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

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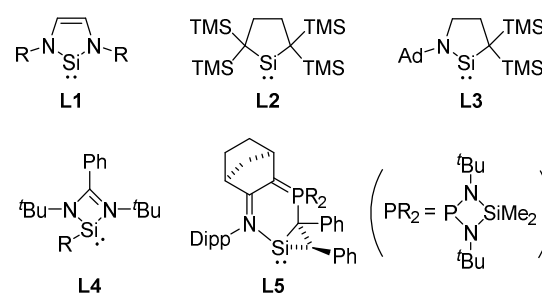
ABSTRACT: The cyclodimerization of diphenylacetylene derivatives catalyzed by a platinum-silylene complex is reported. The reaction proceeds via the cleavage of a carbon-hydrogen bond at the *ortho*-position of an alkynyl group and no additives are needed. Platinum complexes bearing other common ligands, 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, which 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, such as N-heterocyclic silylenes (**L1**), cyclic dialkylsilylenes (**L2**), cyclic amino silylenes (**L3**), and acyclic silylenes have been isolated.² The use of a silylene ligand in transition-metal-catalyzed reactions was also reported. In 2001, Fürstner et al. reported on the preparation of a Pd(0)-NHSi (**L1**: R = ^tBu) 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} A base-stabilized silacycloprop-1-ylidene **L5** was reported by Kato and Baceiredo in 2012.⁵ The 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 a better performance of **L5** compared with other phosphine or N-heterocyclic carbene (NHC) ligands. However, the applications of **L5** in catalysis is limited to hydrosilylation 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.

We report herein that a platinum-**L5** complex is a potent catalyst for use in C-H activation reactions⁷ 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 Ru¹⁰ or Ir¹¹ 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 at 130 °C for 20 h in the presence of 5.0 mol% of Pt(**L5**)(dvtms),

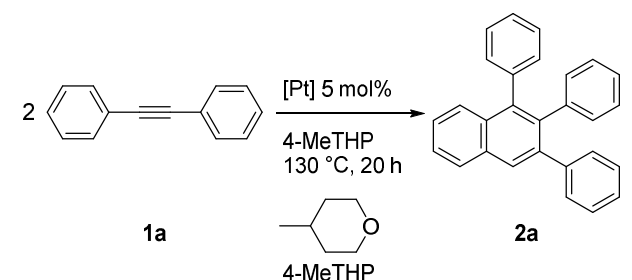
Scheme 1 Selected Stable Silylene Ligands



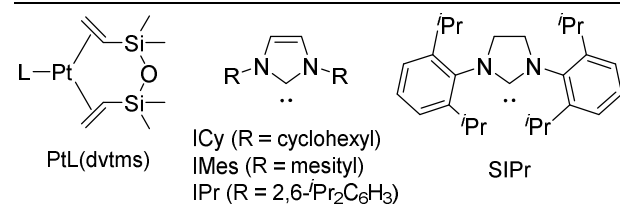
1,2,3-triphenyl-naphthalene was obtained in 72% yield (entry 1, Table 1). In marked contrast, the corresponding NHC-Pt complexes (entries 2-5) and Pt₂(dvtms)₃ (Karstedt's catalyst, entry 6) were completely inactive for the cyclodimerization of **1a** under these conditions. In addition, the use of PPh₃ in conjunction with Karstedt's catalyst failed to promote this reaction. These results clearly highlight the better utility of the silylene ligand **L5** than commonly used NHC and phosphine ligands. The thermal stability of Pt(**L5**)(dvtms) complex has been confirmed by the absence of decomposition after its heating in 4-methyltetrahydropyran at 130 °C for 20 h. It was previously 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 [PtCl₂(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% of 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.

Table 1 Platinum-Catalyzed Cyclodimerization of 1a^a



entry	[Pt]	NMR yield (%) of 2a
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 catalyst)	0
7	PtCl ₂ (MeCN) ₂	0
8	Pt(L5)(dvtms) + Py·HBr 20 mol%	0



^aReaction conditions: **1a** (0.20 mmol), [Pt] (0.010 mmol), 4-MeTHP (0.50 mL) in a screw-capped vial under N₂ for 20 h.
^bYields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

The scope of the platinum-silylene-catalyzed cyclodimerization of diphenylacetylene derivatives was next investigated (Table 2). Substrates bearing an electron-donating group, such as methyl (**1b**) and methoxy groups (**1c**), were applicable to this reaction, although the yields were relatively low compared with that for electron-neutral alkyne **1a** due to the formation of indene derivative **3**¹² as a byproduct. In contrast, electron-deficient alkynes, such as those bearing a trifluoromethyl group (**1d**), were efficiently cyclodimerized without an indene-type byproduct being formed. Halogen atoms, including fluorine (**1e**) and chlorine (**1f**), were tolerated, with the corresponding cyclodimerization products being formed in 87% and 63%, 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 di(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.

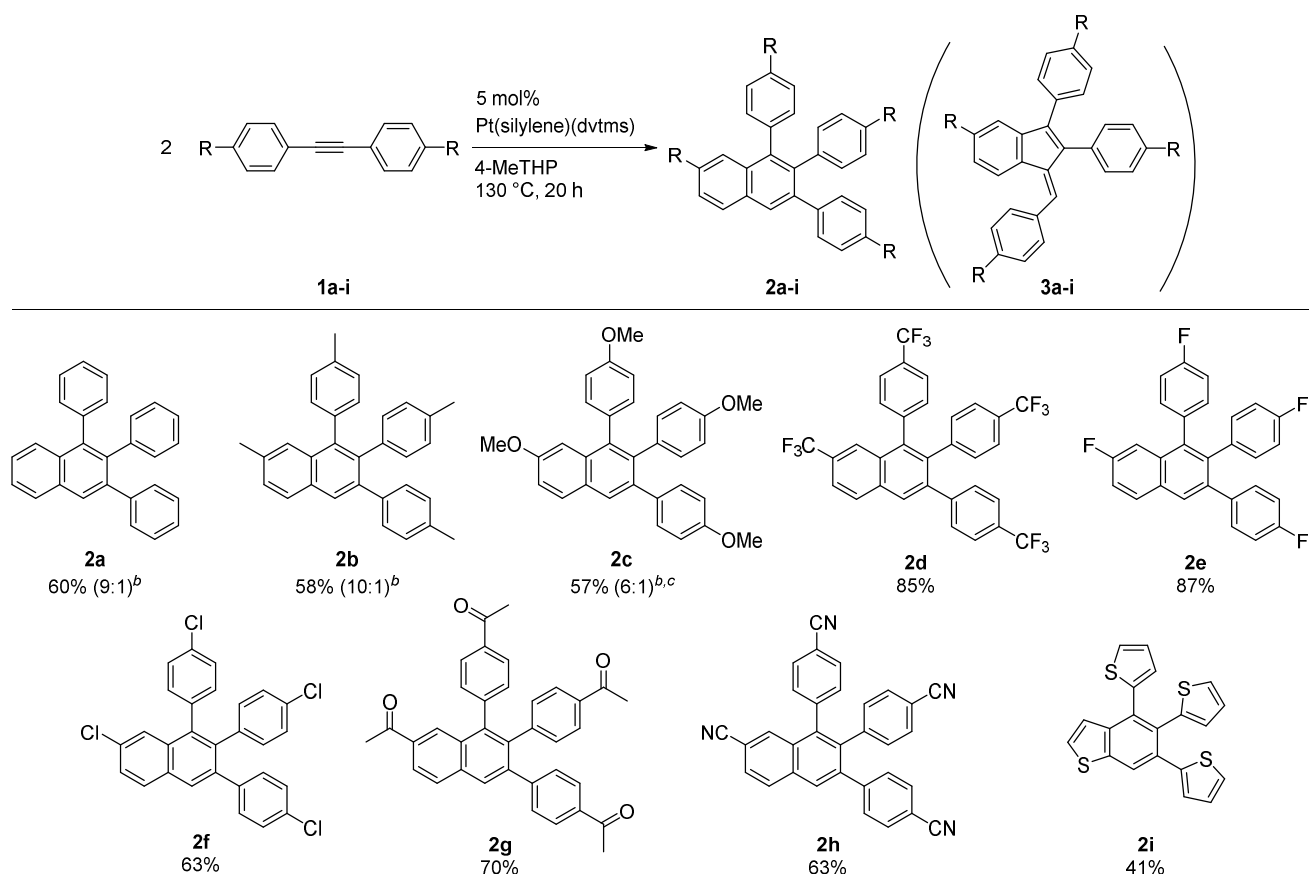
In order to gain insight into mechanistic aspects of this cyclodimerization reaction, deuterium labelling experiments were carried out. The platinum-silylene catalyzed reaction of

2,6,2',6'-tetradeuteroditylacetylene (**1b-d₄**) under the standard reaction conditions led to the formation of a naphthalene derivative with deuterium being incorporated at the 4-position (*i.e.*, **2b-d₄**), in addition to the positions where deuterium atoms were originally located (Scheme 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 rates, deuterium labeling had no significant effect on the yields at the early stage of cyclodimerization reaction (Scheme 2b), which indicates that the turnover-determining step of this reaction is not the C-H bond cleavage step. We next examined substituent effect on the cyclodimerization reaction by comparing the yields of cyclodimerization of **1a**, **1c** and **1d** at 1 and 3 h (Scheme 2c). The yields for alkynes **1a** and **1c** were significantly lower compared with alkyne **1d**, 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 Scheme 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 a platinum center, in which an alkyne serves as an *ortho* directing group,^{11,12,14} to provide Pt(II)-hydride intermediate **B**. The insertion of a second alkyne into an aryl-platinum bond forms alkenyl-Pt 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** with the regeneration of Pt(0). In this reaction, the silylene **L5** served as an efficient ligand. The silylene ligand **L5** is a strong σ -donor, as evidenced by its TEP value of 2072 cm⁻¹ which is lower than the 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 π -backdonation of Pt→silylene than Pt→NHC.⁶ In addition, the silicon center of **L5** is tricoordinate due to 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 both 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 Supporting Information). Given that a kinetic isotope effect was not observed in this reaction (Scheme 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 agreement with the experimental observation that electron-deficient alkynes react more rapidly (Scheme 2c).¹⁶

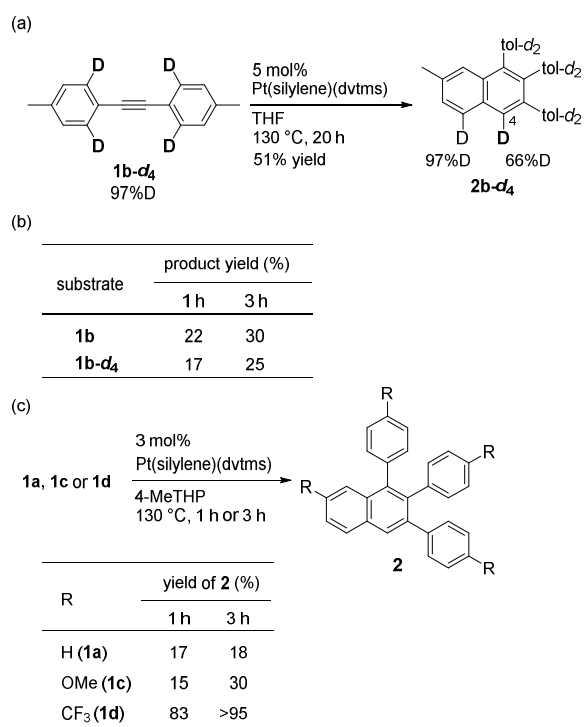
In summary, we have developed the platinum-silylene complex-catalyzed cyclodimerization of diarylacetylenes, leading to the formation of naphthalene derivatives. This reaction involves the cleavage of a C-H bond at the *ortho*-position of aromatic alkynes. The present study demonstrated a potential utility 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.

Table 2 Platinum-Catalyzed Cyclodimerization of Various Alkynes^a

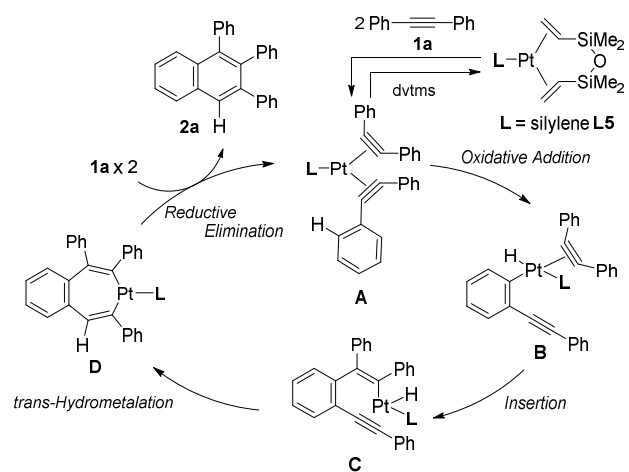


^aReaction conditions: **1a** (0.20 mmol), Pt(silylene)(dvtms) (0.010 mmol), 4-MeTHP (0.50 mL) in a screw-capped vial under N₂ for 20 h. ^bIsolated as a mixture of **2** and **3**. Ratio of **2** and **3** was determined by GC or NMR analysis. ^c0.3mmol scale

Scheme 2 Mechanistic Studies



Scheme 3 Possible Mechanism



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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

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The authors declare no competing financial interests.

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