

Controlling Carbon Monoxide Binding at Di-iron Units Related to the Iron-only Hydrogenase Sub-site

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Complexes used in this study

Complexes **1**, **7** and **8** were synthesised as previously described [1,2]. The complexes **2**, **3**, **5**, **6**, **9** and **B** (X = CH₂OH) are new and were synthesised by an extension of the general method used to synthesise **7** and **8**. The syntheses of [Fe₂(CO)₅{CH₃C(CH₂S)₂CH₂S(C₆H₄)-*p*-CN}], **2** and [Fe₂(CO)₅{CH₃C(CH₂S)₂(2-pyridine)}] **6** are illustrative and these are described in detail.

[Fe₂(CO)₅{CH₃C(CH₂S)₂CH₂S(C₆H₄)-*p*-CN}], **2**.

(a) synthesis of ligand, CH₃C(CH₂S)₂CH₂S(C₆H₄)-*p*-CN, 4-((4-benzonitrilethio)methyl)-4-methyl-1,2-dithiolane

NaH (60 % oil suspension, 0.38 g, 9.4 mmol) was washed with hexane and then dissolved in THF (80 cm³) under a dinitrogen atmosphere. 4-methyl-[1,2] dithiolan-4-yl)methanethiol (0.76 g, 4.6 mmol) was dissolved in THF (5 cm³) , added to the solution of NaH and stirred at room temperature. 4-bromo-nitrobenzene (0.93 g, 5.1 mmol) was dissolved in THF (5 cm³), added to the mixture and stirred at 75 °C overnight. Excess of sodium hydride was quenched by ammonium chloride-saturated water and the product was extracted with dichloromethane. The organic phase was dried (MgSO₄) and purified by flash chromatography (hexane/chloroform 1:2) to give a red-brown solid (0.30 g, 1.1 mmol, 24 %). Microanalysis: C, H, N, Found (calculated) C₁₂H₁₃NS₃ , C, 54.32; H, 5.07; N, 4.96; S, 35.71 (C, 53.90; H, 4.90; N,

5.24; s, 35.97); δ_{H} (400 MHz; solvent CDCl_3 ; standard SiMe_4) 1.37 (3H, s, CH_3), 2.96 (2H, d, J 11.7 Hz, CH_2SS), 3.15 (2H, d, J 11.4 Hz, CH_2SS), 3.24 (2H, s, CH_2SPh), 7.39 (2H, d, J 8.5 Hz, Ph), 7.54 (2H, d, J 8.5 Hz, Ph); $\nu_{\text{max}}/\text{cm}^{-1}$ (CN) 2217 (nujol).

(b) $[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C}(\text{CH}_2\text{S})_2\text{CH}_2\text{S}(\text{C}_6\text{H}_4)\text{-}p\text{-CN}\}]$, **2:** $[\text{Fe}_3(\text{CO})_{12}]$ (0.62 g, 1.2 mmol) was dissolved in toluene (50 cm^3). **I** (0.30 g, 1.1 mmol) was added to the solution. The dark green mixture turned red brown when it was heated at 75 °C for 90 min. The solvent was removed and the compound was purified by flash chromatography under dinitrogen (diethyl ether/hexane 2:1) to give a red-brown powder (0.19 g, 0.37 mmol, 33 %).

$[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C}(\text{CH}_2\text{S})_2\text{CH}_2\text{S}(\text{C}_6\text{H}_4)\text{-}p\text{-CN}\}]$, **2:** Microanalysis: C, H, N Found (calculated), $\text{C}_{17}\text{H}_{13}\text{NO}_5\text{S}_3\text{Fe}_2$, 39.52, 2.76, 2.68 (39.33; 2.52; 2.70) $\nu_{\text{max}}/\text{cm}^{-1}$ (CO) 1933, 1988 and 2051 (CN) 2232 (acetonitrile); δ_{H} (400 MHz; solvent CDCl_3 ; standard SiMe_4) 0.93 (3H, s, CH_3), 1.72 (2H, d, J 14.1 Hz, CH_2SFe), 2.30 (2H, d, J 14.2 Hz, CH_2SFe), 2.40 (2H, s, CCH_2SPh), 7.76 (2H, d, J 8.0 Hz, Ph), 7.90 (2H, d, J 8.3 Hz, Ph).

$[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C}(\text{CH}_2\text{S})_2\text{CH}_2\text{S}(\text{C}_6\text{H}_4)\text{-}p\text{-NO}_2\}]$, **3:** Microanalysis: C, H, N Found (calculated), $\text{C}_{16}\text{H}_{13}\text{NO}_7\text{S}_3\text{Fe}_2$, 35.74; 2.50; 2.67 (35.64; 2.43; 2.60). $\nu_{\text{max}}/\text{cm}^{-1}$ (CO) 1933, 1988 and 2052 (acetonitrile); δ_{H} (400 MHz; solvent CDCl_3 ; standard SiMe_4) 0.95 (3H, s, CH_3), 1.74 (2H, d, J 13.9 Hz, CH_2SFe), 2.32 (2H, d, J 13.9 Hz, CH_2SFe), 2.44 (2H, s, CCH_2SPh), 7.95 (2H, d, J 8.8 Hz, Ph), 8.33 (2H, d, J 8.8 Hz, Ph).

$\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C}(\text{CH}_2\text{S})_2\text{CH}_2\text{S}(\text{C}_6\text{H}_4)\text{-}p\text{-NH}_2\}$, **5:** Microanalysis: C, H, N Found (calculated), $\text{C}_{16}\text{H}_{15}\text{NO}_5\text{S}_3\text{Fe}_2$, 37.76; 2.99; 2.66 (37.74; 2.97; 2.75). $\nu_{\text{max}}/\text{cm}^{-1}$ (CO) 1928, 1983 and 2048 (acetonitrile); δ_{H} (400 MHz; solvent CDCl_3 ; standard SiMe_4) 0.83 (3H, s, CH_3), 1.66 (2H, d, J 13.7 Hz, $\text{CH}_2\text{SCaromatic}$), 2.25 (4H, d, J 13.4 Hz, $2\times\text{CH}_2\text{SFe}$), 3.95 (2H, s, NH_2), 7.95 (2H, d, J 8.8 Hz, Ph), 8.33 (2H, d, J 8.8 Hz, Ph).

Note: complex **4** was generated *in situ* by treatment of **5** with 1.2 equivalents of HBF₄·Me₂O in MeCN under CO at 1 atmosphere.

[Fe₂(CO)₅{CH₃C(CH₂S)₂(2-pyridine)}] (A, X = 2-pyridine), **6**: To a solution of Fe₃(CO)₁₂ (0.216, 0.4mmol) in dry toluene (5ml) was added 2-methyl-2-(pyridin-2-yl)propane-1,3-dithiol (0.079g, 0.4mmol) in dry toluene (10ml) under N₂. The reaction was heated at 110 °C for 4 hours with stirring. After removing the solvent, the reaction residues were purified using flash chromatography (eluting system: ethyl acetate and *n*-hexane at a ratio of 1:4). A greenish brown band was collected. Removal of the solvents under vacuum yielded a black-green solid. The crude product was redissolved in CH₃CN (10ml) and insoluble materials were filtered off under N₂. Both slow evaporation and storing at low temperature (-20 °C) of the filtrate gave single crystals suitable for X-ray diffraction structural determination. Microanalysis: C, H, N Found (calculated), C₁₄H₁₁NO₅S₂Fe₂, 37.40; 2.50; 3.15 (37.44; 2.47; 3.12). FTIR (CH₃CN) ν_{CO}: 2048.6, 1978.2, 1914.1 cm⁻¹; MS (ES⁺): (M+1)/z = 450.8, (M-CO+1)/z = 422.3. Protonation of **6** in dichloromethane using excess HBF₄·Et₂O under CO atmosphere produces the moisture-sensitive hexacarbonyl complex **C** (X = 2-pyridinium) **5**. Storing this solution in dichloromethane at low temperature produces single crystals suitable for structure analysis. The infrared spectrum has the characteristic IR pattern of a diiron hexacarbonyl complex.

[Fe₂(CO)₅{CH₃C(CH₂S)₂(CH₂NH₂)}] (A, X= CH₂NH₂), **9**: Microanalyses: C, H, N Found (calculated), C₁₀H₁₁NO₅S₂Fe₂, 29.63; 2.72; 3.61 (29.95; 2.76; 3.49). FTIR (acetonitrile) ν_{CO}: 2043.9, 1972.1, 1906.5 cm⁻¹. MS (ESI, -): (m+1)/z = 402. ¹H NMR (CDCl₃): 0.704 (s, 3H), 1.692 (d, 2H, J=13.4Hz), 2.173 (broad, 2H), 2.335 (d, 2H, J=13.6Hz), 2.663 (broad, 2H).

Supplementary Material (ESI) for Chemical Communications
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[Fe₂(CO)₆{CH₃C(CH₂S)₂CH₂OH}] (B, X = CH₂OH): Microanalyses: C, H, N

Found (calculated), C₁₁H₁₀O₇S₂Fe₂, 30.68; 2.47; <0.1 (30.72; 2.34; 0.00). FTIR

(CH₃CN) ν_{CO} : 2074.1, 2033.7, 1998 cm⁻¹

[1] M. Razavet, S.C. Davies, D.L. Hughes and C.J. Pickett, *Chem. Commun.*, 2001, 847-848.

[2] M. Razavet, S.C. Davies, D.L. Hughes, J.E. Barclay, D.J. Evans, S.A. Fairhurst, X. Liu and C.J. Pickett, *Dalton Trans.*, 2003, 586-595.