ELECTRONIC SUPPORTING INFORMATION

Intramolecular carboboration of a carbonyl ligand to form boroxycarbenes.

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Materials and Methods.

^{1}H NMR spectra were recorded at 400.13 or 300.13 MHz, ^{13}C NMR spectra were recorded at 100.61 or 75.78 MHz, ^{31}P NMR at 161.98 MHz and ^{19}F NMR at 282.40 or 376.50 MHz. Chemical shifts are reported in ppm and referenced to the solvent peak and to a H_3PO_4 aqueous solution (85%) for ^{31}P NMR experiments and referenced to $CFCl_3$ for ^{19}F NMR. The temperature of the NMR was calibrated with methanol and ethylene glycol standards. All solvents were purified by standard techniques.[1] Reactions were performed under nitrogen in Schlenk flasks. All filtrations were performed through Celite under nitrogen.

Experimental details for the preparation of manganese compounds 1, 3·TfO, 5a, 5b, 6, 7, 8, 9, 10a and 10b.

Compounds **2** and **4** were prepared as previously described.[2]

- **Synthesis of fac-[Mn(CO)$_3$κ$_3$(N,O,O')-{py-CH(OH)CH$_2$COCH$_3$}][OTf], 3·TfO**

Pyridine-2-carboxaldehyde (0.780 g, 7.28 mmol) is solved in 50 ml of hexane and then $[MnBr(CO)_5]$ (2.000 g, 7.28 mmol) is added. The reaction mixture was refluxed for 40 minutes. A brownish precipitate is formed, filtered, washed with hexane (3 x 15 ml), and dried under high vacuum. To a solution of fac-$[MnBr(CO)_3(pyC(H)=O)]$ formed in the previous reaction (0.300 g, 0.920 mmol) in 30 ml of acetone, AgOTf (0.236 g, 0.920 mmol) was added. The resulting suspension was refluxed and stirred for 4h in the dark. Then solvent was removed and the solid extracted with CH_2Cl_2.Hexane is added and solvent partially removed. A yellow precipitate is formed, which is subsequently filtered. (0.371 g, 89%).

IR (Me_2CO, cm^{-1}): 2052, 1958, 1944 (CO).

IR (CH_2Cl_2, cm^{-1}): 2055, 1967, 1943 (CO), 1674 (C=O).

^{1}H NMR (r.t., 300.13 MHz, Me2CO-d6): 9.54 [br, 1H, OH], 9.25 [br, 1H, pyH^{6}], 8.22 [a, 1H, pyH^{4}], 7.88 [br, 1H, pyH^{3}], 7.76 [br,1H, pyH^{5}], 5.80 [br,1H, CH], 3.81 [d(J=19Hz),1H, CH_2], 3.60 [d(J=19Hz),1H, CH_2], 2.37 [s ,3H, CH_3].

Elemental Analysis: Found: C 34.63, H 2.31, N 3.01. Calc. for **$C_{13}H_{11}F_3MnNO_8S$**: C 34.45; H 2,45; N 3.09.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

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[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.

[2] C. M. Álvarez, R. Carrillo, R. García-Rodríguez, D. Miguel, *Chem. Commun*. 2011, **47**, 12765.

- **Synthesis of *fac*-[Mn(CO)$_3$κ$_3$(N,O,O')-{py-CH(OH)CH$_2$COCH$_3$}][ClO$_4$], 3· ClO$_4$**

Pyridine-2-carboxaldehyde (0.780 g, 7.28 mmol) is solved in 50 ml of hexane and then [MnBr(CO)$_5$] (2.000 g, 7.28 mmol) is added. The reaction mixture was refluxed for 40 minutes. A brownish precipitate is formed, filtered, washed with hexane (3 x 15 ml), and dried under high vacuum. To a solution of *fac*-[MnBr(CO)$_3$(pyC(H)=O)] formed in the previous reaction (0.300 g, 0.920 mmol) in 30 ml of acetone, AgClO$_4$ (0.190 g, 0.920 mmol) was added. The resulting suspension was refluxed and stirred for 4h in the dark. Then solvent was removed and the solid extracted with CH$_2$Cl$_2$.Hexane is added and solvent partially removed. A yellow precipitate is formed, which is subsequently filtered. (0.329 g, 88%).

IR (Me$_2$CO, cm^{-1}): 2052, 1958, 1944 (CO).

IR (CH$_2$Cl$_2$, cm^{-1}): 2055, 1967, 1943 (CO), 1674 (C=O).

^{1}H NMR (r.t., 300.13 MHz, Me2CO-*d6*): 9.54 [br, 1H, O*H*], 9.25 [br, 1H, pyH^6], 8.22 [a, 1H, pyH^4], 7.88 [br, 1H, pyH^3], 7.76 [br,1H, pyH^5], 5.80 [br,1H, C*H*], 3.81 [d(*J*=19Hz),1H, CH_2], 3.60 [d(*J*=19Hz),1H, CH_2], 2.37 [s ,3H, CH_3].

Crystalization conditions: CH$_2$Cl$_2$/ hexane at -20ºC.

- **Synthesis of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$, 1**

To a solution of *fac*-[Mn(CO)$_3$κ$_3$(N,O,O')-{py-CH(OH)CH$_2$COCH$_3$}][OTf] (**3·TfO**) (0.200 g, 0.441 mmol) in 30 ml of acetone, an excess of K$_2$CO$_3$ (0.500 g, 3.618 mmol) is added. The solution was stirred for 2 h at room temperature. Then solvent was removed and solid was solved in CH$_2$Cl$_2$. Hexane was added to the transparent solution and solvent was evaporated to obtain compound **2** as a yellow solid. (0.119 g, 89%).

IR (Me$_2$CO, cm^{-1}): 2031, 2014, 1935, 1904 (CO).

IR (CH$_2$Cl$_2$, cm^{-1}): 2033, 2016, 1937, 1906 (CO), 1715 (C=O).

^{1}H NMR (r.t., 300.13 MHz, Me$_2$CO-d_6): 8.91 [d(*J*=5Hz), 2H, pyH^6], 7.57 [td(*J*=8, 1Hz), 2H, pyH^4], 7.34 [t(*J*=6Hz), 2H, pyH^5], 6.94 [d(*J*=8Hz), 2H, pyH^3], 5.18 [dd(*J*=10, 4Hz), 2H, C*H*], 2.85 [dd(*J*=14, 10Hz), 2H, CH_2], 2.35-2.29 [m, 8H, CH_3, CH_2].

Elemental Analysis: Found: C 47.49, H 3.39, N 4.79; Calc. for C$_{24}$H$_{20}$N$_2$O$_{10}$Mn$_2$: C 47.54, H 3.32, N 4.62.

Crystalization conditions: CH$_2$Cl$_2$/ hexane at -20ºC.

- **Synthesis of boroxy-carbene, 5a**

To a solution of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (**1**) (0.200 g, 0.330 mmol) in 20 ml of THF, 0.66 ml of 1.0 M de BEt$_3$ in hexane (0.660 mmol) were added. The reaction mixture was stirred at room temperature for 2 hours, while solution changed its color from yellow to orange. Solvent was partially removed and upon hexane addition, compound **5a** precipitated as a yellow solid. (0.217 g, 82%).

IR (THF, cm^{-1}): 1938, 1846 (CO), 1681 (C=O).

IR (CH_2Cl_2, cm^{-1}): 1936, 1840 (CO), 1682 (C=O).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-d_6): 9.10 [d(J=5Hz), 1H, pyH^6], 7.94 [t(J=8Hz), 1H, pyH^4], 7.61 [d(J=8Hz), 1H, pyH^3], 7.45 [m, 1H, pyH^5], 5.33 [m, 1H, CH], 3.36 [dd(J=20, 4Hz), 1H, CH_2CH], 3.29 [d(J=20Hz), 1H, CH_2CH], 3.00 [m, 2H, CH_2C=Mn], 2.15 [s, 3H, CH_3C=O], 0.90 [t(J=7Hz), 3H, CH_3CH$_2$C=Mn], 0.84 [t(J=7Hz), 3H, CH_3CH$_2$B], 0.73 [t(J=7Hz), 3H, CH_3CH$_2$B], 0.65-0.48 [m, 2H, CH$_3$CH_2B], 0.37 [m, 1H, CH$_3$CH_2B], -0.07 [m, 1H, CH$_3$CH_2B].

^{1}H NMR (r.t., 400.13 MHz, THF-d_8): 9.08 [br, 1H, pyH^6], 7.81 [br, 1H, pyH^4], 7.42 [br, 1H, pyH^3], 7.32 [br, 1H, pyH^5], 5.22 [m, 1H, CH], 3.26 [m, 1H, CH_2CH], 3.06 [m, 1H, CH_2CH], 2.99 [m, 2H, CH_2C=Mn], 2.06 [s, 3H, CH_3C=O], 0.88 [br, 3H, CH_3CH$_2$C=Mn], 0.84 [br, 3H, CH_3CH$_2$B], 0.73 [br, 3H, CH_3CH$_2$B], 0.65-0.48 [m, 2H, CH$_3$CH_2B], 0.37 [m, 1H, CH$_3$CH_2B], -0.10 [m, 1H, CH_3CH$_2$B].

^{13}C RMN (r.t., 100.61 MHz, THF-d_8): 341.49 [C=Mn], 230.22 [br, CO], 223.66 [br, CO], 216.69 [C=O], 165.09 [pyC^2], 150.99 [pyC^6], 138.02 [pyC^4], 123.08 [pyC^5], 120.26 [pyC^3], 74.93 [CH], 49.47 [CH$_2$CMn], 46.78 [CH$_2$CH], 30.03 [CH$_3$CO], 13.25 [br, CH$_2$B], 11.54 [br, CH$_2$B], 9.53 [CH$_3$], 9.21 [CH$_3$], 8.81 [CH$_3$].

Elemental Analysis: Found: C 53.95, H 6.32, N 3.68; Calc. for $C_{18}H_{25}BMnNO_5$: C 53.89, H 6.28, N 3.49.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of boroxy-carbene, 5b**

To a solution of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (**1**) (0.200 g, 0.330 mmol) in 20 ml of THF, 0.66 ml of 1.0 M de BBu$_3$ in hexane (0.660 mmol) were added. The reaction mixture was stirred at room temperature for 2 hours, while solution changed its color from yellow to orange. Solvent was partially removed and upon hexane addition, compound **5a** precipitated as a yellow solid. (0.253 g, 79%).

IR (THF, cm^{-1}): 1938, 1845 (CO), 1682 (C=O).

^{1}H NMR (r.t., 400.13 MHz, THF-d_8): 9.07 [br, 1H, pyH^6], 7.79 [br, 1H, pyH^4], 7.42 [br, 1H, pyH^3], 7.27 [br, 1H, pyH^5], 5.18 [m, 1H, CH], 3.28 [m, 1H, CH_2CH], 3.09 [m, 1H, CH_2CH], 2.92 [m, 2H, CH_2C=Mn], 2.07 [s, 3H, CH_3C=O], 1.66-0.50 [m, 23H, CH_3CH$_2$C=Mn], 0.39 [m, 1H, CH$_3$CH_2B], -0.08 [m, 1H, CH_3CH$_2$B].

^{13}C NMR (r.t., 100.61 MHz, THF-d_8): 341.63 [C=Mn], 230.10 [br, CO], 223.56 [br, CO], 216.67 [C=O], 165.00 [pyC^2], 150.85 [pyC^6], 138.05 [pyC^4], 123.01 [pyC^5], 120.13 [pyC^3], 74.86 [CH], 49.39 [CH$_2$CMn], 46.75 [CH$_2$CH], 30.03 [CH$_3$CO], 29.97 [CH$_2$], 29.05[CH$_2$], 28.91 [CH$_2$], 26.98 [CH$_2$], 26.79 [CH$_2$], 26.61 [CH$_2$], 22.07 [br, CH$_2$B], 21.29 [br, CH$_2$B], 13.94 [CH$_3$], 13.59 [CH$_3$], 13.25 [CH$_3$].

Elemental Analysis: Found: C 59.60, H 7.47, N 2.65; Calc. for $C_{24}H_{37}BMnNO_5$: C 59.40, H 7.68, N 2.89.

- **Synthesis of *fac*-[Mn(CO)$_3$κ$_3$(N,O,O')-{pyCH(OBF$_3$)CH$_2$COCH$_3$}], 6**

To a solution of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (1) (0.100 g, 0.165 mmol) in 20 mL of CH_2Cl_2, $BF_3{\cdot}OEt_2$ (42 μL, 0.330 mmol) was added. The reaction mixture was stirred at room temperature for 2 hours and then solvent was partially removed under vacuum. Upon addition of hexane, compound 6 precipitated as a yellow solid. (0.089 g, 73%).

IR (Me$_2$CO, cm^{-1}): 2049, 1959, 1929 (CO).

IR (CH$_2$Cl$_2$, cm^{-1}): 2052, 1964, 1932 (CO), 1676 (C=O).

^{1}H NMR (r.t., 300.13 MHz, CDCl$_3$): 9.02 [d(*J*=5Hz), 1H, py*H*^{6}], 7.92 [td(*J*=8, 1Hz), 1H, py*H*^{4}], 7.48-7.39 [m, 2H, py*H*^{3}, py*H*^{5}], 5.43 [d(*J*=5Hz), 1H, C*H*], 3.64 [dd(*J*=15, 5Hz), 1H, C*H*$_2$], 2.83 [d(*J*=20Hz), 1H, C*H*$_2$], 2.21 [s ,3H, C*H*$_3$].

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-*d*$_6$): 9.12 [d(*J*=5Hz), 1H, py*H*^{6}], 8.10 [t(*J*=7Hz), 1H, py*H*^{4}], 7.76 [d(*J*=7Hz), 1H, py*H*^{3}], 7.63 [m, 1H, py*H*^{5}], 5.41 [br,1H, C*H*], 3.51 [dd(*J*=20, 4Hz),1H, C*H*$_2$], 3.31 [d(*J*=20Hz), 1H, C*H*$_2$], 2.27 [s ,3H, C*H*$_3$].

^{19}F NMR (r.t., 282.40 MHz, CDCl$_3$): -152.49 [br, 3F ^{10}BF3, 3F ^{11}BF3].

^{19}F NMR (r.t., 376.50 MHz, Me$_2$CO-*d*$_6$): -151.61 [br, 3F ^{10}BF3, 3F ^{11}BF3].

Elemental Analysis: Found: C 38.61, H 2.88, N 3.73; Calc. for $C_{12}H_{10}BF_3MnNO_5$: C 38.85, H 2.72, N 3.78.

Crystalization conditions: CH_2Cl_2/ hexane at 0ºC.

- **Synthesis of *fac*-[Mn(CO)$_3$κ$_3$(N,O,O')-{pyCH(OCH$_3$)CH$_2$COCH$_3$}][OTf], 7**

To a solution of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (**1**) (0.100 g, 0.165 mmol) in 30 ml of CH_2Cl_2, an excess of CH_3OTf (100 μL, 0.912 mmol) was added. The reaction mixture was stirred at room temperature for 6 hours and solvent partially removed under vacuum. Addition of hexane makes compound **7** precipitate as a yellow solid, which was recrystallyzed in a mixture CH_2Cl_2/hexane. (0.088 g, 57%)

IR (CH$_2$Cl$_2$, cm^{-1}): 2056, 1967, 1944 (CO), 1670 (C=O)

^{1}H NMR (r.t., 400.13 MHz, CD$_2$Cl$_2$): 9.04 [br, 1H, py*H*^{6}], 8.03 [br, 1H, py*H*^{4}], 7.75- 7.40 [m, 2H, py*H*^{3}, py*H*^{5}], 4.51 [s, 3H, OC*H*$_3$], 5.36 [br, 1H, C*H*], 3.58-3.02 [m, 2H, C*H*$_2$], 2.25 [br ,3H, C*H*$_3$].

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-*d*$_6$): 9.22 [br, 1H, py*H*^{6}], 8.18 [m, 1H, py*H*^{4}], 7.83 [br, 1H, py*H*^{3}], 7.72 [m, 1H, py*H*^{5}], 5.71 [br, 1H, C*H*], 3.97 [s, 3H, OC*H*$_3$], 3.79 [d(*J*=20Hz), 1H, C*H*$_2$], 3.54 [d(*J*=20Hz), 1H, C*H*$_2$], 2.35 [s ,3H, C*H*$_3$].

Elemental Analysis: Found: C 35.71, H 2.93, N 2.83; Calc. for $C_{14}H_{13}F_3MnNO_8S$: C 35.99, H 2.80; N 3.00.

- **Synthesis of *fac*-[MnBr(CO)$_3$(pyCH$_2$OH)], 8**

[MnBr(CO)$_5$] (2.000 g, 7.28 mmol) is added to a solution of Pyridine-2-methanol (0.794 g, 7.28 mmol) in 50 mL of hexane. The reaction mixture is refluxed for 90 minutes. La mezcla se calienta a reflujo durante 90 minutos. A brownish precipitate is formed, filtered, washed with hexane (3 x 15 ml), and dried under high vacuum. (2.149 g, 90%).

IR (THF, cm^{-1}): 2029, 1935, 1913 (CO).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-*d$_6$*): 9.45 [br, 1H, O*H*], 9.07 [br, 1H, py*H*^{6}], 8.02 [br, 1H, py*H*^{4}], 7.62-7.55 [br, 2H, py*H*^{3}, py*H*^{5}], 5.29 [br, 1H, C*H*^{2}], 5.14 [br, 1H, C*H*^{2}].

Elemental Analysis: Found: C 33.13, H 2.11, N 4.36. Calc. for $C_9H_7BrMnNO_4$: C 32.96, H 2.15, N 4.27.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[Mn(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH$_2$O)]$_2$, 9**

To a solution of complex **8** (0.350 g, 1.07 mmol) in THF (30 mL) an excess of K_2CO_3 (1.5 g) was added. The reaction mixture was stirred at room temperature for 12 hours. Then it is filtered through kieselguhr and solvent partially removed under vacuum. Upon addition of hexane, compoud **9** precipitated as a yellow solid. (0.225 g, 85%).

IR (THF, cm^{-1}): 2031, 2012, 1934, 1914, 1902 (CO).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-*d$_6$*): Major isomer (*cisoid*, 85%): 8.88 [d(*J*=5Hz), 2H, py*H*^{6}], 7.55 [t(*J*=8Hz), 2H, py*H*^{4}], 7.27 [m, 2H, py*H*^{5}], 6.92 [d(*J*=8Hz), 2H, py*H*^{3}], 4.77 [d(*J*=18Hz), 4H, C*H*$_2$]. Minor isomer (*transoid*, 15%): 9.25 [d(*J*=5Hz), 2H, py*H*^{6}], 8.10 [t(*J*=8Hz), 2H, py*H*^{4}], 7.83 [d(*J*=8Hz), 2H, py*H*^{3}], 7.74 [m, 2H, py*H*^{5}], 5.11 [d(*J*=16Hz), 2H, C*H*$_2$], 4.91 [d(*J*=16Hz), 2H, C*H*$_2$].

Elemental Analysis: Found: C 43.52, H 2.71, N 5.51. Calc. for $C_{18}H_{12}Mn_2N_2O_8$: C 43.75, H 2.45, N 5.67.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of boroxy-carbene, 10a**

To a solution of complex **9** (0.035 g, 0.071 mmol) in THF (20 mL), an excess of BEt_3 (1.0 mL of a 1.0 M solution in hexane, 1 mmol) and an excess of PPh_3 (0.056 g, 0.213 mmol). The reaction mixture is stirred at room temperature for 6 hours. Then solvent is partially removed under vacuum and compound **10a** precipitated as a yellow solid upon hexane addition. (0.067 g, 78%).

IR (THF, cm^{-1}): 1933, 1853 (CO).

^{1}H NMR (r.t., 400.13 MHz, THF-*d$_8$*): 8.81 [d(*J*=5Hz), 1H, py*H*^{6}], 7.48-7.20 [m, 16H, PPh$_3$, py*H*^{4}], 7.12 [m, 1H, py*H*^{5}], 6.70 [d(*J*=7Hz), 1H, py*H*^{3}], 4.59 [d(*J*=16Hz), 1H, OC*H*$_2$], 3.81 [d(*J*=16Hz), 1H, OC*H*$_2$], 3.56 [m, 1H, C*H*$_2$C=Mn], 3.27

[m, 1H, C*H*$_2$C=Mn], 1.07-0.99 [m, 6H, 2C*H*$_3$], 0.90-0.51 [m, 5H, C*H*$_3$, CH$_3$C*H*$_2$B], 0.58 [m, 1H, CH$_3$C*H*$_2$B], -0.07 [m, 1H, CH$_3$C*H*$_2$B].

^{13}C NMR (r.t., 100.61 MHz, THF-*d$_8$*): 333.78 [d(*J*=28Hz), *C*=Mn], 231.24 [d(*J*=7Hz), *C*O], 225.08 [d(*J*=15Hz), *C*O], 162.32 [py*C*^{2}], 150.85 [py*C*^{6}], 136.18 [py*C*^{4}], 134.80-127.90 [18C, PPh$_3$], 122.94 [py*C*^{5}], 119.25 [py*C*^{3}], 70.88 [O*C*H$_2$], 48.84 [*C*H$_2$CMn], 12.73 [br, *C*H$_2$B], 12.05 [br, *C*H$_2$B], 9.81 [*C*H$_3$], 9.32 [*C*H$_3$], 8.54 [*C*H$_3$].

^{31}P NMR (r.t., 161.98 MHz, THF-*d$_8$*): 47.63 (s).

Elemental Analysis: Found: C 65.41, H 6.17, N 2.49. Calc. for $C_{33}H_{36}BMnNO_4P$: C 65.26, H 5.97, N, 2.31.

Crystalization conditions: THF/ hexane at -20°C.

- **Synthesis of boroxy-carbene, 10b**

To a solution of complex **9** (0.035 g, 0.071 mmol) in THF (20 ml), an excess of BBu$_3$ (1.0 mL of a 1.0 M solution in ether, 1 mmol) and an excess of PPh$_3$ (0.056 g, 0.213 mmol). The reaction mixture is stirred at room temperature for 8 hours. Then solvent is partially removed under vacuum and compound **10b** precipitated as a yellow solid upon hexane addition and washed with hexane (3 x 15ml). (0.064 g, 65%).

IR (THF, cm^{-1}): 1933, 1853 (CO).

^{1}H NMR (r.t., 400.13 MHz, THF-*d$_8$*): 8.79 [br, 1H, py*H*^{6}], 7.48-7.19 [m, 16H, PPh3, py*H*^{4}], 7.07 [br, 1H, py*H*^{5}], 6.68 [br, 1H, py*H*^{3}], 4.62 [d(*J*=16Hz), 1H, OC*H*$_2$], 3.81 [d(*J*=16Hz), 1H, OC*H*$_2$], 3.57 [m, 1H, C*H*$_2$C=Mn], 3.23 [m, 1H, C*H*$_2$C=Mn], 1.62-0.64 [m, 23H, 2BC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$, C*H*$_3$C*H*$_2$C*H*$_2$CH$_2$C=Mn], 0.58 [m, 1H, C*H*$_2$B], -0.06 [m, 1H, C*H*$_2$B].

^{13}C NMR (r.t., 100.61 MHz, THF-*d$_8$*): 334.00 [d(*J*=28Hz), *C*=Mn], 231.08 [d(*J*=7Hz), *C*O], 225.17 [d(*J*=15Hz), *C*O], 162.08 [py*C*^{2}], 150.64 [py*C*^{6}], 135.98 [py*C*^{4}], 134.80-127.90 [18C, PPh3], 122.72 [py*C*^{5}], 118.96 [py*C*^{3}], 70.62 [O*C*H$_2$], 55.30 [*C*H$_2$CMn], 29.80 [*C*H$_2$], 28.92 [*C*H$_2$], 28.70 [*C*H$_2$], 26.85 [*C*H$_2$], 26.71 [*C*H$_2$], 26.57 [*C*H$_2$], 21.98 [br, *C*H$_2$B], 21.21 [br, *C*H$_2$B], 13.89 [*C*H$_3$], 13.55 [*C*H$_3$], 13.23 [*C*H$_3$].

^{31}P NMR (r.t., 161.98 MHz, THF-*d$_8$*): 47.98 (s).

Elemental Analysis: Found: C 67.93, H 7.19, N 2.28. Calc. for $C_{39}H_{48}BMnNO_4P$: C 67.74, H 7.00, N, 2.03.

Experimental details for the preparation of rhenium compounds 6(Re), 7(Re), 8(Re) and 9(Re).

- **Synthesis of *fac*-[Re(CO)$_3$κ$_3$(N,O,O')-{pyCH(OBF$_3$)CH$_2$COCH$_3$}], 6(Re)**

To a solution of *fac*-[Re(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (**2**) (0.100 g, 0.115 mmol) in 20 mL of CH_2Cl_2, $BF_3{\cdot}OEt_2$ (29 μL, 0.230 mmol) was added. The reaction mixture was stirred at room temperature for 2 hours and then solvent was partially removed under vacuum. Upon addition of hexane, compound 6 precipitated as a white solid. (0.105 g, 91%).

IR (Me$_2$CO, cm^{-1}): 2038, 1933, 1909 (CO).

IR (CH$_2$Cl$_2$, cm^{-1}): 2042, 1938, 1910 (CO), 1669 (C=O).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-*d$_6$*): 8.97 [d(*J*=4Hz), 1H, pyH^6], 8.23 [td(*J*=8, 1Hz), 1H, pyH^4], 7.97 [d(*J*=8Hz), 1H, pyH^3], 7.66 [m, 1H, pyH^5], 5.74 [d(*J*=5Hz), 1H, C*H*], 3.81 [dd(*J*=20, 5Hz), 1H, CH_2], 3.65 [d(*J*=20Hz), 1H, CH_2], 2.38 [s, 3H, CH_3].

^{13}C RMN (r.t., 100.61 MHz, Me$_2$CO-*d$_6$*): 224.65 [*C*=O], 196.57 [*C*O], 196.74 [*C*O], 196.36 [*C*O], 163.32 [pyC^2], 153.30 [pyC^6], 142.21 [pyC^4], 126.43 [pyC^5], 123.28 [pyC^3], 74.82 [*C*H], 48.12 [CH$_2$], 32.09 [CH$_3$].

^{19}F RMN (r.t., 282.40 MHz, Me$_2$CO-*d$_6$*): -152.92 [s, 3F $^{10}BF_3$], -152.98 [s, 3F $^{11}BF_3$].

Elemental Analysis: Found: C 28.65, H 2.19, N 3.91; Calc. for $C_{12}H_{10}BF_3ReNO_5$: C 28.70, H 2.01, N 2.79.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[Re(CO)$_3$κ$_3$(N,O,O')-{pyCH(OCH$_3$)CH$_2$COCH$_3$}][OTf], 7(Re).**

To a solution of *fac*-[Re(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH(O)CH$_2$COCH$_3$]$_2$ (**2**) (0.100 g, 0.115 mmol) in 30 ml of CH_2Cl_2, an excess of CH_3OTf (100 μL, 0.912 mmol) was added. The reaction mixture was stirred at room temperature for 6 hours and solvent partially removed under vacuum. Slow diffusion of hexane at -20^{0}C yields colorless crystals of compound **7(Re)** suitable for X-ray diffraction. (0.082 g, 60%)

IR (CH$_2$Cl$_2$, cm^{-1}): 2046, 1940, 1928 (CO), 1660 (C=O)

^{1}H NMR (r.t., 400.13 MHz, CDCl$_3$): 8.85 [d(*J*=5Hz), 1H, pyH^6], 8.07 [td(*J*=8, 2Hz), 1H, pyH^4], 7.74 [d(*J*=8Hz), 1H, pyH^3], 7.51 [m, 1H, pyH^5], 5.86 [d(*J*=5Hz), 1H, C*H*], 4.20 [s, 3H, OCH_3], 3.90-3.40 [m, 2H, CH_2], 2.31[s ,3H, CH_3]

Elemental Analysis: Found: C 27.98, H 2.11, N 2.43; Calc. for $C_{14}H_{13}F_3ReNO_8S$: C 28.09, H 2.19 N 2.34.

Crystalization conditions: CH_2Cl_2/ hexane at -20ºC.

- **Synthesis of *fac*-[ReBr(CO)$_3$(pyCH$_2$OH)], 8(Re)**

[ReBr(CO)$_5$] (1.000 g, 2.46 mmol) is added to a solution of Pyridine-2-methanol (0.273 g, 2.50 mmol) in 50 mL of hexane. The reaction mixture is refluxed for 10 hours. A white precipitate is formed, filtered, washed with hexane (3 x 15 ml), and dried under high vacuum. (1.028 g, 91%).

IR (THF, cm^{-1}): 2025, 1917, 1893 (CO).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-d_6): 9.18 [br, 1H, OH], 8.88 [d(J=5Hz), 1H, pyH^6], 8.12 [td(J=8, 2Hz), 1H, pyH^4], 7.75 [d(J=8Hz), 1H pyH^3], 7.59 [m, 1H pyH^5], 5.66 [d(J=15Hz), 1H, CH_2], 5.46 [d(J=15Hz), 1H, CH_2].

Elemental Analysis: Found: C 23.46, H 1.79, N 3.25. Calc. for $C_9H_7BrReNO_4$: C 23.54, H 1.54, N, 3.05.

Crystalization conditions: THF/ hexane at -20ºC.

- **Synthesis of *fac*-[Re(CO)$_3$μ(O)κ$_2$(N,O)-(pyCH$_2$O)]$_2$, 9(Re)**

To a solution of complex **8(Re)** (0.275 g, 0.60 mmol) in THF (30 mL) an excess of K_2CO_3 (1.5 g) was added. The reaction mixture was stirred at room temperature for 12 hours. Then it is filtered through kieselguhr and solvent partially removed under vacuum. Upon addition of hexane, compoud **9(Re)** precipitated as a white solid. (0.118 g, 83%).

IR (THF, cm^{-1}): 2028, 2011, 1921, 1903, 1893 (CO).

^{1}H NMR (r.t., 400.13 MHz, Me$_2$CO-d_6): Major isomer (M, transoid, 70%); Minor isomer (m, cisoid, 30%) (M) [d(J=5Hz), 2H, pyH^6], 8.83 (m) [d(J=5Hz), 2H, pyH^6], 8.21 (M) [td(J=8, 2Hz), 2H, pyH^4], 7.98 (M) [d(J=8Hz), 2H, pyH^3], 7.74 (M) [m, 2H, pyH^5], 7.71 (m) [td(J=7, 1Hz), 2H, pyH^4], 7.35 (m) [m, 2H, pyH^5], 7.10 (m) [d(J=8Hz), 2H, pyH^3], 5.81 (M) [d(J=16Hz), 2H, CH_2], 5.43 (m) [d(J=17Hz), 2H, CH_2], 5.38 (M) [d(J=16Hz), 2H, CH_2], 5.10 (m) [d(J=17Hz), 2H, CH_2].

Elemental Analysis: Found: C 28.49, H 1.91, N 3.44. Calc. for $C_{18}H_{12}Re_2N_2O_8$: C 28.57, H 1.60, N 3.70.

Crytallographic data of compounds 1, 3·TfO, 3·ClO$_4$, 5a, 6, 7(Re), 8, 8(Re), 9cis and 10a

Intensity measurement was made with a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT program.[3] A semi-empirical absorption correction was applied with the program SADABS.[4] The structures were solved by direct methods with SIR2002,[5] under WINGX,[6] and refined against F^2 with SHELXTL.[7] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations were made with SHELXTL and PARST[8].

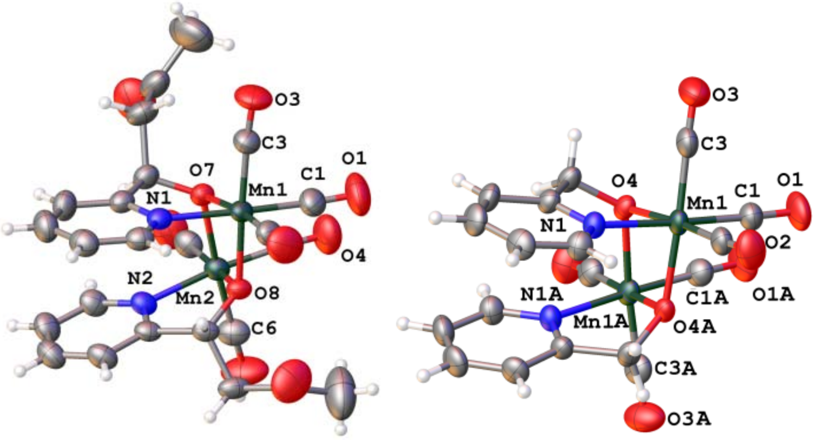

Figure S1.- Perspective view of compound **1** (left), and **9*cis*** (right), showing the atom numbering.

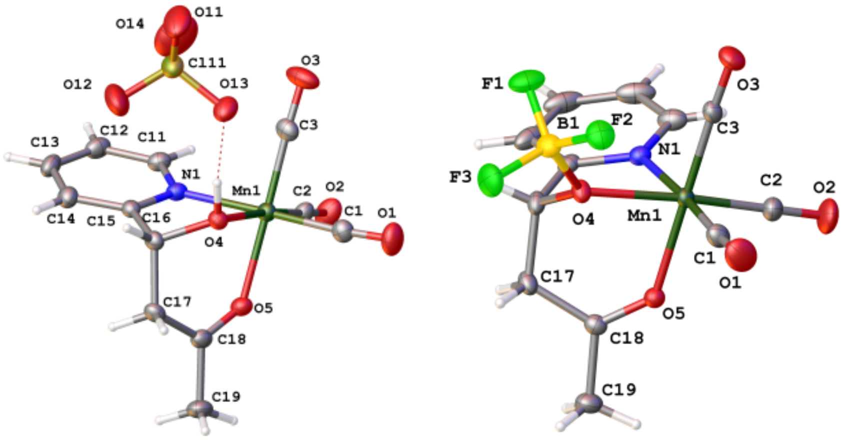

Figure S2.- Perspective view of compound **3ClO$_4$** (left), and **6** (right), showing the atom numbering. Both the proton and the BF$_3$ group, are pointing towards the axial carbonyl ligand.

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[3] SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, 1999.

[4] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 1997.

5 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidory and R. Spagna, SIR2002, A program for automatic solution and refinement of crystal structures. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.

[6] L.J. Farrugia, *J. Appl. Cryst*., 1999, **32**, 837-838.

[7] G. M Sheldrick *Acta Cryst.* 2008, **A64**, 112-122. G. M. Sheldrick, SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, 1998.

[8] *(a)* M. Nardelli, *Comput. Chem.*, 1983, **7**, 95-97. *(b)* M. Nardelli, *J. Appl. Crystallogr*., 1995, **28**, 659.

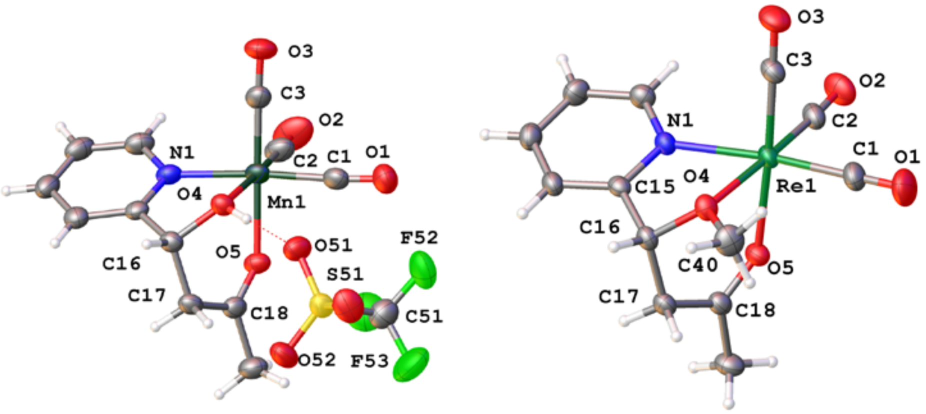

Figure S3.- Perspective view of compound **3OTf** (left), and **7(Re)** (right), showing the atom numbering. Both the proton and the methyl group respectively, are pointing towards one of equatorial carbonyl ligands, not the axial one in these cases.

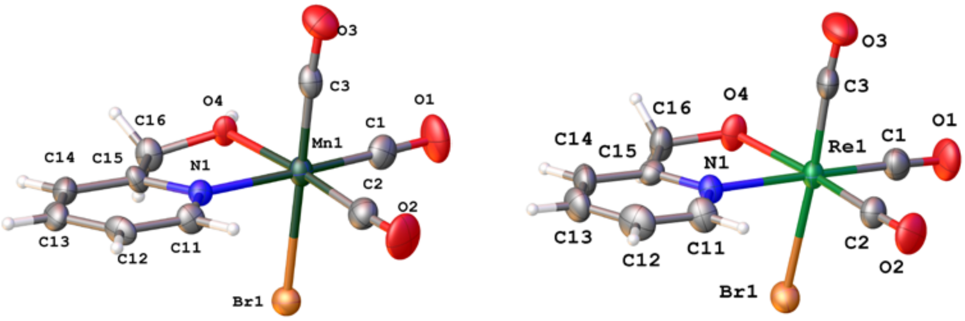

Figure S4.- Perspective view of compounds **8** (left) and **8(Re)** (right), showing the atom numbering.

Table S1. Crystal, measurement and refinement data for the compounds studied by X-ray diffraction (contd.)

	1	**3(ClO4)**	**3OTf**	**5a**	**6**
formula	$C_{24}H_{20}Mn_2N_2O_{10}$	$C_{12}H_{11}ClMnNO_9$	$C_{13}H_{11}F_3MnNO_8S$	$C_{18}H_{25}BMnNO_5$	$C_{12}H_{10}BF_3MnNO_5$
M_f	606.30	403.61	453.23	401.14	370.96
crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	9.020(3)	14.101(2)	13.030(4)	14.745(5)	7.089(7)
b/Å	9.148(3)	9.0131(15)	8.432(3)	8.775(3)	7.997(6)
c/Å	17.351(6)	13.155(2)	16.566(5)	31.476(10)	13.897(10)
α/°	105.056(6)	90.00	90.00	90.00	97.627(16)
β/°	90.211(6)	94.292(4)	105.772(6)	99.237(9)	96.696(15)
γ/°	109.425(6)	90.00	90.00	90.00	105.950(15)
V/Å^3	1297.5(8)	1667.3(5)	1751.4(10)	4020(2)	741.1(12)
T/K	298(2)	298(2)	298(2)	293(2)	293(2)
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	2	4	4	8	2
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
μ(MoKα)/mm^{-1}	1.032	0.997	0.946	0.683	0.947
reflns collected	12983	16251	11433	16037	7344
Indep. Refl.	6312	4135	2542	4935	3630
R_{int}	0.0256	0.0738	0.0392	0.0933	0.0181
R_1 ($I > 2\sigma(I)$)	0.0392	0.0511	0.0339	0.0916	0.0334
$wR(F^2)$ (all data)	0.1035	0.1387	0.0915	0.2124	0.0953
GOF on F^2	1.005	0.939	0.997	1.032	1.037
CCDC number	860498	860499	860500	860501	860502

Table S1.Crystal, measurement and refinement data for the compounds studied by X-ray diffraction (contd.)

	7(Re)	**8**	**8(Re)**	**9*cis***	**10a**
formula	$C_{14}H_{13}F_3NO_8ReS$	$C_9H_7BrMnNO_4$	$C_{13}H_{15}BrNO_5Re$	$C_{18}H_{12}Mn_2N_2O_8$	$C_{37}H_{44}BMnNO_5P$
M_f	598.51	328.01	531.37	494.18	679.45
crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
a/Å	8.830(2)	16.534(6)	9.083(3)	10.874(2)	12.581(6)
b/Å	9.860(2)	11.294(4)	9.093(3)	10.940(2)	17.889(9)
c/Å	11.793(3)	13.542(5)	11.271(4)	15.741(4)	16.664(9)
α/°	109.086(4)	90.00	75.642(5)	90.00	90.00
β/°	104.152(4)	114.688(5)	66.993(5)	91.706(4)	106.245(11)
γ/°	91.234(4)	90.00	74.222(5)	90.00	90.00
V/Å^3	935.0(4)	2297.7(13)	813.9(4)	1871.8(7)	3601(3)
T/K	298(2)	293(2)	298(2)	293(2)	298(2)
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$	$P2_1/n$
Z	2	8	2	4	4
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
μ(MoKα)/mm^{-1}	6.681	4.623	9.938	1.401	0.452
reflns collected	8209	8735	6731	7187	28738
Indep. Refl.	3803	2117	3080	1723	6614
R_{int}	0.0266	0.0872	0.0384	0.0387	0.0593
R_1 ($I > 2\sigma(I)$)	0.0229	0.0481	0.0289	0.0304	0.0527
$wR(F^2)$ (all data)	0.0593	0.1019	0.0717	0.0814	0.1781
GOF on F^2	1.057	0.841	0.987	0.981	0.979
CCDC number	860503	860504	860505	860506	860507