Supplementary information for
Metal-induced tautomerization of oxazole and thiazole molecules to heterocyclic carbenes

Javier Ruiz and Bernabé F. Perandones

Crystal data for 4b: C_{17}H_{13}Cl_{3}MnN_{5}O_{2}S, M = 564.66, monoclinic, P 21/n, a = 10.1874(5), b = 12.8131(5), c = 16.3439(7) Å, β = 93.621(2)°, V = 2129.15(16) Å³, Z = 4, D_c = 1.762 Mg m⁻³, µ = 1.141 mm⁻¹, F(000) = 1136.0, T = 100(2) K, 33014 measured reflections, 3647 independent reflections (R_{int} = 0.0672), R1 = 0.0755, wR2 = 0.2284 (all data), Δe 1.109 and -1.943 e Å⁻³, CCDC 716673. 6b. C_{16}H_{11}F_{6}MnN_{5}O_{3}PS, M = 525.25, triclinic, P -1, a = 8.6199(3), b = 10.0390(3), c = 11.5074(3) Å, α = 78.487(1), β = 80.485(2), γ = 84.597(2)°, V = 960.41(5) Å³, Z = 2, D_c = 1.816 Mg m⁻³, µ = 0.962 mm⁻¹, F(000) = 524.0, T = 100(2) K, 15455 measured reflections, 3416 independent reflections (R_{int} = 0.0275), R1 = 0.0338, wR2 = 0.0648 (all data), Δe 0.315 and -0.321 e Å⁻³, CCDC 716674. 7b. C_{34}H_{25}AuF_{6}MnN_{5}O_{3}PS, M = 983.48, triclinic, P -1, a = 11.0938(3), b = 11.4700(4), c = 15.1096(5) Å, α = 94.041(2), β = 101.191(2), γ = 112.355(2)°, V = 1722.13(10) Å³, Z = 2, D_c = 1.897 Mg m⁻³, µ = 4.848 mm⁻¹, F(000) = 956.0, T = 100(2) K, 57416 measured reflections, 6738 independent reflections (R_{int} = 0.0305), R1 = 0.0398, wR2 = 0.0519 (all data), Δe 0.776 and -0.824 e Å⁻³, CCDC 716675. 8b. C_{21}H_{18}AuClNO_{4}PS, M = 643.81, monoclinic, P 21/n, a = 9.7030(3), b = 16.6091(6), c = 13.9180(4) Å, β = 101.338(2)°, V = 2199.22(12) Å³, Z = 4, D_c = 1.994 Mg m⁻³, µ = 7.007 mm⁻¹, F(000) = 1240, T = 100(2) K, 57620 measured reflections, 4051 independent reflections (R_{int} = 0.0314), R1 = 0.0516, wR2 = 0.0658 (all data), Δe 1.452 and -1.185 e Å⁻³, CCDC 716676.

Synthesis and spectroscopic and analytical data for the new compounds:

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:
4a. ClO₄⁻[Mn(N=CHOCH=CH)(CO)₃(bipy)]ClO₄

To a solution of \( \text{fac-[MnBr(CO)_3(bipy)]} \) (0.10 g, 0.27 mmol) in 10 mL of acetone 0.066 g of AgClO₄ (0.32 mmol) were added and the mixture stirred for 1 hour in the dark. The solution was filtered off to remove the AgBr formed, 1.1 Eq. of oxazole (0.019 mL, d = 1.05 g/mL, 0.29 mmol) were added to the filtrate and the solution stirred for 2 hours. After removal the solvent, the residue was dissolved in 3 mL of CH₂Cl₂. Addition of hexane (10 mL) caused the formation of a yellow solid, which was filtered off and dried under vacuum. Yield: 0.110 g (89%). Anal. (%): Calcd. for C₁₆H₁₁ClMnN₃O₈: C 41.45, H 2.39, N 9.06. Found: C 41.27, H 2.51, N 9.19. IR (CH₂Cl₂): \( \nu \) 2045 (vs), 1959 (s), 1944 (s) cm⁻¹ (CO). \(^1\)H NMR (400 MHz, CD₂Cl₂): \( \delta \) 9.25 (2H, d, \( ^3J_{HH} = 4.8 \), Hₐ bipy), 8.46 (2H, d, \( ^3J_{HH} = 7.7 \), H_d bipy), 8.28 (2H, t, \( ^3J_{HH} = 7.4 \), H_c bipy), 7.88 (1H, s, =CH), 7.79 (2H, t, \( ^3J_{HH} = 6.9 \), H_c bipy), 7.76 (1H, s, =CH), 6.73 (1H, s, =CH).
The procedure was completely analogous to that described above, using $\text{fac-}[\text{MnBr(CO)}_3(\text{bipy})]$ (0.10 g, 0.27 mmol), AgClO$_4$ (0.066 g, 0.32 mmol) and thiazole (0.021 mL, d = 1.198 g/mL, 0.30 mmol). Yield: 0.125 g (98%). Crystals of 4b.ClO$_4$ suitable for X-Ray diffraction study were obtained by slow diffusion of hexane into CH$_2$Cl$_2$ solution of the compound. Anal. (%) Calcd. for C$_{16}$H$_{11}$ClMnN$_3$O$_7$S: C 40.06, H 2.31, N 8.76. Found: C 40.25, H 2.17, N 8.63. IR (CH$_2$Cl$_2$): $\nu$ 2043 (vs), 1957 (s), 1943 (s) cm$^{-1}$ (CO).

$\text{H NMR (400 MHz, CD}_2\text{Cl}_2)$: $\delta$ 9.26 (2H, d, $^3J_{HH} = 4.6$, H$_a$ bipy), 8.40 (2H, d, $^3J_{HH} = 6.3$, H$_b$ bipy), 8.39 (1H, s, =CH), 8.23 (2H, t, $^3J_{HH} = 6.9$, H$_c$ bipy), 7.79 (2H, t, $^3J_{HH} = 6.4$, H$_b$ bipy), 7.51 (1H, s, =CH).

To a solution of 4a.ClO$_4$ (0.10g, 0.22 mmol) in CH$_2$Cl$_2$ (10 mL) potassium tert-butoxide (0.048 g, 0.43 mmol) was added. After 30 minutes of stirring the mixture was filtered and the resulting solution concentrated to 3 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.072 g (92%). Anal. (%) Calcd. for C$_{16}$H$_{10}$MnN$_3$O$_4$: C 52.91, H 2.78, N 11.57. Found: C 52.67, H 2.53, N 11.44. IR (CH$_2$Cl$_2$): $\nu$ 2015 (vs), 1917 (s) cm$^{-1}$ (CO). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 9.10 (2H, d, $^3J_{HH} = 5.4$, H$_a$ bipy), 8.08 (2H, d, $^3J_{HH} = 8.0$, H$_d$ bipy), 7.94 (2H, td, $^4J_{HH} = 1.4$, $^3J_{HH} = 7.9$, H$_c$ bipy), 7.50 (1H, br s, =CH), 7.45-7.40 (2H, m, H$_b$ bipy), 6.60 (1H, br s, =CH). $^{13}$C ($^1$H) NMR (100.64 MHz): $\delta$ 223.8 (s, CO), 213.5 (s, CO), 201.9 (s, C$_{\text{carbene}}$), 155.1 (s, C$_1$ bipy), 153.0 (s, C$_2$ bipy), 140.2 (s, =CH), 137.2 (s, C$_3$ bipy), 125.5 (s, =CH), 125.4 (s, C$_4$ bipy), 121.6 (s, C$_5$ bipy).
5b  \textit{fac-}[\text{Mn(}C=NCH=CHS\text{)(CO)}_3\text{]}(\text{Bipy})]

The procedure was analogous to that described above, using \textbf{4b.ClO}_4\text{(0.10 g, 0.21 mmol), potassium tert-butoxide (0.047 g, 0.42 mmol). Yield: 0.076 g (96%). Anal. (%) Calcd. for C}_{16}H_{10}MnN_3O_3S: C 50.67, H 2.66, N 11.08. Found: C 50.29, H 2.48, N 10.81. IR (CH}_2Cl_2): \nu 2012 (vs), 1915 (s) cm\text{-1} (CO). ^1H NMR (400 MHz, CD}_2Cl_2): \delta 9.18 (2H, d, \text{3J}_{HH} = 5.1, \text{H}_a \text{bipy}), 8.06 (2H, d, \text{3J}_{HH} = 8.0, \text{H}_d \text{bipy}), 7.93 (2H, t, \text{3J}_{HH} = 7.7, \text{H}_c \text{bipy}), 7.53 (1H, d, \text{3J}_{HH} = 2.6, =\text{CH}), 7.45 (2H, t, \text{3J}_{HH} = 6.3, \text{H}_b \text{bipy}), 6.95 (1H, d, \text{3J}_{HH} = 2.6, =\text{CH}).

6a.PF_6  \textit{fac-}[\text{Mn(}CNHCH=CHO\text{)(CO)}_3\text{]}(\text{Bipy})]\text{]PF}_6

To a solution of \textbf{5a} (0.10 g, 0.28 mmol) in CH_2Cl_2 (10 mL) NH_4PF_6 (0.09 g, 0.55 mmol) was added and the mixture stirred for 2 hours. Then the solution filtered off and concentrated to 3 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.135 g (96%). Anal. (%) Calcd. for C_{16}H_{11}F_6MnN_3O_4P: C 37.74, H 2.18, N 8.25. Found: C 37.53, H 2.35, N 8.09. IR (CH_2Cl_2): \nu 2039 (vs), 1958 (s), 1915 (s) cm\text{-1} (CO). IR (KBr): \nu 3377 (m) (NH); 2036 (s), 1938 (s) (CO). ^1H NMR (300 MHz, CD}_2Cl_2): \delta 9.10 (2H, d, \text{3J}_{HH} = 5.1, \text{H}_a \text{bipy}), 8.25 (2H, d, \text{3J}_{HH} = 8.0, \text{H}_d \text{bipy}), 8.13 (2H, t, \text{3J}_{HH} = 7.6, \text{H}_c \text{bipy}), 7.80 (1H, br s, =\text{CH}), 7.64 (2H, t, \text{3J}_{HH} = 6.5, \text{H}_b \text{bipy}), 7.21 (1H, br s, =\text{CH}). ^{13}C \text{ {^{1H}}} \text{NMR (75.47 MHz, CD}_2Cl_2): \delta 220.3 (s, CO), 216.8 (s, C_{\text{carbene}}), 213.1 (s, CO), 155.4 (s, C_1 \text{bipy}), 154.0 (s, C_2 \text{bipy}), 144.5 (s, =\text{CH}), 139.7 (s, C_3 \text{bipy}), 127.8 (s, C_4 \text{bipy}), 123.6 (s, C_5 \text{bipy}), 118.6 (s, =\text{CH}).
6b.PF$_6$ *fac-*[Mn($\text{CNCH=CH}$)(CO)$_3$(Bipy)]PF$_6$

This was similarly prepared from 5b (0.10 g, 0.26 mmol) and NH$_4$PF$_6$ (0.086 g, 0.53 mmol). Reaction time: 3 hours. Yield: 0.134 g (97%). Crystals of 6b.PF$_6$ suitable for X-Ray diffraction study were obtained by slow diffusion of hexane into CH$_2$Cl$_2$ solution of the compound. Anal. (%) Calcd. for C$_{16}$H$_{11}$F$_6$MnN$_3$O$_3$PS: C 36.59, H 2.11, N 8.00. Found: C 36.38, H 2.28, N 7.76. IR (CH$_2$Cl$_2$): v 2035 (vs), 1956 (s), 1933 (s) cm$^{-1}$ (CO). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 11.24 (1H, s, NH), 9.17 (2H, d, $^3$J$_{HH}$ = 5.4, H$_a$ bipy), 8.24 (2H, d, $^3$J$_{HH}$ = 8.0, H$_d$ bipy), 8.14 (2H, t, $^3$J$_{HH}$ = 7.7, H$_c$ bipy), 7.92 (1H, br s, -CH), 7.69 (2H, t, $^3$J$_{HH}$ = 6.4, H$_b$ bipy), 7.39 (1H, d, $^3$J$_{HH}$ = 3.4, =CH). $^{13}$C \{$^1$H\} NMR (75.47 MHz, CD$_2$Cl$_2$): δ 225.5 (s, C carbene), 220.5 (s, CO), 213.7 (s, CO), 155.2 (s, C$_1$ bipy), 154.0 (s, C$_2$ bipy), 139.8 (s, C$_3$ bipy), 136.4 (s, =CH), 128.1 (s, C$_4$ bipy), 123.8 (s, C$_5$ bipy), 123.7 (s, =CH).

7a.PF$_6$ *fac-*[Mn\{NC(AuPPh$_3$)OCH=CH\}(CO)$_3$(Bipy)]PF$_6$

To a solution of 6a.PF$_6$ (0.10 g, 0.20 mmol) in CH$_2$Cl$_2$ (30 mL) 1.1 eq. of AuClPPh$_3$ (0.107 g, 0.22 mmol) were added. Then some KOH (0.20 g, 3.56 mmol) was added and the mixture stirred for 1 hour. Then the solution was filtered off an concentrated to 5 mL. Diethyl ether (15 mL) was added to obtain a yellow solid, which was filtered off and dried under vacuum. Yield: 0.091 g (48%). Anal. (%) Calcd. for C$_{34}$H$_{25}$AuF$_6$MnN$_3$O$_4$P$_2$: C 42.21, H 2.60, N 4.34. Found: C 42.35, H 2.84, N 4.08. IR (CH$_2$Cl$_2$): v 2036 (vs), 1943 (s), 1933 (s) cm$^{-1}$ (CO). $^{31}$P \{$^1$H\} NMR (121.44 MHz): δ 40.2 (s, PPh$_3$). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 9.15 (2H, d, $^3$J$_{HH}$ = 4.3, H$_a$ bipy), 8.24 (2H, d, $^3$J$_{HH}$ = 7.1, H$_d$ bipy), 8.14 (2H, t, $^3$J$_{HH}$ = 6.4, H$_c$ bipy), 7.63-7.56 (16H, m, Ph and =CH), 7.19 (2H, t, $^3$J$_{HH}$ = 5.1, H$_b$ bipy), 6.21 (1H, s, =CH). $^{13}$C \{$^1$H\} NMR (75.47 MHz, CD$_2$Cl$_2$): δ 220.5 (s, CO), 217.6 (s, CO), 208.1
(s, C_{carbene}), 156.0 (s, C_1 bipy), 154.1 (s, C_2 bipy), 141.3 (s, =CH), 140.7 (s, C_3 bipy); 134.6, 132.8, 130.2, 129.4, 128.7 (s, Ph); 127.7 (s, C_4 bipy), 125.3 (s, =CH), 124.1 (s, C_5 bipy).

7b PF_6 \textit{fac-[Mn}[	extit{NC(AuPPh}_3)\text{SCH=CH}(\text{CO})_3\text{Bipy)]PF}_6

The procedure was analogous to the synthesis of 7a PF_6 using 6b PF_6 (0.10 g, 0.19 mmol), AuClPPh_3 (0.104 g, 0.21 mmol) and KOH (0.20 g, 3.56 mmol) in CH_2Cl_2 (20 mL). Yield: 0.096 g (51%). Crystals of 7b PF_6 suitable for X-Ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compound. Anal. (%) Calcd. for C_{34}H_{25}AuF_6MnN_3O_3P_2S: C 41.52, H 2.56, N 4.27. Found: C 41.78 H 2.30, N 4.03. IR (CH_2Cl_2): \nu 2035 (vs), 1945 (s), 1933 (s) cm^{-1} (CO). ^{31}P \{^1H\} NMR (121.44 MHz): \delta 40.1 (s, PPh_3). ^1H NMR (300 MHz, CD_2Cl_2): \delta 9.22 (2H, d, ^3J_{HH} = 5.4, H_a bipy), 8.17 (2H, d, ^3J_{HH} = 8.0, H_d bipy), 8.05 (2H, t, ^3J_{HH} = 7.9, H_c bipy), 7.64-7.50 (16H, m, Ph and =CH), 7.34-7.30 (1H, m, =CH), 7.15 (2H, td, ^3J_{HH} = 6.4, ^4J_{HH} = 1.0, H_b bipy). ^{13}C \{^1H\} NMR (75.47 MHz, CD_2Cl_2): \delta 220.1 (s, CO), 217.8 (s, CO), 210.4 (s, C_{carbene}), 155.6 (s, C_1 bipy), 153.6 (s, C_2 bipy), 144.5 (s, =CH), 140.1 (s, C_3 bipy); 134.2, 132.3, 129.7, 129.0 (s, Ph); 127.2 (s, C_4 bipy), 123.5 (s, C_5 bipy), 120.9 (s, =CH).

8b ClO_4 \textit{[AuPPh}_3(\text{CNHCH=CHS})\text{ClO}_4}

To a solution of 7b PF_6 (0.10 g, 0.10 mmol) in CH_2Cl_2 some HClO_4 (0.05 mL, d = 1.67 g/mL, 70 %, 0.58 mmol) was added and the mixture stirred for 30 minutes. Then the solution was filtered off over kieselgur and hexane (10 mL) added to the solution to obtain a yellow solid corresponding to compound 3 ClO_4, which was filtered off and concentrated under vacuum to 3 mL. Addition of hexane (10 mL) gave a white solid, which was filtered off and dried under vacuum. Yield: 0.040 g (62%). Crystals of 8b ClO_4 suitable for X-Ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2
solution of the compound. Calcd. for C$_{21}$H$_{18}$AuClNO$_4$PS: C 39.18, H 2.82, N 2.18. Found: C 39.43 H 2.97, N 2.01. $^{31}$P $^1$H NMR (121.44 MHz): $\delta$ 40.2 (s, PPh$_3$). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 13.53 (1H, s, NH), 8.34 (1H, d, $^3$J$_{HH}$ = 2.6, =CH), 7.84 (1H, d, $^3$J$_{HH}$ = 2.6, =CH), 7.65-7.50 (15H, m, Ph). $^{13}$C $^1$H NMR (100.64 MHz) = $\delta$ 202.5 (s, C$_{carbene}$), 136.2 (s, =CH), 134.1-128.3 (m, Ph), 117.6 (s, =CH).