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Catalytic Dimerization of Alkynes via C−H Bond Cleavage by a Platinum−Silylene Complex

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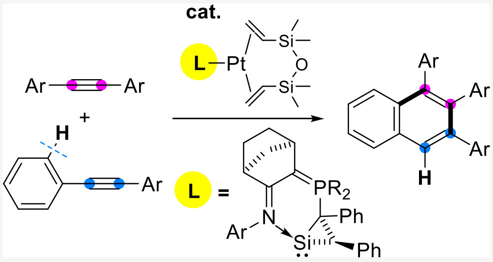
ABSTRACT: The cyclodimerization of diphenylacetylene derivatives catalyzed by a platinum−silylene complex is reported. The reaction proceeds via the cleavage of a carbon−hydrogen bond at the position ortho to an alkynyl group, and no additives are needed. Platinum complexes bearing other common ligands, such as phosphines and NHCs, failed to promote this reaction, highlighting the utility of the silylene ligand in this reaction.



Silylenes are the heavier analogues of carbenes that contain divalent silicon atoms, typically in a singlet ground state. Since the first isolation of a stable divalent silicon compound in 1986,[1] various stable silylenes have been isolated, including N-heterocyclic silylenes (**L1**), cyclic dialkylsilylenes (**L2**), cyclic aminosilylenes (**L3**), and acyclic silylenes (Figure 1).[2] The use of a silylene ligand in transition-metal-catalyzed reactions was also reported. In 2001, Fürstner et al. reported the preparation of a Pd(0)−NHSi (**L1**, R = ^{t}Bu) complex and its use in Suzuki−Miyaura coupling reactions.[3] Since this initial report, several additional catalytic reactions using silylene ligands have been investigated.[4] Three-coordinate base-stabilized silylenes, such as **L4**, are another class of stable silylenes.[2c,d] The base-stabilized silacycloprop-1-ylidene **L5** was reported by Kato and Baceiredo in 2012.[5] Silylene **L5** is an excellent ligand for transition metals, and Cu(I) and Pt(0) complexes of **L5** serve as efficient hydrosilylation catalysts,[6] highlighting the better performance of **L5** compared with other phosphine or N-heterocyclic carbene (NHC) ligands. However, the applications of **L5** in catalysis are limited to hydosilylation reactions of carbonyl compounds and alkenes, and therefore, other types of reactions need to be explored to unveil the full potential of **L5** as a ligand.

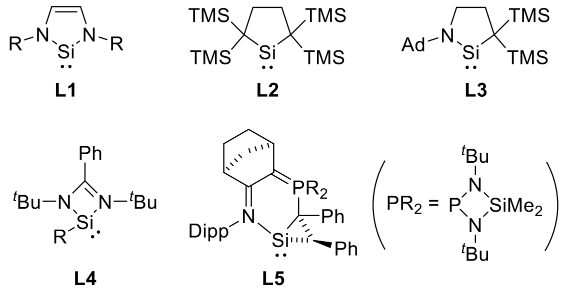


Figure 1. Selected stable silylene ligands.

We report herein that a platinum−**L5** complex is a potent catalyst for use in C−H activation reactions[7] of diphenylacetylene derivatives, which leads to the cyclodimerization of two alkynes to form naphthalene derivatives. Although this type of cyclodimerization of alkynes has been accomplished using Rh,[8] Au,[9] Ru,[10] and Ir[11] catalysts, no platinum complexes that are capable of catalyzing the cyclodimerization of alkynes have been reported to date.

During the course of our investigation of catalytic reactions using Pt(**L5**)(dvtms) (dvtms = 1,3-divinyltetramethyldisiloxane), we found that it efficiently catalyzes the cyclodimerization of diphenylacetylene (**1a**). Thus, when alkyne **1a** was heated in 4-methyltetrahydropyran (4-MeTHP) at 130 °C for 20 h in the presence of 5.0 mol % Pt(**L5**)(dvtms), 1,2,3-triphenylnaphthalene was obtained in 72% yield (entry 1, Table 1). In marked contrast, the corresponding Pt−NHC complexes (entries 2−5) and $Pt_2(dvtms)_3$ (Karstedt's catalyst) (entry 6) were completely inactive for the cyclodimerization of **1a** under these conditions. In addition, the use of PPh_3 in conjunction with Karstedt's catalyst failed to promote this reaction. These results clearly highlight the better utility of silylene ligand **L5** compared with commonly used NHC and phosphine ligands. The thermal stability of the Pt(**L5**)(dvtms) complex was confirmed by the absence of decomposition after its heating in 4-MeTHP at 130 °C for 20 h. It was previously

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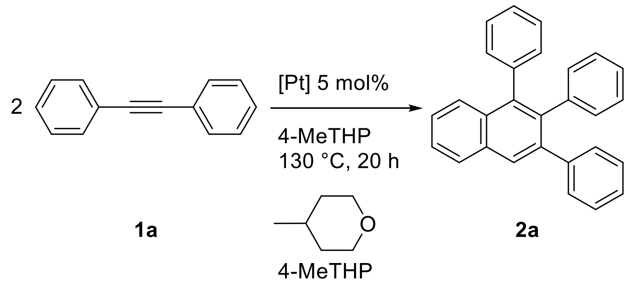
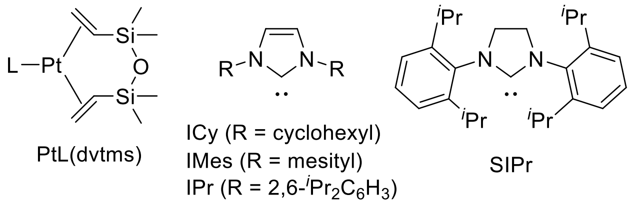
Table 1. Platinum-Catalyzed Cyclodimerization of **1a**[a]



entry	[Pt]	yield of **2a** (%)[b]
1	Pt(**L5**)(dvtms)	72
2	Pt(ICy)(dvtms)	0
3	Pt(IMes)(dvtms)	0
4	Pt(IPr)(dvtms)	0
5	Pt(SIPr)(dvtms)	0
6	$Pt_2(dvtms)_3$ (Karstedt's catalyst)	0
7	$PtCl_2(MeCN)_2$	0
8	Pt(**L5**)(dvtms) + 20 mol % Py·HBr	0

[a]Reaction conditions: **1a** (0.20 mmol), [Pt] (0.010 mmol), and 4-MeTHP (0.50 mL) in a screw-capped vial under N_2 for 20 h. [b]Determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.



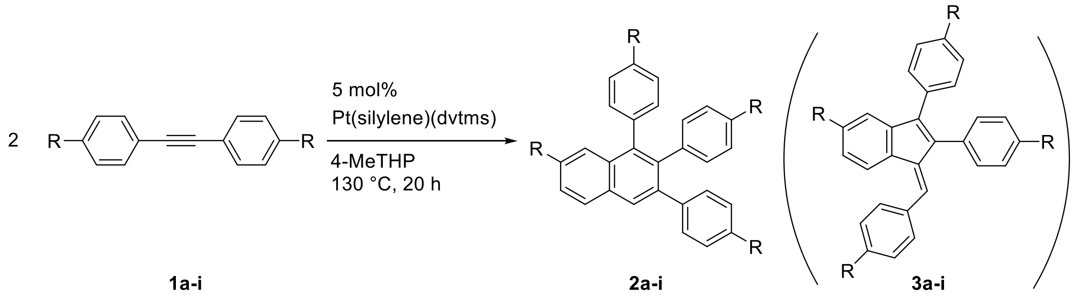
reported that π-acidic Au(I) complexes can catalyze the cyclodimerization of push–pull alkynes.[9] Therefore, we first considered the initiation of the reaction by electrophilic Pt(II) complexes generated in situ. However, this possibility was excluded since electrophilic Pt(II) complexes such as $[PtCl_2(MeCN)_2]$ did not show any catalytic activity (entry 7). It was also reported that Rh(I) complexes, in the presence of a proton source, can generate a Rh(III) hydride as a key reactive species, which initiates the dimerization of alkynes by a hydrorhodation process.[8a,b] To verify the possibility that such a metal hydride species is involved in our platinum system, the reaction was conducted in the presence of 20 mol % Py·HBr. However, the reaction was completely blocked when a proton source was added (entry 8). Therefore, it is unlikely that the reaction is catalyzed by a platinum hydride species that is generated by the reaction of Pt(**L5**)(dvtms) with residual water.

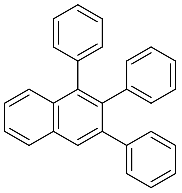
The scope of the platinum–silylene-catalyzed cyclodimerization of diphenylacetylene derivatives was next investigated (Table 2). Substrates bearing electron-donating groups, such as methyl (**1b**) or methoxy groups (**1c**), were applicable to this reaction, although the yields were relatively low compared with that for electron-neutral alkyne **1a** because of the formation of indene derivative **3**[12] as a byproduct. In contrast, electron-deficient alkynes, such as that bearing trifluoromethyl groups (**1d**), were efficiently cyclodimerized without the formation of an indene-type byproduct. Halogen atoms, including fluorine (**1e**) and chlorine (**1f**), were tolerated, with the corresponding cyclodimerization products being formed in 87% and 63% yield, respectively. Acetyl (**1g**) and cyano (**1h**) groups were also compatible. The reaction is not limited to aromatic alkynes, and heteroaromatic substrates also participated in this reaction. When bis(2-thienyl)acetylene (**1i**) was used, benzothiophene was obtained in 41% yield. However, Pt(**L5**)(dvtms) did not show any catalytic activity for the cyclodimerization of aliphatic alkynes and 2-phenyl-1-trimethylsilylacetylene.

In order to gain insight into mechanistic aspects of this cyclodimerization reaction, deuterium labeling experiments were carried out. The platinum–silylene-catalyzed reaction of 2,6,2′,6′-tetradeuteroditolylacetylene (**1b**-d_4) under the standard reaction conditions led to the formation of a naphthalene derivative with deuterium being incorporated at the 4-position (i.e., **2b**-d_4) in addition to the positions where deuterium atoms were originally located (Figure 2a). Although the deuterium content at the 4-position was 66%,[13] the majority of the cleaved deuterium atom is incorporated into the product, indicating that the cleaved hydrogen atom migrates in an intramolecular manner rather than via an intermolecular proton transfer pathway. In terms of the reaction rate, deuterium labeling had no significant effect on the yield at the early stage of the cyclodimerization reaction (Figure 2b), which indicates that the turnover-determining step of this reaction is not the C–H bond cleavage step. We next examined the effect of the substituents on the cyclodimerization reaction by comparing the cyclodimerization yields for **1a**, **1c**, **1d**, and **1e** at 1 and 3 h (Figure 2c). The yields for alkynes **1a** and **1c** were significantly lower than those for alkynes **1d** and **1e**, and the reaction of **1d** was complete within 3 h, revealing that this cyclodimerization is strongly accelerated by electron-withdrawing groups.

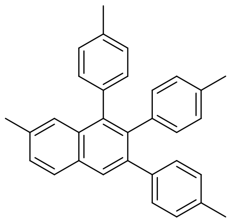
A possible mechanism is shown in Figure 3. First, ligand exchange between dvtms and two alkynes forms $Pt(alkyne)_2$ complex **A**. The ortho C–H bond of alkyne **1a** then oxidatively adds to the platinum center, with an alkyne serving as an ortho directing group,[11,12,14] to provide Pt(II) hydride intermediate **B**. The insertion of a second alkyne into the aryl–platinum bond forms alkenylplatinum complex **C**, which leads to the formation of seven-membered platinacycle **D** via intramolecular trans hydrometalation.[15] Finally, reductive elimination from **D** affords naphthalene **2a** and regenerates Pt(0). In this reaction, silylene **L5** serves as an efficient ligand. The silylene ligand **L5** is a strong σ donor, as evidenced by its Tolman electronic parameter (TEP) value of 2027 cm^{-1}, which is lower than the TEP values for typical NHC ligands (e.g., 2037 cm^{-1} for ICy).[6] Nevertheless, the Pt–vinyl bond distance in Pt(**L5**)(dvtms) (2.123–2.151 Å) is longer than that in Pt(NHC)(dvtms) (2.114–2.132 Å), probably because of the greater Pt → ligand π back-donation with the silylene ligand compared with the NHC ligand.[6] In addition, the silicon center of **L5** is tricoordinate because of the coordination of the imine, rendering the silicon center more sterically demanding than typical NHCs. These electronic and steric features of silylene **L5** would be expected to facilitate the dissociation of dvtms and reductive elimination. We confirmed that Pt(**L5**)(dvtms) and Pt(ICy)(dvtms) release dvtms at similar rates upon the addition of **1a**, indicating that the initial ligand exchange step is not specifically accelerated by **L5** (see the Supporting Information). Since a kinetic isotope effect was not observed in this reaction (Figure 2b), the turnover-limiting step of this catalytic cycle is most probably the reductive elimination step, which would be expected to be facilitated by silylene ligand **L5** as discussed above. This conclusion is also in

Table 2. Platinum-Catalyzed Cyclodimerization of Various Alkynes[a]

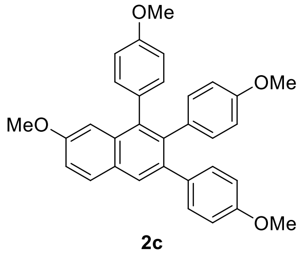




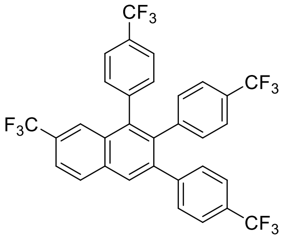
2a
60% (9:1)[b]



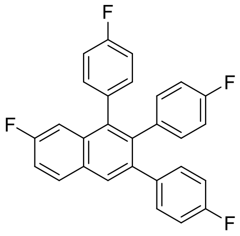
2b
58% (10:1)[b]



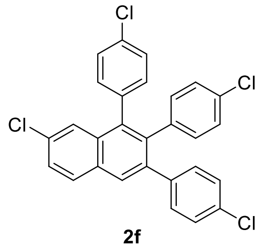
2c
57% (6:1)[b,c]



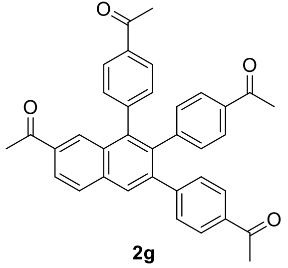
2d
85%



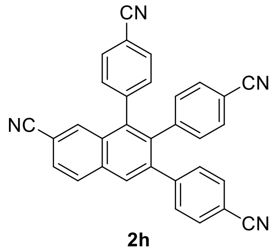
2e
87%



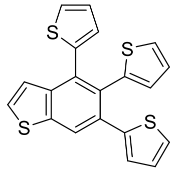
2f
63%



2g
70%



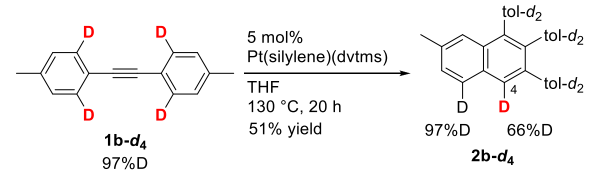
2h
63%



2i
41%

[a]Reaction conditions: **1a** (0.20 mmol), Pt(silylene)(dvtms) (0.010 mmol), and 4-MeTHP (0.50 mL) in a screw-capped vial under N_2 for 20 h. [b]Isolated as a mixture of **2** and **3**. The **2**:**3** ratio was determined by GC or NMR analysis. [c]0.3 mmol scale.

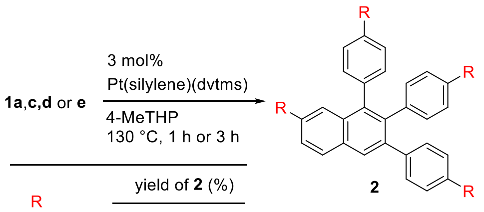
(a)



(b)

substrate	product yield (%)	
	1 h	3 h
1b	22	30
1b-d_4	17	25

(c)



R	yield of **2** (%)	
	1 h	3 h
H (**1a**)	17	18
OMe (**1c**)	15	30
CF_3 (**1d**)	83	>95
F (**1e**)	49	62

Figure 2. Mechanistic studies.

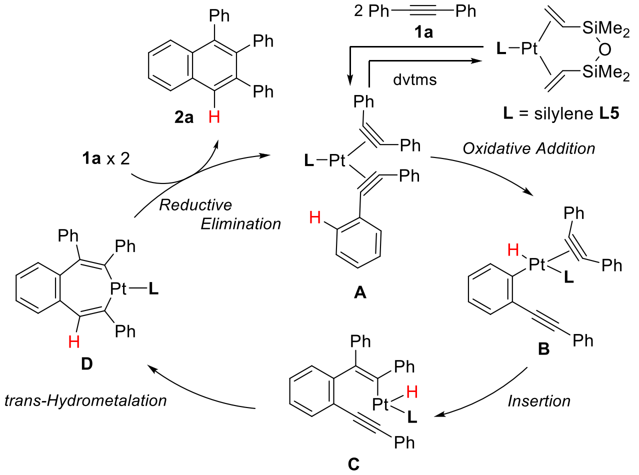


Figure 3. Possible mechanism.

agreement with the experimental observation that electron-deficient alkynes react more rapidly (Figure 2c).[16]

In summary, we have developed the cyclodimerization of diarylacetylenes catalyzed by a platinum–silylene complex, leading to the formation of naphthalene derivatives. This reaction involves cleavage of an aryl C–H bond at the position ortho to the alkyne substituent. The present study demonstrated the potential utility of platinum–silylene complexes in catalytic C–H functionalization.[7] Further studies on platinum−silylene-catalyzed C−H activation are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00195.

> Detailed experimental procedures, characterization of new compounds, and ^{1}H and ^{13}C NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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(13) The deuterium content was decreased, possibly as a result of undesired H/D exchange of the platinum hydride species with dvtms or **L5**. H/D exchange with the solvent is unlikely since running the

reaction in THF-d_8 did not result in deuterium incorporation in the product. See the Supporting Information for details.

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