Supplementary Material

Photocatalytic turnover of CO₂ under visible light by [Re(CO)₃(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))Cl] in tandem with the sacrificial donor BIH

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S1. $^1$H NMR of 2 in CDCl$_3$ (a) with zoomed-in aromatic region (400 MHz, chloroform-d) and image of 2 with assigned peaks and (b) from 0-10 ppm. δ 9.49-9.48 (d, 1H, J=5.1 Hz), 9.46-9.45 (d, 1H, J=4.9 Hz), 9.00-8.98 (dd, 1H, J=9.1, 1.7 Hz), 8.89-8.79 (2H, overlapped), 8.60-8.58 (d, 1H, J=8.9 Hz), 8.50-8.48 (dd, 1H, J=7.9, 5.4 Hz), 8.28-8.26 (d, 1H, J=8.5 Hz), 8.15-8.10 (2H, overlapped), 7.94-7.91 (dd, 1H, J=8.0, 5.4 Hz), 7.82-7.79 (dd, 1H, J=8.4, 5.1 Hz). The appropriate integration of 12 was observed.
S2. $^{13}$C NMR spectrum of 2, acquired in DMSO-$d_6$ exhibiting the appropriate number of peaks. The carbon signals at 197 ppm and 180 ppm are assigned to the carbonyl carbons on the rhenium tricarbonyl core.
S3. FT-IR of 2 (KBr, cm\(^{-1}\)) C≡O: 2026.30; 1919.07, CO-N-CO: 1718.15, C=O: 1678.09, C-NO\(_2\): 1349.89.
S4. Electronic absorption spectrum of 2 in MeOH/DCM (1:9 v:v).
S5. MALDI-TOF mass spectrum of 2 with insert of zoomed-in peaks of interest (650-700 m/z). The expected mass fragment of 690.375 m/z ([Re(CO)$_3$(5-PAN)]$^+$) was observed showing appropriate isotopic distribution as well as other fragments caused by ionization.
S6. $^1$H NMR of BIH (400 MHz, chloroform-d): $\delta$ 2.5670 (s, 6H), 4.88 (s, 1H), 6.43-6.45 (dd, $J = 3.2, 5.4$ Hz, 2H), 6.71-6.73 (dd, $J = 3.2, 5.4$ Hz, 2H), 7.41-7.42 (m, 3H), 7.56-7.59 (m, 2H).
**S7.** $^{13}$C NMR of BIH (400 MHz, chloroform-d, D1=5). The peaks at 33.1485 and 33.5305 correspond to the methyl groups of BIH and the integration was set to 1 in subsequent NMR spectra in which the peaks were used as the internal reference.
Crystal Data Collection, Solution, and Refinement of \([\text{Re(CO)}_3(1-(1,10)\text{phenanthroline-5-(4-nitronaphthalimide)})X]\) (X=Cl or Br)

The following crystallographic work was done by William W. Brennessel at the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester, New York, United States.

Data collection

A crystal (0.149 x 0.05 x 0.041 mm\(^3\)) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections\(^1\). A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.07 and 0.30 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50° steps in \(\omega\) at different \(2\theta, k\), and \(f\) settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the \(xyz\) centroids of 29783 strong reflections from the actual data collection after integration.\(^1\) See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT\(^2\) and refined using SHELXL.\(^3\) The space group \(P-1\) was determined based on intensity statistics. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to \(R1 = 0.0488 (F^2, I > 2s(I))\) and \(wR2 = 0.1249 (F^2, \text{all data})\).
Structure description of [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br)

The asymmetric unit contains one Re complex and one toluene solvate molecule in general positions. The halido ligand site is modeled as a disorder of Br:Cl, 0.80:0.20. This disorder is due to combined batches of 1 and 2 having been made with the starting materials Re(CO)$_5$Cl$_4$ or Re(CO)$_5$Br. Carbonyl ligand C3-O3, which is trans to the halido ligand site, is likely disordered with the halido ligand site, based on the appearance of the ellipsoids and the short C-O distance; however, this disorder was unable to be modeled due to the very small mass of its minor component. The Re-Br and Re-Cl distances were restrained toward the average values obtained from the Cambridge Structural Database$^5$ for terminal ligands on six-coordinate Re centers. The toluene solvate molecule was modeled as disordered over two positions (0.52:0.48).

Structure manipulation and figure generation were performed using Olex2.$^6$ Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028.
**S8.** ORTEP diagram of mixed $[\text{Re(CO)}_3(1\text{-}(1,10)\text{phenanthroline-5-}(4\text{-nitro-naphthalimide}))X]$ ($X=\text{Cl}$ or $\text{Br}$) and a toluene molecule disordered over two positions (0.52:0.48). Anisotropic displacement ellipsoids are drawn at the 50% probability level.
Table 1. Crystal data and structure refinement of [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitronaphthalimide))X] (X=Cl or Br).

| Property                              | Value                  |
|---------------------------------------|------------------------|
| Empirical formula                     | C$_{34}$H$_{20}$Br0.80Cl0.20N$_4$O$_7$Re |
| Formula weight                        | 853.53                 |
| Temperature                           | 100.00(10) K           |
| Wavelength                            | 1.54184 Å              |
| Crystal system                        | triclinic              |
| Space group                           | P-1                    |
| Unit cell dimensions                  | $a = 8.4778(2)$ Å      |
|                                       | $a = 107.983(2)^\circ$ |
|                                       | $b = 13.3551(2)$ Å     |
|                                       | $b = 95.125(2)^\circ$  |
|                                       | $c = 13.9955(3)$ Å     |
|                                       | $g = 96.9490(10)^\circ$|
| Volume                                | 1482.59(5) Å$^3$      |
| Z                                      | 2                      |
| Density (calculated)                  | 1.912 Mg/m$^3$         |
| Absorption coefficient                | 9.949 mm$^{-1}$        |
| $F$(000)                              | 829                    |
| Crystal color, morphology             | yellow, needle         |
| Crystal size                          | 0.149 x 0.05 x 0.041 mm$^3$ |
| Theta range for data collection       | 3.350 to 77.951$^\circ$|
| Index ranges                          | -10 $\leq h \leq$ 10, -16 $\leq k \leq$ 16, -17 $\leq l \leq$ 17 |
| Reflections collected                 | 50161                  |
| Independent reflections               | 6228 [R(int) = 0.0678] |
| Observed reflections                  | 5962                   |
| Completeness to theta = 74.504$^\circ$| 99.8%                  |
| Absorption correction                 | Multi-scan             |
| Max. and min. transmission            | 1.00000 and 0.54834    |
| Refinement method                     | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters        | 6228 / 202 / 494       |
| Goodness-of-fit on $F^2$              | 1.118                  |
| Final $R$ indices [$>2\sigma(I)$]     | $R_1 = 0.0488$, $wR_2 = 0.1235$ |
| $R$ indices (all data)                | $R_1 = 0.0507$, $wR_2 = 0.1249$ |
| Largest diff. peak and hole           | 1.673 and -2.216 e.Å$^{-3}$ |
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br). $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|    | x          | y          | z          | $U_{eq}$ |
|----|------------|------------|------------|----------|
| Re1| 3060(1)    | 2897(1)    | 6356(1)    | 36(1)    |
| O1 | 3161(7)    | 5250(4)    | 7604(4)    | 58(1)    |
| O2 | 257(6)     | 2321(5)    | 7419(4)    | 54(1)    |
| O3 | 5449(7)    | 2675(5)    | 7973(5)    | 59(1)    |
| O4 | 8985(6)    | 479(4)     | 3142(4)    | 48(1)    |
| O5 | 5572(5)    | 2101(3)    | 1662(3)    | 37(1)    |
| O6 | 13931(7)   | 456(4)     | -528(5)    | 60(1)    |
| O7 | 13365(7)   | 1984(5)    | -563(5)    | 66(2)    |
| N1 | 3090(6)    | 1315(4)    | 5288(4)    | 32(1)    |
| N2 | 4876(6)    | 3144(4)    | 5412(4)    | 32(1)    |
| N3 | 7322(5)    | 1354(4)    | 2444(4)    | 29(1)    |
| N4 | 13160(7)   | 1206(5)    | -271(5)    | 51(1)    |
| C1 | 3126(8)    | 4373(6)    | 7151(6)    | 48(2)    |
| C2 | 1306(9)    | 2533(6)    | 7040(5)    | 46(2)    |
| C3 | 4730(9)    | 2747(5)    | 7434(5)    | 38(1)    |
| C4 | 2190(7)    | 406(5)     | 5255(5)    | 35(1)    |
| C5 | 2225(7)    | -560(5)    | 4508(5)    | 38(1)    |
| C6 | 3228(7)    | -601(5)    | 3787(5)    | 38(1)    |
| C7 | 4205(7)    | 338(4)     | 3799(5)    | 32(1)    |
| C8 | 5296(7)    | 377(4)     | 3091(5)    | 32(1)    |
| C9 | 6212(7)    | 1314(4)    | 3159(4)    | 31(1)    |
| C10| 6126(7)    | 2292(4)    | 3944(4)    | 30(1)    |
| C11| 7041(7)    | 3282(4)    | 4046(5)    | 34(1)    |
| C12| 6860(7)    | 4158(5)    | 4823(5)    | 39(1)    |
| C13| 5771(7)    | 4063(5)    | 5496(5)    | 39(1)    |
| C14| 5051(7)    | 2267(4)    | 4641(4)    | 29(1)    |
| C15| 4084(6)    | 1279(4)    | 4577(4)    | 29(1)    |
| C16| 8734(7)    | 913(4)     | 2510(5)    | 34(1)    |
| C17| 9848(7)    | 1003(4)    | 1785(5)    | 32(1)    |
| C18| 9476(7)    | 1474(4)    | 1032(5)    | 35(1)    |
| Atom | C19  | C20  | C21  | C22  | C23  | C24  | C25  | C26  | C27  | Br1   | Cl1   |
|------|------|------|------|------|------|------|------|------|------|-------|-------|
|      | 7986(7) | 1861(5) | 966(5) | 35(1) | 6851(7) | 1796(4) | 1688(5) | 33(1) | 11257(7) | 598(5) | 1819(5) | 39(1) |
|      | 12326(7) | 658(5) | 1123(5) | 43(2) | 11981(7) | 1134(5) | 425(5) | 39(1) | 10542(7) | 1553(5) | 337(5) | 38(1) |
|      | 10067(9) | 2004(6) | -436(5) | 47(2) | 8617(9) | 2348(6) | -484(6) | 49(2) | 7579(8) | 2289(5) | 222(5) | 43(1) |
| Br1  | 987(4) | 3007(2) | 4910(2) | 40(1) | 1110(40) | 3110(30) | 5080(20) | 40(1) | 2370(40) | 4851(19) | 60(20) | 132(10) |
| Cl1  | 2090(20) | 4541(13) | 1000(20) | 82(5) | 790(30) | 4805(18) | 1540(20) | 106(7) | 610(30) | 4510(20) | 2380(20) | 96(5) |
| C28  | 1620(20) | 3937(17) | 2720(20) | 73(5) | 2890(30) | 3686(15) | 2210(19) | 63(5) | 3160(30) | 3983(17) | 1372(19) | 67(4) |
| C31  | 3540(30) | 4781(18) | 490(20) | 121(10) | 3540(30) | 4781(18) | 490(20) | 121(10) | 2710(20) | 4621(12) | 1328(19) | 76(5) |
| C32  | 2710(20) | 4621(12) | 1328(19) | 76(5) | 1560(20) | 5259(15) | 1766(17) | 89(6) | 850(20) | 5090(16) | 2537(18) | 81(5) |
| C33  | 1560(20) | 5259(15) | 1766(17) | 89(6) | 1150(20) | 4285(12) | 2882(19) | 66(4) | 850(20) | 5090(16) | 2537(18) | 81(5) |
| C34  | 2250(30) | 3667(15) | 2525(17) | 65(5) | 3020(30) | 3816(17) | 1758(19) | 70(5) | 3020(30) | 3816(17) | 1758(19) | 70(5) |
Table 3. Bond lengths [Å] and angles [°] for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitronaphthalimide))X] (X=Cl or Br).

| Bond | Distance/Angle |
|------|---------------|
| Re(1)-N(1) | 2.184(5) |
| Re(1)-N(2) | 2.175(5) |
| Re(1)-C(1) | 1.933(8) |
| Re(1)-C(2) | 1.932(7) |
| Re(1)-C(3) | 2.048(8) |
| Re(1)-Br(1) | 2.6107(18) |
| Re(1)-Cl(1) | 2.427(17) |
| O(1)-C(1) | 1.142(9) |
| O(2)-C(2) | 1.127(8) |
| O(3)-C(3) | 0.963(8) |
| O(4)-C(16) | 1.216(7) |
| O(5)-C(20) | 1.205(7) |
| O(6)-N(4) | 1.240(8) |
| O(7)-N(4) | 1.227(8) |
| N(1)-C(4) | 1.339(7) |
| N(1)-C(15) | 1.354(7) |
| N(2)-C(13) | 1.329(8) |
| N(2)-C(14) | 1.360(7) |
| N(3)-C(9) | 1.443(7) |
| N(3)-C(16) | 1.404(7) |
| N(3)-C(20) | 1.412(7) |
| N(4)-C(23) | 1.472(9) |
| C(4)-H(4) | 0.9500 |
| C(4)-C(5) | 1.392(9) |
| C(5)-H(5) | 0.9500 |
| C(5)-C(6) | 1.370(9) |
| C(6)-H(6) | 0.9500 |
| C(6)-C(7) | 1.411(8) |
| C(7)-C(8) | 1.423(8) |
| C(7)-C(15) | 1.407(8) |
| C(8)-H(8) | 0.9500 |
| C(8)-C(9) | 1.362(8) |
| C(9)-C(10) | 1.439(8) |
C(30)-C(31) 1.37(3)  C(2)-Re(1)-C(3) 92.2(3)
C(31)-H(31) 0.9500  C(2)-Re(1)-Br(1) 89.3(2)
C(31)-C(32) 1.36(3)  C(2)-Re(1)-Cl(1) 88.6(10)
C(32)-H(32) 0.9500  C(3)-Re(1)-N(1) 94.5(2)
C(32)-C(33) 1.37(3)  C(3)-Re(1)-N(2) 92.2(2)
C(33)-H(33) 0.9500  C(3)-Re(1)-Br(1) 176.92(18)
C(33)-C(34) 1.38(3)  C(3)-Re(1)-Cl(1) 178.8(9)
C(34)-H(34) 0.9500  C(4)-N(1)-Re(1) 126.3(4)
C(28')-H(28D) 0.9800  C(4)-N(1)-C(15) 118.2(5)
C(28')-H(28E) 0.9800  C(15)-N(1)-Re(1) 115.4(4)
C(28')-H(28F) 0.9800  C(13)-N(2)-Re(1) 126.5(4)
C(28')-C(29') 1.48(4)  C(13)-N(2)-C(14) 117.9(5)
C(29')-C(30') 1.42(2)  C(14)-N(2)-Re(1) 115.6(4)
C(29')-C(34') 1.42(2)  C(16)-N(3)-C(9) 118.8(5)
C(30')-H(30') 0.9500  C(16)-N(3)-C(20) 124.8(5)
C(30')-C(31') 1.35(3)  C(20)-N(3)-C(9) 116.3(5)
C(31')-H(31') 0.9500  O(6)-N(4)-C(23) 116.7(6)
C(31')-C(32') 1.35(2)  O(7)-N(4)-O(6) 122.7(7)
C(32')-H(32') 0.9500  O(7)-N(4)-C(23) 120.6(6)
C(32')-C(33') 1.35(2)  O(1)-C(1)-Re(1) 178.7(7)
C(33')-H(33') 0.9500  O(2)-C(2)-Re(1) 178.2(7)
C(33')-C(34') 1.36(3)  O(3)-C(3)-Re(1) 175.5(7)
C(34')-H(34') 0.9500  N(1)-C(4)-H(4) 118.9
N(1)-Re(1)-Br(1) 82.57(14)  N(1)-C(4)-C(5) 122.3(6)
N(1)-Re(1)-Cl(1) 86.2(8)  C(5)-C(4)-H(4) 118.9
N(2)-Re(1)-N(1) 75.28(18)  C(4)-C(5)-H(5) 120.1
N(2)-Re(1)-Br(1) 86.00(16)  C(6)-C(5)-C(4) 119.8(5)
N(2)-Re(1)-Cl(1) 87.1(10)  C(6)-C(5)-H(5) 120.1
C(1)-Re(1)-N(1) 171.9(2)  C(5)-C(6)-H(6) 120.1
C(1)-Re(1)-N(2) 97.6(2)  C(5)-C(6)-C(7) 119.7(6)
C(1)-Re(1)-C(3) 89.6(3)  C(7)-C(6)-H(6) 120.1
C(1)-Re(1)-Br(1) 93.1(2)  C(6)-C(7)-C(8) 124.0(6)
C(1)-Re(1)-Cl(1) 89.5(8)  C(15)-C(7)-C(6) 116.7(5)
C(2)-Re(1)-N(1) 98.4(2)  C(15)-C(7)-C(8) 119.3(5)
C(2)-Re(1)-N(2) 172.6(2)  C(7)-C(8)-H(8) 119.7
C(2)-Re(1)-C(1) 88.3(3)  C(9)-C(8)-C(7) 120.6(5)
C(9)-C(8)-H(8)  119.7
C(8)-C(9)-N(3)  120.7(5)
C(8)-C(9)-C(10)  121.8(5)
C(10)-C(9)-N(3)  117.5(5)
C(11)-C(10)-C(9)  124.1(5)
C(14)-C(10)-C(9)  118.2(5)
C(14)-C(10)-C(11)  117.7(5)
C(10)-C(11)-H(11)  120.6
C(12)-C(11)-H(11)  120.6
C(11)-C(12)-H(12)  120.0
C(12)-C(11)-H(11)  120.6
C(11)-C(12)-C(13)  119.9(5)
C(11)-C(12)-H(12)  122.7(6)
C(12)-C(13)-H(13)  118.7
C(12)-C(13)-H(13)  112.0
N(2)-C(13)-C(12)  122.7(6)
N(2)-C(13)-H(13)  118.7
C(12)-C(13)-H(13)  118.7
N(2)-C(14)-C(10)  123.0(5)
N(2)-C(14)-C(15)  116.7(5)
C(10)-C(14)-C(15)  120.3(5)
N(1)-C(15)-C(7)  116.8(5)
N(1)-C(15)-C(14)  112.3(5)
C(7)-C(15)-C(14)  119.8(5)
O(4)-C(16)-N(3)  120.2(5)
O(4)-C(16)-C(17)  123.0(5)
N(3)-C(16)-C(17)  116.7(5)
C(18)-C(17)-C(16)  121.2(5)
C(21)-C(17)-C(18)  119.5(6)
C(21)-C(17)-C(16)  119.2(6)
C(17)-C(18)-C(19)  119.7(6)
C(17)-C(18)-C(20)  120.6(5)
C(24)-C(18)-C(19)  119.3(6)
C(18)-C(19)-C(20)  120.6(5)
C(27)-C(19)-C(20)  118.8(6)
O(5)-C(20)-N(3)  119.8(5)
O(5)-C(20)-C(19)  123.4(5)
| Bond                        | Angle         | Bond                        | Angle         |
|-----------------------------|---------------|-----------------------------|---------------|
| C(32)-C(31)-H(31)          | 118.4°        | C(30')-C(29')-C(34')       | 116(2)°       |
| C(31)-C(32)-H(32)          | 121.3°        | C(34')-C(29')-C(28')       | 121.6(17)°    |
| C(31)-C(32)-C(33)          | 117(3)°       | C(29')-C(30')-H(30')       | 119.7°        |
| C(33)-C(32)-H(32)          | 121.3°        | C(31')-C(30')-C(29')       | 120.7(17)°    |
| C(32)-C(33)-H(33)          | 118.9°        | C(31')-C(30')-H(30')       | 119.7°        |
| C(32)-C(33)-C(34)          | 122(2)°       | C(30')-C(31')-H(31')       | 119.6°        |
| C(34)-C(33)-H(33)          | 118.9°        | C(32')-C(31')-C(30')       | 120.7(18)°    |
| C(29)-C(34)-H(34)          | 119.8°        | C(32')-C(31')-H(31')       | 119.6°        |
| C(33)-C(34)-C(29)          | 120(2)°       | C(31')-C(32')-H(32')       | 119.1°        |
| C(33)-C(34)-H(34)          | 119.8°        | C(31')-C(32')-C(33')       | 122(2)°       |
| H(28D)-C(28')-H(28E)       | 109.5°        | C(33')-C(32')-H(32')       | 119.1°        |
| H(28D)-C(28')-H(28F)       | 109.5°        | C(32')-C(33')-H(33')       | 120.3°        |
| H(28E)-C(28')-H(28F)       | 109.5°        | C(32')-C(33')-C(34')       | 119.5(19)°    |
| C(29')-C(28')-H(28D)       | 109.5°        | C(34')-C(33')-H(33')       | 120.3°        |
| C(29')-C(28')-H(28E)       | 109.5°        | C(29')-C(34')-H(34')       | 119.3°        |
| C(29')-C(28')-H(28F)       | 109.5°        | C(33')-C(34')-C(29')       | 121.4(19)°    |
| C(30')-C(29')-C(28')       | 122.7(17)°    | C(33')-C(34')-H(34')       | 119.3°        |
Table 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br). The anisotropic displacement factor exponent takes the form: 

$$-2p^2 \left[ h^2 a^* U_{11} + \ldots + 2hk a^* b^* U_{12} \right]$$

|       | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{23}$  | $U_{13}$  | $U_{12}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| Re1   | 34(1)     | 38(1)     | 40(1)     | 14(1)     | 10(1)     | 11(1)     |
| O1    | 59(3)     | 42(3)     | 65(3)     | -1(2)     | 16(3)     | 14(2)     |
| O2    | 45(3)     | 70(3)     | 58(3)     | 30(3)     | 26(2)     | 12(2)     |
| O3    | 47(3)     | 63(3)     | 69(4)     | 20(3)     | 18(3)     | 18(3)     |
| O4    | 46(3)     | 58(3)     | 59(3)     | 37(2)     | 17(2)     | 23(2)     |
| O5    | 36(2)     | 34(2)     | 46(2)     | 18(2)     | 6(2)      | 10(2)     |
| O6    | 53(3)     | 46(3)     | 74(4)     | 3(3)      | 23(3)     | 8(2)      |
| O7    | 60(3)     | 80(4)     | 82(4)     | 52(4)     | 27(3)     | 16(3)     |
| N1    | 33(2)     | 29(2)     | 38(3)     | 14(2)     | 8(2)      | 9(2)      |
| N2    | 29(2)     | 31(2)     | 38(3)     | 12(2)     | 9(2)      | 4(2)      |
| N3    | 29(2)     | 28(2)     | 36(2)     | 15(2)     | 7(2)      | 8(2)      |
| N4    | 43(3)     | 49(3)     | 56(4)     | 11(3)     | 7(3)      | 5(3)      |
| C1    | 36(3)     | 64(5)     | 47(4)     | 19(3)     | 8(3)      | 11(3)     |
| C2    | 52(4)     | 47(4)     | 44(4)     | 16(3)     | 14(3)     | 16(3)     |
| C3    | 60(4)     | 32(3)     | 26(3)     | 11(2)     | 16(3)     | 9(3)      |
| C4    | 28(3)     | 36(3)     | 52(3)     | 28(3)     | 9(2)      | 8(2)      |
| C5    | 32(3)     | 35(3)     | 58(4)     | 28(3)     | 10(3)     | 9(2)      |
| C6    | 35(3)     | 27(3)     | 56(4)     | 19(3)     | 4(3)      | 7(2)      |
| C7    | 28(3)     | 29(3)     | 42(3)     | 17(2)     | 2(2)      | 7(2)      |
| C8    | 33(3)     | 28(3)     | 37(3)     | 13(2)     | 5(2)      | 8(2)      |
| C9    | 30(3)     | 31(3)     | 35(3)     | 15(2)     | 6(2)      | 6(2)      |
| C10   | 30(3)     | 26(2)     | 37(3)     | 13(2)     | 4(2)      | 6(2)      |
| C11   | 30(3)     | 27(3)     | 46(3)     | 14(2)     | 5(2)      | 3(2)      |
| C12   | 39(3)     | 24(3)     | 52(4)     | 11(3)     | 11(3)     | 1(2)      |
| C13   | 36(3)     | 29(3)     | 48(3)     | 8(3)      | 6(3)      | 3(2)      |
| C14   | 30(3)     | 25(2)     | 36(3)     | 12(2)     | 4(2)      | 8(2)      |
| C15   | 29(3)     | 26(2)     | 34(3)     | 11(2)     | 8(2)      | 9(2)      |
| C16   | 33(3)     | 27(3)     | 42(3)     | 12(2)     | 5(2)      | 8(2)      |
| C17   | 29(3)     | 28(3)     | 38(3)     | 8(2)      | 3(2)      | 4(2)      |
| C18 | 39(3) | 25(3) | 38(3) | 7(2) | 4(2) | 1(2) |
|-----|-------|-------|-------|------|------|------|
| C19 | 35(3) | 28(3) | 41(3) | 11(2) | 6(2) | 3(2) |
| C20 | 35(3) | 26(3) | 40(3) | 14(2) | 4(2) | 4(2) |
| C21 | 35(3) | 35(3) | 46(3) | 10(3) | 5(3) | 9(2) |
| C22 | 27(3) | 35(3) | 57(4) | 4(3) | 5(3) | 4(2) |
| C23 | 35(3) | 36(3) | 40(3) | 7(3) | 7(3) | -2(2) |
| C24 | 36(3) | 33(3) | 40(3) | 7(2) | 8(3) | 1(2) |
| C25 | 48(4) | 49(4) | 48(4) | 24(3) | 11(3) | 0(3) |
| C26 | 53(4) | 49(4) | 56(4) | 33(3) | 12(3) | 9(3) |
| C27 | 45(3) | 41(3) | 53(4) | 27(3) | 10(3) | 10(3) |
| Br1 | 36(1) | 35(1) | 50(1) | 17(1) | -2(1) | 7(1) |
| Cl1 | 36(1) | 35(1) | 50(1) | 17(1) | -2(1) | 7(1) |
| C28 | 180(30) | 82(16) | 150(20) | 67(16) | 5(18) | 8(19) |
| C29 | 74(12) | 52(9) | 103(13) | 13(9) | -23(9) | 4(9) |
| C30 | 83(14) | 73(15) | 160(17) | 35(14) | 2(12) | 26(11) |
| C31 | 53(9) | 72(12) | 156(13) | 25(11) | 10(9) | 18(9) |
| C32 | 51(11) | 44(11) | 102(11) | -2(9) | 2(8) | 3(7) |
| C33 | 55(10) | 40(8) | 77(12) | -5(7) | -8(8) | 12(7) |
| C34 | 58(8) | 39(8) | 86(12) | 3(7) | -6(8) | 4(6) |
| C28' | 150(30) | 74(14) | 160(20) | 50(15) | 53(18) | 43(16) |
| C29' | 64(10) | 45(8) | 108(12) | 17(8) | -9(8) | 4(7) |
| C30' | 75(13) | 62(12) | 157(16) | 66(12) | 23(11) | 25(9) |
| C31' | 43(8) | 62(10) | 160(14) | 65(11) | 16(9) | 13(8) |
| C32' | 43(9) | 36(8) | 119(11) | 31(8) | -4(7) | 5(6) |
| C33' | 53(12) | 39(7) | 86(11) | 5(8) | -19(7) | 6(7) |
| C34' | 67(9) | 36(8) | 93(14) | 2(8) | -7(9) | 12(7) |
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{Re(CO)}_3(1-(1,10)\text{phenanthroline-5-(4-nitro-naphthalimide)})X]$ (X=Cl or Br).

|   | x     | y     | z     | U(eq) |
|---|-------|-------|-------|-------|
| H4 | 1504  | 420   | 5758  | 42    |
| H5 | 1556  | -1188 | 4500  | 45    |
| H6 | 3266  | -1259 | 3280  | 46    |
| H8 | 5387  | -256  | 2566  | 39    |
| H11| 7771  | 3339  | 3582  | 41    |
| H12| 7472  | 4831  | 4907  | 46    |
| H13| 5667  | 4681  | 6035  | 47    |
| H21| 11510 | 276   | 2319  | 47    |
| H22| 13290 | 364   | 1143  | 51    |
| H25| 10768 | 2063  | -916  | 56    |
| H26| 8312  | 2630  | -1006 | 58    |
| H27| 6586  | 2547  | 188   | 52    |
| H28A| 1428 | 5124  | -164  | 198   |
| H28B| 2544 | 4224  | -488  | 198   |
| H28C| 3314 | 5404  | 217   | 198   |
| H30| 36    | 5186  | 1315  | 127   |
| H31| -255  | 4715  | 2745  | 115   |
| H32| 1446  | 3721  | 3298  | 87    |
| H33| 3620  | 3292  | 2439  | 76    |
| H34| 4072  | 3810  | 1045  | 80    |
| H28D| 2810| 4477  | -152  | 181   |
| H28E| 4488 | 4427  | 439   | 181   |
| H28F| 3864 | 5546  | 615   | 181   |
| H30'| 1304 | 5810  | 1512  | 107   |
| H31'| 121  | 5543  | 2840  | 97    |
| H32'| 565  | 4149  | 3390  | 79    |
| H33'| 2488 | 3132  | 2809  | 78    |
| H34'| 3788 | 3373  | 1502  | 85    |
Table 6. Torsion angles [°] for [Re(CO)$_3$(1-(1,10)phenanthroline-5-(4-nitro-naphthalimide))X] (X=Cl or Br).

| Bond | Torsion Angle | Bond | Torsion Angle |
|------|--------------|------|--------------|
| Re1-N1-C4-C5 | 176.3(4) | C8-C9-C10-C14 | -0.8(8) |
| Re1-N1-C15-C7 | -177.0(4) | C9-N3-C16-O4 | 2.2(8) |
| Re1-N1-C15-C14 | 3.0(6) | C9-N3-C16-C17 | -178.2(5) |
| Re1-N2-C13-C12 | -176.8(5) | C9-N3-C20-O5 | -0.9(8) |
| Re1-N2-C14-C10 | 177.9(4) | C9-N3-C20-C19 | 178.9(5) |
| Re1-N2-C14-C15 | -3.2(6) | C9-C10-C11-C12 | -179.8(6) |
| O4-C16-C17-C18 | 177.2(6) | C9-C10-C14-N2 | 179.9(5) |
| O4-C16-C17-C21 | -1.1(9) | C9-C10-C14-C15 | 1.0(8) |
| O6-N4-C23-C22 | 33.9(9) | C10-C11-C12-C13 | -0.5(9) |
| O6-N4-C23-C24 | -145.7(6) | C10-C14-C15-N1 | 179.1(5) |
| O7-N4-C23-C22 | -145.3(7) | C10-C14-C15-C7 | -1.0(8) |
| O7-N4-C23-C24 | 35.1(9) | C11-C10-C14-N2 | -1.1(8) |
| N1-C4-C5-C6 | 1.2(9) | C11-C10-C14-C15 | -179.9(5) |
| N2-C14-C15-N1 | 0.1(8) | C11-C12-C13-N2 | -0.4(10) |
| N2-C14-C15-C7 | -179.9(5) | C13-N2-C14-C10 | 0.2(9) |
| N3-C9-C10-C11 | 0.8(8) | C13-N2-C14-C15 | 179.1(5) |
| N3-C9-C10-C14 | 179.8(5) | C14-N2-C13-C12 | 0.5(9) |
| N3-C16-C17-C18 | -2.4(8) | C14-C10-C11-C12 | 1.2(9) |
| N3-C16-C17-C21 | 179.3(5) | C15-N1-C4-C5 | -1.2(9) |
| N4-C23-C24-C18 | -179.1(5) | C15-C7-C8-C9 | -0.3(8) |
| N4-C23-C24-C25 | 4.0(9) | C16-N3-C9-C8 | -72.7(7) |
| C4-N1-C15-C7 | 0.8(8) | C16-N3-C9-C10 | 106.8(6) |
| C4-N1-C15-C14 | -179.2(5) | C16-N3-C20-O5 | 175.9(5) |
| C4-C5-C6-C7 | -0.7(9) | C16-N3-C20-C19 | -4.4(8) |
| C5-C6-C7-C8 | 179.3(6) | C16-C17-C18-C19 | -0.7(8) |
| C5-C6-C7-C15 | 0.3(8) | C16-C17-C18-C24 | -179.7(5) |
| C6-C7-C8-C9 | -179.3(6) | C16-C17-C21-C22 | 178.9(5) |
| C6-C7-C15-N1 | -0.3(8) | C17-C18-C19-C20 | 1.4(8) |
| C6-C7-C15-C14 | 179.7(5) | C17-C18-C19-C27 | -177.9(6) |
| C7-C8-C9-N3 | 179.8(5) | C17-C18-C24-C23 | 0.5(8) |
| C7-C8-C9-C10 | 0.4(9) | C17-C18-C24-C25 | 177.6(6) |
| C8-C7-C15-N1 | -179.5(5) | C17-C21-C22-C23 | 1.2(9) |
| C8-C7-C15-C14 | 0.5(8) | C18-C17-C21-C22 | 0.5(9) |
| C8-C9-C10-C11 | -179.8(6) | C18-C19-C20-O5 | -179.3(6) |
| Bond                  | Phase Deviation (°) |
|----------------------|---------------------|
| C18-C19-C20-N3       | 0.9(8)              |
| C18-C19-C27-C26      | 0.3(10)             |
| C18-C24-C25-C26      | 0.2(10)             |
| C19-C18-C24-C23      | -178.5(5)           |
| C19-C18-C24-C25      | -1.4(9)             |
| C20-N3-C9-C8         | 104.3(6)            |
| C20-N3-C9-C10        | -76.3(6)            |
| C20-N3-C16-O4        | -174.5(6)           |
| C20-N3-C16-C17       | 5.1(8)              |
| C20-C19-C27-C26      | -179.0(6)           |
| C21-C17-C18-C19      | 177.6(6)            |
| C21-C17-C18-C24      | -1.4(8)             |
| C21-C22-C23-N4       | 178.2(6)            |
| C21-C22-C23-C24      | -2.2(9)             |
| C22-C23-C24-C18      | 1.3(9)              |
| C22-C23-C24-C25      | -175.6(6)           |
| C23-C24-C25-C26      | 177.1(7)            |
| C24-C18-C19-C20      | -179.5(5)           |
| C24-C18-C19-C27      | 1.2(9)              |
| C24-C25-C26-C27      | 1.2(11)             |
| C25-C26-C27-C19      | -1.5(11)            |
| C27-C19-C20-O5       | 0.0(9)              |
| C27-C19-C20-N3       | -179.7(5)           |
| C28-C29-C30-C31      | -179.5(10)          |
| C28-C29-C34-C33      | -178.8(12)          |
| C29-C30-C31-C32      | -2(2)               |
| C30-C29-C34-C33      | 2.0(19)             |
| C30-C31-C32-C33      | 2.0(3)              |
| C31-C32-C33-C34      | -1(3)               |
| C32-C33-C34-C29      | -2(3)               |
| C34-C29-C30-C31      | -0.4(14)            |
| C28'-C29'-C30'-C31'  | -179.5(10)          |
| C28'-C29'-C34'-C33'  | -179.6(12)          |
| C29'-C30'-C31'-C32'  | -3(2)               |
| C30'-C29'-C34'-C33'  | 1.0(18)             |
| C30'-C31'-C32'-C33'  | 5(3)                |
S9. Overlay of DFT-TDA (black) and experimental absorbance spectrum (blue) of 1.
S10. Orbital density plots of 1.
S11. $^{13}\text{C}$ NMR for 1 and 0.15 M (0.75 mmol) BIH. The BIH methyl peaks are 32.86 and 32.91 ppm. Methanol peak is at 49.73 ppm. DCM peak is at 53.61 ppm. CDCl$_3$ peaks are at 76.93, 77.25, and 77.57 ppm. $^{13}\text{COO}^-$ peak is at 159.08 ppm. The remaining peaks between 90-150 ppm are attributed to BIH.
S12. (a) CO$_2$RR procedure without Pre-mixing BIH. At higher concentrations of BIH (1 mmol and above) the solubility limit of BIH in CH$_3$OH/DCM (1:9 v:v) is met, which varies the amount of BIH available to react and the amount of H$^{13}$COO$^-$ produced. Pre-mixing BIH in the solvent for 10 min before adding 1 and $^{13}$CO$_2$ mitigates the variability. (b) Images of the reaction mixture at 0.5 mmol BIH* and 1.0 mmol BIH without pre-mixing† show clear and cloudy solutions, respectively. Pre-mixing the BIH (1.0 mmol), then adding 1, results in a transparent solution‡.
S13. Calibration curve of the $^{13}$C NMR integration of $\text{H}^{13}\text{COO}^-$ supplemented with an internal standard of 0.1 M BIH at a D1 relaxation time of 5 s. The linear regression is $y=6.946x$. The $R^2 = 0.9927$. 
S14. Ion chromatography of a reaction solution containing 1 and BIH after irradiation. Formate was detected while carbonate was not. The peak eluting just before 10 min in A is likely chloride.
S15. A plot of CO (nmol) vs BIH (mmol) upon blue light irradiation of 1 for 30 min. CO amounts were determined by GC analysis of the headspace of a vial containing the reaction mixture.
$^{13}$C NMR of 1 and 0.1 M BIH in CD$_3$OD/DCM (1:9 v:v) after irradiation with blue light for 1.5 hours. The integration of the formate peak at $\sim$160 ppm is greatly diminished from 10.6 (average value for experiments using 0.1 M BIH) to 0.9. The peaks between 112-133 ppm and $\sim$32 ppm are attributed to BIH. The remaining peaks are solvent related.
**S17.** TLC of reaction solution before and after irradiation. DCM/MeOH (1:1, v:v) was used as the mobile phase. The Rf values are listed; \( \mathbf{1} = 0.90 \), BIH = 0.04, BI\(^+\) = 0.59. Spots were determined by UV and iodine vapor.
S18. Electronic absorption spectra of 2 in MeOH/DCM (1:9 v:v) (blue) and the reaction solution containing 2 and 0.3 M BIH after irradiation with blue light (450-460 nm) in MeOH/DCM (1:9 v:v) (red). The MLCT band at 352 nm is bleached and the LC band is red shifted 268 nm to 281 nm.
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