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Synthesis of New Halogenated Pentiptycene Building Blocks

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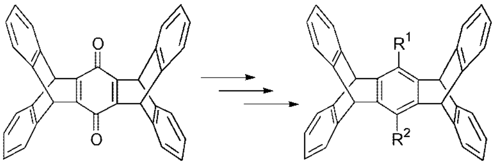
ABSTRACT



12 R^1 = OH, R^2 = Cl
13 R^1 = OH, R^2 = Br
14 R^1 = OH, R^2 = I
15 R^1 = R^2 = Br
16 R^1 = Br, R^2 = I
17 R^1 = R^2 = I

The synthesis of central-ring halogenated pentiptycene phenols 12−14 and dihalogenated pentiptycenes 15−17 is reported. Their utilities as building blocks for preparing new pentiptycene-derived π-conjugated systems through the Sonogashira, Heck, and Suzuki reactions are also demonstrated.

Pentiptycene (**1**) is a member of the iptycene family and possesses a rigid, aromatic, and H-shaped scaffold.[1] Such a structural feature has been applied to the formation of functional molecules such as fluorescent chemosensors,[2] molecular machines,[3] and low dielectric constant materials;[4] to the creation of intriguing supramolecular structures;[5] and to the understanding of structure−property relationships.[6] Interestingly, all of these applications are associated with functionalization of the "sterically shielded" central phenylene ring. As such, the availability of the central-ring prefunctionalized pentiptycene building blocks is crucial in the development of new pentiptycene-based materials.

It has been shown that the readily prepared[7,8] pentiptycene quinone **2** is an excellent precursor for a variety of central-ring functionalized pentiptycene building blocks.[1] Specifically, in addition to the symmetrically disubstituted pentiptycene hydroquinone (**3**) and pentiptycene diacetylene (**4**),[7] a series of unsymmetrically substituted pentiptycenes such as compounds **5−11** have recently been derived from **2** (Scheme 1).[9] However, previous attempts to prepare the halogenated pentiptycene phenols **12−14** and pentiptycene dihalides **15−17** were unsuccessful.[9,10] We report herein the

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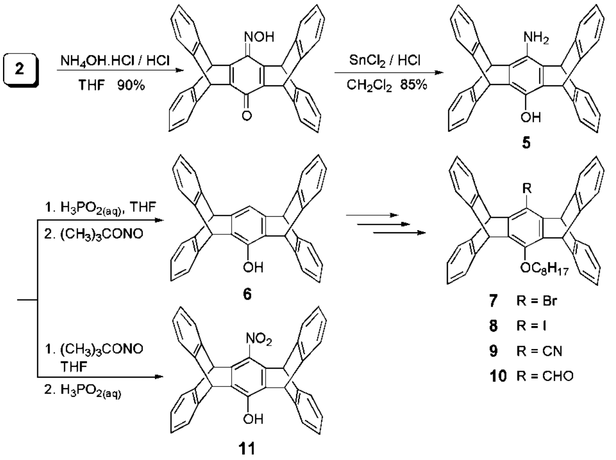
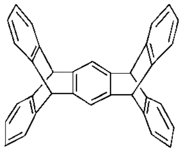
Scheme 1



synthesis of these halogenated pentiptycene building blocks and their potential utility toward the development of new pentiptycene-incorporated π-conjugated systems.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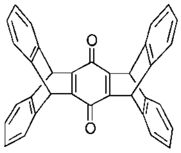
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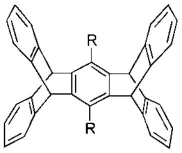
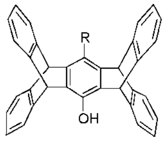
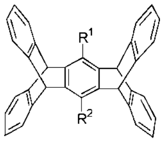
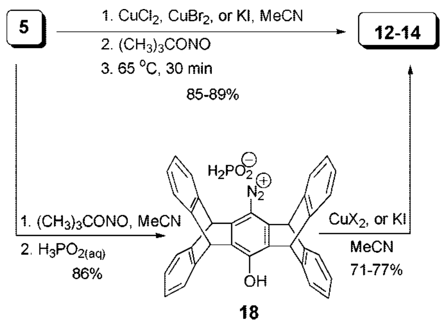

3 R = OH
4 R = CCH

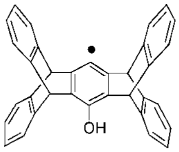

12 R = Cl
13 R = Br
14 R = I


15 R^1 = R^2 = Br
16 R^1 = Br, R^2 = I
17 R^1 = R^2 = I

The halogenated pentiptycene phenols **12**−**14** can be prepared from the deaminative halogenation of **5** either in a one-pot reaction or by a two-step method through the diazonium salt **18** (Scheme 2). The one-pot reaction condition for the synthesis of **12** and **13** is based on the method of Doyle et al.,[11] where *tert*-butyl nitrite is the diazotizing agent, CuBr$_2$ or CuCl$_2$ is the source of halogens, acetonitrile (MeCN) is the solvent, and the reaction temperature is 65 °C. An extension of this method by replacing the cupric halides with KI affords the desired pentiptycene iodide **14**. It should be noted that the same reaction carried out in THF led to other undesired products, including compounds **2**, **3**, **6**, and **11**.[9] Cadogan and Molina have suggested that THF can promote the decomposition of arenediazonium ions to form the corresponding aryl radicals.[12] Indeed, generation of the pentiptycene radical **19** followed by reactions with molecular oxygen, THF, and *tert*-butyl nitrite can nicely account for the products **3** (and the oxidized form **2**), **6**, and **11**, respectively.[9] In other words, in THF the desired reactions between the diazonium ion and cupric halides or KI cannot compete with the THF-promoted pentiptycene radical formation and/or the subsequent reactions. The THF effect on promoting the decomposition of diazonium ions is further evidenced by the fact that the conversion **5** → **11** shown in Scheme 1 is nearly terminated at the stage of the diazonium compound **18** when the solvent is replaced by MeCN (Scheme 2). As a result, the diazonium salt **18** can be isolated as a yellowish solid powder. Interestingly, the powder of **18** displays high thermal stability, as no noticeable decomposition was observed for **18** upon heating up to 300 °C (mp >300 °C) or keeping at 4 °C for as long as 60 days. We believe that, in addition to the hydroxyl substituent,[13] both the steric and electronic factors of the pentiptycene scaffold play a role in its stability, namely, the steric shielding effect due to structural rigidity and bulkiness and the homoconjugative interactions[14] among the peripheral and the central phenylene rings. The conversion of **18** → **12**−**14** can be accomplished simply by stirring acetonitrile solutions of **18** and the corresponding halides (i.e., CuCl$_2$, CuBr$_2$, and KI) at room temperature for 24 h or at 65 °C for 30 min.

Scheme 2




19

The synthesis of pentiptycene dihalides **15**−**17** is outlined in Scheme 3. The key step is the Pd-catalyzed reduction of the triflate group in **20** with triethylsilane, which generates the nitropentiptycene **21**. The reduction reaction is based on the method of Kotsuki et al.,[15] but in our case it requires the more reactive Pd catalyst Pd(PPh$_3$)$_4$ to obtain a reasonable

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(14) The homoconjugative interactions of π groups through the bicycle[2.2.2]octane framework has previously been discussed and termed as "hyperconjugative" interactions. See: Kim, Y.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 452–453.

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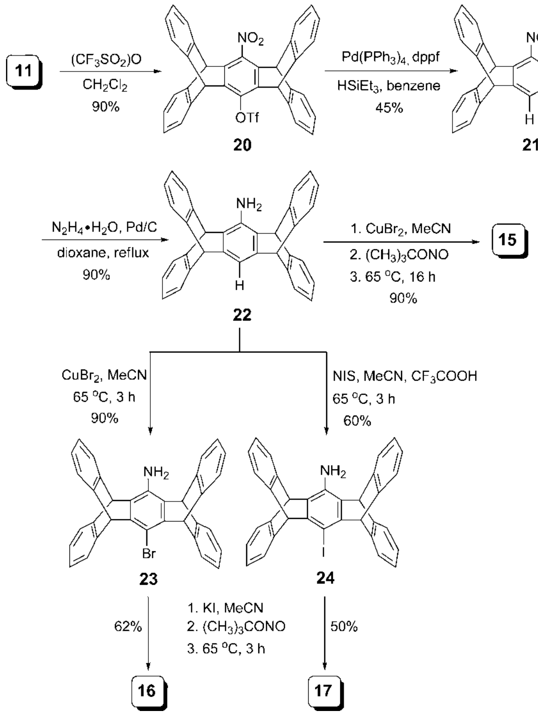
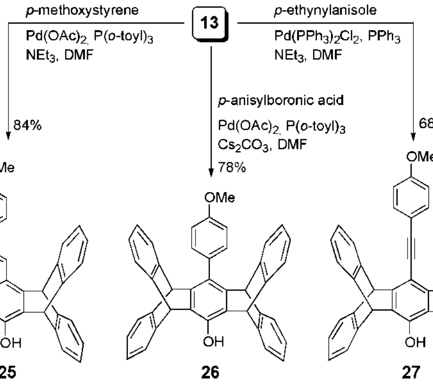
Scheme 3

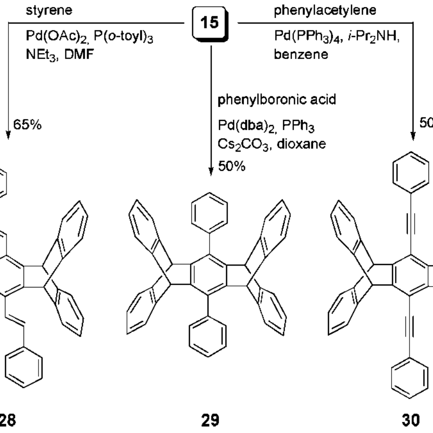


yield (45%). This reaction appears to be more efficient for aryl triflates containing electron-withdrawing substituents, because the corresponding triflate derived from **5** (i.e., an aryl triflate containing an electron-donating amino group) shows no such reactivity. The subsequent reduction of the nitro group provides the pentiptycene aniline **22**. Under the deaminative bromination conditions described for the reaction **5** → **13**, aniline **22** can be readily converted to the desired pentiptycene dibromide **15**. The occurrence of oxidative bromination prior to deaminative bromination for anilines with $CuBr_2$ and *tert*-butyl nitrite in MeCN has previously been observed.[16] With the knowledge of the reaction mechanism,[16] the brominated aniline **23** can be obtained in the absence of *tert*-butyl nitrite, and the subsequent deaminative iodination affords the pentiptycene dihalide **16**. The aniline **23** can also be prepared by reacting **22** with *N*-bromosuccinimide (NBS) in DMF;[17] however, the yield is much lower (40%). Nonetheless, this result inspired us to use *N*-iodosuccinimide (NIS) for the synthesis of **24** from **22**.[18] It should be noted that the use of reagents I_2/Ag_2SO_4[19] and benzyltriethylammonium dichloroiodate (ICl_2^-)[20] for the same purpose led to a mixture of unseparable compounds and unreacted starting material, respectively. The pentiptycene diiodide **17** can then be prepared through the deaminative iodination of **24** under the same condition for the conversion of **23** → **16**.

Scheme 4



Scheme 5



As represented by the building blocks **13** and **15** and the Heck, Suzuki, and Sonogashira reactions,[21] a variety of pentiptycene-incorporated π-conjugated systems (**25**−**30**) can be constructed (Schemes 4 and 5). It should be noted that pentiptycene mono- or ditriflates display little or no such reactivity,[1,2c] although many other aryl triflates have been shown to be alternative substrates for these Pd-catalyzed coupling reactions.[22] In this context, the halogenated pentiptycenes are the critical building blocks toward new pentiptycene-derived π-conjugated systems. In particular, the pentiptycene dihalides **15**−**17** allow one to construct pentiptycene-incorporated π-conjugated polymers of a variety of backbones. Currently, the known pentiptycene-based conjugated polymers are limited to only the alternating arene-pentiptycene poly(*p*-phenyleneethynylene)s (PPEs), prepared from the Sonogashira coupling of the pentiptycene diacetylene **4** and dihalogenated arenes.[2b,7]

In summary, the synthesis of several new pentiptycene halides and dihalides is reported, and their potential utilities

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as building blocks for the construction of new π-conjugated systems are demonstrated. In addition to the halogenated pentiptycenes **12**−**17**, the central-ring functionalized pentiptycene intermediates **18** and **20**−**24** (Schemes 2 and 3) might also find particular utilities in constructing pentiptycene-based materials.

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Supporting Information Available: Experimental procedures and characterization data for **12**−**18** and **20**−**30** and ^{1}H and ^{13}C NMR spectra for new compounds **12**−**18**, **20**−**28**, and **30** This material is available free of charge via the Internet at http://pubs.acs.org.

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