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# 1,2-Palladasilacyclobutene: The Missing Link in the Pd-Catalyzed Annulation of Alkynes for the Silirene-to-Silole Transformation

Marc Devillard,\* Chiara Dinoi, Iker Del Rosal, Clément Orione, Marie Cordier, and Gilles Alcaraz\*



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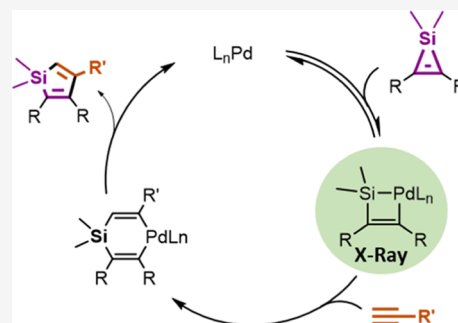


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**ABSTRACT:** The palladium-catalyzed annulation reaction of alkynes enables an attractive approach to siloles. Their access from silirenes and terminal alkynes proved rather general, involving reactive intermediates that have remained elusive to date. Starting from 1,2-bis(3-thienyl)silirene as a source of photochromic siloles, the mechanism of the annulation reaction has been revisited, and palladasilacyclobutenes resulting from the activation of the silirene could be isolated and thoroughly characterized (NMR, X-ray, and DFT). Their role as reactive intermediates and their fate in the course of the reaction were also studied in situ. In combination with in-depth DFT calculations, a clearer picture of the mechanism and the reactive key species is disclosed.



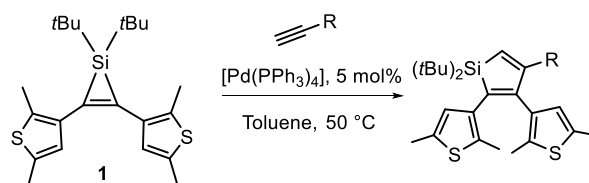
## INTRODUCTION

The chemical behavior of three-membered ring heterocycles is mostly dictated by the release of the ring strain<sup>1</sup> as the main driving force, with a strong influence both of the nature of the embedded heteroelement and of the degree of unsaturation of the cycle.<sup>2</sup> They have proven to be molecules of choice in organic synthesis, offering a wide range of reactivity and a versatile chemistry, especially when combined with catalysis.<sup>3</sup> In particular, they enable the synthesis of higher heterocyclic structures either via intramolecular ring expansion or through insertion reactions in the presence of an unsaturated partner. This approach provides an attractive methodology for the installation of the heteroelement, particularly in the course of new  $\pi$ -conjugated molecules incorporating heavier p-block elements.<sup>4</sup> In this context, the chemistry of silacycles (silicon rings with 3,<sup>5</sup> 4,<sup>6</sup> 5,<sup>6d,7</sup> or more<sup>8</sup> members) is probably the more mature research field driven by that of silacyclopentadienes (siloles) and their peculiar electronic properties.<sup>9</sup> Over the years, this interest has turned siloles into important synthetic targets and has motivated significant efforts toward methodological development.<sup>10</sup> While preparation of siloles relied generally on uncatalyzed transformations involving stoichiometric amounts of organometallic reagents, most recent achievements are based on catalytic routes, mainly using rhodium or palladium complexes.<sup>11</sup> They proceed either (i) intramolecularly from acyclic silanes through arylations of Si–X (X = CH<sub>3</sub>, H) bonds<sup>12</sup> and C–C bond formation between peripheral substituents<sup>13</sup> or (ii) intermolecularly by reaction of an alkyne with a suitable silicon-based reagent.<sup>14</sup> Within this second category, the use of silacyclopentene (silirene) as a direct precursor of siloles is a very attractive strategy, as it takes advantage of both the inherent reactivity of the silicon-containing precursor and the possibilities offered by

the large pool of alkynes. This Pd-catalyzed annulation of an alkyne in the presence of a silirene was reported in the substance as early as 1977 by Seyferth in his seminal studies.<sup>15</sup> Despite more recent efforts to improve the methodology,<sup>16</sup> this promising reaction has remained globally underutilized, with respect to its potential in organic synthesis. In this setting, we have recently described an efficient methodological approach to photochromic siloles<sup>17</sup> with a dithienylethene (DTE) skeleton. The strategy relies on the Pd-catalyzed [3 + 2]-annulation reaction of alkynes with a 1,2-bis(3-thienyl)silirene **1** (Scheme 1).

This divergent methodology proved rather general, tolerant to a variety of functional groups, and could even be extended to the post-polymerization functionalization of PPMA-type

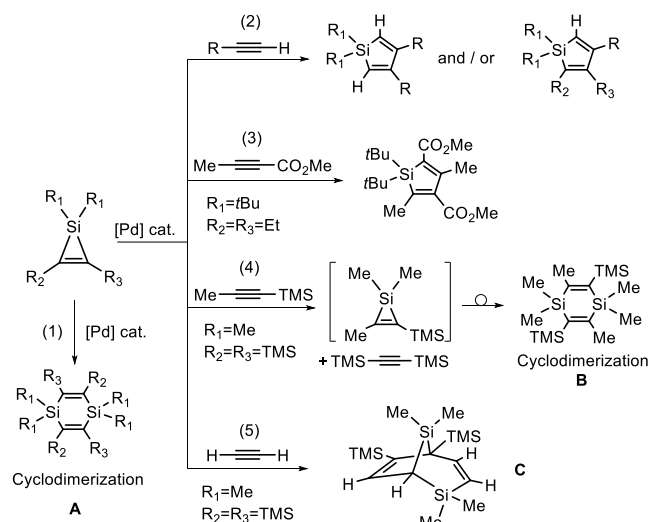
### Scheme 1. Palladium-Catalyzed Synthesis of Photochromic Siloles by Annulation Reaction of Alkynes with a Silacyclopentene



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61 (polypropargylmethacrylamide) polymers displaying terminal  
62 alkyne functionalities.<sup>17</sup> While this transformation can be  
63 formally seen as the regioselective insertion of the C≡C triple  
64 bond of a terminal alkyne into one of the two endocyclic Si–C  
65 single bonds of silirene, some aspects of this chemical  
66 transformation remain unclear when compared with the  
67 mapping of the general reactivity of silirenes with alkynes  
68 under palladium catalysis and the different scenarios related to  
69 the interplay of the silirene/alkyne pair with the metal  
70 (Scheme 2).

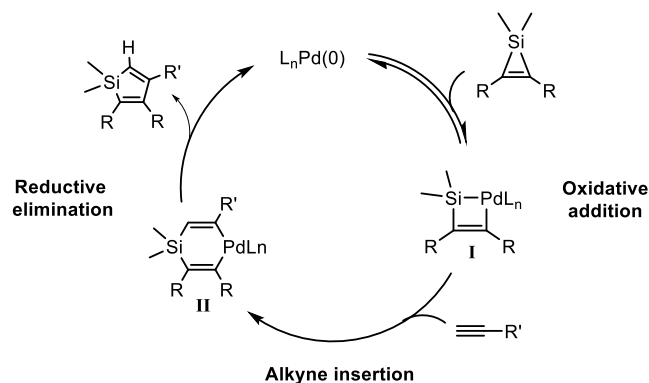
**Scheme 2. Different Scenarios of the Palladium-Catalyzed Reaction of Silirenes with Alkynes (for Route (1) See Refs 15d 21a 21b; for Route (2) See Refs 15a 15b 15d 16a 16b; for Route (3) See Ref 16b; for Route (4) See Ref 21b; and for Route (5) See Ref 18)**



71 Initially, the mechanism of the formation of siloles (Scheme  
72 2—route (2) and (3)) was envisaged to proceed through the  
73 intermediacy of a putative 1,2-palladasilacyclobutene I,  
74 resulting from the oxidative addition (OA) of Pd(0) to the  
75 silirene (Scheme 3).<sup>18</sup>

76 Later, this catalytic reaction was extended successfully by the  
77 group of Woerpel to 1,1-di-*tert*-butyl-silirenes, affording  
78 selective 3-phenylsiloles.<sup>16a,c</sup> On this basis, they proposed a  
79 more complete picture of the catalytic cycle involving the

**Scheme 3. Commonly Accepted Catalytic Cycle for the Palladium-Catalyzed Annulation Reaction of Alkynes with a Silirene**



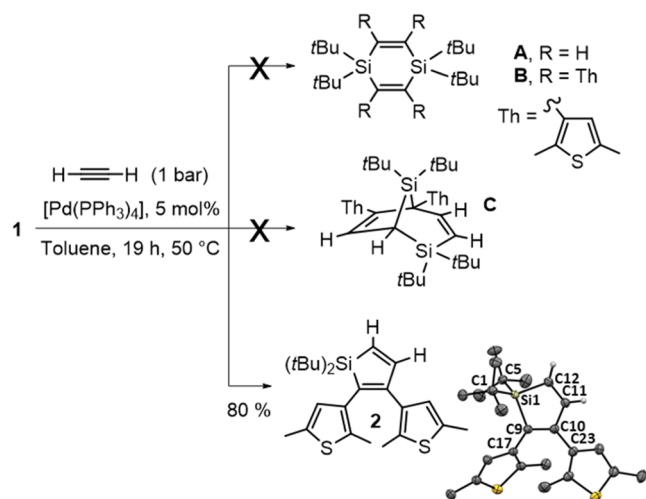
insertion of the alkyne partner into the Pd–Si bond of the 80  
metallacycle I to form a 1,4-palladasilacyclohexadiene II, 81  
followed by a classical reductive elimination step with the 82  
release of the silole product (Scheme 3). This commonly 83  
accepted mechanism remains, however, partly hypothetical due 84  
to the lack of compelling evidence, particularly in the form of 85  
isolated organometallic intermediates and their subsequent 86  
reactivity. On this basis, and in order to gain information on 87  
the mechanism, we performed a series of experiments with 88  
silirene 1 at the catalytic and stoichiometric levels by 89  
combining catalysis and coordination chemistry. We were 90  
indeed able to isolate and fully characterize the first 91  
intermediate I derived from the activation of the silirene and 92  
study its fate upon reaction with an alkyne by multinuclear 93  
NMR spectroscopy. In addition, extensive DFT calculations 94  
enabled us to explain and corroborate our results, providing a 95  
better description of the elementary steps, the nature of the 96  
higher-energy intermediates, and ultimately the whole process. 97

## RESULTS AND DISCUSSION

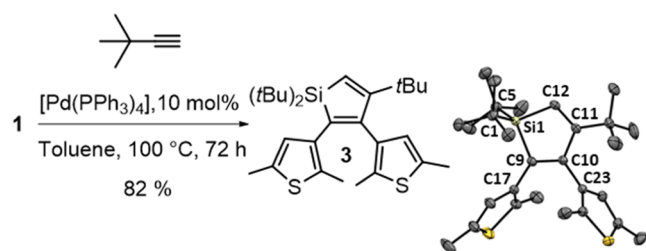
**Palladium-Catalyzed Reaction with Silirene 1 and 98  
Acetylene.** The reactivity of silirenes with alkynes under 99  
palladium-catalyzed conditions is intimately associated with 100  
steric factors, and their behavior strongly depends on the 101  
substitution pattern both at the silicon and at the carbon atoms 102  
of the three-membered ring heterocycle but also on the alkyne 103  
involved in the reaction.<sup>19</sup> In that respect, silirene 1 does not 104  
evolve in solution in the presence of [Pd(PPh<sub>3</sub>)<sub>4</sub>], even upon 105  
prolonged heating at 100 °C. *Si*,*Si*-Di-*tert*-butyl silirenes 106  
display enhanced kinetic stability, and no disilacyclohexadiene 107  
compounds of type A resulting from the silirene [3 + 3]- 108  
cyclodimerization<sup>21</sup> [Scheme 2—route (1)] could be observed 109  
in our case. This trend was confirmed by the reaction of 1 110  
with acetylene (1 bar) under catalytic conditions. In that case, 111  
neither disilacyclohexadiene compounds B [Scheme 2—route 112  
(4)] nor bicyclic compounds of type C [Scheme 2—route (5)] 113  
as in the case of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene 114  
were detected.<sup>18</sup> The corresponding silole 2 was obtained as 115  
the sole product (Figure 1) and isolated in 80% isolated yield 116  
after purification by flash chromatography on silica gel. Single 117  
crystals of 2 could be obtained from a saturated pentane 118  
solution at room temperature, and their structure was 119  
determined by X-ray diffraction analysis. 120

**Steric and Electronic Effects of the Alkyne on the 121  
Annulation Reaction.** The influence of both the steric and 122  
the electronic nature of the terminal alkyne substrate was also 123  
investigated in order to get insight into the mechanism and to 124  
explain the exclusive chemo and regioselectivity observed with 125  
1. First, this study suggests that steric factors play a more 126  
prominent role than we initially thought in our case. This 127  
could be confirmed by the reaction of *tert*-butylacetylene and 128  
trimethylsilylacetylene that bear quaternary substituents 129  
directly linked to the triple bond. While the two substrates 130  
revealed total unreactivity under the standard catalytic 131  
conditions, the *tert*-butyl substituted silole 3 could be finally 132  
formed selectively under forcing conditions (100 °C, 72 h., cat. 133  
loading 10 mol %) and isolated in 82% yield after column 134  
chromatography on silica gel (Figure 2). 3 could be fully 135  
characterized by NMR, HRMS, as well as X-ray diffraction 136  
analyses. 137

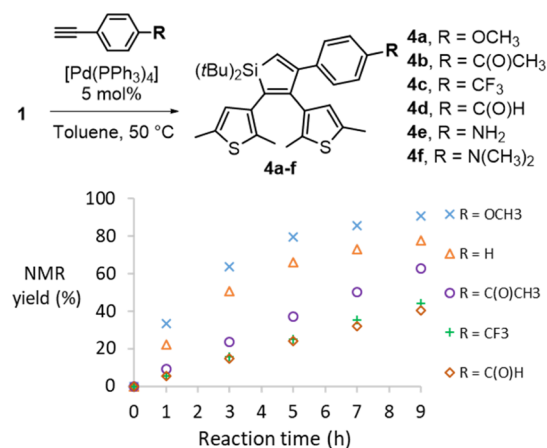
In a second stage, the electronic effects of the alkyne 138  
substituents on the catalytic process were assessed by using 139  
different para-substituted ethynylbenzenes R–pC<sub>6</sub>H<sub>4</sub>–C≡C– 140  
141



**Figure 1.** Reactivity of **1** with acetylene under Pd-catalyzed conditions, giving silole **2**, and X-ray structure of **2** with a displacement ellipsoid plot at a 50% probability level; non-vinyl hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C12 1.872(2), Si1–C9 1.9005(19), C11–C12 1.343(3), C10–C11 1.491(3), C9–C10 1.369(3), C9–C17 1.474(3), C10–C23 1.477(3); C1–Si1–C9 115.53(9), C1–Si1–C5 116.62(9), C1–Si1–C12 108.51(9), C5–Si1–C9 109.74(8), C5–Si1–C12 111.91(9), C9–Si1–C12 91.86(9).



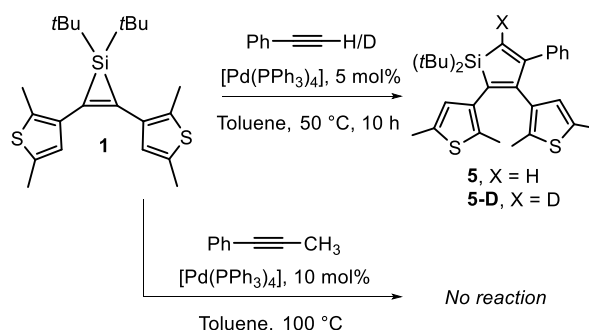
**Figure 2.** Synthesis of silole **3** by Pd-catalyzed annulation of **1** and *tert*-butylacetylene under forcing conditions (left). X-ray structure of **3** (right) with a displacement ellipsoid plot at a 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C9 1.8871(18), Si1–C12 1.8537(19), C9–C10 1.359(2), C10–C11 1.528(2), C11–C12 1.349(3), C9–C17 1.485(2), C10–C23 1.491(2); C1–Si1–C9 113.17(8), C1–Si1–C5 116.98(8), C1–Si1–C12 106.41(8), C5–Si1–C9 111.67(8), C5–Si1–C12 114.81(9), C9–Si1–C12 90.84(8).



**Figure 3.** Synthesis of siloles **4a–f** by Pd-catalyzed annulation of para-substituted phenylacetylenes with **1** (top) and the plot of the catalytic transformations over time (down) for R = OCH<sub>3</sub>, H, C(O)CH<sub>3</sub>, CF<sub>3</sub>, and C(O)H monitored by <sup>1</sup>H NMR spectroscopy (C<sub>6</sub>D<sub>6</sub>, internal standard DCE).

affording the previously described silole **5** and its isotopomer **5-D** (Scheme 4). No KIE could be observed from the rate of

#### Scheme 4. Control Experiments of **1** with Protio-, Deutero-phenylacetylene, and 1-Phenyl-1-propyne



formation, suggesting that acetylenic C–H bond cleavage either does not occur at all or is not involved in the rate-determining step of the reaction. Additionally, and as observed by the group of Palmer and Woerpel, the reaction is clearly limited to terminal alkynes.

Our attempts to react **1** with 1-phenyl-1-propyne left the starting materials unchanged even under forcing conditions (Scheme 4, bottom).

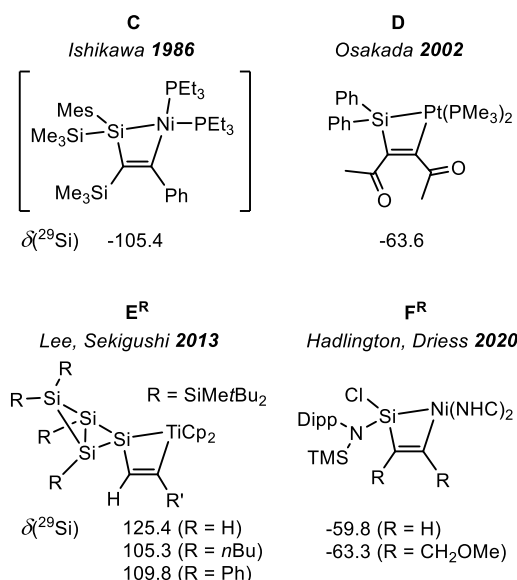
**OA of Palladium to Silirene 1.** At that stage, we turned to coordination chemistry studies in order to address the question of palladacycles of type I (Scheme 3) in the palladium-catalyzed annulation reaction. 1,2-metallacyclobutenes are organometallic complexes with an unsaturated four-membered cyclic structure where a transition metal center is stabilized by two sigma bonds of different nature,  $\sigma$ -C–M and  $\sigma$ -Si–M, respectively. Although often invoked,<sup>6c,16b,23</sup> these complexes are rare and limited in number. A first description was reported by Ishikawa<sup>24</sup> in the case of nickelasilacyclobutene **C** generated from a silirene and [(PEt<sub>3</sub>)<sub>4</sub>Ni(0)] (Figure 4).

It revealed instability and was only characterized in situ by NMR spectroscopy. Since then, other examples have appeared (D, E<sup>R</sup>, and F<sup>R</sup>),<sup>25</sup> but only four of them have been structurally characterized so far in the case of Pt (D), Ti (E<sup>H</sup>), and Ni (F<sup>H</sup> and F<sup>CH<sub>2</sub>OMe</sup>) (Figure 4). They are either obtained by the [2 +

63

142 H (Figure 3, top). As previously reported, the catalytic transformation is tolerant to various functional groups, and we were pleased to observe the full conversion to aryl-substituted siloles **4a–f** that were isolated in quantitative yield, except **4d** (22% isolated yield) due to its degradation over silica gel during the purification step. They were all characterized by multinuclear NMR spectroscopy and HRMS analysis (see S6–S9). The NMR monitoring of the reaction shows that electron-rich substrates react faster, with the following tendency: –OMe > –H > –C(O)CH<sub>3</sub> > –C(O)H ~ –CF<sub>3</sub> (Figure 3, bottom).<sup>22</sup>

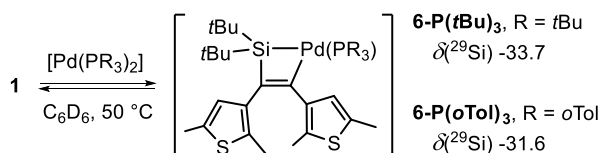
To gain further information on the mechanism of the reaction and more particularly on the coordination of the alkyne to the palladium in the catalytic process, the kinetic isotope effect (KIE) associated with a possible C–H bond cleavage of the alkyne moiety was evaluated. The study was conducted independently with protio and deutero phenylacetylene, Ph–C≡C–H, and Ph–C≡C–D, respectively,



**Figure 4.** Previously described 1,2-metallasilacyclobutenes **C–F** and corresponding  $^{29}\text{Si}$  NMR of the Si–M silicon nucleus.

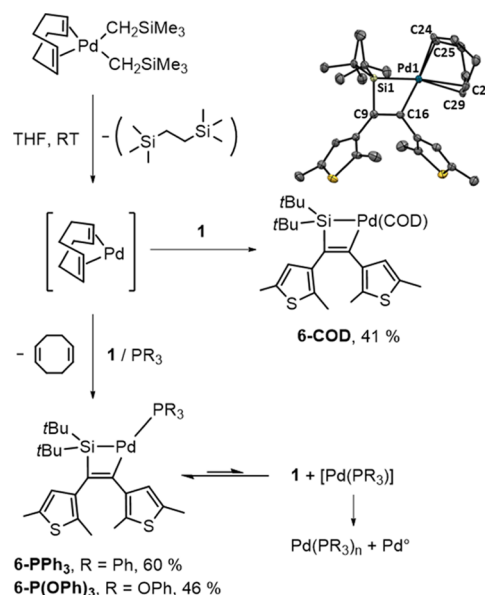
186 2]-cycloaddition of the Si=M bond of a terminal silylene (M  
187 = Ni, Ti) with the C≡C triple bond of an alkyne or, in the  
188 case of Pt, by ring closure involving a  $\gamma$ -Si–H bond activation  
189 from a 3-sila-1-propenyl(silyl)platinum precursor and silane  
190 elimination. After perusal of the literature, we first assumed  
191 that 1,2-palladasilacyclobutenes should be accessed by OA of  
192 an adapted palladium precursor to silirene **1**. We first started to  
193 study the reactivity of silirene **1** with low-coordinated  
194 palladium (0) complexes  $[(\text{PR}_3)_2\text{Pd}]$  (R = *t*Bu, *o*Tol) that  
195 are known to easily undergo OA reactions (Scheme 5).

### Scheme 5. Preparation of **6-P(*t*Bu)<sub>3</sub>** and **6-P(*o*Tol)<sub>3</sub>** by Reaction of **1** and $[\text{Pd}(\text{PR}_3)_2]$



196 The reaction monitoring at 50 °C by  $^{31}\text{P}\{^1\text{H}\}$  NMR of **1**  
197 with both complexes independently revealed the appearance of  
198 a new species displaying a resonance signal at  $\delta$  80.9 (R = *t*Bu)  
199 and  $\delta$  25.3 (R = *o*Tol) in addition to the remaining starting  
200 materials. The conversion to the product was estimated to be  
201 40% and 82% for R = *t*Bu and R = *o*Tol, respectively.<sup>26</sup> In the  
202  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum, new singlet resonance signals at  $\delta$   
203  $-33.7$  (R = *t*Bu) and  $\delta$   $-31.6$  (R = *o*Tol), low field shifted  
204 regarding the starting material ( $\delta$   $-69.9$ ), were observed.  
205 Except for the special case of titanasilacyclobutenes **E<sup>R</sup>** that  
206 exhibit a peculiar deshielded signal for the Ti-bound Si atom,  
207 the observed values are downfield shifted compared to the  
208 values from the other group 10 metallocyclobutenes **C**, **D**, and  
209 **F<sup>R</sup>** (Figure 4).<sup>27</sup> This feature could be attributed to the nature  
210 of the exocyclic silicon SiRR' substituents. Despite this  
211 discrepancy, the spectroscopic data from the full NMR  
212 characterization are consistent with a 1,2-palladacyclobutene  
213 structure for **6-P(*t*Bu)<sub>3</sub>** and **6-P(*o*Tol)<sub>3</sub>** with a monophosphine-  
214 coordinated palladium center. Unfortunately, attempts to  
215 isolate any of the two compounds by crystallization gave

solid  $\text{Pd}(\text{PR}_3)_n$  ( $n = 2, 3$ ) complexes. NMR analysis of the 216  
mother liquors revealed only the presence of **1** in solution with 217  
minor decomposition products. This result is in agreement 218  
with previous NMR spectroscopic analyses (vide supra) and 219  
again suggests that the OA process leading to **6-P(*t*Bu)<sub>3</sub>** and **6-** 220  
**P(*o*Tol)<sub>3</sub>** is an equilibrated process. In view of these results, we 221  
reasoned that the excess phosphine ligand in solution could be 222  
the cause of the difficulties encountered in isolating complex **6**. 223  
We hypothesized that this point could be circumvented by the 224  
use of a “phosphine-free” palladium(0) precursor in the 225  
presence of a stoichiometric amount of a chosen phosphine. 226  
We then turned to the use of the thermally unstable 227  
 $[(\text{COD})\text{Pd}(\text{CH}_2\text{TMS})_2]$  dialkyl complex<sup>28</sup> as the convenient 228  
precursor of the active 14 electron  $[(\text{COD})\text{Pd}]$  transient 229  
complex by simple reductive elimination of  $(\text{TMS}-\text{CH}_2)_2$  230  
(Figure 5, top).<sup>29</sup> A clean reaction occurs between **1** and 231 15

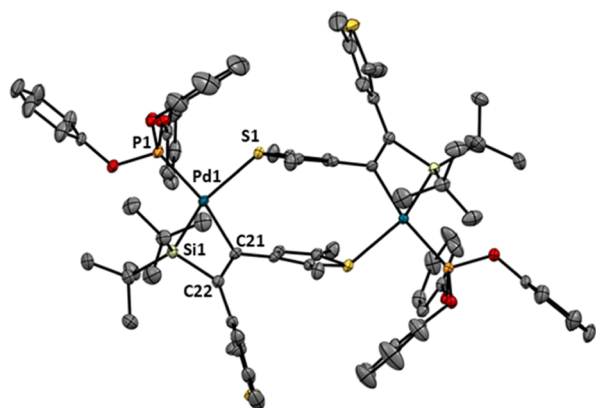


**Figure 5.** Decomposition of  $[(\text{COD})\text{PdR}_2]$  to  $[(\text{COD})\text{Pd}]$  and its reactivity with (i) **1** affording **6-COD** (right) and (ii) **1** and  $\text{PR}_3$  (R = Ph, OPh) affording **6-PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>** (bottom). X-ray structure of **6-COD** (top right) with a displacement ellipsoid plot at a 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C24 2.309(3), Pd1–C25 2.351(2), Pd1–C28 2.454(3), Pd1–C29 2.510(3), Pd1–Si1 2.3237(9), Pd1–C16 2.064(3), Si1–C9 1.859(3), C9–C16 1.352(4); Si1–C9–C16 91.54(18), C9–C16–Pd1 116.37(18), C16–Pd1–Si1 63.75(8).

$[(\text{COD})\text{Pd}(\text{CH}_2\text{TMS})_2]$  in THF at room temperature (Figure 232  
**5**, right), as shown by the  $^1\text{H}$  NMR monitoring and the 233  
appearance of a singlet resonance signal at  $\delta$   $-34.8$  in the 234  
 $^{29}\text{Si}\{^1\text{H}\}$  NMR in agreement with the values obtained in the 235  
case of **6-P(*t*Bu)<sub>3</sub>** and **6-P(*o*Tol)<sub>3</sub>**. After work-up, **6-COD** could 236  
be isolated as colorless crystals in 41% yield, and its structure 237  
was determined by X-ray diffraction analysis. In the solid state, 238  
the palladium is in a distorted square-planar environment with 239  
an acute C16Pd1Si1 angle of  $63.75(8)^\circ$  [ $\Sigma_\alpha(\text{LPdL}) = 360^\circ$ ]. 240  
The Si1Pd1 distance of 2.3237(9) Å is in the range of 241  
previously characterized silyl palladium(II) complexes (2.25– 242  
2.43 Å). Within the four-membered metallacycle, the C9Si1 243  
bond of 1.859(3) Å is slightly elongated relative to the 244  
endocyclic Si–C bonds in **1** (1.82 Å in average), whereas the 245  
Si1C16 distance of 2.327(3) Å largely exceeds the sum of 246

247 covalent radii of the two atoms (1.84 Å,  $R = 1.26$ ), confirming  
 248 the cleavage of this bond. The C=C double bond length of  
 249 1.352(4) Å is identical to that in **1** [1.352(2) Å] with the  
 250 exocyclic thienyl groups in an antiparallel conformation as in  
 251 DTE derivatives.<sup>30</sup> The geometry around the C9 olefinic  
 252 carbon atom deviates strongly from the ideal  $sp^2$  arrangement  
 253 with an acute C16C9Si1 angle of 88.09(9)°. This particular  
 254 feature is more pronounced than in the case of the heavier  
 255 platinum derivative **D** (97.8(5)°) but comparable to the case  
 256 of the lighter nickel complexes **F** (average of 89.3°).

257 Following a similar synthetic strategy, **1** can be treated with  
 258 [(COD)Pd(CH<sub>2</sub>TMS)<sub>2</sub>] in the presence of a stoichiometric  
 259 amount of phosphine ligands, leading to the exchange of the  
 260 cyclooctadiene ligand (Figure 5, bottom). With one equivalent  
 261 of Ph<sub>3</sub>P or (PhO)<sub>3</sub>P, the monophosphine complexes **6-PPh<sub>3</sub>**  
 262 and **6-P(OPh)<sub>3</sub>** could be obtained in 65 and 46% yield,  
 263 respectively, and fully characterized by NMR spectroscopy.  
 264 The NMR spectra of **6-PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>** are contaminated  
 265 with a small amount of palladium(0) phosphine complexes  
 266 Pd(PR<sub>3</sub>)<sub>*n*</sub> (R = Ph, OPh), as well as silirene **1** (~5%). This can  
 267 be explained by the existence of an equilibrium between **6-**  
 268 **PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>** and their reductive elimination products  
 269 **1** and [Pd(PR<sub>3</sub>)<sub>*n*</sub>] that lead to the slow decomposition of **6-**  
 270 **PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>** and the release of Pd<sup>0</sup> (Figure 5).<sup>31</sup> For  
 271 the two complexes **6-PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>**, the <sup>29</sup>Si NMR  
 272 display a resonance signal at a similar chemical shift (**6-PPh<sub>3</sub>** δ  
 273 -27.2, **6-P(OPh)<sub>3</sub>** δ -26.9) and as a doublet due to scalar  
 274 coupling to the <sup>31</sup>P nucleus (<sup>2</sup>*J*<sub>SiP</sub> = 2.1 Hz, **6-PPh<sub>3</sub>**; <sup>2</sup>*J*<sub>SiP</sub> = 4.7  
 275 Hz, **6-P(OPh)<sub>3</sub>**), indicative of the expected P-Pd-Si  
 276 connectivity. Single crystals of **6-P(OPh)<sub>3</sub>** suitable for X-ray  
 277 diffraction analysis were grown at -30 °C from a saturated  
 278 pentane/THF solution and their X-ray structure determined at  
 279 150 K (Figure 6).

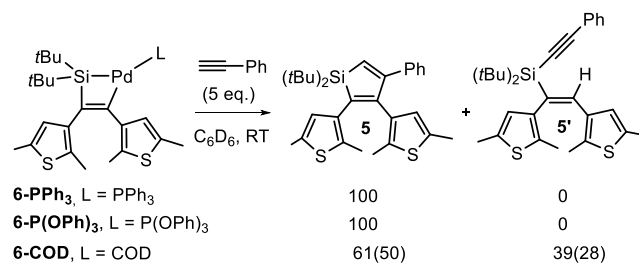


**Figure 6.** X-ray structure of **6-P(OPh)<sub>3</sub>** with a displacement ellipsoid plot at a 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1-C21 2.085(2), Pd1-Si1 2.3380(7), Pd1-S1 2.6384(7), Pd1-P1 2.2548(7), Si1-C22 1.857(2), C22-C21 1.362(3), P1-Pd1-S1 104.38(2), C21-Pd1-S1 100.47(7), C21-Pd1-Si1 64.42(7), P1-Pd1-Si1 104.38(2), C21-C22-Si1 93.41(16).

280 In the solid state, it displays a dimeric structure revealing an  
 281 intermolecular thienyl-to-palladium S → Pd coordination  
 282 [Pd1S1 2.6384(7) Å; Pd2S3 2.6438(7) Å] with the thienyl  
 283 ligand in *trans*-position to the silyl ligand. The 1,2-  
 284 palladasilacyclobutene four-membered ring of **6-P(OPh)<sub>3</sub>**  
 285 exhibits similar geometric features as those of **6-COD**. To  
 286 further explore the catalytic cycle, we continued by assessing

the reactivity of the palladacycles with terminal alkynes in  
 stoichiometric experiments (Scheme 6).

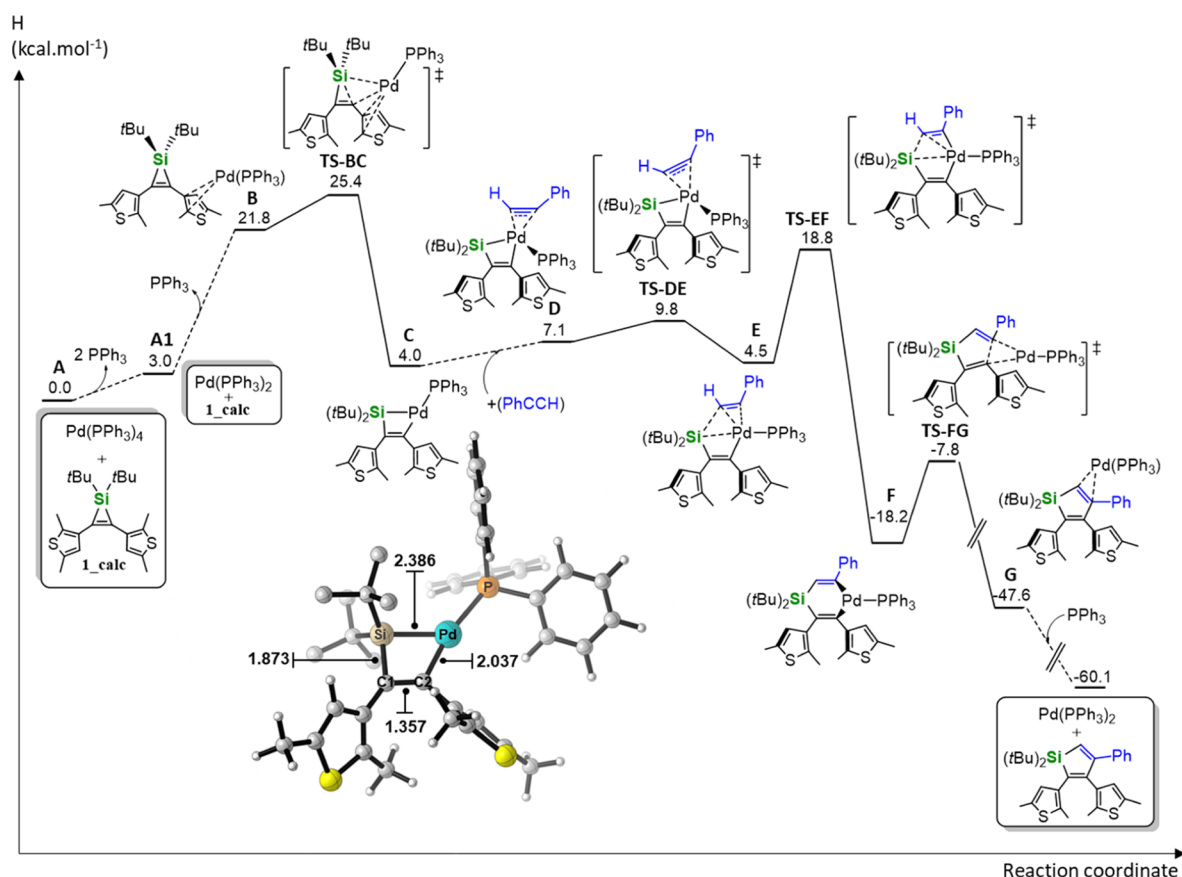
### Scheme 6. Reactivity of Metallasilacyclobutene **6-L** (L = PPh<sub>3</sub>, P(OPh)<sub>3</sub>, and COD) with Phenyl Acetylene



Both complexes **6-PPh<sub>3</sub>** and **6-P(OPh)<sub>3</sub>** react readily with  
 phenylacetylene at room temperature ( $t \approx 5$  and 30 min,  
 respectively) to form selectively the model silole **5** as observed  
 in the implemented catalytic conditions. Interestingly, the  
 same reaction with **6-COD** is much slower and gives a mixture  
 of **5** and an acyclic structural isomer **5'** in 50 and 28%  
 isolated yield, respectively (see S20 for details). The structure of **5'**  
 was determined thanks to HRMS and multinuclear NMR analyses.  
 In particular, the <sup>3</sup>*J*<sub>SiH</sub> coupling constant of 6.9 Hz indicates  
 that the central olefin has retained its stereochemistry with the  
 thienyl groups in the *cis* position.

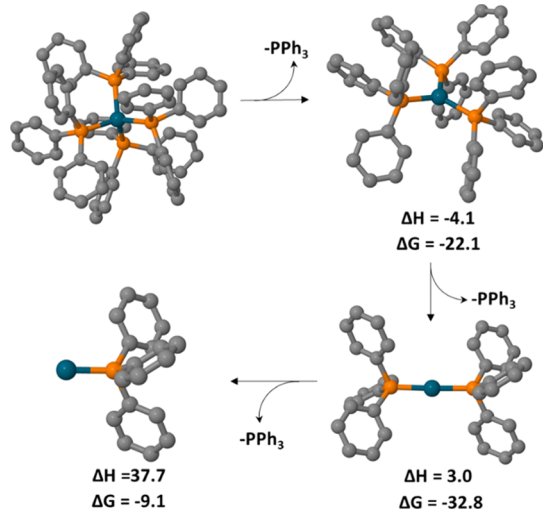
These results strongly support the involvement of a  
 monophosphine-ligated 1,2-palladasilacyclobutene key inter-  
 mediate in the palladium-catalyzed annulation reaction. With  
 the objective of detecting intermediates derived from the  
 palladacycle, the reaction between **6-PPh<sub>3</sub>** and phenyl  
 acetylene was monitored by NMR, at low temperature, in  
 CD<sub>2</sub>Cl<sub>2</sub>. At 203 K, the <sup>1</sup>H NMR revealed the presence of  
 resonance signals attributed to the model silole **5**<sup>33</sup> together  
 with the remaining **6-PPh<sub>3</sub>** in a 1.33:1 ratio. Besides remaining  
**6-PPh<sub>3</sub>**, the <sup>31</sup>P NMR spectra exhibit an AB spin system with a  
 coupling constant (<sup>2</sup>*J*<sub>PP</sub> = 18.4 Hz) that is indicative of the  
 presence of a Pd complex with two phosphines in the *cis*  
 position. Based on multinuclear NMR 2D experiments  
 (HMQC <sup>1</sup>H-<sup>31</sup>P, HSQC, and HMBC <sup>1</sup>H-<sup>13</sup>C) and after  
 comparison to experimental data available in the literature,<sup>34</sup>  
 the Pd(0)-alkyne  $\pi$ -complex [(Ph<sub>3</sub>P)<sub>2</sub>Pd( $\eta^2$ -PhC≡CH)]  
 could be identified unambiguously (see S21-S25). It most  
 likely results from ligand redistribution after the release of the  
 silole ring between residual [Pd(PPh<sub>3</sub>)<sub>*n*</sub>] and the excess of  
 phenylacetylene present in the medium. This experiment  
 clearly shows that the elementary steps occurring in the  
 catalytic cycle after the formation of the 1,2-palladasilacyclo-  
 butene intermediate by OA require only little kinetic energy in  
 the case of phenylacetylene. In that respect, the instability of  
 1,4-palladasilacyclohexadiene (type II species, Scheme 3)  
 toward reductive elimination and silole formation is reminis-  
 cent of the behavior of nickel analogues,<sup>25d</sup> contrary to the  
 platinum ones that proved stable at room temperature.<sup>25b</sup>

**Theoretical Insight into the Reaction Mechanism.** In  
 order to get more insights into the reaction mechanism, DFT  
 calculations at the B3PW91 level of theory have been  
 performed, and the corresponding enthalpy profile computed  
 with silirene **1** and phenylacetylene is shown in Figure 7 (for  
 the Gibbs free energy profile, see Figure S127 in the  
 Supporting Information).



**Figure 7.** DFT-computed enthalpy profile ( $\text{kcal mol}^{-1}$ ) of the Pd-catalyzed annulation reaction of phenylacetylene with silirene **1**; optimized structure of **C** and bond lengths within the Si–C–C–Pd metallacycle.

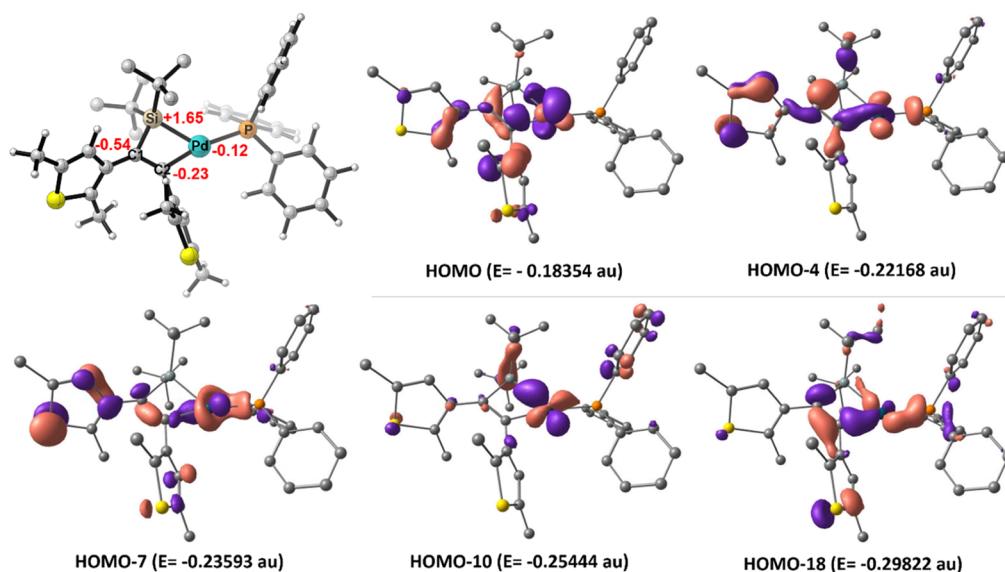
335 **Phosphine Dissociation.** Since the  $[\text{Pd}(\text{PPh}_3)_4]$  com-  
 336 pound is electronically saturated, the first step consists in the  
 337 release of phosphine ligands to generate a reactive species. In  
 338 order to evaluate the lability of the phosphine ligands bound to  
 339 the Pd center, we computed the  $\text{PPh}_3$  dissociation energy  
 340 starting from  $\text{Pd}(\text{PPh}_3)_4$ . As shown in Figure 8, the



**Figure 8.** DFT-computed enthalpy and Gibbs free energy values for the  $\text{PPh}_3$  dissociation reaction starting from the  $\text{Pd}(\text{PPh}_3)_4$  compound. The  $\Delta H$  and  $\Delta G$  values refer to the starting  $\text{Pd}(\text{PPh}_3)_4$  compound.

dissociation of one, two, and three  $\text{PPh}_3$  ligands displays a  
 $\Delta H$  of  $-4.1$ ,  $+3.0$ , and  $+37.7 \text{ kcal mol}^{-1}$  ( $\Delta G$  of  $-22.1$ ,  $-32.8$ ,  
 and  $-9.1 \text{ kcal mol}^{-1}$ ), respectively, indicating that the starting  
 $\text{Pd}(\text{PPh}_3)_4$  compound spontaneously loses two  $\text{PPh}_3$  ligands in  
 solution to afford the  $\text{Pd}(\text{PPh}_3)_2$  species (**A1** in Figure 7),  
 which is in line with literature data.<sup>35</sup> The replacement of the  
 third phosphine by silirene **1** to form **B** is an energetically  
 costly step ( $21.8 \text{ kcal mol}^{-1}$ ), which prepares the following OA  
 reaction.

**OA and 1,2-Palladasilacyclobutene Formation.** In  
 accordance with the experimental results reported above for  
 the synthesis of **6-PtBu<sub>3</sub>** and **6-P(oTol)<sub>3</sub>**, the 1,2-palladasila-  
 cyclobutenes species **C** (**6-PPh<sub>3</sub>**) is in equilibrium with the  
 in situ-formed  $\text{Pd}(\text{PPh}_3)_2$  species **A1**, with the displacement  
 of the equilibrium toward the OA product **C** requiring thermal  
 conditions ( $50 \text{ }^\circ\text{C}$ ), given the presence of a large amount of  
 free phosphine in solution. This OA reaction involves an early  
 transition state where the C–Si bond is only slightly elongated  
 with a low associated barrier of  $3.6 \text{ kcal mol}^{-1}$  (**TS-BC**)  
 compared to **B**. For comparison purposes, the possibility of a  
 first step involving the reaction between  $\text{Pd}(0)$  and the  
 terminal alkyne was also considered (see Figure S128 in the  
 Supporting Information). Starting from a diphosphine  
 palladium (0)  $\pi$ -complex  $[(\text{Ph}_3\text{P})_2\text{Pd}(\eta^2\text{-PhC}\equiv\text{CH})]$  **H**, the  
 OA of the C–H bond to form the palladium (II) hydride  
 $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}\equiv\text{CPh})]$  (**H**) was, however, revealed to be  
 highly endothermic ( $18.0 \text{ kcal mol}^{-1}$ ) with an associated  
 kinetic barrier of  $19.9 \text{ kcal mol}^{-1}$  (**TS-HI**). This unfavorable  
 step and the failure to localize the subsequent intermediates



**Figure 9.** Geometry, NPA charge analysis, and representative MOs of the 1,2-metallasilacyclobutene **C** (isodensity value = 0.05 au).

370 made us rule out this alternative option. Due to its peculiar  
371 structure, the OA product **C** has been analyzed in more detail.

372 **1,2-Palladasilacyclobutene Scaffold.** As shown in  
373 **Figure 7**, the 1,2-palladasilacyclobutene **C** compound (6-  
374 **PPh<sub>3</sub>**) displays a distorted T-shape environment around  
375 palladium with an acute C2PdSi angle of 60.69°. The SiPd  
376 distance (2.386 Å) is slightly longer than that measured  
377 experimentally for **6-COD** (2.3237(9) Å) and **6-P(OPh)<sub>3</sub>**  
378 (2.3380(7) Å) but still within the range of previously  
379 characterized silyl palladium(II) complexes (2.25–2.43 Å).  
380 Within the four-membered metallacycle, the C1–Si bond  
381 length of 1.873 Å is slightly elongated with respect to the  
382 endocyclic Si–C bonds of the computed silirene compound  
383 **1<sub>calc</sub>** (1.844 Å), whereas the C2Si distance of 2.255 Å largely  
384 exceeds the sum of covalent radii of the two atoms (1.84 Å, R  
385 = 1.26 Å). The C=C double bond length (1.357 Å) is  
386 identical to the one obtained for the computed silirene  
387 molecule (1.359 Å). The geometry around the C1 olefinic  
388 carbon atom is highly constrained, displaying an acute C2C1Si  
389 angle of 87.0°. To explore in depth the nature of the bonds  
390 involved in the Si–C–C–Pd cycle, we performed a NPA  
391 charge and MO analysis of **C** (**Figure 9**).

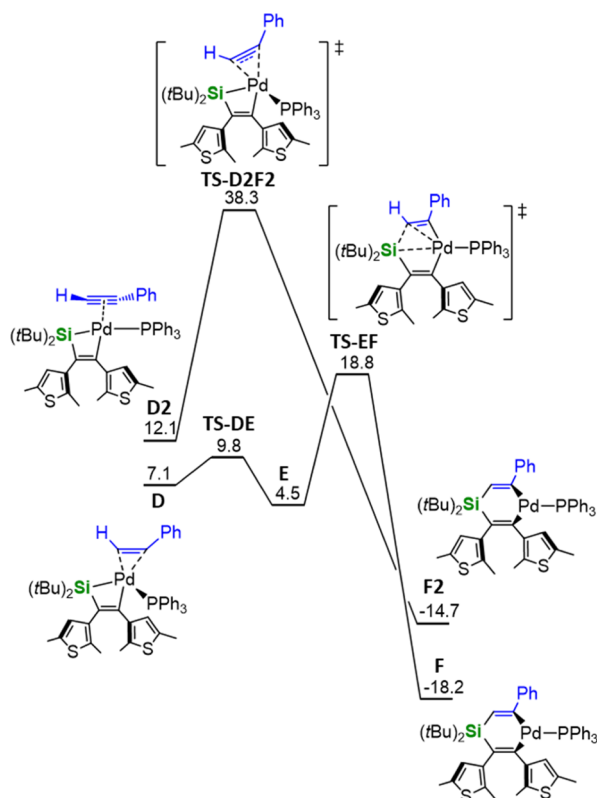
392 The computed natural charges indicate a positive charge of  
393 1.65 for the electropositive Si center, together with a slight  
394 polarization of the C1–C2 bond, with the C1 carbon carrying  
395 a more negative charge (−0.54) than the C2 carbon (−0.23).  
396 The computed molecular orbitals responsible for the bonding  
397 within the Si–C1–C2–Pd cycle are shown in **Figure 8**. The  
398 HOMO, HOMO-4, HOMO-7, HOMO-10, and HOMO-18  
399 orbitals describe the sigma bonding system of the four-  
400 membered 1,2-palladasilacyclobutene skeleton<sup>36,37</sup> (**Figure 8**),  
401 whereas the HOMO-1 and the HOMO-17 orbitals account for  
402 the  $\pi$  interaction between C1 and C2 (see **Figure S129** in the  
403 Supporting Information). No orbital overlapping is detected  
404 between the Si and C2 atoms, despite the large SiC2 distance  
405 observed experimentally in the X-ray structures of **6** (vide  
406 supra), ruling out any possibility of bonding between these two  
407 centers.

408 **Alkyne Insertion Process.** From **C** (6-**PPh<sub>3</sub>**), the alkyne  
409 may then insert into the Pd–Si bond of the metallacycle to  
410 form the 1,4-palladasilacyclohexadiene species. The process

occurs in three steps, involving (i) the coordination of the  
411 alkyne to **C**; (ii) the insertion of the alkyne into the Pd–Si  
412 bond with the retention of the Pd–Si bond (**TS-DE**), and (iii)  
413 the breaking of the Pd–Si bond (**TS-EF**) to afford the 1,4-  
414 palladasilacyclohexadiene species **F**. As shown in **Figure 7**, after  
415 the formation of **D**<sup>38</sup> via the endothermic coordination of the  
416 alkyne to **C** in a  $\eta^2$  side-on fashion (7.1 kcal mol<sup>−1</sup> with respect  
417 to the entrance channel **A**), the two-step insertion of the  
418 alkyne into the Pd–Si bond takes place through two kinetically  
419 accessible barriers of 9.8 and 18.8 kcal mol<sup>−1</sup>. The alternative  
420 scenario involving the alkyne insertion into the Pd–C bond  
421 has been excluded due to its unreasonably high kinetic barrier  
422 of 39.6 kcal mol<sup>−1</sup> (see **Figures S132 and S133** in the  
423 Supporting Information). The resulting 1,4-palladasilacyclo-  
424 hexadiene species **F** is exothermic by −18.2 kcal mol<sup>−1</sup> and  
425 represents the driving force of the reaction. Two regioisomers  
426 are possible depending on whether the terminal alkyne carbon  
427 binds the Si atom (**Figure 7**) or the Pd atom (see **Figures S134**  
428 and **S135** in Supporting Information). As shown in **Figures 7**  
429 and **S134** in the Supporting Information, the formation of the  
430 regio-isomer displaying the terminal alkyne carbon bonded to  
431 the Si atom is more favorable, both kinetically and  
432 thermodynamically (**TS-DE** = 9.8 kcal mol<sup>−1</sup>; **TS-EF** = 18.8  
433 kcal mol<sup>−1</sup>; **F** = −18.2 kcal mol<sup>−1</sup> vs **TS-DIE1** = 28.6 kcal  
434 mol<sup>−1</sup>; **TS-E1F1** = 32.3 kcal mol<sup>−1</sup>; **F1** = −12.4 kcal mol<sup>−1</sup>);  
435 the steric repulsion between the *t*Bu groups at the Si center  
436 and the phenyl substituent of the alkyne plays an important  
437 role.

438 **Reductive Elimination Step.** From species **F** in **Figure 7**,  
439 an easy reductive elimination process may then occur with a  
440 kinetic barrier of 10.4 kcal mol<sup>−1</sup>, leading to the exothermic  
441 formation of the experimentally observed silole product (**G** =  
442 −47.6 kcal mol<sup>−1</sup>). The relative orientation of the two thienyl  
443 substituents is likely to play an important role when tetra-  
444 coordinate Pd species are involved. This is related to the well-  
445 known conformational preference of the DTE skeleton for two  
446 possible antiparallel orientations of the thienyl groups,<sup>30</sup>  
447 resulting in two possible diastereomeric structures when  
448 tetracoordinated Pd species are involved. As shown by the  
449 comparison between the enthalpy profiles in **Figure 10** (see  
450 **Figures S136 and S137** in the Supporting Information for the  
451





**Figure 10.** DFT-computed enthalpy profiles for the formation of 1,4-palladasilacyclohexadiene F from  $\pi$ -complex D with the two possible antiparallel orientation of the thienyl groups.

corresponding Gibbs free energy profiles), the different orientation of the thienyl groups particularly affects the alkyne insertion step.

Starting from the alkyne  $\pi$ -complex D2, indeed, the phenylacetylene insertion becomes a one-step process with an associated kinetic barrier of 38.2 kcal mol<sup>-1</sup> (TS-D2F2), which cannot compete with the pathway starting from D, displaying a kinetic barrier of 18.8 kcal mol<sup>-1</sup> (TS-EF).

**Electronic and Steric Effects in the Insertion Step of the Alkyne.** In line with the experimental observations, we computed the annulation reaction of different para-substituted ethynylbenzenes R-*p*C<sub>6</sub>H<sub>4</sub>-C≡C-H (R = CF<sub>3</sub> and OMe). As shown in Figures S138–S141 in the Supporting Information, compared to the phenylacetylene analogues, the energies of intermediates D<sub>CF3</sub> and D<sub>OMe</sub> differ by less than 2 kcal mol<sup>-1</sup> (5.9 and 7.5 kcal mol<sup>-1</sup>, respectively, compared to 7.1 kcal mol<sup>-1</sup> for D) and the energies of alkyne insertion transition states, TS-DE<sub>CF3</sub>, TS-EF<sub>CF3</sub> and TS-DE<sub>OMe</sub>, TS-EF<sub>OMe</sub> by less than 4 kcal mol<sup>-1</sup> (8.8 and 10.1 kcal mol<sup>-1</sup> compared to 9.8 kcal mol<sup>-1</sup> for TS-DE and 16.5 and 19.7 compared to 18.8 kcal mol<sup>-1</sup> for TS-EF). According to the literature,<sup>39</sup> these values are of the same order of magnitude as the accuracy of the DFT method used here, indicating that the electronic effects of the alkyne substituents observed experimentally are too small to be rationalized by DFT methods. The same conclusion applies to the effect of PPh<sub>3</sub> and P(OPh)<sub>3</sub> phosphines. As shown in the comparison of the enthalpy profiles of the Pd-catalyzed annulation reaction of Ph-C≡C-H with silirene 1 in the presence of PPh<sub>3</sub> and P(OPh)<sub>3</sub> (Figure S142), the effect of phosphine on the reaction and, more particularly, on the stabilization of the

intermediates is too small to allow a clear differentiation by means of DFT calculations. To further confirm the presence of one phosphine coordinated to the Pd center during the alkyne insertion process, we computed the phosphine dissociation from adduct D (D4) and the following PhCCH insertion reaction without the PPh<sub>3</sub> coordination. As shown in the enthalpy profile in Figure S143, while the phosphine dissociation from D to D4 is athermic, the following PhCCH insertion becomes kinetically unfavorable, with the corresponding transition state enthalpy passing from 9.8 kcal mol<sup>-1</sup> (TS-DE) to 36.4 kcal mol<sup>-1</sup> (TS-D4E4). To get more insight into the steric factors, we also computed the annulation reaction of *tert*-butylacetylene (see Figures S144 and S145 in the Supporting Information). This time the energy of intermediate D<sub>tBu</sub> is significantly higher than that of intermediate D (11.3 vs 7.1 kcal mol<sup>-1</sup>), and the formation of the 1,4-palladasilacyclohexadiene compound involves higher kinetic barriers (14.2 and 23.6 kcal mol<sup>-1</sup> for TS-DE<sub>tBu</sub> and TS-EF<sub>tBu</sub> vs 9.8 and 18.8 kcal mol<sup>-1</sup> for TS-DE and TS-EF). Compared to phenylacetylene, therefore, the more forcing conditions needed with *tert*-butylacetylene, (100 °C, 72 h., cat. loading 10 mol %) may be accounted for by both its more endothermic coordination and its less kinetically favorable insertion barriers.

## CONCLUSIONS

In summary, this work contributes to a better understanding of the Pd-catalyzed silole synthesis from alkynes and silacyclopropenes in terms of scope, limitations, and mechanism. The influence of the alkyne substrate was first evaluated, revealing that the reaction is nicely functional group tolerant. When conducted under an acetylene atmosphere, no scrambling of the reagents is observed, with the corresponding silole being the sole product of the reaction. The steric and electronic environment at the alkyne group has a significant impact on the reaction kinetics: while electron-rich alkynes react faster, sterically hindered alkynes display considerably lower reaction rates. In particular, a slow reaction is observed with the bulky *t*Bu-C≡C-H whereas no reaction is detected in the case of Me<sub>3</sub>Si-C≡C-H. From a mechanistic point of view, the question of the involvement in the process of the hitherto unknown 1,2-palladasilacyclobutene intermediate was duly addressed. Four monophosphine-coordinated 6-PR<sub>3</sub> (R = *o*Tol, *t*Bu, Ph, and OPh) and one cyclooctadiene-ligated 6-COD 1,2-palladasilacyclobutene could be prepared and characterized by multinuclear NMR spectroscopy. The OA of Pd(0) precursors to silacyclopropene 1 was found to be equilibrated in all cases. The nature of the 1,2-palladasilacyclobutenes could be ultimately ascertained by the X-ray diffraction analysis of 6-P(OPh)<sub>3</sub> and 6-COD. Under stoichiometric conditions, 6-PPh<sub>3</sub> reacts cleanly with phenylacetylene to afford the expected silole, thus strongly supporting the involvement of 1,2-palladasilacyclobutene as a key intermediate of the catalytic cycle. The putative 1,4-palladasilacyclohexadiene intermediate resulting from the alkyne insertion could not be observed, most likely due to fast reductive elimination and silole formation even at low temperatures. For greater rationalization, we carried out a DFT study on the involved reaction mechanism by computing different possible mechanistic pathways and comparing the theoretical data with the experimental ones. The computational results indicate that the Pd-catalyzed annulation reaction of alkynes with silirene 1 occurs in three main steps, involving

(i) the OA of Pd(0) to the silirene; (ii) the insertion of the alkyne into the Pd–Si bond; and (iii) the reductive elimination on the 1,4-palladasilacyclohexadiene compound with the exothermic release of the silole product. The starting Pd(PPh<sub>3</sub>)<sub>4</sub> compound spontaneously evolves in solution to the Pd(PPh<sub>3</sub>)<sub>2</sub> species as the prelude of the OA of silirene via the endothermic loss of an additional phosphine. The resulting 1,2-palladasilacyclobutene species C is in equilibrium with the in situ-formed Pd(PPh<sub>3</sub>)<sub>2</sub> compound, with the displacement of the equilibrium toward the OA product requiring high thermal conditions (50 °C), given the presence of a large amount of free phosphine in solution. The subsequent alkyne insertion reaction occurs selectively into the Pd–Si bond of C, with the resulting 1,4-palladasilacyclohexadiene species displaying the terminal alkyne carbon bonded to the silicon atom. In accordance with the experimental results, therefore, the computational data confirm that the alkyne insertion is a chemo- and regio-selective reaction, with the formation of the experimentally observed silole strongly favored.

## EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox. CD<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, and THF d<sup>8</sup> were dried over calcium dihydride, distilled, and stored over 3 Å molecular sieves prior to use. Tetrahydrofuran was dried over calcium dihydride and distilled prior to use. All other solvents were purged with argon and dried using an MBRAUN solvent purification system. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer or a Bruker Avance III HD 500 NMR spectrometer. All <sup>29</sup>Si NMR spectra have been recorded with proton decoupling. Chemical shifts were expressed in parts per million, calibrated to residual <sup>1</sup>H (5.32 ppm for CD<sub>2</sub>Cl<sub>2</sub>, 7.16 ppm for C<sub>6</sub>D<sub>6</sub>, and 1.72 and 3.58 for THF d<sup>8</sup>) and <sup>13</sup>C (53.84 ppm for CD<sub>2</sub>Cl<sub>2</sub>, 128.06 ppm for C<sub>6</sub>D<sub>6</sub>, and 25.31 and 67.21 for THF d<sup>8</sup>), 85% H<sub>3</sub>PO<sub>4</sub>, and external tetramethylsilane solvent signals, respectively. Mass spectra were recorded on a MAXIS 4G or an Ultraflex III mass spectrometer. Elemental analyses were performed at the ScanMat-CRMPO on a Thermo Fisher Flash 1112 Series. Silirene 1<sup>17</sup> and [(COD)Pd(CH<sub>2</sub>TMS)<sub>2</sub>]<sup>29b</sup> were prepared according to literature procedures.

**Compound 2.** A Schlenk tube loaded with a solution of silirene 1 (60.0 mg, 0.154 mmol) and palladium tetrakis(triphenylphosphine) (8.9 mg, 7.7 × 10<sup>-3</sup> mmol, 5.0 mol %) in toluene (2 mL) was pressurized with acetylene (1 bar), and the resulting mixture was stirred for 19 h at 50 °C, giving a dark solution. The volatiles were then removed under reduced pressure, and the residue was then purified by column chromatography on silica gel (SiO<sub>2</sub>, 15 g, gradient: pentane 100% → pentane/DCM (95/5), R<sub>f</sub> (pentane) = 0.52), giving the expected compound as a crystalline white solid in 80% yield. Single crystals suitable for X-ray diffraction studies were obtained from a saturated pentane solution at room temperature.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ (ppm) 1.08 (s, 18H, CH<sub>3</sub> tBu), 1.66 (s, 3H, CH<sub>3</sub>-Th), 1.95 (s, 3H, CH<sub>3</sub>-Th), 2.32 (s, 3H, CH<sub>3</sub>-Th), 2.38 (s, 3H, CH<sub>3</sub>-Th), 6.18 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 10.5 Hz, Si-CH), 6.36 (s, 1H, H Th), 6.63 (s, 1H, H Th), 7.09 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 10.5 Hz, Si-C(H)=CH); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) 14.3 (s, CH<sub>3</sub>-Th), 14.7 (s, CH<sub>3</sub>-Th), 15.2 (s, CH<sub>3</sub>-Th), 15.4 (s, CH<sub>3</sub>-Th), 19.7 (s, C tBu), 29.1 (s, CH<sub>3</sub> tBu), 126.6 (s, CH Ph), 126.9 (s, CH Th), 129.7 (s, Si-CH), 130.0, 133.4, 135.4, 135.5, 135.7, 137.8, 138.0 and 148.9 (s, Cquat.), 152.0 (s, Si-C(H)=CH); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 79 MHz): δ (ppm) 21.8 (s). HRMS (ESI, CH<sub>2</sub>Cl<sub>2</sub>) calcd for [C<sub>24</sub>H<sub>34</sub>Si<sub>2</sub>]<sup>+</sup>, 414.18657; found, 414.1866 (0 ppm).

**Compound 3.** To a solution of silirene 1 (50.0 mg, 0.129 mmol) and 3,3-dimethyl-but-1-yne (79.2 μL, 0.643 mmol, 5.00 equiv) in C<sub>6</sub>D<sub>6</sub> (0.65 mL) was added tetrakis(triphenylphosphine) palladium (0) (14.9 mg, 1.29 × 10<sup>-2</sup> mmol, 10.0 mol %) under stirring, and the

resulting mixture was stirred for 3 days at 100 °C, giving a bright yellow mixture. The solution was concentrated to dryness, and the residue was purified by column chromatography on silica gel [SiO<sub>2</sub>, 15 g, eluent petroleum ether (100%), R<sub>f</sub> = 0.60], giving the expected compound as a white solid in 82% yield. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of pentane at -30 °C.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ (ppm) 0.99 (s, 9H, CH<sub>3</sub> tBu), 1.05 (s, 9H, CH<sub>3</sub> tBu), 1.18 (s, 9H, CH<sub>3</sub> tBu), 2.01 (s, 3H, CH<sub>3</sub>-Th), 2.05 (s, 3H, CH<sub>3</sub>-Th), 2.30 (s, 3H, CH<sub>3</sub>-Th), 2.33 (s, 3H, CH<sub>3</sub>-Th), 5.94 (s with <sup>29</sup>Si sat., 1H, <sup>2</sup>J<sub>Hsi</sub> = 10.5 Hz, H vinyl), 6.41 (s, 1H, H Th), 6.51 (s, 1H, H Th); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) 14.7 (s, CH<sub>3</sub>-Th), 15.1 (s, CH<sub>3</sub>-Th), 15.3 (s, CH<sub>3</sub>-Th), 15.7 (s, CH<sub>3</sub>-Th), 19.6 (s, C tBu), 19.9 (s, C tBu), 28.9 (s, CH<sub>3</sub> tBu), 29.5 (s, CH<sub>3</sub> tBu), 30.6 (s, CH<sub>3</sub> tBu), 37.2 (s, C tBu), 121.4 (s, CH vinyl), 126.6 (s, CH Th), 128.6 (s, Cquat.), 129.0 (s, CH Th), 132.5, 133.2, 134.7, 138.6 and 138.7 (s, Cquat.), 143.5 (s, C-Si), 154.6 (s, Cquat.), 171.4 (s, Cquat.). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz): δ (ppm) 13.3 (s). HRMS (ESI, CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (90/10)) calcd for [C<sub>28</sub>H<sub>42</sub>Si<sub>2</sub>+Na]<sup>+</sup>, 493.23894; found, 493.2394 (1 ppm); calcd for [C<sub>28</sub>H<sub>42</sub>Si<sub>2</sub>+K]<sup>+</sup>, 509.21288; found, 509.2130 (0 ppm). Anal. Calcd for [C<sub>28</sub>H<sub>42</sub>Si<sub>2</sub>]; C, 71.42; H, 8.99; Si, 13.62. Found: C, 71.60; H, 9.00; Si, 13.16.

**Compound 4a–f: General Procedure.** To a solution of silirene 1 (50.0 mg, 0.129 mmol) and alkyne (0.129 mmol, 1.00 equiv) in toluene (1.6 mL) was added palladium tetrakis(triphenylphosphine) (7.4 mg, 6.4 × 10<sup>-3</sup> mmol, 5.0 mol %) under stirring, and the resulting mixture was stirred for 24 h at 50 °C, giving a bright yellow solution. The volatiles were then removed under reduced pressure giving an oily residue that was purified by column chromatography on silica gel (see underneath for chromatography conditions for each compound). These compounds were obtained in quantitative yield, but the aldehyde 4d that partially decomposes on silica gel was isolated in only 22% yield.

**Compound 4a (R = OMe).** After flash chromatography on silica gel {SiO<sub>2</sub>, 15 g; gradient DCM/pentane (10/90) → DCM/pentane (20/80); R<sub>f</sub> [DCM/pentane (20/80)] = 0.60}, the product was obtained as a white solid. Single crystals suitable for X-ray diffraction were obtained from a saturated diethylether solution at -20 °C.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ (ppm) 1.09 (s, 9H, CH<sub>3</sub> tBu), 1.14 (s, 9H, CH<sub>3</sub> tBu), 1.74 (s, 3H, CH<sub>3</sub>-Th), 1.79 (s, 3H, CH<sub>3</sub>-Th), 2.20 (s, 3H, CH<sub>3</sub>-Th), 2.39 (s, 3H, CH<sub>3</sub>-Th), 2.89 (s, 3H, OCH<sub>3</sub>), 5.96 (s, 1H, H Th), 5.99 (s with <sup>29</sup>Si sat., 1H, <sup>2</sup>J<sub>Hsi</sub> = 11.2 Hz, H vinyl), 6.50 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, H Ph), 6.64 (s, 1H, H Th), 6.89 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, H Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) 14.5 (s, CH<sub>3</sub>-Th), 14.6 (s, CH<sub>3</sub>-Th), 15.2 (s, CH<sub>3</sub>-Th), 15.4 (s, CH<sub>3</sub>-Th), 19.9 (s, C tBu), 20.1 (s, C tBu), 29.1 (s, CH<sub>3</sub> tBu), 29.3 (s, CH<sub>3</sub> tBu), 40.7 (s, OCH<sub>3</sub>), 111.6 (s, CH Ph), 126.0 (s, CH vinyl), 127.2 (s, CH Th), 128.1 (s, CH Th), 128.7 (s, CH Ph), 130.0 (s, C Th), 130.5 (s, C Ph), 133.1, 134.1, 135.1, 137.4 and 138.1 (s, C-Th), 140.2 (s, C-Si), 150.0 (s, C Ph), 151.4 (s, Si-CH = C-Ph), 163.1 (s, Si-C=C-Th); <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 79 MHz): δ (ppm) 16.7 (s). HRMS (ESI, CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (95/5)) calcd for [C<sub>31</sub>H<sub>40</sub>SiOS<sub>2</sub>+H]<sup>+</sup>, 521.23626; found, 521.2361 (0 ppm). Anal. Calcd for [C<sub>31</sub>H<sub>40</sub>SiOS<sub>2</sub>]; C, 71.48; H, 7.74. Found: C, 71.36; H, 7.82.

**Compound 4b (R = COMe).** After flash chromatography on silica gel [SiO<sub>2</sub>, 15 g; gradient DCM/pentane (50/50) → DCM/pentane (70/30); R<sub>f</sub> (DCM/pentane (50/50)) = 0.60], the product was obtained a clear yellow oil.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ (ppm) 1.10 (s, 9H, CH<sub>3</sub> tBu), 1.16 (s, 9H, CH<sub>3</sub> tBu), 1.73 (s, 3H, CH<sub>3</sub>-Th), 1.79 (s, 3H, CH<sub>3</sub>-Th), 2.16 (s, 3H, CH<sub>3</sub>-Th), 2.39 (s, 3H, CH<sub>3</sub>-Th), 2.53 (s, 3H, C(O)CH<sub>3</sub>), 5.91 (s, 1H, H Th), 6.24 (s with <sup>29</sup>Si sat., 1H, <sup>2</sup>J<sub>Hsi</sub> = 10.7 Hz, H vinyl), 6.65 (s, 1H, H Th), 7.11 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, H Ph), 7.73 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, H Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) 14.5 (s, CH<sub>3</sub>-Th), 14.6 (s, CH<sub>3</sub>-Th), 15.1 (s, CH<sub>3</sub>-Th), 15.4 (s, CH<sub>3</sub>-Th), 20.0 (s, C tBu), 20.1 (s, C tBu), 26.8 (s, C(O)CH<sub>3</sub>), 29.0 (s, CH<sub>3</sub> tBu), 29.3 (s, CH<sub>3</sub> tBu), 127.0 (s, CH Th), 127.6 (s, CH Th), 127.7 (s, CH Ph), 128.0 (s, CH Ph), 130.3 (s, C



821 11.7 Hz, Si-C=C), 152.6 (d,  $J_{\text{CP}} = 55.0$  Hz, Si-C=C);  $^{29}\text{Si}\{^1\text{H}\}$   
822 NMR ( $\text{C}_6\text{D}_6$ , 79 MHz):  $\delta$  (ppm) -31.6 (s);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  
823 162 MHz):  $\delta$  (ppm) 25.3 (s).

824 **Compound 6-COD.** THF (2 mL) was added to a neat mixture of  
825 silirene **1** (30.0 mg,  $7.72 \times 10^{-2}$  mmol) and (1,5-cyclooctadiene)-  
826 bis(trimethylsilylmethyl)palladium(II) (30.0 mg,  $7.72 \times 10^{-2}$  mmol,  
827 1.00 equiv), and the resulting solution was stirred for 1 h at room  
828 temperature, giving a dark solution. The solvent was evaporated under  
829 vacuum, and the residue thus obtained was further dried for 10 h  
830 under vacuum, giving a sticky brown residue. The residue was  
831 extracted with pentane (2 mL), and the pentane solution was filtered  
832 and placed at  $-30$  °C, giving the expected compound as colorless  
833 blocks in 41% yield. Single crystals suitable for X-ray diffraction  
834 analysis were obtained in the same conditions.

835  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, 243 K):  $\delta$  (ppm) 1.07 (s, 18H,  $\text{CH}_3$   
836 Si*t*Bu), 1.96 (s, 3H,  $\text{CH}_3$ -Th), 1.98 (s, 3H,  $\text{CH}_3$ -Th), 2.06–2.20  
837 (br., 2H,  $\text{CH}_2$  COD), 2.20–2.40 (br., 4H,  $\text{CH}_2$  COD), 2.29 (s, 3H,  
838  $\text{CH}_3$ -Th), 2.30 (s, 3H,  $\text{CH}_3$ -Th), 2.52–2.66 (br., 2H,  $\text{CH}_2$  COD),  
839 4.88–5.67 (br., 2H,  $\text{CH}$  COD), 5.90 (br., 2H,  $\text{CH}$  COD), 6.27 (s,  
840 1H,  $\text{H}$  Th), 6.43 (s, 1H,  $\text{H}$  Th);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz,  
841 243 K):  $\delta$  (ppm) 14.0 (s,  $\text{CH}_3$ -Th), 14.7 (s,  $\text{CH}_3$ -Th), 15.2 (s,  
842  $\text{CH}_3$ -Th), 15.2 (s,  $\text{CH}_3$ -Th), 23.3 (s br.,  $\text{C}$  Si*t*Bu), 27.4 (br.,  $\text{CH}_2$   
843 COD), 30.0 (br.,  $\text{CH}_2$  COD), 30.7 (s,  $\text{CH}_3$  Si*t*Bu), 105.1 (s br.,  $\text{CH}$   
844 COD), 122.2 (s br.,  $\text{CH}$  COD), 123.2 (s,  $\text{C}_{\text{quat}}$ ), 125.4 (s,  $\text{CH}$  Th),  
845 126.4 (s,  $\text{C}_{\text{quat}}$ ), 126.5 (s,  $\text{CH}$  Th), 133.8, 133.8, 140.8, 146.4, 151.6  
846 and 161.3 (s,  $\text{C}_{\text{quat}}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 99 MHz, 243 K):  $\delta$   
847 (ppm) -34.8 (s).

848 **Compound 6-PPh<sub>3</sub>.** To a solution of silirene **1** (40.0 mg, 0.103  
849 mmol) and triphenylphosphine (27.0 mg, 0.103 mmol, 1.00 equiv) in  
850 THF (2.5 mL) was added (1,5-cyclooctadiene)bis-  
851 (trimethylsilylmethyl)palladium(II) (40.1 mg, 0.103 mmol, 1.00  
852 equiv) as a powder in one portion, and the resulting mixture was  
853 stirred for 1 h at room temperature, giving a clear green solution.

854 The volatiles were then eliminated under reduced pressure, and the  
855 residue was then dried under vacuum ( $2 \times 10^{-2}$  mbar) for 10 h,  
856 giving a green solid. This solid was then washed two times with  
857 pentane (2 times 1 mL), giving the expected compound as a clear  
858 yellow powder in 65% yield (51 mg). All the attempts to grow single  
859 crystals of **6-PPh<sub>3</sub>** for X-ray diffraction analysis furnished crystals of  
860 the known complex  $[\text{Pd}(\text{PPh}_3)_3]$ .

861  $^1\text{H}$  NMR (THF- $d^8$ , 400 MHz):  $\delta$  (ppm) 1.04 (s, 18H,  $\text{CH}_3$  *t*Bu),  
862 1.86 (s, 3H,  $\text{CH}_3$ -Th), 2.13 (s, 3H,  $\text{CH}_3$ -Th), 2.32 (s, 3H,  $\text{CH}_3$ -  
863 Th), 2.34 (s, 3H,  $\text{CH}_3$ -Th), 6.56 (s, 1H,  $\text{H}$  Th), 6.58 (s, 1H,  $\text{H}$  Th),  
864 7.31–7.43 (m, 9H,  $\text{H}$  *p*Ph and  $\text{H}$  *m*Ph), 7.54–7.64 (m, 6H,  $\text{H}$  *o*Ph);  
865  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d^8$ , 100 MHz):  $\delta$  (ppm) 14.7 (s,  $\text{CH}_3$ -Th),  
866 14.9 (s,  $\text{CH}_3$ -Th), 15.0 (s,  $\text{CH}_3$ -Th), 15.1 (s,  $\text{CH}_3$ -Th), 24.7 (s,  $\text{C}$   
867 *t*Bu), 31.1 (s,  $\text{CH}_3$  *t*Bu), 127.3 (s,  $\text{CH}$  Th), 127.6 (s,  $\text{CH}$  Th), 128.7  
868 (d,  $J_{\text{CP}} = 1.7$  Hz,  $\text{C}_{\text{quat}}$ ), 129.2 (s,  $\text{C}_{\text{quat}}$ ), 129.2 (d,  $J_{\text{CP}} = 9.6$  Hz,  
869  $\text{CH}$  *m*Ph), 130.6 (d,  $J_{\text{CP}} = 1.4$  Hz,  $\text{CH}$  *p*Ph), 134.7 (s,  $\text{C}_{\text{quat}}$ ), 135.0  
870 (d,  $J_{\text{CP}} = 15.9$  Hz,  $\text{CH}$  *o*Ph), 135.3 (d,  $J_{\text{CP}} = 31.2$  Hz,  $\text{C}-\text{P}$ ), 135.4 (s,  
871  $\text{C}_{\text{quat}}$ ), 137.0 (s br.,  $\text{C}_{\text{quat}}$ ), 138.9 (d,  $J_{\text{CP}} = 9.9$  Hz,  $\text{C}_{\text{quat}}$ ), 146.3  
872 (d,  $J_{\text{CP}} = 11.5$  Hz, Si-C=C), 156.0 (d,  $J_{\text{CP}} = 63.4$  Hz, Si-C=C);  
873  $^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $d^8$ , 79 MHz):  $\delta$  (ppm) -27.2 (d,  $J_{\text{SiP}} = 2.1$  Hz);  
874  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d^8$ , 162 MHz):  $\delta$  (ppm) 24.0 (s, **6-PPh<sub>3</sub>**).

875 **NMR Evidence for the Existence of an Equilibrium.** In the  
876 NOESY  $^1\text{H}, ^1\text{H}$  NMR spectrum, exchange correlations are observed  
877 between PPh<sub>3</sub> aromatic proton resonance signals of **6-PPh<sub>3</sub>** and  
878  $[\text{Pd}(\text{PPh}_3)_n]$ ; exchange correlations are observed between thienyl  
879 -CH<sub>3</sub> protons resonance signals of **6-PPh<sub>3</sub>** and **6-PPh<sub>3</sub>**.

880 In the NOESY  $^{31}\text{P}, ^{31}\text{P}$  NMR spectrum, exchange correlations are  
881 observed between the PPh<sub>3</sub> resonance signal of **6-PPh<sub>3</sub>** and  
882  $[\text{Pd}(\text{PPh}_3)_n]$ .

883 **Compound 6-P(OPh)<sub>3</sub>.** To a solution of silirene **1** (100 mg, 0.257  
884 mmol) and triphenylphosphite (67.4  $\mu\text{L}$ , 79.8 mg, 0.257 mmol, 1.00  
885 equiv) in THF (7 mL) was added (1,5-cyclooctadiene)bis-  
886 (trimethylsilylmethyl)palladium(II) (100 mg, 0.257 mmol, 1.00  
887 equiv) as a powder in one portion, and the resulting mixture was  
888 stirred for 2 h at room temperature, giving a clear yellow solution.  
889 The crude mixture was then filtered, and the resulting solution was  
890 concentrated to dryness over 30 min at room temperature. The

resulting residue was extracted with pentane (15 mL) at room 891  
temperature and filtered, and the yellow pentane solution was placed 892  
in the freezer at  $-40$  °C, affording colorless crystals in a few hours. 893  
The mother liquor was then eliminated via a syringe, and the crystals 894  
were washed 4 times with  $-40$  °C cold pentane (4 times 5 mL). The 895  
crystals were then dried under vacuum at  $0$  °C for 5 h. NMR analysis 896  
of the crystalline material revealed the presence of about 5% of 897  
 $[\text{Pd}(\text{P}(\text{OPh})_3)_3]$  in addition to the expected compound (46% yield). 898  
Attempts to separate the two complexes were unsuccessful. Crystals of 899  
**6-P(OPh)<sub>3</sub>** suitable for X-ray diffraction were obtained from a 900  
saturated THF/pentane solution at  $-30$  °C. 901

The compound **6-P(OPh)<sub>3</sub>** was characterized by NMR at  $-40$  °C 902  
in THF  $d^8$ . In the case of  $^{29}\text{Si}$  NMR, no resonance signal could be 903  
observed at low temperature, and the spectrum was recorded at room 904  
temperature over a few hours, resulting in the partial decomposition 905  
of the compound due to its thermal instability. Fast  $^1\text{H}$  and  $^{31}\text{P}$  NMR 906  
spectra could also be recorded at room temperature in  $\text{CD}_2\text{Cl}_2$  for a 907  
better resolution (see S101–104). 908

$^1\text{H}$  NMR (THF- $d^8$ , 400 MHz, 233 K):  $\delta$  (ppm) 1.30 (s, 18H,  $\text{CH}_3$   
909 *t*Bu), 1.68 (s, 3H,  $\text{CH}_3$ -Th), 1.75 (s, 3H,  $\text{CH}_3$ -Th), 2.19 (s, 3H,  
910  $\text{CH}_3$ -Th), 2.34 (s, 3H,  $\text{CH}_3$ -Th), 6.08 (s, 1H,  $\text{H}$  Th), 6.55 (s, 1H,  $\text{H}$   
911 Th), 7.17–7.24 (m, 3H,  $\text{H}$  *p*Ph), 7.35–7.45 (m, 12H,  $\text{H}$  *o*Ph and  $\text{H}$   
912 *m*Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d^8$ , 100 MHz, 233 K):  $\delta$  (ppm) 14.4 (s,  
913  $\text{CH}_3$ -Th), 14.7 (s,  $\text{CH}_3$ -Th), 14.9 (s,  $\text{CH}_3$ -Th), 15.3 (s,  $\text{CH}_3$ -Th),  
914 24.2 (s,  $\text{C}$  *t*Bu), 31.2 (s,  $\text{CH}_3$  *t*Bu), 121.8 (br.,  $\text{CH}$  *o*Ph or  $\text{CH}$  *m*Ph),  
915 125.4 (s,  $\text{CH}$  *m*Ph), 126.1 (br.,  $\text{C}_{\text{quat}}$ ), 127.1 (s,  $\text{CH}$  Th), 127.8 (s,  
916  $\text{CH}$  Th or  $\text{C}_{\text{quat}}$ ), 127.9 (s,  $\text{CH}$  Th or  $\text{C}_{\text{quat}}$ ), 130.3 (s,  $\text{CH}$  *o*Ph or  
917  $\text{CH}$  *m*Ph), 133.4 (br.,  $\text{C}_{\text{quat}}$ ), 134.5 (s,  $\text{C}_{\text{quat}}$ ), 141.0 (d br.,  $J_{\text{CP}} =$   
918 12.3 Hz,  $\text{C}_{\text{quat}}$ ), 143.4 (br.,  $\text{C}_{\text{quat}}$ ), 151.8 (d,  $J_{\text{CP}} = 3.5$  Hz,  $\text{C}-\text{P}$ ),  
919 165.3 (d,  $J_{\text{CP}} = 151.7$  Hz,  $\text{C}_{\text{quat}}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 79 MHz,  
920 293 K):  $\delta$  (ppm) -26.9 (d,  $J_{\text{SiP}} = 4.7$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d^8$ ,  
921 162 MHz, 233 K):  $\delta$  (ppm) 126.8 (s). One quaternary carbon was  
922 not observed. 923

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at 926  
<https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c00045>. 927

Experimental details and characterization data and 928  
Cartesian coordinates for the calculated structure 929  
obtained by DFT calculations (PDF). 930

### Accession Codes

CCDC 2184696–2184699 contain the supplementary crys- 931  
tallographic data for this paper. These data can be obtained 932  
free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by 933  
emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The 934  
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## 961 Notes

962 The authors declare no competing financial interest.

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1291 the overlapping of a Si p orbital with both the C1 sp hybrid on one  
1292 side and the Pd d orbital on the other side. The HOMO-4 accounts  
1293 for the Si–C1 and Pd–C2 bonds, involving a first overlapping  
1294 between a sp hybrid on C1 and a p orbital on Si and a second  
1295 overlapping between a sp hybridized orbital on C2 and a d orbital on  
1296 the Pd metal. The HOMO-7 orbital mainly describes the C1–C2  
1297 bond, through the interaction between sp orbitals, whereas the  
1298 HOMO-10 mainly describes the Si–Pd bond, via the interaction  
1299 between a p orbital on the Si center and a d orbital on Pd. The  
1300 HOMO-18 orbital, finally, displays the overlapping of a C2 sp  
1301 hybridized orbital with both a Pd d orbital on one side and a C1 sp  
1302 hybridized orbital on the other side, together with an additional slight  
1303 bonding interaction between the same C1 sp hybridized orbital and a  
1304 Si p orbital.
- (37) For sake of clarity, the LUMO is also depicted in Figure S3-  
1305 DFT. It consists of an antibonding interaction between the Si and Pd  
1306 atoms together with a bonding interaction between Pd and  
1307 phosphorus.
- (38) To get more insight into the coordination of the alkyne to C  
1309 (**6-PPh<sub>3</sub>**), we computed the molecular orbitals of complex **D**. As  
1310 shown in Figure S5-DFT, the orbital accounting for the bonding with  
1311 phenylacetylene is the homo-7 one, resulting from the overlapping  
1312 between the homo orbital of C and the lumo orbital of phenyl-  
1313 acetylene. Only the Pd metal interacts with phenylacetylene, a Pd d  
1314 orbital overlapping the  $\pi^*$  orbital of the alkyne C–C bond.
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