

## A Thallium(I)-Mediated Route to $\sigma$ -Arylalkynyl Complexes of Bipyridyltricarboxylrhenium(I).

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### Table of Contents:

General Experimental Considerations.	S2
Synthetic Details.	S3
Table S1. Selected characterization data for various tricarboxyl(dipyridyl)rhenium(I) derivatives.	S8
X-Ray Crystallography- General Considerations.	S9
Table S2. Crystallographic Data and Refinement Parameters.	S10
Figure S1. ORTEP diagram with atom labeling and selected bond distances and angles for (5,5'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]•0.5 acetone.	S11
Figure S2. Asymmetric unit with atom labeling and selected bond distances and angles of (6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> (Br)•0.5 THF.	S12
Figure S3. ORTEP diagram with atom labeling and selected bond distances and angles of (6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]•0.41 THF.	S13
Figure S4. ORTEP diagram with atom labeling and selected bond distances and angles of (6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> (PO <sub>2</sub> F <sub>2</sub> ).	S14
Figure S5. ORTEP diagram with atom labeling and selected bond distances and angles for (4,4'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(HpzAn <sup>Me</sup> )].	S15
Figure S6. ORTEP diagram with atom labeling and selected bond distances and angles for (bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]--(CH <sub>2</sub> OCH <sub>2</sub> Cp <sub>3</sub> ) <sub>2</sub> ].	S16
Table S3. Rhenium-Alkynyl "bending" Angles.	S17

## General Experimental Considerations:

Solvents were dried and distilled prior to use except where indicated. The syntheses of the rhenium complexes were carried out under nitrogen atmosphere using standard Schlenk techniques. Literature procedures were used to prepare  $\text{Re}(\text{CO})_5\text{Br}$ ,<sup>S1</sup> 5,5'-Br<sub>2</sub>bipyridyl,<sup>S2</sup>  $(\text{X}_2\text{-bipy})\text{Re}(\text{CO})_3\text{Br}$  (X = H, Me, Br),<sup>S3</sup>  $\text{H}(\text{pzAn}^{\text{Me}})$  (HpzAnMe = 2-pyrazolyl-4-methylaniline),<sup>S4</sup> and 3,5-(pz<sub>3</sub>CCH<sub>2</sub>OCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C≡CH,<sup>S5</sup> while all other chemicals were obtained commercially and used as received. Elemental analysis was performed by Midwest Microlab Inc., Indianapolis, IN. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. Infrared spectra were recorded on samples as KBr pellets and as Nujol mulls using a Nicolet Magna-IR 560 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian 300 MHz spectrometer. Chemical shifts were referenced to solvent resonances at:  $\delta_{\text{H}}$  7.27,  $\delta_{\text{C}}$  77.23 for CDCl<sub>3</sub>;  $\delta_{\text{H}}$  2.05,  $\delta_{\text{C}}$  29.92 for acetone-d<sub>6</sub> or  $\delta_{\text{H}}$  1.94,  $\delta_{\text{C}}$  118.9 for CD<sub>3</sub>CN. Absorption measurements were recorded on an Agilent 8453 spectrometer. Steady-State emission spectra were obtained on a JASCO FP-6500 spectrofluorometer. Electrochemical measurements were collected with a BAS CV-50V instrument for ca. 0.2 mM THF solutions of the complexes, with 0.25 M NBu<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte, in a three-electrode cell comprised of an Ag/AgCl electrode, a platinum working electrode and a glassy carbon counter electrode. Mass spectrometric measurements recorded in ESI(+) mode were obtained on a Micromass Q-Tof spectrometer.

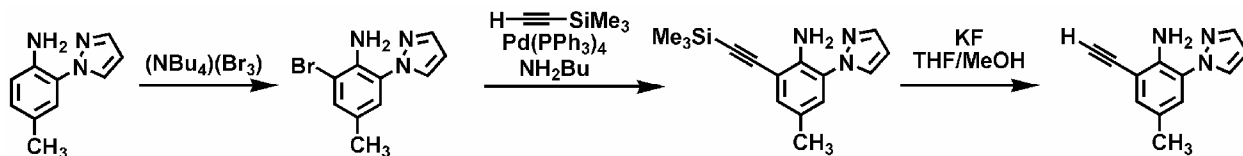
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## Synthetic Details:

### Starting materials:

The compound 2-ethynyl-6-pyrazolyl-4-methylaniline was prepared according to Scheme S1, as detailed below.

### Scheme S1.



**2-Bromo-6-pyrazolyl-4-methylaniline.** A mixture of 1.03g (5.95 mmol)  $\text{H}(\text{pzAn}^{\text{Me}})$  and 2.87g (5.95 mmol)  $(\text{NBu}_4)(\text{Br}_3)$  in 2:1  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  were stirred 0.5 h at room temperature. Purification by silica gel column chromatography ( $R_f = 0.83$ , 3/1 hexanes/ethyl acetate) afforded 1.50 g (91 %) of the desired compound as a colorless solid. Recrystallization by cooling hot hexanes solution gives colorless needles. Mp, 49-50 °C. Anal. Calcd. (found) for  $\text{C}_{10}\text{H}_{10}\text{BrN}_3$ : C, 47.64 (46.76); H, 4.00 (4.12); N 16.67 (16.42).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.75 (d,  $J = 1$  Hz, 1H,  $\text{H}_3\text{-pz}$ ), 7.69 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-pz}$ ), 7.27 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-An}$ ), 6.96 (d,  $J = 2$  Hz, 1H,  $\text{H}_3\text{-An}$ ), 6.44 (dd,  $J = 2$ , 1 Hz, 1H,  $\text{H}_4\text{-pz}$ ), 5.03 (br s, 2H,  $\text{NH}_2$ ), 2.26 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$  141.1 ( $\text{C}_3\text{-pz}$ ), 137.2 ( $\text{C}_1\text{-An}$ ), 132.4 ( $\text{C}_5\text{-An}$ ), 130.4 ( $\text{C}_4\text{-An}$ ), 128.0 ( $\text{C}_2\text{-An}$ ), 124.4 ( $\text{C}_5\text{-pz}$ ), 117.9 ( $\text{C}_6\text{-An}$ ), 111.1 ( $\text{C}_3\text{-An}$ ), 106.9 ( $\text{C}_4\text{-pz}$ ), 20.3 ( $-\text{CH}_3$ ).

**2-(2-trimethylsilylethynyl)-6-pyrazolyl-4-methylaniline.** A mixture of 4.0 g (16 mmol) 2-bromo-6-pyrazolyl-4-methylaniline, 4.5 ml (32 mmol) trimethylsilylacetylene, and 0.37 g (0.32 mmol, 2 mol %)  $\text{Pd}(\text{PPh}_3)_4$  were stirred in refluxing n-butylamine for 1 d. Purification by silica gel column chromatography ( $R_f = 0.56$ , 5/1 hexanes/ethyl acetate) afforded 4.0 g (94%) of the desired compound as an orange oil. Anal. Calcd. (found) for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{Si}$ : C, 66.87 (66.98); H, 7.11 (7.12); N 15.60 (15.44).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.73 (d,  $J = 1$  Hz, 1H,  $\text{H}_3\text{-pz}$ ), 7.69 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-pz}$ ), 7.14 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-An}$ ), 6.97 (d,  $J = 2$  Hz, 1H,  $\text{H}_3\text{-An}$ ), 6.43 (dd,  $J = 2$ , 1 Hz, 1H,  $\text{H}_4\text{-pz}$ ), 5.02 (br s, 2 H,  $\text{NH}_2$ ), 2.23 (s, 3 H,  $\text{CH}_3$ ), 0.26 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$  141.0 ( $\text{C}_3\text{-pz}$ ), 140.8 ( $\text{C}_1\text{-An}$ ), 132.0 ( $\text{C}_5\text{-An}$ ), 130.0 ( $\text{C}_4\text{-An}$ ), 126.5 ( $\text{C}_2\text{-An}$ ), 125.6 ( $\text{C}_5\text{-pz}$ ), 110.2 ( $\text{C}_6\text{-An}$ ), 110.1 ( $\text{C}_3\text{-An}$ ), 106.7 ( $\text{C}_4\text{-pz}$ ), 101.5 ( $\text{C}\equiv\text{C}$ ), 100.8 ( $\text{C}\equiv\text{C}$ ), 20.4 ( $\text{CH}_3$ ), 0.3 ( $\text{Si}(\text{CH}_3)_3$ ).

**2-ethynyl-6-pyrazolyl-4-methylaniline.** A mixture of 4.0 g (15 mmol) 2-(2-trimethylsilylethynyl)-6-pyrazolyl-4-methylaniline and 1.3 g (22 mmol)  $\text{KF}$  were heated at reflux 12 hr in 1/1  $\text{THF}/\text{MeOH}$ . Purification by silica gel column chromatography ( $R_f = 0.67$ , 2/1 hexanes/ethyl acetate) afforded 2.4 g (82%) of the desired product as a brown oil. Anal. Calcd. (found) for  $\text{C}_{12}\text{H}_{11}\text{N}_3$ : C, 73.07 (73.41); H, 5.62 (5.74); N 21.31 (21.54).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.74 (d,  $J = 1$  Hz, 1H,  $\text{H}_3\text{-pz}$ ), 7.70 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-pz}$ ), 7.16 (d,  $J = 2$  Hz, 1H,  $\text{H}_5\text{-An}$ ), 7.00 (d,  $J = 2$  Hz, 1H,  $\text{H}_3\text{-An}$ ), 6.43 (dd,  $J = 2$ , 1 Hz, 1H,  $\text{H}_4\text{-pz}$ ), 5.17 (br s, 2 H,  $\text{NH}_2$ ), 3.41 (s, 1 H,  $\text{CC-H}$ ), 2.25 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$  141.2 ( $\text{C}_3\text{-pz}$ ),

140.8 (C<sub>1</sub>-An), 132.2 (C<sub>5</sub>-An), 129.9 (C<sub>4</sub>-An), 126.4 (C<sub>2</sub>-An), 126.1 (C<sub>6</sub>-An) , 125.7 (C<sub>5</sub>-pz), 108.9 (C<sub>3</sub>-An), 106.6 (C<sub>4</sub>-pz), 83.1 (C≡C), 80.3 (C≡C-H), 20.2 (CH<sub>3</sub>).

**(5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br).** A mixture of 0.205 g (0.67 mmol) 5,5'-Br<sub>2</sub>bipy and 0.250 g (0.62 mmol) Re(CO)<sub>5</sub>Br in 20 mL toluene were heated at reflux under nitrogen 4h. The resulting yellow-orange mixture was allowed to cool room temperature and was filtered. The insoluble portion was washed with 5 mL toluene, two 10 mL portions hexanes, and was dried under vacuum to leave 0.303 g (75 %) of (5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br) as a yellow microcrystalline solid. Mp, dec 340-365 °C. Anal. Calcd. (found) for C<sub>13</sub>H<sub>6</sub>Br<sub>3</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 23.51 (23.44); H, 0.91 (1.01); N 4.22 (4.12). <sup>1</sup>H NMR (CH<sub>3</sub>CN) 9.23 (d, *J* = 2 Hz, 2 H, H<sub>6</sub>-bipy), 8.70 (d, *J* = 9 Hz, 2 H, H<sub>3</sub>-bipy), 8.56 (dd, *J* = 9, 2 Hz, H<sub>4</sub>-bipy). <sup>13</sup>C NMR (CH<sub>3</sub>CN) δ<sub>C</sub> 154.4, 129.8, 129.1, 126.4, 126.1 (CO not obs). IR (KBr, cm<sup>-1</sup>) ν<sub>C-O</sub> = 2016, 1907. UV-Vis (THF), λ<sub>max</sub> 416 nm (ε = 1700 M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid): λ<sub>max</sub> = 549 nm.

**(6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br).** A mixture of 0.252 g (1.37 mmol) 6,6'-Me<sub>2</sub>bipy and 0.556 g (1.37 mmol) Re(CO)<sub>5</sub>Br in 20 mL toluene were heated at reflux under nitrogen 4h. The resulting yellow-orange mixture was allowed to cool room temperature and was filtered. The insoluble portion was washed with 5 mL toluene, two 10 mL portions of hexanes, and was dried under vacuum to leave 0.696 g (95%) of (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br) as a yellow microcrystalline solid. Mp, dec 361-373 °C. Anal. Calcd. (found) for C<sub>15</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>3</sub>Re: C, 33.71 (33.82); H, 2.26 (2.32); N 5.24 (5.33). <sup>1</sup>H NMR (CH<sub>3</sub>CN) 8.19 (d, *J* = 8 Hz, 2H, H<sub>3,3'</sub>-bipy), 8.00 (dd, *J* = 8 Hz, *J* = 8 Hz, 2H, H<sub>4,4'</sub>-bipy), 7.59 (d, *J* = 8 Hz, 2H, H<sub>3</sub>-bipy), 3.05 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (CO not obs) 163.4, 159.0, 140.7, 127.9, 122.6, 30.7. IR (KBr, cm<sup>-1</sup>) ν<sub>C-O</sub> = 2021, 1906. UV-Vis (THF), λ<sub>max</sub> 380 nm (ε = 1600 M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid): λ<sub>max</sub> = 530 nm. Single crystals of a THF solvate suitable for X-Ray diffraction were grown by layering a THF solution with diethyl ether.

## Rhenium Alkynyls:

### (bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>).

**Method 1a. TlPF<sub>6</sub>/THF solution.** A mixture of 0.403 g (0.796 mmol) (bipy)Re(CO)<sub>3</sub>(Br), 0.280 g (0.802 mmol) TlPF<sub>6</sub>, 0.18 mL (1.6 mmol;  $\rho$  = 0.93 g/mL) phenylacetylene, 20 mL THF, 1 mL NEt<sub>3</sub> were heated at reflux for 2d (without precautions to avoid air or light). After cooling to room temperature, the mixture was filtered. The insoluble portion (TlBr) was washed with THF, ethyl acetate, and MeOH to ensure quantitative transfer of soluble products. After adsorbing the mixture onto silica gel, the desired product was subject to column chromatography where it eluted as a yellow-orange band using either ethyl acetate ( $R_f$  = 0.67) or 3:2 hexanes:acetone ( $R_f$  = 0.7) to give 0.235 g (56%) as a yellow orange powder after removing solvent and drying under vacuum. Note: for incomplete reactions, (bipy)Re(CO)<sub>3</sub>(Br) elutes next ( $R_f$  = 0.33 ethyl acetate;  $R_f$  = 0.4 in 3:2 hexanes:acetone). A second run using 0.080 g (0.16 mmol) (bipy)Re(CO)<sub>3</sub>(Br), 0.060 g (0.19 mmol) TlPF<sub>6</sub>, 0.030 mL (0.27 mmol) phenylacetylene, afforded 0.043 g (52 %) of the desired product. Average: 54%. Mp, dec. 245-256 °C. Anal. Calcd. (found) for C<sub>21</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 47.81 (47.99); H, 2.48 (2.53); N 5.31 (5.35). <sup>1</sup>H NMR (acetone-d<sub>6</sub>) 9.13 (dd,  $J$  = 6, 1 Hz, 2H, H<sub>6</sub>-bipy), 8.69 (dd,  $J$  = 8, 1 Hz, 2H, H<sub>3</sub> - bipy), 8.30 (ddd,  $J$  = 8, 8, 2 Hz, 2H, H<sub>4</sub>-bipy), 7.75 (ddd,  $J$  = 8, 6 Hz, 1 Hz, 2H, H<sub>5</sub>-bipy), 6.89 (m, 5H, Ph). <sup>13</sup>C NMR (acetone-d<sub>6</sub>) 197.6, 194.6, 156.1, 153.3, 139.3, 131.2, 128.8, 127.7, 126.8, 124.6, 124.0, 105.0, 99.5. IR (KBr, cm<sup>-1</sup>)  $\nu_{C-O}$  = 2009, 1907. UV-Vis (THF):  $\lambda_{max}$  422 nm ( $\epsilon$  = 1700 M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid):  $\lambda_{max}$  = 524 nm.

**Method 1b. Ag(OSO<sub>2</sub>CF<sub>3</sub> = OTf)/THF solution.** A mixture of 0.505 g (0.997 mmol) (bipy)Re(CO)<sub>3</sub>(Br), 0.257 g (1.00 mmol) AgOTf, 0.21 mL (2.00 mmol;  $\rho$  = 0.93 g/mL) phenylacetylene, 20 mL THF, 1 mL NEt<sub>3</sub> were heated at reflux for 2d under nitrogen atmosphere and with the exclusion of light (aluminum foil-wrapped apparatus). The resulting mixture was worked up as in Method 1a to give 0.150g (29 %) of the desired product.

**Method 2. TlPF<sub>6</sub>/Neat amine.** A mixture of 0.080 g (0.16 mmol) (bipy)Re(CO)<sub>3</sub>(Br), 0.059 g (17 mmol) TlPF<sub>6</sub>, 0.04 mL (0.36 mmol) phenylacetylene in 5 mL EtN(iPr)<sub>2</sub> was heated at reflux 15 h, then was worked up as in Method 1a to give 0.054 g (64%) of the desired product.

**(4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>).** A reaction performed according to Method 1a but with 0.206 g (0.385 mmol) (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.136 g (0.389 mmol) TlPF<sub>6</sub>, 0.09 mL (0.8 mmol;  $\rho$  = 0.93 g/mL) phenylacetylene, afforded 0.140 g (65 %) of (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>) as a yellow solid after purification by column chromatography ( $R_f$  = 0.75, ethyl acetate, SiO<sub>2</sub> plate). A second run using 0.220 g (0.410 mmol) (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.150 g (0.429 mmol) TlPF<sub>6</sub>, 0.09 mL (0.8 mmol) phenylacetylene, afforded 0.215 g (94 %) of the desired product. Average 79%. Mp, dec. 190-196 °C. Anal. Calcd. (found) for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 49.72 (49.85); H, 3.08 (3.12); N 5.04 (5.26). <sup>1</sup>H NMR (CD<sub>3</sub>CN) 8.85 (d,  $J$  = 6 Hz, 2H, H<sub>6</sub>-bipy), 8.28 (s, 2H, H<sub>3</sub>-bipy), 7.42 (d,  $J$  = 6 Hz, 2H, H<sub>5</sub>-bipy), 7.02 (m, 3H, Ph), 6.80 (m, 2H, Ph), 2.55 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN) 199.9, 194.4, 153.2, 152.7, 150.6, 139.3, 136.2, 131.8, 128.8, 125.9, 125.3, 105.7, 100.6, 21.7. IR (KBr, cm<sup>-1</sup>)  $\nu_{C-O}$  = 2006, 1888. UV-Vis (THF):  $\lambda_{max}$  417 nm ( $\epsilon$  = 1200, M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid):  $\lambda_{max}$  = 560 nm.

**(5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>).** A reaction performed according to Method 1a but with 0.280 g (0.524 mmol) (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.190 g (0.544 mmol) TlPF<sub>6</sub>, 0.11 mL (1.0 mmol;  $\rho$  = 0.93 g/mL) phenylacetylene, afforded 0.249 g (85%) of (5,5'-

**Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)** as a yellow solid after purification by column chromatography (*R<sub>f</sub>* = 0.79, ethyl acetate on SiO<sub>2</sub> plate). A second run using 0.110 g (0.210 mmol) (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.081 g (0.23 mmol) TIPF<sub>6</sub>, 0.06 mL (0.5 mmol) phenylacetylene, afforded 0.085 g (77 %) of the desired product. Average 81%. Mp, dec. 265-273 °C. Anal. Calcd. (found) for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 49.72 (50.03); H, 3.08 (2.97); N 5.04 (5.03). <sup>1</sup>H NMR (acetone-d<sub>6</sub>) 8.93 (d, *J* = 2 Hz, 2H, H<sub>6</sub>, -bipy), 8.50 (d, *J* = 8 Hz, 2H, H<sub>3</sub>-bipy), 8.07 (dd, *J* = 8, 2 Hz, 2H, H<sub>4</sub>-bipy), 6.95 (m, 3H, Ph), 6.81 (m, 2H, Ph), 2.55 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (acetone-d<sub>6</sub>) 199.1, 193.5, 153.7, 152.9, 139.7, 137.8, 131.2, 128.9, 127.7, 126.1, 124.6, 123.0, 105.0, 17.6. IR (KBr, cm<sup>-1</sup>) ν<sub>C-O</sub> = 2005, 1894. UV-Vis (THF): λ<sub>max</sub> 412 nm (ε = 1500, M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid): λ<sub>max</sub> = 560 nm. Single crystals of an acetone solvate suitable for X-Ray diffraction were grown by layering an acetone solution with diethyl ether.

**(5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)**. A reaction performed according to Method 1a but with 0.180 g (0.271 mmol) (5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.100 g (0.286 mmol) TIPF<sub>6</sub>, 0.060 mL (0.60 mmol; ρ = 0.93 g/mL) phenylacetylene, afforded 0.110 g (59%) of (5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>) as a red-orange solid after purification by column chromatography (*R<sub>f</sub>* = 0.79 ethyl acetate, SiO<sub>2</sub> plate). A second run using 0.070 g (0.11 mmol) (5,5'-Br<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.041 g (0.12 mmol) TIPF<sub>6</sub>, 0.02 mL (0.18 mmol) phenylacetylene, afforded 0.044 g (59 %) of the desired product. Average 59%. Mp, dec. 238-240 °C. Anal. Calcd. (found) for C<sub>21</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 36.80 (36.44); H, 1.62 (1.26); N 4.09 (3.78). <sup>1</sup>H NMR (CD<sub>3</sub>CN) 9.10 (d, *J* = 2 Hz, 2H, H<sub>6</sub>-bipy), 8.31 (m, 4 H, H<sub>3</sub>- and H<sub>4</sub>-bipy), 7.03 (m, 3H, Ph), 6.83 (m, 2H, Ph). <sup>13</sup>C NMR (CD<sub>3</sub>CN) 154.4, 147.7, 129.8, 129.1, 126.2. IR (KBr, cm<sup>-1</sup>) ν<sub>C-O</sub> = 2006, 1890. UV-Vis (THF): λ<sub>max</sub> 447 nm (ε = 2000, M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid): λ<sub>max</sub> = 609 nm.

**(6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)**. A reaction performed according to Method 1a but with 0.246 g (0.461 mmol) (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.170 g (0.487 mmol) TIPF<sub>6</sub>, 0.10 mL (0.91 mmol; ρ = 0.93 g/mL) phenylacetylene, afforded 0.178 g (70%) of (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>) as a yellow solid. A second run using 0.268 g (0.501 mmol) (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.175 g (0.501 mmol) TIPF<sub>6</sub>, 0.11 mL (1.0 mmol; ρ = 0.93 g/mL) phenylacetylene, afforded 0.217 g (78 %) of the desired product. Average 72%. *R<sub>f</sub>* = 0.70 (ethyl acetate). Single crystals suitable for X-Ray diffraction were grown by layering an acetone solution with hexanes. Mp, dec 217-220 °C. Anal. Calcd. (found) for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>Re: C, 49.72 (50.12); H, 3.08 (3.26); N 5.04 (4.82). <sup>1</sup>H NMR (acetone-d<sub>6</sub>) 8.44 (d, *J* = 8 Hz, 2 H, H<sub>3</sub>-bipy), 8.11 (dd, *J* = 8, 8 Hz, 2H, H<sub>4</sub>-bipy), 7.69 (d, *J* = 8 Hz, 2H, H<sub>5</sub>-bipy), 6.98 (m, 3H, Ph), 6.84 (m, 2H, Ph), 3.06 (s, 6 H, 6,6'-CH<sub>3</sub>). <sup>13</sup>C NMR (acetone-d<sub>6</sub>) 199.7, 194.1, 154.3, 153.7, 140.5, 138.8, 131.8, 128.9, 126.8, 125.8, 123.8, 106.2, 101.6, 18.4. IR (KBr, cm<sup>-1</sup>) ν<sub>C-O</sub> = 2008, 1900. UV-Vis, λ<sub>max</sub> (414) (ε = 1900, M<sup>-1</sup>cm<sup>-1</sup>). Emission (solid): λ<sub>max</sub> = 557 nm.

**(6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(PO<sub>2</sub>F<sub>2</sub>)**. A mixture of 0.10 g (0.19 mmol) (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br), 0.72 g (0.20 mmol) TIPF<sub>6</sub> in 10 mL THF was heated at reflux for 2 d. After cooling and filtration to remove TlBr, ca. 2 g silica gel was added to the filtrate and solvent was removed to adsorb the yellow product mixture. After transferring onto a fresh pad of silica gel, trace unreacted (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br) was eluted with ethyl acetate, then 0.084 g (83% based on Re) (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(PO<sub>2</sub>F<sub>2</sub>) eluted in the yellow luminescent band near the solvent front after flushing with THF (*R<sub>f</sub>* ca. 0.95, THF, SiO<sub>2</sub>). Single crystals suitable for X-Ray diffraction were grown by layering a THF solution with hexanes. Mp, dec. 210-215 °C. Anal. Calcd.

(found) for  $C_{15}H_{12}F_2N_2O_5PRe$ : C, 32.44 (32.16); H, 2.18 (2.01); N 5.04 (5.32).  $^1H$  NMR ( $CD_3CN$ ) 8.22 (d,  $J = 8$  Hz, 2 H,  $H_3$ -bipy), 8.07 (dd,  $J = 8, 8$  Hz, 2H,  $H_4$ -bipy), 7.61 (d,  $J = 8$  Hz, 2H,  $H_5$ -bipy), 3.06 (s, 6 H,  $CH_3$ ).  $^{13}C$  NMR ( $CD_3CN$ ) (CO not obs) 159.0, 141.5, 130.8, 128.0, 122.8, 30.3.  $^{19}F$  NMR ( $CD_3CN$ ) -85.33 (d,  $J_{F-P} = 960$  Hz).  $^{31}P$  NMR ( $CD_3CN$ ) -15.0 (t,  $J_{P-F} = 960$  Hz). IR (KBr,  $cm^{-1}$ )  $\nu_{C-O} = 2031, 1944, 1898$ . UV-Vis (THF):  $\lambda_{max}$  355 nm ( $\epsilon = 1300$ ,  $M^{-1}cm^{-1}$ ). Emission (solid):  $\lambda_{max} = 530$  nm.

Note: Hydrolysis of the  $PF_6$  anion to the  $PO_2F_2$  anion has been previously observed see for example: (a) Reger, D. L.; Huff, M. F.; Lebiada, L. *Acta. Cryst. C* **1991**, C47, 1167 and (b) Blake, A.J.; Baum, G.; Champness, N.R.; Chung, S.S.M.; Cooke, P.A.; Fenske, D.; Khobystov, A.N.; Lemonovskii, D.A.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4285. In the current case, hydrolysis occurs from the interaction between [(6,6'- $Me_2$ bipy)Re(solvent)(CO) $_3$ ]( $PF_6$ ) (solvent =  $CH_3CN$  or THF) with silica gel since the intact  $PF_6$  salts can be isolated, as will be addressed separately.

**(bipy)Re(CO) $_3$ [C $\equiv$ C( $C_6H_5$ )-3,5-( $CH_2OCH_2Cpz_3$ ) $_2$ ].** A reaction performed according to Method 1a but with 0.345 g (0.681 mmol) (bipy)Re(CO) $_3$ (Br), 0.250 g (0.716 mmol)  $TiPF_6$ , 0.426g (0.726 mmol)  $HC\equiv C(C_6H_5)$ -3,5-( $CH_2OCH_2Cpz_3$ ) $_2$ , afforded 0.250 g (35 %) of (bipy)Re(CO) $_3$ [C $\equiv$ C( $C_6H_5$ )-3,5-( $CH_2OCH_2Cpz_3$ ) $_2$ ] as a yellow solid after purification by silica gel column chromatography ( $R_f = 0.58$ , ethyl acetate). Single crystals suitable for X-Ray diffraction were grown by vapor diffusion of  $Et_2O$  into a cold ( $4^\circ C$ ) acetone solution. Mp, 178-181  $^\circ C$ . Anal. Calcd. (found) for  $C_{46}H_{39}N_{14}O_5Re$ : C, 52.41 (52.69); H, 3.73 (3.56); N 18.60 (18.39).  $^1H$  NMR (acetone- $d_8$ ) 9.06 (dd,  $J = 6, 1$  Hz, 2H,  $H_6$ -bipy), 8.41 (dd,  $J = 8, 1$  Hz, 2H,  $H_3$ -bipy), 8.16 (ddd,  $J = 8, 8, 2$  Hz, 2H,  $H_4$ -bipy), 7.60 (ddd,  $J = 8, 6, 1$  Hz, 2H,  $H_5$ -bipy), 7.57 (d,  $J = 1$  Hz, 6H,  $H_3$ -pz), 7.38 (d,  $J = 2$  Hz, 6H,  $H_5$ -pz), 6.60 (s, 1H, Ph), 6.53 (s, 2H, Ph), 6.31 (dd,  $J = 2$  Hz, 1 Hz, 6H,  $H_4$ -pz), 4.90 (s, 4H,  $CH_2$ ), 4.28 (s, 4H,  $CH_2$ ).  $^{13}C$  NMR (acetone- $d_8$ ) 199.7, 193.8, 156.7, 153.9, 141.5, 140.0, 137.9, 131.8, 130.8, 129.4, 128.2, 126.8, 124.6, 124.3, 106.8, 105.5, 104.1, 74.0, 73.8. IR (KBr,  $cm^{-1}$ )  $\nu_{C-O} = 2005, 1896$ . UV-Vis (THF):  $\lambda_{max}$  423 nm ( $\epsilon = 2400$ ,  $M^{-1}cm^{-1}$ ). Emission (solid):  $\lambda_{max} = 555$  nm.

**(4,4'- $Me_2$ bipy)Re(CO) $_3$ [C $\equiv$ C(HpzAn $^{Me}$ )].** A reaction performed according to Method 1a but with 0.139 g (0.260 mmol) (4,4'- $Me_2$ bipy)Re(CO) $_3$ (Br), 0.095 g (0.270 mmol)  $TiPF_6$ , 0.062 g (0.314 mmol)  $HC\equiv C(HpzAn^{Me})$ , afforded 0.063 g (37 %) of (6,6'- $Me_2$ bipy)Re(CO) $_3$ ( $C_2C_6H_5$ ) as a yellow solid after column chromatography using silica gel ( $R_f = 0.7$ , ethyl acetate). A second run using 0.255 g (0.477 mmol) (4,4'- $Me_2$ bipy)Re(CO) $_3$ (Br), 0.170 g (0.487 mmol)  $TiPF_6$ , 0.110 g (0.558 mmol)  $HC\equiv C(HpzAn^{Me})$ , afforded 0.067 g (23 %) of the desired product. Average 30%. Single crystals suitable for X-Ray diffraction were grown by layering an acetone solution of the compound with hexanes. Mp, dec. 212-220  $^\circ C$ . Anal. Calcd. (found) for  $C_{27}H_{22}N_5O_3Re$ : C, 49.84 (49.66); H, 3.41 (3.09); N 10.76 (10.57).  $^1H$  NMR (acetone- $d_6$ ) 8.96 (d,  $J = 6$  Hz, 2H,  $H_6$ -bipy), 8.54 (s, 2H,  $H_3$ -bipy), 7.82 (d,  $J = 2$  Hz, 1H,  $H_3$ -pz), 7.62 (d,  $J = 2$  Hz, 1H,  $H_5$ -pz), 7.57 (d,  $J = 6$  Hz, 2H,  $H_5$ -bipy), 6.73 (d,  $J = 1$  Hz, 1H,  $H_3$ -An), 6.64 (d,  $J = 1$  Hz, 1H,  $H_5$ -An), 6.38 (dd,  $J = 2, 1$  Hz, 1H,  $H_4$ -pz), 4.74 (br s, 2H,  $NH_2$ -An), 2.82 (s, 3H,  $CH_3$ -An), 2.60 (s, 6H,  $CH_3$ -bipy).  $^{13}C$  NMR (acetone- $d_6$ ) 199.7, 194.3, 153.3, 152.4, 145.7, 142.6, 140.41, 130.5, 128.9, 125.4, 122.4, 121.8, 106.6, 101.0, 82.2, 78.9, 21.4, 20.2. IR (KBr,  $cm^{-1}$ )  $\nu_{C-O} = 2004, 1899$ . UV-Vis (THF):  $\lambda_{max}$  417 nm ( $\epsilon = 2800$ ,  $M^{-1}cm^{-1}$ ). Emission (solid):  $\lambda_{max} = 550$  nm.

**Table S1.** Selected characterization data for various tricarbonyl(dipyridyl)rhenium(I) derivatives.

Compound	IR ( $\nu_{\text{CO}}$ , $\text{cm}^{-1}$ , KBr)	$E_{1/2}$ (V vs Ag/AgCl) <sup>a</sup>	UV, $\lambda_{\text{max}}$ MLCT (THF)	Emission, <sup>b</sup> $\lambda_{\text{max}}$ (solid)
(bipy)Re(CO) <sub>3</sub> Br	2019, 1907	1.58, -1.36	394	524
(bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]	2009, 1898	1.23, -1.48	422	563
(bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>3</sub> )-3,5-(CH <sub>2</sub> OCH <sub>2</sub> Cp <sub>z</sub> ) <sub>2</sub> ]	2005, 1896	1.14, -1.52	423	555
(4,4'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> Br	2018, 1889	1.55, -1.46	388	519
(4,4'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]	2006, 1888	1.10, -1.56	417	560
(4,4'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(HpzAn <sup>Me</sup> )]	2004, 1899	1.17, -2.07	404	550
(5,5'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> Br	2020, 1903	1.57, -1.45	386	529
(5,5'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]	2005, 1894	1.10, -1.59	412	560
(5,5'-Br <sub>2</sub> bipy)Re(CO) <sub>3</sub> Br	2016, 1907	1.50, -1.26	416	549
(5,5'-Br <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]	2006, 1890	1.17, -1.20	447	609
(6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> Br	2021, 1906	1.64, -1.45	380	530
(6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]	2008, 1900	1.12, -1.46	414	557
(6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> (PO <sub>2</sub> F <sub>2</sub> )	2031, 1944, 1898	1.96, -1.41, -1.56	355	530

a. only anodic peak potentials are reported for irreversible oxidations. NBu<sub>4</sub>PF<sub>6</sub> supporting electrolyte, 100 mV/s. b. MLCT

**X-ray Crystallography.** The X-ray crystallographic studies of (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.5acetone, (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>Br•0.5THF, (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.41THF, (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(PO<sub>2</sub>F<sub>2</sub>), and (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(HpzAn<sup>Me</sup>)] were carried out at 100K with a Bruker AXS 3-circle diffractometer equipped with a SMART2<sup>S6</sup> CCD detector using Cu(Kα) radiation while that of (bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>3</sub>)-3,5-(CH<sub>2</sub>OCH<sub>2</sub>Cpz<sub>3</sub>)<sub>2</sub>] was carried out at 296 K using Mo(Kα) source radiation. Numerical absorption correction has been applied to the data for (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>Br•0.5THF, (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.41THF while the data for the remainder of compounds were corrected for absorption effects with SADABS<sup>S6</sup> while the data for the remaining compounds were not corrected for absorption effects. All structures were solved by direct methods (SHELXS)<sup>S7</sup> and refined by a full-matrix least-squares procedure (SHELXL) using Intel/HP Pentium PC computers. The X-ray crystallographic parameters and the details of data collection and structure refinement are presented in Table S-2. Atom labeling and selected bond distances and angles are presented in Figures S1-S6.

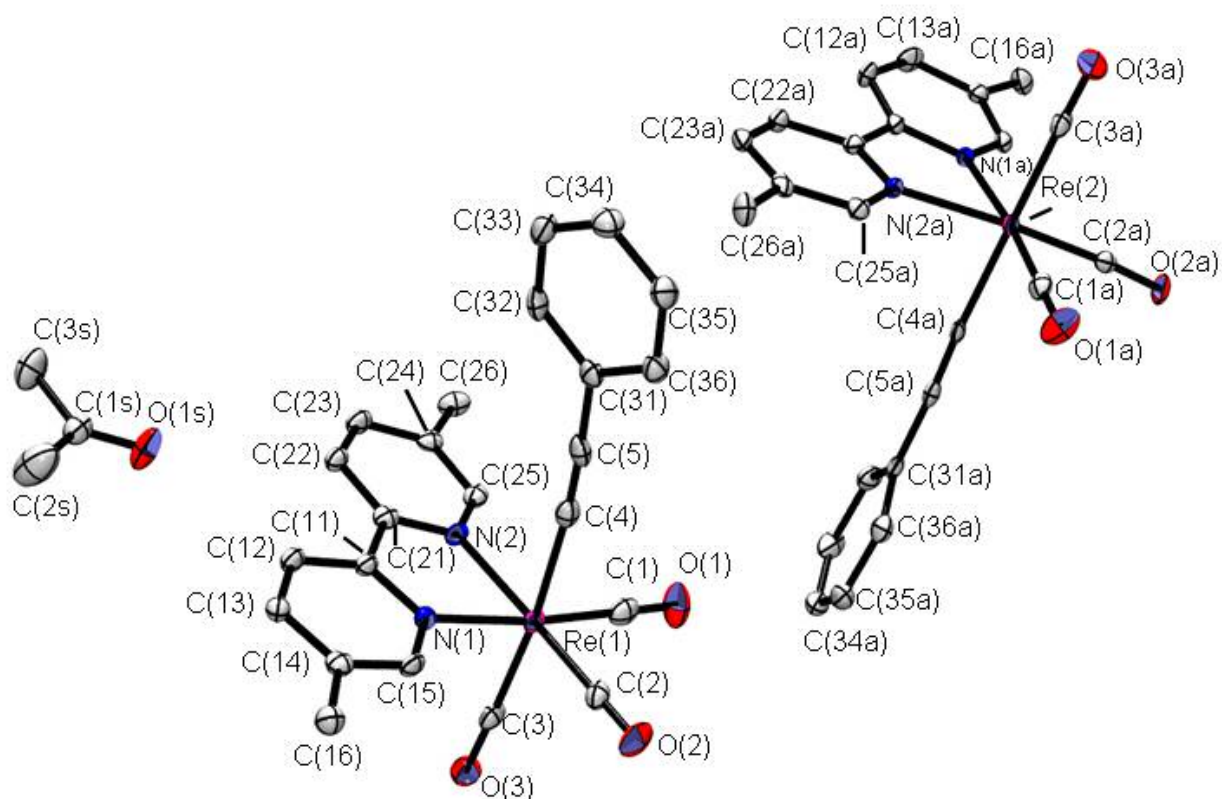
## References:

- [S6] SMART Version 5.630, SAINT+ Version 6.45, and SADABS Version 2.05. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
- [S7] Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

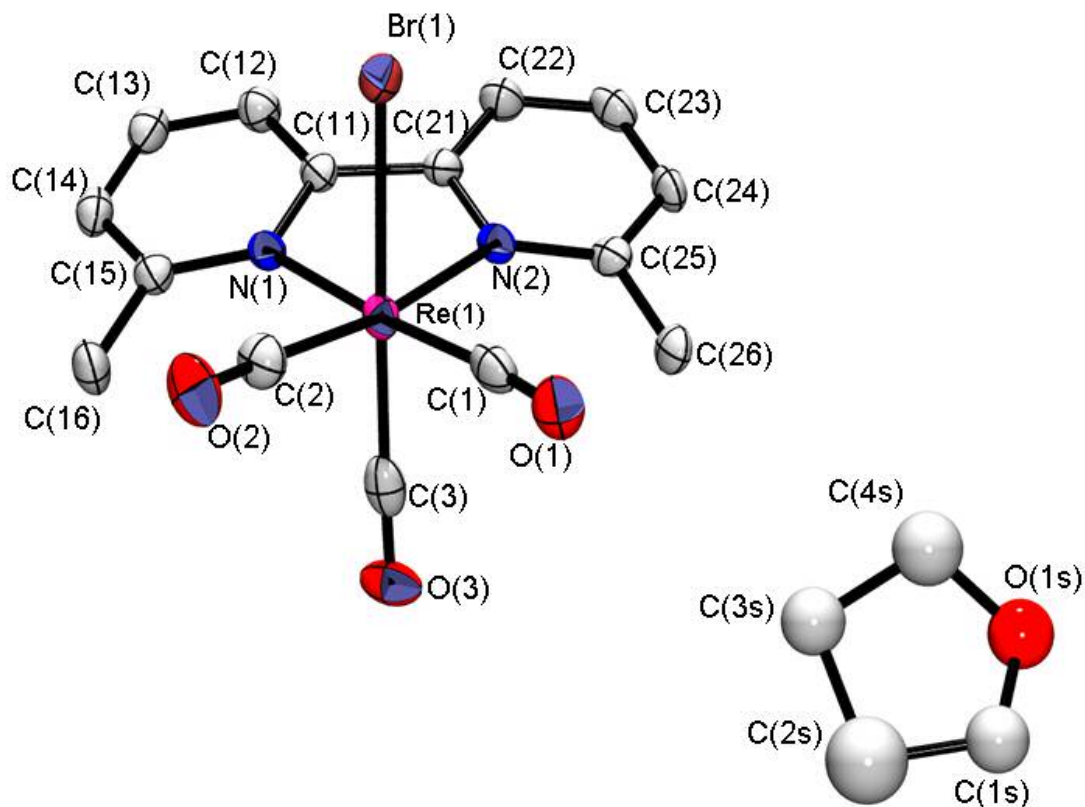
Table S2. Crystallographic Data and Refinement Parameters for (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.5acetone (**A**), (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>Br•0.5THF (**B**), (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.41THF (**C**), (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(PO<sub>2</sub>F<sub>2</sub>) (**D**), (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(HpzAn<sup>Me</sup>)] (**E**), and (bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)-3,5-(CH<sub>2</sub>OCH<sub>2</sub>Cpz<sub>3</sub>)<sub>2</sub>] (**F**).

Compound	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>
Formula	C <sub>24.5</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3.5</sub> Re	C <sub>17</sub> H <sub>16</sub> BrN <sub>2</sub> O <sub>3.5</sub> Re	C <sub>24.64</sub> H <sub>20.28</sub> N <sub>2</sub> O <sub>3.41</sub> Re	C <sub>15</sub> H <sub>12</sub> F <sub>2</sub> N <sub>2</sub> O <sub>5</sub> PRe	C <sub>27</sub> H <sub>22</sub> N <sub>5</sub> O <sub>3</sub> Re	C <sub>45</sub> H <sub>37</sub> N <sub>14</sub> O <sub>5</sub> Re
Formula weight	584.63	570.43	585.11	555.44	650.70	1040.09
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P -1	P -1	P 21/n	P 21/n	C 2/c	P2(1)/c
a, Å	10.4542(5)	8.2628(2)	16.52200(10)	13.2407(2)	16.4742(4)	18.2497(7)
b, Å	11.2095(6)	9.5792(2)	13.81230(10)	8.89470(10)	14.2705(3)	10.8047(4)
c, Å	19.9781(11)	11.4401(2)	19.5082(2)	14.9325(2)	21.3045(5)	23.2347(9)
α, deg	77.721(3)	79.7850(10)	90	90	90	90
β, deg	82.260(2)	88.9520(10)	104.4480(10)	104.3370(10)	91.8490(10)	107.3970(10)
γ, deg	73.989(3)	87.2710(10)	90	90	90	90
V, Å <sup>3</sup>	2191.7(2)	890.09(3)	4311.11(6)	1703.86(4)	5006.0(2)	4371.9(3)
Z	4	2	8	4	8	4
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	296(2)
ρ calcd, Mg m <sup>-3</sup>	1.772	2.128	1.803	2.165	1.727	1.580
λ, Å	1.54178	1.54178	1.54178	1.54178	1.54178	0.71073 <sup>c</sup>
μ (Cu Kα), mm <sup>-1</sup>	11.101	16.167	11.284	15.330	9.815	2.843
R[I>2σ(I)] <sup>a</sup> (all data)	0.0193 (0.0206)	0.0342 (0.0387)	0.0208 (0.0224)	0.0237 (0.0274)	0.0285 (0.0330)	0.0401 (0.0580)
wR <sup>b</sup> (all data)	0.0477 (0.0484)	0.0816 (0.0836)	0.0471 (0.0477)	0.0553 (0.0567)	0.0606 (0.0622)	0.0978 (0.1062)

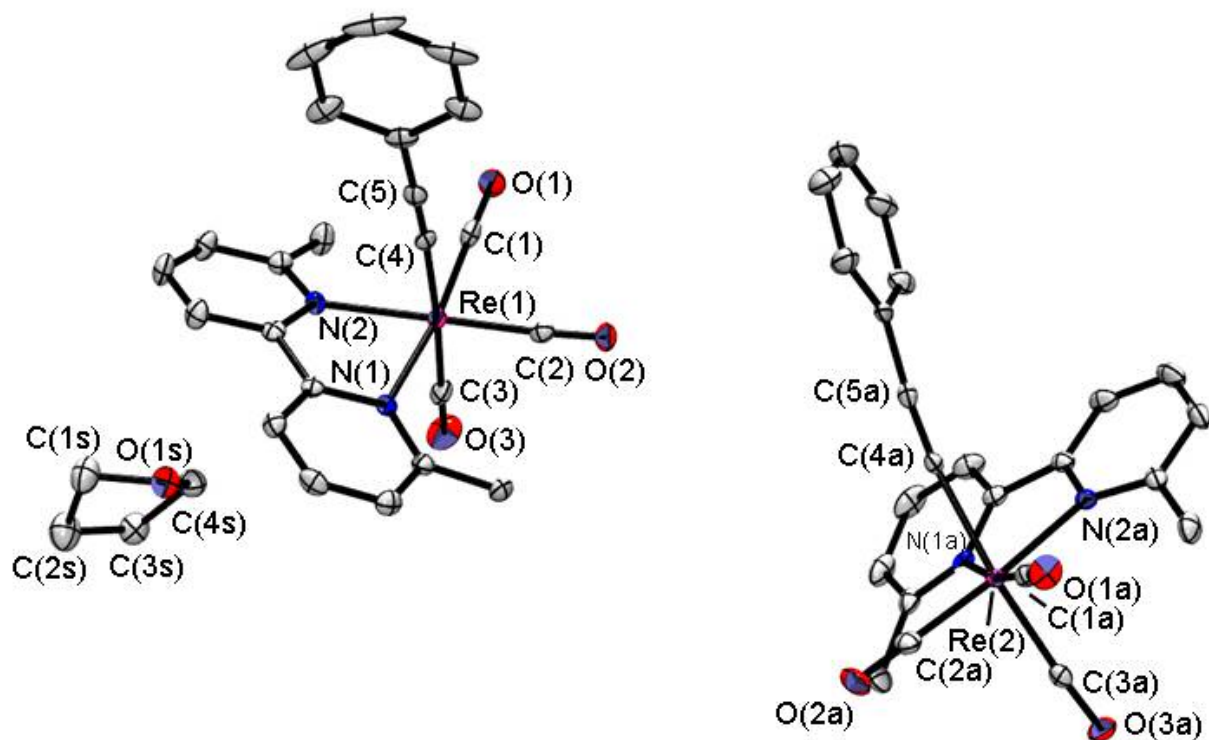
<sup>a</sup> R =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> wR =  $[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$  <sup>c</sup> Mo Kα



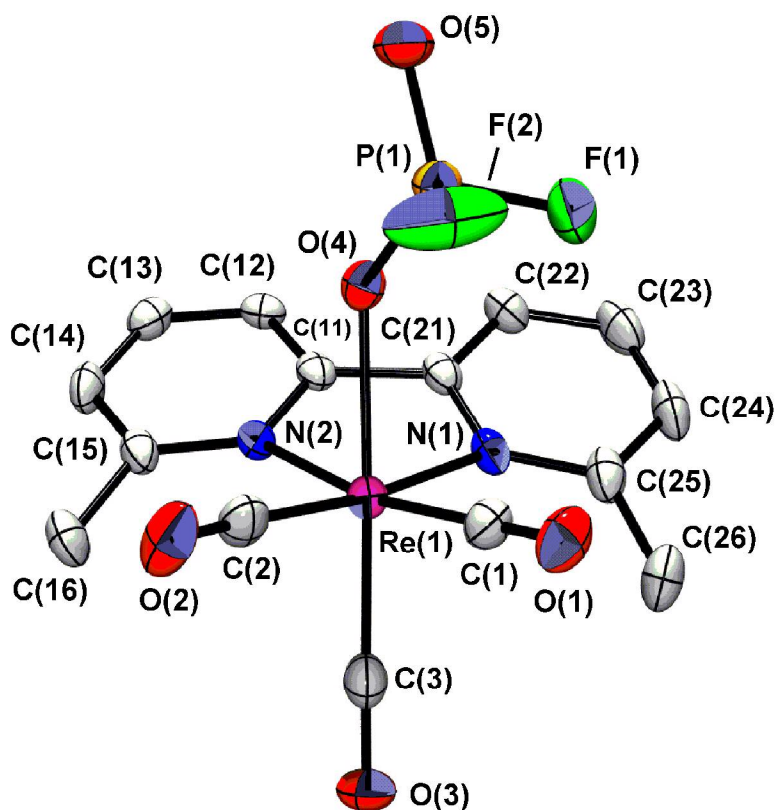
**Figure S1.** ORTEP diagram (50% probability ellipsoids) with atom labeling for (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.5 acetone. Hydrogens removed for clarity. Selected bond distances (Å): Re(1)-C(1) = 1.930(4), Re(1)-C(2) = 1.920(3), Re(1)-C(3) = 1.957(4), Re(1)-C(4) = 2.137(4), Re(1)-N(1) = 2.175(3), Re(1)-N(2) = 2.186(2), C(1)-O(1) = 1.148(4), C(2)-O(2) = 1.151(4), C(3)-O(3) = 1.153(4), C(4)-C(5) = 1.204(5), Re(2)-C(1a) = 1.923(4), Re(2)-C(2a) = 1.909(3), Re(2)-C(3a) = 1.971(3), Re(2)-C(4a) = 2.137(3), Re(2)-N(1a) = 2.184(2), Re(2)-N(2a) = 2.195(2), C(1a)-O(1a) = 1.143(4), C(2a)-O(2a) = 1.149(4), C(3a)-O(3a) = 1.142(4), C(4a)-C(5a) = 1.206(5). Selected angles (deg): C(2)-Re(1)-C(1) = 87.49(14), C(2)-Re(1)-C(3) = 91.42(13), C(1)-Re(1)-C(3) = 92.99(14), C(2)-Re(1)-C(4) = 91.08(13), C(1)-Re(1)-C(4) = 93.33(13), C(2)-Re(1)-N(1) = 98.59(12), C(3)-Re(1)-N(1) = 89.63(12), C(4)-Re(1)-N(1) = 83.85(11), C(1)-Re(1)-N(2) = 98.99(12), C(3)-Re(1)-N(2) = 92.36(11), C(4)-Re(1)-N(2) = 84.45(11), N(1)-Re(1)-N(2) = 74.75(10), C(5)-C(4)-Re(1) = 174.2(3), C(2a)-Re(2)-C(1a) = 85.06(13), C(2a)-Re(2)-C(3a) = 91.00(13), C(1a)-Re(2)-C(3a) = 91.73(14), C(2a)-Re(2)-C(4a) = 88.51(12), C(1a)-Re(2)-C(4a) = 89.24(13), C(2a)-Re(2)-N(1a) = 101.63(11), C(3a)-Re(2)-N(1a) = 89.70(11), C(4a)-Re(2)-N(1a) = 89.40(10), C(1a)-Re(2)-N(2a) = 98.70(12), C(3a)-Re(2)-N(2a) = 94.43(11), C(4a)-Re(2)-N(2a) = 85.99(10), N(1a)-Re(2)-N(2a) = 74.49(9), C(5a)-C(4a)-Re(2) = 175.4(3).



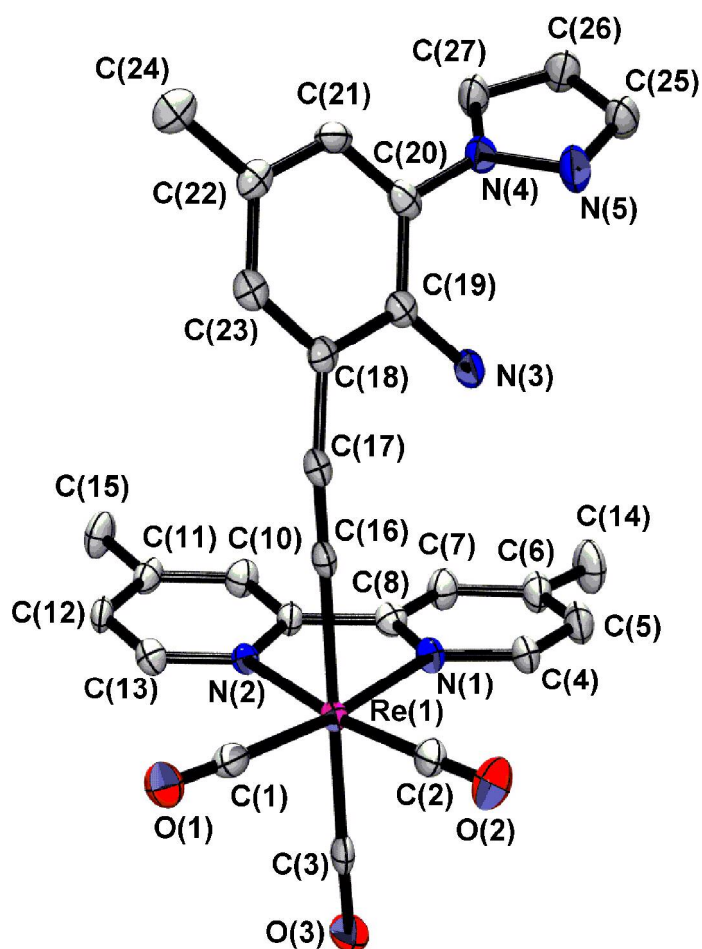
**Figure S2.** Asymmetric unit with atom labeling of (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(Br)•0.5 THF. Hydrogens removed for clarity. Thermal ellipsoids are drawn at 50% probability. Only one component of the disorder of THF is shown. Selected bond distances (Å): Re(1)-C(1) = 1.922(8), Re(1)-C(2) = 1.925(7), Re(1)-C(3) = 1.930(9), Re(1)-N(1) = 2.205(5), Re(1)-N(2) = 2.208(5), Re(1)-Br(1) = 2.6115(8), C(1)-O(1) = 1.149(9), C(2)-O(2) = 1.144(9), C(3)-O(3) = 1.121(9). Selected angles (deg): C(1)-Re(1)-C(2) = 82.0(3), C(1)-Re(1)-C(3) = 88.0(3), C(2)-Re(1)-C(3) = 91.6(3), C(1)-Re(1)-N(2) = 102.3(2), C(3)-Re(1)-N(2) = 95.3(2), C(2)-Re(1)-N(1) = 100.5(3), C(3)-Re(1)-N(1) = 94.8(2), N(2)-Re(1)-N(1) = 74.9(2), C(1)-Re(1)-Br(1) = 91.4(2), C(2)-Re(1)-Br(1) = 89.7(2), N(2)-Re(1)-Br(1) = 83.43(14), N(1)-Re(1)-Br(1) = 85.73(14), C(3)-Re(1)-Br(1) = 178.5(2).



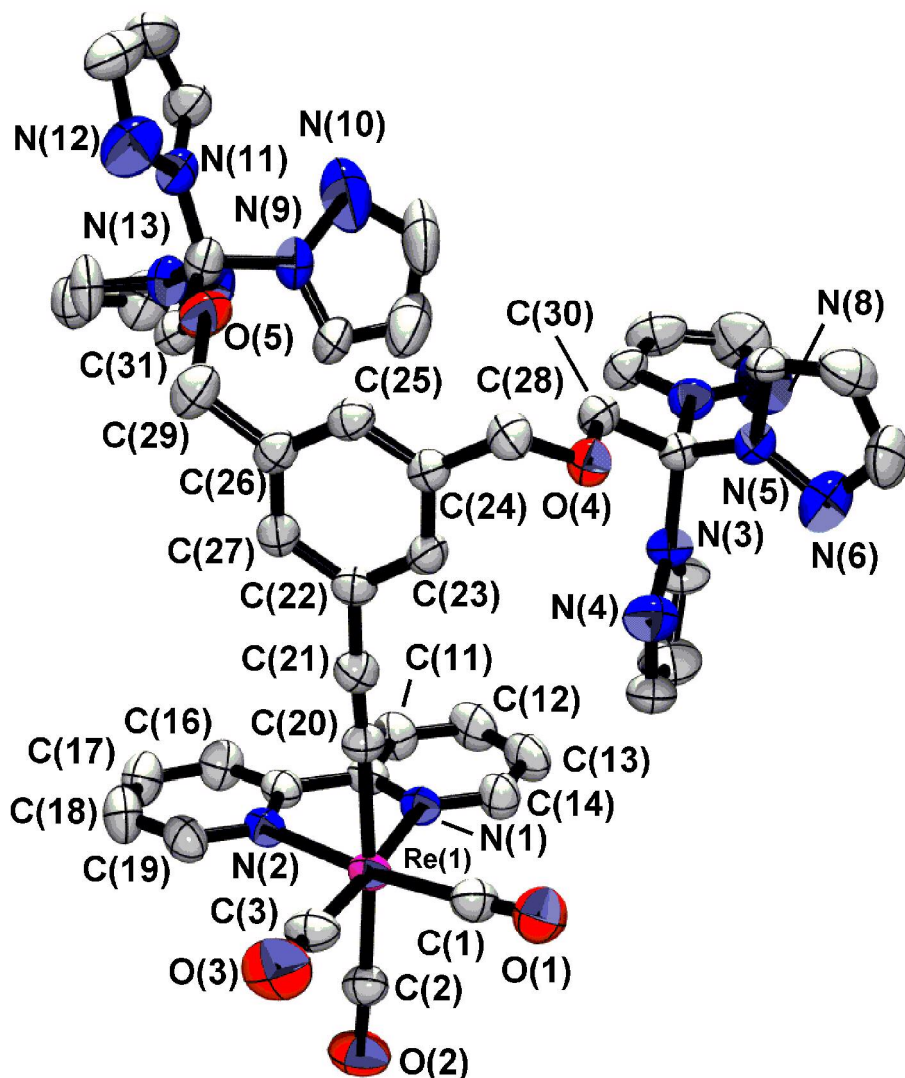
**Figure S3.** ORTEP diagram (50% probability ellipsoids) with atom labeling of (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.41THF with hydrogens removed for clarity. Selected bond distances (Å): Re(1)-C(1) = 1.920(4), Re(1)-C(2) = 1.916(3), Re(1)-C(3) = 1.967(3), Re(1)-C(4) = 2.127(3), Re(1)-N(1) = 2.209(2), Re(1)-N(2) = 2.211(3), C(1)-O(1) = 1.149(4), C(2)-O(2) = 1.147(4), C(3)-O(3) = 1.138(4), C(4)-C(5) = 1.211(5), Re(2)-C(1a) = 1.914(3), Re(2)-C(2a) = 1.921(3), Re(2)-C(3a) = 1.966(3), Re(2)-C(4a) = 2.143(3), Re(2)-N(1a) = 2.212(2), Re(2)-N(2a) = 2.212(3), C(1a)-O(1a) = 1.149(4), C(2a)-O(2a) = 1.149(4), C(3a)-O(3a) = 1.147(4), C(4a)-C(5a) = 1.201(4). Selected angles (deg): C(2)-Re(1)-C(1) = 83.09(13), C(2)-Re(1)-C(3) = 90.80(13), C(1)-Re(1)-C(3) = 91.51(14), C(2)-Re(1)-C(4) = 92.08(13), C(1)-Re(1)-C(4) = 91.13(13), C(2)-Re(1)-N(1) = 102.03(11), C(3)-Re(1)-N(1) = 95.41(12), C(4)-Re(1)-N(1) = 81.72(10), C(1)-Re(1)-N(2) = 99.63(12), C(3)-Re(1)-N(2) = 92.35(12), C(4)-Re(1)-N(2) = 84.65(10), N(1)-Re(1)-N(2) = 74.87(9), C(5)-C(4)-Re(1) = 177.0(3), C(2a)-Re(2)-C(1a) = 85.65(14), C(2a)-Re(2)-C(3a) = 91.57(13), C(1a)-Re(2)-C(3a) = 93.52(13), C(2a)-Re(2)-C(4a) = 93.73(12), C(1a)-Re(2)-C(4a) = 92.04(12), C(2a)-Re(2)-N(1a) = 100.12(12), C(3a)-Re(2)-N(1a) = 94.57(11), C(4a)-Re(2)-N(1a) = 81.13(10), C(1a)-Re(2)-N(2a) = 99.09(12), C(3a)-Re(2)-N(2a) = 89.79(11), C(4a)-Re(2)-N(2a) = 82.73(10), N(1a)-Re(2)-N(2a) = 74.79(9), C(5a)-C(4a)-Re(2) = 168.1(3).



**Figure S4.** ORTEP diagram (50% probability ellipsoids) with atom labeling of (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>(PO<sub>2</sub>F<sub>2</sub>) with hydrogens removed for clarity. Selected bond distances (Å): Re(1)-C(1) = 1.923(5), Re(1)-C(2) = 1.924(5), Re(1)-C(3) = 1.913(5), Re(1)-O(4) = 2.174(3), Re(1)-N(1) = 2.206(3), Re(1)-N(2) = 2.191(3), C(1)-O(1) = 1.147(6), C(2)-O(2) = 1.141(5), C(3)-O(3) = 1.143(5), O(4)-P(1) = 1.467(3), O(5)-P(1) = 1.447(3). Selected angles (deg): C(2)-Re(1)-C(1) = 83.99(18), C(2)-Re(1)-C(3) = 88.08(18), C(1)-Re(1)-C(3) = 88.06(19), C(2)-Re(1)-O(4) = 92.85(15), C(1)-Re(1)-O(4) = 95.13(15), C(2)-Re(1)-N(1) = 101.68(16), C(3)-Re(1)-N(1) = 99.70(16), O(4)-Re(1)-N(1) = 77.06(11), C(1)-Re(1)-N(2) = 98.28(15), C(3)-Re(1)-N(2) = 97.54(16), O(4)-Re(1)-N(2) = 81.42(11), N(1)-Re(1)-N(2) = 75.35(12), O(5)-P(1)-O(4) = 119.88(18).



**Figure S5.** ORTEP diagram (50% probability ellipsoids) with atom labeling for (4,4'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(HpzAn<sup>Me</sup>)]. Hydrogens removed for clarity. Selected bond distances (Å): Re(1)-C(1) = 1.924(5), Re(1)-C(2) = 1.919(5), Re(1)-C(3) = 1.973(5), Re(1)-C(16) = 2.138(5), Re(1)-N(1) = 2.182(4), Re(1)-N(2) = 2.185(4), C(1)-O(1) = 1.153(6), C(2)-O(2) = 1.146(6), C(3)-O(3) = 1.142(6), C(16)-C(17) = 1.197(6). Selected angles (deg): C(2)-Re(1)-C(1) = 88.7(2), C(2)-Re(1)-C(3) = 89.0(2), C(1)-Re(1)-C(3) = 91.53(19), C(2)-Re(1)-C(16) = 94.22(18), C(1)-Re(1)-C(16) = 91.35(18), C(2)-Re(1)-N(1) = 98.48(17), C(3)-Re(1)-N(1) = 92.07(17), C(16)-Re(1)-N(1) = 84.67(15), C(1)-Re(1)-N(2) = 98.34(18), C(3)-Re(1)-N(2) = 93.95(17), C(16)-Re(1)-N(2) = 82.51(15), N(1)-Re(1)-N(2) = 74.30(14), C(17)-C(16)-Re(1) = 173.4(4).



**Figure S6.** ORTEP diagram (50% probability ellipsoids) with atom labeling for (bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>3</sub>)-3,5-(CH<sub>2</sub>OCH<sub>2</sub>Cpz<sub>3</sub>)<sub>2</sub>]. Hydrogens removed for clarity. Selected bond distances (Å): Re(1)-C(1) = 1.908(5), Re(1)-C(2) = 1.943(5), Re(1)-C(3) = 1.911(5), Re(1)-C(20) = 2.140(4), Re(1)-N(1) = 2.176(3), Re(1)-N(2) = 2.166(4), C(1)-O(1) = 1.156(6), C(2)-O(2) = 1.142(6), C(3)-O(3) = 1.143(6), C(20)-C(21) = 1.193(6). Selected angles (deg): C(2)-Re(1)-C(1) = 92.3(2), C(2)-Re(1)-C(3) = 86.25(18), C(1)-Re(1)-C(3) = 88.3(2), C(3)-Re(1)-C(20) = 93.01(16), C(1)-Re(1)-C(20) = 92.56(18), C(2)-Re(1)-N(1) = 93.19(15), C(1)-Re(1)-N(1) = 97.10(16), C(20)-Re(1)-N(1) = 87.09(13), C(2)-Re(1)-N(2) = 90.28(17), C(3)-Re(1)-N(2) = 100.10(17), C(20)-Re(1)-N(2) = 85.05(14), N(1)-Re(1)-N(2) = 74.53(13), C(21)-C(20)-Re(1) = 176.0(3).

As one reviewer pointed out, the rhenium-alkynyl appears bent towards the bipyridyl group in some cases while in other cases it is not. We attribute this effect to intermolecular noncovalent (packing) interactions rather to any intramolecular interaction, since in two cases, (5,5'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.5acetone and (6,6'-Me<sub>2</sub>bipy)Re(CO)<sub>3</sub>[C≡C(C<sub>6</sub>H<sub>5</sub>)]•0.41THF, there are two independent molecules in the unit cell, yet each exhibits a different degree of alkynyl “bending” (crudely measured by the Re-C(alkynyl)-C<sub>ipso</sub>(Phenyl) angle, as collected in Table S3).

Table S3. Rhenium-Alkynyl “bending” Angles.

Compound	Re-C(alkynyl)-C <sub>ipso</sub> (Phenyl) (deg)
(5,5'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]•0.5acetone ( <b>A</b> )	173.88 (molecule A)
	172.71 (molecule B)
(6,6'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]•0.41THF ( <b>C</b> )	163.97 (molecule A)
	176.71 (molecule B)
(4,4'-Me <sub>2</sub> bipy)Re(CO) <sub>3</sub> [C≡C(HpzAn <sup>Me</sup> )] ( <b>E</b> )	168.70
(bipy)Re(CO) <sub>3</sub> [C≡C(C <sub>6</sub> H <sub>5</sub> )]-3,5-(CH <sub>2</sub> OCH <sub>2</sub> Cp <sub>3</sub> ) <sub>2</sub> ] ( <b>F</b> )	174.84