Supporting Information for

Aldehyde Deformylation and Catalytic C-H Activation Resulting from a Shared Cobalt(II) Precursor

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Figure S1. $^1$H NMR spectrum of 1 in CD$_3$CN (294 K, 400 MHz). Peak frequencies: 95.0, 86.6, 84.0, 82.4, 78.6, 75.9, 74.3, 72.4, 67.8, 66.5, 63.3, 59.4, 58.8, 48.3, 40.0, 38.1, 35.2, 32.2, 31.5, 27.7, 25.1, 23.2, 22.5, 21.0, 19.3, 16.4, 15.1, 14.0, 13.4, 12.4, 11.3, 10.0, -1.1, -1.5, -3.4, -4.6, -11.1, -13.1, -13.7, -25.3.

Figure S2. X-band EPR spectrum of 1 as a frozen MeCN solution at 4 K. The major feature is at $g = 4.3$. 
Figure S3. UV/vis spectra of 1 in MeCN (red) and MeOH (blue) and 2 in MeCN (green). Data acquired under air at 298 K with a 1.0 cm cuvette. The data were collected from 0.033 mM solutions of 1 and a 0.10 mM solution of 2.

Figure S4. $^1$H NMR spectrum of 2 in CD$_3$CN (294 K, 400 MHz). Peak assignments: 8.08 (1H, t, $J = 7.8$ Hz), 7.78 (2H, d, $J = 7.2$ Hz), 7.67 (1H, d, $J = 8.0$ Hz), 7.45 (8H, m), 7.18 (1H, d, $J = 5.2$ Hz), 7.09 (4H, m), 6.49 (1H, d, $J = 7.6$ Hz), 5.19 (1H, d, $J = 12$ Hz), 4.63 (1H, d, $J = 12$ Hz), 4.58 (1H, d, $J = 16$ Hz), 4.02 (2H, dd, $J_1 = 16$ Hz, $J_2 = 5.8$ Hz), 3.79 (1H, d, $J = 16$ Hz), 3.68 (1H, d, $J = 14$ Hz), 3.44 (1H, t, $J = 5.4$ Hz), 3.32 (1H, d, $J = 14$ Hz), 2.57 (1H, t, $J = 12$ Hz), 2.09 (substantial overlap with MeCN peak prevents accurate integration, t, $J = 4.8$ Hz), 1.67 (1H, d, $J = 14$ Hz), 1.31 (1H, d, $J = 12$ Hz), 1.1-0.79 (5H, m).
Figure S5. IR spectrum of 1 (KBr). The 2026 cm$^{-1}$ feature is assigned to the Co(II)-bound MeCN molecules. The 1609 cm$^{-1}$ feature is assigned to the C-N stretches for the coordinated pyridine rings.
Figure S6. IR spectrum of 2 (KBr). The 1605 cm$^{-1}$ feature is assigned to the C-N stretches for the coordinated pyridine rings.

Figure S7. IR spectrum of the free bbpc ligand (KBr).
Figure S8. $^1$H NMR spectrum (400 MHz) of the reaction between 5 mM I and 5 mM PhIO in 294 K CD$_3$CN.
Figure S9. Expanded view of the aromatic region from Figure S8. The major peaks have been assigned to either iodobenzene (PhI) or iodosobenzene (PhIO), which is sparingly soluble in MeCN.
Figure S10. Mass spectrometry (ESI) of [Co(bbpc)(MeCN)$_2$](ClO$_4$) (1) in MeCN. Formic acid was added to ionize previous samples. The 580.2110 m/z feature is assigned to [Co(bbpc)(formate)]$^+$ (calculated m/z = 580.2249); the 593.2341 m/z feature is assigned to [Co(bbpc)(MeCN)(OH)]$^+$ (calculated m/z = 593.2565).

Figure S11. Mass spectrometry (ESI) of [Co(bbpc)(O$_2$)]$^+$ (2) in MeCN. The 567.2093 m/z feature is assigned to [Co(bbpc)(O$_2$)]$^+$ (calculated m/z = 567.2170).
Figure S12. Mass spectrometry (ESI) of the reaction between 2.0 mM PhIO and 1.0 mM [Co(bbpc)(MeCN)₂](ClO₄)₂ (1) in 3:7 MeOH/MeCN. The feature labeled 297.1263 was further investigated and is presented in an expanded form in Figure S13. The following assignments were made: 267.5994 m/z = [Co(bbpc)]²⁺ (calculated m/z = 267.6136), 353.1089 m/z = [Co(bbpc-2Bz)]⁺ ([C₁₈H₂₂N₄Co]⁺, calculated m/z = 353.1176), 443.1614 m/z = [Co(bbpc-Bz-H)]⁺ ([C₂₅H₂₈N₄Co]⁺, calculated m/z = 443.1646), 459.1520 m/z = [Co(bbpc-Ph+H)]⁺ ([C₂₆H₃₂N₄Co]⁺, calculated m/z = 459.1959), 476.2996 m/z = bbpc (calculated m/z = 476.2940), 541.1263 m/z = [Co(bbpc-Bz-2H)(ClO₄)]⁺ ([C₂₅H₂₇ClN₄O₄Co]⁺, calculated m/z = 541.1053).

Figure S13. Mass spectrometry (ESI) of the reaction between 1.0 mM 1 and 2.0 mM PhIO in 3:7 MeOH/MeCN. The bottom feature is the same reaction using PhIO pre-mixed with 10 µL of ¹⁸O-labelled H₂O. The 296.6 m/z feature is assigned to [Co(bbpc)(MeCN)(OH)]²⁺ (calculated m/z = 296.6); the 297.6 m/z feature is assigned to [Co(bbpc)(MeCN)(¹⁸OH)]³⁺ (calculated m/z = 297.6).
**Figure S14.** Spectrophotometric analysis of the reaction between 2.0 mM [Co(bbpc)(O2)]$^+$ (2) and 400 mM cyclohexanecarboxaldehyde (CCA) in 298 K MeCN. Scans were acquired every 30 s. The inset shows the change in absorbance at 505 nm. The data can be fit to a pseudo-first-order decay with $k_{\text{obs}} = 1.0 \times 10^{-3}$ s$^{-1}$.

**Figure S15.** Spectrophotometric analysis of the reaction between 2.0 mM [Co(bbpc)(O2)]$^+$ (2) and 100 mM 2-phenylpropionaldehyde (2-PPA) in 298 K MeCN. Scans were acquired every 30 s. The inset shows the change in absorbance at 505 nm. The data can be fit to a pseudo-first-order decay with $k_{\text{obs}} = 3.1 \times 10^{-3}$ s$^{-1}$. 
Figure S16. Plot of observed rate constants ($k_{obs}$) for the pseudo-first order decay of 2 versus the concentration of 2-phenylpropionaldehyde (2-PPA). All reactions were run at 298 K in MeCN under air.

Figure S17. Spectrophotometric analysis of the reaction between 2.0 mM [Co(bbpc)(O$_2$)]$^+$ (2) and 400 mM benzaldehyde in 298 K MeCN. Scans were acquired every 30 s. The inset shows the change in absorbance at 505 nm. The data can be fit to a pseudo-first-order decay with $k_{obs} = 3.2 \times 10^{-3}$ s$^{-1}$. 
Figure S18. MS analysis of the reaction between 2.0 mM 2 and CCA. The following assignments were made: 353.1165 m/z = [Co(bbpc-2Bz)]\(^+\) ([C\(_{18}\)H\(_{22}\)N\(_4\)Co]\(^+\), calculated m/z = 353.1176), 443.1635 m/z = [Co(bbpc-Bz-H)]\(^+\) ([C\(_{25}\)H\(_{28}\)N\(_4\)Co]\(^+\), calculated m/z = 443.1646). This suggests oxidation of the bbpc ligand at the benzyl positions.