Supplementary information for

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

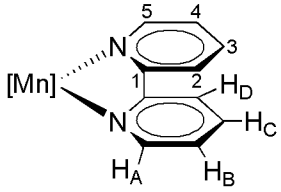
Javier Ruiz and Bernabé F. Perandones

Crystal data for 4b: $C_{17}H_{13}Cl_3MnN_3O_7S$, M = 564.66, monoclinic, P 21/n, a = 10.1874(5), b = 12.8131(5), c = 16.3439(7) Å, β = 93.621(2)º, V = 2129.15(16) Å^3, 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, w$R2$ = 0.2284 (all data), Δe 1.109 and -1.943 e Å^{-3}, CCDC 716673. **6b**. $C_{16}H_{11}F_6MnN_3O_3PS$, 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)º, V = 960.41(5) Å^3, 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, w$R2$ = 0.0648 (all data), Δe 0.315 and –0.321 e Å^{-3}, CCDC 716674. **7b** $C_{34}H_{25}AuF_6MnN_3O_3P_2S$, 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)º, V = 1722.13(10) Å^3, 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, w$R2$ = 0.0519 (all data), Δe 0.776 and –0.824 e Å^{-3}, CCDC 716675. **8b** $C_{21}H_{18}AuClNO_4PS$, M = 643.81, monoclinic, P 21/n, a = 9.7030(3), b = 16.6091(6), c = 13.9180(4) Å, β = 101.338(2)º, V = 2199.22(12) Å^3, 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, w$R2$ = 0.0658 (all data), Δe 1.452 and –1.185 e Å^{-3},CCDC 716676.

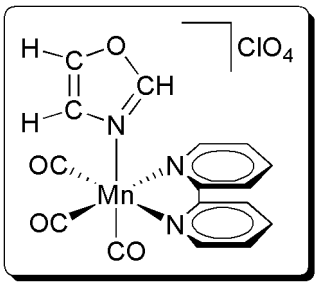
Synthesis and spectroscopic and analytical data for the new compounds:

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:

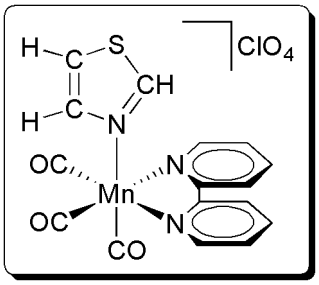


4a.ClO_4 ***fac*-[Mn(N=CHOCH=CH)$(CO)_3$(Bipy)]ClO_4**



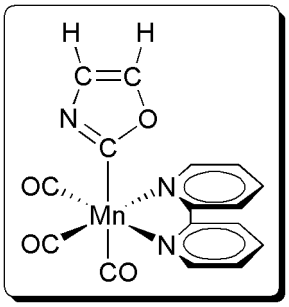
To a solution of *fac*-[MnBr$(CO)_3$(bipy)] (0.10 g, 0.27 mmol) in 10 mL of acetone 0.066 g of $AgClO_4$ (0.32 mmol) were added and the mixture stirred for 1 hour in the dark. The solution was filtered off to remove the AgBr formed, 1.1 Eq. of oxazole (0.019 mL, d = 1.05 g/mL, 0.29 mmol) were added to the filtrate and the solution stirred for 2 hours. After removal the solvent, the residue was dissolved in 3 mL of CH_2Cl_2. 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 $C_{16}H_{11}ClMnN_3O_8$: C 41.45, H 2.39, N 9.06. Found: C 41.27, H 2.51, N 9.19. IR (CH_2Cl_2): ν 2045 (vs), 1959 (s), 1944 (s) cm^{-1} (CO). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.25 (2H, d, $^3J_{HH}$ = 4.8, H_a 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).

4b.ClO_4 ***fac*-[Mn(N=CHSCH=CH)$(CO)_3$(Bipy)]ClO_4**



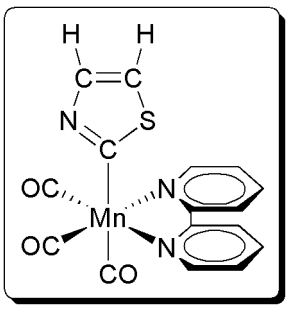
The procedure was completely analogous to that described above, using *fac*-[MnBr$(CO)_3$(bipy)] (0.10 g, 0.27 mmol), $AgClO_4$ (0.066 g, 0.32 mmol) and thiazole (0.021 mL, d = 1.198 g/mL, 0.30 mmol). Yield: 0.125 g (98%). Crystals of **4b.ClO_4** suitable for X-Ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compound. Anal. (%) Calcd. for $C_{16}H_{11}ClMnN_3O_7S$: C 40.06, H 2.31, N 8.76. Found: C 40.25, H 2.17, N 8.63. IR (CH_2Cl_2): ν 2043 (vs), 1957 (s), 1943 (s) cm^{-1} (CO). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 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).

5a ***fac*-[Mn(C=NCH=CHO)$(CO)_3$(Bipy)]**



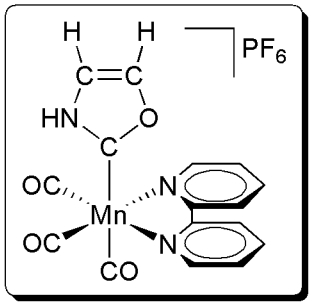
To a solution of **4a.ClO_4** (0.10g, 0.22 mmol) in CH_2Cl_2 (10 mL) potassium *tert*-butoxide (0.048 g, 0.43 mmol) was added. After 30 minutes of stirring the mixture was filtered and the resulting solution concentrated to 3 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.072 g (92%). Anal. (%) Calcd. for $C_{16}H_{10}MnN_3O_4$: C 52.91, H 2.78, N 11.57. Found: C 52.67, H 2.53, N 11.44. IR (CH_2Cl_2): ν 2015 (vs), 1917 (s) cm^{-1} (CO). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 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). $^{13}C\{^1H\}$ NMR (100.64 MHz): δ 223.8 (s, CO), 213.5 (s, CO), 201.9 (s, $C_{carbene}$), 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 ***fac*-[Mn(C=NCH=CHS)(CO)$_3$(Bipy)]**



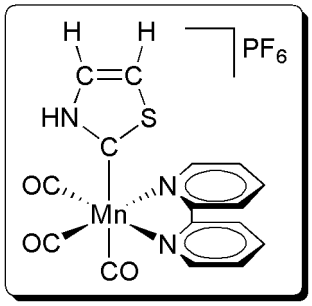
The procedure was analogous to that described above, using **4b.ClO$_4$** (0.10 g, 0.21 mmol), potassium *tert*-butoxide (0.047 g, 0.42 mmol). Yield: 0.076 g (96%). Anal. (%) Calcd. for $C_{16}H_{10}MnN_3O_3S$: C 50.67, H 2.66, N 11.08. Found: C 50.29, H 2.48, N 10.81. IR (CH_2Cl_2): ν 2012 (vs), 1915 (s) cm^{-1} (CO). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.18 (2H, d, $^3J_{HH}$ = 5.1, H_a bipy), 8.06 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 7.93 (2H, t, $^3J_{HH}$ = 7.7, H_c bipy), 7.53 (1H, d, $^3J_{HH}$ = 2.6, =CH), 7.45 (2H, t, $^3J_{HH}$ = 6.3, H_b bipy), 6.95 (1H, d, $^3J_{HH}$ = 2.6, =CH).

6a.PF$_6$ ***fac*-[Mn(CNHCH=CHO)(CO)$_3$(Bipy)]PF$_6$**



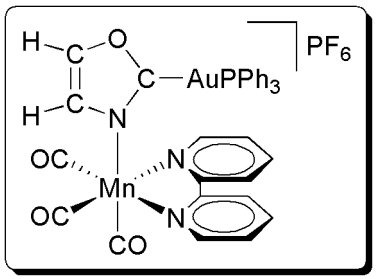
To a solution of **5a** (0.10 g, 0.28 mmol) in CH_2Cl_2 (10 mL) NH_4PF_6 (0.09 g, 0.55 mmol) was added and the mixture stirred for 2 hours. Then the solution filtered off and concentrated to 3 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.135 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): ν 2039 (vs), 1958 (s), 1915 (s) cm^{-1} (CO). IR (KBr): ν 3377 (m) (NH); 2036 (s), 1938 (s) (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.10 (2H, d, $^3J_{HH}$ = 5.1, H_a bipy), 8.25 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 8.13 (2H, t, $^3J_{HH}$ = 7.6, H_c bipy), 7.80 (1H, br s, =CH), 7.64 (2H, t, $^3J_{HH}$ = 6.5, H_b bipy), 7.21 (1H, br s, =CH). ^{13}C {^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 220.3 (s, CO), 216.8 (s, $C_{carbene}$), 213.1 (s, CO), 155.4 (s, C_1 bipy), 154.0 (s, C_2 bipy), 144.5 (s, =CH), 139.7 (s, C_3 bipy), 127,8 (s, C_4 bipy), 123.6 (s, C_5 bipy), 118.6 (s, =CH).

6b.PF$_6$ *fac*-**[Mn(CNHCH=CHS)(CO)$_3$(Bipy)]PF$_6$**



This was similarly prepared from **5b** (0.10 g, 0.26 mmol) and NH_4PF_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_2Cl_2 solution of the compound. Anal. (%) Calcd. for $C_{16}H_{11}F_6MnN_3O_3PS$: C 36.59, H 2.11, N 8.00. Found: C 36.38, H 2.28, N 7.76. IR (CH_2Cl_2): ν 2035 (vs), 1956 (s), 1933 (s) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 11.24 (1H, s, NH), 9.17 (2H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.24 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 8.14 (2H, t, $^3J_{HH}$ = 7.7, H_c bipy), 7.92 (1H, br s, =CH), 7.69 (2H, t, $^3J_{HH}$ = 6.4, H_b bipy), 7.39 (1H, d, $^3J_{HH}$ = 3.4, =CH). ^{13}C {^{1}H} NMR (75.47 MHz, CD_2Cl_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).

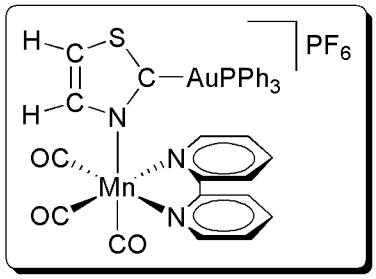
7a.PF$_6$ *fac*-**[Mn{NC(AuPPh$_3$)OCH=CH}(CO)$_3$(Bipy)]PF$_6$**



To a solution of **6a.PF$_6$** (0.10 g, 0.20 mmol) in CH_2Cl_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 $C_{34}H_{25}AuF_6MnN_3O_4P_2$: C 42.21, H 2.60, N 4.34. Found: C 42.35, H 2.84, N 4.08. IR (CH_2Cl_2): ν 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_2Cl_2): δ 9.15 (2H, d, $^3J_{HH}$ = 4.3, H_a bipy), 8.24 (2H, d, $^3J_{HH}$ = 7.1, H_d bipy), 8.14 (2H, t, $^3J_{HH}$ = 6.4, H_c bipy), 7.63-7.56 (16H, m, Ph and =CH), 7.19 (2H, t, $^3J_{HH}$ = 5.1, H_b bipy), 6.21 (1H, s, =CH). ^{13}C {^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 220.5 (s, CO), 217.6 (s, CO), 208.1

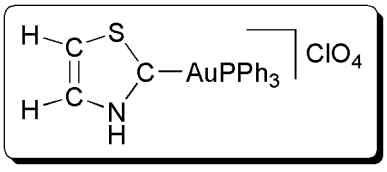
(s, $C_{carbene}$), 156.0 (s, C_1 bipy), 154.1 (s, C_2 bipy), 141.3 (s, =CH), 140.7 (s, C_3 bipy);134.6, 132.8, 130.2, 129.4, 128.7 (s, Ph); 127.7 (s, C_4 bipy), 125.3 (s, =CH), 124.1 (s, C_5 bipy).

7b.PF$_6$ *fac*-**[Mn{NC(AuPPh$_3$)SCH=CH}(CO)$_3$(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): ν 2035 (vs), 1945 (s), 1933 (s) cm^{-1} (CO). ^{31}P {^1H} NMR (121.44 MHz): δ 40.1 (s, PPh_3). ^1H NMR (300 MHz, CD_2Cl_2): δ 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): δ 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$_4$ **[AuPPh$_3$(CNHCH=CHS)]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 $C_{21}H_{18}AuClNO_4PS$: C 39.18, H 2.82, N 2.18. Found: C 39.43 H 2.97, N 2.01. ^{31}P $\{^1H\}$ NMR (121.44 MHz): δ 40.2 (s, PPh_3). ^1H NMR (300 MHz, CD_2Cl_2): δ 13.53 (1H, s, NH), 8.34 (1H, d, $^3J_{HH}$ = 2.6, =CH), 7.84 (1H, d, $^3J_{HH}$ = 2.6, =CH), 7.65-7.50 (15H, m, Ph). $^{13}C\{^1H\}$ NMR (100.64 MHz) = δ 202.5 (s, $C_{carbene}$), 136.2 (s, =CH), 134.1-128.3 (m, Ph), 117.6 (s, =CH).