A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201901565
Angew. Chem. 10.1002/ange.201901565

Link to VoR: http://dx.doi.org/10.1002/anie.201901565
http://dx.doi.org/10.1002/ange.201901565

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Rhodaelectrocatalysis for Annulative C–H Activation: Polycyclic Aromatic Hydrocarbons by Versatile Double Electrocatalysis

Wei-Jun Kong, Lars H. Finger, João C. A. Oliveira, and Lutz Ackermann*[a]

Abstract: The rapid access to structurally diversified polycyclic aromatic hydrocarbons (PAHs) in a controlled manner is of key significance in materials sciences. Herein, we describe a strategy featuring two distinct electrocatalytic C–H transformations for the synthesis of novel nonplanar PAHs. Thus, the combination of rhodaelectrooxidative C–H activation/[2+2+2] alkyne annulation of easily accessible boronic acids, along with electrocatalytic cyclodehydrogenation provided modular access to diversely substituted PAHs with electricity as sustainable oxidant. The unique molecular topology as well as the photophysical and electronic properties of the thus obtained PAHs were fully analyzed. The unique power of the metallaelectrocatalysis was reflected by the chemo-selective assembly of synthetically useful iodo-substituted PAHs.

Polycyclic aromatic hydrocarbons (PAHs) have found widespread applications in optoelectronics, bioimaging and catalysis.[1] The physicochemical properties of PAHs are determined by their shape, π-extension and edge topology, which strongly depend on their mode of fabrication. Thus, the bottom-up synthesis of PAHs with atomic precision has attracted considerable attention in molecular engineering and materials sciences. The syntheses of PAHs have thus far largely relied on multistep protocols involving Diels-Alder cycloadditions, cyclotrimerizations or cross-couplings.[2] Recently, catalytic C–H activation has emerged as a transformative tool for the rapid construction of extended π-systems, with major contributions by Itami[3] and You,[4] among others.[5] However, the sustainable nature of this approach is largely compromised by the need for prefunctionalized substrates and/or metal oxidants, such as silver(I) salts, which generate stoichiometric amounts of undesired chemical waste.

In recent years, the use of electricity as redox agent to power chemical reactions[6] has undergone a renaissance.[7],[8] Significant recent impetus was gained by the merger of electrocatalysis with organometallic C−H activation, avoiding the use of toxic and expensive metal oxidants.[9],[10] While electrochemical polymerization was exploited for the synthesis of conducting materials,[11] the bottom-up assembly of atomically precise PAH motifs by electrooxidative catalysis has thus far unfortunately proven elusive. In sharp contrast, we have now devised a novel strategy for merging two distinct electrocatalyses towards the chemo-selective assembly of decorated PAHs. Thus, the development of an unprecedented rhodaelectro-catalyzed[12] C−H activation for the annulative[13] [2+2+2] cycloaddition of user-friendly boronic acids set the stage for an electro-catalyzed dehydrogenation in a resource-economical manner. Salient features of our findings include a) a rapid, modular access to PAHs via double electrocatalysis, b) electricity as sustainable oxidant, c) the formation of six new C–C bonds in a programmable fashion, and d) outstanding levels of chemo-selectivity by metallaelectrocatalysis.

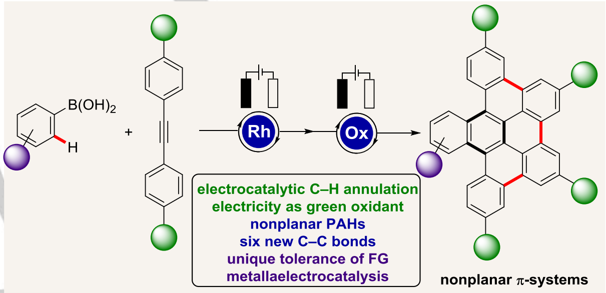

Figure 1. Rhodaelectro-catalyzed C−H activation for selective PAH assembly.

We initiated our studies by probing various reaction parameters for the envisioned electrochemical rhodium-catalyzed C−H activation with boronic acid **1a** for the [2+2+2] alkyne **2a** annulation in a traceless fashion (Table 1, and the Supporting Information).[14] Preliminary observations revealed that the C−H activation benefited from protic solvents, with a combination of *tert*-amyl alcohol and H_2O giving the best results (entries 1-7). Among a variety of additives, KOAc resulted in the optimal performance (entries 8 to 11). Control experiments verified the indispensable role of electricity and the rhodium catalyst (entries 12 and 13). Notably, the reaction proceeded also well with the boronic acid as limiting reagent even at a decreased temperature and under air (entry 14 and entry 15). In stark contrast, ruthenium, iridium or palladium based catalysts fell short in the efficient assembly of product **3aa**.[14]

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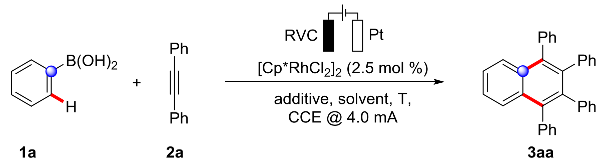
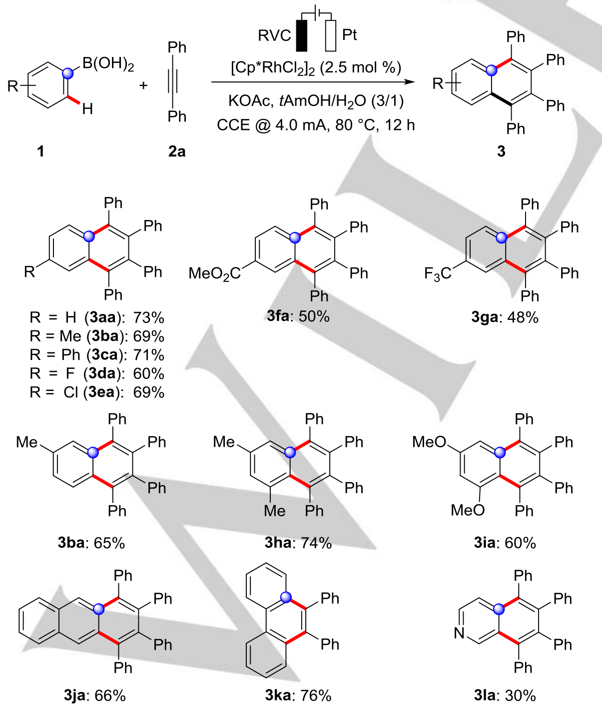
Table 1. Optimization of the rhodaelectro-catalyzed [2+2+2] cycloaddition.[a]



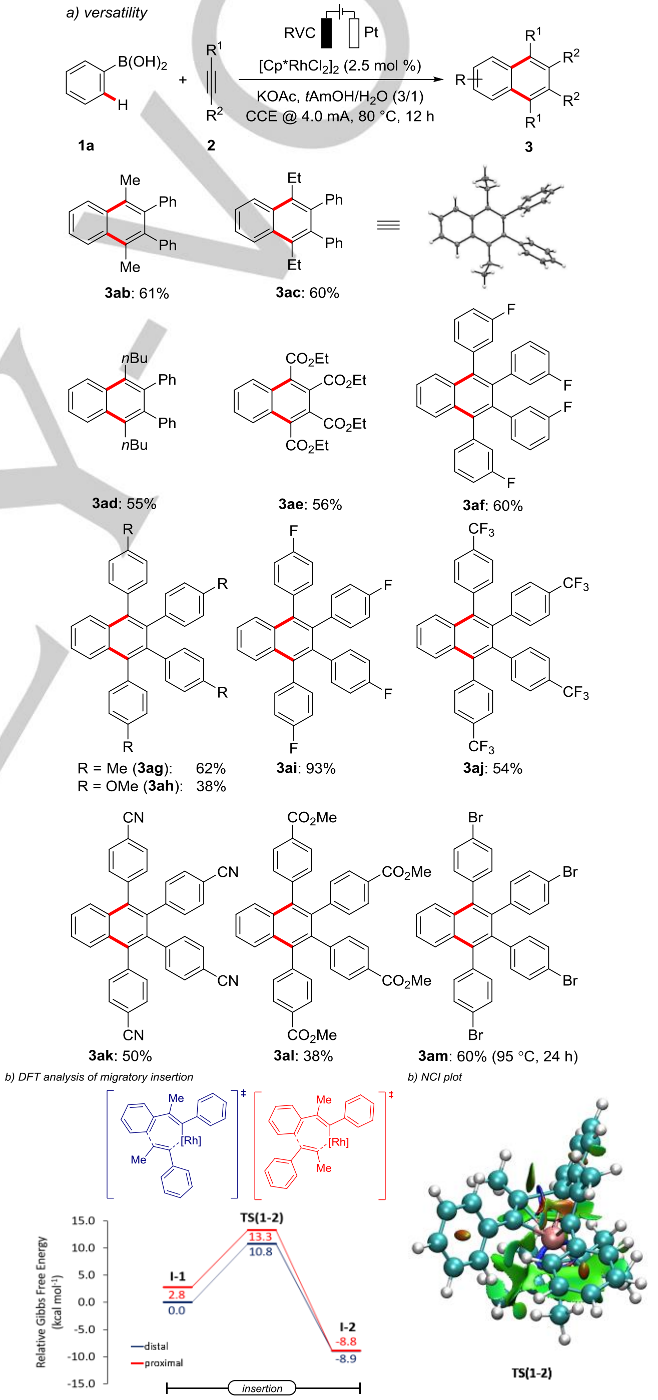
Entry	Additive	T (°C)	Solvent	**3aa** [%]
1	NaOAc	100	DMF	21
2	NaOAc	80	*i*PrOH	11
3	NaOAc	100	*t*AmOH	48
4	NaOAc	100	H_2O	47
5	NaOAc	100	*t*AmOH/H_2O (1/1)	65
6	NaOAc	100	*t*AmOH/H_2O (3/1)	72
7	NaOAc	100	*t*AmOH/H_2O (7/1)	70
8	NaOPiv	100	*t*AmOH/H_2O (3/1)	45
9	K_2HPO_4	100	*t*AmOH/H_2O (3/1)	71
10	KOAc	100	*t*AmOH/H_2O (3/1)	75
11	---	100	*t*AmOH/H_2O (3/1)	55
12	KOAc	100	*t*AmOH/H_2O (3/1)	23[b]
13	KOAc	100	*t*AmOH/H_2O (3/1)	---[c]
14	**KOAc**	**80**	***t*AmOH/H_2O (3/1)**	**73**[d]
15	KOAc	80	*t*AmOH/H_2O (3/1)	71[e]

[a] **1a** (0.5 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), additive (2.0 equiv), solvent (4.0 mL), undivided cell, RVC anode, Pt cathode, constant current = 4.0 mA, 16 h, under N_2, isolated yield. [b] Without electricity. [c] Without $[Cp^*RhCl_2]_2$. [d] With **1a** (0.25 mmol), **2a** (1.0 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), 12 h. [e] Under air, with **1a** (0.25 mmol), **2a** (1.0 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), 12 h.



Scheme 1. Rhodaelectro-catalyzed C−H activation of boronic acids **1**.

With the optimized reaction conditions for the electrochemical annulative C−H activation in hand, its versatility was explored with boronic acids **1** (Scheme 1). Thus, electronically differentiated substrates **1** gave the desired products **3** with high levels of chemo-selectivities. The annulative C−H activation of the *meta*-substituted arenes proceeded with excellent positional selectivity being controlled by steric interactions. Yet, the congested di-*meta*-arenes **1h** and **1i** were converted with high efficacy likewise (**3ha** and **3ia**). While 2-naphthalene boronic acid **1j** afforded tetraphenylanthracene (**3ja**), *ortho*-phenyl arylboronic acid **1k** underwent a chemo-selective mono-alkyne annulation to furnish the phenanthrene **3ka**.

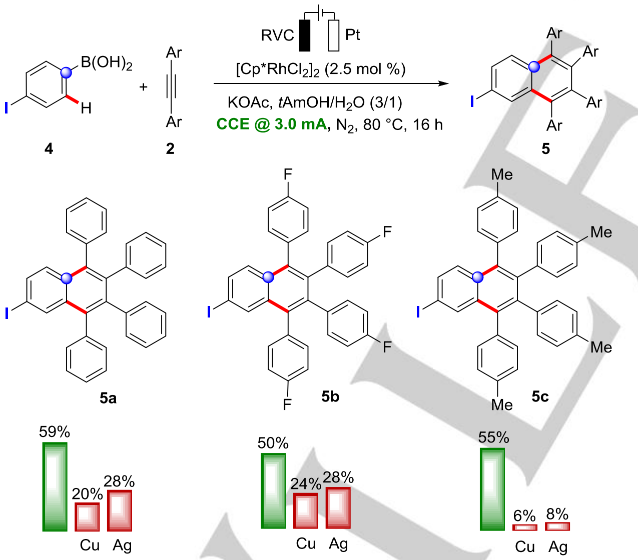


Scheme 2. a) Rhodaelectro-catalyzed C−H activation with alkynes **2**. b) Computed Gibbs free energies ($\Delta G_{353.15K}$) in kcal mol^{-1} for the regioselectivity of the second alkyne migratory insertion, calculated at the

PW6B95-D3BJ/def2-QZVPP+SMD(water)//TPSS-D3BJ/def2-SVP level of theory. c) Visualization of the non-covalent interactions calculated through the NCI-plot for the major isomer. Strong and week attractive interactions are given in blue and green respectively, while red corresponds to strong repulsive interactions.[14]

Subsequently, a variety of alkynes was evaluated in the rhodaelectro-catalyzed C−H activation (Scheme 2a). Hence, challenging unsymmetrical alkynes **2b**-**2d** delivered the corresponding symmetrical products with high levels of double regio-selectivities.[14] This pronounced regio-selectivity features were rationalized by DFT analysis[14] in terms of attractive non-covalent interactions in the key migratory insertion transition state (Scheme 2b,c). The electron-deficient diethyl acetylenedicarboxylate **2e** was well tolerated likewise (**3ae**). The chemo-selective nature of the electrocatalysis was mirrored by its full tolerance of valuable electrophilic functional groups, such as bromo, ester and cyano, which should prove invaluable for further late-stage modifications.

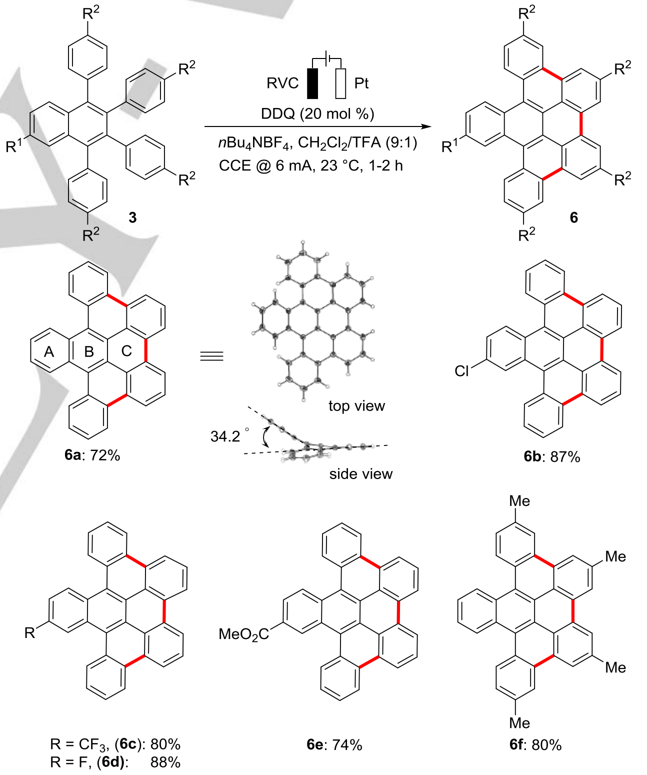
The unique synthetic utility of the rhodaelectrocatalysis manifold was clearly reflected by the chemo-selective C–H transformation of highly sensitive iodo-substituted boronic acid **4** (Scheme 3). Thus, the desired products **5a**-**5c** were obtained with outstanding levels of chemo-selectivity by metallaelectrocatalysis, leaving the sensitive C−I bond intact. In contrast, typical chemical oxidants fell short in delivering the desired iodo-substituted products. These findings highlight the outstanding power of the mild electrochemical redox regime as compared to conventional chemical oxidants.



Scheme 3. The rhodaelectrocatalysis allows access to functionalized products with high selectivity, while chemical oxidants deliver the products in low yields. Conditions for the chemical oxidations: Cu: $Cu(OAc)_2.H_2O$ (2.0 equiv), *t*AmOH/H_2O (3/1), 80 °C, 16 h; Ag: AgOAc (2.0 equiv), *t*AmOH/H_2O (3/1), 80 °C, 16 h.

After having established the robust rhodaelectro-catalyzed [2+2+2] cycloaddition, we turned our attention towards extending the π-conjugation of the thus-formed products **3** by dehydrogenation[15],[16] of the aryl moieties. Here, we obtained the desired product **6a** in the presence of catalytic quantities of the redox mediator DDQ[16b] at room temperature (Scheme 4). Thereby, a wealth of decorated PAHs was accessed under metal-free, mild conditions (**6b**-**6e**), fully tolerating synthetically meaningful halo groups.

The structure of the cyclodehydrogenated product **6a** was unambiguously established by X-ray diffraction analysis, showing a nonplanar PAH with two fused [4]helicene subcomponents (Scheme 4).[17] The dihedral angle between the A and C rings was found to be 34.2°, indicating huge potential towards chirality[18] and curvature dependent optoelectronic properties.[19] The optoelectronic features of the synthesized PAHs **6a**–**6f** are characterized by an absorption range from 350 to 450 nm (Figure 3a and Supporting Information), which results in a light green color. The emission wavelengths of **6a**–**6f** range from 420 to 550 nm with two partly overlapping peaks. The redox behavior of PAHs **6a** to **6f** was further investigated by cyclic voltammetry (Figure 3b and Supporting Information). The compounds are reduced at half-wave potentials between $E_{1/2} = –2.31$ V (**6a**) and $E_{1/2} = –1.93$ V (**6f**, Figure 3b) vs. ferrocene, while being oxidized between $E_{1/2} = 0.62$ V (**6a** and **6f**) and $E_{1/2} = 0.82$ V (**6c**) vs. ferrocene.



Scheme 4. DDQ-catalyzed electrochemical cyclodehydrogenation.

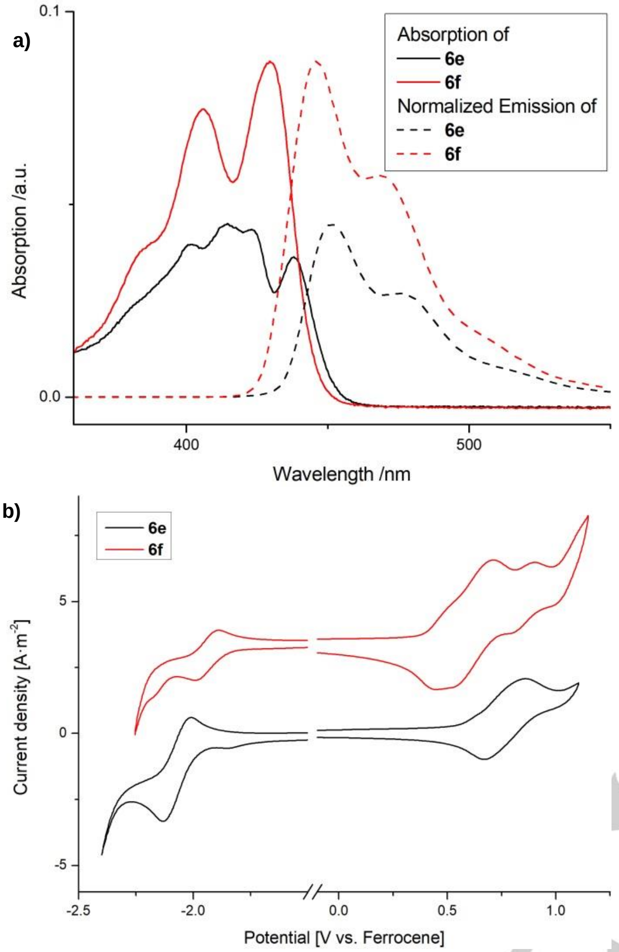


Figure 3. a) Photoabsorption spectra of PAHs **6e** and **6f** in CH_2Cl_2 (straight line) and normalized emission spectra in CH_2Cl_2 (dashed line); b) cyclic voltammograms of **6e** and **6f** vs. ferrocene in CH_2Cl_2 containing 0.1 mol/L $n$$Bu_4NPF_6$, scan rate 0.1 V/s.

In summary, we have devised a novel strategy towards the assembly of decorated PAHs by two distinct electrocatalytic C–H transformations. Thus, the development of an unprecedented rhodaelectro-catalyzed C–H activation for annulative [2+2+2] cycloaddition set the stage for the cyclodehydrogenative synthesis of novel nonplanar PAHs from simple arylboronic acids and alkynes. This strategy features a user-friendly setup, ample scope and electricity as green oxidant. The outstanding power of the metallaelectrocatalysis was mirrored by the chemo-selective C–H functionalization/annulation with sensitive iodo-boronic acids. Our findings thus clearly indicate the superiority of the metallaelectroxidation regime over conventional chemical oxidants in terms of waste product minimization and robustness towards a sustainable future.

Acknowledgements

Generous support by the DFG (SPP 1807, Gottfried-Wilhelm-Leibniz award to LA) is gratefully acknowledged. We thank Dr. Christopher Golz (University Göttingen) for assistance with the X-ray diffraction analysis.

Keywords: Electrochemistry • C−H Activation • Polycyclic Aromatic Hydrocarbons • Rhodium • Dehydrogenation

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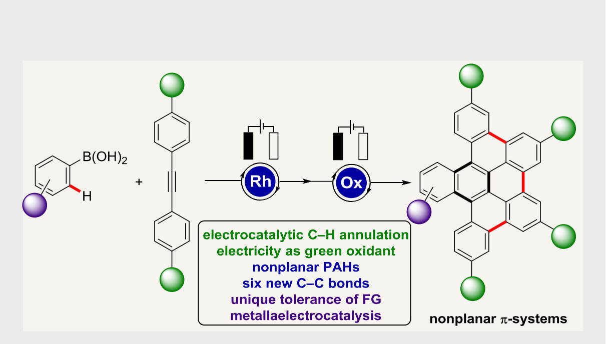

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The combination of rhodaelectrooxidative C–H activation/[2+2+2] alkyne annulation of easily accessible boronic acids, along with electrocatalytic cyclodehydrogenation provided modular access to diversely substituted PAHs with electricity as sustainable oxidant.