Electronic Supplementary Information for Dalton Transactions

Supporting Information for

Ligand-Mediated Decarbonylation as an Efficient Synthetic Method to Re(I) and Re(II) Dicarbonyl Complexes

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Contents

Materials and Methods

All reagents and solvents were purchased from standard sources and used as received. CH_2Cl_2 was distilled under a nitrogen atmosphere prior to use. IR spectra were recorded on a Perkin-Elmer BX II spectrometer from KBr pellets. NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. [(tacn)$Re^{I}(CO)_3$]Br (**1**)[1] and [(dien)$Re^{I}(CO)_3$]Br (**1a**) [2] were prepared according to reported procedures.

[1] K. Wieghardt, C. Pomp, B. Nuber, J. Weiss, *Inorg. Chem.* 1986, **25**, 1659-1661.

[2] S. Mundwiler, L. Candreia, P. Hafliger, K. Ortner and R. Alberto, *Bioconjugate. Chem.,* 2004, **15**, 195-202.

[(tacn)-N-CO-$Re^{III}(CO)_2Br$]Br (2). 200mg of **1** (0.42 mmol) were dissolved in 15ml of water. To this solution 32μL of Br_2 (0.63 mmol) were added and the resulting mixture stirred for 30min at RT. Complex **2** was isolated by filtration as a bright yellow microcrystalline powder, washed with a small amount (ca. 2mL) of cold water and dried under vacuum. Yield: 140 mg, 60%. Anal. Calc. for $C_9H_{14}Br_2N_3O_3Re_1$ (558.24): C 19.36%, H 2.53%, N 7.53% Found: C 19.20%, H 2.43%, N 7.11%. IR (solid state, KBr, cm^{-1}): 2073, 1975 (C≡O), 1765 (C=O).

[(tacn) $Re^{I}(CO)_2Br$] (3). 100mg of **2** (0.18 mmol) were stirred in a 1M NaOH solution (10mL) for 24h. Complex **3** was then collected by filtration, washed with a small amount of cold water and dried under vacuum. Yield: 81 mg, quantitative. Anal. Calc. for $C_8H_{15}Br_1N_3O_2Re_1$ (451.33): C 21.29%, H 3.35%, N 9.31% Found: C 21.09%, H 3.33%, N 9.17%. ^{1}H NMR, 500 MHz (DMSO, δ ppm): 6.82 (s, NH, 1H), 5.84 (s, NH, 2H), 2.93-2.90 (m, CH, 2H), 2.79-2.75 (m, CH, 5H), 2.65-2.56 (m, CH, 5H). IR (solid state, KBr, cm^{-1}): 1883, 1770 (C≡O).

[(tacn)$Re^{II}(CO)_2Br$]PF_6 (4). In a glovebox; 120mg of **3** (0.27 mmol) and 88mg of $[Cp_2Fe]PF_6$ (0.27 mmol) were stirred in CH_2Cl_2 (10 mL) at RT for two days or until the solution turned completely orange. Complex **4** was then collected by filtration, washed with a small amount of cold CH_2Cl_2 and cold ether and dried under vacuum. Yield: 158 mg, quantitative. Anal. Calc. for $C_8H_{15}Br_1F_6N_3O_2P_1Re_1$ (596.30): C 16.11%, H 2.54%, N 7.05% Found: C 15.97%, H 2.51%, N 6.90%. IR (solid state, KBr, cm^{-1}): 1999, 1866 (C≡O).

Complexes [(dien)-N-CO-$Re^{III}(CO)_2Br$]Br (**2a**), [(dien)$Re^{I}(CO)_2Br$] (**3a**) and [(dien)$Re^{II}(CO)_2Br$]PF_6 (**4a**) were synthesized as described for **2**, **3** and **4** respectively.

[(dien)-N-CO-Re^{III}(CO)$_2$Br]Br (2a). Anal. Calc. for $C_7H_{12}Br_2N_3O_3Re_1$ (532.20): C 15.80%, H 2.27%, N 7.90% Found: C 16.92%, H 3.47%, N 9.11%. IR (solid state, KBr, cm^{-1}): 2066, 1994 (C≡O), 1774 (C=O).

[(dien)Re^{I}(CO)$_2$Br] (3a). Anal. Calc. for $C_6H_{13}Br_1N_3O_2Re_1$ (425.30): C 16.94%, H 3.08%, N 9.88% Found: C 17.09%, H 3.25%, N 9.71%. ^{1}H NMR, 500 MHz (DMSO, δ ppm): 6.70 (s, NH, 1H), 4.60 (s, NH, 2H), 3,50 (s, NH, 2H), 2.71 (s, CH, 8H). IR (solid state, KBr, cm^{-1}): 1856, 1755 (C≡O).

[(dien)Re^{II}(CO)$_2$Br]PF$_6$ (4a). Anal. Calc. for $C_6H_{13}Br_1F_6N_3O_2P_1Re_1$ (570.26): C 12.64%, H 2.30%, N 7.37% Found: C 12.41%, H 2.31%, N 6.96%. IR (solid state, KBr, cm^{-1}): 2010, 1867 (C≡O).

Table S1 Mulliken atomic spin densities:

1 C 0.009472	14 H 0.001385
2 H -0.000168	15 N -0.046066
3 H 0.000018	16 H 0.000417
4 C 0.003824	17 N -0.021949
5 H -0.000613	18 N -0.029372
6 H 0.003009	19 C -0.005311
* 7 Re 0.864396*	20 H -0.000173
8 C -0.019733	21 H -0.000124
9 C -0.012520	22 C 0.018391
10 O 0.029034	23 H 0.000353
11 O 0.035165	24 H -0.000400
* 12 Br 0.169450*	25 C -0.004793
13 H 0.001006	26 H 0.000213

27 H 0.000068	29 H -0.000455
28 C 0.005387	30 H 0.000089

Sum of Mulliken spin densities= 1.00000

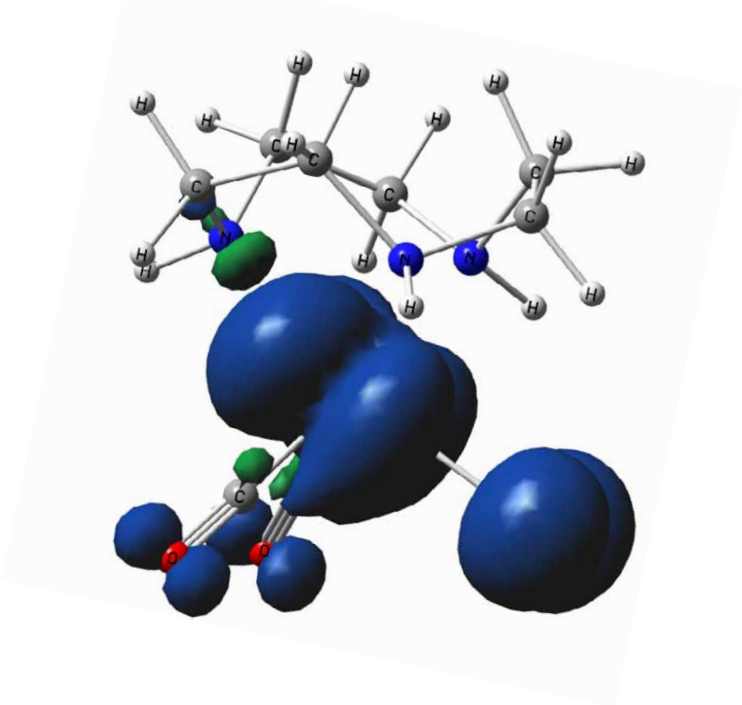

Figure S1. Theoretical calculated spin density surface of the cation of **4.**