Supplementary Information

Selective formation of formamidines, carbodiimides and formimidates from isocyanide complexes of Mn(I) mediated by Ag$_2$O

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Synthesis and characterization of the new compounds

General Considerations

All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer Spectrum 100 and Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. Mass spectra were recorded on Bruker model Impact II (ESI and APCI) and MAT95XP (FAB) apparatus. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants $J$ are given in Hz. NMR multiplicities are abbreviated as follows: $s = $ singlet, $d = $ doublet, $dd = $ doublet of doublets, $t = $ triplet, $q = $ quartet, $m = $ multiplet, $br = $ broad. Chemical shifts of the NMR spectra were referenced to internal SiMe$_4$ ($^1$H and $^{13}$C) or external H$_3$PO$_4$ ($^{31}$P). Assignments are based on $^1$H,$^1$H-COSY, $^1$H,$^{13}$C-HMBC, $^1$H,$^{13}$C-HSQC and DEPT experiments. All reagents were obtained commercially and used without further purification. Compounds $[3a]$CO$_4$ and $[3d]$ClO$_4$ were prepared as described in reference 12b of the manuscript.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of such materials should be prepared and these should be handled with great caution.

For the NMR spectra the atom-labeling in 2,2′-bipyridine ligand is as follows:

Synthesis of compound $[3b]$ClO$_4$. To a solution of fac-$[\text{Mn}\{\text{C(NHC}_{10}\text{H}_{7})(\text{NHCH}_{3})\}($bipy$)($CO$_3$)$]$ClO$_4$ ($[2b]$ClO$_4$, 0.10 g, 0.17 mmol) in CH$_2$Cl$_2$ (10 mL)
Ag₂O (21 mg, 0.09 mmol) was added, and the resulting mixture stirred for 3 h. The solution was filtered and then concentrated under vacuum to 3 mL. Addition of hexane (10 mL) afforded a yellow solid. Yield: 95 mg (95%). The ¹H NMR indicates the presence of two isomers in an approximate ratio 4:1. The major isomer (shown in the figure) corresponds to coordination of the formamidine through the N-Naphthyl group, whereas the minor one features N-Methyl coordination of the corresponding formamidine tautomer. A sample of the major isomer for ¹H NMR measurements was obtained by successive recrystallizations in CH₂Cl₂/Et₂O. IR (CH₂Cl₂, cm⁻¹): ν(CO) 2036 (vs), 1946 (s), 1935 (s). ¹H NMR (300 MHz, CD²Cl₂, δ, ppm): Major isomer (80%): δ = 8.99 (d, 3J(H,H) = 5.2 Hz, 1H, Hₐ bipy), 8.83 (d, 3J(H,H) = 5.2 Hz, 1H, Hₐ bipy), 8.20-8.16 (m, 2H, Hₐ bipy), 8.11 (t, 3J(H,H) = 7.6 Hz, 1H, Hₖ bipy), 8.04 (t, 3J(H,H) = 7.6 Hz, 1H, Hₚ bipy), 7.75-7.73 (m, 1H, Naph), 7.59-7.54 (m, 2H, Hₖ bipy and Naph), 7.48-7.39 (m, 4H, Hₖ bipy and Naph). Minor isomer (20%): δ = 9.22 (d, 3J(H,H) = 5.0 Hz, 2H, Hₐ bipy), 8.36 (d, 3J(H,H) = 7.9 Hz, 2H, Hₚ bipy), 8.22 (t, 3J(H,H) = 8.1 Hz, 2H, Hₖ bipy), 7.77-7.70 (m, Hₚ bipy), 7.10-7.08 (m, 2H, Naph), 7.19 (d, 3J(H,H) = 13.0 Hz, 1H, NCHN). ¹³C{¹H} NMR (100.61 MHz, CD²Cl₂, ppm): Major isomer (80%): δ = 220.1 (s, CO), 218.2 (s, CO), 159.3 (s, NCHN), 156.1 (s, C₁ bipy), 154.0 (s, C₃ bipy), 141.9 (s, C_ipso Naph), 140.5, 140.4 (s, C₃ bipy), 134.0, 131.8 (s, C Naph), 130.8, 128.2, 126.9 (s, CH Naph), 127.8, 127.7 (s, C₄ bipy), 123.9, 123.8 (s, C₂ bipy), 122.9, 122.0 (s, CH Naph), 32.9 (s, NCH₃). Minor isomer (20%): 156.2 (s, C₁ bipy), 153.9 (s, C₃ bipy), 140.9 (s, C₃ bipy), 124.5 (s, C₂ bipy), 118.9 (s, CH Naph), 114.0 (s, CH Naph), 39.7 (s, NCH₃). MS (ESI): m/z: 479.0901 [M - ClO₄]⁺

Synthesis of compound [3c]ClO₄. This was similarly prepared starting from fac-[Mn{CNH(4-MeOC₆H₄)(NHCH₃)}(bipy)(CO)₃]ClO₄ ([2c]ClO₄, 0.10 g, 0.18 mmol) and Ag₂O (21 mg, 0.09 mmol). Yield: 93 mg (93%). IR (CH₂Cl₂, cm⁻¹): ν(CO) 2036 (vs), 1946 (s), 1938 (sh). ¹H NMR (400 MHz, CD₂Cl₂, ppm): Major isomer (60%): δ = 8.92 (d, 3J(H,H) = 5.4 Hz, 2H, Hₐ bipy), 8.27-8.25 (m, 2H, Hₚ bipy), 8.15 (t, 3J(H,H) = 7.3 Hz, 2H, Hₖ bipy), 7.58 (t, 3J(H,H) = 6.7 Hz, 2H, Hₖ bipy), 7.11 (d, 3J(H,H) = 13.1 Hz, 1H,
NCHN), 6.55 (d, $^3J(H,H) = 8.7$ Hz, 2H, C$_6$H$_5$), 5.96 (d, $^3J(H,H) = 8.7$ Hz, 2H, C$_6$H$_4$), 4.59 (br, 1H, NH), 3.69 (s, 3H, OCH$_3$), 2.79 (d, $^3J(H,H) = 4.9$ Hz, 3H, NCH$_3$). Minor isomer (40%): $\delta = 9.18$ (d, $^3J(H,H) = 5.4$ Hz, 2H, H$_A$ bipy), 8.22 (t, $^3J(H,H) = 8.4$ Hz, 2H, Hc bipy), 7.72 (t, $^3J(H,H) = 8.4$ Hz, 2H, C$_6$H$_4$), 6.99 (br, 1H, NH), 6.90 (d, $^3J(H,H) = 10.7$ Hz, 1H, NCHN), 6.82 (d, $^3J(H,H) = 8.9$ Hz, 2H, C$_6$H$_4$), 3.75 (s, 3H, OCH$_3$), 2.60 (s, 3H, NCH$_3$).

**13C$^{1H}$ NMR (100.61 MHz, CD$_2$Cl$_2$, ppm):**

Major isomer (75%): $\delta = 220.1$ (s, CO), 218.0 (s, CO), 158.3 (C ipso), 159.7 (s, NCHN), 156.0 (s, C$_1$ bipy), 153.9 (s, C$_5$ bipy), 140.5 (s, C$_3$ bipy), 137.0 (s, C$_{ipso}$), 128.0 (s, C$_4$ bipy), 125.0 (s, C$_6$H$_4$), 123.8 (s, C$_2$ bipy), 115.6 (s, C$_6$H$_5$), 56.0 (s, OCH$_3$), 32.7 (s, NCH$_3$).

Minor isomer (25%): 157.7 (s, C ipso), 156.2 (s, C$_1$ bipy), 153.8 (s, C$_5$ bipy), 153.7 (s, NCHN), 140.9 (s, C$_3$ bipy), 132.0 (s, C$_{ipso}$), 128.2 (s, C$_4$ bipy), 124.3 (s, C$_2$ bipy), 120.5 (s, C$_6$H$_4$), 115.4 (s, C$_6$H$_4$), 56.0 (s, OCH$_3$), 39.0 (s, NCH$_3$).

**MS (ESI):** $m/z$: 459.0863 [M – ClO$_4$]$^+$

**Synthesis of compound [3e]ClO$_4$.** This was similarly prepared starting from fac-

$[\text{Mn(CNH(CH$_2$C$_6$H$_5$)(NHCH$_3$))(CO)$_3$(bipy)}]\text{ClO}_4$ ([2e]ClO$_4$, 0.10 g, 0.18 mmol) and Ag$_2$O (21 mg, 0.09 mmol), maintaining the reaction mixture at 0 °C. Yield: 63 mg (63%). Crystals of [3e]ClO$_4$ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound. Yield: 63 mg (63%). IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu$(CO) 2036 (vs), 1943 (s), 1937 (sh).

**1H NMR (400 MHz, CD$_2$Cl$_2$, ppm):** $\delta = 9.07$ (d, $^3J(H,H) = 4.6$ Hz, 2H, H$_A$ bipy), 8.28 (d, $^3J(H,H) = 7.9$ Hz, 2H, H$_B$ bipy), 8.14 (t, $^3J(H,H) = 7.6$ Hz, 2H, Hc bipy), 7.62 (t, $^3J(H,H) = 6.1$ Hz, 2H, H$_B$ bipy), 7.30 (s, 3H, C$_6$H$_5$), 7.00 (s, 2H, C$_6$H$_5$), 6.42 (d, $^3J(H,H) = 12.0$ Hz, 1H, NCHN), 6.06 (br, 1H, NH), 4.19 (d, $^3J(H,H) = 4.6$ Hz, 2H, CH$_2$Bn), 2.45 (s, 3H, NCH$_3$).

**13C$^{1H}$ NMR (100.61 MHz, CD$_2$Cl$_2$, ppm):** $\delta = 219.9$ (s, CO), 217.6 (s, CO), 157.4 (s, NCHN), 155.8 (s, C$_1$ bipy), 153.6 (s, C$_3$ bipy), 140.5 (s, C$_3$ bipy), 138.3 (s, C$_{ipso}$), 129.2, 128.2, 127.8 (s, Ph), 127.9 (s, C$_4$ bipy), 123.9 (s, C$_2$ bipy), 49.4 (s, CH$_2$Bn), 38.5 (s, NCH$_3$). MS (ESI): $m/z$: 443.0924 [M – ClO$_4$]$^+$

**Liberation of formamidine 4b.** A solution of [3b]ClO$_4$ (80 mg, 0.14 mmol) in 15 ml of CH$_3$CN was heated under reflux for 45 min. The solution was then evaporated to dryness under vacuum. Extraction with diethyl ether (2 x 5 mL) afforded 4b as a white
solid. The remaining residue corresponding to fac-[Mn(NCMe)(bipy)(CO)₃]ClO₄ can be transformed to [2b]ClO₄ by reaction with 2-Naphthyl isocyanide. Yield: 21 mg (85%). ¹H NMR (400 MHz, CD₂Cl₂, ppm, 298K): δ = 7.79-7.72 (4H, NCHN and Naph), 7.42 (t, ³J(H,H) = 7.4 Hz, 1H, Naph), 7.33 (t, ³J(H,H) = 7.2 Hz, 1H, Naph), 7.26 (s, 1H, Naph), 7.21 (d, ³J(H,H) = 7.6 Hz, 1H, Naph), 4.75 (br, 1H, NH), 3.00 (s, 3H, CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, ppm, 193K): δ = 151.6 (s, NCHN), 149.3, 133.9, 129.5 (s, C Naph), 128.3, 127.2, 126.6, 125.8, 123.6, 123.0, 115.2 (s, CH Naph), 28.0 (s, NCH₃). MS (APCI): m/z: 185.1078 [M + H]^+.

Liberation of formamidine 4c. This was similarly performed from [3c]ClO₄ (80 mg, 0.14 mmol). Yield: 19 mg (84%). ¹H NMR (400 MHz, CD₂Cl₂, ppm, 298K): δ = 7.61 (s, 1H, NCHN), 6.82 (q, AB, C₆H₄), 4.66 (br, 1H, NH), 3.74 (s, 3H, OCH₃), 2.91 (s, 3H, CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, ppm, 193K): δ = 154.7 (s, C ipso), 151.0 (s, NCHN), 144.7 (s, C ipso), 121.4, 113.5 (s, C₆H₄), 55.1 (s, OCH₃), 27.9 (s, NCH₃). MS (APCI): m/z: 165.1031 [M + H]^+.

Formation of carbodiimide 6a. To a solution of fac-[Mn{CNH(C₆H₅)(NHCH₃)}(bipy)(CO)₃]ClO₄ ([2a]ClO₄, 0.20 g, 0.38 mmol) in CH₂Cl₂ (10 mL) an excess of KOH (0.2 g, 3.56 mmol) was added and the resulting mixture stirred for 45 min. The formation of the deprotonated diaminocarbene (formamidinile) derivative 5a was monitored by IR spectroscopy. The solution was then filtered and poured into a Schlenk containing Ag₂O (88 mg, 0.38 mmol). The mixture was stirred for 1 h. The solvent was then evaporated to dryness under vacuum and the residue extracted with hexane (2 x 5 mL) and filtered. The solution was evaporated to dryness and the residue chromatographed on a silica gel column. Elution with CH₂Cl₂ gave the carbodiimide 6a as a colorless oil. Yield: 33 mg (66%). IR (CH₂Cl₂, cm⁻¹): ν(NCN) 2146 (s), 2134 (sh). ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 7.29 (t, ³J(H,H) = 7.8 Hz, 2H, m-Ph), 7.11 (t, ³J(H,H) = 7.4 Hz, 1H, p-Ph), 7.08 (d, ³J(H,H) = 7.5 Hz, 2H, o-Ph), 3.15 (s, 3H, NCH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, ppm): δ = 141.3 (s, C ipso), 136.7 (s, NCN), 129.9 (s, m-Ph), 125.1 (s, p-Ph), 124.0 (s, o-Ph), 32.9 (s, NCH₃). MS (APCI): m/z: 133.0791 [M + H]^+.
Formation of carbodiimide 6b. This was similarly obtained using \( \text{fac-}[\text{Mn}(\text{C(NH}_{10}\text{H}_{7})(\text{NHCH}_{3})](\text{CO})_{3}(\text{bipy})]\text{ClO}_4 \) ([2b]ClO_4, 0.20 g, 0.35 mmol) and \( \text{Ag}_2\text{O} \) (80 mg, 0.35 mmol). Yield: 30 mg (48%). IR (CH_2Cl_2, cm^{-1}): \( \nu(\text{NCN}) 2141 \text{ (s)} \). 

\(^1\)H NMR (400 MHz, CD_2Cl_2, ppm): \( \delta = 7.81-7.73 \text{ (3H, Naph)}, 7.49-7.38 \text{ (3H, Naph)}, 7.26 \text{ (dd, }^3J(\text{H,H}) = 8.7 \text{ Hz, }^4J(\text{H,H}) = 2.2 \text{ Hz, 1H, Naph)}, 3.20 \text{ (s, 3H, NCH}_3 \). \n
\(^{13}\)C{\(^1\)H} NMR (100.61 MHz, CD_2Cl_2, ppm): \( \delta = 138.8, 134.7, 131.5 \text{ (s, C Naph)}, 136.6 \text{ (s, NCN)}, 129.7, 128.2, 127.6, 127.1, 125.6, 123.8, 120.8 \text{ (s, CH Naph)}, 33.0 \text{ (s, NCH}_3 \). MS (APCI): \( m/z: 183.0918 [\text{M} + \text{H}]^+ \).

Formation of carbodiimide 6c. This was similarly obtained using \( \text{fac-}[\text{Mn}(\text{CNH}(\text{p-MeOC}_{6}\text{H}_{4}))(\text{NHCH}_{3})](\text{CO})_{3}(\text{bipy})]\text{ClO}_4 \) ([2c]ClO_4, 0.20 g, 0.36 mmol) and \( \text{Ag}_2\text{O} \) (83 mg, 0.36 mmol). Yield: 31 mg (53%). IR (CH_2Cl_2, cm^{-1}): \( \nu(\text{NCN}) 2140 \text{ (s)}, 2120 \text{ (sh)} \). 

\(^1\)H NMR (400 MHz, CD_2Cl_2, ppm): \( \delta = 7.01 \text{ (d, }^3J(\text{H,H}) = 8.7 \text{ Hz, 2H, }\text{C}_6\text{H}_4\), 6.82 \text{ (d, }^3J(\text{H,H}) = 8.7 \text{ Hz, 2H, }\text{C}_6\text{H}_4\), 3.77 \text{ (s, 3H, OCH}_3 \), 3.12 \text{ (s, 3H, NCH}_3 \). 

\(^{13}\)C{\(^1\)H} NMR (100.61 MHz, CD_2Cl_2, ppm): \( \delta = 157.5, 133.6 \text{ (s, C ipso)}, 137.8 \text{ (s, NCN)}, 124.9 \text{ (s, CH }\text{C}_6\text{H}_4\), 115.1 \text{ (s, CH }\text{C}_6\text{H}_4\), 56.0 \text{ (s, OCH}_3 \), 33.1 \text{ (s, NCH}_3 \). MS (APCI): \( m/z: 163.0868 [\text{M} + \text{H}]^+ \).

Formation of carbodiimide 6f. This was similarly obtained using \( \text{fac-}[\text{Mn}(\text{C(NH}_{6}\text{H}_3(\text{CH}_3)\text{Cl})(\text{NHCH}_{3})](\text{CO})_{3}(\text{bipy})]\text{ClO}_4 \) ([2f]ClO_4, 0.20 g, 0.36 mmol) and \( \text{Ag}_2\text{O} \) (83 mg, 0.36 mmol). Yield: 27 mg (47%). IR (CH_2Cl_2, cm^{-1}): \( \nu(\text{NCN}) 2166 \text{ (s)}, 2148 \text{ (sh)} \). 

\(^1\)H NMR (400 MHz, CD_2Cl_2, ppm): \( \delta = 7.00 \text{ (d, }^3J(\text{H,H}) = 7.5 \text{ Hz, 2H, m-Xylyl)}, 6.90 \text{ (t, }^3J(\text{H,H}) = 6.9 \text{ Hz, 1H, p-Xylyl)}, 3.08 \text{ (s, 3H, NCH}_3 \), 2.31 \text{ (s, 6H, CH}_3\text{Xylyl)}. \n
\(^{13}\)C{\(^1\)H} NMR (100.61 MHz, CD_2Cl_2, ppm): \( \delta = 157.6, 133.6 \text{ (s, C ipso Xylyl)}, 137.8 \text{ (s, NCN)}, 124.6 \text{ (s, CH }\text{C}_6\text{H}_4\), 115.1 \text{ (s, CH }\text{C}_6\text{H}_4\), 56.0 \text{ (s, OCH}_3 \), 33.1 \text{ (s, NCH}_3 \). MS (APCI): \( m/z: 161.1078 [\text{M} + \text{H}]^+ \).

Formation of carbodiimide 6g. This was similarly prepared using \( \text{fac-}[\text{Mn}(\text{C(NH}_{6}\text{H}_3\text{Cl})(\text{CH}_3))(\text{NHCH}_{3})](\text{CO})_{3}(\text{bipy})]\text{ClO}_4 \) ([2g]ClO_4, 0.20 g, 0.35 mmol) and \( \text{Ag}_2\text{O} \) (80 mg, 0.35 mmol). Yield: 35 mg (56%). IR (CH_2Cl_2, cm^{-1}): \( \nu(\text{NCN}) 2162 \text{ (s)}, 2145 \text{ (sh)} \). 

\(^1\)H NMR (300 MHz, CD_2Cl_2, ppm): \( \delta = 7.22 \text{ (d, }^3J(\text{H,H}) = 7.5 \text{ Hz, 2H, m-Xylyl}), 6.90 \text{ (t, }^3J(\text{H,H}) = 6.9 \text{ Hz, 1H, p-Xylyl)}, 3.08 \text{ (s, 3H, NCH}_3 \), 2.31 \text{ (s, 6H, CH}_3\text{Xylyl)}. \n
\(^{13}\)C{\(^1\)H} NMR (100.61 MHz, CD_2Cl_2, ppm): \( \delta = 157.6, 133.6 \text{ (s, C ipso Xylyl)}, 137.8 \text{ (s, o-Xylyl)}, 128.6 \text{ (s, m-Xylyl)}, 124.6 \text{ (s, p-Xylyl)}, 33.1 \text{ (s, NCH}_3 \), 19.2 \text{ (s, CH}_3\text{Xylyl)}. MS (APCI): \( m/z: 161.1078 [\text{M} + \text{H}]^+ \).
= 8.0 Hz, 1H, m-C₆H₃), 7.07 (d, 3J(H,H) = 7.6 Hz, 1H, m-C₆H₃), 6.93 (t, 3J(H,H) = 7.8 Hz, 1H, p-C₆H₃), 3.13 (s, 3H, NCH₃), 2.30 (s, 3H, CH₃). 13C{¹H} NMR (100.61 MHz, CD₂Cl₂, ppm): δ = 136.8, 134.9, 129.6 (s, C C₆H₃), 129.4 (s, m-C₆H₃), 127.7 (s, m-C₆H₃), 125.0 (s, p-C₆H₃), 32.8 (s, NCH₃), 19.4 (s, CH₃). MS (APCI): m/z: 181.0528 [M + H]⁺

Synthesis of compound 7a. To a solution of fac-[Mn(CNPh)(CO)₃(bipy)]ClO₄ ([1a]ClO₄, 0.10 g, 0.20 mmol) in MeOH (1 mL) a two fold excess of sodium was added (10 mg, 0.43 mmol). The color of the solution instantaneously changed from yellow to red. 15 mL of CH₂Cl₂ were added to the reaction mixture and the resulting solution was then washed with water (3 x 15 mL). The organic phase was dried with Na₂CO₃ and then filtered through diatomaceous earth. The solution was concentrated to 1 mL under vaccum and hexane (5 mL) added to obtain a redish solid. Red crystals of 7a suitable for X-ray diffusion were formed by slow diffusion of hexane into a dichlorometane solution of the compound. Yield: 68 mg (79%). IR (CH₂Cl₂, cm⁻¹): ν(CO) 2008 (vs), 1912 (vs), 1906 (sh). ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 8.71 (d, 3J(H,H) = 5.4 Hz, 2H, Hₐ bipy), 7.96 (d, 3J(H,H) = 8.0 Hz, 2H, Hₐ bipy), 7.80 (t, 3J(H,H) = 7.6 Hz, 2H, Hₗ bipy), 7.11 (t, 3J(H,H) = 6.4 Hz, 2H, Hₘ bipy), 6.86 (t, 3J(H,H) = 7.6 Hz, 2H, m-Ph), 6.74 (t, 3J(H,H) = 7.2 Hz, 1H, p-Ph), 6.25 (d, 3J(H,H) = 7.5 Hz, 2H, o-Ph), 3.30 (s, 3H, OCH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, ppm): δ = 224.7 (s, CO), 213.4 (s, CO), 202.7 (s, NCO), 154.8 (s, C₁ bipy), 154.2 (s, C₅ bipy), 152.6 (s, Cₘₚₙₜ), 137.0 (s, C₃ bipy), 128.7 (s, m-Ph), 124.9 (s, C₄ bipy), 121.7 (s, o-Ph), 121.6 (s, C₂ bipy), 120.1 (s, p-Ph), 52.9 (s, OCH₃). MS (ESI): m/z: 398.0331 [M – OCH₃]⁺

Synthesis of compound 7b. This was prepared in a similar way as 7a from fac-[Mn(CNNaph)(CO)₃(bipy)]ClO₄ ([1b]ClO₄, 0.10 g, 0.18 mmol), methanol (1 mL) and sodium (10 mg, 0.43 mmol). Yield: 72 mg (83%). IR (CH₂Cl₂, cm⁻¹): ν(CO) 2008 (vs), 1912 (vs), 1907 (sh). ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 8.59 (d, 3J(H,H) = 5.0 Hz, 2H, Hₐ bipy), 7.92 (d, 3J(H,H) = 7.9 Hz, 2H, Hₐ bipy), 7.72-7.68 (m, 3H, Hₗ bipy and Naph), 7.46 (d, 3J(H,H) = 8.1 Hz, 1H, Naph), 7.36-7.32 (m, 2H, Naph), 7.27 (t, 3J(H,H) = 7.3 Hz, 1H, Naph), 6.80 (t, 3J(H,H) = 6.3 Hz, 2H, Hₘ bipy), 6.68 (s, 1H, Naph), 6.47 (d, 3J(H,H) = 7.7 Hz, 1H, Naph), 3.37 (s, 3H, OCH₃).
13C\textsuperscript{1}H) NMR (100.61 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): δ = 224.8 (s, CO), 213.3 (s, CO), 203.3 (s, NCO), 154.9 (s, C\textsubscript{1} bipy), 154.2 (s, C\textsubscript{5} bipy), 150.2, 134.9, 129.5 (s, C Naph), 137.2 (s, C\textsubscript{3} bipy), 128.1, 127.9, 127.3, 126.0, 124.3, 123.3, 116.4 (s, CH Naph), 124.8 (s, C\textsubscript{4} bipy), 121.5 (s, C\textsubscript{2} bipy), 53.1 (s, OCH\textsubscript{3}). MS (ESI): m/z: 480.0755 [M + H]\textsuperscript{+}.

**Synthesis of compound 7a\textsuperscript{*}**. This was prepared in a similar way as 7a from fac-[Mn(CNPh)(CO)\textsubscript{3}(bipy)]ClO\textsubscript{4} ([1a]ClO\textsubscript{4}, 0.10 g, 0.20 mmol), ethanol (4 mL) and sodium (10 mg, 0.43 mmol). Yield: 59 mg (66%). IR (CH\textsubscript{2}Cl\textsubscript{2}, cm\textsuperscript{-1}): ν(CO) 2007 (vs), 1908 (vs). 1H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): δ = 8.73 (d, 3J(H,H) = 5.1 Hz, 2H, H\textsubscript{A} bipy), 7.98 (d, 3J(H,H) = 8.0 Hz, 2H, H\textsubscript{D} bipy), 7.81 (t, 3J(H,H) = 7.7 Hz, 2H, H\textsubscript{C} bipy), 7.14 (t, 3J(H,H) = 6.5 Hz, 2H, H\textsubscript{B} bipy), 6.88 (t, 3J(H,H) = 7.5 Hz, 2H, m-Ph), 6.75 (t, 3J(H,H) = 7.0 Hz, 2H, CH\textsubscript{2}), 0.89 (t, 3J(H,H) = 7.0 Hz, 3H, CH\textsubscript{3}). 13C\textsuperscript{1}H) NMR (100.61 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): δ = 224.8 (s, CO), 213.5 (s, CO), 202.0 (s, C\textsubscript{carbeno}), 154.9 (s, C\textsubscript{1} bipy), 154.3 (s, C\textsubscript{5} bipy), 152.9 (s, C\textsubscript{ipso}), 136.9 (s, C\textsubscript{3} bipy), 128.7 (s, m-Ph), 124.9 (s, C\textsubscript{4} bipy), 122.0 (s, o-Ph), 121.5 (s, C\textsubscript{2} bipy), 120.2 (s, p-Ph), 60.3 (s, CH\textsubscript{2}), 14.7 (s, CH\textsubscript{3}). MS (ESI): m/z: 444.0750 [M + H]\textsuperscript{+}.

**Synthesis of compound [8a]BF\textsubscript{4}**. To a solution of 7a (70 mg, 0.16 mmol) in 12 mL of CH\textsubscript{2}Cl\textsubscript{2} was added HBF\textsubscript{4}-OEt\textsubscript{2} (34 µL, d = 1.18 g/mL, 0.25 mmol). The color of the solution changed instantaneously from red to yellow. The solution was then concentrated to 1 mL and further addition of hexane (5 mL) caused the formation of a yellow solid, which was washed with diethyl ether (2 x 5 mL). The NMR data (see below) show the presence of two isomers in an approximate ratio of 9:1. Slow diffusion of hexane into a dichloromethane solution of the compound afforded yellow crystals suitable for an X-ray analysis. Yield: 81 mg (96%). IR (CH\textsubscript{2}Cl\textsubscript{2}, cm\textsuperscript{-1}): ν(CO) 2033 (vs), 1952 (s), 1930 (s). 1H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): Major isomer (90%): δ = 9.75 (br, 1H, NH), 8.59 (d, 3J(H,H) = 5.1 Hz, 2H, H\textsubscript{A} bipy), 8.18 (d, 3J(H,H) = 7.9 Hz, 2H, H\textsubscript{D} bipy), 8.02 (t, 3J(H,H) = 7.5 Hz, 2H, H\textsubscript{C} bipy), 7.42 (t, 3J(H,H) = 7.3 Hz, 1H, p-Ph), 7.37-7.32 (m, 4H, H\textsubscript{B} bipy and m-Ph), 7.10 (d, 3J(H,H) = 7.4 Hz, 2H, o-Ph), 3.77 (s, 3H, OCH\textsubscript{3}). Minor isomer (10%): δ = 9.15 (d, 3J(H,H) = 4.7 Hz, 2H, H\textsubscript{A} bipy), 8.51 (d, 3J(H,H) = 8.0 Hz, 2H, H\textsubscript{D} bipy), 8.24 (br, 2H, H\textsubscript{C} bipy), 7.73 (br, 2H, H\textsubscript{D} bipy), 7.27-7.20 (m, m-Ph and p-Ph), 6.80 (d, 3J(H,H) = 7.9
Hz, 2H, o-Ph), 4.24 (s, 3H, OCH₃). ^{13}C{^1}H NMR (100.61 MHz, CD₂Cl₂, ppm): Major isomer (90%): δ = 238.9 (s, C_carbene), 221.0 (s, CO), 213.8 (s, CO), 155.5 (s, C₁ bipy), 153.9 (s, C₃ bipy), 139.2 (s, C₃ bipy), 137.3 (s, C_ipso), 130.1 (s, m-Ph), 129.4 (s, p-Ph), 128.3 (s, C₄ bipy), 127.0 (s, o-Ph), 123.1 (s, C₂ bipy), 57.3 (s, OCH₃). Minor isomer (10%): 154.5 (s, C₅ bipy), 140.8 (s, C₃ bipy), 124.8 (s, o-Ph), 62.6 (s, OCH₃). MS (ESI): m/z: 430.0594 [M - BF₄]⁺.

**Synthesis of compound [8b]BF₄.** This was prepared in a similar way from 7b (72 mg, 0.13 mmol) and HBF₄·OEt₂ (31 µL, d = 1.18 g/mL, 0.23 mmol). Yield: 67 mg (81%).

IR (CH₂Cl₂, cm⁻¹): ν(CO) 2033 (vs), 1953 (vs), 1929 (s).

^{1}H NMR (400 MHz, CD₂Cl₂, ppm): Major isomer (95%): δ = 9.92 (br, 1H, NH), 8.44 (d, 3J(H,H) = 4.6 Hz, 2H, H_A bipy), 8.14 (d, 3J(H,H) = 7.8 Hz, 2H, H_D bipy), 7.91 (br, 3H, H_C bipy and Naph), 7.75 (br, 2H, Naph), 7.61-7.57 (m, 3H, Naph), 7.14 (d, 3J(H,H) = 7.8 Hz, 1H, Naph), 7.07 (t, 3J(H,H) = 5.8 Hz, 2H, H_B bipy) 3.82 (s, 3H, OCH₃). Minor isomer (5%): δ = 9.17 (br, 2H, H_A bipy), 4.24 (s, 3H, OCH₃).

^{13}C{^1}H NMR (100.61 MHz, CD₂Cl₂, ppm): Major isomer (95%): δ = 239.2 (s, C_carbene), 221.2 (s, CO), 213.7 (s, CO), 155.4 (s, C₁ bipy), 153.6 (s, C₃ bipy), 139.1 (s, C₃ bipy), 134.5, 133.6, 133.4 (s, C_Naph), 130.0, 128.7, 128.3, 127.9, 127.8, 127.1, 125.5 (s, CH Naph), 126.7 (s, C₄ bipy), 123.1 (s, C₂ bipy), 57.5 (s, OCH₃). Minor isomer (5%): δ = 154.4 (s, C₃ bipy), 140.8 (s, C₃ bipy), 62.7 (s, OCH₃). MS (ESI): m/z: 480.0750 [M – BF₄]⁺.

**Synthesis of compound [8a’]BF₄.** This was prepared in a similar way as [8a]BF₄ from 7a’ (70 mg, 0.16 mmol) and HBF₄·OEt₂ (33 µL, d = 1.18 g/mL, 0.24 mmol). Yield: 80 mg (95%).

IR (CH₂Cl₂, cm⁻¹): ν(CO) 2032 (vs), 1951 (s), 1929 (s).

^{1}H NMR (400 MHz, CD₂Cl₂, ppm): Major isomer (93%): δ = 9.69 (br, 1H, NH), 8.62 (d, 3J(H,H) = 5.4 Hz, 2H, H_A bipy), 8.21 (d, 3J(H,H) = 8.0 Hz, 2H, H_D bipy), 8.03 (t, 3J(H,H) = 7.8 Hz, 2H, H_C bipy), 7.44-7.33 (5H, H_B bipy, m-Ph and p-Ph), 7.13 (d, 3J(H,H) = 7.5 Hz, 2H, o-Ph), 3.96 (q, 3J(H,H) = 6.8 Hz, 2H, CH₂), 0.99 (t, 3J(H,H) = 6.8 Hz, 3H, CH₃). Minor isomer (7%): δ = 9.16 (br, 2H, H_A bipy), 8.46 (d, 3J(H,H) = 8.0 Hz, 2H, H_D bipy), 7.72 (br, 2H, H_B bipy), 7.24-7.17 (m, m-Ph and p-Ph), 6.81 (d, 3J(H,H) = 7.7 Hz, 2H, o-Ph), 4.55 (q, 3J(H,H) = 6.9 Hz, 2H, CH₂), 1.20 (t, 3J(H,H) = 6.9 Hz, 3H, CH₃). ^{13}C{^1}H NMR (100.61 MHz, CD₂Cl₂, ppm): Major isomer (93%): δ = 238.1 (s, C_carbene), 221.1 (s, CO), 213.8 (s, CO), 155.7 (s, C₁ bipy), 154.5 (s, C₅ bipy), 140.8 (s, C₃ bipy), 124.8 (s, o-Ph), 62.6 (s, OCH₃).
153.8 (s, C₅ bipy), 139.3 (s, C₃ bipy), 137.5 (s, Cipso), 130.1 (s, m-Ph), 129.5 (s, p-Ph), 128.5 (s, o-Ph), 127.0 (s, C₄ bipy), 123.1 (s, C₂ bipy), 66.3 (s, CH₂), 13.6 (s, CH₃).

Minor isomer (7%): \( \delta = 154.4 \) (s, C₅ bipy), 140.7 (s, C₃ bipy), 124.9 (s, C₂ bipy), 124.6 (s, o-Ph), 72.6 (s, CH₂), 15.3 (s, CH₃). MS (ESI): \( m/z: 444.0748 \ [M – BF₄]^+ \).

**Synthesis of compound [9a]BF₄.** To a solution of [8a]BF₄ (0.10 g, 0.19 mmol) in CH₂Cl₂ (10 mL) Ag₂O (23 mg, 0.10 mmol) was added and the mixture stirred for 4 h. The solution was then filtered and evaporated to dryness under vacuum. Hexane (5 mL) was added to the residue and the mixture stirred to obtain a yellow solid. Yellow crystals of [8a]BF₄ suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 93 mg (93%). IR (CH₂Cl₂, cm⁻¹): \( \nu(CO) \) 2040 (vs), 1950 (s), 1943 (sh).

\( ^1H \) NMR (400 MHz, CD₂Cl₂, ppm): \( \delta = 8.86 \) (d, \( ^3J(H,H) = 5.1 \) Hz, 2H, Hₐ bipy), 8.21 (d, \( ^3J(H,H) = 8.1 \) Hz, 2H, Hₕ bipy), 8.08 (t, \( ^3J(H,H) = 7.9 \) Hz, 2H, Hₗ bipy), 7.69 (s, 1H, NCHO), 7.46 (t, \( ^3J(H,H) = 6.5 \) Hz, 2H, Hₖ bipy), 7.04 (t, \( ^3J(H,H) = 7.4 \) Hz, 1H, p-Ph), 6.96 (t, \( ^3J(H,H) = 7.6 \) Hz, 2H, m-Ph), 6.24 (d, \( ^3J(H,H) = 8.0 \) Hz, 2H, o-Ph), 4.07 (s, 3H, OCH₃).

\( ^{13}C\{^1H \} \) NMR (75.46 MHz, CD₂Cl₂, ppm): \( \delta = 219.4 \) (br, CO), 169.8 (s, NCHO), 156.0 (s, C₁ bipy), 145.6 (s, C₃ bipy), 140.5 (s, C₃ bipy), 129.6 (s, m-Ph), 127.4 (s, C₄ bipy), 127.2 (s, p-Ph), 123.8 (s, o-Ph and C₂ bipy), 61.6 (s, OCH₃). MS (ESI): \( m/z: 430.0594 \ [M – BF₄]^+ \).

**Synthesis of compound [9b]BF₄.** This was prepared in a similar way from [8b]BF₄ (0.10 g, 0.18 mmol) and Ag₂O (21 mg, 0.09 mmol). Yield: 91 mg (91%). IR (CH₂Cl₂, cm⁻¹): \( \nu(CO) \) 2039 (vs), 1949 (s), 1941 (sh).

\( ^1H \) NMR (400 MHz, CD₂Cl₂, ppm): \( \delta = 8.83 \) (br, 2H, Hₐ bipy), 8.12 (m, 2H, Hₕ bipy), 7.97 (s, 2H, Hₗ bipy), 7.79 (br, 1H, NCHN), 7.72 (br, 2H, Naph), 7.51-7.44 (4H, Naph), 7.32 (br, 2H, Hₖ bipy), 6.58 (d, \( ^3J(H,H) = 7.8 \) Hz, 1H, Naph), 6.47 (s, 1H, Naph), 4.08 (s, 3H, OCH₃). \( ^{13}C\{^1H \} \) NMR (100.61 MHz, CD₂Cl₂, ppm): \( \delta = 219.8 \) (s, CO), 218.9 (s, CO), 170.0 (s, NCHO), 156.1 (s, C₁ bipy), 154.7 (s, C₃ bipy), 142.8, 133.4, 131.8 (s, Naph), 140.4 (s, C₃ bipy), 129.5, 128.1, 127.9, 127.8, 127.0, 122.5, 121.7 (s, CH Naph), 127.2 (s, C₄ bipy), 123.7 (s, C₂ bipy), 61.6 (s, OCH₃). MS (ESI): \( m/z: 480.0751 \ [M – BF₄]^+ \).
Synthesis of compound [9a’]BF$_4$. This was prepared in a similar way from [8a’]BF$_4$ (0.10 g, 0.19 mmol) and Ag$_2$O (23 mg, 0.10 mmol). Yield: 75 mg (75%). IR (CH$_2$Cl$_2$, cm$^{-1}$): v(CO) 2040 (vs), 1947 (s), 1943 (s).

$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, ppm): δ = 8.87 (d, $^3$J(H,H) = 4.9 Hz, 2H, H$_b$ bipy), 8.22 (d, $^3$J(H,H) = 8.0 Hz, 2H, H$_D$ bipy), 7.74 (s, 1H, NCHO), 7.45 (t, $^3$J(H,H) = 6.3 Hz, 2H, H$_B$ bipy), 7.05 (t, $^3$J(H,H) = 7.0 Hz, 1H, p-Ph), 6.96 (t, $^3$J(H,H) = 7.4 Hz, 2H, o-Ph), 4.36 (q, $^3$J(H,H) = 7.0 Hz, 2H, CH$_2$), 1.49 (t, $^3$J(H,H) = 7.0 Hz, 3H, CH$_3$).

$^{13}$C{$^{1}$H} NMR (100.61 MHz, CD$_2$Cl$_2$, ppm): δ = 219.9 (br, CO), 168.7 (s, NCHO), 156.1 (s, C$_1$ bipy), 154.6 (s, C$_3$ bipy), 145.7 (s, C$_{ipso}$), 140.5 (s, C$_s$ bipy), 129.6 (s, m-Ph), 127.4 (s, C$_4$ bipy), 127.2 (s, o-Ph), 123.9 (s, o-Ph and C$_2$ bipy), 71.9 (s, CH$_2$), 15.5 (s, CH$_3$). MS (ESI): m/z: 444.0749 [M − BF$_4$]$^+$.  

Liberation of formimidate 10b. A solution of [9b]BF$_4$ (80 mg, 0.14 mmol) in acetonitrile (15 mL) was stirred for 2 h at room temperature. The solvent was evaporated to dryness under vacuum and the resulting residue extracted with diethyl ether (2 x 5 mL) and filtered. Evaporation of the solvent afforded a slightly orange oil. Yield: 24 mg (91%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, ppm, 298K): δ = 7.87 (s, 1H, NCHO), 7.82-7.72 (m, 3H, Naph), 7.46 (t, $^3$J(H,H) = 7.4 Hz, 1H, Naph), 7.40 (t, $^3$J(H,H) = 7.2 Hz, 1H, Naph), 7.33 (s, 1H, Naph), 7.20 (d, $^3$J(H,H) = 8.6 Hz, 1H, Naph), 3.93 (s, 3H, OCH$_3$). $^{13}$C{$^{1}$H} NMR (100.61 MHz, CD$_2$Cl$_2$, ppm, 298K): δ = 156.3 (s, NCHO), 146.4, 134.8, 131.6 (s, C Naph), 129.4, 128.1, 127.8, 126.8, 125.2, 123.0, 117.6 (s, CH Naph), 54.3 (s, OCH$_3$). MS (APCI): m/z: 186.0920 [M + H]$^+$. 

S11
1H NMR (CD$_2$Cl$_2$) spectrum of Compound [3b]ClO$_4$ (major isomer)

$^{13}$C{1H} NMR (CD$_2$Cl$_2$) spectrum of Compound [3b]ClO$_4$ (major isomer)
\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)) spectrum of **Compound [3b]ClO\(_4\)**

\(^{13}\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\)) spectrum of **Compound [3b]ClO\(_4\)**
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [3c]ClO$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [3c]ClO$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [3e]ClO$_4$

$^{13}$C(1H) NMR (CD$_2$Cl$_2$) spectrum of Compound [3e]ClO$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 4b

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 193 K) spectrum of Compound 4b
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 4c

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 193 K) spectrum Compound 4c

S17
$^1$H NMR (CD$_2$Cl$_2$) spectrum of **Compound 6a**

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of **Compound 6a**
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 6b

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 6b
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 6c

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 6c
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 6f

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 6f
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 6g

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 6g
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 7a

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 7a
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 7b

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 7b
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 7a’

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 7a’
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [8a]BF$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [8a]BF$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [8b]BF$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [8b]BF$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [8a$'$]BF$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [8a$'$]BF$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [9a]BF$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [9a]BF$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [9b]BF$_4$

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [9b]BF$_4$
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound [9a’]BF$_4$.

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound [9a’]BF$_4$.
$^1$H NMR (CD$_2$Cl$_2$) spectrum of Compound 10b

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) spectrum of Compound 10b