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A Selvaraj, Marie Cordier, Marc Devillard, Gilles Alcaraz. Synthesis of Photochromic Phosphines by Pd-Catalyzed Annulation Reaction of Alkynes bearing Phosphinyl Substituent with a Silacyclopropene. Chemistry - A European Journal, In press, 10.1002/chem.202302374 . hal-04196552

HAL Id: hal-04196552

<https://hal.science/hal-04196552>

Submitted on 20 Sep 2023

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RESEARCH ARTICLE

Synthesis of Photochromic Phosphines by Pd-Catalyzed Annulation Reaction of Alkynes bearing Phosphinyl Substituent with a Silacyclopropene

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Dedicated to Prof. Hansjörg Grützmacher in appreciation of his many years contribution to phosphorus chemistry and its deeper understanding.

Abstract: The synthesis of phosphines with light controlled basicity is presented in this study. A methodological approach for the preparation of these unconventional photochromic phosphines based on a dithienylethene organic moiety is reported. It relies on the palladium-catalyzed annulation of **alkynyl phosphines** in the presence of a **2,3-Dithienylsilacyclopropene**. Accordingly, a diphenylphosphino moiety is connected to the organic photochrome thanks to different linkers. Their influence on the photochromism and on the phosphinyl group basicity is studied and evaluated based on experimental an NMR descriptor as well as DFT calculations.

Introduction

Phosphines constitute a central class of molecules for coordination chemistry and catalysis. As ligands^{[1]–[4]} or as organocatalysts,^{[5]–[7]} the chemical modification of phosphines remains a very active area of research and their use is the subject of constant progress fueled by the most recent advances in synthetic methodology.^{[8]–[12]} While this strategy is well known and widely studied, controlling stereoelectronic properties remotely and reversibly remains a real challenge. Although light control of the properties of various molecular systems is particularly appealing,^{[13]–[16]} relatively little work has been done in the field of phosphines.^[17] They mainly concentrate on photoswitchable phosphines derived of azobenzenes,^{[18]–[25]} dithienylethenes (DTE)^{[26]–[28]} and 1,1'-biindanes.^{[29]–[31]} Their preparation generally involves a two-step sequence starting with halogen-lithium exchange from suitable aryl- or thienylhalides, followed by a trapping of the organolithium with a chlorophosphine. More suitable catalytic approaches for their synthesis are so far strictly limited to well-established phosphination of iodoarenes with diphenylphosphine. In the case of DTEs, which are among the most widely studied photochromic systems, the examples reported have mainly focused on the introduction of phosphorus into the thienyl groups. Only one case of phosphino-functionalized DTE, other than on thienyl groups, has been described to date starting from 1,2-bis(2,5-dimethyl-3-thienyl)acetylene that is involved in a zirconium/copper transmetalation process.^[32] The lack of alternative syntheses for efficiently accessing new phosphino-functionalized DTE models limits their study and hampers their further development.

In this setting, we have recently described and studied in-depth an effective methodological approach to photochromic siloles with a dithienylethene (DTE) backbone.^{[33][34]} The synthesis relies on a palladium-catalyzed annulation reaction of alkynes in the presence of a 2,3-dithienylsilacyclopropene **1** (Figure 1, A). With high yields and tolerance to a variety of functional groups such as ketones, aldehydes, alcohols, amines and amides, this reaction should provide an interesting synthetic tool for new models of photochromic phosphines.

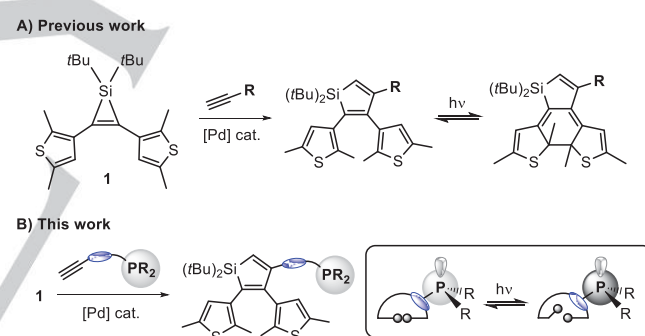


Figure 1. A) Synthesis of photochromic siloles by Pd-catalyzed annulation reaction of terminal alkynes in presence of a silirene; B) Transposition of the strategy to the synthesis of photochromic phosphines using **alkynyl phosphines**.

As part of our program on the silacyclopropenes chemistry, we have shown here that a series of DTE with phosphino-functionalized silole ring could be efficiently produced from silirene **1** and alkynes bearing a phosphinyl substituent (**alkynyl phosphines**). Photocontrol of phosphine basicity (Figure 1, B) is evaluated within this series of unconventional phosphines and discussed as a function of the spacer between the phosphorus and the silole core. Finally, the experimental results are compared with those of the theoretical study carried out in parallel on the basis of the phosphine X-ray structures obtained in order to draw general trends in the behavior of these unconventional phosphines.

Results and Discussion

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In a first attempt, we targeted a photochromic phosphino-functionalized silole incorporating a methylene spacer between the phosphinyl group and the silole heterocycle. The protected (propargyl)diphenylphosphine substrate was prepared in two steps as the corresponding phosphine-borane adduct^{[35][36]} and further engaged in the Pd-catalyzed reaction under optimized conditions (Figure 2). The ³¹P NMR monitoring of the reaction showed the gradual consumption of the starting material at δ 19.4 and the clean appearance of a new broad resonance signal at δ 17.8. In ¹H NMR, a set of four singlet resonance signals for the thienyl methyl groups indicating the lower symmetry of the product **2-BH₃** regarding the starting material **1**.

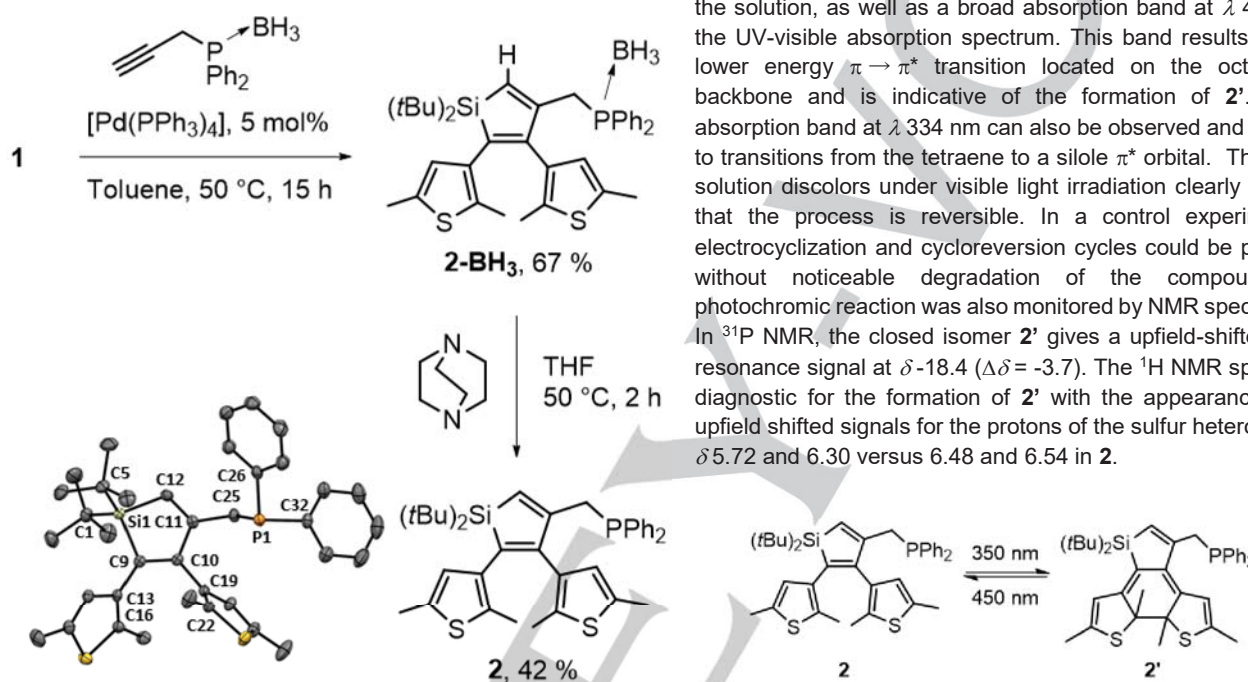


Figure 2. Two-step synthesis of **2** from silirene **1** in the presence of propargylphosphine-borane under palladium catalysis and subsequent deprotection in the presence of DABCO. Solid-state structure (150 K) of **2** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C25 1.8663(16), P1-C26 1.8381(17), P1-C32 1.8402(17), Si-C1 1.9010(17), Si-C5 1.9170(18), Si1-C9 1.8953(16), Si1-C12 1.8532(17), C9-C10 1.361(2), C10-C11 1.513(2), C11-C12 1.344(2), C11-C25 1.508(2); C10C11C25 120.27(14), C11C25P1 114.94(11), C26P1C25 102.99(8), C32P1C25 96.81(7), C26P1C32 101.47(8); C9C10C19C22 61.4(2), C10C9C13C16 52.0(2), C10C11C25P1 63.04(17), C26P1C25C11 89.17(13).

After completion of the reaction, **2-BH₃** was purified by column chromatography on silica gel and obtained as a white powder in 67% isolated yield. The structure of **2-BH₃** was supported by multinuclear NMR spectroscopy, by HR-MS (ESI) analysis that afforded the expected m/z for [**2-BH₃**]⁺ and was finally ascertained by X-ray diffraction analysis of single crystals grown at -30 °C (See S38 for details). Reaction of **2-BH₃** with 1,4-diazabicyclo[2.2.2]octane (DABCO) in THF led to the clean deprotection of the phosphine and the formation of unprotected **2** that could be purified by crystallization in 42% yield. Single crystals of **2** were obtained and studied by X-ray diffraction analysis (Figure 2). In the solid state, the thienyl groups are twisted with respect to the plane defined by the silole ring by 53.3 ° (left) and 59.2 ° (right) and positioned in an antiparallel conformation.^[37] The phosphinyl group is also out of the plane

defined by the silole ring with a C12C11C25P1 torsion angle of -115.27(16) °. The P-CH₂ [C25P1 1.8663(16) Å], P-C_{Ph} [P1-C26 1.8381(17) and P1-C32 1.8402(17)] bond lengths are in the range of P-C_{Alk} and P-C_{Ph} bond lengths reported for R-CH₂-PPH₂ (1.625-1.901 Å, mean 1.853 Å). The pyramidalization of phosphorus [$\Sigma\alpha$ (CPC) = 301.3 °] is featureless and in the range of reported values (mean 304.4 °).

The solution behaviour of **2** under photochemical conditions was then assessed by UV absorption spectroscopy (Figure 2). The UV-Visible spectrum of **2** recorded in dichloromethane displays an intense band in the UV region at λ_{max} 354 nm attributed to $\pi \rightarrow \pi^*$ transitions located on the thienyl aromatic rings. Irradiation of the sample at λ 350 nm led to the appearance of a yellow color in the solution, as well as a broad absorption band at λ 454 nm in the UV-visible absorption spectrum. This band results from the lower energy $\pi \rightarrow \pi^*$ transition located on the octatetraene backbone and is indicative of the formation of **2'**. Another absorption band at λ 334 nm can also be observed and attributed to transitions from the tetraene to a silole π^* orbital. The cuvette solution discolors under visible light irradiation clearly indicating that the process is reversible. In a control experiment, 10 electrocyclization and cycloreversion cycles could be performed without noticeable degradation of the compound. The photochromic reaction was also monitored by NMR spectroscopy. In ³¹P NMR, the closed isomer **2'** gives a upfield-shifted singlet resonance signal at δ -18.4 ($\Delta\delta$ = -3.7). The ¹H NMR spectrum is diagnostic for the formation of **2'** with the appearance of new upfield shifted signals for the protons of the sulfur heterocycles at δ 5.72 and 6.30 versus 6.48 and 6.54 in **2**.

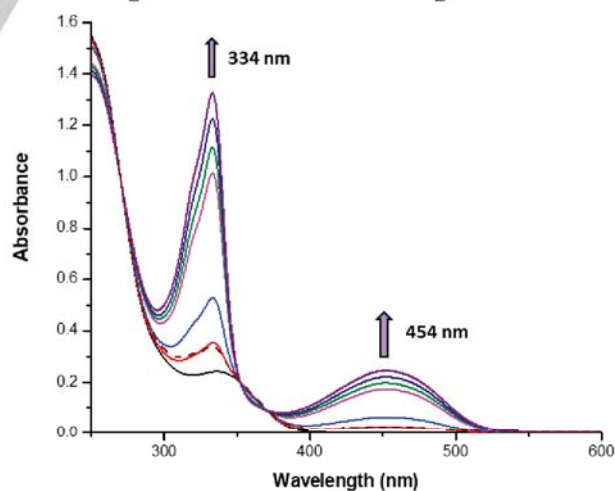
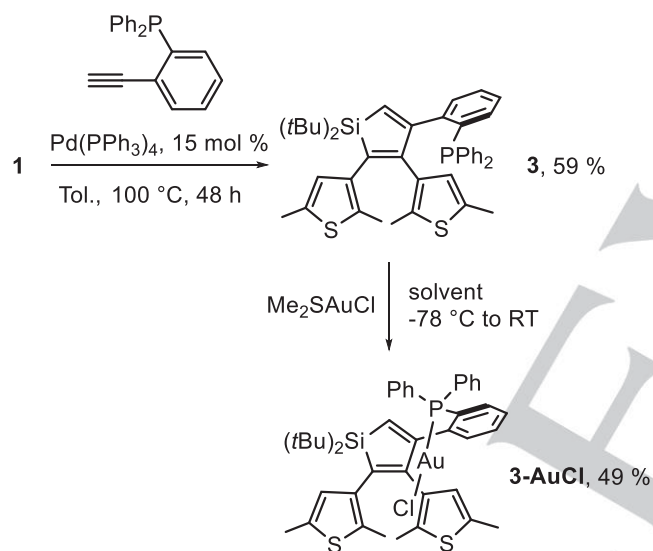


Figure 3. Reversible transformation of **2** into **2'** under light irradiation and UV/Vis spectral changes upon irradiation of a dichloromethane solution of **2** at 350 nm.

We then targeted a parent compound featuring a conjugated phenylene spacer between the silole and the phosphinyl group. For this purpose, (2-ethynylphenyl)diphenylphosphine was prepared in 80% yield as a brown oil from the known (2-

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(trimethylsilylethynyl)phenyl)diphenylphosphine.^[38] Alkyne deprotection was carried out using tetrabutylammonium fluoride (TBAF) under optimized conditions to avoid the formation of undesired phospholane oxide.^[39] This new substrate was engaged in the Pd-catalyzed annulation reaction with silirene **1** and after optimization of the reaction conditions, phosphino-silole **3** could be obtained in good yield under forcing conditions (15 mol% catalyst loading, $\theta = 100\text{ }^\circ\text{C}$), validating the compatibility of the catalytic reaction with a free phosphine substrate (Scheme 1). The ^{31}P NMR spectrum of **3** displays a set of two singlet resonance signals at δ -13.1 and -13.3 due to hindered rotation around the C–C bond connecting the silole and the aryl ring. Combined with the two possible antiparallel conformations of the thienyl rings, this leads to the presence of diastereoisomers in solution. ^1H and ^{31}P variable temperature NMR experiments revealed signals coalescence at 313 K which gives a rotational barrier of approximately $\Delta G^\ddagger = 16\text{ kcal.mol}^{-1}$ (see S71-72 for details). A similar rotation barrier of $16.4\text{ kcal.mol}^{-1}$ was obtained from a DFT calculated mechanism at the B3LYP/6-311g(d,p) level of theory (see S115 for details).



Scheme 1. Synthesis of triarylphosphine **3** by reaction of **1** with (2-ethynylphenyl)diphenylphosphine under palladium-catalyzed conditions and formation of the gold(I) complex **3-AuCl** by reaction between **3** and Me_2SAuCl .

A single crystal of **3** was analyzed by X-ray diffraction analysis (Figure 4, left). In the solid state, **3** displays a very constrained steric environment around phosphorus with the ortho-substituted aryl bridge and the silole heterocycle close to orthogonality (angle between planes of 78.0 °). The corresponding $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^2}$ bond bridging the two aromatics is elongated [C10-C25 1.4911(17) Å], but remains in the range of reported values for silole-phenyl linkages (1.437-1.567 Å).

The use of **3** as a metal ligand was then evaluated via a simple linear coordination with gold(I) (Scheme 1). Despite the bulkiness of **3**, its reaction with $[\text{Me}_2\text{SAuCl}]$ at room temperature readily affords the corresponding phosphine gold(I) chloride complex **3-AuCl**. In contrast to **3**, the ^{31}P NMR spectrum of **3-AuCl** exhibits a single resonance signal at δ 27.8 suggesting that a dynamic resolution took place upon coordination, with one of the diastereoisomers of **3** being more reactive than the other. **3-AuCl** could be obtained in 49% yield as a yellow powder and was fully

characterized including by X-ray diffraction analysis (Figure 4, right).

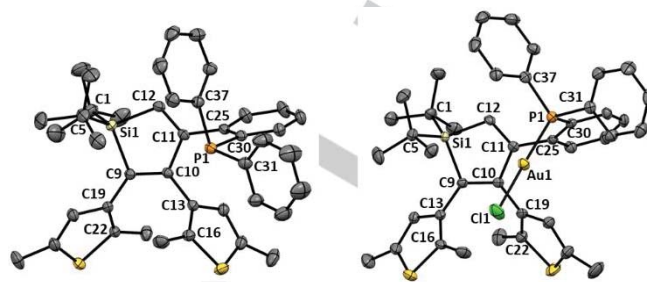
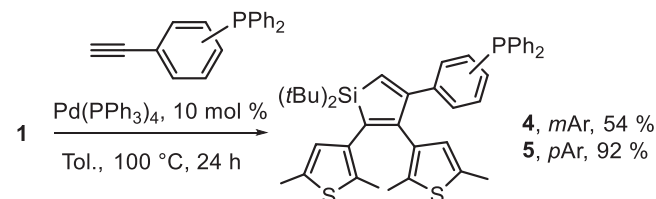


Figure 4. a) Solid-state structure (150 K) of **3** (left) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: P1-C30 1.8338(13), P1-C31 1.8299(14), P1-C37 1.8387(14), Si1-C1 1.9007(16), Si1-C5 1.9156(15), Si1-C9 1.8903(13), Si1-C12 1.8596(14), C9-C10 1.3613(17), C10-C11 1.5076(17), C11-C12 1.3440(18), C11-C25 1.4911(17), C10C11C25 120.83(11), C11C25C30 121.11(11), C25C30P1 117.33(9), C30P1C31 100.57(6), C30P1C37 100.26(6), C31P1C37 102.56(6), C9C10C13C16 -54.72(19), C10C9C19C22 -47.9(2), C12C11C25C30 100.82(16); b) Solid-state structure (150 K) of **3-AuCl** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and a dichloromethane molecule are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: P1-C30 1.823(2), P1-C31 1.819(2), P1-C37 1.811(2), P1-Au1 2.2337(7), Au1-Cl1 2.2855(7), Si1-C1 1.913(2), Si1-C5 1.899(3), Si1-C9 1.880(2), Si1-C12 1.861(2), C9-C10 1.365(3), C10-C11 1.510(3), C11-C12 1.346(3), C11-C25 1.496(3), P1Au1Cl1 175.98(2), C10C11C25 121.54(19), C11C25C30 123.5(2), C25C30P1 122.27(16), C30P1C31 104.07(10), C30P1C37 108.33(10), C31P1C37 105.70(11), C9C10C19C22 -48.3(4), C10C9C13C16 -50.6(4), C12C11C25C30 -59.3(3).

Position isomers of phosphino-silole **3** were then targeted following the same synthetic strategy. Compound **4** and **5** with a *meta*- and a *para*-phenylene linker were prepared, respectively. They could be obtained from (3-ethynylphenyl)diphenylphosphine and (4-ethynylphenyl)diphenylphosphine, respectively (Scheme 2). After column chromatography on silica gel, **4** and **5** were obtained in a pure form in 54% and 92% yield, respectively. They were fully characterized by multinuclear NMR, HR-MS and X-ray diffraction analyses. As expected, and in contrast to **3**, the ^{31}P NMR spectra of **4** and **5** display a single resonance signal indicating free rotation around the C(silole)–C(ArPPh₂) bond in solution.



Scheme 2. Synthesis of triarylphosphine **4** and **5** by reaction of **1** with (3-ethynylphenyl)diphenylphosphine and (4-ethynylphenyl)diphenylphosphine, respectively, under palladium-catalyzed conditions.

Triarylphosphines **3**, **4** and **5** were all found to be photochromic in solution and light stable. Closed isomers **3'**, **4'** and **5'** were characterized by the typical low energy absorption bands at λ_{max} 454, 452, and 454 nm, respectively (Figure 5). In ^{31}P NMR, their formation could also be evidenced by the appearance of new resonance signals at δ -13.5 and -14.0 for **3'**, present as diastereoisomers in solution analogously to **3**, and at δ -5.1 and δ -6.1 for **4'** and **5'**, respectively.

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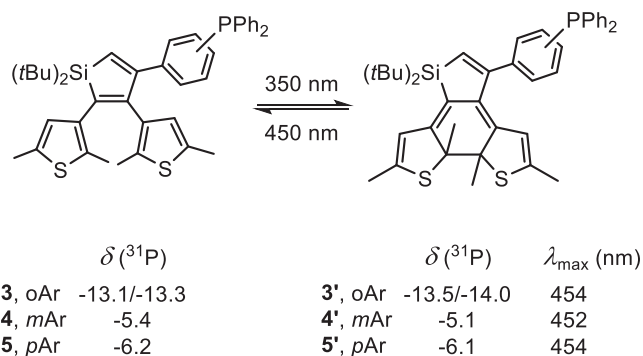


Figure 5. Photochromic transformation of **3**, **4** and **5** and corresponding changes in ^{31}P NMR chemical shift and λ_{max} of the closed isomers **3'**, **4'**, and **5'** extracted from the UV-vis electronic absorption spectrum.

With the family of compounds **2-5** in hand, we turned to the evaluation of the influence of the photochromism on the properties of the phosphinyl group and more particularly on its Lewis basicity. Among different experimental descriptors of phosphine basicity, measurement of the $^1J_{\text{PSe}}$ NMR coupling constant of the corresponding phosphine selenide is particularly sensitive to subtle changes in the chemical environment of the phosphorus atom, and has the advantage of being easily implemented.^{[40]-[42]} Phosphine selenides **2-Se**, **3-Se**, **4-Se** and **5-Se** were then prepared by reaction of the corresponding phosphines with elemental selenium. They were fully characterized by multinuclear NMR spectroscopy and by X-ray diffraction analysis in the case of **2-Se** and **3-Se** (see S38 details). In each case, the phosphine selenide was found to be photochromic in solution and the $^1J_{\text{PSe}}$ coupling constants could be extracted from the ^{31}P NMR spectrum of a sample containing the two isomers after UV irradiation (see Figure 6a for the example of **3-Se/3'-Se**). The values in Hz are listed below with the corresponding $\Delta_{\text{c-o}}$ (Hz) difference between “closed” and “open” isomer (Figure 5b). In the case of the methylene bridge model compound, **2-Se**, the $\Delta_{\text{c-o}}$ value is close to zero ($\Delta_{\text{c-o}} = -0.7$ Hz) indicating that open and closed isomers are marginally different in terms of phosphorus donating ability. This result was somewhat expected with a methylene bridge that allows no electronic conjugation between the silole ring and the phosphinyl group, and is also flexible enough to respond to small changes in the steric environment of the phosphorus. The situation is radically different with phenylene spacers with non-negligible $\Delta_{\text{c-o}}$ values measured. It is important to note that the $\Delta_{\text{c-o}}$ values measured are positive overall, indicating that the phosphinyl group in the “open” isomer is more basic than in the “closed” one. This decrease in basicity of the phosphinyl group towards the closed isomer is similar for meta and para derivatives ($\Delta_{\text{c-o}} = 2.3$ and 2.7 Hz respectively) and comparable in magnitude to the difference between $\text{PPh}_2(\text{o-tolyl})$ and PPh_3 .^[40]

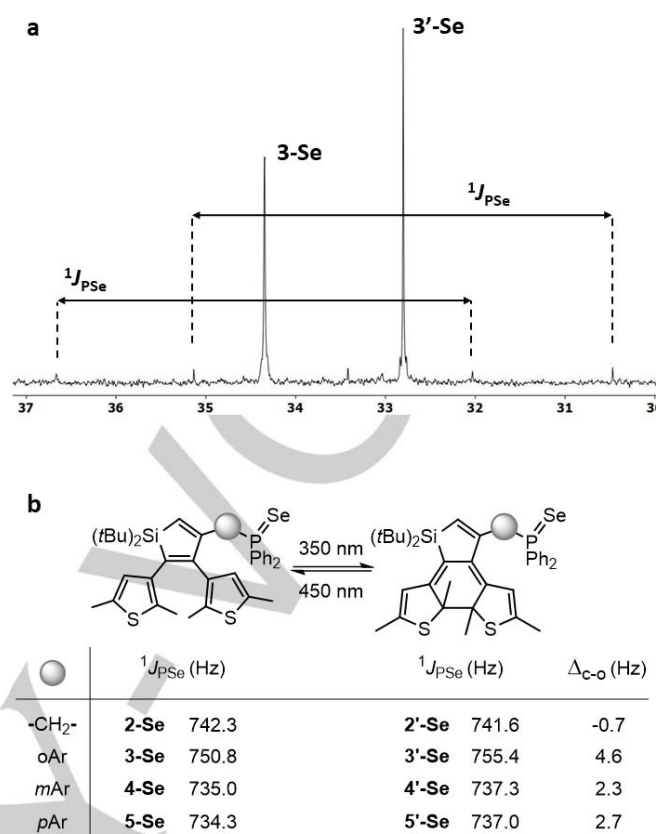


Figure 6. a) ^{31}P NMR spectrum of the mixture of **3-Se** and **3'-Se** after irradiation at λ 350 nm; b) $^1J_{\text{PSe}}$ coupling constants of the open and closed isomer extracted from the ^{31}P NMR spectra of mixtures of **2-Se/2'-Se**, **3-Se/3'-Se**, **4-Se/4'-Se** and **5-Se/5'-Se**.

In the case of the ortho derivative **3-Se**, the decrease is more pronounced ($\Delta_{\text{c-o}} = 4.6$ Hz) compared to the meta **4-Se** ($\Delta_{\text{c-o}} = 2.3$ Hz) and para **5-Se** ($\Delta_{\text{c-o}} = 2.7$ Hz) derivatives, respectively, probably due to the higher steric hindrance in the compound. The structure of compounds **2-5** and **2'-5'** have been optimized by DFT calculations at the B3LYP/6-311G(d,p) level of theory. The bond lengths and angles are reproduced with accuracy with a mean deviation of 0.67% on bond distances and 0.64% on angles for compound **2** taken as benchmark (see SI111 for details). Compounds **2_{opt}-5_{opt}** and **2'_{opt}-5'_{opt}** have been compared on the basis of their occupied Kohn-Sham molecular orbital (HOMO-2, HOMO-1 and HOMO). The situation being comparable within the series, only **2_{opt}** and **2'_{opt}** MOs are displayed in figure 7. In the open isomer, the lone pair of phosphorus is present almost exclusively in the HOMO-1 level and is a phosphorus centered orbital with small contributions from the adjacent aryl groups. The HOMO-2 and HOMO levels are located on the thienyl groups (combination of π^* orbitals) and on the whole DTE backbone (antibonding π system), respectively. Among the closed isomers **2'_{opt}-5'_{opt}**, the lone pair of phosphorus corresponds to the HOMO-2. HOMO-1 and HOMO levels correspond to the π -system of the DTE backbone which is fully delocalized on the tetraene linkage and the silicon heterocycle. Overall, no substantial conjugation is observed between the phosphinyl group and the photochromic substituent for any of the compounds **2_{opt}-5_{opt}** and **2'_{opt}-5'_{opt}**, suggesting that the experimentally observed difference in basicity between open and closed isomers is more of steric origin.

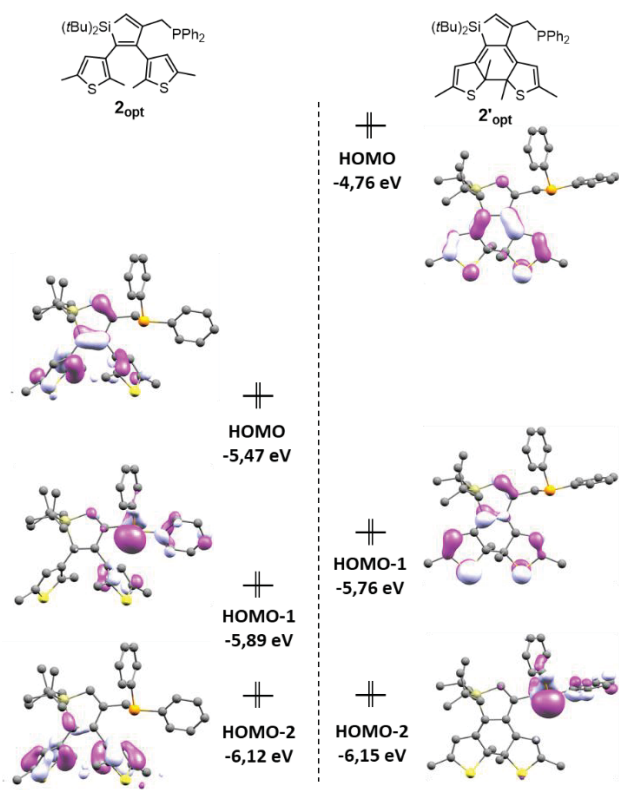
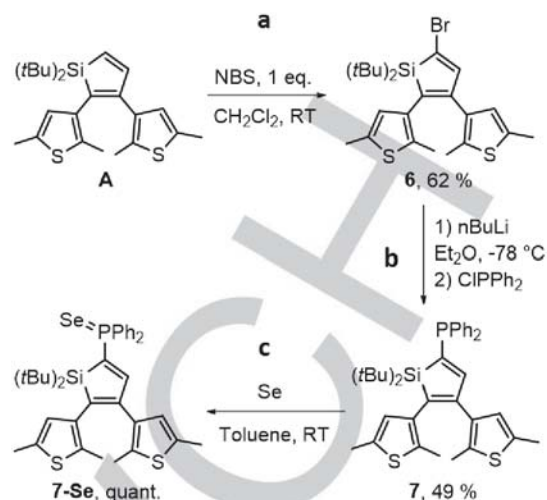


Figure 7. Kohn-Sham molecular orbitals HOMO-2, HOMO-1 and HOMO of compounds **2_{opt}** and **2'_{opt}** (isodensity value = 0.05 au).

In the light of these observations, the option of removing any spacer and connecting the phosphinyl group directly to the silole heterocycle was evaluated. We assumed that such a design would lead to an increased influence of the stereoelectronic changes inherent to the photocyclization on the basicity of the phosphinyl group. The reactivity of (ethynyl)diphenylphosphine $\text{Ph}_2\text{P}-\text{C}\equiv\text{C}-\text{H}$ in the presence of silirene **1** was evaluated under various catalytic conditions but no reaction could be observed even under forcing conditions and after an extended period of time. Increasing catalyst loading did not improve the reaction outcome while reaction temperatures above 50°C resulted in the gradual decomposition of the phosphine substrate. We thought that the lack of reactivity of this substrate could be linked to excessive steric hindrance at the alkyne and its lack of accessibility due to its direct connection with the phosphinyl group. It has previously been shown that this annulation reaction is sensitive to the presence of sterically demanding substituents directly linked to the alkyne triple bond.^{[34][43][44]} In order to circumvent that difficulty, the synthetic strategy starting from the unsubstituted **2,3-Dithienylsilole** was evaluated. 2,3-dithienylsilole **A** was previously described in our group and obtained in good yield via the annulation reaction of acetylene in the presence of **1**.^[34] **A** was reacted with NBS under stoichiometric conditions, in dichloromethane, at room temperature (Scheme 3, a). The reaction resulted in the regiospecific bromination of compound **A** at the silicon adjacent carbon of the silole heterocycle. Compound **6** was isolated in 62% yield and was fully characterized by multinuclear NMR and the regiospecificity of the bromination was ascertained by X-ray diffraction analysis of the compound (Figure 8, a).^[45]



Scheme 3. a) Synthesis of brominated compound **6** by bromination of a 2,3-dithienylsilole **A**; b) Synthesis of phosphine **7** by a sequence of lithium/bromine exchange and electrophilic trapping; c) Synthesis of phosphine selenide **7-Se**.

After optimization of the reaction conditions, brominated compound **6** could be successfully converted to the corresponding 2-phosphinosilole **7** via a sequential lithium/bromine exchange followed by an electrophilic trapping with ClPPh_2 (Scheme 3, b). **7** could be isolated in 49% yield as a dark yellow powder after column chromatography on silica gel. It was fully characterized by multinuclear NMR, HR-MS as well as X-ray diffraction analyses (Figure 8, b).

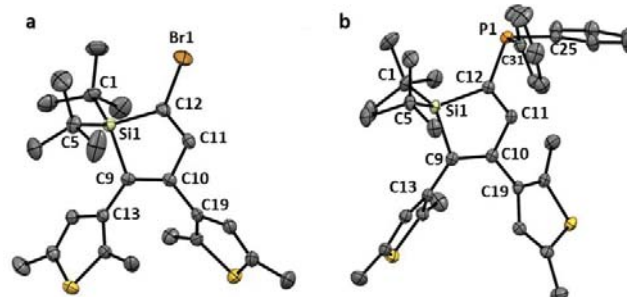


Figure 8. a) Solid-state structure (150 K) of **6** (left) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-C1 1.911(2), Si1-C5 1.902(2), Si1-C9 1.898(2), Si1-C12 1.879(2), C9-C10 1.361(3), C10-C11 1.484(3), C11-C12 1.324(3), C12-Br1 1.896(2); b) Solid-state structure (150 K) of **7** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C31 1.8404(14), P1-C25 1.8323(14), Si1-C1 1.9192(15), Si1-C5 1.9019(14), Si1-C9 1.8979(14), Si1-C12 1.8804(14), C9-C10 1.3626(19), C10-C11 1.4852(19), C11-C12 1.3473(18), C12-P1 1.8200(14), C12P1C31 101.45(6), C12P1C25 101.18(6), C25P1C31 102.64(6); C31P1C12C11 -92.30(13), C25P1C12C11 13.22(13).

In the solid state, the silole ring of **7** and the P1C25 bond are close to coplanarity with a dihedral angle of 16.7° with the phosphorus lone pair adopting a synclinal disposition with respect to the C12-Si1 axis. The behavior of **7** under light irradiation was then assessed. Under UV light irradiation, a weak band centered at 467 nm appeared along with a colour change from colourless to very pale yellow, indicating a weak absorption in the visible range. The reversibility of this phenomenon under visible light irradiation clearly indicates that **7** is photochromic. In the ^{31}P NMR spectrum, the change of color is concomitant with the appearance of a new

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singlet at δ -16.4 ($\Delta\delta$ = -1.3). At the photostationary state, the conversion of **7** is quite low (11%), which explains the weak absorption band observed previously. The corresponding phosphine selenide **7-Se** could be obtained via the aforementioned reaction in the presence of elemental selenium and obtained quantitatively. The compound is photochromic in solution and the $^1J_{\text{PSe}}$ coupling constants of both open and closed isomers could be extracted from the ^{31}P NMR spectrum ($\Delta\epsilon$ -o = -2.9 Hz). In this case, the trend is opposite to what was observed for compounds **2-5** and suggests that the phosphinyl group is more basic in the closed isomer **7'** than in the open one **7**. We reasoned that this could be due to additional conjugation between the phosphorus lone pair and the extended aromatic system of the silole-bridged DTE within closed isomer **7'**. The Kohn-Sham molecular orbitals analysis of open isomer **7** shows a situation similar to **2-5** with a HOMO-1 corresponding to the lone pair of phosphorus (see S114 for details). However, in the closed isomer **7'**, the lone pair is no more confined to HOMO-2 as in **2'-5'** but is also present in the HOMO-1 due to a favorable mixing with the adjacent C=C π -orbital of the vinyl silane moiety (see Figure 8). This phenomenon is only negligible within the open isomer of **7** likely due to the partial aromaticity of the silole heterocycle. The situation is reminiscent of the borole-bridged DTE reported by Branda and coworkers.^[46]

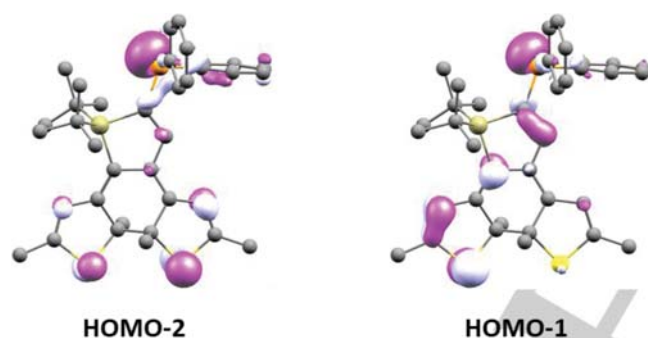


Figure 8. Kohn-Sham HOMO-2 and HOMO-1 molecular orbitals for closed isomers **7'** (isodensity value = 0.05 au).

Conclusion

In conclusion, we have here reported a family of unconventional photochromic phosphines based on the dithienylethene backbone. The present synthetic methodology takes advantage of the Pd-catalyzed alkyne annulation reaction in the presence of a 2,3-dithienylsilacyclopentene recently reported by our group and successfully transposed to **alkynyl phosphine** substrates. This strategy enables the easy modification of the linker connecting the phosphinyl group to the photochromic organic backbone by a simple modification of the alkyne. It thus enables a comparative study of the influence of photochromism on the basicity of phosphorus by varying the type of connectors. This influence was evaluated on the basis of an experimental descriptor of the basicity, the $^1J_{\text{PSe}}$ NMR coupling constant value of the corresponding phosphine selenides, and theoretically, thanks to MO analysis. This study reveals that the flexible methylene -CH₂-linker (**2**) does not allow any communication between the photochromic moiety and the phosphinyl group whereas the aryl bridges do. For the *o*/*m*/*p*-Ph linkers (**3-5**), the descriptor suggests

that the open isomer of the corresponding DTE-phosphine is more basic than the closed one with a pronounced effect in the case of the most sterically constrained *o*-Ph derivative. Within the series, the influence seems to be more of steric than electronic origin. A linker free DTE-phosphine was finally prepared starting from the 2,3-dithienylsilole via a bromination/phosphination two step sequence. This photochromic silylphosphine displays a reverse behaviour with the closed isomer revealing to be more basic than the open one. This feature arises from the substantial conjugation between the phosphine lone pair and the extended π -system of the photochrom in its closed form.

Experimental Section

The authors have cited additional references within the Supporting Information.^[52-58]

General considerations

The synthesis of 1,1-di-*tert*-butyl-2,3-bis(2,5-dimethylthiophen-3-yl)-1*H*-silirene **1** has been previously reported in the group.^[33] ((trimethylsilyl)ethynyl)diphenylphosphine and ethynyl(diphenyl)phosphine,^[47] diphenylphosphine-borane,^[36] (2-(2-bromophenyl)ethynyl)trimethylsilane,^[48] and (2-((trimethylsilyl)ethynyl)phenyl)diphenylphosphine^[35] were synthesized according to the reported procedures. (diphenyl)propargylphosphine-borane^[35] was synthesized according to literature by replacing propargyl bromide by propargyl chloride. The syntheses of (4-ethynylphenyl)diphenylphosphine and (3-ethynylphenyl)diphenylphosphine have been previously reported^[49] but prepared in this work following a different strategy. ((4-bromophenyl)ethynyl)trimethylsilane,^[50] (4-((trimethylsilyl)ethynyl)phenyl)diphenylphosphine and (4-ethynylphenyl)diphenylphosphine^[51] were synthesized according to previously reported procedures with minor modifications. The same synthetic strategies were adapted to synthesize ((3-bromophenyl)ethynyl)trimethylsilane, (3-((trimethylsilyl)ethynyl)phenyl)diphenylphosphine and (3-ethynylphenyl)diphenylphosphine respectively. The synthesis of 1,1-di-*tert*-butyl-2,3-bis(2,5-dimethylthiophen-3-yl)-1*H*-silole has been previously described in our group.^[34]

Deposition	Numbers	<url
https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202302374	2282534 (for 2-BH₃), 2282535 (for 2), 2282536 (for 2-Se), 2282537 (for 3), 2282538 (3-Se), 2282539 (for 3-AuCl), 2282540 (for 5), 2282541 (for 6), 2282542 (for 7)	contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe
http://www.ccdc.cam.ac.uk/structures	Access	Structures service</url>

Compound 2-BH₃

To a solution of diphenyl(propargyl)phosphine-borane (75.0 mg, 0.310 mmol, 1.10 equiv.) in toluene (5 mL), **1** (135 mg, 0.340 mmol, 1.00 eq.) was added. It was followed by the addition of palladium tetrakis(triphenylphosphine) (20.1 mg, 1.70 x 10⁻² mmol, 5.00 mol%) to the reaction mixture, which was then stirred at 50 °C for 15 hours. The reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum giving a yellow-colored oily residue. The crude residue was purified by column chromatography on silica gel (L 44 x W 25 mm; mSiO₂ = 7.5 g; eluent EtOAc/Pentane 0.5/99.5 (V/V)) giving the

desired compound as a white powder in 67 % yield (140 mg). Single crystals suitable for X-ray diffraction were obtained from a saturated pentane solution at -30 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.90 (s, 9H, C_H₃ tBu), 1.02 (s, 9H, C_H₃ tBu), 1.73 (s, 3H, C_H₃ Th), 1.81 (s, 3H, C_H₃-Th), 2.32 (s, 3H, C_H₃ Th), 2.34 (s, 3H, C_H₃ Th), 3.37 (ABq, 2H, ²J_{HH} = 14 Hz, P-CH₂), 6.10 (d with ²⁹Si sat. ²J_{HSi} = 15.2 Hz, ⁴J_{HP} = 3.7 Hz, 1H, Si-CH vinyl), 6.27 (s, 1H, CH Th), 6.49 (s, 1H, CH Th), 7.38-7.59 (m, 10H, C_H_{o/m/p}-Ph). In ¹H{¹¹B} NMR spectrum, the protons of BH₃ were observed at δ = 0.97 ppm; ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.7 (s, C_H₃ Th), 14.7 (s, C_H₃ Th), 15.2 (s, C_H₃ Th), 15.3 (s, C_H₃ Th), 19.7 (s, C tBu), 28.7 (s, C_H₃ tBu), 29.4 (s, C_H₃ tBu), 29.7 (d, ¹J_{CP} = 35.1 Hz, P-CH₂), 126.8 (s, CH Th), 127.4 (s, CH Th), 129.0 (d, ¹J_{CP} = 8.2 Hz, CH_m-Ph), 129.1 (d, ¹J_{CP} = 8.2 Hz, CH_m-Ph), 129.7 (d, ¹J_{CP} = 54.0 Hz, P-C_{ipso}), 129.7 (s, C_{quat} Th), 130.7 (d, ³J_{CP} = 7.5 Hz, Si-CH), 130.9 (d, ¹J_{CP} = 54.0 Hz, P-C_{ipso}), 131.3 (d, ¹J_{CP} = 2.3, CH_p-Ph), 131.5 (d, ¹J_{CP} = 2.3 Hz, CH_p-Ph), 131.7 (d, ¹J_{CP} = 2.4 Hz, CH_pPh), 132.6 (d, ²J_{CP} = 8.8 Hz, CH_o-Ph), 132.8 (d, ²J_{CP} = 9.0 Hz, CH_o-Ph), 133.5 (d, ¹J_{CP} = 9.6 Hz, CH_pPh), 134.5, 135.1, 135.4, 135.6 and 137.7 (s, C_{quat} Th), 139.8 (s, Si-C_{quat}), 151.1 (d, ²J_{CP} = 5.1 Hz, C_{quat} Silole) and 151.5 (d, ³J_{CP} = 3.7 Hz, C_{quat} Silole); ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 17.8 (br.); ¹¹B{¹H} NMR (CD₂Cl₂, 128 MHz): δ = -38.3 (br.).

HRMS (ESI), solvent CH₂Cl₂: exact mass (monoisotopic) calcd. for M⁺(C₃₇H₄₈PS₂Si), 626.27919; found 626.2793 (0 ppm); exact mass (monoisotopic) calcd. for [M-BH₃+H]⁺ (C₃₇H₄₆PS₂Si), 613.25424; found 613.2539 (1 ppm); Anal. Calcd. for [C₃₇H₄₈PS₂Si]; C, 70.90; H, 7.72; Found: C, 70.66; H, 7.75.

Compound 2

DABCO (51.0 mg, 0.450 mmol, 3.00 equiv.) was added to a solution of **2.BH₃** (95.3 mg, 0.150 mmol, 1.00 equiv.) in THF (6.2 mL). The reaction mixture was stirred for 2h at 50 °C. The completion of the reaction was monitored by ³¹P{¹H} NMR. The reaction mixture was then allowed to cool to room temperature and the solvent was evaporated. The product was dissolved in pentane (2 mL) and left for crystallization at -30 °C. Crystals in the form of white blocks were obtained in 42 % yield (39.2 mg). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated pentane solution at -30 °C.

¹H NMR, 400 MHz): δ = 0.90 (s, 9H, C_H₃ tBu), 1.00 (s, 9H, C_H₃ tBu), 1.83 (s, 3H, C_H₃ Th), 1.97 (s, 3H, C_H₃ Th), 2.35 (s, 3H, C_H₃ Th), 2.36 (s, 3H, C_H₃ Th), 3.08 (s, 2H, P-CH₂), 5.73 (d with ²⁹Si sat. ²J_{HSi} = 15.2 Hz, ⁴J_{HP} = 4.3 Hz, 1H, Si-CH vinyl), 6.48 (s, 1H, CH Th), 6.55 (s, 1H, CH Th), 7.18-7.39 (m, 10H, C_H_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.6 (d, ¹J_{CP} = 2.5 Hz, C_H₃ Th), 14.9 (s, C_H₃ Th), 15.2 (s, C_H₃ Th), 15.3 (s, C_H₃ Th), 19.5 (s, C tBu), 28.7 (s, C_H₃ tBu), 29.5 (s, C_H₃ tBu), 35.5 (d, ¹J_{CP} = 15.2 Hz, P-CH₂), 126.4 (d, ³J_{CP} = 12.8 Hz, Si-CH), 126.8 (s, CH Th), 127.5 (d, ⁵J_{CP} = 2.1 Hz, CH Th), 128.6 (d, ³J_{CP} = 4.1 Hz, CH_m-Ph), 128.6 (d, ³J_{CP} = 4.3 Hz, CH_m-Ph), 128.7 (s, CH_p-Ph), 128.9 (s, CH_p-Ph), 129.6 (s, C_{quat} Th), 133.0 (d, ²J_{CP} = 19.5 Hz, CH_o-Ph), 133.6 (d, ²J_{CP} = 19.5 Hz, CH_o-Ph), 134.0 (d, ⁴J_{CP} = 1.5 Hz, C_{quat} Th), 134.9, 135.0, 136.3 and 138.0 (s, C_{quat} Th), 139.3 (d, ¹J_{CP} = 55.6 Hz, P-C_{ipso}), 139.5 (d, ¹J_{CP} = 55.8 Hz, P-C_{ipso}), 140.0 (s, Si-C_{quat}), 151.8 (s, ³J_{CP} = 3.3 Hz, C_{quat} Silole), 158.1 (d, ²J_{CP} = 8.0 Hz, C_{quat} Silole); ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = -14.7 (s); ²⁹Si{¹H} NMR (CD₂Cl₂, 79 MHz): δ = 17.0 (d, ⁴J_{SiP} = 1.5 Hz).

HRMS (ESI), solvent CH₂Cl₂: exact mass (monoisotopic) calcd. for [M+H]⁺ (C₃₇H₄₆PS₂Si), 613.25424; found 613.2540 (0 ppm); Anal. Calcd. for [C₃₇H₄₅PS₂Si]; C, 72.50; H, 7.40. Found: C, 72.77; H, 7.39.

Compound 2-Se

A suspension of compound **2** (260 mg, 0.420 mmol, 1.00 equiv.) and selenium (270 mg, 3.39 mmol, 8.00 equiv.) in toluene (10 mL) was heated for 3 hours at 60 °C under stirring. The resulting solution was then allowed

to cool down to room temperature and the volatiles were removed. The residue obtained was extracted with DCM and the excess of selenium was removed by filtration. DCM was removed under pressure and the solid residue that remained was purified by column chromatography on silica gel (L 90 mm x W 25 mm; mSiO₂ = 12 g; eluent DCM/Pentane 50/50 (V/V)) giving the desired compound as a yellow solid in 45 % yield (130 mg). Single crystals suitable for X-ray diffraction analysis were obtained from a pentane/DCM solvent mixture at -30 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.92 (s, 9H, C_H₃ tBu), 1.04 (s, 9H, C_H₃ tBu), 1.71 (s, 3H, C_H₃ Th), 1.74 (s, 3H, C_H₃ Th), 2.32 (s, 3H, C_H₃ Th), 2.34 (s, 3H, C_H₃ Th), 3.79 (ABq, 2H, ²J_{HH} = 14 Hz, 2H, P-CH₂), 6.25 (s, 1H, CH Th), 6.46 (d overlap with CH Th, 1H, Si-CH vinyl), 6.47 (s, 1H, CH Th), 7.36-7.46 (m, 6H, C_H_{o/m/p}-Ph), 7.63-7.69 (m, 4H, C_H_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ = 14.7 (s, C_H₃ Th), 14.8 (s, C_H₃ Th), 15.3 (s, C_H₃ Th), 15.3 (s, C_H₃ Th), 19.6 (s, C tBu), 19.7 (s, C tBu), 28.7 (s, C_H₃ tBu), 29.4 (s, C_H₃ tBu), 35.7 (d, ¹J_{CP} = 46.8 Hz, P-CH₂), 126.8 (s, CH Th), 127.4 (s, CH Th), 128.8 (d, ²J_{CP} = 12.0 Hz, CH_o-Ph), 128.8 (d, ²J_{CP} = 12.0 Hz, CH_o-Ph), 129.7 (s, C_{quat} Th), 131.4 (d, ³J_{CP} = 9.0 Hz, Si-CH), 131.5 (d, ⁴J_{CP} = 2.9 Hz, CH_p-Ph), 131.6 (d, ⁴J_{CP} = 2.9 Hz, CH_p-Ph), 131.9 (d, ³J_{CP} = 10.2 Hz, CH_m-Ph), 132.4 (d, ³J_{CP} = 10.2 Hz, CH_m-Ph), 133.6 (d, ¹J_{CP} = 71.0 Hz, P-C_{ipso}), 134.5, 135.1, 135.4, 135.5 and 137.7 (s, C_{quat} Th), 139.5 (s, Si-C_{quat}), 150.1 (d, ²J_{CP} = 7.5 Hz, C_{quat} Silole), 151.1 (d, ³J_{CP} = 5.8 Hz, C_{quat} Silole). One P-C_{ipso} was not observed; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 34.1 (s with ⁷⁷Se sat., ¹J_{PSe} = 741.8 Hz).

HRMS (ASAP, 200 °C): exact mass (monoisotopic) calcd. for [M⁺] (C₃₇H₄₅PS₂SiSe), 692.1634; found 692.1631 (0 ppm); exact mass (monoisotopic) calcd. for [M+H]⁺ (C₃₇H₄₆PS₂SiSe) 693.17131; found 693.1678 (4 ppm); exact mass (monoisotopic) calcd. for [M-H]⁺ (C₃₇H₄₄PS₂SiSe) 691.15511; found 691.1553 (0 ppm); Anal. Calcd. for [C₃₇H₄₅PS₂SiSe]; C, 64.23; H, 6.56. Found: C, 64.13; H, 6.48.

Compound 3

To a solution of (2-ethynylphenyl)diphenylphosphine (132 mg, 0.460 mmol, 1.80 eq.) in toluene (12 mL), **1** (100 mg, 0.250 mmol, 1.00 eq.) was added. To this reaction mixture, palladium tetrakis(triphenylphosphine) (44.5 mg, 3.80 x 10⁻² mmol, 15.0 mol%) was added. The resulting mixture was then stirred at 100 °C for 48 hours. Toluene was then removed under vacuum giving a red colored oily residue that was purified by column chromatography on silica gel (L 180 x W 25 mm; mSiO₂ = 30 g; eluent DCM/Pentane 15/85 (V/V)) giving the desired compound as a white powder in 59 % yield (100 mg). Single crystals suitable for X-ray diffraction were obtained from a saturated pentane solution at -30 °C.

NMR characterization: In solution compound **3** exists as isomers in equilibrium. Hence, a set of resonance signals were observed for each isomer (major : minor = 1 : 0.6). Major isomer: ¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.96 (s, 9H, C_H₃ tBu), 1.07 (s, 9H, C_H₃ tBu), 1.71 (s, 3H, C_H₃ Th), 1.95 (s, 3H, C_H₃ Th), 2.10 (s, 3H, C_H₃ Th), 2.38 (s, 3H, C_H₃ Th), 5.73 (s, 1H, Si-CH), 5.87 (s, 1H, CH Th), 6.68 (s, 1H, CH Th), 6.77-7.35 (m, 14H, C_H_{o/m/p}-Ph); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ = -13.3 (s); Minor isomer: ¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.96 (s, 9H, C_H₃ tBu), 1.15 (s, 9H, C_H₃ tBu), 1.81 (s, 3H, C_H₃ Th), 1.89 (s, 3H, C_H₃ Th), 2.12 (s, 3H, C_H₃ Th), 2.38 (s, 3H, C_H₃ Th), 5.54 (s, 1H, Si-CH), 6.28 (s, 1H, CH Th); 6.65 (s, 1H, CH Th), 6.77-7.35 (m, 14H, C_H_{o/m/p}-Ph); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ = -13.1 (s). The carbon resonance signals could not be unambiguously assigned due to the complexity of the of the spectrum. For details, see the supporting information.

HRMS [MALDI, matrice DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile)]: exact mass (monoisotopic) calcd. for M⁺ (C₄₂H₄₇PS₂Si), 674.26206; found 674.262 (0 ppm); exact mass (monoisotopic) calcd. for [M-H]⁺ [C₄₂H₄₆PS₂Si], 673.25479; found 673.256 (3 ppm); Anal. Calcd. for [C₄₂H₄₇PS₂Si]; C, 75.07; H, 7.10. Found: C, 75.10; H, 6.99.

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Compound 3-Se

A suspension of compound **3** (41.3 mg, 6.00×10^{-2} mmol, 1.00 equiv.) and selenium (38.0 mg, 4.80×10^{-1} mmol, 8.00 equiv.) in toluene (10 mL) was heated at 60 °C under stirring for 15 hours. The resulting solution was then allowed to cool down to room temperature and the volatiles were removed. The residue obtained was extracted with DCM and the excess of selenium was removed by filtration. DCM was removed under pressure and the solid residue that remained was purified by column chromatography on silica gel (L 110 mm x W 25 mm; mSiO₂ = 15 g; eluent DCM/Pentane 20/80 (V/V)) giving the desired compound as yellow solid in a quantitative yield. Single crystals suitable for X-ray diffraction were obtained from a saturated pentane solution at -30 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.87 (s, 9H, CH₃ tBu), 1.06 (s, 9H, CH₃ tBu), 1.87 (s, 3H, CH₃ Th), 1.88 (s, 3H, CH₃ Th), 2.12 (s, 3H, CH₃ Th), 2.37 (s, 3H, CH₃ Th), 4.95 (s, 1H, Si-CH), 6.55-6.58 (m, 1H, CHPh), 6.62 (s, 1H, CHTh), 6.89-7.13 (m, 3H, CH_{o/m/p}-Ph), 7.27 (s, 1H, CHTh), 7.43-7.61 (m, 6H, CH_{o/m/p}-Ph), 7.66-7.71 (m, 2H, CH_{o/m/p}-Ph), 7.89-7.95 (m, 2H, CH_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.7 (s, CH₃ Th), 14.9 (s, CH₃ Th), 15.0 (s, CH₃ Th), 15.3 (s, CH₃ Th), 20.2 (s, C tBu), 21.2 (s, C tBu), 29.3 (s, CH₃ tBu), 30.0 (s, CH₃ tBu), 125.6 (d, ²J_{CP} = 12.2 Hz, CH_o-Ph), 126.8 (s, CH Th), 128.3 (s, C_{quat} Th), 128.7 (d, ²J_{CP} = 12.2 Hz, CH_o-Ph), 128.9 (s, CHTh), 129.1 (s, CH_p-Ph), 130.2 (d, ⁴J_{CP} = 2.8 Hz, CH_p-Ph), 130.6 (s, C_{quat} Th), 131.4 (d, ⁴J_{CP} = 2.6 Hz, CH_p-Ph), 131.5 (d, ³J_{CP} = 10.4 Hz, CH_m-Ph), 131.8 (d, ³J_{CP} = 10.4 Hz, CH_m-Ph), 132.3 (s, Si-CH), 133.2 (d, ³J_{CP} = 10.0 Hz, CH_m-Ph), 133.3 (d, ³J_{CP} = 10.1 Hz, CH_m-Ph), 133.3 (d, ¹J_{CP} = 67.3 Hz, P-C_{ipso}), 133.4 (d, ²J_{CP} = 11.0 Hz, CH_o-Ph), 134.9 (s, C_{quat} Th), 135.1 (d, ¹J_{CP} = 77.0 Hz, P-C_{ipso}), 137.2, 138.0 and 139.0 (s, C_{quat} Th), 147.1 (d, ³J_{CP} = 11.0 Hz, C_{quat} Silole), 150.8 (s, Si-C_{quat}), 160.8 (d, ⁴J_{CP} = 4.5 Hz, C_{quat} Silole). One quaternary carbon C_{quat} Ph was not observed; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 34.3 (s with ⁷⁷Se sat., ¹J_{PSe} = 750.7 Hz).

HRMS (ASAP, 210 °C): exact mass (monoisotopic) calcd. for [M+H]⁺ (C₄₂H₄₈SiPS₂⁸⁰Se), 755.18641; found 755.1862 (0 ppm); Anal. Calcd. for [C₄₂H₄₇PS₂SiSe]; C, 66.90; H, 6.28. Found: C, 67.16; H, 6.39.

Compound 3-AuCl

A mixture of **3** (15.3 mg, 2.00×10^{-2} mmol, 1.00 equiv.) and chloro(dimethylsulfide) gold(I) (6.60 mg, 2.00×10^{-2} mmol, 1.00 equiv.) in DCM (2 mL) were stirred at room temperature for 1 hour. The completion of the reaction was monitored by ³¹P NMR. On completion, DCM was evaporated and the residue obtained was extracted with a mixture of pentane and DCM. The volatiles were evaporated to obtain the desired complex as a yellow powder in 49 % yield (10.0 mg). Single crystals suitable for X-ray diffraction were obtained from a saturated pentane solution at -30 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 0.95 (s, 9H, CH₃ tBu), 1.05 (s, 9H, CH₃ tBu), 1.86 (s, 3H, CH₃ Th), 1.87 (s, 3H, CH₃ Th), 2.17 (s, 3H, CH₃ Th), 2.37 (s, 3H, CH₃ Th), 5.06 (s with ²⁹Si sat. ²J_{HSi} = 10.0 Hz, 1H, Si-CH), 6.62 (s, 1H, CHTh), 6.64-6.68 (m, 1H, CH_{o/m/p}-Ph), 6.83 (s, 1H, CHTh), 6.89-6.94 (m, 1H, CH_{o/m/p}-Ph), 7.08-7.20 (m, 2H, CH_{o/m/p}-Ph), 7.45-7.64 (m, 8H, CH_{o/m/p}-Ph), 7.72-7.78 (m, 2H, CH_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.6 (s, CH₃ Th), 15.1 (s, CH₃ Th), 15.3 (s, CH₃ Th), 15.5 (s, CH₃ Th), 20.0 (s, C tBu), 20.3 (s, C tBu), 29.4 (s, CH₃ tBu), 29.8 (s, CH₃ tBu), 125.9 (d, ¹J_{CP} = 62.7 Hz, P-C_{ipso}), 126.6 (d, ³J_{CP} = 9.7 Hz, CH_m-Ph), 126.8 (s, CHTh), 127.7 (s, CHTh), 129.6 (d, ³J_{CP} = 11.0 Hz, CH_m-Ph), 129.9 (d, ²J_{CP} = 12.0 Hz, CH_o-Ph), 130.5 (d, ³J_{CP} = 9.3 Hz, CH_m-Ph), 130.6 (d, ⁴J_{CP} = 2.0 Hz, CH_p-Ph), 131.0 (d, ¹J_{CP} = 61.7 Hz, P-C_{ipso}), 131.2 (d, ¹J_{CP} = 64.4 Hz, P-C_{ipso}), 131.5 (s, C_{quat} Th), 131.7 (d, ⁴J_{CP} = 2.0 Hz, CH_p-Ph), 132.4 (d, ⁴J_{CP} = 2.3 Hz, CH_p-Ph), 133.9 (s, C_{quat} Th), 134.3 (d, ⁴J_{CP} = 7.4 Hz, CH_m-Ph), 134.4 (s, C_{quat} Th), 134.7 (d, ²J_{CP} = 13.9 Hz, CH_o-Ph), 134.8 (d, ²J_{CP} = 14.7 Hz, CH_o-Ph), 135.1 (s, C_{quat} Th), 136.3 (s, Si-CH), 136.4 and 137.1 (s, C_{quat} Th), 140.8 (s, Si-C_{quat}), 147.8 (d, ²J_{CP} = 15.6 Hz, C_{quat} Ph), 149.4 (s, C_{quat} Silole), 160.2 (d, ³J_{CP} = 6.5 Hz, C_{quat} Silole); ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 27.8 ppm (s).

Compound 4

To a solution of 3-(ethynylphenyl)diphenylphosphine (60.0 mg, 0.209 mmol, 1.50 equiv.) in toluene (10 mL), **1** (54.0 mg, 0.139 mmol, 1.00 equiv.) was added. To this reaction mixture, palladium tetrakis(triphenylphosphine) (16.0 mg, 1.39×10^{-2} mmol, 10.0 mol%) was added. The resulting mixture was then stirred at 100 °C for 24 hours. Toluene was removed under vacuum giving a brown oily residue that was purified by column chromatography on silica gel (L 120 x W 25 mm; mSiO₂ = 21 g; eluent DCM/Pentane 10/90 (V/V)) giving the desired compound as a white powder with a yield of 54 % (50.0 mg).

¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.05 (s, 9H, CH₃ tBu), 1.14 (s, 9H, CH₃ tBu), 1.70 (s, 3H, CH₃ Th), 1.71 (s, 3H, CH₃ Th), 2.14 (s, 3H, CH₃ Th), 2.38 (s, 3H, CH₃ Th), 5.85 (d, $J_{HH} < 1.0$ Hz, 1H, CHTh), 6.06 (s with ²⁹Si sat. ²J_{HSi} = 11.0 Hz, 1H, Si-CH), 6.61 (d, $J_{HH} < 1.0$ Hz, 1H, CHTh), 6.96-6.99 (m, 1H, CH_{o/m/p}-Ph), 7.03-7.09 (m, 2H, CH_{o/m/p}-Ph), 7.12-7.15 (m, 1H, CH_{o/m/p}-Ph), 7.16-7.24 (m, 4H, CH_{o/m/p}-Ph), 7.29-7.38 (m, 4H, CH_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.5 (s, CH₃ Th), 14.5 (s, CH₃ Th), 15.1 (s, CH₃ Th), 15.3 (s, CH₃ Th), 19.9 (s, C tBu), 20.0 (s, C tBu), 28.9 (s, CH₃ tBu), 29.3 (s, CH₃ tBu), 127.0 (s, CHTh), 127.7 (s, CHTh), 127.9 (d, ³J_{CP} = 6.5 Hz, CH_m-Ph), 128.3 (s, CH_p-Ph), 128.8 (d, ³J_{CP} = 6.5 Hz, CH_m-Ph), 129.0 (d, ³J_{CP} = 6.9 Hz, CH_m-Ph), 129.0 (s, CH_p-Ph), 129.4 (s, CH_p-Ph), 129.7 (s, Si-CH), 130.1 (s, C_{quat} Th), 132.3 (d, ²J_{CP} = 17.0 Hz, CH_o-Ph), 133.3 (s, C_{quat} Th), 133.5 (d, ²J_{CP} = 23.0 Hz, CH_o-Ph), 133.9 (d, ²J_{CP} = 9.8 Hz, CH_o-Ph), 134.1 (d, ²J_{CP} = 10.0 Hz, CH_o-Ph), 134.3 and 135.2 (s, C_{quat} Th), 136.4 (d, ¹J_{CP} = 11.5 Hz, P-C_{ipso}), 136.7 and 137.8 (s, C_{quat} Th), 137.8 (d, ²J_{CP} = 20.3 Hz, P-C_{ipso}), 140.3 (s, C_{quat} Silole), 142.7 (d, ³J_{CP} = 7.7 Hz, C_{quat} Ph), 150.6 (s, Si-C_{quat}), 163.1 (s, C_{quat} Silole). One P-C_{ipso} was not observed; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = -5.4 (s).

HRMS (ASAP, 200 °C): exact mass (monoisotopic) calcd. for [M+H]⁺ (C₄₂H₄₈SiPS₂), 675.27044; found 675.2696 (0 ppm); Anal. Calcd. for [C₄₂H₄₇PS₂Si]; C, 74.73; H, 7.02. Found: C, 74.45; H, 6.99.

Compound 4-Se

A suspension of **4** (36.0 mg, 5.33×10^{-2} mmol, 1.00 equiv.) and selenium (33 mg, 4.26×10^{-1} mmol, 8.00 equiv.) in toluene (6 mL) was heated at 60 °C under stirring for 15 hours. The resulting mixture was then allowed to cool to room temperature and the volatiles were removed. The residue obtained was extracted with DCM and the excess of selenium was removed by filtration. DCM was removed under reduced pressure and the solid residue that remained was purified by column chromatography on silica gel (L 110 mm x W 25 mm; mSiO₂ = 15 g; eluent DCM/Petroleum ether 50/50 (V/V)) giving the desired compound as pale-yellow oil in a quantitative yield.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.04 (s, 9H, CH₃ tBu), 1.14 (s, 9H, CH₃ tBu), 1.69 (s, 3H, CH₃ Th), 1.69 (s, 3H, CH₃ Th), 2.14 (s, 3H, CH₃ Th), 2.37 (s, 3H, CH₃ Th), 5.82 (d, $J_{HH} < 1.0$ Hz, 1H, CHTh), 6.11 (s with ²⁹Si sat. ²J_{HSi} = 11.0 Hz, 1H, Si-CH), 6.59 (d, $J_{HH} < 1.0$ Hz, 1H, CHTh), 7.12 (d, ³J_{HH} = 14.2 Hz, 1H, CH_{o/m/p}-Ph), 7.27-7.33 (m, 2H, CH_{o/m/p}-Ph), 7.40-7.62 (m, 11H, CH_{o/m/p}-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.5 (s, CH₃ Th), 14.5 (s, CH₃ Th), 15.2 (s, CH₃ Th), 15.3 (s, CH₃ Th), 19.9 (s, C tBu), 20.0 (s, C tBu), 28.8 (s, CH₃ tBu), 29.3 (s, CH₃ tBu), 126.9 (s, CHTh), 127.6 (s, CHTh), 128.3 (d, ²J_{CP} = 12.9 Hz, CH_o-Ph), 128.7 (d, ³J_{CP} = 4.8 Hz, CH_m-Ph), 128.9 (d, ³J_{CP} = 4.7 Hz, CH_m-Ph), 130.2 (s, C_{quat} Th), 130.9 (s, Si-CH), 130.9 (s, CH_p-Ph), 131.0 (s, C_{quat} Th), 131.3 (d, ²J_{CP} = 11.4 Hz, CH_o-Ph), 131.6 (s, CH_p-Ph), 131.8 (s, CH_p-Ph), 131.8 (d, ³J_{CP} = 8.2 Hz, CH_m-Ph), 132.9 (d, ²J_{CP} = 10.9 Hz, CH_o-Ph), 133.0 (d, ²J_{CP} = 10.9 Hz, CH_o-Ph), 133.0 (d, ²J_{CP} = 80.3 Hz, P-C_{ipso}), 134.6, 135.4, 136.4 and 137.6 (s, C_{quat} Th), 140.7 (s, C_{quat} Silole), 142.5 (d, ³J_{CP} = 12.3 Hz, C_{quat} Ph), 149.9 (s, Si-C_{quat}), 162.2 (s, C_{quat} Silole). Two P-C_{ipso} were not observed; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 35.6 (s with ⁷⁷Se sat., ¹J_{PSe} = 735.1 Hz).

1 HRMS (ASAP, 210 °C): exact mass (monoisotopic) calcd. for [M+H]⁺
 2 (C₄₂H₄₈SiPS₂Se), 755.18696; found 755.1856 (1 ppm); Anal. Calcd. for
 3 [C₄₂H₄₇PS₂SiSe]; C, 66.90; H, 6.28. Found: C, 67.26; H, 6.23.

4 Compound 5

5 To a solution of 4-(ethynylphenyl)diphenylphosphine (55.0 mg, 0.193
 6 mmol, 1.50 equiv.) in toluene (10 mL), **1** (50.0 mg, 0.128 mmol, 1.00
 7 equiv.) was added. To this reaction mixture, palladium
 8 tetrakis(triphenylphosphine) (14.7 mg, 1.28 x 10⁻⁵ mmol, 10.0 mol%) was
 9 added. The resulting mixture was then stirred at 100 °C for 24 hours.
 10 Toluene was then removed under vacuum giving a yellow oily residue that
 11 was purified by column chromatography on silica gel (L 180 x W 25 mm;
 12 mSiO₂ = 30 g; eluent DCM/Petroleum ether 10/90 (V/V)). The desired
 13 compound was obtained as a white powder in 92 % yield (80.0 mg). Single
 14 crystals suitable for X-ray diffraction were obtained from a saturated
 15 pentane solution at -30 °C.

16 ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.08 (s, 9H, C_H₃ tBu), 1.16 (s, 9H, C_H₃
 17 tBu), 1.73 (s, 3H, C_H₃ Th), 1.79 (s, 3H, C_H₃ Th), 2.17 (s, 3H, C_H₃ Th), 2.39
 18 (s, 3H, C_H₃ Th), 5.89 (d, J_{HH} < 1.0 Hz, 1H, C_H Th), 6.17 (s with ²⁹Si sat.
 19 ²J_{H_{Si}} = 10.9 Hz, 1H, Si-C_H), 6.65 (d, J_{HH} < 1.0 Hz, 1H, C_H Th), 6.97-7.00
 20 (m, 2H, C_H_{o(m-p-Ph)}), 7.07-7.11 (m, 2H, C_H_{o(m-p-Ph)}), 7.23-7.37 (m, 10H, C_H_{o(m-p-Ph)});
 21 ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.5 (s, C_H₃ Th), 14.6 (s, C_H₃
 22 Th), 15.1 (s, C_H₃ Th), 15.4 (s, C_H₃ Th), 19.9 (s, C tBu), 20.0 (s, C tBu),
 23 28.9 (s, C_H₃ tBu), 29.3 (s, C_H₃ tBu), 127.0 (s, C_H Th), 127.9 (s, C_H Th),
 24 128.1 (d, ³J_{CP} = 7.0 Hz, C_H_{m-Ph}), 128.8 (d, ³J_{CP} = 6.6 Hz, C_H_{m-Ph}), 129.0 (s
 25 with ²⁹Si sat. ¹J_{C_{Si}} = 6.9 Hz, Si-C_H), 129.6 (s, C_H_{p-Ph}), 130.1 (s, C_{quat} Th),
 26 132.3 (d, ⁴J_{CP} = 5.8 Hz, C_{quat}), 133.1 (d, ²J_{CP} = 19.7 Hz, C_H_{o-Ph}), 133.4 (s,
 27 C_{quat}), 133.9 (d, ²J_{CP} = 19.5 Hz, C_H_{o-Ph}), 133.9 (d, ²J_{CP} = 19.5 Hz, C_H_{o-Ph}),
 28 134.4 and 135.3 (s, C_{quat} Th), 135.4 (d, ¹J_{CP} = 10.4 Hz, P-C_{ipso}), 136.7 and
 29 137.8 (s, C_{quat} Th), 138.0 (d, ¹J_{CP} = 11.6 Hz, P-C_{ipso}), 140.2 (s, C_{quat} Silole),
 30 142.9 (s, C_{quat} Ph), 150.5 (s, Si-C_{quat}), 162.9 (s, C_{quat} Silole); ³¹P{¹H} NMR
 31 (CD₂Cl₂, 162 MHz): δ = -6.2 (s).

32 HRMS [ASAP, 200 °C]: exact mass (monoisotopic) calcd. for [M+H]⁺
 33 (C₄₂H₄₈SiPS₂), 675.26989; found 675.2696 (0 ppm); M⁺. (C₄₂H₄₇PS₂Si),
 34 674.26206; found 674.2628 (1 ppm); exact mass (monoisotopic) calcd. for
 35 [M-C₄H₉]⁺ (C₃₈H₃₈PS₂Si), 617.19164; found 617.1926 (2 ppm); Anal. Calcd.
 36 for [C₄₂H₄₇PS₂Si]; C, 74.73; H, 7.02. Found: C, 74.98; H, 6.95.

37 Compound 5-Se

38 A suspension of **5** (42.8 mg, 6.00 x 10⁻² mmol, 1.00 equiv.) and selenium
 39 (40.0 mg, 6.00 x 10⁻² mmol, 8.00 equiv.) in toluene (10 mL) was heated
 40 overnight at 60 °C under stirring. The resulting solution was then allowed
 41 to cool down to room temperature and the volatiles were removed. The
 42 residue obtained was extracted with DCM and the excess of selenium was
 43 removed by filtration. DCM was removed under pressure and the solid
 44 residue that remained was purified by column chromatography on silica
 45 gel (L 110 mm x W 25 mm; mSiO₂ = 15 g; eluent DCM/Petroleum ether
 46 50/50 (V/V)) giving the desired compound as pale-yellow solid in a
 47 quantitative yield.

48 ¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.08 (s, 9H, C_H₃ tBu), 1.17 (s, 9H, C_H₃
 49 tBu), 1.73 (s, 3H, C_H₃ Th), 1.79 (s, 3H, C_H₃ Th), 2.16 (s, 3H, C_H₃ Th), 2.39
 50 (s, 3H, C_H₃ Th), 5.88 (s, 1H, C_H Th), 6.24 (s with ²⁹Si sat. ²J_{H_{Si}} = 10.9 Hz,
 51 1H, Si-C_H), 6.65 (s, 1H, C_H Th), 7.08-7.11 (m, 2H, C_H_{o(m-p-Ph)}), 7.42-7.53
 52 (m, 8H, C_H_{o(m-p-Ph)}), 7.62-7.69 (m, 4H, C_H_{o(m-p-Ph)}); ¹³C{¹H} NMR (CD₂Cl₂,
 53 100 MHz): δ = 14.5 (s, C_H₃ Th), 14.6 (s, C_H₃ Th), 15.1 (s, C_H₃ Th), 15.4
 54 (s, C_H₃ Th), 19.9 (s, C tBu), 20.1 (s, C tBu), 28.9 (s, C_H₃ tBu), 29.3 (s, C_H₃
 55 tBu), 126.9 (s, C_H Th), 127.7 (s, C_H Th), 128.0 (d, ³J_{CP} = 13.3 Hz, C_H_{m-Ph}),
 56 128.9 (d, ³J_{CP} = 12.0 Hz, C_H_{m-Ph}), 129.5 (d, J_{CP} = 78.7 Hz, P-C_{ipso}),
 57 130.2 (s, C_{quat} Th), 131.3 (s, Si-C_H), 131.9 (d, ⁴J_{CP} = 3.1 Hz, C_H_{p-Ph}), 132.1
 58 (d, ²J_{CP} = 11.4 Hz, C_H_{o-Ph}), 132.7 (d, J_{CP} = 76.2 Hz, P-C_{ipso}), 132.7 (d,
 59 J_{CP} = 77.0 Hz, P-C_{ipso}), 132.8 (d, ²J_{CP} = 10.8 Hz, C_H_{o-Ph}), 132.8 (d, ²J_{CP} =
 60 10.9 Hz, C_H_{o-Ph}), 133.6, 134.7, 135.5, 136.6 and 137.6 (s, C_{quat} Th), 140.6
 61 (s, C_{quat} Silole), 145.7 (d, ⁴J_{CP} = 3.2 Hz, C_{quat} Ph), 150.0 (s, Si-C_{quat}), 162.1

(d, ⁵J_{CP} = 1.5 Hz, C_{quat} Silole); ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 34.6
 (s with ⁷⁷Se sat., ¹J_{P_{Se}} = 733.2 Hz).

HRMS (ESI), solvent CH₂Cl₂: exact mass (monoisotopic) calcd. for [M+H]⁺
 (C₄₂H₄₈PSiS₂⁸⁰Se), 755.18641; found 755.1858 (1 ppm); exact mass
 (monoisotopic) calcd. for [M-C₄H₉]⁺ (C₃₈H₃₈SiPS₂⁸⁰Se), 697.10816; found
 697.1079 (0 ppm); Anal. Calcd. for [C₄₂H₄₇PS₂Si]; C, 66.90; H, 6.28.
 Found: C, 67.15; H, 6.33.

Compound 6

To a Schlenk loaded with a solution of 1,1-di-*tert*-butyl-2,3-bis(2,5-
 dimethylthiophen-3-yl)-1*H*-silole **A** (310 mg, 0.740 mmol, 1.00 equiv.) in
 DCM (6.5 mL), *N*-bromosuccinimide (140 mg, 0.780 mmol, 1.05 equiv.)
 was added giving a dark yellow solution. The resulting reaction mixture
 was stirred for 15 hours at room temperature. The volatiles were then
 removed under reduced pressure giving an oily yellow residue that was
 purified by column chromatography on silica gel (L 140 mm x W 25 mm;
 mSiO₂ = 20 g; eluent 100 % Pentane). The expected compound was
 obtained as a yellow powder in 62 % yield (230 mg). Single crystals
 suitable for X-ray diffraction were obtained from a saturated pentane
 solution at -30 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.15 (s, 18H, C_H₃ tBu), 1.69 (s, 3H, C_H₃
 Th), 1.95 (s, 3H, C_H₃ Th), 2.31 (s, 3H, C_H₃ Th), 2.38 (s, 3H, C_H₃ Th), 6.33
 (s, 1H, C_H Th), 6.63 (s, 1H, C_H Th), 7.22 (s with ²⁹Si sat. ²J_{H_{Si}} = 9.0 Hz,
 1H, Si-C_H); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.3 (s, C_H₃ Th), 14.7
 (s, C_H₃ Th), 15.2 (s, C_H₃ Th), 15.4 (s, C_H₃ Th), 19.9 (s, C tBu), 28.6 (s,
 C_H₃ tBu), 124.4 (s, C_{quat} Silole), 125.8 (s, C_H Th), 126.0 (s, C_H Th), 130.1
 and 133.4 (s, C_{quat} Th), 134.6 (s, C_{quat} Silole), 135.2, 135.4, 136.3 and
 136.8 (s, C_{quat} Th), 148.5 (s, C-Br), 150.8 (s, Si-C_H).

HRMS (ESI), solvent CH₃OH/CH₂Cl₂ (90/10): exact mass (monoisotopic)
 calcd. for [M⁺] (C₂₄H₃₃BrSiS₂), 492.09763; found 492.0975 (1 ppm); Anal.
 Calcd. for [C₂₄H₃₃BrSiS₂]; C, 58.40; H, 6.74. Found: C, 58.35; H, 6.84.

Compound 7

To a stirred solution of compound **6** (0.15 g, 0.30 mmol, 1.0 equiv.) in
 diethyl ether (10 mL), 2.5 M *n*-butyl lithium in *n*-hexane (0.12 mL, 0.30
 mmol, 1.0 eq.) was added dropwise over 10 minutes at -78 °C. The
 reaction mixture was allowed to warm up to 0 °C and stirred over 4h at the
 same temperature. Then, the reaction mixture was again cooled to -78 °C
 and chlorodiphenylphosphine (54 μL, 0.30 mmol, 1.0 eq.) was added
 dropwise. The reaction solution was left to warm up slowly to room
 temperature under stirring overnight giving a brown colored solution with
 lithium chloride as precipitate. The reaction mixture was then filtered and
 the volatiles were evaporated under reduced pressure giving an oily yellow
 residue. The crude compound was purified by column chromatography on
 silica gel (L 145 mm x W 25 mm; mSiO₂ = 25 g; eluent DCM/Hexane 10/90
 (V/V)). The solvent was then evaporated to dryness leading to the desired
 compound as a dark yellow powder in 49 % yield (90 mg).

¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.05 (s, 18H, C_H₃ tBu), 1.67 (s, 3H, C_H₃
 Th), 1.87 (s, 3H, C_H₃ Th), 2.23 (s, 3H, C_H₃ Th), 2.38 (s, 3H, C_H₃ Th), 6.07
 (s, 1H, C_H Th), 6.65 (s, 1H, C_H Th), 7.80 (d with ²⁹Si sat. ³J_{H_{Si}} = 12.0 Hz,
³J_{H_P} = 12.5 Hz, 1H, Si-C_H), 7.33-7.45 (m, 10H, C_H_{o(m-p-Ph)}); ¹³C{¹H} NMR
 (CD₂Cl₂, 100 MHz): δ = 14.2 (s, C_H₃ Th), 14.7 (s, C_H₃ Th), 15.1 (s, C_H₃
 Th), 15.4 (s, C_H₃ Th), 20.2 (s, C tBu), 29.2 (s, C_H₃ tBu), 126.7 (s, C_H Th),
 126.8 (s, C_H Th), 128.7 (d, ³J_{CP} = 6.4 Hz, C_H_{m-Ph}), 129.0 (s, C_H_{p-Ph}), 130.5
 and 133.5 (s, C_{quat} Th), 134.6 (d, ²J_{CP} = 20.1 Hz, C_H_{o-Ph}), 135.4, 135.4,
 137.5 and 137.8 (s, C_{quat} Th), 138.4 (d, ¹J_{CP} = 42.2 Hz, P-C_{ipso} Silole),
 140.3 (d, ³J_{CP} = 4.2 Hz, C_{quat} Silole), 149.7 (d, ³J_{CP} = 4.9 Hz, C_{quat} Silole),
 158.9 (d, ²J_{CP} = 5.2 Hz, Si-C_H). One P-C_{ipso} was not observed; ³¹P{¹H}
 NMR (CD₂Cl₂, 162 MHz): δ = -15.2 (s).

HRMS [ASAP, 200 °C]: exact mass (monoisotopic) calcd. for [M+H]⁺ (C₃₆H₄₄SiPS₂), 599.23914; found 599.2386 (0 ppm); Anal. Calcd. for [C₃₆H₄₃SiPS₂]; C, 72.20; H, 7.24. Found: C, 71.99; H, 7.31.

Compound 7-Se

A suspension of 5 (20.4 mg, 3.00 x 10⁻² mmol, 1.00 equiv.) and selenium (21.5 mg, 2.70 x 10⁻¹ mmol, 8.00 equiv.) in toluene (4 mL) was stirred overnight at room temperature. The volatiles were removed and the residue obtained was extracted with DCM. The excess of selenium was removed by filtration. The DCM was removed under pressure and the solid residue that remained was purified by column chromatography on silica gel (L 55 mm x W 25 mm; mSiO₂ = 8 g; eluent DCM/Hexane 50/50 (V/V)) giving the desired compound as dark yellow solid in a quantitative yield.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.10 (br., 18H, C_H₃ tBu), 1.69 (s, 3H, C_H₃ Th), 1.85 (s, 3H, C_H₃ Th), 2.21 (s, 3H, C_H₃ Th), 2.38 (s, 3H, C_H₃ Th), 5.95 (d, J_{HH} = 1.3 Hz, 1H, C_H Th), 6.64 (d, J_{HH} < 1.0 Hz, 1H, C_H Th), 6.95 (d with ²⁹Si sat. ³J_{H_{Si}} = 12.0 Hz, ³J_{HP} = 24.0 Hz, 1H, Si-C_H), 7.46-8.08 (br., 10H, C_H₂/m/p-Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ = 14.2 (s, C_H₃ Th), 14.6 (s, C_H₃ Th), 15.1 (s, C_H₃ Th), 15.4 (s, C_H₃ Th), 20.3 (s, C tBu), 28.9 (s, C_H₃ tBu), 126.4 (s, C_H Th), 126.7 (s, C_H Th), 128.7 (d, ²J_{CP} = 12.0 Hz, C_H₂-Ph), 131.0-135.0 (br. C_H_{m-Ph} and C_H_{p-Ph}), 131.5 (s, C_{quat}), 133.3 (s, C_{quat}. Silole), 133.8, 135.6, 136.0, 136.7 and 137.5 (s, C_{quat}. Th), 144.7 (s, C_{quat}. Silole), 148.5 (d, ¹J_{CP} = 20.8 Hz, P-C_{ipso} Silole), 164.3 (d, ²J_{CP} = 1.8 Hz, Si-C_H). One P-C_{ipso} was not observed; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 30.6 (s with ⁷⁷Se sat., ¹J_{PSe} = 715.5 Hz).

HRMS [ASAP, 250 °C]: exact mass (monoisotopic) calcd. for [M+H]⁺ (C₃₆H₄₄SiPS₂⁸⁰Se), 679.15566; found 679.1548 (0 ppm); exact mass (monoisotopic) calcd. for [M-C₄H₉]⁺ (C₃₂H₃₅SiPS₂⁸⁰Se), 622.08523; found 622.0847 (0 ppm).

Acknowledgements

We thank Dr. P. Jéhan and F. Lambert (CRMPO, Rennes) for the HR-MS, V. Dorcet for the measurement of crystals of compounds **2-Se** and **6**, M. Escadeillas for the elemental analyses, R. Marchal and the CTI group of the ISCR for the computational resources.

Keywords: Phosphines • Siloles • Annulation reaction • Photochromism • Dithienylethenes

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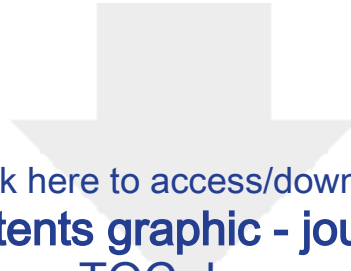
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