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Cyclopropanation of Strained Alkenes by Palladium-Catalyzed Reaction of 3-Trimethylsilyl- or 3-Pinacolatoboryl-1-arylallyl Acetates

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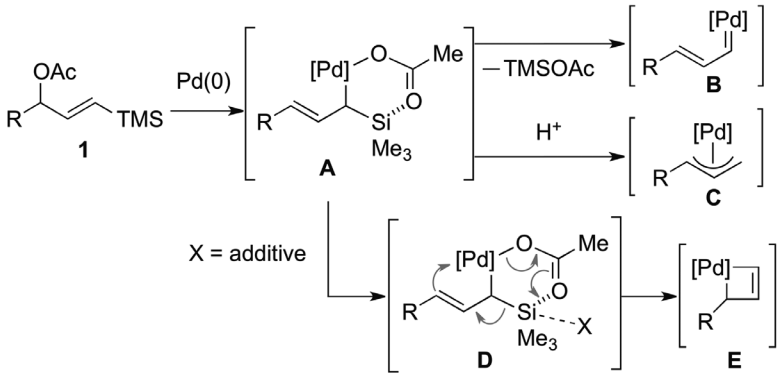
Abstract: The palladium-catalyzed cyclopropanation of strained alkenes with 3-trimethylsilyl- or 3-pinacolatoboryl-1-arylallyl acetate derivatives is described. This reaction gives cyclopropanation products in good to high yields with a single diastereomer, and the key step is likely to involve the formation of a palladacyclobutene complex from the α-trimethylsilyl- or α-pinacolatoboryl-σ-allylpalladium complex.

Keywords: allylsilanes; cyclopropanation; palladacyclobutenes; palladium carbenoids; π-allylpalladium species

π-Allylpalladium intermediates have been widely studied due to their possible involvement in a large number of important organic transformations involving the formation of C–C and C–heteroatom bonds. Changing the behavior of such allyl species on palladium complexes has the potential of altering their reactivity pattern. Bis-π-allylpalladium complexes,[1] trimethylenemethane-palladium complexes[2] and pincer-type π-allylpalladium complexes[3] are representative examples. In 1983, Trost reported the generation of Pd-complexed vinylcarbene species **B** *via* the α-elimination of acetoxytrimethylsilane from α-trimethylsilyl-σ-allylpalladium intermediate **A** (Scheme 1).[4] Although the reactivity of metal carbenoids mainly depends on the functionality of the carbene and the nature of the metal that donates the electron into the empty *p* orbital of the carbene carbon atom,[5] the Pd-complexed vinylcarbene species **B** generated from **1** and a palladium complex apparently exhibits a different reactivity from typical palladium carbenoids.[6,7]

Recently, Fillion demonstrated the ambiphilic vinylcarbenoid nature of an α-tributylstannyl-π-allylpalladium complex.[7b] In light of these results, it is evident that the carbon atom between the palladium and the trimethysilyl group in Trost's *gem*-dimetallic intermediate **A** has a Brønsted base character, and can therefore subsequently undergo protodesilylation to produce π-allylpalladium intermediate **C** in the pres-



Scheme 1. Working hypothesis.

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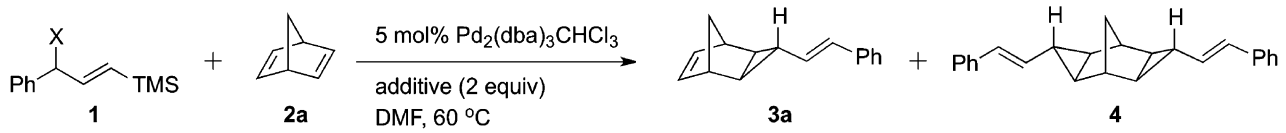
Table 1. Optimization of the reaction conditions.[a]



Entry	X	1	Additive	Time [h]	3a [%][b]	4 [%][b]
1	OCOMe	**1a**	CsF	3	78	0
2[c]	OCOMe	**1a**	CsF	6	47	24
3[d]	OCOMe	**1a**	CsF	10	27	14
4	OCOMe	**1a**	KF	24	35	0
5	OCOMe	**1a**	TBAT[e]	6	68	0
6	OCOMe	**1a**	Cs_2CO_3	20	33	0
7[f]	OCOMe	**1a**	–	36	20	0
8	OCO_2Et	**1b**	CsF	4	74	0
9	OCONHTs	**1c**	CsF	3	74	0
10	OCONHPh	**1d**	CsF	2	54	0
11	OCON(Me)Ph	**1e**	CsF	4	58	0
12	OCSNHPh	**1f**	CsF	12	0	0
13	Br	**1g**	CsF	12	0	0
14	OEt	**1h**	CsF	12	0	0

[a] Reaction was performed with **1** (0.5 mmol), **2a** (1.5 mmol), $Pd_2(dba)_3CHCl_3$ (0.025 mmol) and additive (1.0 mmol) in DMF (2.5 mL) at 60 °C.
[b] Isolated yield.
[c] 2 equiv. of **2a** to **1a** were used.
[d] 1 equiv. of **2a** to **1a** was used.
[e] TBAT = tetrabutylammonium difluorotriphenylsilicate.
[f] Reaction was carried out at 80 °C.

ence of nucleophiles such as β-keto esters or β-diesters that possess acidic protons. In this case, the Tsuji–Trost reaction is induced rather than C–H insertion of the palladium carbenoid.

On the basis of these reactivity principles, we envisioned that palladacyclobutene intermediate **E** might be generated from α-trimethylsilyl-σ-allylpalladium intermediate **A** *via* an S_E2'-type reaction in which the allylsilane moiety acts as an intramolecular hard nucleophile that can attack the palladium complex if the silicon atom can be activated appropriately.[8] To the best of our knowledge, there are very few previous reports regarding the reactivity of palladacyclobutene intermediates.[9]

After several attempts, we finally found that the reaction of **1a** (1 equiv.) with 2,5-norbornadiene **2a** (3 equiv.) in the presence of cesium fluoride (2 equiv.) and $Pd_2(dba)_3CHCl_3$ (5 mol%) in DMF under an argon atmosphere at 60 °C provided the cyclopropanation product **3a** in 78% isolated yield as a single diastereomer (Table 1, entry 1). Cyclopropanation occurred exclusively on the *exo* face of **2a**, and the stereochemistry was determined to be *anti* by NOE experiments. Three equivalents of **2a** were needed to obtain **3a** in high yield. The yield of **3a** was found to decrease significantly and the double cyclopropanation product **4** was formed in considerable yield when **2a** was reduced to less than three equivalents (entries 1–3). Among the additives tested, cesium fluoride was found to provide **3a** in high yield (entries 1 and 4–6). Furthermore, addition of a fluoride source as an additive was found to be essential for the present reaction (entry 7). Importantly, intermediate **A** must allow the intramolecular coordination of a carbonyl oxygen to the silicon atom in order to generate palladacyclobutene intermediate **E** (entries 8–14). The use of π-allylpalladium chloride dimer as a catalyst afforded similar results to $Pd_2(dba)_3CHCl_3$, whereas other palladium complexes gave diminished yields of **3a**.[10] Furthermore, addition of a phosphine ligand was found to enhance the Brønsted base character of the carbon atom between the palladium and trimethylsilyl group, which resulted in protodesilylation to produce cinnamyl acetate.[11]

Under the optimized reaction conditions, the substrate scope of the present Pd-catalyzed cyclopropanation of **2a** is summarized in Table 2. The present reaction was found to proceed independently of the electronic nature of the substituent at the aromatic position. For example, the aryl-containing substrates bearing electron-donating groups **1i–1l** and electron-withdrawing groups **1m–1r** afforded the desired products **3b–3k** in good to high yields (entries 1–10). Notably, bromo-containing substrate **1q** afforded product **3j** in good yield while leaving the C–Br bond intact (entry 9). Moreover, the present cyclopropanation

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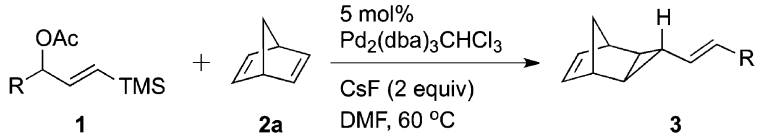
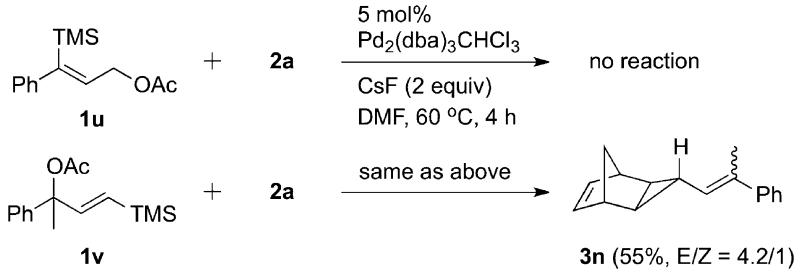
Table 2. Pd-catalyzed cyclopropanation of **2a** with **1**.[a]



Entry	R	1	Time [h]	3 [%][b]
1	2-MeC_6H_4	**1i**	4	**3b** (81)
2	4-$MeOC_6H_4$	**1j**	3	**3c** (78)
3	2,6-$Me_2C_6H_3$	**1k**	6	**3d** (55)
4	2-PhC_6H_4	**1l**	5	**3e** (60)
5	3-$MeOC_6H_4$	**1m**	4	**3f** (77)
6	3,5-$(MeO)_2C_6H_3$	**1n**	4	**3g** (50)
7	4-FC_6H_4	**1o**	4	**3h** (75)
8	4-ClC_6H_4	**1p**	4	**3i** (70)
9[c]	4-BrC_6H_4	**1q**	4	**3j** (52)
10	4-$CF_3C_6H_4$	**1r**	6	**3k** (55)
11	2-thiofuryl	**1s**	8	**3l** (53)
12	2-furyl	**1t**	8	**3m** (50)

[a] Reaction was performed with **1** (0.5 mmol), **2a** (1.5 mmol), $Pd_2(dba)_3CHCl_3$ (0.025 mmol) and additive (1.0 mmol) in DMF (2.5 mL) at 60 °C.
[b] Isolated yield.
[c] 4 Å molecular sieves (250 mg) was used.



Scheme 2. Pd-catalyzed cyclopropanation of **2a** with **1u** and **1v**.

also proceeded in the presence of heteroaromatic groups such as 2-thiofuryl **1s** and 2-furyl **1t** to give the corresponding cyclopropanation products **3l** and **3m**, respectively, in good yield (entries 11 and 12). Interestingly, all the cyclopropanation products were isolated as a single diastereomer, which suggests that the present reaction would proceed *via* a different mechanism from Fillion's palladium vinylcarbenoid pathway. Unfortunately, the use of substrates bearing an alkyl group in place of the aryl group resulted in complex mixtures, possibly due to lack of an aryl effect[12] or a β-hydrogen elimination in intermediate **E**. Similarly, the sterically demanding substrate **1u** proved to be unreactive (Scheme 2). On the other hand, the use of **1v** produced the desired product in good yield as a 4.2:1 mixture of (*E*)-**3n** and (*Z*)-**3n** isomers. It should be noted that cyclopropanation occurred exclusively on the *exo* face of **2a**, and that the *anti*-cyclopropanes (*E*)-**3n** and (*Z*)-**3n** were obtained respectively as a single diastereomer.

We then explored the scope of this Pd-catalyzed intermolecular cyclopropanation with a variety of alkenes (Table 3). In sharp contrast to the typical reactivity of palladium carbenoids,[6] the present reaction generally proceeds with strained alkenes.

For example, no cyclopropanation occurred when the reaction of **1a** with styrene was tested.[10] On the other hand, use of strained alkenes **2b**–**2e** led to the desired products **3o**–**3r**, respectively, in good to high yields (entries 1-4). In all cases, the cyclopropanation product was isolated as a single diastereomer. It is worth noting that **3r** was obtained with excellent chemoselectivity (entry 4).

To gain further insight into the nature of the reactive species involved in this process, the reaction of **2a** with cinnamaldehyde tosylhydrazone sodium salt **5**

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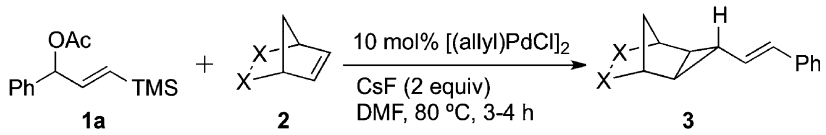
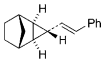
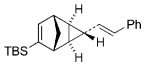
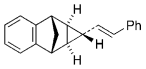
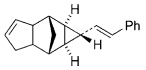
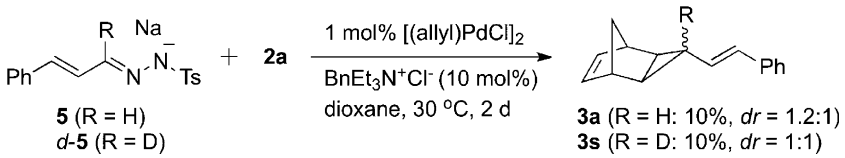
Table 3. Reaction of **1a** with various alkenes **2**.[a]

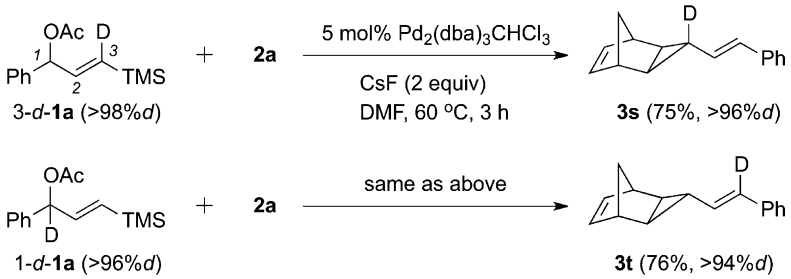


Entry	Alkene	2	Product	3 [%][b]
1		**2b**		**3o** (80)
2		**2c**		**3p** (40)
3		**2d**		**3q** (65)
4		**2e**		**3r** (58)

[a] Reaction was performed with **1a** (1.0 mmol), **2** (3.0 mmol), $[(allyl)PdCl]_2$ (0.1 mmol), CsF (2.0 mmol) in DMF (5.0 mL) at 80 °C.
[b] Isolated yield.



Scheme 3. Cyclopropanation of **2a** using diazo compound precursors **5** and *d*-**5**.



Scheme 4. Deuterium labelling experiments.

that is known to generate styryldiazomethane in the presence of a phase-transfer catalyst was examined (Scheme 3).[13] We were surprised to find that cyclopropanation of **2a** with styryldiazomethane afforded **3a** as a mixture of diastereomers ($dr = 1.2:1$), and *anti*-cyclopropane was the major product. Moreover, **3s** was obtained without scrambling of the deuterium atom.[14] Similarly, when the reaction of deuterium-labelled 3-*d*-**1a** and 1-*d*-**1a** with **2a** was examined, no scrambling of the deuterium atom between C-1 and C-3 was also observed in the respective products **3s** and **3t** in either case (Scheme 4). These mechanistic experiments strongly support our working hypothesis shown in Scheme 1. To further verify our working hypothesis, the palladium-catalyzed dimerization of **1a** in the absence of **2a** was examined because transition metal complexed vinylcarbenes generated from a transition metal complex with styryldiazomethane are prone to dimerization.[13a] However, no dimerization product was observed and instead a trace amount of cinnamyl acetate was obtained although metallacyclobutene intermediates are known to rearrange to form metal vinylalkylidene complexes,[15] This result suggests that **2a** is not only the substrate of cyclopropanation but also may play an important role as a ligand to generate palladacyclobutene intermediate **E**.[16]

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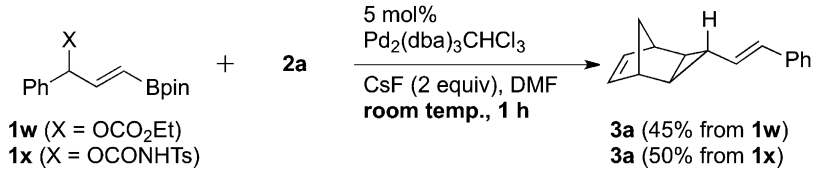
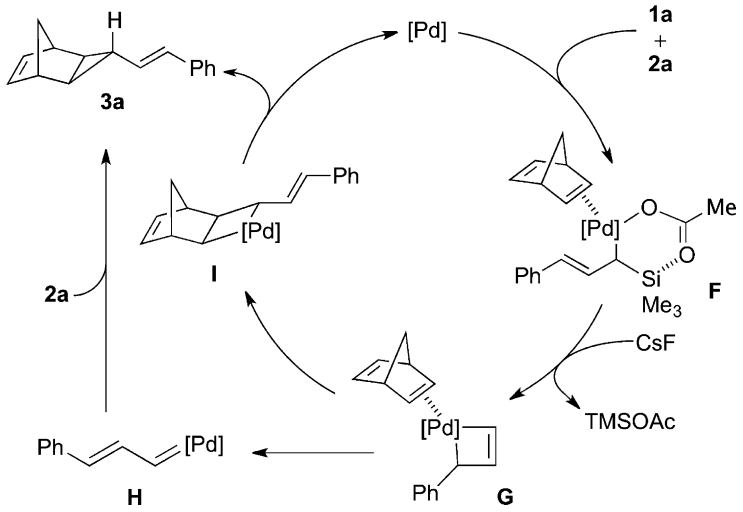


Scheme 5. Reactions of **2a** with **1** bearing a pinacolatoboryl group.



Scheme 6. A plausible reaction mechanism.

In light of the above findings, we considered that if the present cyclopropanation proceeds dominantly through palladacyclobutene intermediate **E** and this formation step would be the rate-limiting step, then the allylborane species produced upon complexation of **1w** to the palladium complex would be more reactive than the corresponding allylsilane species. In order to prove this hypothesis, the reaction of **1w** with **2a** was examined (Scheme 5). We were pleased to find that the reaction proceeded smoothly to give **3a** in moderate yield after 1 h at room temperature. Likewise, the reaction of **1x** with **2a** also afforded **3a** in moderate yield at room temperature (Table 1, entry 9 *versus* Scheme 5). Thus, a mechanism involving a palladacyclobutene intermediate **E** may account for the observed different reactivities.

Scheme 6 depicts a plausible catalytic cycle for the present cyclopropanation of **2a**. Dimetallic species **F** bearing an allylsilane moiety, which is formed initially *via* the π-allylpalladium intermediate, is transformed into palladacyclobutene intermediate **G** in the presence of cesium fluoride. Compound **2a** then inserts into **G** to produce palladacylobutane intermediate **I**, which subsequently undergoes reductive elimination upon coordination of another molecule of **2a** to the palladium complex to furnish product **3a**. This is likely to be a facile process since reductive elimination is generally accelerated by π-acidic ligands.[17] An alternative pathway involving Pd-complexed vinylcarbene intermediate **H** generated from **G** should be also taken into consideration. However, this process usually affords the **3a** as a mixture of diastereomers (Scheme 3).

In summary, we have developed a palladium-catalyzed cyclopropanation of strained alkenes with 3-trimethylsilyl- or 3-pinacolatoboryl-1-arylallyl acetates, which gives cyclopropanation product as a single diastereomer. The key step in the present reaction is likely to involve the formation of a palladacyclobutene complex generated from the α-trimethylsilyl- or α-pinacolatoboryl-σ-allylpalladium complex. Further efforts to expand the synthetic utility of the present methodology are underway.

Experimental Section

Typical Procedure

In a 20-mL Schlenk tube were charged $Pd_2(dba)_3CHCl_3$ (5 mol%), CsF (1 mmol), 2,5-norbornadiene **2a** (1.5 mmol) and dry DMF (2.5 mL) under an argon atmosphere. The resulting suspension was stirred at room temperature for 15 min, and the substrate **1a** (0.5 mmol) was then added. The reaction mixture was heated at 60 °C, and the reaction mixture was allowed to stir for the time specified. After reaction completion, as monitored by TLC, the reaction mix-

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ture was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with diethyl ether (2× 20 mL), and the combined organic extracts were washed with brine (2×20 mL). After the organic layer had been dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography to give **3a** as a colorless oil.

The Supporting Information contains the experimental details, product characterization and NMR spectra.

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[10] See the Supporting Information.

[11] Use of cinnamyl acetate instead of **1a** under the same reaction conditions as shown in Table 1 resulted in no reaction.

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[16] The use of 2,2′-bipyridine instead of **2a** as a ligand (1 equiv. to Pd) afforded 1,6-diphenyl-1,3,5-hexatriene in 88% as a mixture of (1*E*,3*E*,5*E*) and (1*E*,3*Z*,5*E*) isomers (2.8:1). This shows the reactivity of the palladium carbenoid, which will be reported in due course.

[17] An alternative mechanism involves insertion of **2a** to a π-allylpalladium intermediate that would be produced by palladium complexing with cinnamyl acetate generated from protodesilylation of **1a**. However, this process preferentially produces a [2+2]cycloadduct rather than a cyclopropanation product, thus making this possibility rather unlikely. For details, see: N. Tsukada, T. Sato, Y. Inoue, *Tetrahedron Lett.* **2000**, *41*, 4181–4184.

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