

Cascade Carbopalladation Reaction between Alkynes and *gem*-Dibromoolefins: Facile Access to Monoannulated Pentalenes

Pablo Rivera-Fuentes,^{†,§} Margarete von Wantoch Rekowski,^{†,§} W. Bernd Schweizer,[†] Jean-Paul Gisselbrecht,[‡] Corinne Boudon,[‡] and François Diederich^{*,†}

Laboratorium für Organische Chemie, ETH Zürich, Hönggerberg, HCI, 8093 Zürich, Switzerland, and Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie-UMR 7177, C.N.R.S., Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

diederich@org.chem.ethz.ch

Received June 18, 2012

ABSTRACT



A carbopalladation cascade reaction of easily accessible *gem*-dibromoolefins and alkynes furnishes monobenzo- and mononaphthopentalenes. The new chromophores accessed by this short route exhibit small HOMO–LUMO gaps and redox amphoteric behavior with tunable redox potentials.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous structures in molecular organic electronics.¹ The vast majority of these PAHs are based on fused six-membered rings, while the opto-electronic properties of polycyclic unsaturated hydrocarbons consisting of fused five-membered

rings (polyquinenes)² have remained largely unexplored.³ Pentalene is the simplest polyquinene, and its derivatives have recently attracted considerable attention due to their interesting opto-electronic properties. Symmetrically substituted pentalenes fused to two other benzenoid aromatic systems can be conveniently accessed by palladium⁴ and nickel-mediated⁵ homocoupling reactions. These materials are both good electron donors and electron acceptors (redox amphoteric behavior) with small HOMO–LUMO gaps,^{5,6} possessing interesting charge transport properties, and are suitable for application in organic field-effect transistors (OFETs).⁷

We became interested in exploring the opto-electronic properties of asymmetrically substituted pentalenes fused to only one benzenoid aromatic system. However, only a few approaches for the synthesis of such compounds have

[†] ETH Zürich.

[‡] Université de Strasbourg.

[§] P.R.-F. and M.v.W.R. contributed equally.

(1) For recent reviews, see: (a) Pisula, W.; Feng, X.; Müllen, K. *Chem. Mater.* **2011**, *23*, 554–567. (b) Hoheisel, T. N.; Schrettl, S.; Szilluweit, R.; Frauenrath, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 6496–6515.

(2) Moss, G. P.; Smith, P. A. S.; Tavernier, D. *Pure Appl. Chem.* **1995**, *67*, 1307–1375.

(3) For classic and recent papers on pentalene and polyquinene synthesis, see: (a) Brand, K. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3071–3077. (b) Bally, T.; Chai, S.; Neuenschwander, M.; Zhu, Z. *J. Am. Chem. Soc.* **1997**, *119*, 1869–1875. (c) Saito, M.; Hashimoto, Y.; Tajima, T.; Ishimura, K.; Nagase, S.; Minoura, M. *Chem.—Asian. J.* **2012**, *7*, 480–483. (d) Hashmi, A. S. K.; Wietek, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 555–562. (e) LeGoff, E. *J. Am. Chem. Soc.* **1962**, *84*, 3975–3976. (f) Hafner, K.; Bangert, K. F.; Orfanos, V. *Angew. Chem., Int. Ed.* **1967**, *6*, 451–452. (g) Hafner, K.; Süß, H. U. *Angew. Chem., Int. Ed.* **1973**, *12*, 575–577. (h) Hafner, K.; Suda, M. *Angew. Chem., Int. Ed.* **1976**, *15*, 314–315. (i) Hafner, K.; Goltz, M. *Angew. Chem., Int. Ed.* **1982**, *21*, 695–696. (j) Fu, X.; Cook, J. M. *Aldrichimica Acta* **1992**, *25*, 43–54. (k) Cao, H.; Flippen-Anderson, J.; Cook, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 3230–3231. (l) Cao, H.; Van Ornum, S. G.; Deschamps, J.; Flippen-Anderson, J.; Laib, F.; Cook, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 933–943.

(4) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797.

(5) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem.—Eur. J.* **2009**, *15*, 2653–2661.

(6) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012–11014.

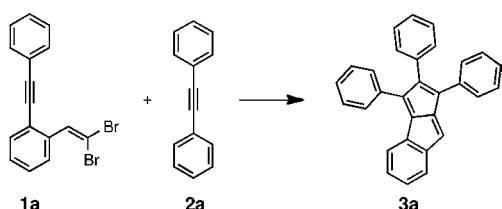
(7) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 7728–7732.

been reported using pyrolysis^{8a-c} or multistep syntheses.^{8f-j} Hence, we decided to develop a simple and rapid method that allows preparation of this kind of molecules starting from readily available reactants. Carbopalladation cascade reactions are powerful methods for the construction of carbocycles,⁹ usually consisting of an initial oxidative addition, one or more carbopalladation steps, and a reductive elimination. In this sense, carbopalladation cascades often rely on the presence of carbon-halide bonds for the oxidative addition and multiple carbon-carbon bonds for the carbopalladation steps. Among the many organohalide derivatives that can be used to start the cascade, *gem*-dibromoolefins¹⁰ are especially interesting and have been used in a variety of palladium-catalyzed cascades to afford *N*-fused heterocyclic systems,¹¹ methyleneindenes,¹² isocoumarins,¹³ benzofurans,¹⁴ oxazolones,¹⁵ methyleneisoindolin-1-ones,¹⁶ indoles,¹⁷ and thiophenes,¹⁸ among many other heterocycles. To the best of our knowledge, *gem*-dibromoolefins have never been used for the construction of pentalene derivatives.

We began our investigations on the reaction of *gem*-dibromoolefin **1a** and diphenylacetylene **2a** (Table 1). Initial experiments using catalytic or stoichiometric amounts of palladium did not deliver any reaction product (Table 1, entries 1 and 2). We noticed that the reaction requires addition of a reducing agent (1,4-hydroquinone, isopropanol, or zinc dust) to proceed; however, only zinc dust gave reasonable yields (Table 1, entries 3–8). On the other hand, a control experiment using only zinc dust proved the necessity of the palladium catalyst for product

formation (Table 1, entry 9). With these results in hand, we started to explore the optimal conditions. Different reaction parameters such as solvent, temperature, and source of palladium (Table 1, entries 10–13) were examined; however, no improvement was observed.

Table 1. Investigated Reaction Conditions for the Carbopalladation Cascade Reaction



entry	catalyst ^a	temp [°C]	solvent	reducing agent ^b	yield ^c [%]
1	[Pd(PPh ₃) ₂ Cl ₂]	100	toluene	none	0
2	[Pd(PPh ₃) ₂ Cl ₂] ^d	100	toluene	none	0
3	[Pd(PPh ₃) ₂ Cl ₂]	25	toluene	zinc dust	traces ^e
4	[Pd(PPh₃)₂Cl₂]	100	toluene	zinc dust	42
5	[Pd(PPh ₃) ₂ Cl ₂]	100	toluene	1,4-hydroquinone	14
6	[Pd(dba) ₂]	100	toluene	1,4-hydroquinone	10
7	[Pd(PPh ₃) ₂ Cl ₂]	100	toluene	isopropanol	8
8	[Pd(dba) ₂]	100	toluene	isopropanol	traces ^e
9	none	100	toluene	zinc dust	0
10	[Pd(PPh ₃) ₂ Cl ₂]	100	1,4-dioxane	zinc dust	traces ^e
11	[Pd(PPh ₃) ₂ Cl ₂]	130	DMF	zinc dust	traces ^e
12	[Pd(MeCN) ₂ Cl ₂]	100	toluene	zinc dust	25
13	[Pd(dba) ₂]	100	toluene	zinc dust	22

(8) For papers on the synthesis of monoannulated pentalenes: (a) Brown, R. F. C.; Eastwood, F. W. *Pure Appl. Chem.* **1996**, *68*, 261–266. (b) Bapat, J. B.; Brown, R. F. C.; Bulmer, G. H.; Childs, T.; Coulston, K. J.; Eastwood, F. W.; Taylor, D. K. *Aust. J. Chem.* **1997**, *50*, 1159–1182. (c) Blake, M. E.; Bartlett, K. L.; Jones, M., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 6485–6490. (d) Shukla, B.; Tsuchiya, K.; Koshi, M. *J. Phys. Chem. A* **2011**, *115*, 5284–5293. (e) Comandini, A.; Malewicki, T.; Brezinsky, K. *J. Phys. Chem. A* **2012**, *116*, 2409–2434. (f) LeGoff, E. *J. Am. Chem. Soc.* **1962**, *84*, 1505–1506. (g) Ried, W.; Freitag, D. *Tetrahedron Lett.* **1967**, *8*, 3135–3136. (h) Ried, W.; Freitag, D. *Chem. Ber.* **1968**, *101*, 756–762. (i) Ried, W.; Schaefer, H.-J. *Synthesis* **1970**, *3*, 142. (j) Wu, T.-C.; Tai, C.-C.; Tiao, H.-C.; Chang, Y.-T.; Liu, C.-C.; Li, C.-H.; Huang, C.-H.; Kuo, M.-Y.; Wu, Y.-T. *Chem.—Eur. J.* **2011**, *17*, 7220–7227.

(9) For a review on carbopalladation cascade reactions, see: Bräse, S.; de Meijere, A. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons, Inc.: New York, 2002; Vol. 1, pp 1369–1403.

(10) The chemistry of *gem*-dihaloolefins has been recently reviewed: Chelucci, G. *Chem. Rev.* **2012**, *112*, 1344–1462.

(11) Chai, D. I.; Lautens, M. *J. Org. Chem.* **2009**, *74*, 3054–3061.

(12) (a) Bryan, C. S.; Lautens, M. *Org. Lett.* **2010**, *12*, 2754–2757. (b) Ye, S.; Ren, H.; Wu, J. *J. Comb. Chem.* **2010**, *12*, 670–675. (c) Ye, S.; Yang, X.; Wu, J. *Chem. Commun.* **2010**, *46*, 2950–2952.

(13) Wang, L.; Shen, W. *Tetrahedron Lett.* **1998**, *39*, 7625–7628.

(14) Thielges, S.; Meddah, E.; Bissere, P.; Eustache, J. *Tetrahedron Lett.* **2004**, *45*, 907–910.

(15) Chai, D. I.; Hoffmeister, L.; Lautens, M. *Org. Lett.* **2011**, *13*, 106–109.

(16) Sun, C.; Xu, B. *J. Org. Chem.* **2008**, *73*, 7361–7364.

(17) (a) Fang, Y.-Q.; Lautens, M. *J. Org. Chem.* **2008**, *73*, 538–549. (b) Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2005**, *7*, 3549–3552. (c) Fayol, A.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 4203–4206. (d) Bryan, C. S.; Lautens, M. *Org. Lett.* **2008**, *10*, 4633–4636. (e) Arthuis, M.; Pontakis, R.; Florent, J.-C. *Org. Lett.* **2009**, *11*, 4608–4611.

(18) (a) Bryan, C. S.; Braunger, J. A.; Lautens, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7064–7068. (b) Zeng, F.; Alper, H. *Org. Lett.* **2011**, *13*, 2868–2871.

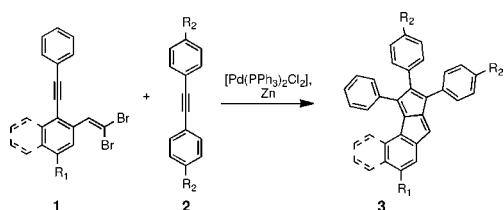
^a 0.05 equiv (unless otherwise stated). ^b 1 equiv. ^c Isolated yields (unless otherwise stated). ^d 1 equiv. ^e Traces were detected by TLC and ¹H NMR but no product was isolated. dba = dibenzylideneacetone. DMF = *N,N*-dimethylformamide.

We next investigated the generality of this carbopalladation cascade using various *gem*-dibromoolefins **1** and internal alkynes **2** (Table 2). The transformation indeed provides a variety of pentalene derivatives that are otherwise inaccessible or tedious to prepare. Another advantage of this method is the availability of the starting materials, which are either commercially available or can be prepared in a few steps following well-established protocols.

The reaction possibly follows a mechanism similar to that proposed for the homocoupling of haloalkynes reported by Levi and Tilley,⁴ although the requirement of zinc dust suggests that zinc might trigger an alternative mechanistic pathway. We propose that the first step in the catalytic cycle (Scheme 1) involves coordination of palladium to the alkyne moiety of the *gem*-dibromoolefin (A), directing the oxidative addition to the desired CBr bond (B).¹⁹ The next step is the intramolecular carbopalladation

(19) A similar directing effect has been observed in related substrates: (a) Nuss, J. M.; Rennels, R. A.; Levine, B. H. *J. Am. Chem. Soc.* **1993**, *115*, 6991–6992. (b) Torii, S.; Okumoto, H.; Tadokoro, T.; Nishimura, A.; Rashid, M. A. *Tetrahedron Lett.* **1993**, *34*, 2139–2142.

Table 2. Carbopalladation Cascade Reaction To Access Monoannulated Pentalenes 3



entry	gem-dibromoolefin	alkyne	product	yield ^a [%]
1	1a: phenyl, R ¹ = H	2a: R ² = H	3a: R ¹ = H, R ² = H	42
2	1a: phenyl, R ¹ = H	2b: R ² = Me	3b: R ¹ = H, R ² = Me	32
3	1a: phenyl, R ¹ = H	2c: R ² = F	3c: R ¹ = H, R ² = F	21
4	1b: phenyl, R ¹ = F	2a: R ² = H	3d: R ¹ = F, R ² = H	40
5	1b: phenyl, R ¹ = F	2b: R ² = Me	3e: R ¹ = F, R ² = Me	27
6	1b: phenyl, R ¹ = F	2c: R ² = F	3f: R ¹ = F, R ² = F	17
7	1c: phenyl, R ¹ = OMe	2a: R ² = H	3g: R ¹ = OMe, R ² = H	35
8	1c: phenyl, R ¹ = OMe	2b: R ² = Me	3h: R ¹ = OMe, R ² = Me	20
9	1c: phenyl, R ¹ = OMe	2c: R ² = F	3i: R ¹ = OMe, R ² = F	20
10	1d: naphthyl, R ¹ = H	2a: R ² = H	3j: R ¹ = H, R ² = H	23
11	1d: naphthyl, R ¹ = H	2b: R ² = Me	3k: R ¹ = H, R ² = Me	20

^a Yields correspond to isolated, pure products. Reagents and conditions: [Pd(PPh₃)₂Cl₂] (0.05 equiv), zinc dust (1 equiv), alkyne (20 equiv), toluene, 100 °C, 24 h.

at the alkyne, forming a transient fulvene (C), followed by intermolecular carbopalladation with an alkyne (D). For termination, we suggest three plausible routes: (a) Oxidative addition of zinc to the CBr bond (E), followed by an intramolecular Negishi-type sequence; (b) Intramolecular carbopalladation at the fulvene (F), followed by zinc-assisted reductive elimination; (c) Two-electron reduction of the Pd(II) intermediate by zinc, a second oxidative addition, formation of a palladacycle (G), and reductive elimination. Further mechanistic investigations are currently underway.

Monobenzopentalenes²⁰ **3a–i** were isolated as dark green solids that are stable both in solution and in the solid state under ambient conditions. Mononaphthopentalenes **3j,k** are greenish-brown solids that are stable in the solid state but decompose slowly when kept in solution at room temperature. Crystals suitable for X-ray diffraction were grown of **3a** and **3j** (Figure 1),²¹ confirming the planar structure of the tri- and tetracyclic scaffolds, respectively.

Pentalenes and some of their annulated derivatives are planar, cyclic hydrocarbons with 4n π-electrons and can be considered antiaromatic. The X-ray data of **3a** and **3j** show bond length alternation in the pentalene cores (see the Supporting Information (SI)), which is consistent with antiaromaticity (for NICS values, see the SI).

(20) Monobenzo- and mononaphthopentalene are trivial names. For IUPAC names of these compounds, see the Supporting Information.

(21) CCDC 871620 (**3a**) and 871621 (**3j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ or via www.ccdc.cam.ac.uk/data_request/cif.

Scheme 1. Proposed Catalytic Cycle with Three Plausible Termination Steps

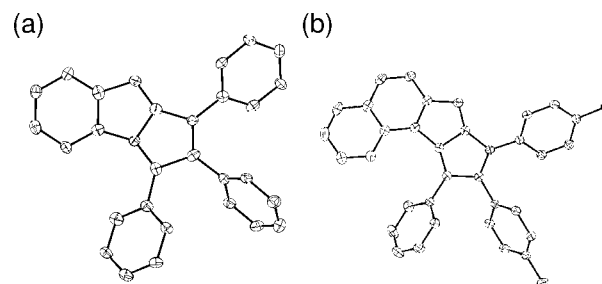
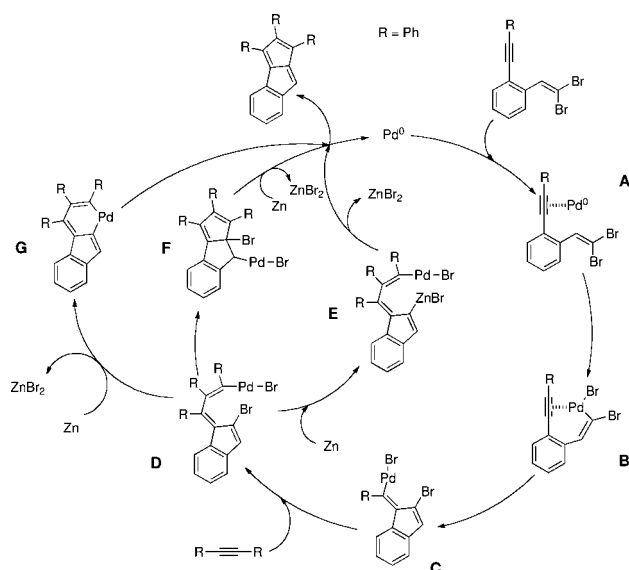


Figure 1. X-ray crystal structures of **3a** (a) and **3j** (b). Arbitrary numbering, atomic displacement parameters obtained at 100 K are drawn at 30% probability level (for details, including bond lengths, see the SI).

UV/vis spectra (see the SI) of the synthesized monoannulated pentalene derivatives display broad low-energy absorptions with λ_{max} values around 600 nm for **3a–i** and 660 nm for **3j,k**, with end absorptions reaching beyond 1000 nm. Time-dependent DFT (TD-DFT) calculations²² at the CAM-B3LYP/6-31G* level of theory revealed that this absorption is associated with the HOMO–LUMO transition (see the SI), which is symmetry forbidden (as is usually the case for 4n π-chromophores) and therefore has a low extinction coefficient. These results account for optical HOMO–LUMO gaps of ca. 2.1 and 1.8 eV for compounds **3a–i** and **3j,k**, respectively. These values are smaller than those of dibenzo- and dinaphthopentalenes⁵ and comparable to those of the recently reported

(22) All calculations were carried out using Gaussian 09, Revision A.02, Frisch, M. J. et al. Gaussian, Inc., Wallington, CT, 2009. For the full reference, see the Supporting Information.

6,12-diethynylindeno[1,2-*b*]fluorenes and indeno[2,1-*a*]fluorenes (~2.1 eV in both cases).²³

Cyclic voltammetry (CV) and rotating disk voltammetry (RDV) were measured for derivatives **3a–j**. CV results for some selected compounds are summarized in Table 3 (for the full data set and RDV results, see the SI).

Table 3. Overview of the First Reduction and Oxidation Potentials from Cyclic Voltammetry (CV) and Summary of Electrochemical and Optical Energy Gaps

entry	3	E_{ox} [V] ^f	E_{Red} [V] ^f	ΔE_{redox} [V] ^d	ΔE_{opt} [V] ^e
1	3a	+0.61 ^b	−1.51 ^c	2.12	2.22
2	3f	+0.67 ^b	−1.45 ^c	2.12	2.07
3	3g	+0.46 ^b	−1.57 ^c	2.03	2.04
4	3j	+0.44 ^b	−1.44 ^b	1.88	1.84

^a Electrochemical data obtained at a scan rate of 0.1 V s^{−1} in CH₂Cl₂ + 0.1 M Bu₄NPF₆ on a glassy carbon working electrode. All potentials are given versus the Fc⁺/Fc couple used as internal standard. Complete set of electrochemical data, including second oxidation and reduction potentials (when detected), and RDV data can be found in the SI. ^b Redox potential for reversible electron transfer. ^c Irreversible peak potential. ^d The electrochemical gap, ΔE_{redox} , is defined as the potential difference between the first oxidative and first reductive redox potentials. ^e The optical gap, ΔE_{opt} , is defined as the energy corresponding to the lowest-energy absorption (λ_{max}).

The values shown in Table 3 reveal that derivatives **3a** and **3j** display a strong redox amphoteric behavior similar to dibenzo[*a,e*]pentalenes.⁵ Derivative **3a** shows an oxidation potential of +0.61 V that can be lowered to +0.46 V by incorporation of a single methoxy group in compound **3g**. Analogously, the presence of fluorine and *p*-fluorophenyl

substituents in compound **3f** gives a reduction potential of −1.45 V (compared to −1.51 V in **3a**). Interestingly, substituents increase or decrease the reduction and oxidation potentials in a concerted manner, allowing the HOMO–LUMO gap to remain essentially unchanged. The electrochemical energy gaps around 2.1 eV for derivatives **3a–i** are consistent with the optical values (Table 3). Mononaphthopentalene **3j** undergoes oxidation at +0.44 V and reduction at −1.44 V, giving a smaller HOMO–LUMO gap of 1.88 eV, also in agreement with the optical value (Table 3).

In summary, we developed a simple and rapid synthesis of monobenzo- and mononaphthopentalenes based on a carbopalladation cascade reaction between *gem*-dibromoolefins and alkynes. This methodology allows for the preparation of asymmetrically substituted pentalene derivatives with only one fused aromatic system, starting from readily available reactants. The pentalenes prepared by this method display small HOMO–LUMO gaps and redox amphoteric behavior. Further investigations in our laboratories include the incorporation of pentalene units in push–pull chromophores and extension of this methodology to the preparation of polyquinenes containing two or more fused pentalene units.

Acknowledgment. This work was supported by a grant from the Swiss National Science Foundation. P.R.-F. thanks the *Stipendienfonds der Schweizerischen Chemischen Industrie* (SSCI) for a doctoral fellowship. Dedicated to Prof. Dr. Dieter Seebach on the occasion of his 75th birthday.

Supporting Information Available. Synthesis, NMR spectra, X-ray crystallographic details, CIF file, DFT and TD-DFT calculations, UV/vis spectra, and full electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>

The authors declare no competing financial interest.

(23) (a) Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11103–11106. (b) Shimizu, A.; Tobe, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 6906–6910. (c) Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong, Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. *J. Am. Chem. Soc.* **2012**, *134*, 10349–10352. (d) Nishida, J.-i.; Tsukaguchi, S.; Yamashita, Y. *Chem.—Eur. J.* **2012**, *18*, 8964–8970.