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Electro-Catalyzed Hypervalent Iodine Orchestrated for Ruthenaelectro-Catalyzed C–H Oxygenation

Leonardo Massignan,[+] Xuefeng Tan,[+] Tjark H. Meyer, Rositha Kuniyil, Antonis M. Messinis, and Lutz Ackermann*

Abstract: *The catalytic generation of hypervalent iodine(III) reagents by anodic electro-oxidation was orchestrated towards an unprecedented electro-catalytic C–H oxygenation of weakly-coordinating aromatic amides and ketones. Thus, catalytic quantities of iodoarenes in concert with catalytic amounts of ruthenium(II) complexes set the stage for versatile C–H activations with ample scope and high functional group tolerance. Detailed mechanistic studies by experiment and computation substantiated iodoarenes as the electrochemically relevant species towards C–H oxygenations with electricity as sustainable oxidant and molecular hydrogen as the sole by-product. para-Selective C–H oxygenations proved likewise viable in the absence of directing groups.*

Organic electrochemistry has emerged as an increasingly viable tool for molecular synthesis.[1] In addition to the unique potential of electrosynthesis, it is attractive due to the storable, and sustainable properties of electricity.[2] Thus, the effective conversion of renewable electricity into value-added chemical products holds major prospect for a sustainable energy economy.[1h] In this scenario, the merger of electrosynthesis and metal-catalyzed C–H activation[3] has recently been identified as a particularly powerful approach for the resource-economical transformation of ubiquitous, but otherwise inert C–H bonds.[4] Despite of indisputable advances by Mei, Sanford, and Ackermann,[5] electrochemical C–H oxygenations[6] of challenging arenes by weak-coordination[7] have thus far proven elusive. Hence, the reported metalla-catalyzed C–H oxygenations largely required cost-intensive palladium complexes and were inherently limited to strongly-coordinating *N*-directing groups, such as oximes and pyridines.[5] In sharp contrast, C–H oxygenations by synthetically-useful weak *O*-coordination have not been realized in terms of sustainable electro-catalysis. Instead, highly-reactive hypervalent iodine(III) reagents,[8],[9] such as (diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]benzene, are required in overstoichiometric quantities, which calls for strong chemical oxidants for their syntheses and leads to equimolar amounts of undesired halogenated waste products during the C–H functionalization process. Contrarily, we herein present a mechanistically-distinct strategy to address this molecular challenge that orchestrates the catalytic electro-regeneration[10] of hypervalent iodine(III) reagents with ruthenium(II)-catalyzed[11],[12] C–H functionalizations. Salient features of our findings include (*a*) first electro-catalyzed C–H oxygenations by weak coordination, (*b*) user-friendly electrochemical generation of hypervalent iodine reagents, (*c*) ioda/ruthenaelectro-catalyzed C–H functionalizations that combine the advantages of ruthenium-catalyzed C–H activation with the electro-catalytic hypervalent iodine chemistry, and (*d*) mechanistic studies by experiment, computation, cyclic voltammetry and *in-operando* NMR spectroscopy.

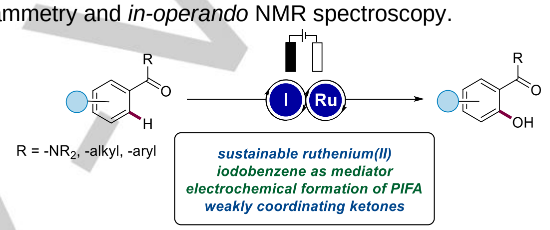

Figure 1. Orchestrating ioda(III)/ruthena(II)-electro-catalytic C–H activation.

We initiated our studies by exploring various reaction conditions for the envisioned electrochemical orchestrated C–H oxygenation of substrate **1a** in a user-friendly undivided cell setup (Table 1, and Table S1 in the Supporting Information).[13] Preliminary experimentation indicated that the reaction could indeed be accomplished in the presence of catalytic amounts of iodobenzene and ruthenium(II) carboxylate (entry 1). The ideal current density was found at 2.67 mA·cm^{-2} (entries 2-3), and the C–H activation proceeded equally well under constant potential conditions at a 2.0 V working potential (entry 4). Interestingly, the platinum-plate as anode was found to be beneficial in comparison to the reticulated vitreous carbon (RVC) anode (entries 5-6). Here, detailed infrared spectroscopic analysis of the RVC anode indicated its electrocatalytic modification.[13] Control experiments confirmed the essential role of the electricity, the ruthenium catalyst, and the iodoarene (entries 7-9). Furthermore, iodobenzene was found to be the only co-catalyst that enabled the desired C–H oxygenation, while benzoquinone (entry 10) as well as chlorine, bromine or chalcogenide redox catalysis[14] fell short in converting substrate **1a** (entries 11 and 12).[12] Notably, the replacement of electricity by the typical chemical oxidants *m*CPBA or Oxone resulted in considerably inferior efficacy (entries 13-14).

Table 1. Optimization of ioda/ruthenaelectro-catalyzed C–H oxygenation.[a]

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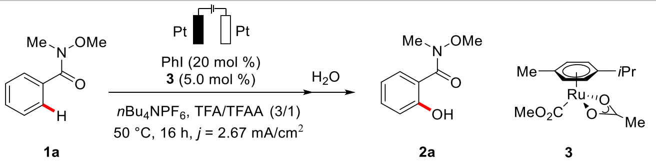
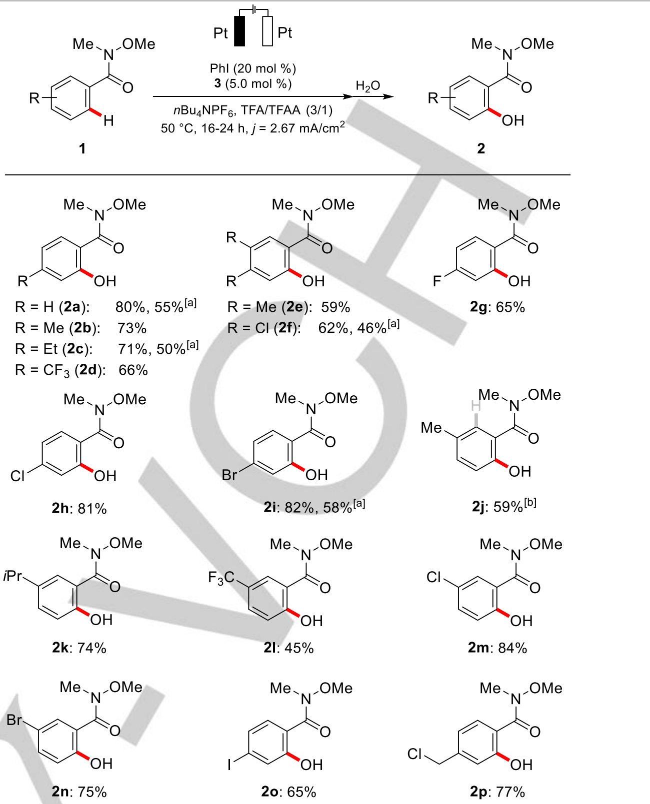


Entry	Deviation from standard conditions	Yield[b]
1	**none**	**80%**
2	j = 4.00 mA·cm^{-2}	51%
3	j = 1.33 mA·cm^{-2}	37%
4	CPE at 2.0 V	86%[c]
5	RVC anode instead of Pt	24%
6	RVC anode instead of Pt, without PhI	28%
7	no current	---
8	without [Ru]	---
9	without PhI	---
10	1,4-Benzoquinone instead of PhI	---
11	PhBr or PhCl instead of PhI	---
12	PhS-SPh or PhSe-SePh instead of PhI	---
13	*m*CPBA instead of electricity	15%
14	Oxone instead of electricity	32%

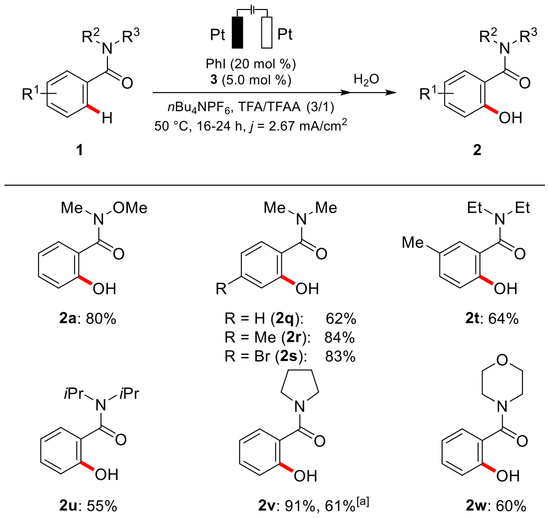
[a] Undivided cell, **1a** (0.50 mmol), iodobenzene (20 mol %), **3** (5.0 mol %) electrolyte (1.0 equiv), solvent (3.0 mL), 50 °C, 16 h, Pt-plate electrodes (10 mm x 15 mm x 0.125 mm), constant current electrolysis (CCE) at 4 mA. [b] Yield of isolated product. [c] CPE = constant potential electrolysis at 2.0 V vs Ag/Ag$^+$. TFA = trifluoroacetic acid. TFAA = trifluoroacetic anhydride.

With the optimized reaction conditions in hand, we probed the versatility of the co-catalytic[15] electrochemical C–H oxygenation system with a representative set of weakly-*O*-coordinating amides **1** (Scheme 1). Differently decorated amides bearing *para*- and *meta*-substituents were thus efficiently transformed towards products **2a-k**. Useful electrophilic functional groups, such as chloro, bromo and even iodo substituents as well as sensitive benzyl chlorides, were fully tolerated, an invaluable asset in terms of future late-stage modifications (**2l-p**).



Scheme 1. Electro-catalyzed C–H activation of Weinreb amides **1**. [a] Without *n*Bu$_4$NPF$_6$. [b] Regio-isomer **2j'** was isolated in 2% yield.

It is noteworthy that the reaction was not limited to Weinreb amides **1**. Indeed, differently substituted amides **1q-w** were efficiently converted to the corresponding oxygenated arenes **2** with excellent efficiency likewise (Scheme 2).



Scheme 2. Electrooxidative C–H activation of various amides **1**. [a] Without *n*Bu$_4$NPF$_6$.

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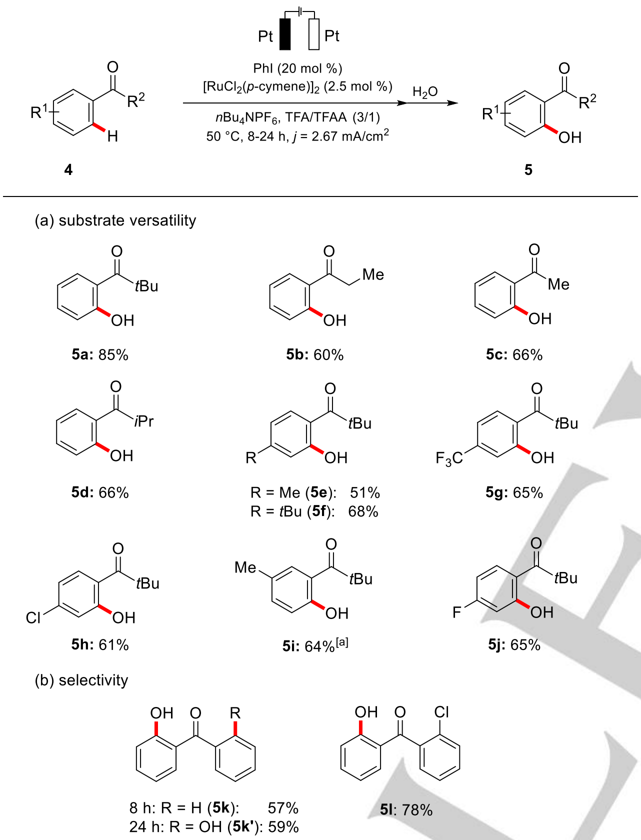
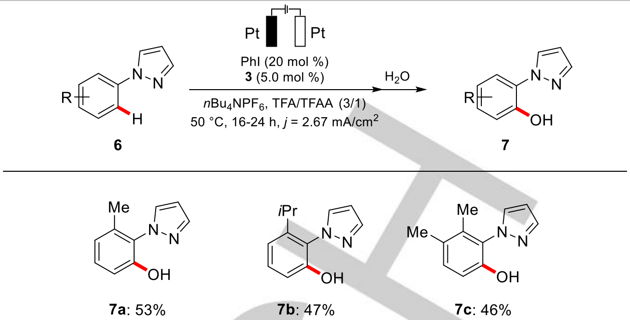
To our delight, the outstanding robustness of the iodine(III)/ruthenium(II)-catalyzed C–H oxygenation co-catalytic system was further highlighted by its ability to also transform weakly coordinating ketones **4** (Scheme 3).[7] The versatility of the electro-catalysis was hence reflected by the successful use of differently decorated ketones **4**. Thereby, various substitution patterns were well tolerated to deliver products **5e-j**. The inherent selectivity features were probed by intramolecular competition experiments with diaryl-ketones **4k** and **4l**, both being functionalized with an excellent mono- and chemo-selectivity. The regio-selectivity in the C–H transformation of the unsymmetrically-substituted substrate **4l** further illustrated the inherent preference for electron-rich arenes (*vide infra*).



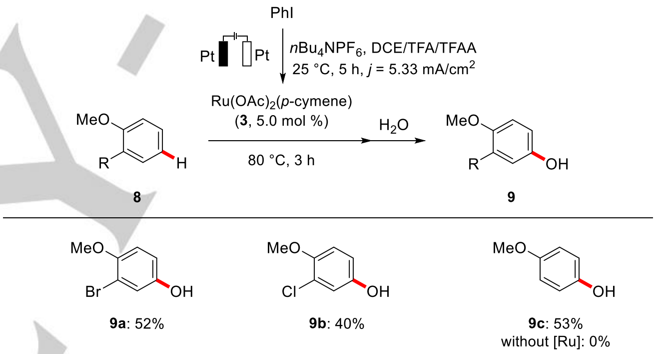
Scheme 3. Ruthenaelectro-catalyzed C–H activation of ketones **4**. [a] 3 mA.

Moreover, the ruthenaelectro-catalyzed C–H oxygenation enabled the modification of synthetically useful pyrazole derivatives **6** (Scheme 4).



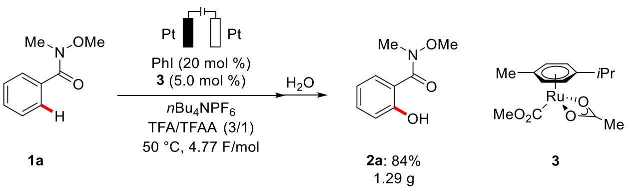
Scheme 4. Ruthenaelectro-catalyzed C–H activation of pyrazolyl substrates **6**.

It is noteworthy that the ruthenaelectro-catalyzed C–H functionalization was not limited to chelation-assisted *ortho*-oxygenation. Indeed, the directing group-free[6f] functionalization in the challenging remote position was likewise sequentially accomplished with excellent levels of site-selectivity, while the ruthenium catalyst was found to be essential (Scheme 5).



Scheme 5. Directing group-free remote C–H oxygenation.

The scalability of the orchestrated electrochemical C–H oxygenation was demonstrated by the gram-scale synthesis of product **2a** without loss in efficiency (Scheme 6).



Scheme 6. Gram-scale iodine/ruthena-electro-catalyzed C–H oxygenation.

Given the efficiency of the unprecedented C–H oxygenation electrochemical system, we became interested in delineating its mode of action. To this end, first, the assessment of the deuterated Weinreb amide in the catalytic reaction unravelled a reversible C–H activation step (Scheme 7a). This finding contrasts with C–H oxygenations enabled by the chemical oxidant PIFA, for which H/D scrambling was not observed.[6g] Second, kinetic studies provided strong support for a fast and reversible C–H metalation with a minor kinetic isotope effect (KIE) of only

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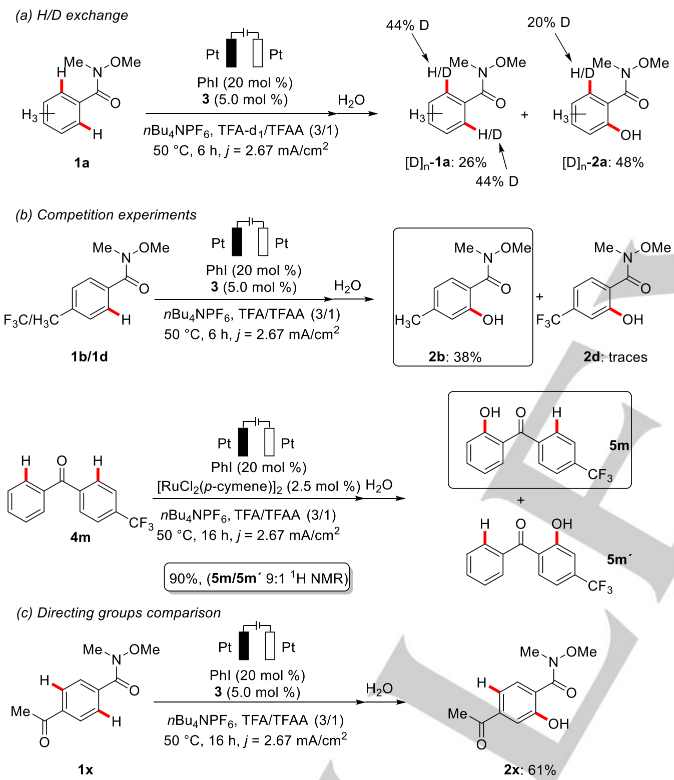
$k_H/k_D \approx 1.6$.[13] These observations overall suggest that the C–H activation is not the rate-determining step, but rather the oxidation of the cyclometalated species. These experimental data are again in contrast with the use of chemical oxidants for which the C–H activation was proposed to be the rate-limiting step with a KIE of $k_H/k_D \approx 3.0$.[6f] Thirdly, competition experiments, using either the Weinreb amides **1b** and **1d** or the difunctionalized ketone **4m**, highlighted electron-rich substrates being preferentially functionalized (*vide supra*, Scheme 7b), which can be rationalized in terms of a base-assisted internal electrophilic-type substitution (BIES) to be operative for the C–H metalation.[16] Forth, an intramolecular competition experiment with substrate **1x** revealed the Weinreb amide as more powerful coordination for the iodine-ruthenium-co-catalyzed C–H transformation (Scheme 7c). Fifth, we probed the possibility of *p*-cymene dissociation.[17] Thus, detailed gas-chromatographic analysis did not provide evidence for free *p*-cymene at any point in the reaction mixture.[12]

cyclic voltammetry (Figure 2b).[12] To this end, the oxidation of different aryl halides was recorded.[13] In trifluoroacetic acid, only iodobenzene showed irreversible anodic oxidation with an onset potential of E = 1.25 V *vs.* ferrocene. By means of computation we also confirmed that the oxidation potential of the iodobenzene is 200 mV lower than the ruthenium(II/IV) manifold,[12] substantiating the iodine-co-catalysis. Notably, other organic halides are known to undergo oxidation at considerably higher potentials,[18, 12] reflecting the unique catalytic competence of iodine reagents (*vide supra*, Table 1). The amide **1a** and electron-deficient iodoarenes showed significally higher potentials for anodic oxidation as compared with unsubstituted and electron-rich iodoarenes. A mixture of iodobenzene and amide **1a** did not lead to significant changes in the voltammogram, which is in agreement with the control experiments summarized in Table 1. Cyclic voltammetry of the independently prepared ruthenacycle **10** in DCE provided support for its facile oxidation.[13]



Scheme 7. Summary of the mechanistic findings.

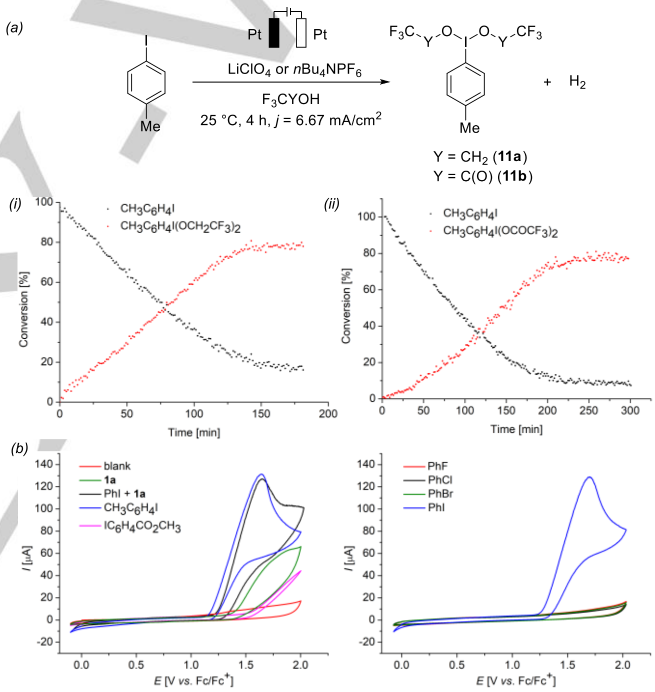
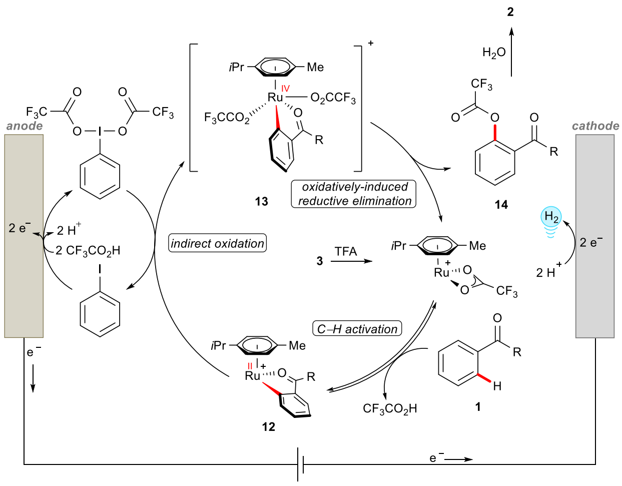


Figure 2. a) *in-operando* NMR-studies using constant current electrolysis at 10 mA in trifluoroethanol (TFE) or trifluoroacetic acid (TFA) respectively. NMR conversion was determined using CH_2Br_2 as the internal standard. i) Reaction profile of anodic formation of $CH_3C_6H_4I(OCH_2CF_3)_2$ (**11a**). ii) Reaction profile of anodic synthesis/formation of $CH_3C_6H_4I(OCOCF_3)_2$ (**11b**). b) Cyclic voltammetry (TFA, 0.1 m nBu$_4$NPF$_6$, 100 mV/s) using glassy carbon as the working electrode. Cyclic voltammograms of different reaction components and their mixtures as well as haloarenes.

Next, we studied the reaction profile for the direct anodic generation of hypervalent iodine reagents by *in-operando* NMR spectroscopy (Figure 2a).[12] This combination of electrochemistry and *in-situ* spectroscopy offered the possibility to study the generation of otherwise unstable electrochemically generated iodine(III) reagents. Initially, the anodic oxidation of iodobenzene in trifluoroethanol (TFE) was monitored and showed almost full conversion of the aryl halide after 2.5 h at 10 mA (Figure 2a,i).[10a] Subsequently, the anodic generation of hypervalent iodine **11b** from TFA and iodobenzene was completed with only slightly prolonged reaction times within 2.5 h (Figure 2a,ii). Thereafter, we examined the electrochemical C–H oxygenation by means of

Based on our detailed mechanistic studies, we propose a plausible catalytic cycle for the ioda/ruthena-electrocatalyzed C–H oxygenation as depicted in Scheme 8. The mechanism rationale commences with the C–H activation on amide **1** by a ruthenium(II) carboxylate. Meanwhile, iodobenzene undergoes a two electron transfer anodic oxidation generating the hypervalent iodine(III). The iodine(III) reagent then mediates the oxidation of

12 by carboxylate-transfer to the ruthena(II)cycle, delivering ruthenium(IV) intermediate **13**, which thereby undergoes rapid oxidatively-induced reductive elimination to furnish product **2** after hydrolysis. Lastly, the regeneration of the active catalyst takes place. The formation of molecular hydrogen as the only stoichiometric by-product was confirmed by gas-chromatographic headspace analysis,[12] bearing great potential for paired electrochemical approaches.[19]



Scheme 8. Plausible catalytic cycle.

In conclusion, we have devised a novel electrochemical co-catalytic system for the C–H oxygenation of synthetically useful amides and ketones by challenging weak-*O*-coordination. The versatile iodine(III)/ruthenium(II)-electro-catalyzed C–H functionalization occurred by orchestrating the catalytic generation of hypervalent iodine(III) reagents with sustainable electricity as cost-effective terminal oxidant, with the formation of molecular hydrogen as the sole by-product. Detailed mechanistic studies by experiment, computation and flow-NMR spectroscopy provided - in contrast to chemical oxidation - support for a fast and reversible C–H ruthenation. The ruthenium catalysis also allowed for the electrochemical remote C–H oxygenations in the absence of directing groups.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: oxygenation • C–H activation • electrocatalysis • electrochemistry • ruthenium • hypervalent iodine

[1] a) K. D. Moeller, *Chem. Rev.* **2018**, *118*, 4817-4833; b) A. Wiebe, T. Gieshoff, S. Mohle, E. Rodrigo, M. Zirbes, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2018**, *57*, 5594-5619; c) S. Tang, Y. Liu, A. Lei, *Chem* **2018**, *4*, 27-45; d) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230-13319; e) E. J. Horn, B. R. Rosen, P. S. Baran, *ACS Cent. Sci.* **2016**, *2*, 302-308; f) R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492-2521; g) S. R. Waldvogel, B. Janza, *Angew. Chem. Int. Ed.* **2014**, *53*, 7122-7123; h) T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, *Chem. Rev.* **2010**, *110*, 6474-6502, and cited references.

[2] a) T. H. Meyer, L. H. Finger, P. Gandeepan, L. Ackermann, *Trends Chem.* **2019**, *1*, 63-76; b) J. Chen, S. Lv, S. Tian, *ChemSusChem* **2019**, *12*, 115-132; c) C. Ma, P. Fang, T.-S. Mei, *ACS Catal.* **2018**, *8*, 7179-7189.

[3] a) Ł. Woźniak, N. Cramer, *Trends Chem.* **2019**; b) P. Gandeepan, L. Ackermann, *Chem* **2018**, *4*, 199-222; c) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, *117*, 9247-9301; d) Q.-Z. Zheng, N. Jiao, *Chem. Soc. Rev.* **2016**, *45*, 4590-4627; e) B. Ye, N. Cramer, *Acc. Chem. Res.* **2015**, *48*, 1308-1318; f) G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11726-11743; g) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369; h) P. Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110*, 824-889; i) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826; j) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094-5115; k) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074-1086.

[4] a) Y. Qiu, J. Struwe, L. Ackermann, *Synlett* **2019**, *30*, 1164-1173; b) N. Sauermann, T. H. Meyer, Y. Qiu, L. Ackermann, *ACS Catal.* **2018**, *8*, 7086-7103; c) Q.-L. Yang, P. Fang, T.-S. Mei, *Chin. J. Chem.* **2018**, *36*, 338-352.

[5] a) C. Tian, U. Dhawa, J. Struwe, L. Ackermann, *Chin. J. Chem.* **2019**, *37*, 552-556; b) A. Shrestha, M. Lee, A. L. Dunn, M. S. Sanford, *Org. Lett.* **2018**, *20*, 204-207; b) Q.-L. Yang, Y.-Q. Li, C. Ma, P. Fang, X.-J. Zhang, T.-S. Mei, *J. Am. Chem. Soc.* **2017**, *139*, 3293-3298; c) Q. L. Yang, Y. Q. Li, C. Ma, P. Fang, X. J. Zhang, T. S. Mei, *J. Am. Chem. Soc.* **2017**, *139*, 3293-3298; d) Y.-Q. Li, Q.-L. Yang, P. Fang, T.-S. Mei, D. Zhang, *Org. Lett.* **2017**, *19*, 2905-2908; e) N. Sauermann, T. H. Meyer, C. Tian, L. Ackermann, *J. Am. Chem. Soc.* **2017**, *139*, 18452-18455, and cited references.

[6] a) G. G. Dias, T. Rogge, R. Kuniyil, C. Jacob, R. F. S. Menna-Barreto, E. N. da Silva Júnior, L. Ackermann, *Chem. Commun.* **2018**, *54*, 12840-12843; b) Y.-H. Sun, T.-Y. Sun, Y.-D. Wu, X. Zhang, Y. Rao, *Chem. Sci.* **2016**, *7*, 2229-2238; c) Y.-F. Liang, X. Wang, Y. Yuan, Y. Liang, X. Li, N. Jiao, *ACS Catal.* **2015**, *5*, 6148-6152; d) F. Yang, K. Rauch, K. Kettelhoit, L. Ackermann, *Angew. Chem. Int. Ed.* **2014**, *53*, 11285-11288; e) X. Yang, Y. Sun, Z. Chen, Y. Rao, *Adv. Synth. Catal.* **2014**, *356*, 1625-1630; f) W. Liu, L. Ackermann, *Org. Lett.* **2013**, *15*, 3484-3486; g) F. Yang, L. Ackermann, *Org. Lett.* **2013**, *15*, 718-720; h) P. Y. Choy, F. Y. Kwong, *Org. Lett.* **2013**, *15*, 270-273; i) H.-Y. Zhang, H.-M. Yi, G.-W. Wang, B. Yang, S.-D. Yang, *Org. Lett.* **2013**, *15*, 6186-6189; j) V. S. Thirunavukkarasu, L. Ackermann, *Org. Lett.* **2012**, *14*, 6206-6209; k) V. S. Thirunavukkarasu, J. Hubrich, L. Ackermann, *Org. Lett.* **2012**, *14*, 4210-4213; l) F. Mo, L. J. Trzepkowski, G. Dong, *Angew. Chem. Int. Ed.* **2012**, *51*, 13075-13079; m) G. Shan, X. Yang, L. Ma, Y. Rao, *Angew. Chem. Int. Ed.* **2012**, *51*, 13070-13074; n) J. M. Racowski, N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18022-18025; o) T. Yoneyama, R. H. Crabtree, *J. Mol. Catal. A* **1996**, *108*, 35-40. A recent review: p) F. Yang, H. Zhang, X. Liu, B. Wang, L. Ackermann, *Chin. J. Org. Chem*. **2019**, *39*, 59-73, and cited references.

[7] a) S. D. Sarkar, W. Liu, S. I. Kozhushkov, L. Ackermann, *Adv. Synth. Catal.* **2014**, *356*, 1461-1479; b) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788-802.

[8] a) D. P. Hari, P. Caramenti, J. Waser, *Acc. Chem. Res.* **2018**, *51*, 3212-3225; b) X. Li, P. Chen, G. Liu, *Beilstein J. Org. Chem.* **2018**, *14*, 1813-1825; c) N. Früh, J. Charpentier, A. Togni, in *Hypervalent Iodine Chemistry* (Ed.: T. Wirth), Springer, Cham, **2016**, pp. 167-186; d) Y. Li, D. P. Hari, M. V. Vita, J. Waser, *Angew. Chem. Int. Ed.* **2016**, *55*, 4436-4454; e) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328-3435; f) F. V. Singh, T. Wirth, *Chem. Asian J.* **2014**, *9*, 950-971; g) T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Tetrahedron* **2009**, *65*, 10797-10815; h) V. V. Zhdankin, *Chem. Rev.* **2002**, *102*, 2523-2584.

[9] R. D. Richardson, T. Wirth, *Angew. Chem. Int. Ed.* **2006**, *45*, 4402-4404.

[10] a) M. Elsherbini, B. Winterson, H. Alharbi, A. A. Folgueiras-Amador, C. Génot, T. Wirth, *Angew. Chem. Int. Ed.* **2019**, *58*, 9811–9815; b) R. Francke, *Curr. Opin. Electrochem.* **2019**, *15*, 83-88; c) M. Elsherbini, T. Wirth, *Chem. Eur. J.* **2018**, *24*, 13399-13407; d) J. D. Haupt, M. Berger, S. R. Waldvogel, *Org. Lett.* **2018**, *21*, 242-245; e) R. Mockel, E. Babaoglu, G. Hilt, *Chem. Eur. J.* **2018**, *24*, 15781-15785; f) T. Wirth, W.-C. Gao, Z.-Y. Xiong, S. Pirhaghani, *Synthesis* **2018**, *51*, 276-284; g) T. Broese, R. Francke, *Org. Lett.* **2016**, *18*, 5896-5899; h) Y. I. K. Inoue, S. Nishiyama, *Org. Lett.* **2010**, *12*, 436-439; i) D. Kajiyama, K. Inoue, Y. Ishikawa, S. Nishiyama, *Tetrahedron* **2010**, *66*, 9779-9784.

[11] For recent representative references, see: a) A. S. Trita, A. Biafora, M. Pichette Drapeau, P. Weber, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2018**, *57*, 14580-14584; b) J. A. Leitch, C. G. Frost, *Chem. Soc. Rev.*

2017, *46*, 7145-7153; c) J. A. Leitch, C. L. McMullin, A. J. Paterson, M. F. Mahon, Y. Bhonoah, C. G. Frost, *Angew. Chem. Int. Ed.* **2017**, *56*, 15131-15135; d) R. Manikandan, M. Jeganmohan, *Chem. Commun.* **2017**, *53*, 8931-8947; e) P. Nareddy, F. Jordan, M. Szostak, *ACS Catal.* **2017**, *7*, 5721-5745; f) P. Nareddy, F. Jordan, S. E. Brenner-Moyer, M. Szostak, *ACS Catal.* **2016**, *6*, 4755-4759; g) M. Simonetti, G. J. P. Perry, X. C. Cambeiro, F. Juliá-Hernández, J. N. Arokianathar, I. Larrosa, *J. Am. Chem. Soc.* **2016**, *138*, 3596-3606; h) M.-L. Louillat, A. Biafora, F. Legros, F. W. Patureau, *Angew. Chem. Int. Ed.* **2014**, *53*, 3505-3509; i) B. Li, P. H. Dixneuf, *Chem. Soc. Rev.* **2013**, *42*, 5744-5767; j) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879-5918; k) L. Ackermann, *Top. Organomet. Chem.* **2007**, *24*, 35-60, and cited references.

[12] Recent ruthena-electrocatalysis: a) M. J. Luo, M. Hu, R. J. Song, D. L. He, J. H. Li, *Chem. Commun.* **2019**, *55*, 1124-1127; b) M.-J. Luo, T.-T. Zhang, F.-J. Cai, J.-H. Li, D.-L. He, *Chem. Commun.* **2019**, *55*, 7251-7254; c) R. Mei, J. Koeller, L. Ackermann, *Chem. Commun.* **2018**, *54*, 12879-12882; d) F. Xu, Y.-J. Li, C. Huang, H.-C. Xu, *ACS Catal.* **2018**, *8*, 3820-3824; e) Y. Qiu, C. Tian, L. Massignan, T. Rogge, L. Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 5818-5822.

[13] For detailed information, see the Supporting Information.

[14] a) C. Chen, J.-C. Kang, C. Mao, J.-W. Dong, Y.-Y. Xie, T.-M. Ding, Y.-Q. Tu, Z.-M. Chen, S. Zhang, *Green Chem.* **2019**, *21*, 4010–4019; b) P. Becker, T. Duhamel, C. Martínez, K. Muñiz, *Angew. Chem. Int. Ed.* **2018**, *57*, 5166-5170.

[15] M. M. Lorion, K. Maindan, A. R. Kapdi, L. Ackermann, *Chem. Soc. Rev.* **2017**, *46*, 7399-7420.

[16] a) L. Wang, B. Carrow, *ACS Catal.* **2019**, *9*, 6821–6836; b) K. Naksomboon, J. Poater, F. M. Bickelhaupt, M. Á. Fernández-Ibáñez, *J. Am. Chem. Soc.* **2019**, *141*, 6719-6725; c) E. Tan, O. Quinonero, M. Elena de Orbe, A. M. Echavarren, *ACS Catal.* **2018**, *8*, 2166-2172; d) D. Zell, M. Bursch, V. Müller, S. Grimme, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 10378-10382; e) W. Ma, R. Mei, G. Tenti, L. Ackermann, *Chem. Eur. J.* **2014**, *20*, 15248-15251.

[17] a) M. Simonetti, D. M. Cannas, X. Just-Baringo, I. J. Vitorica-Yrezabal, I. Larrosa, *Nat. Chem.* **2018**, *10*, 724-731; b) J. McIntyre, I. Mayoral-Soler, P. Salvador, A. Poater, D. J. Nelson, *Catal. Sci. Tech.* **2018**, *8*, 3174-3182; c) H. H. Al Mamari, E. Diers, L. Ackermann, *Chem. Eur. J.* **2014**, 20, 9739-9743; d) L. Ackermann, R. Born, P. Álvarez-Bercedo, *Angew. Chem. In. Ed.* **2007**, *46*, 6364-6367.

[18] H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714-723.

[19] T. Wu, B. H. Nguyen, M. C. Daugherty, K. D. Moeller, *Angew. Chem. Int. Ed.* **2019**, *58*, 3562–3565.

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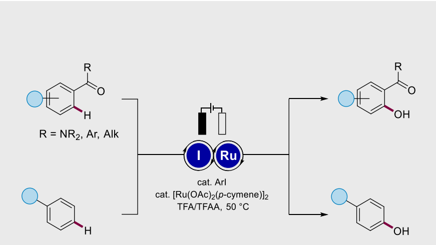

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Electro-Catalyzed Hypervalent Iodine Orchestrated for Ruthenaelectro-Catalyzed C–H Oxygenation

Dual catalysis: The joined action of catalytic amounts of iodoarenes and ruthenium(II) carboxylates enabled the expedient C**–**H oxygenation by weak coordination with amides and ketones.