through the less energetic three-center transition state TS1, which is accessed through previous intermediate 1 (Figure 4). Among the transition states TS1 computed for three different catalytic systems, the lowest energy values are associated with the cc and oc states, at 7.4 and 7.8 kcal/mol, respectively, while the **oo** isomer requires 10.6 kcal/mol. As the transition state for the oxidative addition of the bisligated complex leads to the formation of the fully coordinated ciscoordinated Pd^{II} species 2, ligand dissociation is a prerequisite for subsequent steps, which was found to be slightly less energy demanding for the cc system (13.2 kcal/mol for cc species vs 14.4 kcal/mol for **oo** species). Then, formed intermediate **3** isomerizes through the transition state TS3 (energy barrier $\approx 2.8-4.7$ kcal/mol), and upon tin coordination, transmetallation takes

place with the highest energy barrier among all the steps. In particular, the energy barrier for the cyclic transition state **TS5** involving the closed-state Pd^0 species is 13.5 kcal/mol, which is lower than for the open-state catalytic system (15.4 kcal/mol). Lastly, reductive elimination of the intermediate **6** was observed to take place through the transition state **TS7**, with an energy barrier difference of only 0.3 kcal/mol between the closed- and open-state isomers. In conclusion, our computational analysis revealed that the barriers for the most energy-demanding steps of the investigated Stille coupling reaction – i.e., oxidative addition, ligand dissociation and transmetallation – are lower for the catalytic palladium species bearing closed-state **DTE-COCF3** ligands. This is in agreement with our experimental results, which showed higher catalytic activity for the **cc**-enriched state of the [PdCl₂(**DTE-COCF3**)₂] pre-catalyst. Nevertheless, the differences in energy barriers computed for the open- and closed-state isomers of the system along the catalytic cycle are moderate (\approx 1-3 kcal/mol), which in combination with incomplete DTE photocyclization should account for the limited modulation of reactivity accomplished in our experiments.



Figure 4. Calculated Gibbs energy profile for the Stille coupling reaction in solution (THF) using $[PdCl_2(DTE^{\circ}-COCF_3)_2]$ or $[PdCl_2(DTE^{\circ}-COCF_3)_2]$ as a pre-catalyst, where L^x is $DTE^{\circ}-COCF_3$ (black line) or $DTE^{\circ}-COCF_3$ (blue line).

Conclusions

Dithienylethenes were used to prepare the photoisomerizable phosphine ligands DTE-COCF₃ and DTE-C₆F₅, where the electronic communication between the phosphorus atom and electronwithdrawing groups is switched on and off by reversible open- to closed-state conversion. As a result, the σ -donating ability of these phosphines can be efficiently modulated upon light irradiation, in agreement with DFT calculations, improving the behavior observed for the analogous DTE-Ph ligand bearing an EWG-free dithienylethene moiety. Interestingly, when coordinated to palladium(II), the resulting bisphosphine complexes preserve ligand's capacity to undergo ring-cyclization under illumination, albeit resulting in incomplete phototransformation into their dual closed-state isomer. Finally, when testing the synthesized complexes as precatalysts in the Stille coupling reaction between phenyl iodide and tributylvinyltin, a clear modulation in reaction rate was observed upon photoisomerization of the compounds bearing DTE-COCF₃ and DTE-C₆F₅ ligands. In particular, the catalytic activity of the complexes increased for the closed state of these ligands, which could be rationalized by DFT calculations. Therefore, these results validate our molecular design towards photoswitchable catalysis, which can be extended to other metals and reactions in future.

EXPERIMENTAL SECTION

Synthesis

A detailed description of the synthesis of ligands and complexes is given in the Supporting Information.

Single crystal X-ray diffraction analysis

The data were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-K α radiation and ω -scan rotation. Data reduction was performed with CrysAlisPro⁶³ including the program SCALE3 ABSPACK for an empirical absorption correction. As a result of the extremely thin crystal, for [PdCl₂(**DTE⁰-C**₆**F**₅)₂] a numerical absorption correction was applied as well using a multifaceted crystal model based on expressions derived by R.C. Clark and J.S. Reid.⁶⁴ All structures were solved by dual space methods with SHELXT⁶⁵ and the refinement was performed with SHELXL⁶⁵. Hydrogen atoms were calculated on idealized positions using the riding model. Structure figures were generated with DIAMOND-4⁶⁶ and Mercury (version 2022.2.0).⁶⁷

CCDC deposition numbers given in Table S1 contain the supplementary crystallographic data for this These data be obtained free of charge via paper. can https://summary.ccdc.cam.ac.uk/structure-summary-form from the Cambridge (or Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Photochemical characterization

Photoswitching was monitored by UV-vis and NMR spectroscopy. The photostationary state PSS^{oc} composition was determined through ³¹P or ¹⁹F NMR spectroscopy from a PSS^{oc} state produced by irradiating a toluene- d_8 solution in an NMR tube with the appropriate wavelength. Spectra of the closed state isomers shown in Figures S23-S28 were estimated from the PSS^{oc} and open state UV-vis spectra. Photoisomerization quantum yields were determined by monitoring the variation of the UV-vis absorption spectra of ligands and complexes in cyclohexane upon irradiation with UV (for photocyclization, $\lambda_{exc} = 312$ or 355 nm) or visible light (for

photocycloreversion, $\lambda_{exc} = 532$ nm). In the case of the free ligands bearing one DTE unit, spectral data was fitted to a simple kinetic model previously reported.⁶⁸ For the complexes containing two DTE groups, a more complex kinetic model had to be used to separately determine the photoisomerization quantum yields of their **oo**, **oc** and **cc** isomers.⁶⁹ To apply this model, we assumed the UV-vis absorption spectrum of each DTE unit in the complexes to be independent of the isomerization state of the other - i.e., the extinction coefficients of open DTE units are the same in the **oo** and **oc** states, while those of closed DTE groups are equal in the **oc** and **cc** states, as suggested by carried out TD-DFT calculations and observed in previous works on DTE dimers.⁷⁰ In all the cases, the irradiation intensities used in our photoisomerization and photocycloreversion processes of 1,2-bis(2-methyl-5-trifluoroacetylthien-3-yl)cyclopentene in toluene as a reference ($\Phi^{oc} = 0.37$ and $\Phi^{co} = 0.031$).³³

Computational details

DFT calculations were carried out using the Gaussian16 program package.⁷¹ Geometry optimizations were conducted without any constraints using the B3LYP functional⁷²⁻⁷⁴ with Grimme's D3 correction to account for dispersion effects.⁷⁵ Optimizations were performed in THF using the solvation model density (SMD) continuum model⁷⁶ with basis set 1 (BS1). BS1 included the 6-31G(d,p) basis set for the main group atoms^{77,78} (H, C, O, F, P, S) and the Stuttgart-Dresden SDD effective core potential (ECP) and its corresponding double- ζ basis set,⁷⁹ with a set of *d* polarization functions⁸⁰ for I and Sn and *f* polarization functions⁸¹ for Pd. Frequency calculations were performed for all the optimized geometries to determine the stationary points as either minima or transition states. Energies in THF were refined through single-point calculations of the optimized BS1 geometries with an extended basis set (BS2). BS2

consisted of the def2-TZVP for main group atoms, and the quadruple-ζ def2-QZVP basis set for Pd, together with the def2 ECP.⁸² Gibbs energies in THF were calculated by adding thermal and entropic correction from BS1 to the BS2 energies in THF. An additional correction of 1.9 kcal/mol was applied to all the Gibbs energies to change the standard state from the gas phase (1 atm) to the condensed phase (1 M) at 298.15 K.⁸³ Frontier molecular orbitals and natural bond orbital (NBO)⁸⁴ analysis were calculated at the B3LYP-D3/BS1 level in THF using the SMD continuum model. TD-DFT calculations were carried out using the CAM-B3LYP functional⁸⁵ with Grimme's D3 correction to account for dispersion effects.⁷⁵ The first 15 electronic transitions were calculated in cyclohexane using the SMD continuum model with the BS1 described above.

General procedure for catalytic studies

In an NMR tube, 0.033 mL iodobenzene (0.30 mmol, 1.0 eq.), 0.097 mL tributylvinyltin (0.33 mmol, 1.1 eq.), 5 mol % [Pd] catalyst and 0.05 g (0.03 mmol, 0.1 eq.) 1,3,5-trimethoxybenzene were dissolved in 1 mL dry, degassed THF- d_8 . The reactions were carried out in the dark and monitored every 2 hours by ¹H, ³¹P{¹H} and, when applicable, ¹⁹F NMR spectroscopy. The reaction yields are an average of two replicates.

ASSOCIATED CONTENT

The following files are available free of charge.

Synthetic procedures, additional experimental details, photochemical and catalytic studies, additional theoretical data and NMR spectra (PDF).

CCDC deposition numbers 2310549 – 2310551 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via

https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

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Author Contributions

A. S. – performed the experimental work, DFT calculations, data analysis and prepared the original draft; J. H. – performed data analysis, supervised the project and prepared the original draft; P. L. – performed single crystal X-ray analysis and interpreted the structural data; A. L. – supervised computational studies and revised the draft; R.M.S, E.H.-H. – supervised the project, revised the draft and acquired funding. All authors have read and approved the final version.

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SYNOPSIS

Two photoisomerizable phosphine ligands were synthesized based on dithienylethenes, whose electronic communication with strong electron-withdrawing groups is switched on and off upon light irradiation. As a result, the σ -donating ability of these phosphines can be efficiently light-controlled. This behavior was transferred to palladium(II) catalytic complexes and exploited to photomodulate the reaction rate of a model Stille reaction.

ToC GRAPHICS

