

Electrosynthesis

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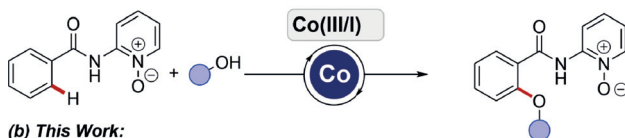
Insights into Cobalta(III/IV/II)-Electrocatalysis: Oxidation-Induced Reductive Elimination for Twofold C–H Activation

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Abstract: The merger of cobalt-catalyzed C–H activation and electrosynthesis provides new avenues for resource-economical molecular syntheses, unfortunately their reaction mechanisms remain poorly understood. Herein, we report the identification and full characterization of electrochemically generated high-valent cobalt(III/IV) complexes as crucial intermediates in electrochemical cobalt-catalyzed C–H oxygenations. Detailed mechanistic studies provided support for an oxidatively-induced reductive elimination via highly-reactive cobalt(IV) intermediates. These key insights set the stage for unprecedented cobalt/electro two-fold C–H/C–H activation.

C–H activation has emerged as a transformative tool in molecular sciences^[1] with notable applications to inter alia medicinal chemistry,^[2] material sciences^[3] and late-stage modifications.^[4] Significant recent momentum was gained by the merger of electrosynthesis^[5] with metal-catalyzed C–H activation with sustainable electricity as the terminal oxidant,^[6] with major advances in Earth-abundant^[7] cobalt catalysis.^[8] Despite of indisputable progress, the mechanistic understanding^[9] of their elementary steps continues to be underdeveloped,^[10] strongly contrasting with their precious 4d and 5d metal homologs.^[11] Particularly, oxidation-induced reductive elimination has recently been identified as key for rhodium- and iridium-mediated C–H activation, as described among others by Chang, Jones, and Tilset. In this context, we and Xu have very recently proposed the formation of high-valent rhodium(IV) complexes for rhodaelectro-catalyzed C–H activations.^[12,13] Thus, mechanistic studies revealed the key anodic oxidation of rhodium(III) complexes to the high-valent rhoda(IV) species.^[12] Cobalt-catalyzed C–H activations were thus far largely^[14] suggested to occur by a cobalt(II/III/I) catalytic cycle (Figure 1).^[15] In this context, detailed mechanistic studies on Cp*-free^[16] cobalt-catalyzed C–H activations continue to be scarce, despite of notable contributions by Daugulis,^[15g] Maiti,^[17] Ribas,^[18] among others,^[14g,19] while

(a) Previously Proposed Cobalt-Catalyzed C–O Formation Pathways



(b) This Work:

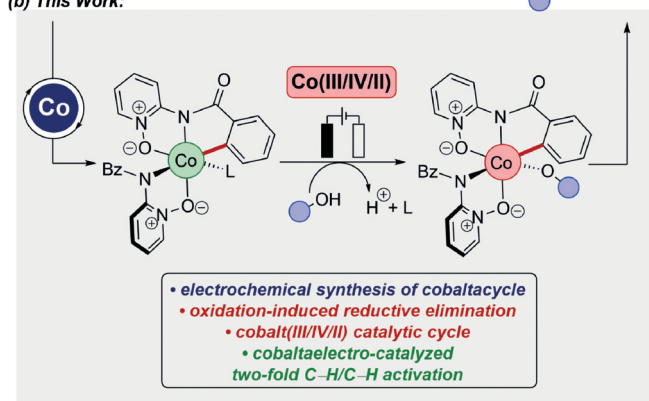


Figure 1. Oxidation-induced reductive elimination for cobalt/electro-catalysis.

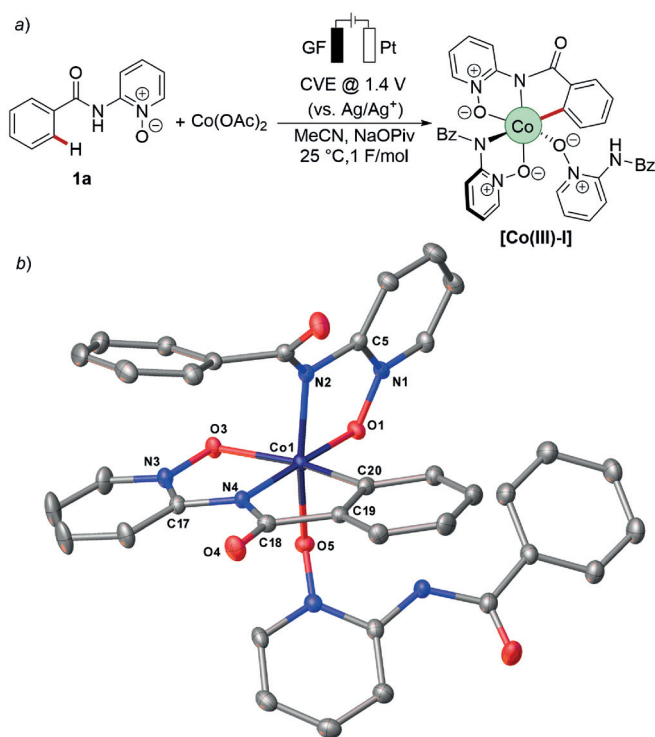
single electron transfer (SET) reactions are predominantly proposed for base-metal-induced C–Het bond formations.^[20] In sharp contrast, we have now unraveled oxidation-induced reductive elimination for cobalt-catalyzed electrochemical C–H activation. Salient features of our findings include a) the isolation and full characterization of electrochemically generated high-valent cyclometalated cobalt(III) complexes, b) electroanalytical characterization of cobalt(IV) intermediates, and c) an oxidatively-induced reductive elimination pathway for cobalta(III/IV/II) electrocatalysis, which d) mechanistically guided twofold C–H/C–H activations by cobalt/electro-catalyzed C–H arylations.

We set out to rationalize the stoichiometric electrochemical synthesis of the cyclometalated cobalt(III) complex [Co^{III}-I] from amide **1a** (Scheme 1a). Acetonitrile was found as the solvent of choice. After considerable experimentation, we were able to isolate and fully characterize the envisioned 18-electron cobalta(III)-cycle [Co^{III}-I]. The potentiostatic electrolysis at low potential and the thus mild reaction conditions were key to prevent overoxidation and byproduct formation (vide infra). The overall electrolysis was stopped upon consumption of 1.0 F mol⁻¹. In addition to electrospray ionization mass spectrometry (ESI-MS), the structure of [Co^{III}-I] was unambiguously confirmed by full NMR-spectroscopic and single-crystal X-ray characterization (Scheme 1b).

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Scheme 1. a) Electrochemical synthesis of cobaltacycle **[Co^{III}-I]** via C–H activation. b) X-ray crystal structure analysis of **[Co^{III}-I]** (50% probability ellipsoids).^[25] Hydrogen atoms were omitted for clarity. Bz = –C(O)Ph.

Motivated by our findings, we became intrigued to investigate the redox potential of **[Co^{III}-I]** by means of cyclic voltammetry (Figure 2). Hence, at potentials of $E_{p,ox} = 0.95$ V vs. SCE an irreversible oxidation wave arises, which was assigned to complex **[Co^{III}-I]**. The experimental oxidation potentials are in good agreement with the ones that we calculated for **[Co^{III}-I]**, (exp: $E_{p,2} = 0.89$ V vs. SCE, 100 mV s^{-1} , calc: $E_{p,2} = 0.89$ V vs. SCE).^[21] The small shoulder at $E_{p,ox} = 0.76$ V vs. SCE, however, could be assigned to intermediate **[Co^{III}-II]**, in which the mono-coordinated substrate **1a** was substituted by the solvent MeOH. The dissociation of the oxygen-coordinated (O5) substrate **1a** is in accordance with ESI-MS, NMR and computational studies on the calculated redox potentials.^[21] The irreversible oxidation waves were assigned to the anodic generation of Co^{IV} complexes.^[22] As can be concluded from the voltammograms, the electrochemical reaction is chemically irreversible, even at higher scan rates of up to 1.0 V s^{-1} , indicating that subsequent chemical reactions quickly consume the oxidized cobalt(IV)-complexes on the CV time scale. When the CV-experiments were performed at a lower temperature of 273 K (Figure 2b), we observed a reversible Co^{III}/Co^{IV} redox-event with a scan-rate of 1.6 V s^{-1} . At lower scan-rates, the oxidation was still irreversible. However, with a further decrease in temperature to $T = 195$ K, we were able to characterize a reversible redox event with even lower scan-rates, highlighting the stability of the proposed high-valent cobalt(IV) complex.^[21]

To explore the influence of the substitution pattern of the benzamide **1a** on the redox behavior, we prepared a series of

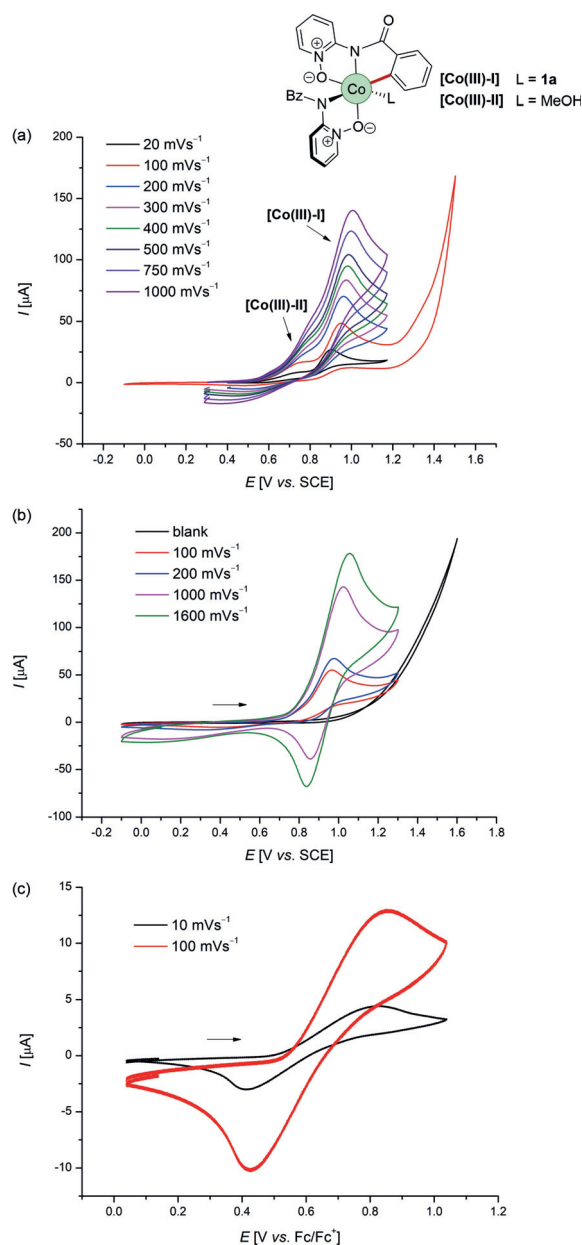
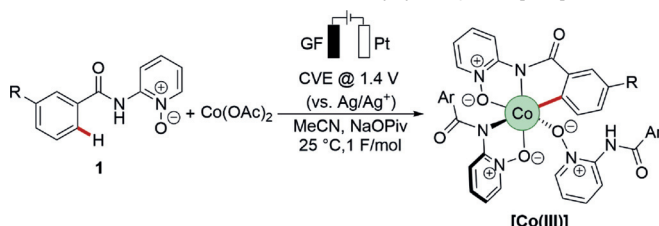


Figure 2. CVs of the electrochemically generated cobaltacycles **[Co^{III}-I]** and **[Co^{III}-II]** in MeOH (3.5 mM) at different scan rates. The voltammograms were recorded in 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$. a) At 298 K. b) At 273 K. c) At 195 K.

differently decorated cyclometalated cobalt complexes **[Co^{III}-I]**–**[Co^{III}-VII]** (Table 1).

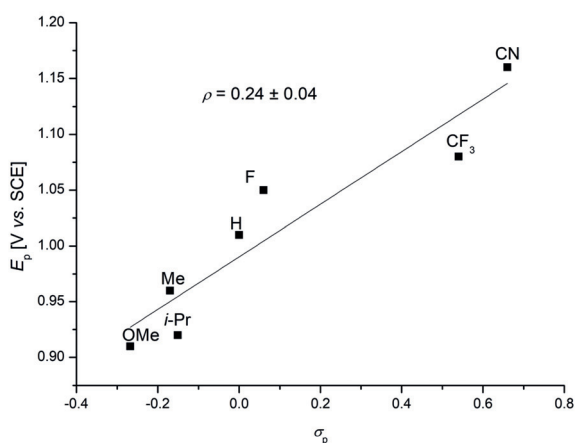
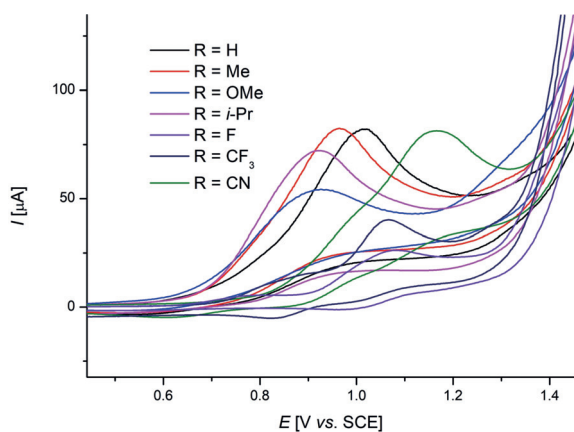
A Hammett plot analysis of voltammetric peak potential versus the σ_{para} values for a series of different substituents was performed (Figure 3).^[23] The positive slope clearly indicates that electron-donating substituents facilitate the electro-oxidation, while electron-withdrawing substituents remove electron-density on the ligated cobalt and thereby increase the required oxidation potential of the complex.

The relevance of the thus electro-chemically prepared cobalt(III) complexes towards cobalt-electrocatalyzed C–O formation was emphasized by detailed mass-spectrometric analysis of stoichiometric experiments with simple $\text{Co}(\text{OAc})_2$

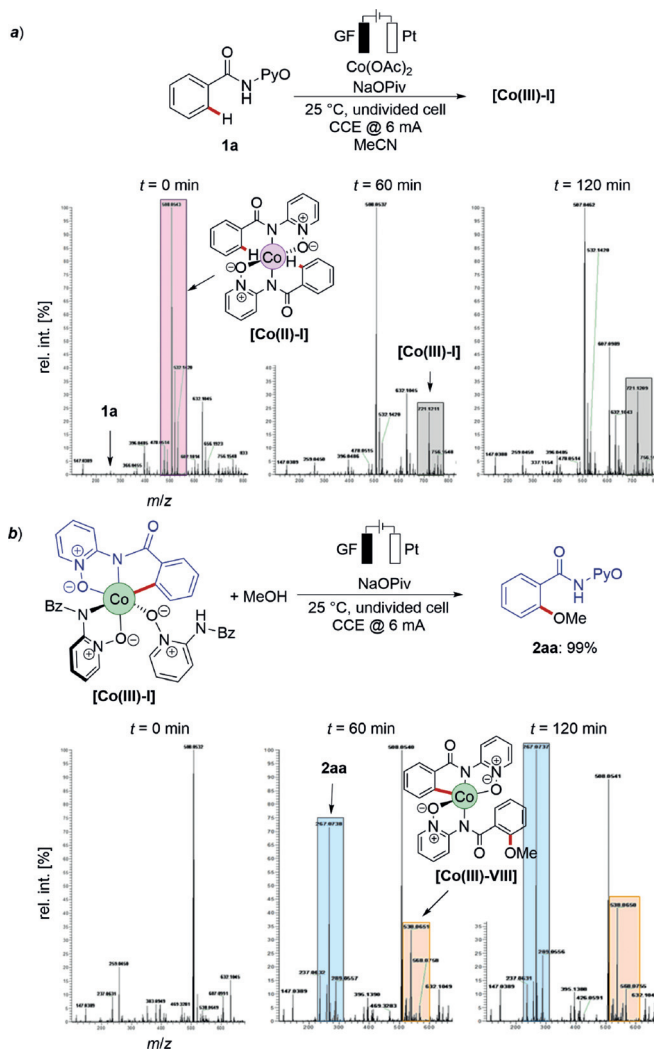
Table 1: Electro-C–H activation for cobalt(III) complexes $[\text{Co}^{\text{III}}]$.^[a]


Entry	R	$[\text{Co}^{\text{III}}]$	Yield [%]
1	H	$[\text{Co}^{\text{III}}\text{-I}]$	46
2	Me	$[\text{Co}^{\text{III}}\text{-III}]$	51
3	<i>i</i> Pr	$[\text{Co}^{\text{III}}\text{-IV}]$	28
4	OMe	$[\text{Co}^{\text{III}}\text{-V}]$	13 ^[b]
5	CN	$[\text{Co}^{\text{III}}\text{-VI}]$	19
6	CF ₃	$[\text{Co}^{\text{III}}\text{-VII}]$	13

[a] Reaction conditions: Undivided cell, **1** (1.0 mmol), $\text{Co}(\text{OAc})_2$ (0.5 equiv), NaOPiv (1.0 equiv), MeCN (13 mL), 25 °C, constant potential electrolysis (CVE) at 1.4 V vs. Ag/Ag^+ , 1 F mol^{-1} , graphite felt anode, Pt-plate cathode. Yields of isolated complexes are given. [b] C–H acyloxylation was detected in 3% conversion.

**Figure 3.** CVs of the substituted cobalt(III) cycles $[\text{Co}^{\text{III}}]$ in MeOH (3.5 mM) at 100 mVs^{-1} in 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$.

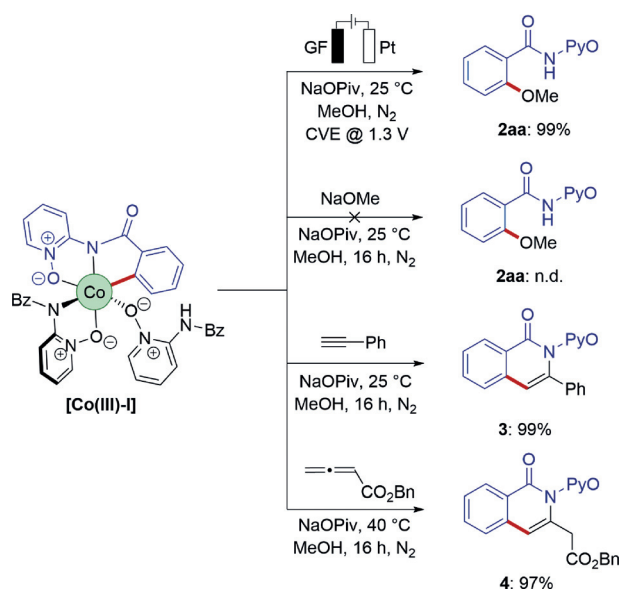
versus $[\text{Co}^{\text{III}}\text{-I}]$ in the presence of MeOH as the solvent (Scheme 2). Thus, upon formation of cobalt(II) bisamide $[\text{Co}^{\text{II}}\text{-I}]$ in MeCN, anodic oxidation allowed for the generation of cyclometalated $[\text{Co}^{\text{III}}\text{-I}]$. It is noteworthy that the

**Scheme 2.** ESI-MS monitoring of possible cobaltacycle formation. a) Formation of $[\text{Co}^{\text{III}}\text{-I}]$ upon anodic oxidation of $[\text{Co}^{\text{II}}\text{-I}]$ in MeCN. b) Oxidation-induced C–H alkoxylation of $[\text{Co}^{\text{III}}\text{-I}]$ in MeOH.

electrosynthesis only occurred in the presence of NaOPiv as the additive.^[21] These findings and the Hammett plot analysis (Figure 3) provide support for a base-assisted internal electrophilic-type substitution (BIES) C–H activation.^[24]

Noteworthy, the formation of the C–H alkoxyated product **2aa** was solely achieved when electricity was applied, providing support for an oxidation-induced reductive elimination within a cobalt(III/IV/II) regime (Scheme 3). Interestingly, analogous transformations of the cyclometalated cobalt complex $[\text{Co}^{\text{III}}\text{-I}]$ with alkynes or allenes quantitatively delivered the corresponding annulated products in the absence of additional oxidants. Collectively, these findings are indicative of different mechanisms being operative for the C–O versus C–C formations. Here, decoordination of substrate **1a** likely induced coordination of the alkyne or allene substrate, along with insertion and reductive elimination to deliver products **3** and **4**, respectively.

To rationalize the nature of the C–O forming reductive elimination step, DFT calculations at the PBE0-D3(BJ)/def2-TZVP + SMD(MeOH)/PBE0-D3(BJ)/def2-SVP level of



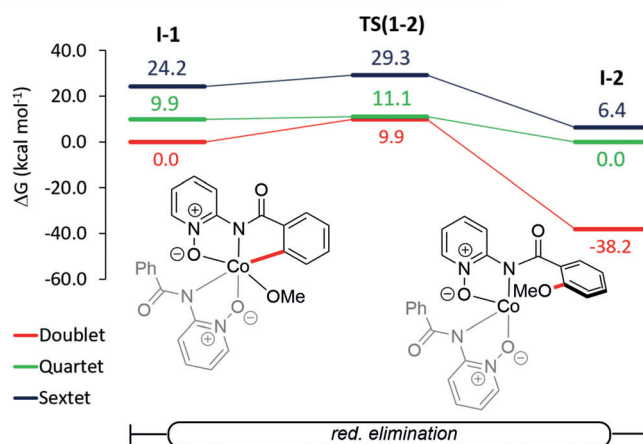
Scheme 3. $[\text{Co}^{\text{III}}\text{-I}]$ for C–O versus C–C bond formation.

theory were performed. These computational studies were in good agreement with our experimental findings (Figure 4).^[21] Hence, oxidatively-induced reductive elimination through a $\text{Co}^{\text{III}}/\text{Co}^{\text{IV}}/\text{Co}^{\text{II}}$ manifold proved to be highly plausible with an activation barrier of $9.9 \text{ kcal mol}^{-1}$. Noncovalent interactions between the π -systems of the two coordinated substrates could be identified to stabilize the relevant transition state structure.

During the synthesis of the cyclometalated cobalt(III)-complexes $[\text{Co}^{\text{III}}]$ we noticed the formation of a significant amount of by-product, especially with the electron-rich substrates **1** (Table 1, entries 2 and 3). Based on our CV-studies, we hypothesized a possible oxidation of $[\text{Co}^{\text{III}}\text{-I}]$ to a high-valent cobalt(IV) complex, which would induce oxidation-induced reductive elimination for homo-couplings of the coordinated substrates, while leading to a paramagnetic cobalt(II) complex. To reduce our hypothesis into practice, we probed various solvents and adjusted the reaction temperature. The use of solvents other than polar-aprotic MeCN proved to be unsuitable (Table 2, entries 2–4). Interestingly, at a reaction temperature of 60°C (Table 2, entry 5) the desired complex $[\text{Co}^{\text{II}}\text{-II}]$ was isolated in high yield, after cobalt-electro-double C–H activation. The structure of $[\text{Co}^{\text{II}}\text{-II}]$ was unambiguously verified by single-crystal X-ray characterization (Figure 5). Overall, the isolation of cobalt(II) $[\text{Co}^{\text{II}}\text{-II}]$ provides further strong support for an oxidation-induced reductive elimination from a high-valent cobalt(IV) intermediate, likely featuring two Co–C bonds.

In summary, we have identified, isolated and fully characterized key C–H activated intermediates of cobalt-electrocatalyzed C–H activation. Thus, well-defined cyclometalated cobalt(III) complexes were structurally characterized by X-ray diffraction analysis. Their cyclovoltammetric features, kinetic analysis, and mass spectrometric studies were supportive of an oxidation-induced reductive elimination within a cobalt(III/IV/II) manifold. The resulting cobalt(II) complex was also isolated and fully characterized by X-ray

a) Oxidatively-induced reductive elimination



b) NCIPlot

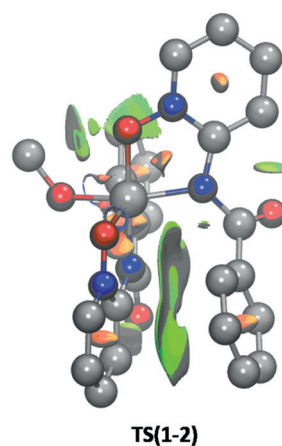


Figure 4. a) Computed Gibbs free energies ($\Delta G_{298.15}$) in kcal mol^{-1} for oxidatively-induced reductive elimination elementary step from $[\text{Co}^{\text{III}}\text{-I}]$ and b) visualization of noncovalent interactions determined through a NCI plot. In the latter, strong and weak attractive interactions are depicted in blue and green, respectively, while red corresponds to strong repulsive interactions. All values include dispersion corrections.

diffraction analysis. Our experimental and computational mechanistic insights are of direct relevance to cobalt-electrocatalyzed C–O formations, and enabled the development of unprecedented cobalt-electro-mediated double C–H/C–H arylations.

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Table 2: Cobalt electro-induced two-fold C–H activation.^[a]

Entry	Solvent	T [°C]	[Co ^{II} -II] [%]
1	MeCN	25	20
2	CH ₂ Cl ₂	40	–
3	HFIP	40	–
4	EtOH	40	– ^[b]
5	MeCN	60	73

[a] Reaction conditions: Undivided cell, **1a** (0.5 mmol), Co(OAc)₂·4 H₂O (0.5 equiv), NaOPiv (2.0 equiv), solvent (5 mL), constant current electrolysis (CCE) at 4 mA, 14 h, graphite felt anode, Pt-plate cathode. Yields of isolated complex are given. [b] C–H ethoxylation formed **2ab** in 70% isolated yield.

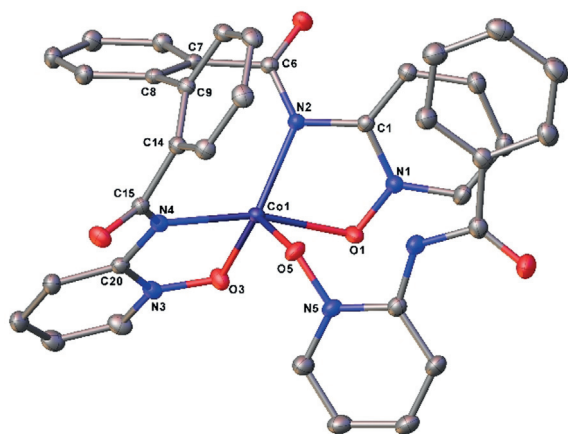


Figure 5. X-ray crystal structure analysis of [Co^{II}-II] (50% probability ellipsoids).^[25] Hydrogen atoms were omitted for clarity.

Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation · cobalt · electrosynthesis · mechanism · oxidative catalysis

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