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Practical and Convenient Synthesis of 1,6-Di- or 1,2,5,6-Tetraarylhexa-1,3,5-trienes by the Dimerization of Pd(0)-Complexed Alkenylcarbenes Generated from π-Allylpalladium Intermediates

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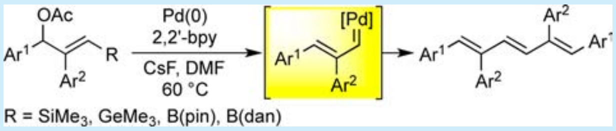
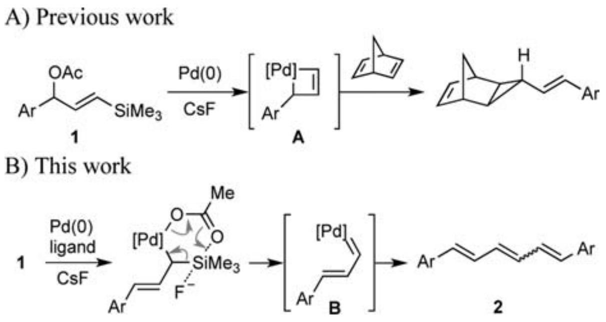
Supporting Information

ABSTRACT: Pd(0)-complexed 3-aryl or 2,3-diaryl propenylcarbenes generated from α-silyl-, α-germyl-, or α-boryl-σ-allylpalladium intermediates undergo self-dimerization to provide 1,6-di- or 1,2,5,6-tetraarylhexa-1,3,5-trienes in good to high yields. This method allows the use of a π-allylpalladium intermediate for a carbenoid precursor. Furthermore, the obtained 1,2,5,6-tetraarylhexa-1,3,5-trienes exhibit aggregation-induced emission enhancement property.



Recently, significant research interest has been focused on π-conjugated compounds since they exhibit interesting fluorescence properties. A number of π-conjugated hydrocarbons are known to display intriguing fluorescence properties.[1] 1,6-Diarylhexa-1,3,5-trienes serve as fluorescent probes in biological studies,[2] and 1,3,4,6-tetraarylhexa-1,3,5-trienes have a structure consisting of organic fluorophores, which exhibit aggregation-induced emission enhancement.[3] Although several synthetic approaches to 1,6-diarylhexa-1,3,5-trienes have been developed, substrate scope is narrow, and some methods require elaborate substrates.[4−9] Thus, more general protocols for the synthesis of 1,6-diarylhexa-1,3,5-trienes are still of high interest. Among their reported methods, the dimerization of the Pd(0)-complexed 3-aryl propenylcarbene appears to be an ideal approach due to its high functional group tolerance. Moreover, in the past decade, Pd(II)-carbene complexes have emerged as a promising intermediate for cross-coupling reactions;[10,11] however, few studies have focused on the generation of Pd(0)-carbene intermediates.[12] To date, developments in the generation of Pd(0)-carbene intermediates have been restricted to diazo esters. Representative examples are transmetalation from group 6 Fisher metal carbene complex to a Pd(0) complex and decomposition of in situ generated diazo compounds by the Pd(0) complex.[12e−i] Recently, a unique strategy involving a Pd(0)-carbene intermediate to access to 1,6-diarylhexa-1,3,5-trienes was developed by Fillion. Specifically, the strategy involved the generation of Pd(0)-complexed 3-aryl propenylcarbenes generated from an γ-aryl-α-stannyl-σ-allylpalladium intermediate.[12a] This method allows the utilization of readily available substrates rather than diazo compounds to provide 1,6-diarylhexa-1,3,5-trienes and showed reasonable generality in the substrate scope. On the other hand, our group reported the Pd-catalyzed stereoselective cyclopropanation of strained alkenes with 3-trimethylsilyl-1-arylallyl acetate **1** (Scheme 1A).[13] The key step of this reaction appears to involve the formation of a putative palladacyclobutene intermediate **A** from the α-trimethylsilyl-σ-allylpalladium intermediate. Given our result and Fillion's finding, we hypothesized that reducing the electrophilicity of the Pd atom in σ-allylpalladium intermediate would preferentially induce the formation of Pd(0)-complexed 3-aryl propenylcarbene **B**, which subsequently leads to carbene self-dimerization via disproportionation of **B** to provide the desired product **2** (Scheme 1B). Herein, we report the palladium-catalyzed practical and convenient synthesis of a wide range of 1,6-diarylhexa-1,3,5-trienes **2** from readily available starting materials **1**. The application to the synthesis of 1,2,5,6-tetraarylhexa-1,3,5-trienes to display the aggregation-induced emission enhancement is considered, and the physical properties of 1,2,5,6-tetraarylhexa-1,3,5-trienes are also discussed.

Scheme 1. Strategy for the Generation of Pd(0)-Carbene



To test our hypothesis, we initially examined the effect of ligands and additives, as shown in Table 1. The reaction of **1a** in the presence of 5 mol % of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ did not provide the desired product 1,6-diphenylhexa-1,3,5-triene **2a** (entry 1); however, to our delight, the treatment of **1a** with 5

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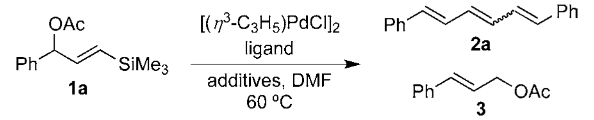
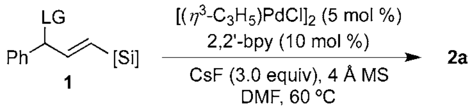
Table 1. Optimization of Reaction Conditions[a]



entry	ligand	additives[b]	time (h)	2a (%)[c]	3 (%)
1	–	–	12	trace	0
2	DPPE[d]	CsF	3.5	36	41
3	TMEDA[e]	CsF	6	trace	0
4	phen[f]	CsF	1	74	10
5	2,2′-bpy[g]	CsF	0.5	76	22
6	2,2′-bpy	CsF, 4 Å MS	0.5	88	0
7	2,2′-bpy	4 Å MS	19	48	52
8	2,2′-bpy	TBAF	1	0	0
9	2,2′-bpy	TBAT[h]	1	34	10
10[i]	2,2′-bpy	KF, 4 Å MS	24	40	0
11	2,2′-bpy	CsF, 4 Å MS	5.5	76	10

[a] Conditions: **1a** (1 mmol), [(η^3-C_3H_5)PdCl]$_2$ (5 mol %), ligand (10 mol %), MF (M = Cs or K, 3 mmol), DMF (5 mL), 60 °C. [b] 4 Å MS (500 mg) was used. [c] **2a** was isolated as a (*E,E,E*)-isomer. [d] DPPE = 1,2-bis(diphenylphosphino)ethane. [e] TMEDA = *N,N,N′,N′*-tetramethylethylenediamine. [f] phen = 1,10-phenanthroline. [g] 2,2′-bpy = 2,2′-bipyridine. [h] TBAT = tetrabutylammonium difluorotriphenylsilicate. [i] [(η^3-C_3H_5)PdCl]$_2$ (2.5 mol %) and 2,2′-bpy (5 mol %) were used.

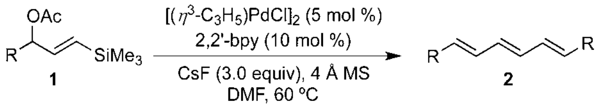
Table 2. Leaving Group and Silyl Group Effects on Pd-Catalyzed Dimerization of 1[a]



entry	1	LG	[Si]	time (min)	2a (%)[b]
1	**1b**	OCO$_2$Et	SiMe$_3$	30	84
2	**1c**	OCONHPh	SiMe$_3$	50	65
3	**1d**	OCONHBz	SiMe$_3$	60	57
4	**1e**	OCSNHPh	SiMe$_3$	50	0
5	**1f**	Br	SiMe$_3$	60	0
6	**1g**	OAc	SiMe$_2$Ph	45	88
7	**1h**	OAc	SiMe$_2{}^t$Bu	180	81
8	**1i**	OAc	Si^{i}Pr$_3$	240	45

[a] Conditions: **1** (1 mmol), [(η^3-C_3H_5)PdCl]$_2$ (5 mol %), 2,2′-bpy (10 mol %), CsF (3 mmol), 4 Å MS (500 mg), DMF (5 mL), 60 °C. [b] **2a** was isolated as a (*E,E,E*)-isomer.

Table 3. Substrate Scope and Limitations[a]



entry	1	R	time (h)	2[b]	yield (%)
1	**1j**	2-Me-C_6H_4	0.5	**2b**	88
2	**1k**	2-allyl-C_6H_4	0.5	**2c**	60
3	**1l**	2-(*i*-propenyl)-C_6H_4	0.5	**2d**	70
4	**1m**	2-Ph-C_6H_4	0.5	**2e**	68
5	**1n**	2,6-Me$_2$-C_6H_3	3	**2f**	86
6	**1o**	4-F-C_6H_4	0.5	**2g**	88
7	**1p**	4-CF$_3$-C_6H_4	0.5	**2h**	92
8	**1q**	2-MeO-C_6H_4	0.5	**2i**	91
9	**1r**	3-BnO-C_6H_4	1	**2j**	50
10	**1s**	3-MOMO-C_6H_4	0.5	**2k**	77
11	**1t**	4-MOMO-C_6H_4	0.5	**2l**	62
12	**1u**	4-MeO-C_6H_4	0.5	**2m**	36[c]
13	**1v**	2-thienyl	0.5	**2n**	73
14	**1w**	3-thienyl	12	**2o**	40[d]
15	**1x**	2-furyl	0.5	**2p**	75
16	**1y**	3-furyl	2	**2q**	35
17	**1z**	3-pyridyl	0.5	**2r**	75

[a] The same reaction conditions with those in Table 2. [b] **2** was isolated as a (*E,E,E*)-isomer. [c] Yield was determined after hydrogenation. [d] **1w** was recovered in 60% yield.

mol % of [(η^3-C_3H_5)PdCl]$_2$, 10 mol % of DPPF, and 3.0 equiv of CsF in DMF at 60 °C for 3.5 h gave desired product **2a** in 36% yield along with cinnamyl acetate **3** in 41% yield (entry 2). Presumably, the enhanced Brønsted base character of the carbon atom between bidentate *phosphine*-ligated palladium and a trimethylsilyl group led to protodesilylation to produce **3**. While the screening of phosphine ligands did not improve the yield of **2a**, we were pleased to find that use of 2,2′-*bipyridine* as a ligand increased the yield of **2a** (entries 3−5). Among the additives tested, cesium fluoride furnished **2a** in high yield (entries 6−10). When the catalyst loading was reduced to 2.5 mol %, **3** was formed in considerable yield (entry 11).[14] Although **2a** was obtained as a mixture of (*E,E,E*)-**2a** and (*E,Z,E*)-**2a** ((*E,E,E*)/(*E,Z,E*) = 4/1 in entry 6) in all cases, the isomerization of **2a** consisted of a mixture of stereoisomers was occurred easily with (*E,E,E*)-**2a** during the acidic work up and silica-gel column chromatography.[15]

We then explored the effect of leaving groups and sustituents on the silyl group (Table 2). Importantly, the formation of *gem*-dimetallic species in α-trimethylsilyl-σ-allylpalladium intermediate plays a crucial role in the formation of **B** because the reaction of a cinnamyl acetate **3** under optimal reaction conditions resulted in no reaction.[5b] Furthermore, the intramolecular coordination of a carbonyl oxygen atom to the silicon atom was likely to be involved in the formation of **B** (entries 1−5). As expected, the use of more robust silyl groups such as DMPS, TBDMS and TIPS required a prolonged reaction time and diminished the yield of **2a** (entries 6−8).

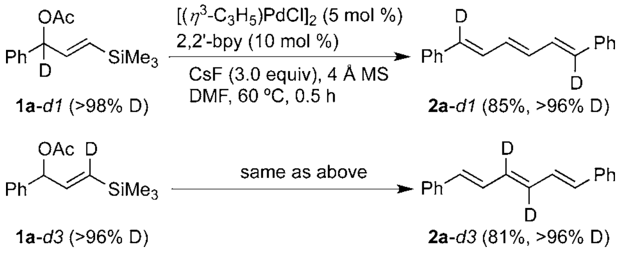
Under the optimized reaction conditions, substitution effects on the phenyl ring of **1** were probed (Table 3). Alkyl-, alkenyl-, and phenyl-substituted substrates at the *ortho*-position provided the corresponding products in good to high yields (entries 1−5). In addition, the present reaction was found to proceed independently of the electronic nature of the substituent on the phenyl ring, and the corresponding products were obtained in good to high yields (entries 6−11). On the other hand, the introduction of methoxy group at the *para*-position resulted in diminished yield (entry 12).

Furthermore, furyl-, thienyl-, and 3-pyridyl-substituted substrates also participated in the present reaction (entries 13−17). However, reaction with 2-pyridyl-substituted substrate was rather difficult, and (*Z*)-1-(2-pyridyl)-1-propenyl acetate was obtained in 27% yield.

Next, insights into the nature of the reactive species were gathered through the reaction of deuterium-labeled **1a**-d_1 and **1a**-d_3. The scrambling of the deuterium atom between C-1 and C-3 in the respective products **2a**-d_1 and **2a**-d_3 was not observed in either case (Scheme 2).[16]

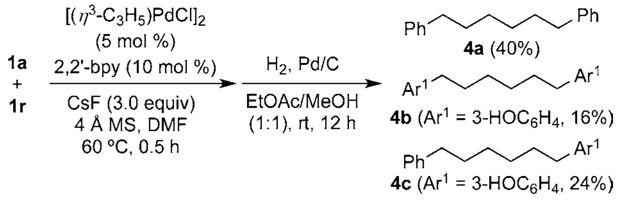
Furthermore, a crossover experiment was conducted using a 1:1 mixture of **1a** and **1r** to clarify the dimerization mechanism in the dimerization of present Pd(0)-complexed 3-aryl propenylcarbene (Scheme 3). Under optimal reaction con-

Scheme 2. Deuterium Labeling Experiments



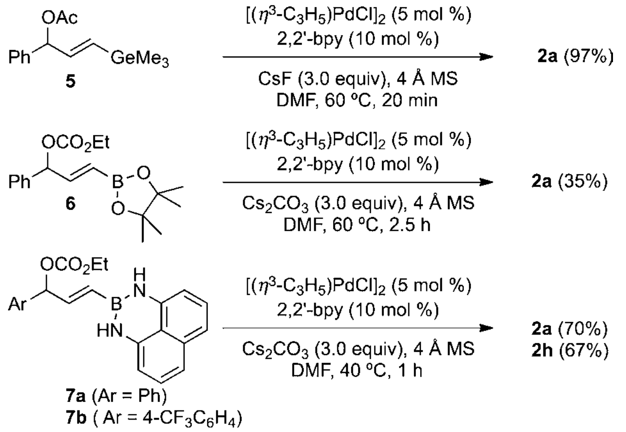
ditions, products **4a**, **4b**, and crossover product **4c** were isolated respectively after hydrogenation.

Scheme 3. Crossover Experiment



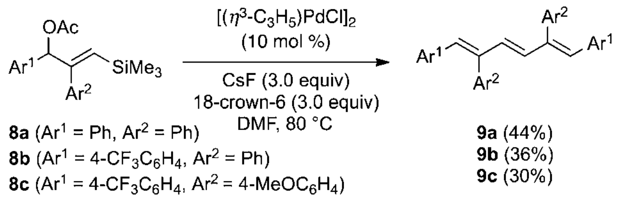
Next, we extend the present reaction to investigate carbon−metalloid bond activation such as C−Ge and C−B bonds (Scheme 4). Substrate **5** with a trimethylgermyl group instead of the trimethylsilyl group at the alkene terminus provided the corresponding product **2a** in excellent yield. On the other hand, the use of substrate **6** with a pinacolatoboryl group at the alkene terminus produced **2a** in 35% isolated yield in the presence of Cs_2CO_3 as a base. Interestingly, although the boryl group masked by 1,8-*diaminonaphthalene* is known to serve as a robust protecting group, particularly under basic conditions,[17] the reaction of substrates **7a** and **7b** proceeded under milder conditions than that of **6** and gave **2a** and **2h** in 70 and 67% isolated yield, respectively.

Scheme 4. Pd-Catalyzed Dimerization of Substrates 5−7 Possessing a Germyl and Boryl Group at the Alkene Terminus



Finally, application for the synthesis of 1,2,5,6-tetraarylhexa-1,3,5-trienes **9a−c** was examined (Scheme 5). Substrates **8a−c** were easily prepared by three steps involving silylstannylation[18] and modified Stille coupling[19] from readily available 1-aryl-2-propyn-1-ol. The Pd-catalyzed reaction of **8a−c** in the presence of CsF and 18-crown-6 afforded the **9a−c**, respectively, in moderate yield.[20] The structure of **9a** was unambiguously confirmed by X-ray diffraction analysis (Figure 1).[21] The triene moiety of **9a** was found to adapt a completely planar conformation, whereas the terminal benzene rings were distorted with dihedral angles of 27.4°. Another dihedral angle of the remaining 2,5-diphenyl groups to the plane of the triene moiety was 71.8°.

Scheme 5. Application to the Synthesis of 1,2,5,6-Tetraarylhexa-1,3,5-trienes 9a−9c



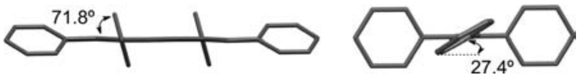


Figure 1. X-ray structure of **9a** (hydrogens are omitted for clarity): side view of the molecule (left) and view from the long axis of the molecule (right).

Interestingly, compounds **9a−9c** in the solid state emitted blue light, although the solution of **9a−9c** in $CHCl_3$ did not exhibit fluorescence.[20−22] Next, the fluorescence spectra of **9a** were measured in a mixed solvent of THF and water to confirm aggregation-induced emission enhancement.[20] As a result, a THF solution of **9a** did not exhibit luminescence, whereas the fluorescence intensity increased when up to 70 vol % water was added to the THF solution. Further addition of water resulted in a decrease in fluorescence intensity. This result demonstrated that **9a** exhibits an aggregation-induced emission enhancement property. The crystal packing of **9a** also supported this result.[20]

In conclusion, we developed a convenient and practical method for the synthesis of 1,6-diarylhexa-1,3,5-trienes by the self-dimerization of Pd(0)-complexed 3-aryl propenylcarbene generated from α-silyl-, α-germyl-, or α-boryl-σ-allylpalladium intermediates. Furthermore, we demonstrated that a π-allylpalladium intermediate could be used for cyclopropanation of strained alkenes,[13] as well as to serve as a carbenoid precursor. Finally, the present reaction could be applied to the synthesis of 1,2,5,6-tetraarylhexa-1,3,5-trienes, which exhibit aggregation-induced emission enhancement. We are currently synthesizing a series of 1,2,5,6-tetraarylhexa-1,3,5-trienes that could be applied to display highly fluorescent organic solids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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