ORGANIC
LETTERS

2009
Vol. 11, No. 6
1429−1432

Synthesis of New Halogenated Pentiptycene Building Blocks

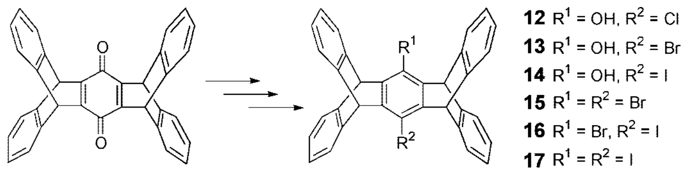
Jye-Shane Yang,*,† Jyu-Lun Yan,‡ Ying-Xue Jin,*,†,§ Wei-Ting Sun,† and Ming-Che Yang†

Department of Chemistry, National Taiwan University, Taipei, Taiwan, 10617,
Department of Chemistry, National Central University, Chungli, Taiwan, 32001, and
College of Chemistry and Engineering, Haerbin Normal University,
Harbin, China 150025

jsyang@ntu.edu.tw; tgh.123@163.com

Received January 20, 2009

ABSTRACT



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

---

† National Taiwan University.
‡ National Central University.
§ Haerbin Normal University.

[1] (a) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432. (b) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, 1641–1654. (c) Yang, J.-S.; Yan, J.-L. *Chem. Commun.* **2008**, 1501–1512.

[2] (a) Yang, J.-S.; Lin, C.-S.; Hwang, C.-Y. *Org. Lett.* **2001**, *3*, 889–892. (b) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev* **2007**, *107*, 1339–1386. (c) Zyryanov, G. V.; Palacios, M. A.; Anzenbacher, P., Jr. *Org. Lett.* **2008**, *10*, 3681–3684.

[3] (a) Annunziata, R.; Benaglia, M.; Cinquini, M.; Raimondi, L.; Cozzi, F. *J. Phys. Org. Chem.* **2004**, *17*, 749–751. (b) Yang, J.-S.; Huang, Y.-T.; Ho, J.-H.; Sun, W.-T.; Huang, H.-H.; Lin, Y.-C.; Huang, S.-J.; Huang, S.-L.; Lu, H.-F.; Chao, I. *Org. Lett.* **2008**, *10*, 2279–2282.

[4] Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 14113–14119.

[5] (a) Yang, J.-S.; Liu, C.-P.; Lee, G.-H. *Tetrahedron Lett.* **2000**, *41*, 7911–7915. (b) Yang, J.-S.; Lee, C.-C.; Yau, S.-L.; Chang, C.-C.; Lee, C.-C.; Leu, J.-M. *J. Org. Chem.* **2000**, *65*, 871–877.

[6] (a) Zhao, X.; Cardolaccia, T.; Farley, R. T.; Abboud, K. A.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 2619–2627. (b) Yang, J.-S.; Yan, J.-L.; Hwang, C.-Y.; Chiou, S.-Y.; Liau, K.-L.; Tsai, H.-H. G.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2006**, *128*, 14109–14119.

[7] Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873.

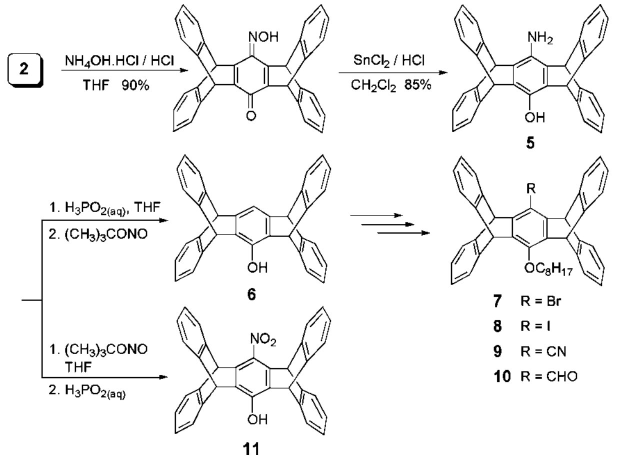
[8] (a) Wiehe, A.; Senge, M. O.; Kurreck, H. *Liebigs Ann. Recl.* **1997**, 1951–1963. (b) Zhu, X.-Z.; Chen, C.-F. *J. Org. Chem.* **2005**, *70*, 917–924.

[9] Yang, J.-S.; Ko, C.-W. *J. Org. Chem.* **2006**, *71*, 844–847.

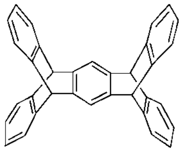
[10] Williams, V. E.; Swager, T. M. *Macromolecules* **2000**, *33*, 4069–4073.

10.1021/ol900127m CCC: $40.75

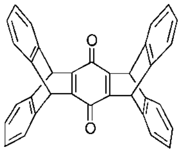
Scheme 1



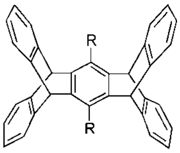
synthesis of these halogenated pentiptycene building blocks and their potential utility toward the development of new pentiptycene-incorporated π-conjugated systems.



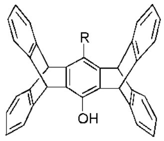
1



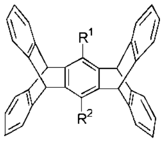
2



3 R = OH
4 R = CCH



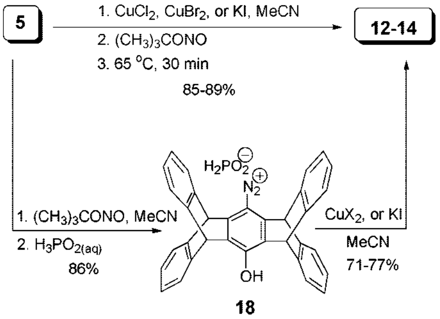
12 R = Cl
13 R = Br
14 R = I

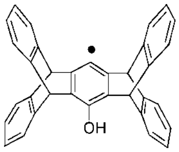


15 R^1 = R^2 = Br
16 R^1 = Br, R^2 = I
17 R^1 = R^2 = I

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

---

[11] Doyle, M. P.; Siegfried, B.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2426–2431.

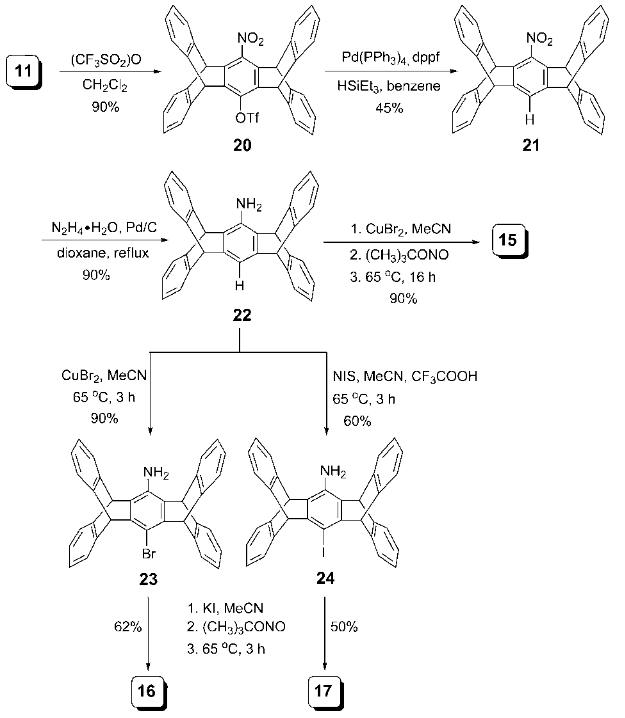
[12] Cadogan, J. I. G.; Molina, G. A. *J. Chem. Soc., Perkin I* **1973**, 541–542.

[13] Bräse, S.; Dahmen, S.; Popescu, C.; Schroen, M.; Wortmann, F.-J. *Chem. Eur. J.* **2004**, *10*, 5285–5296.

[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.

[15] Kotsuki, H.; Datta, P. K.; Hayakawa, H.; Suenaga, H. *Synthesis* **1995**, 1348–1350.

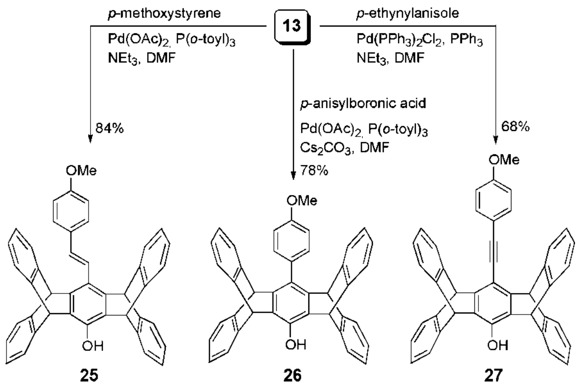
Scheme 3



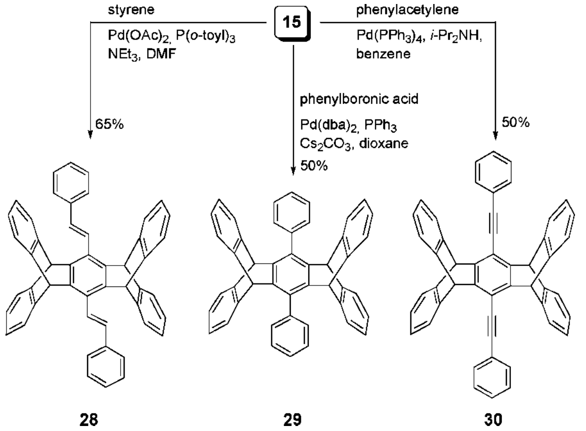
yield (45%). This reaction appears to be more efficient for aryl triflates containing electron-withdrawing substituents, because the corresponding triflate derived from **5** (i.e., an aryl triflate containing an electron-donating amino group) shows no such reactivity. The subsequent reduction of the 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**.

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]

Scheme 4



Scheme 5



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

---

(16) Doyle, M. P.; Van Lente, M. A.; Mowat, R.; Fobare, W. F. *J. Org. Chem.* **1980**, *45*, 2570–2575.

(17) Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733–4735.

(18) Castanet, A.-S.; Colobert, F.; Broutin, P.-E. *Tetrahedron Lett.* **2002**, *43*, 5047–5048.

(19) Sy, W.-W. *Synth. Commun.* **1992**, *22*, 3215–3219.

(20) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600–602.

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.

Acknowledgment. We thank the National Science Council of Taiwan, Academia Sinica, and National Taiwan University for financial support.

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.

OL900127M

---

(21) Hegedus, L. S. In *Organometallics in Synthesis*, Schlosser, M., Ed.; John Wiley & Sons: New York, 1994; Chapter 5.

(22) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133–173.