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

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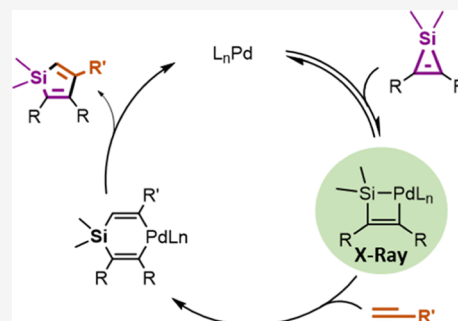


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ABSTRACT: The palladium-catalyzed annulation reaction of alkynes enables an attractive approach to siloles. Their access from silirenes and terminal alkynes proved rather general, involving reactive intermediates that have remained elusive to date. 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.



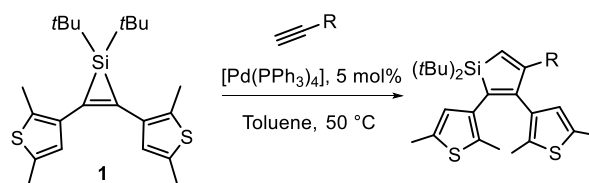
INTRODUCTION

The chemical behavior of three-membered ring heterocycles is mostly dictated by the release of the ring strain¹ 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.² 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.³ 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 π -conjugated molecules incorporating heavier p-block elements.⁴ In this context, the chemistry of silacycles (silicon rings with 3,⁵ 4,⁶ 5,^{6d,7} or more⁸ members) is probably the more mature research field driven by that of silacyclopentadienes (siloles) and their peculiar electronic properties.⁹ Over the years, this interest has turned siloles into important synthetic targets and has motivated significant efforts toward methodological development.¹⁰ 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.¹¹ They proceed either (i) intramolecularly from acyclic silanes through arylations of Si–X (X = CH₃, H) bonds¹² and C–C bond formation between peripheral substituents¹³ or (ii) intermolecularly by reaction of an alkyne with a suitable silicon-based reagent.¹⁴ 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.¹⁵ Despite more recent efforts to improve the methodology,¹⁶ 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 siloles¹⁷ 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

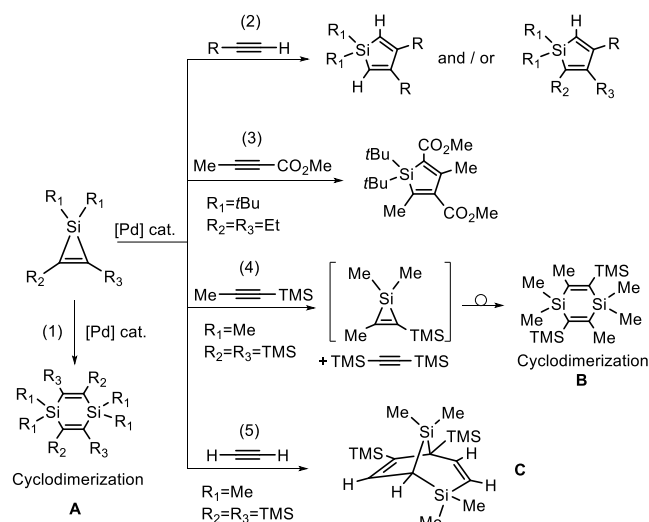
Scheme 1. Palladium-Catalyzed Synthesis of Photochromic Siloles by Annulation Reaction of Alkynes with a Silacyclopentene



Received: January 5, 2023

61 (polypropargylmethacrylamide) polymers displaying terminal
62 alkyne functionalities.¹⁷ 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).

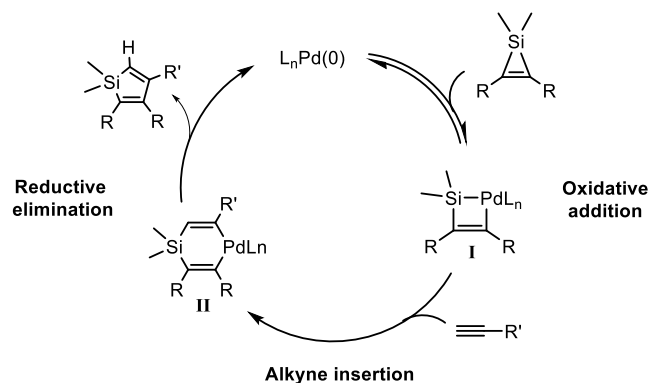
Scheme 2. Different Scenarios of the Palladium-Catalyzed Reaction of Silirenes with Alkynes (for Route (1) See Refs 15d 21a 21b; for Route (2) See Refs 15a 15b 15d 16a 16b; for Route (3) See Ref 16b; for Route (4) See Ref 21b; and for Route (5) See Ref 18)



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).¹⁸

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.^{16a,c} 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.¹⁹ In that respect, silirene 1 does not 104
evolve in solution in the presence of [Pd(PPh₃)₄], 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
cyclodimerization²¹ [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.¹⁸ 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–pC₆H₄–C≡C– 140
141

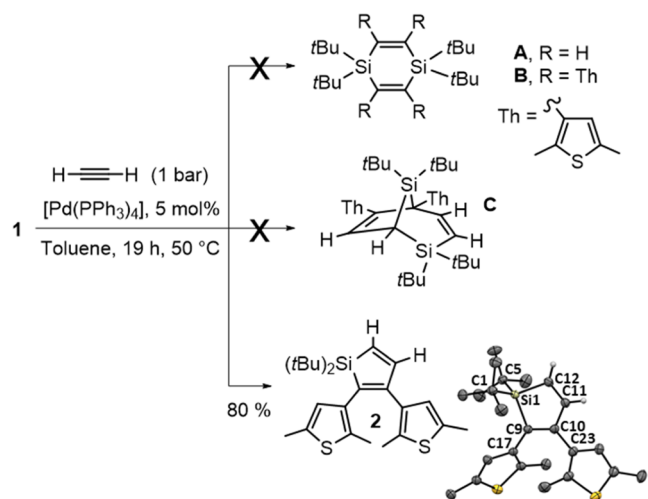


Figure 1. Reactivity of **1** with acetylene under Pd-catalyzed conditions, giving silole **2**, and X-ray structure of **2** with a displacement ellipsoid plot at a 50% probability level; non-vinyl hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C12 1.872(2), Si1–C9 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).

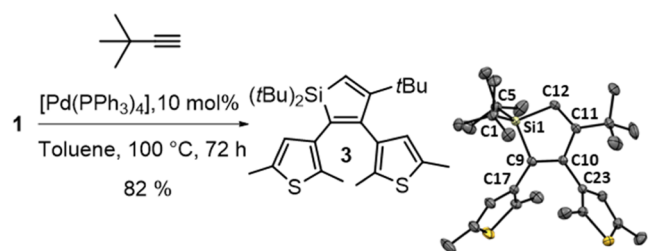


Figure 2. Synthesis of silole **3** by Pd-catalyzed annulation of **1** and *tert*-butylacetylene under forcing conditions (left). X-ray structure of **3** (right) with a displacement ellipsoid plot at a 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: 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).

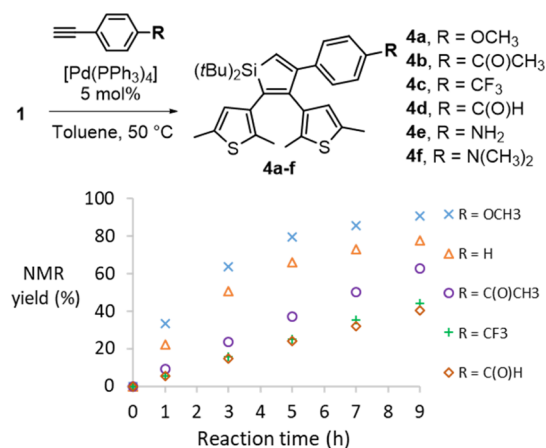
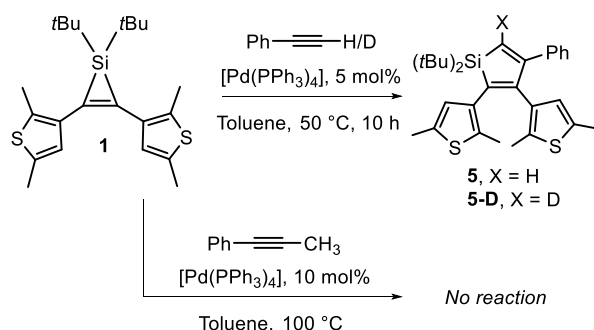


Figure 3. Synthesis of siloles **4a–f** by Pd-catalyzed annulation of para-substituted phenylacetylenes with **1** (top) and the plot of the catalytic transformations over time (down) for R = OCH₃, H, C(O)CH₃, CF₃, and C(O)H monitored by ¹H NMR spectroscopy (C₆D₆, internal standard DCE).

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-, Deuterio-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-metallasilacyclobutenes are organometallic complexes with an unsaturated four-membered cyclic structure where a transition metal center is stabilized by two sigma bonds of different nature, σ -C–M and σ -Si–M, respectively. Although often invoked,^{6c,16b,23} these complexes are rare and limited in number. A first description was reported by Ishikawa²⁴ in the case of nickelasilacyclobutene **C** generated from a silirene and [(PEt₃)₄Ni(0)] (Figure 4).

It revealed instability and was only characterized in situ by NMR spectroscopy. Since then, other examples have appeared (**D**, **E^R**, and **F^R**),²⁵ but only four of them have been structurally characterized so far in the case of Pt (**D**), Ti (**E^H**), and Ni (**F^H** and **F^{CH₂OMe}**) (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)CH₃ > –C(O)H ~ –CF₃ (Figure 3, bottom).²²

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 deuterio phenylacetylene, Ph–C≡C–H, and Ph–C≡C–D, respectively,

C

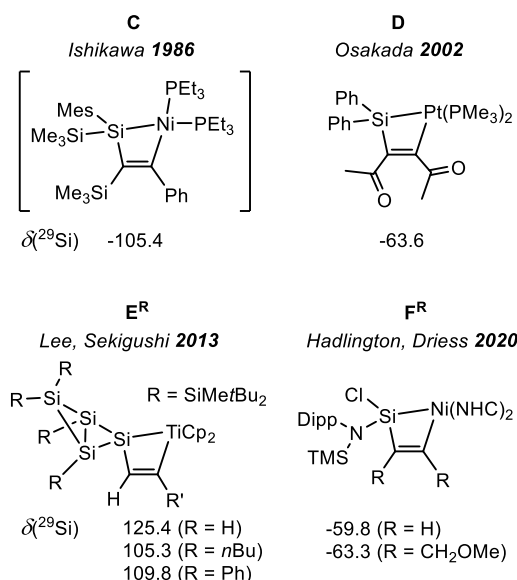
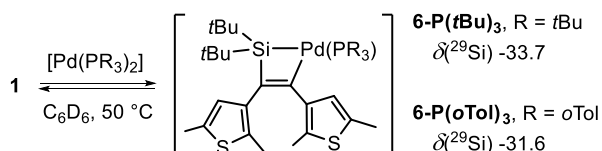


Figure 4. Previously described 1,2-metallasilacyclobutenes **C–F** and corresponding ^{29}Si NMR of the Si–M silicon nucleus.

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 γ -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)₃** and **6-P(*o*Tol)₃** 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 δ 80.9 (R = *t*Bu)
199 and δ 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.²⁶ In the
202 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, new singlet resonance signals at δ
203 -33.7 (R = *t*Bu) and δ -31.6 (R = *o*Tol), low field shifted
204 regarding the starting material (δ -69.9), were observed.
205 Except for the special case of titanasilacyclobutenes **E^R** 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^R** (Figure 4).²⁷ 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)₃** and **6-P(*o*Tol)₃** 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)₃** and **6-** 220
P(*o*Tol)₃ 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 complex²⁸ 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).²⁹ A clean reaction occurs between **1** and 231 15

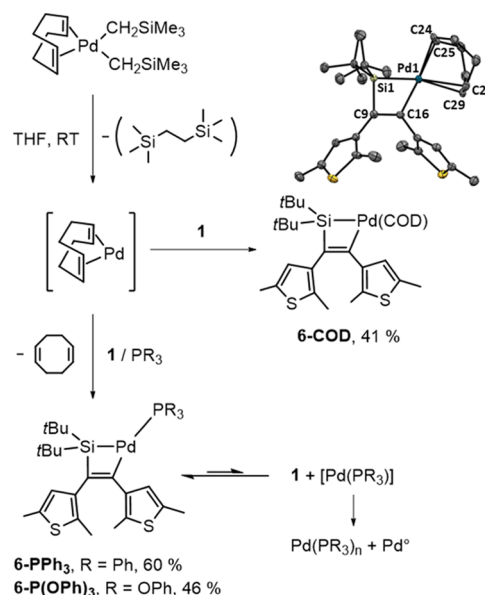


Figure 5. Decomposition of $[(\text{COD})\text{PdR}_2]$ to $[(\text{COD})\text{Pd}]$ and its reactivity with (i) **1** affording **6-COD** (right) and (ii) **1** and PR_3 (R = Ph, OPh) affording **6-PPh₃** and **6-P(OPh)₃** (bottom). X-ray structure of **6-COD** (top right) with a displacement ellipsoid 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 ^1H NMR monitoring and the 233
appearance of a singlet resonance signal at δ -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)₃** and **6-P(*o*Tol)₃**. 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.³⁰ 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(CH₂TMS)₂] 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 Ph₃P or (PhO)₃P, the monophosphine complexes **6-PPh₃**
 262 and **6-P(OPh)₃** could be obtained in 65 and 46% yield,
 263 respectively, and fully characterized by NMR spectroscopy.
 264 The NMR spectra of **6-PPh₃** and **6-P(OPh)₃** are contaminated
 265 with a small amount of palladium(0) phosphine complexes
 266 Pd(PR₃)_{*n*} (*R* = Ph, OPh), as well as silirene **1** (~5%). This can
 267 be explained by the existence of an equilibrium between **6-**
 268 **PPh₃** and **6-P(OPh)₃** and their reductive elimination products
 269 **1** and [Pd(PR₃)_{*n*}] that lead to the slow decomposition of **6-**
 270 **PPh₃** and **6-P(OPh)₃** and the release of Pd⁰ (Figure 5).³¹ For
 271 the two complexes **6-PPh₃** and **6-P(OPh)₃**, the ²⁹Si NMR
 272 display a resonance signal at a similar chemical shift (**6-PPh₃** δ
 273 -27.2, **6-P(OPh)₃** δ -26.9) and as a doublet due to scalar
 274 coupling to the ³¹P nucleus (²*J*_{SiP} = 2.1 Hz, **6-PPh₃**; ²*J*_{SiP} = 4.7
 275 Hz, **6-P(OPh)₃**), indicative of the expected P-Pd-Si
 276 connectivity. Single crystals of **6-P(OPh)₃** 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).

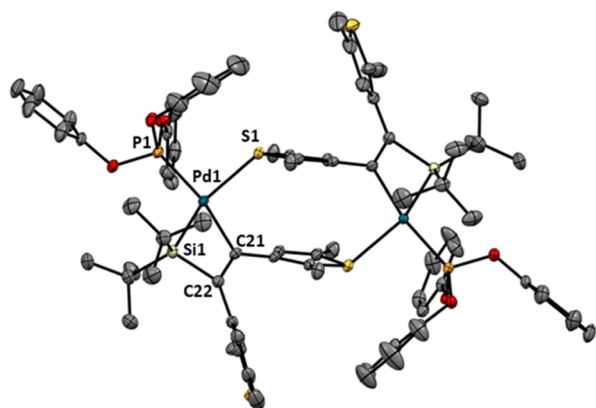


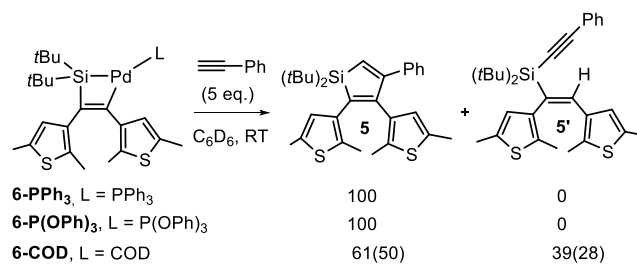
Figure 6. X-ray structure of **6-P(OPh)₃** with a displacement ellipsoid plot at a 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1-C21 2.085(2), Pd1-Si1 2.3380(7), Pd1-S1 2.6384(7), Pd1-P1 2.2548(7), Si1-C22 1.857(2), C22-C21 1.362(3), P1-Pd1-S1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

287
 288 86

Scheme 6. Reactivity of Metallasilacyclobutene **6-L** (**L** = **PPh₃**, **P(OPh)₃**, and **COD**) with Phenyl Acetylene



Both complexes **6-PPh₃** and **6-P(OPh)₃** 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 ³*J*_{SiH} 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-PPh₃** and phenyl
 acetylene was monitored by NMR, at low temperature, in
 CD₂Cl₂. At 203 K, the ¹H NMR revealed the presence of
 resonance signals attributed to the model silole **5**³³ together
 with the remaining **6-PPh₃** in a 1.33:1 ratio. Besides remaining
6-PPh₃, the ³¹P NMR spectra exhibit an AB spin system with a
 coupling constant (²*J*_{PP} = 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 ¹H-³¹P, HSQC, and HMBC ¹H-¹³C) and after
 comparison to experimental data available in the literature,³⁴
 the Pd(0)-alkyne π -complex [(Ph₃P)₂Pd(η 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(PPh₃)_{*n*}] 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,^{25d} contrary to the
 platinum ones that proved stable at room temperature.^{25b}

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).

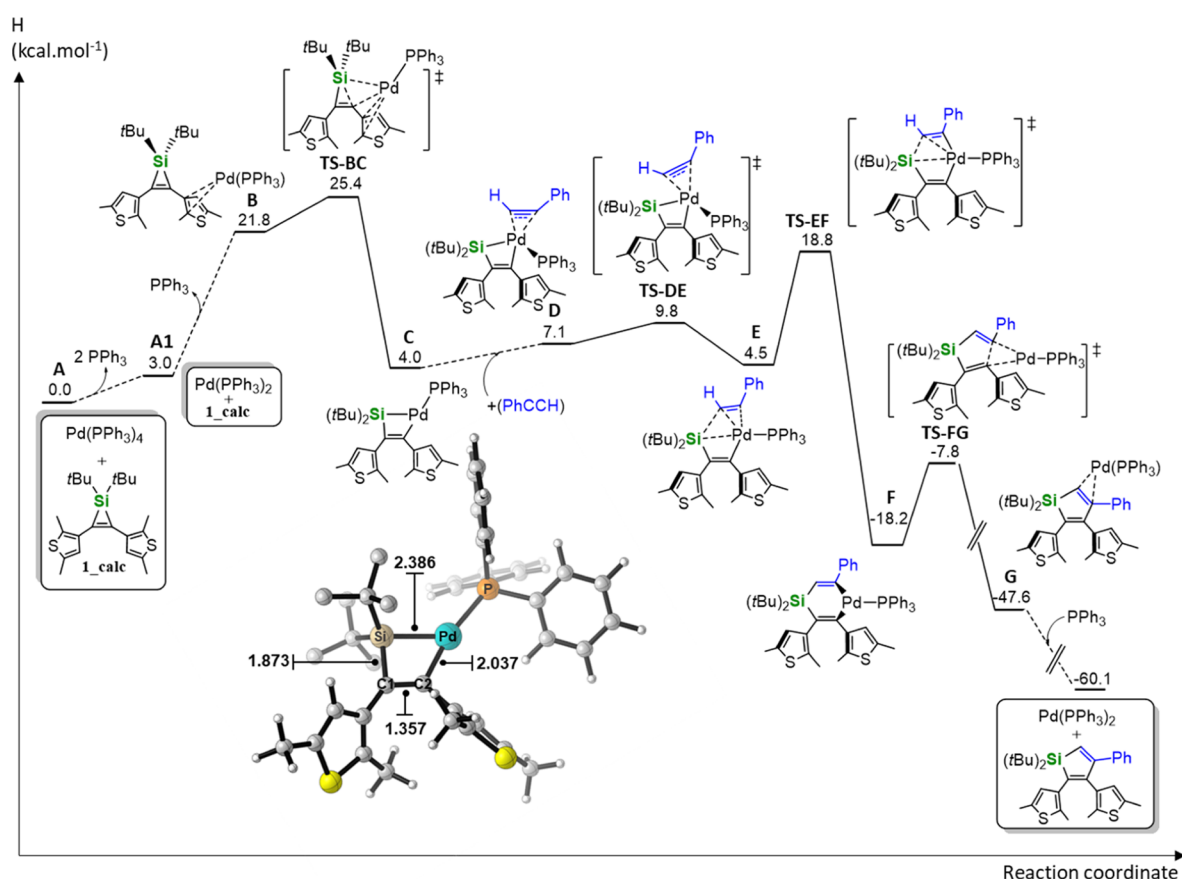


Figure 7. DFT-computed enthalpy profile (kcal mol^{-1}) of the Pd-catalyzed annulation reaction of phenylacetylene with silirene **1**; optimized structure of **C** and bond lengths within the Si–C–C–Pd metallacycle.

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 PPh_3 dissociation energy
 340 starting from $\text{Pd}(\text{PPh}_3)_4$. As shown in Figure 8, the

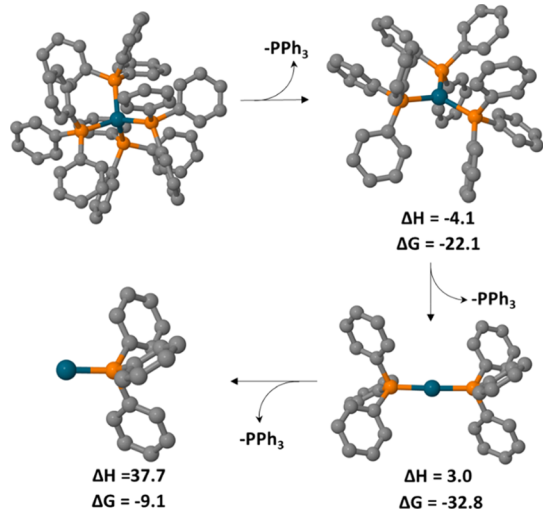


Figure 8. DFT-computed enthalpy and Gibbs free energy values for the PPh_3 dissociation reaction starting from the $\text{Pd}(\text{PPh}_3)_4$ compound. The ΔH and ΔG values refer to the starting $\text{Pd}(\text{PPh}_3)_4$ compound.

dissociation of one, two, and three PPh_3 ligands displays a
 ΔH of -4.1 , $+3.0$, and $+37.7$ kcal mol^{-1} (ΔG of -22.1 , -32.8 ,
 and -9.1 kcal mol^{-1}), respectively, indicating that the starting
 $\text{Pd}(\text{PPh}_3)_4$ compound spontaneously loses two 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.³⁵ The replacement of the
 third phosphine by silirene **1** to form **B** is an energetically
 costly step (21.8 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-PtBu₃** and **6-P(oTol)₃**, the 1,2-palladasila-
 cyclobutenes species **C** (**6-PPh₃**) 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 $^\circ\text{C}$), 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 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) π -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 kcal mol^{-1}) with an associated
 kinetic barrier of 19.9 kcal mol^{-1} (**TS-HI**). This unfavorable
 step and the failure to localize the subsequent intermediates

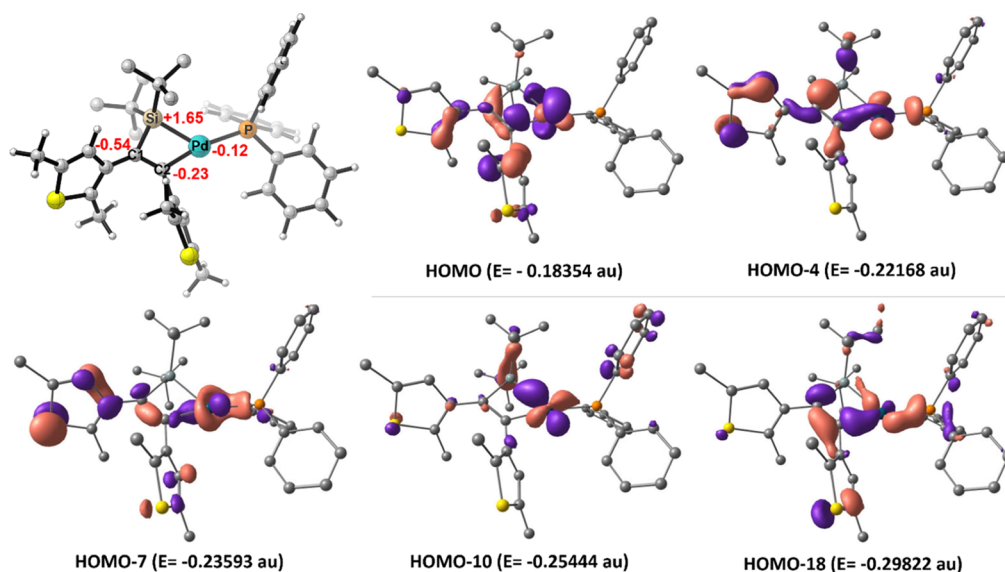


Figure 9. Geometry, NPA charge analysis, and representative MOs of the 1,2-metallasilacyclobutene **C** (isodensity value = 0.05 au).

made us rule out this alternative option. Due to its peculiar structure, the OA product **C** has been analyzed in more detail. **1,2-Palladasilacyclobutene Scaffold.** As shown in **Figure 7**, the 1,2-palladasilacyclobutene **C** compound (**6-PPh₃**) displays a distorted T-shape environment around palladium with an acute C2PdSi angle of 60.69°. The SiPd distance (2.386 Å) is slightly longer than that measured experimentally for **6-COD** (2.3237(9) Å) and **6-P(OPh)₃** (2.3380(7) Å) but still within the range of previously characterized silyl palladium(II) complexes (2.25–2.43 Å). Within the four-membered metallacycle, the C1–Si bond length of 1.873 Å is slightly elongated with respect to the endocyclic Si–C bonds of the computed silirene compound **1_{calc}** (1.844 Å), whereas the C2Si distance of 2.255 Å largely exceeds the sum of covalent radii of the two atoms (1.84 Å, R = 1.26 Å). The C=C double bond length (1.357 Å) is identical to the one obtained for the computed silirene molecule (1.359 Å). The geometry around the C1 olefinic carbon atom is highly constrained, displaying an acute C2C1Si angle of 87.0°. To explore in depth the nature of the bonds involved in the Si–C–C–Pd cycle, we performed a NPA charge and MO analysis of **C** (**Figure 9**).

The computed natural charges indicate a positive charge of 1.65 for the electropositive Si center, together with a slight polarization of the C1–C2 bond, with the C1 carbon carrying a more negative charge (−0.54) than the C2 carbon (−0.23). The computed molecular orbitals responsible for the bonding within the Si–C1–C2–Pd cycle are shown in **Figure 8**. The HOMO, HOMO-4, HOMO-7, HOMO-10, and HOMO-18 orbitals describe the sigma bonding system of the four-membered 1,2-palladasilacyclobutene skeleton^{36,37} (**Figure 8**), whereas the HOMO-1 and the HOMO-17 orbitals account for the π interaction between C1 and C2 (see **Figure S129** in the Supporting Information). No orbital overlapping is detected between the Si and C2 atoms, despite the large SiC2 distance observed experimentally in the X-ray structures of **6** (vide supra), ruling out any possibility of bonding between these two centers.

Alkyne Insertion Process. From **C** (**6-PPh₃**), the alkyne may then insert into the Pd–Si bond of the metallacycle to form the 1,4-palladasilacyclohexadiene species. The process

occurs in three steps, involving (i) the coordination of the alkyne to **C**; (ii) the insertion of the alkyne into the Pd–Si bond with the retention of the Pd–Si bond (**TS-DE**), and (iii) the breaking of the Pd–Si bond (**TS-EF**) to afford the 1,4-palladasilacyclohexadiene species **F**. As shown in **Figure 7**, after the formation of **D**³⁸ via the endothermic coordination of the alkyne to **C** in a η^2 side-on fashion (7.1 kcal mol^{−1} with respect to the entrance channel A), the two-step insertion of the alkyne into the Pd–Si bond takes place through two kinetically accessible barriers of 9.8 and 18.8 kcal mol^{−1}. The alternative scenario involving the alkyne insertion into the Pd–C bond has been excluded due to its unreasonably high kinetic barrier of 39.6 kcal mol^{−1} (see **Figures S132** and **S133** in the Supporting Information). The resulting 1,4-palladasilacyclohexadiene species **F** is exothermic by −18.2 kcal mol^{−1} and represents the driving force of the reaction. Two regioisomers are possible depending on whether the terminal alkyne carbon binds the Si atom (**Figure 7**) or the Pd atom (see **Figures S134** and **S135** in Supporting Information). As shown in **Figures 7** and **S134** in the Supporting Information, the formation of the regio-isomer displaying the terminal alkyne carbon bonded to the Si atom is more favorable, both kinetically and thermodynamically (**TS-DE** = 9.8 kcal mol^{−1}; **TS-EF** = 18.8 kcal mol^{−1}; **F** = −18.2 kcal mol^{−1} vs **TS-DIE1** = 28.6 kcal mol^{−1}; **TS-E1F1** = 32.3 kcal mol^{−1}; **F1** = −12.4 kcal mol^{−1}); the steric repulsion between the *t*Bu groups at the Si center and the phenyl substituent of the alkyne plays an important role.

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

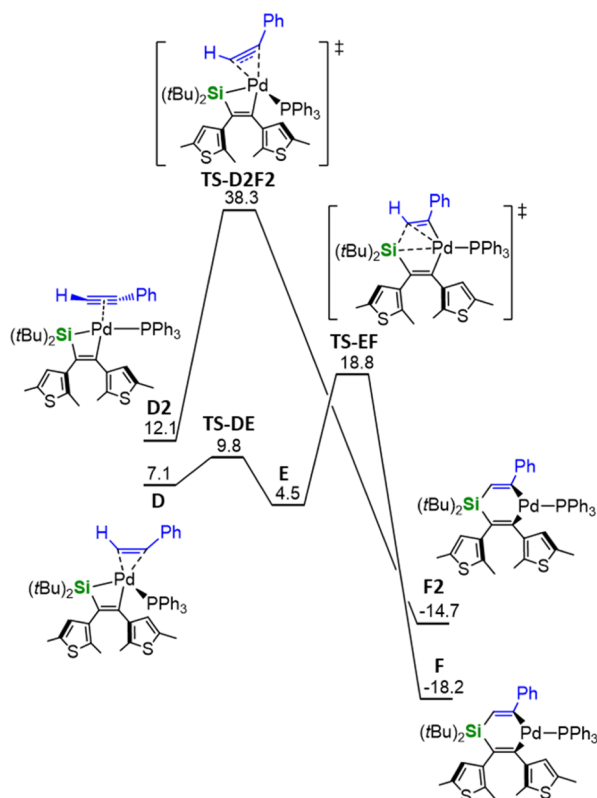


Figure 10. DFT-computed enthalpy profiles for the formation of 1,4-palladasilacyclohexadiene F from π -complex D with the two possible antiparallel orientation of the thienyl groups.

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

Starting from the alkyne π -complex D2, indeed, the phenylacetylene insertion becomes a one-step process with an associated kinetic barrier of 38.2 kcal mol⁻¹ (TS-D2F2), which cannot compete with the pathway starting from D, displaying a kinetic barrier of 18.8 kcal mol⁻¹ (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*C₆H₄-C≡C-H (R = CF₃ and OMe). As shown in Figures S138–S141 in the Supporting Information, compared to the phenylacetylene analogues, the energies of intermediates D_{CF3} and D_{OMe} differ by less than 2 kcal mol⁻¹ (5.9 and 7.5 kcal mol⁻¹, respectively, compared to 7.1 kcal mol⁻¹ for D) and the energies of alkyne insertion transition states, TS-DE_{CF3}, TS-EF_{CF3} and TS-DE_{OMe}, TS-EF_{OMe} by less than 4 kcal mol⁻¹ (8.8 and 10.1 kcal mol⁻¹ compared to 9.8 kcal mol⁻¹ for TS-DE and 16.5 and 19.7 compared to 18.8 kcal mol⁻¹ for TS-EF). According to the literature,³⁹ 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 PPh₃ and P(OPh)₃ 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 PPh₃ and P(OPh)₃ (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 PPh₃ 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⁻¹ (TS-DE) to 36.4 kcal mol⁻¹ (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_{tBu} is significantly higher than that of intermediate D (11.3 vs 7.1 kcal mol⁻¹), and the formation of the 1,4-palladasilacyclohexadiene compound involves higher kinetic barriers (14.2 and 23.6 kcal mol⁻¹ for TS-DE_{tBu} and TS-EF_{tBu} vs 9.8 and 18.8 kcal mol⁻¹ 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 Me₃Si-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-PR₃ (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)₃ and 6-COD. Under stoichiometric conditions, 6-PPh₃ 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(PPh₃)₄ compound spontaneously evolves in solution to the Pd(PPh₃)₂ 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(PPh₃)₂ 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. CD₂Cl₂, C₆D₆, and THF d⁸ 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. ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer or a Bruker Avance III HD 500 NMR spectrometer. All ²⁹Si NMR spectra have been recorded with proton decoupling. Chemical shifts were expressed in parts per million, calibrated to residual ¹H (5.32 ppm for CD₂Cl₂, 7.16 ppm for C₆D₆, and 1.72 and 3.58 for THF d⁸) and ¹³C (53.84 ppm for CD₂Cl₂, 128.06 ppm for C₆D₆, and 25.31 and 67.21 for THF d⁸), 85% H₃PO₄, 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**¹⁷ and [(COD)Pd(CH₂TMS)₂]^{29b} 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 × 10⁻³ 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 (SiO₂, 15 g, gradient: pentane 100% → pentane/DCM (95/5), R_f (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.

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) 1.08 (s, 18H, CH₃ tBu), 1.66 (s, 3H, CH₃-Th), 1.95 (s, 3H, CH₃-Th), 2.32 (s, 3H, CH₃-Th), 2.38 (s, 3H, CH₃-Th), 6.18 (d, 1H, ³J_{HH} = 10.5 Hz, Si-CH), 6.36 (s, 1H, H Th), 6.63 (s, 1H, H Th), 7.09 (d, 1H, ³J_{HH} = 10.5 Hz, Si-C(H)=CH); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ (ppm) 14.3 (s, CH₃-Th), 14.7 (s, CH₃-Th), 15.2 (s, CH₃-Th), 15.4 (s, CH₃-Th), 19.7 (s, C tBu), 29.1 (s, CH₃ 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); ²⁹Si NMR (CD₂Cl₂, 79 MHz): δ (ppm) 21.8 (s). HRMS (ESI, CH₂Cl₂) calcd for [C₂₄H₃₄Si₂]⁺, 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 C₆D₆ (0.65 mL) was added tetrakis(triphenylphosphine) palladium (0) (14.9 mg, 1.29 × 10⁻² 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 [SiO₂, 15 g, eluent petroleum ether (100%), R_f = 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.

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) 0.99 (s, 9H, CH₃ tBu), 1.05 (s, 9H, CH₃ tBu), 1.18 (s, 9H, CH₃ tBu), 2.01 (s, 3H, CH₃-Th), 2.05 (s, 3H, CH₃-Th), 2.30 (s, 3H, CH₃-Th), 2.33 (s, 3H, CH₃-Th), 5.94 (s with ²⁹Si sat., 1H, ²J_{Hsi} = 10.5 Hz, H vinyl), 6.41 (s, 1H, H Th), 6.51 (s, 1H, H Th); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ (ppm) 14.7 (s, CH₃-Th), 15.1 (s, CH₃-Th), 15.3 (s, CH₃-Th), 15.7 (s, CH₃-Th), 19.6 (s, C tBu), 19.9 (s, C tBu), 28.9 (s, CH₃ tBu), 29.5 (s, CH₃ tBu), 30.6 (s, CH₃ 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.). ²⁹Si NMR (C₆D₆, 79 MHz): δ (ppm) 13.3 (s). HRMS (ESI, CH₃OH/CH₂Cl₂ (90/10)) calcd for [C₂₈H₄₂Si₂+Na]⁺, 493.23894; found, 493.2394 (1 ppm); calcd for [C₂₈H₄₂Si₂+K]⁺, 509.21288; found, 509.2130 (0 ppm). Anal. Calcd for [C₂₈H₄₂Si₂]; 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 × 10⁻³ 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 {SiO₂, 15 g; gradient DCM/pentane (10/90) → DCM/pentane (20/80); R_f [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.

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) 1.09 (s, 9H, CH₃ tBu), 1.14 (s, 9H, CH₃ tBu), 1.74 (s, 3H, CH₃-Th), 1.79 (s, 3H, CH₃-Th), 2.20 (s, 3H, CH₃-Th), 2.39 (s, 3H, CH₃-Th), 2.89 (s, 3H, OCH₃), 5.96 (s, 1H, H Th), 5.99 (s with ²⁹Si sat., 1H, ²J_{Hsi} = 11.2 Hz, H vinyl), 6.50 (d, 2H, ³J_{HH} = 8.9 Hz, H Ph), 6.64 (s, 1H, H Th), 6.89 (d, 2H, ³J_{HH} = 8.9 Hz, H Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ (ppm) 14.5 (s, CH₃-Th), 14.6 (s, CH₃-Th), 15.2 (s, CH₃-Th), 15.4 (s, CH₃-Th), 19.9 (s, C tBu), 20.1 (s, C tBu), 29.1 (s, CH₃ tBu), 29.3 (s, CH₃ tBu), 40.7 (s, OCH₃), 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); ²⁹Si NMR (CD₂Cl₂, 79 MHz): δ (ppm) 16.7 (s). HRMS (ESI, CH₃OH/CH₂Cl₂ (95/5)): calcd for [C₃₁H₄₀SiOS₂+H]⁺, 521.23626; found, 521.2361 (0 ppm). Anal. Calcd for [C₃₁H₄₀SiOS₂]; C, 71.48; H, 7.74. Found: C, 71.36; H, 7.82.

Compound 4b (R = COMe). After flash chromatography on silica gel [SiO₂, 15 g; gradient DCM/pentane (50/50) → DCM/pentane (70/30); R_f (DCM/pentane (50/50)) = 0.60], the product was obtained a clear yellow oil.

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) 1.10 (s, 9H, CH₃ tBu), 1.16 (s, 9H, CH₃ tBu), 1.73 (s, 3H, CH₃-Th), 1.79 (s, 3H, CH₃-Th), 2.16 (s, 3H, CH₃-Th), 2.39 (s, 3H, CH₃-Th), 2.53 (s, 3H, C(O)CH₃), 5.91 (s, 1H, H Th), 6.24 (s with ²⁹Si sat., 1H, ²J_{Hsi} = 10.7 Hz, H vinyl), 6.65 (s, 1H, H Th), 7.11 (d, 2H, ³J_{HH} = 8.5 Hz, H Ph), 7.73 (d, 2H, ³J_{HH} = 8.5 Hz, H Ph); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ (ppm) 14.5 (s, CH₃-Th), 14.6 (s, CH₃-Th), 15.1 (s, CH₃-Th), 15.4 (s, CH₃-Th), 20.0 (s, C tBu), 20.1 (s, C tBu), 26.8 (s, C(O)CH₃), 29.0 (s, CH₃ tBu), 29.3 (s, CH₃ 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

681 Th), 131.5 (s, $\underline{\text{CH}}$ vinyl), 133.5 (s, $\underline{\text{C}}$ Th), 134.9 (s, $\underline{\text{C}}$ Th), 135.5 (s, $\underline{\text{C}}$ Th), 135.8 (s, $\underline{\text{C}}-\text{C}(\text{O})\text{CH}_3$), 136.6 (s, $\underline{\text{C}}$ Th), 137.6 (s, $\underline{\text{C}}$ Th), 140.8 (s, $\underline{\text{C}}-\text{Si}$), 146.9 (s, $\underline{\text{C}}$ Ph), 150.1 (s, $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$), 162.4 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$), 197.9 (s, $\underline{\text{C}}=\text{O}$); ^{29}Si NMR (CD_2Cl_2 , 79 MHz): δ (ppm) 685 17.7 (s). HRMS (ESI, CH_2Cl_2): calcd for $[\text{C}_{32}\text{H}_{40}\text{SiO}_5]^+$, 686 532.22844; found, 532.2283 (0 ppm). Anal. Calcd for $[\text{C}_{28}\text{H}_{42}\text{SiS}_2]$; 687 C, 72.13; H, 7.57. Found: C, 72.41; H, 7.56.

688 **Compound 4c** ($R = \text{CF}_3$). After flash chromatography on silica gel 689 $[\text{SiO}_2$, 15 g; eluent, DCM/pentane (5/95); $R_f = 0.8$], the product was 690 obtained as a white solid.

691 ^1H NMR (CD_2Cl_2 , 400 MHz): δ (ppm) 1.10 (s, 9H, $\underline{\text{CH}_3}$ tBu), 692 1.17 (s, 9H, $\underline{\text{CH}_3}$ tBu), 1.74 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 1.79 (s, 3H, $\underline{\text{CH}_3}-$ 693 Th), 2.16 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.39 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 5.89 (s, 1H, $\underline{\text{H}}$ 694 Th), 6.24 (s with ^{29}Si sat., 1H, $^2J_{\text{HSi}} = 10.6$ Hz, $\underline{\text{H}}$ vinyl), 6.66 (s, 1H, 695 $\underline{\text{H}}$ Th), 7.14 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, $\underline{\text{H}}$ Ph), 7.41 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, 696 $\underline{\text{H}}$ Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ (ppm) 14.5 (s, $\underline{\text{CH}_3}-$ 697 Th), 14.6 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.1 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.4 (s, $\underline{\text{CH}_3}-\text{Th}$), 20.0 698 (s, $\underline{\text{C}}$ tBu), 20.1 (s, $\underline{\text{C}}$ tBu), 29.0 (s, $\underline{\text{CH}_3}$ tBu), 29.3 (s, $\underline{\text{CH}_3}$ tBu), 699 124.5 (q, $^4J_{\text{CF}} = 3.8$ Hz, $\underline{\text{CH}}$ Ph), 124.9 (q, $^1J_{\text{CF}} = 271.7$ Hz, $\underline{\text{CF}_3}$), 700 126.9 (s, $\underline{\text{CH}}$ Th), 127.6 (s, $\underline{\text{CH}}$ Th), 128.2 (s, $\underline{\text{CH}}$ Ph), 128.7 (q, $^2J_{\text{CF}}$ 701 = 32.0 Hz, $\underline{\text{C}}-\text{CF}_3$), 130.3 (s, $\underline{\text{C}}$ Th), 131.5 (s, $\underline{\text{CH}}$ vinyl), 133.5, 135.0, 702 135.5, 136.5 and 137.6 (s, $\underline{\text{C}}$ Th), 140.8 (s, $\underline{\text{C}}-\text{Si}$), 145.9 (s, $\underline{\text{C}}$ Ph), 703 150.0 (s, $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$), 162.0 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$); ^{29}Si NMR 704 (CD_2Cl_2 , 79 MHz): δ (ppm) 17.7 (s); $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 705 376 MHz): δ (ppm) -62.7 (s). HRMS (ESI, CH_2Cl_2): calcd for 706 $[\text{C}_{31}\text{H}_{37}\text{F}_3\text{SiS}_2]^+$, 558.20526; found, 558.2053 (0 ppm). Anal. Calcd 707 for $[\text{C}_{28}\text{H}_{42}\text{SiS}_2]$; C, 66.63; H, 6.67. Found: C, 66.97; H, 6.83.

708 **Compound 4d** ($R = \text{CHO}$). After flash chromatography on silica gel 709 $[\text{SiO}_2$, 15 g; eluent, pentane/ethyl acetate (97/3); $R_f = 0.47$], the 710 product was obtained as a fluffy pale-yellow solid.

711 ^1H NMR (CD_2Cl_2 , 400 MHz): δ (ppm) 1.10 (s, 9H, $\underline{\text{CH}_3}$ tBu), 712 1.17 (s, 9H, $\underline{\text{CH}_3}$ tBu), 1.73 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 1.80 (s, 3H, $\underline{\text{CH}_3}-$ 713 Th), 2.15 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.40 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 5.90 (s, 1H, $\underline{\text{H}}$ 714 Th), 6.28 (s with ^{29}Si sat., 1H, $^2J_{\text{HSi}} = 10.6$ Hz, $\underline{\text{H}}$ vinyl), 6.66 (s, 1H, 715 $\underline{\text{H}}$ Th), 7.19 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, $\underline{\text{H}}$ Ph), 7.66 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, 716 $\underline{\text{H}}$ Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ (ppm) 14.1 (s, $\underline{\text{CH}_3}-$ 717 Th), 14.2 (s, $\underline{\text{CH}_3}-\text{Th}$), 14.7 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.0 (s, $\underline{\text{CH}_3}-\text{Th}$), 19.6 718 (s, $\underline{\text{C}}$ tBu), 19.7 (s, $\underline{\text{C}}$ tBu), 28.5 (s, $\underline{\text{CH}_3}$ tBu), 28.9 (s, $\underline{\text{CH}_3}$ tBu), 719 126.5 (s, $\underline{\text{CH}}$ Th), 127.1 (s, $\underline{\text{CH}}$ Th), 128.1 (s, $\underline{\text{CH}}$ Ph), 128.7 (s, $\underline{\text{CH}}$ 720 Ph), 129.9 (s, $\underline{\text{C}}$ Th), 131.6 (s, $\underline{\text{CH}}$ vinyl), 133.1, 134.5, 134.7, 135.1, 721 136.1 and 137.1 (s, $\underline{\text{C}}$ Th), 140.4 (s, $\underline{\text{C}}-\text{Si}$), 147.9 (s, $\underline{\text{C}}$ Ph), 149.5 (s, 722 $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$), 161.9 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$), 191.8 (s, $\underline{\text{C}}=\text{O}$); ^{29}Si NMR 723 (CD_2Cl_2 , 79 MHz): δ (ppm) 17.8 (s). HRMS (ESI, CH_2Cl_2): calcd 724 for $[\text{C}_{31}\text{H}_{38}\text{OSiS}_2]^+$, 518.21279; found, 518.2126 (0 ppm). Anal. 725 Calcd for $[\text{C}_{28}\text{H}_{42}\text{SiS}_2]$; C, 71.76; H, 7.38. Found: C, 72.22; H, 7.26.

726 **Compound 4e** ($R = \text{NH}_2$). After flash chromatography on silica gel 727 $[\text{SiO}_2$, 15 g; eluent, DCM/pentane/methanol (20/79/1); $R_f = 0.1$], 728 the product was obtained as an oil.

729 ^1H NMR (CD_2Cl_2 , 400 MHz): δ (ppm) 1.09 (s, 9H, $\underline{\text{CH}_3}$ tBu), 730 1.14 (s, 9H, $\underline{\text{CH}_3}$ tBu), 1.73 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 1.79 (s, 3H, $\underline{\text{CH}_3}-$ 731 Th), 2.19 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.38 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 3.64 (s br., 2H, 732 $\underline{\text{NH}_2}$), 5.94 (s, 1H, $\underline{\text{H}}$ Th), 6.00 (s with ^{29}Si sat., 1H, $^2J_{\text{HSi}} = 11.0$ Hz, 733 $\underline{\text{H}}$ vinyl), 6.45 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, $\underline{\text{H}}$ Ph), 6.63 (s, 1H, $\underline{\text{H}}$ Th), 6.80 734 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, $\underline{\text{H}}$ Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 735 (ppm) 14.5 (s, $\underline{\text{CH}_3}-\text{Th}$), 14.6 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.2 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.4 736 (s, $\underline{\text{CH}_3}-\text{Th}$), 19.9 (s, $\underline{\text{C}}$ tBu), 20.1 (s, $\underline{\text{C}}$ tBu), 29.1 (s, $\underline{\text{CH}_3}$ tBu), 29.3 737 (s, $\underline{\text{CH}_3}$ tBu), 114.0 (s, $\underline{\text{CH}}$ Ph), 126.5 (s, $\underline{\text{CH}}$ vinyl), 127.2 (s, $\underline{\text{CH}}$ 738 Th), 128.0 (s, $\underline{\text{CH}}$ Th), 129.0 (s, $\underline{\text{CH}}$ Ph), 130.0 (s br., $\underline{\text{C}}$ Th), 132.6 739 (s, $\underline{\text{C}}$ Ph), 133.1 (s, $\underline{\text{C}}$ Th), 134.1 (s br., $\underline{\text{C}}$ Th), 135.1 (s, $\underline{\text{C}}$ Th), 137.3 740 (s, $\underline{\text{C}}$ Th), 138.1 (s, $\underline{\text{C}}$ Th), 140.2 (s, $\underline{\text{C}}-\text{Si}$), 146.0 (s, $\underline{\text{C}}$ Ph), 151.3 (s, 741 $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$), 163.1 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$); ^{29}Si NMR (CD_2Cl_2 , 79 742 MHz): δ (ppm) 16.8 (s). HRMS (ESI, $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (95/5)): 743 calcd for $[\text{C}_{30}\text{H}_{39}\text{NSiS}_2\text{H}]^+$, 506.2366; found, 506.2365 (0 ppm). 744 Anal. Calcd for $[\text{C}_{30}\text{H}_{39}\text{SiS}_2\text{H}]^+$; C, 71.23; H, 7.77, N, 2.77. Found: C, 745 70.91; H, 7.62, N, 2.27.

746 **Compound 4f** ($R = \text{N}(\text{CH}_3)_2$). After flash chromatography on silica 747 gel $[\text{SiO}_2$, 15 g; eluent, DCM/pentane (50/50); $R_f = 0.9$], the product 748 was obtained as a yellowish oil.

749 ^1H NMR (CD_2Cl_2 , 400 MHz): δ (ppm) 1.09 (s, 9H, $\underline{\text{CH}_3}$ tBu), 750 1.15 (s, 9H, $\underline{\text{CH}_3}$ tBu), 1.73 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 1.78 (s, 3H, $\underline{\text{CH}_3}-$

Th), 2.18 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.39 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 3.75 (s, 6H, 751 $\text{N}(\underline{\text{CH}_3})_2$), 5.92 (s, 1H, $\underline{\text{H}}$ Th), 6.06 (s with ^{29}Si sat., 1H, $^2J_{\text{HSi}} = 11.0$ 752 Hz, $\underline{\text{H}}$ vinyl), 6.64 (s, 1H, $\underline{\text{H}}$ Th), 6.67 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, $\underline{\text{H}}$ Ph), 753 6.94 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, $\underline{\text{H}}$ Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 754 MHz): δ (ppm) 14.5 (s, $\underline{\text{CH}_3}-\text{Th}$), 14.6 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.1 (s, $\underline{\text{CH}_3}-$ 755 Th), 15.4 (s, $\underline{\text{CH}_3}-\text{Th}$), 19.9 (s, $\underline{\text{C}}$ tBu), 20.1 (s, $\underline{\text{C}}$ tBu), 29.0 (s, $\underline{\text{CH}_3}$ 756 tBu), 29.3 (s, $\underline{\text{CH}_3}$ tBu), 55.5 (s, $\text{N}(\underline{\text{CH}_3})_2$), 112.9 (s, $\underline{\text{CH}}$ Ph), 127.1 757 (s, $\underline{\text{CH}}$ Th), 127.8 (s, $\underline{\text{CH}}$ vinyl), 127.9 (s, $\underline{\text{CH}}$ Th), 129.1 (s, $\underline{\text{CH}}$ Ph), 758 130.1 (s, $\underline{\text{C}}$ Th), 133.2 (s, $\underline{\text{C}}$ Th), 134.3 (s, $\underline{\text{C}}$ Th), 134.9 (s, $\underline{\text{C}}$ Ph), 759 135.2 (s, $\underline{\text{C}}$ Th), 137.1 (s, $\underline{\text{C}}$ Th), 138.0 (s, $\underline{\text{C}}$ Th), 140.3 (s, $\underline{\text{C}}-\text{Si}$), 760 151.0 (s, $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$), 159.0 (s, $\underline{\text{C}}$ Ph), 162.8 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$); 761 ^{29}Si NMR (CD_2Cl_2 , 79 MHz): δ (ppm) 16.9 (s). HRMS (ESI, 762 $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (5/95)): calcd for $[\text{C}_{32}\text{H}_{43}\text{SiS}_2\text{H}]^+$, 534.2679; 763 found, 534.2679 (0 ppm). 764

Compound 5-D. The synthesis and purification of **5-D** were 765 transposed from the described procedure for the protio-derivative **5** 766 with $\text{Ph}-\text{C}\equiv\text{C}-\text{D}$ as a starting material instead of $\text{Ph}-\text{C}\equiv\text{C}-\text{H}$. 767

^1H NMR (CD_2Cl_2 , 400 MHz): δ (ppm) 1.10 (s, 9H, $\underline{\text{CH}_3}$ -tBu), 768 1.16 (s, 9H, $\underline{\text{CH}_3}$ -tBu), 1.73 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 1.78 (s, 3H, $\underline{\text{CH}_3}-$ 769 Th), 2.16 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.39 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 5.90 (s, 1H, $\underline{\text{H}}$ - 770 Th), 6.65 (s, 1H, $\underline{\text{H}}$ -Th), 6.99–7.05 (m, 2H, $\underline{\text{H}}-\text{mPh}$), 7.11–7.19 (m, 771 3H, $\underline{\text{H}}-\text{oPh}$ and $\underline{\text{H}}-\text{pPh}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 772 (ppm) 14.5 (s, $\underline{\text{CH}_3}-\text{Th}$), 14.6 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.1 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.4 773 (s, $\underline{\text{CH}_3}-\text{Th}$), 19.9 (s, $\underline{\text{C}}$ -tBu), 20.1 (s, $\underline{\text{C}}$ -tBu), 29.0 (s, $\underline{\text{CH}_3}$ -tBu), 29.3 774 (s, $\underline{\text{CH}_3}$ -tBu), 127.0 (s, $\underline{\text{CH}}$ -pPh), 127.1 (s, $\underline{\text{CH}}$ -Th), 127.6 (s, $\underline{\text{CH}}$ - 775 oPh), 127.9 (s, $\underline{\text{C}}-\text{Th}$), 127.9 (s, $\underline{\text{CH}}-\text{mPh}$), 128.9 (triplet 111, $^1J_{\text{CD}}$ 776 = 22.6 Hz, $\underline{\text{CD}}$ -vinyl), 130.1 (s, $\underline{\text{C}}_2-\text{Th}$), 133.3 (s, $\underline{\text{C}}_2-\text{Th}$), 134.4 (s, 777 $\underline{\text{C}}_5-\text{Th}$), 135.3 (s, $\underline{\text{C}}_5-\text{Th}$), 137.0 (s, $\underline{\text{C}}_3-\text{Th}$), 137.9 (s, $\underline{\text{C}}_3-\text{Th}$), 778 140.3 (s, $\underline{\text{C}}-\text{Si}$), 142.3 (s, $\underline{\text{C}}-\text{ipsoPh}$), 150.8 (s, $\text{Si}-\text{C}=\underline{\text{C}}-\text{Th}$), 163.3 779 (s, $\text{Si}-\text{CH}=\underline{\text{C}}-\text{Ph}$). HRMS (ASAP, 90 °C): exact mass (mono- 780 isotopic) calcd for $[\text{C}_{30}\text{H}_{37}\text{DSiS}_2]^+$, 491.22415; found, 491.2246 (1 781 ppm). 782

Compound 6-PtBu₃. A solution of silirene **1** (20.0 mg, 5.15×10^{-2} 783 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (26.2 mg, $5.15 \times$ 784 10^{-2} mmol, 1.00 equiv) in C_6D_6 (0.65 mL) was heated for 13 h at 50 785 °C, giving yellow solution. **6-PtBu₃** was characterized in situ by 786 multinuclear NMR spectroscopy, showing a conversion toward the 787 OA product of 40%. 788

^1H NMR (C_6D_6 , 400 MHz): δ (ppm) 1.26 (d, 27H, $^3J_{\text{HP}} = 11.7$ 789 Hz, $\underline{\text{CH}_3}$ PtBu), 1.53 (s, 18H, $\underline{\text{CH}_3}$ SiBu), 2.14 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 790 2.17 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.19 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.29 (s, 3H, $\underline{\text{CH}_3}-$ 791 Th), 6.55 (s, 1H, $\underline{\text{H}}$ Th), 6.94 (s, 1H, $\underline{\text{H}}$ Th); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 792 100 MHz): δ (ppm) 14.5 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.0 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.3 (s, 793 $\underline{\text{CH}_3}-\text{Th}$), 15.4 (s, $\underline{\text{CH}_3}-\text{Th}$), 24.5 (s, $\underline{\text{C}}$ SiBu), 31.8 (s, $\underline{\text{CH}_3}$ SiBu), 794 32.8 (d, $^2J_{\text{CP}} = 8.3$ Hz, $\underline{\text{CH}_3}$ PtBu), 37.3 (s, $\underline{\text{C}}$ PtBu), 127.3 (s, $\underline{\text{CH}}$ 795 Th), 127.7 (s, $\underline{\text{CH}}$ Th), 128.4 (s, $\underline{\text{C}}\text{quat.}$), 128.9 (s, $\underline{\text{C}}\text{quat.}$), 134.3 (s, 796 $\underline{\text{C}}\text{quat.}$), 134.6 (s, $\underline{\text{C}}\text{quat.}$), 134.8 (d, $J_{\text{CP}} = 2.4$ Hz, $\underline{\text{C}}\text{quat.}$), 138.7 (d, 797 $J_{\text{CP}} = 8.8$ Hz, $\underline{\text{C}}\text{quat.}$), 146.4 (d, $J_{\text{CP}} = 12.8$ Hz, $\text{Si}-\underline{\text{C}}=\text{C}$), 151.5 (d, J_{CP} 798 = 46.1 Hz, $\text{Si}-\text{C}=\underline{\text{C}}$); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79 MHz): δ (ppm) 799 -33.7 (s); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ (ppm) 80.9 (s). 800

Compound 6-P(otol)₃. A solution of silirene **1** (20.0 mg, $5.15 \times$ 801 10^{-2} mmol) and bis(tri-*o*-tolyl-phosphine)palladium(0) (36.8 mg, 802 5.15×10^{-2} mmol, 1.00 equiv) in C_6D_6 (0.65 mL) was heated for 4 h 803 at 50 °C, giving yellow solution. **6-P(otol)₃** was characterized in situ 804 by multinuclear NMR spectroscopy, showing a conversion toward the 805 OA product of 82%. 806

^1H NMR (C_6D_6 , 400 MHz): δ (ppm) 1.35 (s, 18H, $\underline{\text{CH}_3}$ SiBu), 807 1.97 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.15 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.18 (s, 3H, $\underline{\text{CH}_3}-$ 808 Th), 2.25 (s, 3H, $\underline{\text{CH}_3}-\text{Th}$), 2.46 (s, 3H, $\underline{\text{CH}_3}$ tolyl), 6.56 (s, 1H, $\underline{\text{H}}$ 809 Th), 6.96 (s, 1H, $\underline{\text{H}}$ Th); the ortho tolyl proton resonance signals 810 could not be unambiguously assigned due to the complexity of the 811 aromatic region of the spectrum; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 812 (ppm) 14.7 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.1 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.1 (s, $\underline{\text{CH}_3}-\text{Th}$), 15.3 813 (s, $\underline{\text{CH}_3}-\text{Th}$), 23.7 (d, $^3J_{\text{CP}} = 11.8$ Hz, $\underline{\text{CH}_3}$ tolyl), 24.7 (s, $\underline{\text{C}}$ SiBu), 814 31.3 (s, $\underline{\text{CH}_3}$ SiBu), 126.0 (d, $J_{\text{CP}} = 8.9$ Hz, $\underline{\text{CH}}$ tolyl), 127.0 (s, $\underline{\text{CH}}$ 815 Th), 127.5 (s, $\underline{\text{CH}}$ Th), 128.5 (s br., $\underline{\text{C}}\text{quat.}$), 129.3 (s, $\underline{\text{C}}\text{quat.}$), 130.0 816 (d, $^1J_{\text{CP}} = 28.7$ Hz, $\text{P}-\underline{\text{C}}$), 130.4 (s br., $\underline{\text{CH}}$ tolyl), 131.9 (d, $^3J_{\text{CP}} = 5.8$ 817 Hz, $\underline{\text{CH}}$ tolyl), 134.8 (s, $\underline{\text{C}}\text{quat.}$), 134.9 (s, $\underline{\text{C}}\text{quat.}$), 135.5 (d, $J_{\text{CP}} = 818 14.7$ Hz, $\underline{\text{CH}}$ tolyl), 137.8 (d, $J_{\text{CP}} = 1.2$ Hz, $\underline{\text{C}}\text{quat.}$), 138.7 (d, $J_{\text{CP}} = 819 9.3$ Hz, $\underline{\text{C}}\text{quat.}$), 142.9 (d, $J_{\text{CP}} = 11.6$ Hz, $\underline{\text{C}}$ otolyl), 146.0 (d, $J_{\text{CP}} = 820$

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 (C_6D_6 , 79 MHz): δ (ppm) -31.6 (s); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 ,
823 162 MHz): δ (ppm) 25.3 (s).

824 **Compound 6-COD.** THF (2 mL) was added to a neat mixture of
825 silirene **1** (30.0 mg, 7.72×10^{-2} mmol) and (1,5-cyclooctadiene)-
826 bis(trimethylsilylmethyl)palladium(II) (30.0 mg, 7.72×10^{-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 ^1H NMR (CD_2Cl_2 , 500 MHz, 243 K): δ (ppm) 1.07 (s, 18H, CH_3
836 Si*t*Bu), 1.96 (s, 3H, CH_3 -Th), 1.98 (s, 3H, CH_3 -Th), 2.06–2.20
837 (br., 2H, CH_2 COD), 2.20–2.40 (br., 4H, CH_2 COD), 2.29 (s, 3H,
838 CH_3 -Th), 2.30 (s, 3H, CH_3 -Th), 2.52–2.66 (br., 2H, CH_2 COD),
839 4.88–5.67 (br., 2H, CH COD), 5.90 (br., 2H, CH COD), 6.27 (s,
840 1H, H Th), 6.43 (s, 1H, H Th); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz,
841 243 K): δ (ppm) 14.0 (s, CH_3 -Th), 14.7 (s, CH_3 -Th), 15.2 (s,
842 CH_3 -Th), 15.2 (s, CH_3 -Th), 23.3 (s br., C Si*t*Bu), 27.4 (br., CH_2
843 COD), 30.0 (br., CH_2 COD), 30.7 (s, CH_3 Si*t*Bu), 105.1 (s br., CH
844 COD), 122.2 (s br., CH COD), 123.2 (s, C_{quat}), 125.4 (s, CH Th),
845 126.4 (s, C_{quat}), 126.5 (s, CH Th), 133.8, 133.8, 140.8, 146.4, 151.6
846 and 161.3 (s, C_{quat}); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 99 MHz, 243 K): δ
847 (ppm) -34.8 (s).

848 **Compound 6-PPh₃.** 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 (2×10^{-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-PPh₃** for X-ray diffraction analysis furnished crystals of
860 the known complex $[\text{Pd}(\text{PPh}_3)_3]$.

861 ^1H NMR (THF- d^8 , 400 MHz): δ (ppm) 1.04 (s, 18H, CH_3 *t*Bu),
862 1.86 (s, 3H, CH_3 -Th), 2.13 (s, 3H, CH_3 -Th), 2.32 (s, 3H, CH_3 -
863 Th), 2.34 (s, 3H, CH_3 -Th), 6.56 (s, 1H, H Th), 6.58 (s, 1H, H Th),
864 7.31–7.43 (m, 9H, H *p*Ph and H *m*Ph), 7.54–7.64 (m, 6H, H *o*Ph);
865 $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d^8 , 100 MHz): δ (ppm) 14.7 (s, CH_3 -Th),
866 14.9 (s, CH_3 -Th), 15.0 (s, CH_3 -Th), 15.1 (s, CH_3 -Th), 24.7 (s, C
867 *t*Bu), 31.1 (s, CH_3 *t*Bu), 127.3 (s, CH Th), 127.6 (s, CH Th), 128.7
868 (d, $J_{\text{CP}} = 1.7$ Hz, C_{quat}), 129.2 (s, C_{quat}), 129.2 (d, $J_{\text{CP}} = 9.6$ Hz,
869 CH *m*Ph), 130.6 (d, $J_{\text{CP}} = 1.4$ Hz, CH *p*Ph), 134.7 (s, C_{quat}), 135.0
870 (d, $J_{\text{CP}} = 15.9$ Hz, CH *o*Ph), 135.3 (d, $J_{\text{CP}} = 31.2$ Hz, $\text{C}-\text{P}$), 135.4 (s,
871 C_{quat}), 137.0 (s br., C_{quat}), 138.9 (d, $J_{\text{CP}} = 9.9$ Hz, C_{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): δ (ppm) -27.2 (d, $J_{\text{SiP}} = 2.1$ Hz);
874 $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d^8 , 162 MHz): δ (ppm) 24.0 (s, **6-PPh₃**).

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_3 aromatic proton resonance signals of **6-PPh₃** and
878 $[\text{Pd}(\text{PPh}_3)_n]$; exchange correlations are observed between thienyl
879 - CH_3 protons resonance signals of **6-PPh₃** and **6-PPh₃**.

880 In the NOESY $^{31}\text{P}, ^{31}\text{P}$ NMR spectrum, exchange correlations are
881 observed between the PPh_3 resonance signal of **6-PPh₃** and
882 $[\text{Pd}(\text{PPh}_3)_n]$.

883 **Compound 6-P(OPh)₃.** To a solution of silirene **1** (100 mg, 0.257
884 mmol) and triphenylphosphite (67.4 μL , 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)₃ suitable for X-ray diffraction were obtained from a 900
saturated THF/pentane solution at -30 °C. 901

The compound **6-P(OPh)₃** was characterized by NMR at -40 °C 902
in THF d^8 . In the case of ^{29}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 ^1H and ^{31}P NMR 906
spectra could also be recorded at room temperature in CD_2Cl_2 for a 907
better resolution (see S101–104). 908

^1H NMR (THF- d^8 , 400 MHz, 233 K): δ (ppm) 1.30 (s, 18H, CH_3
909 *t*Bu), 1.68 (s, 3H, CH_3 -Th), 1.75 (s, 3H, CH_3 -Th), 2.19 (s, 3H,
910 CH_3 -Th), 2.34 (s, 3H, CH_3 -Th), 6.08 (s, 1H, H Th), 6.55 (s, 1H, H
911 Th), 7.17–7.24 (m, 3H, H *p*Ph), 7.35–7.45 (m, 12H, H *o*Ph and H
912 *m*Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d^8 , 100 MHz, 233 K): δ (ppm) 14.4 (s,
913 CH_3 -Th), 14.7 (s, CH_3 -Th), 14.9 (s, CH_3 -Th), 15.3 (s, CH_3 -Th),
914 24.2 (s, C *t*Bu), 31.2 (s, CH_3 *t*Bu), 121.8 (br., CH *o*Ph or CH *m*Ph),
915 125.4 (s, CH *m*Ph), 126.1 (br., C_{quat}), 127.1 (s, CH Th), 127.8 (s,
916 CH Th or C_{quat}), 127.9 (s, CH Th or C_{quat}), 130.3 (s, CH *o*Ph or
917 CH *m*Ph), 133.4 (br., C_{quat}), 134.5 (s, C_{quat}), 141.0 (d br., $J_{\text{CP}} =$
918 12.3 Hz, C_{quat}), 143.4 (br., C_{quat}), 151.8 (d, $J_{\text{CP}} = 3.5$ Hz, $\text{C}-\text{P}$),
919 165.3 (d, $J_{\text{CP}} = 15.1$ Hz, C_{quat}); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 79 MHz,
920 293 K): δ (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): δ (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- 932
tallographic data for this paper. These data can be obtained 933
free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by 934
emailing data_request@ccdc.cam.ac.uk, or by contacting The 935
Cambridge Crystallographic Data Centre, 12 Union Road, 936
Cambridge CB2 1EZ, UK; fax: +44 1223 336033. 937

AUTHOR INFORMATION

Corresponding Authors

Marc Devillard – ISCR (Institut des Sciences Chimiques de 940
Rennes)—UMR 6226, Université de Rennes I, CNRS, F- 941
35042 Rennes, France; orcid.org/0000-0002-3821-0885;
942 Email: marc.devillard@univ-rennes1.fr 943

Gilles Alcaraz – ISCR (Institut des Sciences Chimiques de 944
Rennes)—UMR 6226, Université de Rennes I, CNRS, F- 945
35042 Rennes, France; orcid.org/0000-0001-8705-5917;
946 Email: gilles.alcaraz@univ-rennes1.fr 947

Authors

Chiara Dinoi – LCPNO, CNRS & INSA, Université de 948
Toulouse, F-31077 Toulouse, France 949

Iker Del Rosal – LCPNO, CNRS & INSA, Université de 950
Toulouse, F-31077 Toulouse, France; orcid.org/0000-0001-6898-4550 951
952 953

954 Clément Orione – ScanMAT-CRMPO, Université de Rennes
955 1, F-35042 Rennes, France
956 Marie Cordier – ISCR (Institut des Sciences Chimiques de
957 Rennes)—UMR 6226, Université de Rennes 1, CNRS, F-
958 35042 Rennes, France

959 Complete contact information is available at:
960 <https://pubs.acs.org/10.1021/acs.inorgchem.3c00045>

961 Notes

962 The authors declare no competing financial interest.

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1244 complex is actually in equilibrium regarding to ligand redistribution
1245 and $[Pd(PR_3)_n]$ species as well as free phosphine can be observed.

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1290 two sp hybridized orbitals, as well as the Si–C1 and Si–Pd bonds, via
1291 the overlapping of a Si p orbital with both the C1 sp hybrid on one

side and the Pd d orbital on the other side. The HOMO-4 accounts
for the Si–C1 and Pd–C2 bonds, involving a first overlapping
between a sp hybrid on C1 and a p orbital on Si and a second
overlapping between a sp hybridized orbital on C2 and a d orbital on
the Pd metal. The HOMO-7 orbital mainly describes the C1–C2
bond, through the interaction between sp orbitals, whereas the
HOMO-10 mainly describes the Si–Pd bond, via the interaction
between a p orbital on the Si center and a d orbital on Pd. The
HOMO-18 orbital, finally, displays the overlapping of a C2 sp
hybridized orbital with both a Pd d orbital on one side and a C1 sp
hybridized orbital on the other side, together with an additional slight
bonding interaction between the same C1 sp hybridized orbital and a
Si p orbital.

(37) For sake of clarity, the LUMO is also depicted in Figure S3-
DFT. It consists of an antibonding interaction between the Si and Pd
atoms together with a bonding interaction between Pd and
phosphorus.

(38) To get more insight into the coordination of the alkyne to C
(6-PPh₃), we computed the molecular orbitals of complex **D**. As
shown in Figure S5-DFT, the orbital accounting for the bonding with
phenylacetylene is the homo-7 one, resulting from the overlapping
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