Supporting Information of

Mixed-Valence [Fe^IFe^{II}] Hydrogenase Active Site Model Complexes Stabilized by a Bidentate Carborane bis-Phosphine Ligand

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UV/vis spectra of the *o*-carborane diiron complexes [$Fe_2(dt)(CO)_4(BC)$] 1-3:

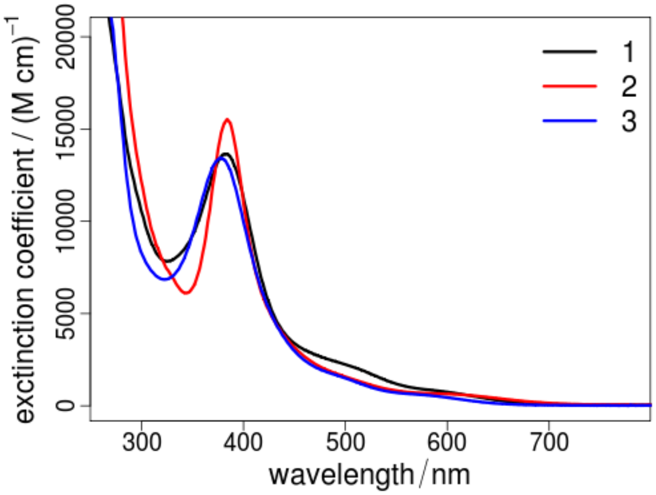

Figure S 1 Absorption spectra of **1** (black), **2** (red), **3** (blue) dissolved in dichloromethane. The three complexes differ in their dithiolate bridge: pdt = 1,3-propyldithiolate = **1**, bdt = 1,2-benzenedithiolate = **2** and edt = 1,2-ethyldithiolate = **3**.

^{13}C-NMR data (carbonyl region) of the dinuclear complexes [$Fe_2(dt)(CO)_4(BC)$] 1-3 and of [$Fe(BC)(CO)_3$] 5:

Table S 1 Selected ^{13}C-NMR signals of [$Fe_2(dt)(CO)_4(BC)$] (bridge = pdt **1**, bdt **2**, edt **3**).

Compound in $CDCl_3$	^{13}**C-NMR*** δ / ppm
1	210.07, 210.24
1’	207.80
2	209.76, 209.87
2’	207.56
3	218.47, 218.31
3’	208.40
5	216.90
4’	205.10

$*$ The values of the hexacarbonyl precursors [$Fe_2(dt)(CO)_6$] (dt = dithiolate, pdt = propyl-1,3-dt **1’**, bdt = benzene-1,2-dt **2’**, edt = ethyl-1,2-dt **3’** and cdt = *o*-carborane-1,2-dt **4’**) are given for comparison.

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Crystallographic data of 5

Monocrystals of [Fe(BC)$(CO)_3$] **5** were obtained by slow evaporation of a mixture of dichloromethane and n-hexane. The respective crystal structure data has been stored at the Cambridge Crystallographic Data Centre with the deposition number CCDC822991.

Table S 2 Crystallographic data and refinement details for **5**

Compound	**5**
Formula	$C_{29}H_{30}B_{10}FeO_3P_2$
M_w (g/mol); F(000)	652.42; 2672
T (K); wavelength (Å)	100; 0.71073
Crystal System	Orthorhombic
Space Group	Pbca
Unit Cell: a (Å)	10.7762(5)
b (Å)	17.3586(8)
c (Å)	33.5473(16)
β (°)	90
V (Å^3); Z; $d_{calcd.}$ (g/cm^3)	6275.3(5); 8; 1.381
θ range (°); completeness	2.25 to 27.50; 0.974
collected reflections; R_{int}	122210; 0.0601
unique reflections; R_{int}	9984; 0.069
μ(mm^{-1}); Abs. Corr.	0.615; Semi-empirical
R_1(F); wR(F^2) [I>2σ(I)]	0.0337; 0.0590
R_1(F); wR(F^2) (all data)	0.0813; 0.0930
GoF(F^2)	0.929
Residual electron density (e^-/Å^3)	0.442 and -0.393

Table S 3 Selected bond lengths (Å) and angles (°) for [Fe(BC)$(CO)_3$] **5**

Compound	**5**
Fe(1)-P(1)	2.1948(5)
Fe(1)-P(2)	2.1974(5)
Fe(1)-CCO [a]	1.773(18)
C=O_{all} [b]	1.1518(20)
P(1)-Fe(2)-P(2)	90.821(17)

[a] average over all three Fe(1)-CCO bonds, [b] average over all three C=O bonds

FTIR spectroelectrochemistry

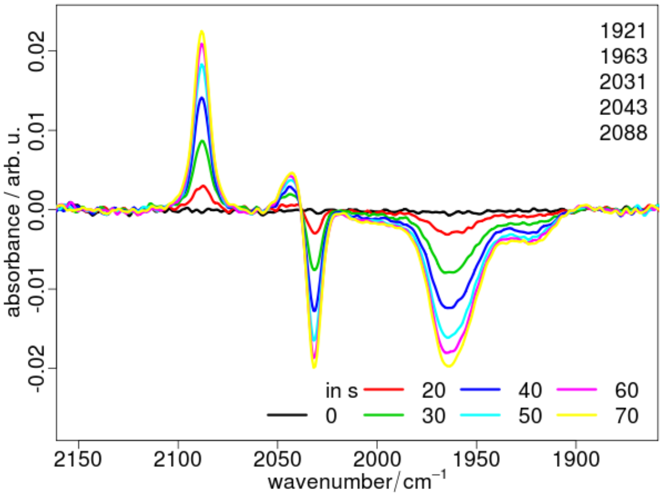

Figure S 2 FTIR-SEC spectra recorded during oxidation of a 1.0 mM solution of **1** in CH_2Cl_2 under inert conditions. The negative bands correspond to the depletion of the starting material. The wavenumbers in the upper right corner represent the maxima of the corresponding IR bands.

^{1}H-NMR spectra of the dinuclear complexes [Fe_2(dt)$(CO)_4$(BC)] 1-3 in $CDCl_3$ solution:

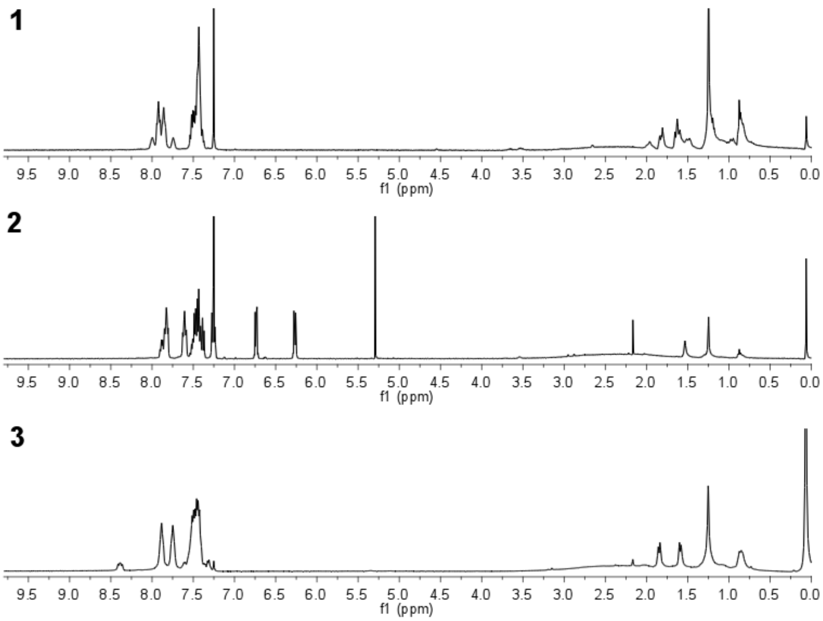

Figure S 3 ^{1}H-NMR spectra (400 MHz, $CDCl_3$ solution, at 298 K) of the complexes **1**-**3**.

^{31}P{^{1}H}-NMR spectra of the dinuclear complexes [Fe_2(dt)$(CO)_4$(BC)] 1-3 in $CDCl_3$ solution:

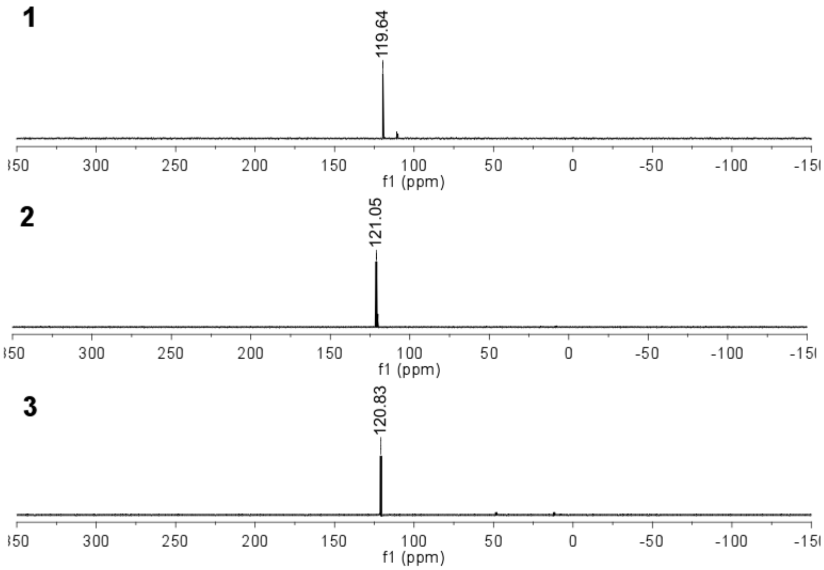

Figure S 4 ^{31}P{^{1}H}-NMR spectra (161.8 MHz, $CDCl_3$ solution) of the complexes **1**-**3**.