JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Iridium-Catalyzed Borylation of Pyrene: Irreversibility and the Influence of Ligand on Selectivity

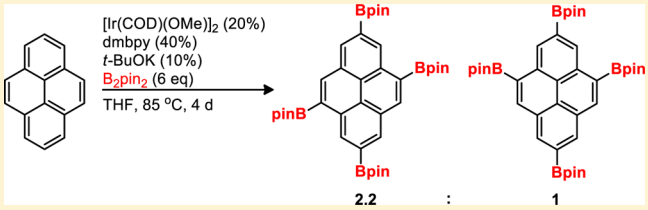
Lei Ji,[†] Katharina Fucke,[†,‡] Shubhankar Kumar Bose,[†] and Todd B. Marder*[,†]

[†]Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[‡]School of Medicine, Pharmacy and Health, Durham University, University Boulevard, Stockton-on-Tees, TS17 6BH, United Kingdom

Supporting Information

ABSTRACT: The iridium-catalyzed borylation of pyrene, using 4,4′-dimethyl-2,2′-bipyridine as the ligand, in the presence of *t*-BuOK, gave a mixture of 2,4,7,9-*tetrakis*(Bpin)-pyrene (**c4**) and its 2,4,7,10-isomer (**m4**) in a 2.2:1 ratio, and the selectivity of the Ir-catalyzed borylation of pyrene is kinetically determined and can be influenced to some extent by the nature of the ligand.



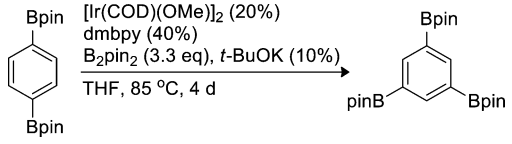
Aromatic boronic acids and their esters are of great importance due to their increasing applications in Suzuki−Miyaura and heteroatom coupling reactions, conjugate additions, and functional group transformations.[1] The Ir-catalyzed direct C−H borylation of aromatic compounds using bis(pinacolato)diboron (B_2pin_2) is a convenient way to synthesize aryl and heteroaryl boronates.[2] The regioselectivity of this reaction results predominantly from steric factors, especially at elevated temperature.[2] Underlying electronic selectivity in the borylation reactions is best observed if the reactions are performed at room temperature, and the selectivity is diametrically opposed to classical aromatic electrophilic substitution.[3] The differences in selectivity of the Ir-catalyzed arene/heteroarene C−H borylation compared to the classical electrophilic aromatic substitution therefore make it a useful complementary approach to prepare functionalized aromatic compounds.

Methodologies for synthesizing pyrene derivatives have also attracted tremendous attention due to their applications in organic electronics including organic light-emitting diodes, organic photovoltaics, and organic field-effect transistors.[4] Furthermore, the extremely long fluorescence lifetime of pyrene and the high sensitivity of the fluorescence vibronic band shape to environment allows derivatives to be used as fluorescent probes.[5] However, most of the pyrene derivatives prepared to date are substituted at either one or more of the 1-, 3-, 6-, or 8-positions because these four symmetry equivalent positions are the sites of electrophilic bromination.[4] Pyrene derivatives with substitution at other positions, such as the 4-, 5-, 9-, and 10-positions (K-region) and 2- and 7-positions (C2 and C7 lie in the nodal plane of both the HOMO and LUMO), are usually synthesized via "indirect methods", by adopting activation steps such as reduction/oxidation.[4] In contrast, the aforementioned steric selectivity of the Ir-catalyzed arene C−H borylation reaction has allowed us to borylate pyrene at the 2- and 7-positions directly[6] and to prepare a range of derivatives showing useful structural and interesting photophysical properties.[7] Liu, Marder and co-workers have recently shown that Ir-catalyzed pyrene C−H borylation can take place at the 4-position (K-region) if the 2- and 7-positions are already occupied by Bpin or *t*-Bu groups.[8,9] In the latter case, excess B_2pin_2 and longer reaction times led to a mixture of bisborylated 2,7-di(*tert*-butyl)pyrenes.

Recently, a report by Eliseeva and Scott revealed the reversibility of the Ir-catalyzed aromatic C−H borylation, when a large amount of catalyst is employed along with added *t*-BuOK, using 4,4′-dimethyl-2,2′-bipyridine (dmbpy) as the ligand, in the presence of an excess of B_2pin_2, providing a convenient method to prepare highly borylated compounds such as 1,3,5,7,9-*pentakis*(Bpin)corannulene, 1,3,5-*tris*(Bpin)-benzene, etc.[10] Their report triggered our investigations on the reversibility of the reaction. First, we confirmed that 1,4-*bis*(Bpin)benzene is completely converted to 1,3,5-*tris*(Bpin)-benzene (Scheme 1) under their conditions, and, thus, the reversibility of the borylation reaction for this particular substrate.

Scott et al. also reported that polyborylation of pyrene (**1**) yielded almost pure 2,4,7,9-*tetrakis*(Bpin)pyrene (**c4**),[10] and none of the 2,4,7,10-*tetrakis*(Bpin)pyrene (**m4**) isomer of **c4** was observed (Scheme 2). The authors did not investigate the

Scheme 1. Conversion of 1,4-*bis*(Bpin)benzene to 1,3,5-*tris*(Bpin)benzene by Exploiting Reversibility[10]



Received: October 20, 2014
Published: December 2, 2014

   dx.doi.org/10.1021/jo5024014 | *J. Org. Chem.* 2015, 80, 661−665

Scheme 2. Borylation of Pyrene with Excess B_2pin_2 in the Presence of *t*-BuOK[10]

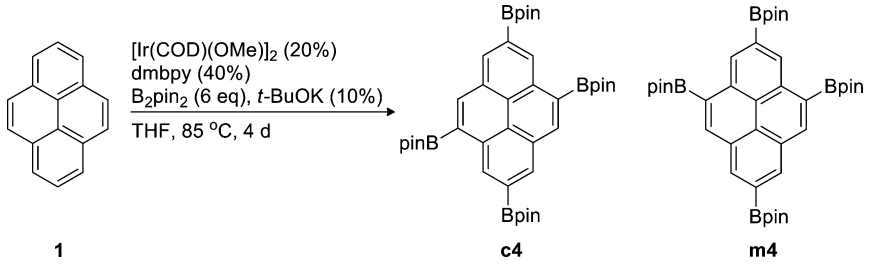
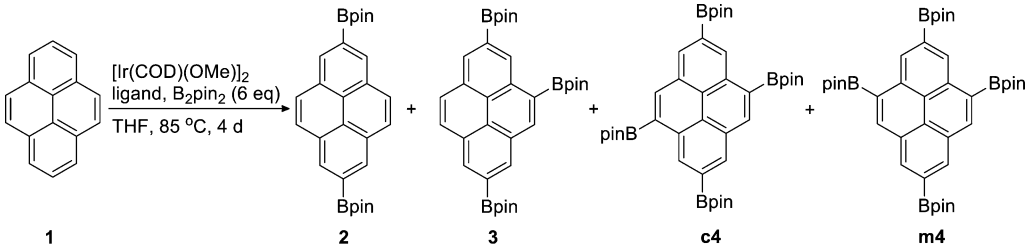


Table 1. Iridium Catalyzed Borylation of Pyrene Using Different Reaction Conditions[a]



					ratio[b]			
entry	$[Ir]_2$ (mol %)	ligand (mol %)	*t*-BuOK (mol %)	[pyrene] (M)	**2**	**3**	**c4**	**m4**
1[c]	20	dmbpy (40)	10	1	0	0.4	2.2	1
2	20	dmbpy (40)	0	1	0	0.3	1.4	1
3	2.5	dtbpy (5)	0	0.1	0.1	1	1.8	1
4[d]	20	dtbpy (40)	10	1	0	0.6	1.9	1

[a]Reaction conditions: pyrene, **1** (0.4 mmol, 1 equiv), $[Ir]_2 = [Ir(COD)(OMe)]_2$, ligand, B_2pin_2 (6 equiv), THF (0.4 mL), at 85 °C for 4 d. Neither pyrene nor 2-(Bpin)pyrene were detected in the crude products. [b]The **2**:**3**:**c4**:**m4** ratios are calculated based on ^{1}H NMR spectra of the crude reaction products (see Supporting Information for details). [c]Average ratio of three repeated reactions (the **c4**:**m4** ratios of these three repeated reactions were 2.0:1, 2.2:1, 2.4:1, respectively). [d]Average ratio of two repeated reactions (the **c4**:**m4** ratios of these two repeated reactions were 2.0:1 and 1.7:1, respectively).

crude product directly after the reaction was finished, but instead followed a workup procedure including solvent removal and washing of the crude product with methanol, giving a white solid after filtration, which was almost pure **c4**. In addition to that, they reported DFT calculations which showed that the energy of **c4** is only 0.5 kcal·mol^{-1} lower than that of the **m4** isomer, resulting in a calculated thermodynamic **c4**:**m4** ratio of 2:1, i.e., the expected ratio if the reaction is indeed reversible and the two isomers are in equilibrium. They claimed that their calculated energy difference must therefore be underestimated, as in their reaction they observed only **c4**.

The Scott result conflicts with previous studies of the borylation of naphthalene and tetracene, in the absence of *t*-BuOK, which gave mixtures of 2,6- and 2,7-*bis*(Bpin)-naphthalene or the analogous tetracenes in almost equal proportions.[6] As Eliseeva and Scott had not checked the crude products, the composition of their reaction mixture before workup was not clear.[10] Finding this result especially intriguing, we performed the reaction using their conditions, and along with **c4**, we also observed the **m4** isomer in the crude reaction mixture (*vide infra*). We repeated their reaction three times (Table 1, entry 1) and detected both **c4** and **m4** in a 2.2:1 ratio by ^{1}H NMR spectra of the crude reaction mixtures. Furthermore, the structures of **c4** and **m4** were confirmed by single-crystal X-ray diffraction (Figure 1).

In one of our repetition experiments (Table 1, entry 1), the crude reaction mixture was divided into two equal parts: A and B. Part A was examined by ^{1}H NMR spectroscopy, which showed it to be a mixture of **c4**:**m4** in a ratio of 2.2:1 (Figure 2a). Part B was worked up in the same way as reported by Eliseeva and Scott:[10] the crude reaction mixture was evaporated to dryness under reduced pressure, and the resulting solid was washed with methanol; the ^{1}H NMR spectrum of the precipitate showed **c4** to be the main component (Figure 2b), while the ^{1}H NMR spectrum of the evaporated methanol washings showed **m4** to be the main component (Figure 2c). Thus, we found that, due to the solubility of **m4** in methanol, **m4** was selectively washed out of the crude product during the workup process.

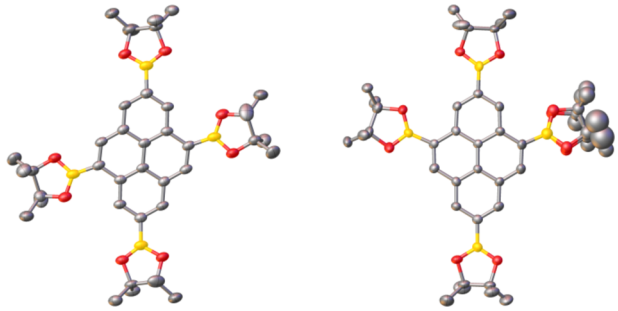


Figure 1. Molecular structures of **c4** (left) and **m4** (right). One of the pinacol groups in **m4** shows disorder. Hydrogen atoms are omitted for clarity. Element (color): carbon (gray), oxygen (red), boron (yellow). Atomic displacement ellipsoids are drawn at 50% probability.

Further investigations were carried out in order to determine whether or not the reaction results in an equilibrium mixture of **c4**:**m4**. We thus attempted to convert pure **c4** or **m4** (88%

dx.doi.org/10.1021/jo5024014 | J. Org. Chem. 2015, 80, 661−665

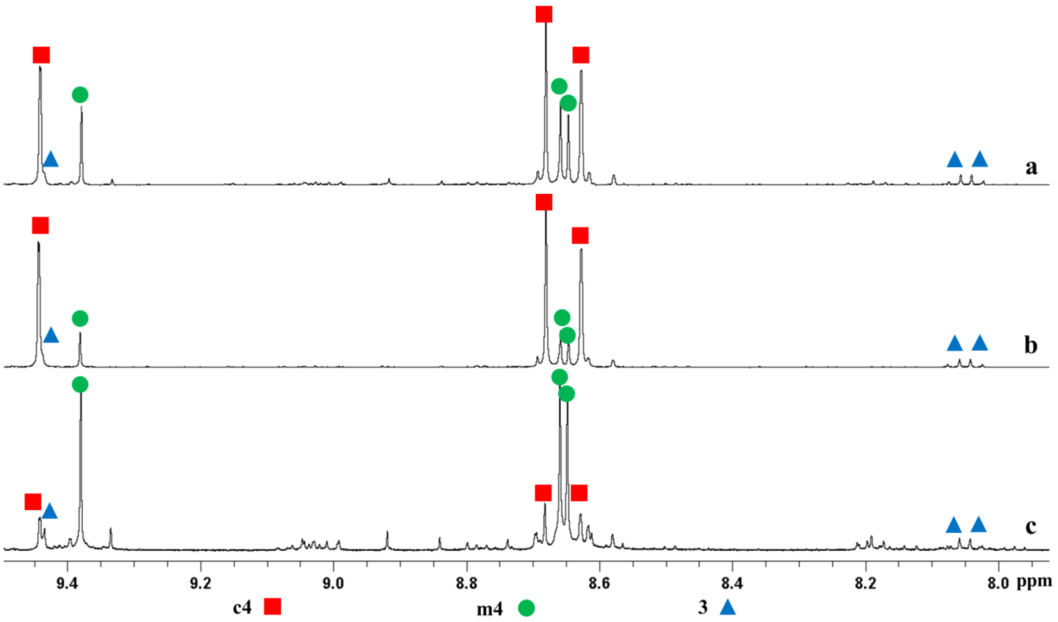


Figure 2. ^{1}H NMR spectra of Table 1, entry 1: (a) before workup; (b) the precipitate after washing with methanol and filtration; (c) the evaporated methanol washings.

pure, *vide infra*) to a mixture of **c4**:**m4** in a thermodynamic equilibrium ratio under the same conditions as those in Scheme 2. However, there was no change observed in either case; i.e., **c4** was not converted to **m4**, nor was **m4** converted to **c4**. Therefore, the Ir-catalyzed (20 mol %) borylation of pyrene, at least at the 4- and 9/10-positions, is in fact not reversible, even in the presence of *t*-BuOK and large amounts of B_2pin_2.

Thus, the **c4**:**m4** ratios are determined by kinetic selectivity. Eliseeva and Scott provide suitable evidence for the reversibility of the borylation of benzene (which we confirmed, *vide supra*), biphenyl, and corannulene, but the reaction is not reversible for **c4** and **m4**. It would appear that steric factors may play a significant role in the reverse (i.e., proteodeborylation) reaction.

As **c4** and **m4** are potentially useful intermediates for the synthesis of organic materials, further investigations were carried out in order to develop good conditions to produce **c4** and **m4**. Performing the reaction in the absence of *t*-BuOK (Table 1, entry 2) results in a decreased amount of **c4** and a final **c4**:**m4** ratio of 1.4:1. This result suggests that addition of *t*-BuOK to the reaction has a modest but measurable impact on the kinetic selectivity of the 4-fold borylation. However, 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) proved to be an effective ligand for the Ir-catalyzed tetraborylation of pyrene even in a dilute solution, and with a much lower catalyst loading. Thus, when 2.5% of the catalyst and 5% of dtbpy were used in a much more dilute solution (Table 1, entry 3) with an excess of B_2pin_2, the reaction produced a **2**:**3**:**c4**:**m4** ratio of 0.1:1:1.8:1. Large amounts of **c4** and **m4** can be synthesized using this set of conditions, and pure **c4** and 88% pure **m4** can be readily isolated. The presence of *t*-BuOK does not affect the **c4**:**m4** ratio when using dtbpy as the ligand (Table 1, entry 4 compared to Table 1, entry 3).

The kinetic selectivity when using dmbpy as the ligand is affected by the presence of *t*-BuOK. The dmbpy anion, which could be produced by the deprotonation of dmbpy, would be much more electron donating than dmbpy.[10] It is possible that the kinetic selectivity may be affected, to some extent, by the electron donating strength of the ligand, although we cannot yet exclude alternative factors. Suginome also noted increased activity for the borylation of di-isobutyl ether when very small amounts of *t*-BuOK were added to the reactions in which $[Ir(OMe)(COD)]_2$/3,4,7,8-tetramethylphenanthroline was used as the catalyst precursor, although the explanation of this effect is not yet apparent.[11]

In conclusion, our study shows that the Ir-catalyzed borylation of pyrene at least at the 4, 9/10-positions is not reversible, despite the reversibility of the Ir-catalyzed borylation of some other substrates, e.g., 1,4-*bis*(Bpin)benzene, under the same conditions. As Eliseeva and Scott suggested, the dmbpy ligand may be deprotonated by *t*-BuOK and thus become a stronger donor. Thus, the kinetic selectivity of Ir-catalyzed C–H borylation may be affected by the donor strength of the ligand, although steric interactions between the ligand and substrate may also be important. We also note that details of the catalyst activation process itself may require consideration when using very high loadings.

EXPERIMENTAL SECTION

Material and Methods. Pyrene, dtbpy, and dmbpy were checked by ^{1}H NMR spectroscopy and used as received. Commercially available *t*-BuOK was dried and sublimed under vacuum and subsequently stored under nitrogen. THF was dried over sodium/benzophenone and deoxygenated using the freeze–pump–thaw method. B_2pin_2 was kindly provided by AllyChem Co. Ltd. (Dalian, China). $[Ir(COD)(OMe)]_2$ was synthesized according to the literature procedure[12] and recrystallized from freshly distilled THF. All NMR spectra were recorded at ambient temperature using a 500 NMR spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). Mass spectrometric analysis was performed in EI mode, and the high-resolution mass spectrometric (HRMS) analysis was performed in ESI mode.

General Experimental Procedures for Examples Described in Table 1. In an argon-filled glovebox, a 5 mL thick-walled reaction

dx.doi.org/10.1021/jo5024014 | J. Org. Chem. 2015, 80, 661–665

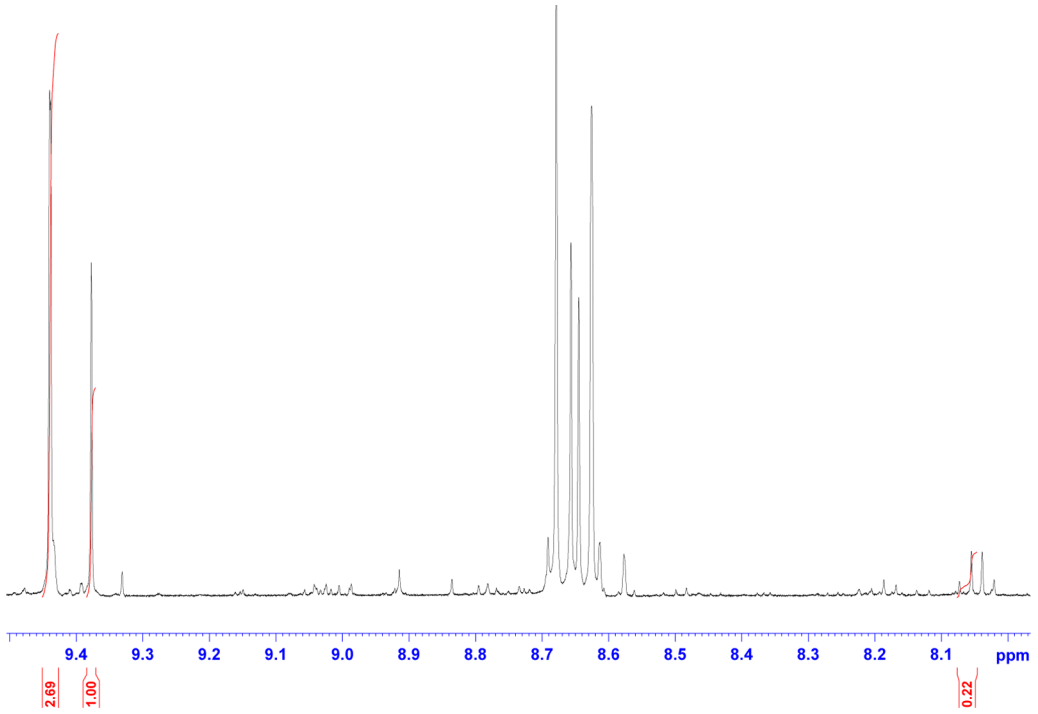


Figure 3. Aromatic region of the ^{1}H NMR spectrum of the crude products in Table 1, entry 1.

tube of the type normally used in a microwave reactor was charged with $[Ir(OMe)COD]_2$, dmbpy (or dtbpy in the case of entry 3), B_2pin_2, and *t*-BuOK. THF was then added, and the vessel was crimp-sealed with a septum cap and stirred at 50 °C for 10 min. Afterwards, pyrene was added, and the vessel was resealed, taken out of the glovebox, and heated at 85 °C in an oil bath for 4 days. After cooling, dichloromethane (2 mL) was added, and the mixture was stirred for 5 min to dissolve all of the solids; 0.5 mL of this solution was evaporated to dryness under vacuum, and the ^{1}H NMR spectrum of the crude product was obtained from this sample. The ratio of **2**:**3**:**c4**:**m4** contained in this solid was calculated by integration of the aromatic region of ^{1}H NMR spectra with good signal-to-noise ratios (Figure 3 is an example).

The doublet at δ = 9.45 (J = 1 Hz) ppm belongs to **c4**, the singlet at δ = 9.38 ppm belongs to **m4**, and the smaller peak at δ = 9.44 ppm (this peak is partly overlapping with the peak of **c4** at 9.45 ppm) and the AB multiplet at *ca.* 8.06 ppm belong to **3**.[8] Thus, the ratio of **3**:**c4**:**m4** in the mixture is as follows: **3**:**c4**:**m4** = $2S_{8.07}$:($S_{9.45}$ − $S_{9.44}$):$S_{9.38}$ = $2S_{8.04}$:($S_{9.45}$ − $S_{8.04}$):$S_{9.38}$ = $2S_{8.07}$:($S_{9.45}$ − $S_{8.07}$):$S_{9.38}$.

Scale-up of Experiment as per Table 1, entry 3, and the Purification and Characterization of c4 and m4. In an argon-filled glovebox, a Young's tube was charged with $[Ir(OMe)COD]_2$ (66 mg, 0.1 mmol, 2.5%), dtbpy (54 mg, 0.2 mmol, 5%) and B_2pin_2 (6.09 g, 24 mmol, 6 equiv). THF (20 mL) was then added, and the vessel was sealed and stirred at 50 °C for 10 min. Afterwards, pyrene (810 mg, 4 mmol, 1 equiv) was added, and the vessel was sealed, taken out of the glovebox, and heated at 85 °C in an oil bath for 4 days. After the reaction was finished, **c4** (1.01 g, 96% purity, yield 36%) was isolated as a white solid by filtration and then washed with methanol (100 mL). Pure **c4** (0.35 g, 13%) was isolated by slow diffusion of methanol into a dichloromethane solution of 96% pure **c4**. The mother liquor was evaporated to dryness under vacuum and washed with hexane/ethanol 1:1 as the solvent to obtain **m4** as a white powder (285 mg, 88% purity, yield 10%).

2,2′,2″,2‴-(Pyrene-2,4,7,9-tetrayl)*tetrakis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[10] (c4). ^{1}H NMR δ = 9.45 (d, 2H, J = 1 Hz), 8.68 (s, 2H), 8.63 (s, 2H), 1.51 (s, 24H), 1.44 (s, 24H) ppm; ^{13}C NMR δ = 139.0, 133.4, 133.1, 132.0, 130.1, 127.5, 126.7, 84.01, 83.97, 25.21, 25.18 ppm. Anal. Calcd for $C_{40}H_{54}B_4O_8$: C, 68.04; H, 7.71. Found: C, 67.81; H, 7.70. MS (EI$^+$): m/z 706 (100%).

2,2′,2″,2‴-(Pyrene-2,4,7,10-tetrayl)*tetrakis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (m4). ^{1}H NMR δ = 9.38 (s, 2H), 8.67 (s, 2H), 8.66 (s, 2H), 1.52 (s, 24H), 1.45 (s, 12H), 1.43 (s, 12H) ppm. ^{13}C NMR δ = 137.8, 133.3, 133.0, 132.3, 129.97, 128.6, 127.9, 127.2, 126.4, 126.2, 84.13, 84.03, 83.8, 25.3, 25.19, 25.15 ppm. HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{40}H_{54}B_4O_8$: 706.42103; Found 706.42090.

Note: It has thus far proven difficult to obtain significant amounts in a purity greater than 88%, although we have confirmed its structure by a single crystal X-ray diffraction study.

X-ray Crystallography. Single crystals of **c4** were obtained by slow diffusion of methanol into a chloroform solution, and those of **m4** by slow diffusion of hexane into a dichloromethane solution. Crystals suitable for X-ray diffraction were selected, coated in perfluoropolyether oil, mounted on sample holders, and placed directly into the precooled cryostream at 100 K. Diffraction data for **c4** were collected on a three circle diffractometer with mirror monochromated Mo Kα radiation (λ = 0.71073 Å) from a microfocus sealed X-ray tube run at 50 kV and 1 mA, and equipped with an area detector. Diffraction data for **m4** were collected on a three circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) from a rotating anode run at 50 kV and 40 mA, and equipped with an area detector. Utilizing Olex2,[13] the structures were solved with the Olex2.solve Charge Flipping algorithm, and refined with Olex2.refine using Gauss−Newton minimization. All non-hydrogen atom positions were located from the Fourier maps and refined anisotropically. Hydrogen atom positions were calculated using a riding model in geometric positions and refined isotropically.

*X-ray Data for **c4**.* $C_{40}H_{54}B_4O_8$, M = 706.17, monoclinic, $P2_1/n$, a = 11.952(3) Å, b = 11.320(3) Å, c = 15.039(3) Å, β = 106.308(7)°, V = 1952.9(8) Å^3, T = 100 K, Z = 2, μ(Mo Kα) = 0.080 mm^{-1}, 24 599 reflections measured, 3840 unique (*Rint* = 0.0581) which were used in all calculations. The final *wR*2 was 0.2476 (all data) and *R*1 was 0.0768 ($I \geq 2\sigma(I)$).

*X-ray Data for **m4**.* $C_{41}H_{55}B_4O_8$, M = 719.09, monoclinic, $P2_1/c$, a = 17.173(2) Å, b = 12.1653(13) Å, c = 22.267(2) Å, β = 110.548(5)°, V = 4356.0(9) Å^3, T = 100 K, Z = 4, μ(Mo Kα) = 0.073 mm^{-1}, 98884 reflections measured, 8537 unique (*Rint* = 0.2907) which were used in all calculations. The final *wR*2 was 0.4176 (all data) and *R*1 was 0.1138 ($I \geq 2\sigma(I)$). The crystal showed twinning and disorder in one Bpin

dx.doi.org/10.1021/jo5024014 | J. Org. Chem. 2015, 80, 661−665

substituent; however, the position of the borylation is unambiguous and the boron atom position is fully occupied. The Bpin residue shows disorder over at least two positions and is modeled in two orientations with approximately 50% occupancy each. The terminal methyl groups show large mobility; thus, this part of the model was kept isotropic.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of **c4** and **m4**, as well as the ^{1}H NMR of the crude products of all the entries, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: todd.marder@uni-wuerzburg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.K.B. thanks the Alexander von Humboldt Foundation (AvH) for a postdoctoral fellowship. T.B.M. thanks AllyChem Co. Ltd. for a generous gift of B_2pin_2. Generous financial support by the Bavarian State Ministry of Science, Research, and the Arts for the Collaborative Research Network "Solar Technologies go Hybrid" is gratefully acknowledged.

■ REFERENCES

(1) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (b) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, 2nd ed.; Wiley-VCH: Weinheim, 2011.

(2) (a) Nguyen, P.; Blom, H. P.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329−9330. (b) Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391−3393. (c) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1999**, *121*, 7696−7697. (d) Cho, J.-Y.; Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **2000**, *122*, 12868−12869. (e) Tse, M. K.; Cho, J.-Y.; Smith, M. R., III. *Org. Lett.* **2001**, *3*, 2831−2833. (f) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305−308. (g) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390−391. (h) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890−931. (i) Hitosugi, S.; Nakamura, Y.; Matsuno, T.; Nakanishi, W.; Isobe, H. *Tetrahedron Lett.* **2012**, *53*, 1180−1182. (j) Preshlock, S. M.; Ghaffari, B.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E., Jr.; Smith, M. R., III. *J. Am. Chem. Soc.* **2013**, *135*, 7572−7582. (k) Larsen, M. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 4287−4289.

(3) Tajuddin, H.; Harrisson, P.; Bitterlich, B.; Collings, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci.* **2012**, *3*, 3505−3515.

(4) (a) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260−7314. (b) Casas-Solvas, J. M.; Howgego, J. D.; Davis, A. P. *Org. Biomol. Chem.* **2014**, *12*, 212−232.

(5) (a) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039−2044. (b) Perry, M.; Carra, C.; Chrétien, M. N.; Scaiano, J. C. *J. Phys. Chem. A* **2007**, *111*, 4884−4889.

(6) (a) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172−2174. (b) Kimoto, T.; Tanaka, K.; Sakai, Y.; Ohno, A.; Yoza, K.; Kobayashi, K. *Org. Lett.* **2009**, *11*, 3658−3661.

(7) (a) Crawford, A. G.; Dwyer, A. D.; Liu, Z.; Steffen, A.; Beeby, A.; Pålsson, L.-O.; Tozer, D. J.; Marder, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 13349−13362. (b) Batsanov, A. S.; Howard, J. A. K.; Albesa-Jové, D.; Collings, J. C.; Liu, Z.; Mkhalid, I. A. I.; Thibault, M.-H.; Marder, T. B. *Cryst. Growth Des.* **2012**, *12*, 2794−2802. (c) Crawford, A. G.; Liu, Z.; Mkhalid, I. A. I.; Thibault, M.-H.; Schwarz, N.; Alcaraz, G.; Steffen, A.; Collings, J. C.; Batsanov, A. S.; Howard, J. A. K. *Chem.—Eur. J.* **2012**, *18*, 5022−5035.

(8) Liu, Z.; Wang, Y.; Chen, Y.; Liu, J.; Fang, Q.; Kleeberg, C.; Marder, T. B. *J. Org. Chem.* **2012**, *77*, 7124−7128.

(9) Pd-catalyzed arylation at the 4-position, proposed to proceed via a Heck type mechanism, is also an efficient way to prepare 4-substituted pyrene derivatives: Mochida, K.; Kawasumi, K.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 10716−10719.

(10) Eliseeva, M. N.; Scott, L. T. *J. Am. Chem. Soc.* **2012**, *134*, 15169−15172.

(11) Ohmura, T.; Torigoe, T.; Suginome, M. *Chem. Commun.* **2014**, *50*, 6333−6336.

(12) Uson, R.; Oro, L. A.; Cabeza, J. A.; Bryndza, H. E.; Stepro, M. P. *Inorg. Synth.* **1985**, *23*, 126−130.

(13) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. *Appl. Crystallogr.* **2009**, *42*, 339−341.