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Substituent Effects in the Preparation of Naphthacenes by the Coupling Reaction of Diyne-Derived Zirconacyclopentadienes with Tetraiodobenzene

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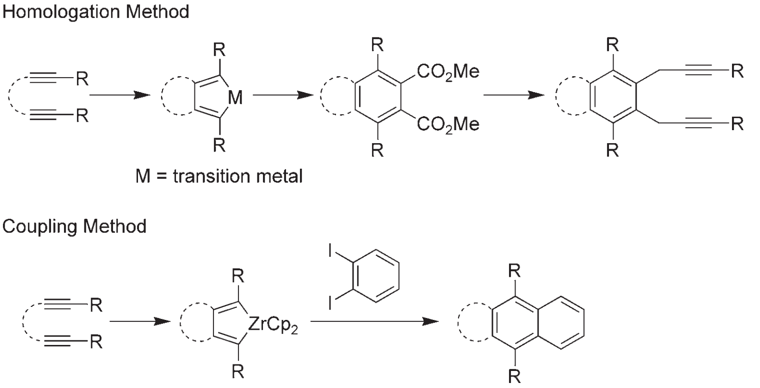
Dedicated to Professor Teruaki Mukaiyama on the occasion of his 80th birthday

Abstract: The synthesis of a series of substituted naphthacene derivatives through the coupling reaction of zirconacyclopentadienes with diiodobenzenes is reported. A reaction of bis(propargyl)benzenes with zirconacene dibutyl afforded the corresponding tricyclic zirconacyclopentadienes, which reacted with *o*-diiodobenzenes to afford the corresponding dihydronaphthacenes. The yields of the coupling reactions were dependent on the substituents on both of the zirconacycles and *o*-diiodobenzenes. The reactions of diphenyl-substituted zirconacycles gave higher yields than those of the α,α′-dialkyl-substituted derivatives. The iodide functions thus introduced allowed further introduction of substituents by well-established cross-coupling reactions after construction of the naphthacene skeletons.

Keywords: aromatic compounds · coupling reactions · polycyclic compounds · substituent effects · zirconium

Introduction

Substituted naphthacene derivatives have attracted much attention in the context of organic semiconductors, as crystalline tetraphenyl-substituted naphthacene (rubrene) has shown the highest FET (field effect transistor) mobility among organic compounds.[1] Unfortunately, however, preparative methods for substituted naphthacene derivatives have not been well developed yet.[2–5]



Scheme 1. Homologation method and coupling method for aromatic-ring extension.

Recently we focused on aromatic-ring-extension reactions and developed an homologation method[6] and a coupling method[7] for the formation of substituted anthracenes, naphthacenes, and pentacenes (Scheme 1). These methods involve the formation of metalacyclopentadienes such as zirconacyclopentadienes from alkynes or diynes. The homologation method consists of benzene-ring formation by the reaction of metalacyclopentadienes with alkynes.[8] On the other hand, the coupling reaction involves the coupling of zirconacyclopentadienes with diiodobenzene or tetraiodobenzene.[7]

During the course of our investigation into the reactivity of tricyclic zirconacyclopentadienes, which can be conveniently prepared from diyne derivatives, towards tetraiodo-

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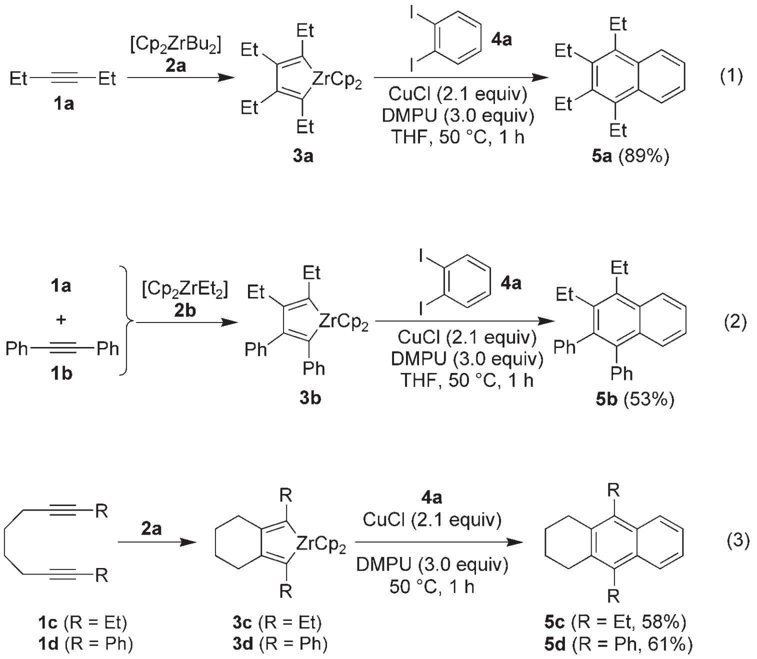
benzene, we found a remarkable effect of the phenyl substituent on the coupling reactions of zirconacyclopentadienes.

Results and Discussion

Comparison of Alkyl-Substituted Zirconacyclopentadienes with Phenyl-Substituted Zirconacyclopentadienes

We have reported the coupling reaction of zirconacyclopentadienes with diiodobenzene in the presence of CuCl and DMPU (*N*,*N*′-dimethyl-*N*,*N*′-propyleneurea). In the previous results, no significant positive effects of aryl substituents on the zirconacyclopentadienes were observed. For example, the reaction of tetraethyl-substituted zirconacyclopentadiene **3a** with *o*-diiodobenzene (**4a**) gave the corresponding naphthalene **5a** in a higher yield than that of diphenyl-substituted **3b** to produce naphthalene **5b** as shown in [Eq. (1)] and [Eq. (2)].



Abstract in Japanese:

ジルコナシクロペンタジエンと1,2,4,5-テトラヨードベンゼンとのカップリング反応を用いて、一連のナフタセン誘導体を合成した。*o*-ビス（プロパルギル）ベンゼン誘導体とジルコノセンジブチルとの反応により、対応する3環式ジルコナシクロペンタジエンを調製し、これとテトラヨードベンゼンとの反応から、対応するジヒドロナフタセンが得られた。このカップリング反応の収率には、ジルコナサイクル上の置換基効果が観測された。α,α'-ジアルキル置換ジルコナサイクルよりも、α,α'-ジフェニル置換体のほうが、より高い収率でカップリング生成物を与えた。これにより導入されたヨウ素を足がかりとして、ナフタセン骨格を構築した後に、クロスカップリング反応によってさらに置換基導入することが可能となった。

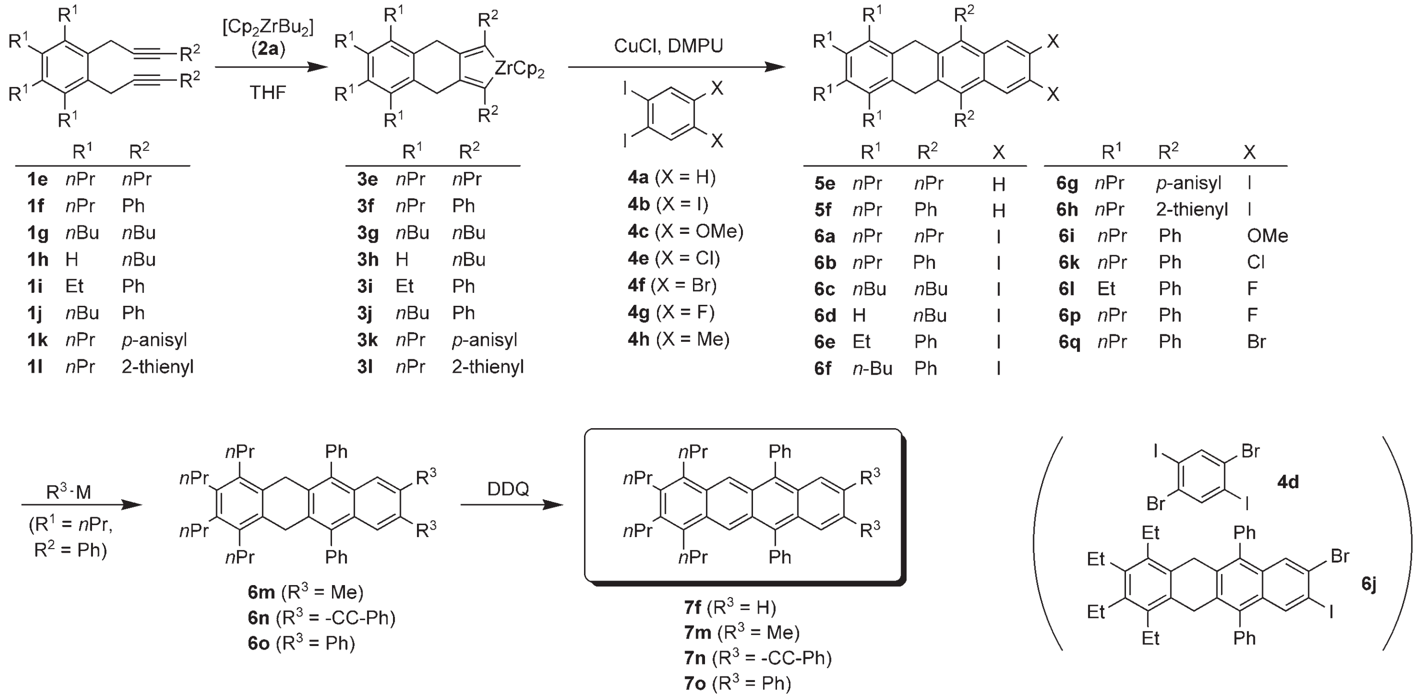
In the case of bicyclic zirconacyclopentadienes **3c** and **3d** ([Eq. (3)]), there is almost no difference between the reactions of ethyl-substituted zirconacyclopentadiene **3c** and phenyl-substituted **3d**.

In this study, we carried out the coupling reaction of tricyclic zirconacyclopentadienes **3**, which are conveniently prepared from diynes **1**, with substituted diiodobenzenes **4** (Scheme 2). Interestingly, it was found that these reactions showed significant substituent effects in the both zirconacyclopentadienes **3** and diiodobenzenes **4**, as described below.

As summarized in Table 1, the yields of the coupling reaction of zirconacycle **3** were strongly dependent on the substituents of **3** and the coupling partners, that is, diiodo- or tetraiodobenzene (**4a** or **4b**). When the reaction of dipropyl-substituted zirconacycle **3e** (R = *n*Pr) with diiodobenzene **4a** was carried out in the presence of CuCl (2 equiv) in THF at 50 °C for 1 h, the corresponding coupling product, dihydronaphthacene **5e** was obtained in good yield (Table 1, entry 1). Similarly, the reaction of phenyl-substituted zirconacycle **3f** (R = Ph; Table 1, entry 2) gave the product **5f** in almost the same yield as that of **5e**, and no considerable differences were observed in these reactions with diiodobenzene **4a**.

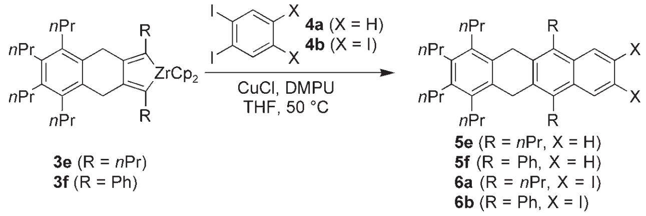
However, in the reactions with tetraiodobenzene **4b** the reactivity of these zirconacyclopentadienes was quite different. Alkyl-substituted zirconacyclopentadiene **3e** gave the product **6a** in just 38 % yield (Table 1, entry 3). In contrast, the yield from the reaction of phenyl-substituted zirconacycle **3f** surprisingly increased to 88 % (Table 1, entry 4).

The other results of the coupling of tricyclic zirconacycles **3** with tetraiodobenzene **4b** are summarized in Table 2. The remarkable difference in the reactivity of the alkyl- and phenyl-substituted zirconacyclopentadienes can also be seen in these examples. For example, the reactions of alkyl-substituted zirconacycles **3g** and **3h** gave the corresponding products **6c** and **6d**, respectively, in moderate yields (Table 2, entries 1 and 2). On the other hand, the phenyl-substituted derivatives **3i** and **3j** afforded the coupling products **6e** and **6f**, respectively, in high yields (Table 2, entries 3 and 4). Furthermore, *p*-anisyl-, and 2-thienyl groups also showed similar positive effects on this coupling reaction, and produced the corresponding dihydronaphthacenes **6g** and **6h** in high yields.



Scheme 2. Zirconium-mediated synthesis of naphthacene derivatives by coupling with diiodobenzenes **4**.

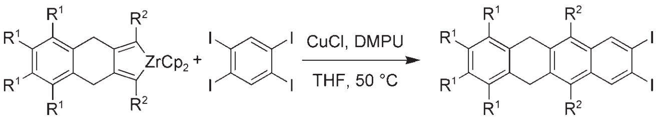
Table 1. Coupling reactions with zirconacycles **3**.



Entry	R	X	Product	Yield [%][a]
1	*n*Pr	H	**5e**	64
2	Ph	H	**5f**	65
3	*n*Pr	I	**6a**	38
4	Ph	I	**6b**	88

[a] Yields of isolated products.

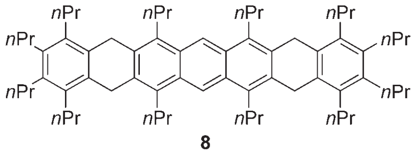
Table 2. Effects of the substituents of zirconacycles on the coupling with tetraiodobenzene.



Entry	R^1	R^2	Product	Yield [%]
1	*n*Bu	*n*Bu	**6c**	52
2	H	*n*Bu	**6d**	41
3	Et	Ph	**6e**	71
4	Ph	Ph	**6f**	84
5	*n*Bu	*p*-anisyl	**6g**	76
6	*n*Pr	2-thienyl	**6h**	67

Substituent Effects of Zirconacyclopentadienes and Diiodobenzenes

The unusual phenomena observed in the reactions of tricyclic zirconacyclopentadienes **3** and di- or tetraiodobenzene **4a** or **4b** can be summarized as follows: 1) Alkyl-substituted tricyclic zirconacyclopentadienes, such as **3e**, reacted with diiodobenzene **4a** to give the coupling products in about 65 % yield. However, with tetraiodobenzene **4b**, the yields went down to 40–50 %. 2) In contrast, when phenyl-substituted tricyclic zirconacyclopentadienes reacted with tetraiodobenzene under the same conditions, the yields increased to 70–90 %, whereas the reactions with diiodobenzene **4a** afforded the coupling product in 65 % yield. To elucidate the origin of these substituent effects, we investigated by-products in the reaction of alkyl-substituted zirconacyclopentadiene **3e** with tetraiodobenzene **4b**. Interestingly, the formation of double coupling product **8** with a heptacyclic skeleton proceeded in 24 % yield (on the basis of NMR spectroscopic analysis). On the other hand, no such product was observed in the reaction with phenyl-substituted zirconacycle **3f**. This result suggests that the alkyl-substituted zirconacyclopentadiene **3e** is more reactive than the phenyl-substituted **3f** because of the electron-donating nature of the alkyl group, and zirconacycle **3e** could react with the single coupling product **6a**. Therefore, the yield of **6a** decreased.



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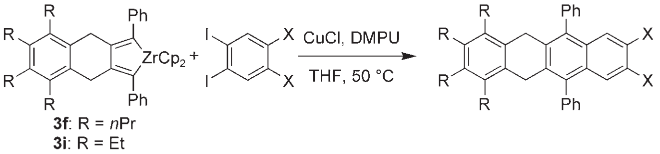
In the case of phenyl-substituted zirconacycle **3f**, the reactivity is not high enough to react with the single coupling product **6b**. This is the reason why the yield of the coupling of **3f** with **4b** did not decrease. To understand the reason for the improvement of the yield of the coupling of phenyl-substituted zirconacycle **3f** with tetraiodobenzene **4b**, we carried out the coupling reaction with a series of substituted diiodobenzenes with substituents at C4 and C5 (Table 3).

Table 3. Coupling of zirconacycles **3f** and **3i** with various diiodobenzenes.

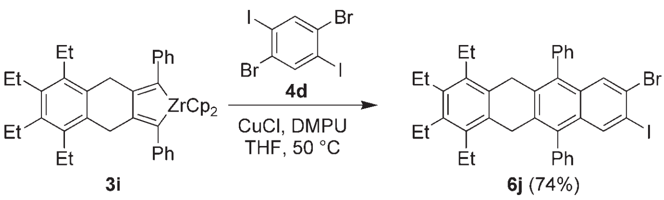


3f: R = *n*Pr
3i: R = Et

Entry	R	X	Product	Yield [%]
1	*n*Pr	OMe	**6i**	29
2	*n*Pr	Me	**6m**	58
3	*n*Pr	H	**5e**	65
4	*n*Pr	Br	**6q**	75
5	*n*Pr	Cl	**6k**	89
6	*n*Pr	F	**6p**	71
7	Et	F	**6l**	83

When the substituents on the diiodobenzene were electron-donating groups such as methoxy and methyl, the yields of the products **6i** and **6m** were low to moderate (Table 3, entries 1 and 2). With diiodobenzene **4a** itself, the yield of **5e** was reasonably good (Table 3, entry 3). In contrast, when the substituents were electron-withdrawing groups, such as Br, Cl, and F, the yields were quite high (Table 3, entries 4–7). This clearly showed that the reactivity of *o*-diiodobenzenes towards phenyl-substituted zirconacyclopentadienes was highly dependent on the substituents. This can be attributed to an enhancement of the electrophilicity of the carbon–iodine bonds by the electron-withdrawing groups.

Furthermore, the coupling of **3i** with 1,4-dibromo-2,5-diiodobenzene (**4d**) proceeded as well ([Eq. (4)]), and the corresponding bromoiododihydronaphthacene **6j** was obtained in high yield. The *o*-dibromo function is tolerated under these conditions (Table 3, entry 4), and the result showed that at least one of the halogen atoms should be iodine in the coupling partner of the zirconacycles to promote the reaction, as we reported previously.[7a]

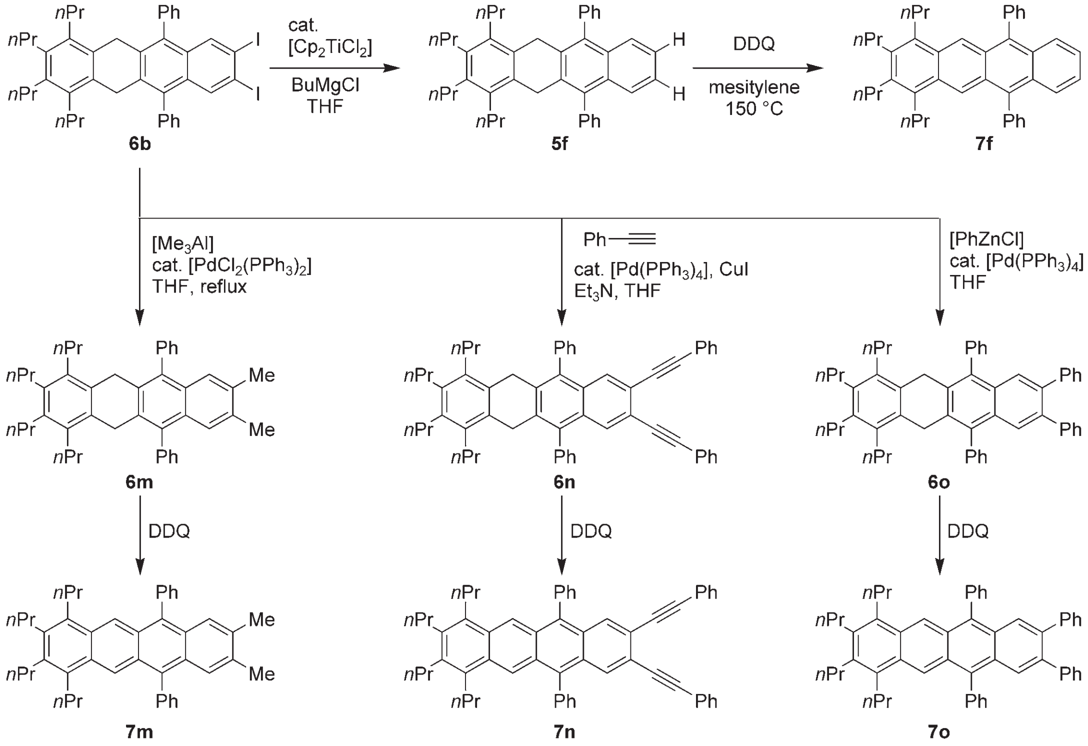


3i **6j** (74%)

(4)

Preparation of Substituted Naphthacene Derivatives

The obtained diiodonaphthacene derivatives **6** with phenyl groups on the internal ring of the naphthacene skeleton were converted into various substituted naphthacene (Scheme 3). Reductive removal of two iodine atoms of **6b** proceeded smoothly by reaction with *n*BuMgCl in the presence of a catalytic amount of $[Cp_2TiCl_2]$[9] to afford dihydro-



Scheme 3. Synthesis of various naphthacenes from diiodide **6b**.

naphthacene **5f**. Carbon–carbon bond formations were also performed by means of well-established Pd-catalyzed cross-coupling reactions, such as methylation with $[Me_3Al]$,[10] Sonogashira coupling with phenylacetylene, and Negishi coupling with [PhZnCl]to produce the corresponding products **6m**, **6n**, and **6o**, respectively, in excellent yields. Finally, the resulting dihydronaphthacenes were aromatized with DDQ in mesitylene at 150 °C to afford a series of naphthacene derivatives **7f**, **7m**, **7n**, and **7o**.

Conclusions

In the present work, we found significant substituent effects in the coupling reactions of tricyclic zirconacyclopentadienes **3** with diiodobenzenes **4** in the presence of CuCl and DMPU. Both of the substituents on zirconacycles **3** and diiodobenzenes **4** considerably affected the product yields, and the combination of aryl substituents on the zirconacycles **3** and electron-withdrawing groups on the diiodobenzenes **4** gave superior results to afford the corresponding dihydronaphthacene derivatives in high yields.

Among the obtained dihydronaphthacenes, diiodo derivatives have a suitable functionality for further modification of the substituents (Scheme 3). This route provides an efficient and effective method not only to synthesize a series of substituted naphthacene derivatives, but also to modify and tune the physical properties of the naphthacenes as organic semiconductors. Further development of the present synthetic method and applications of the synthesized naphthacenes for organic electronic materials are under investigation.

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