Restricted Rotation of an $Fe(CO)_2(PL_3)$-subunit in [FeFe]-Hydrogenase Active Site Mimics by Intramolecular Ligation

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Supporting Info

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^{31}P-NMR spectra

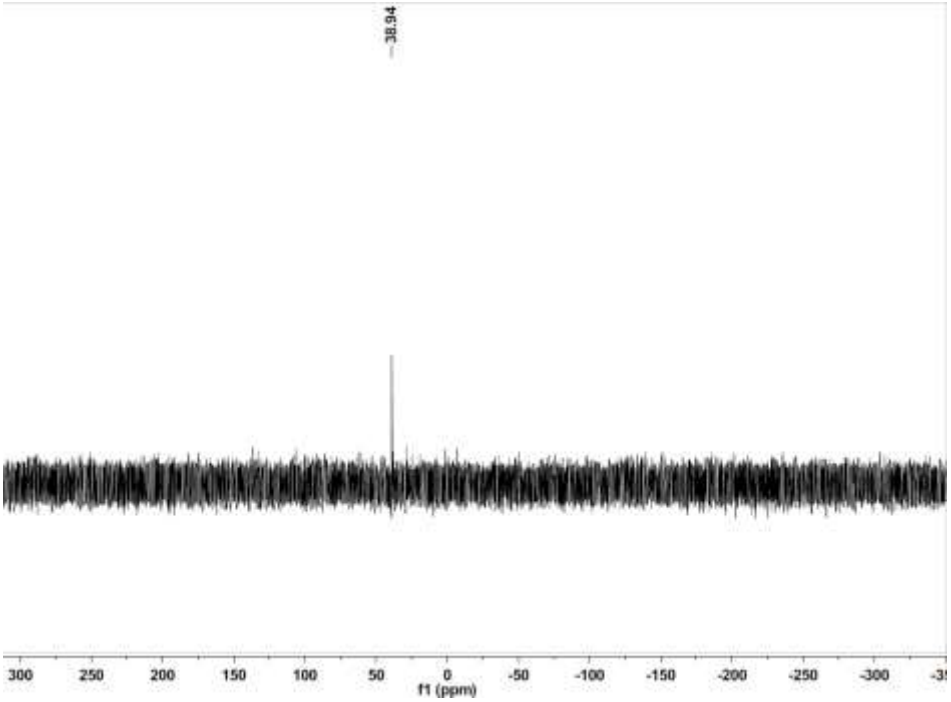


Figure S1: Fe_2(propylamide-mabdt)$(CO)_5(PPh_2Me)$ (6) ($CDCl_3$)

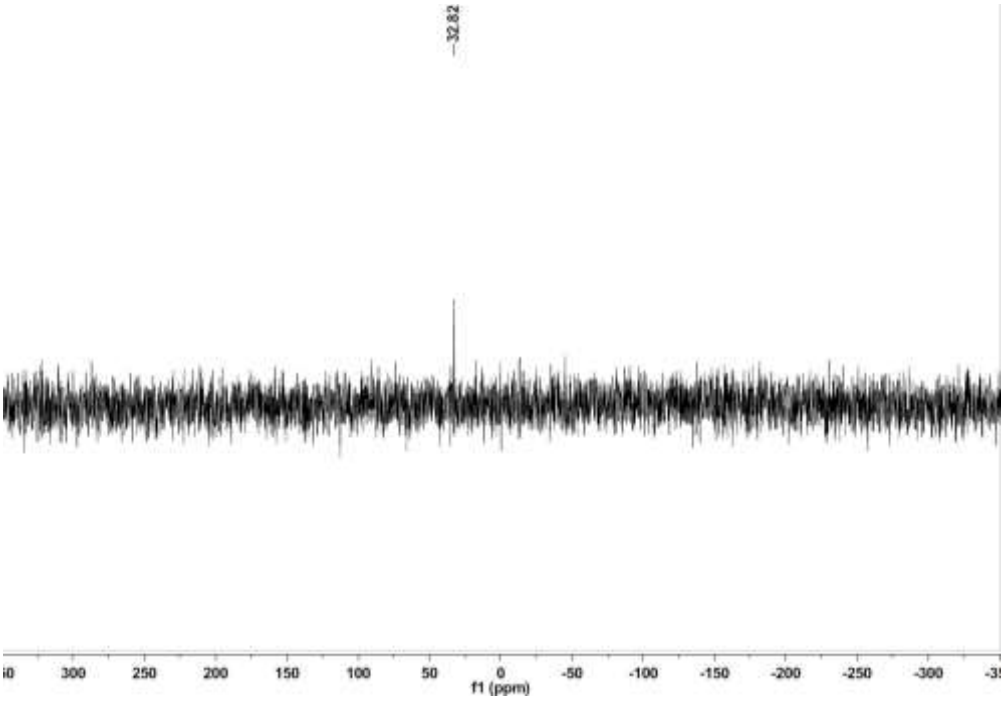


Figure S2: Fe_2(propyl-tethered-mabdt-PPh_2)$(CO)_5$ (3) ($CDCl_3$)

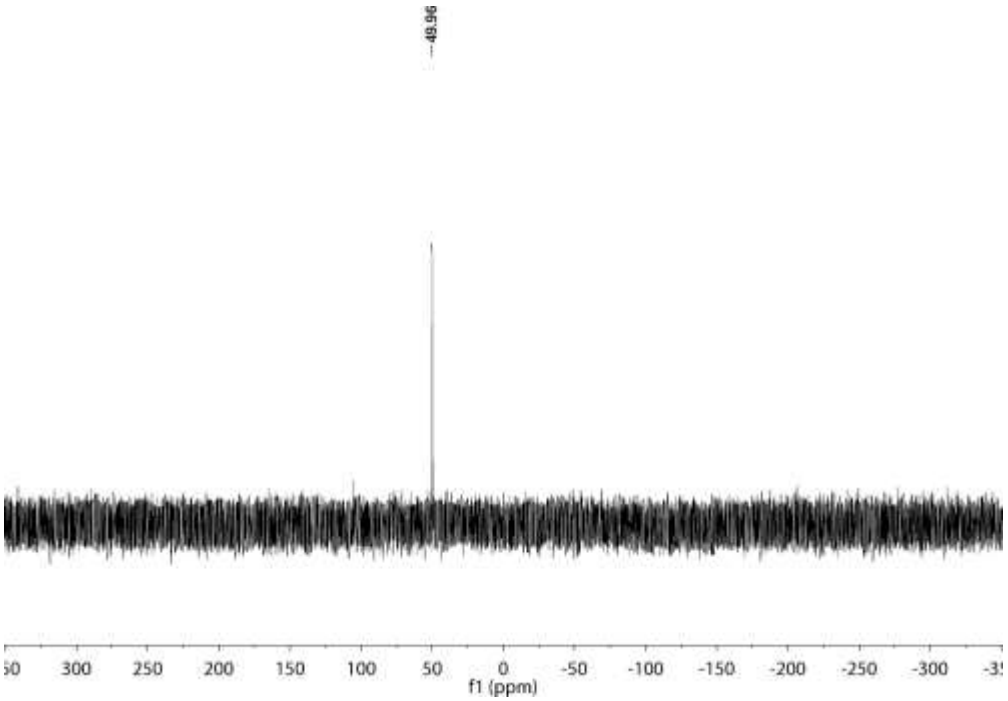


Figure S3: Fe_2(butyl-tethered-mabdt-PPh_2)$(CO)_5$ (4) (CD_2Cl_2)

Electrochemical data

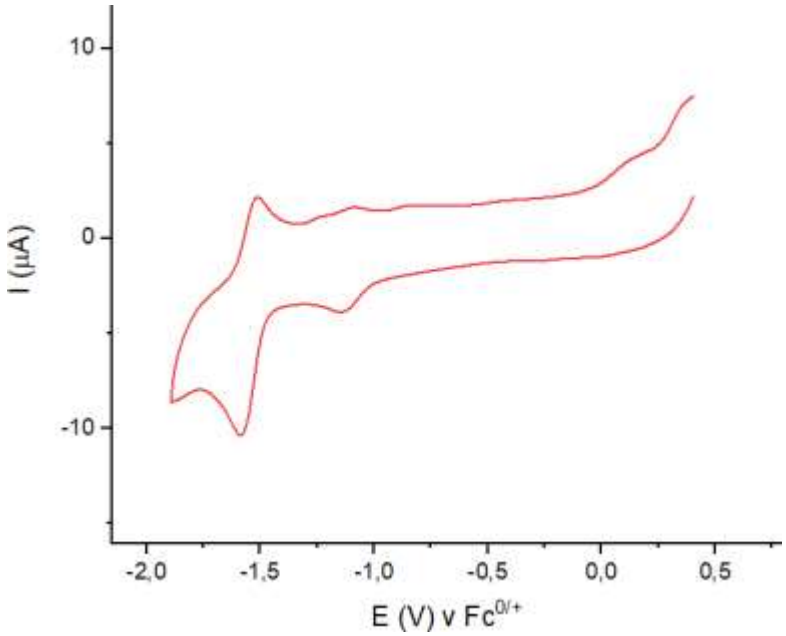


Figure S4: Cyclic voltammogram of complex **3** in 0.1M $TBAPF_6$ in MeCN, 1mM FeFe, 100 mV/s scan rate.

DFT calculations

The geometry optimized structure of the ground state is well in accordance with X-ray structure (view table S1).

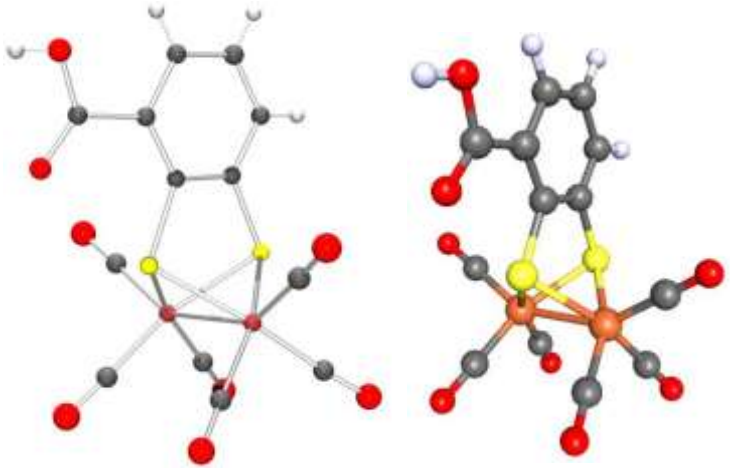


Figure S5. Left: Crystal structure of $Fe_2(mcbdt)(CO)_6$ and Right: Geometry optimized structure.

Table S1. Comparison of computed ground state structure with X-ray crystallographic data[8]

bond/angle[a]	X-ray[b]	DFT (this study)
Fe-Fe	2.4986(8)	2.5200
Fe1-S1	2.2622(10)	2.2977
Fe1-S2	2.2636(10)	2.2844
S-C	1.781(4)	1.7942
Fe-C[d]	1.802(4)	1.7852
C-O[d]	1.135(5)	1.1548
S-Fe-S[e]	81.15(4)	80.29
Fe-S-Fe[e]	56.493(3)	60.74
S-Fe-C_a [e]		102.12
C_a -Fe-C_b [e]		98.47
C_b -Fe-C_b [e]		90.82

[a]Bond lengths, Å; angles, degrees. [b]Experimental geometric parameters are averaged to C_{2V} symmetry for the molecule. C_a refers to the apical COs in the local square-based pyramid geometry of each Fe, and C_b refers to the basal COs. [c]See Experimental Section for details of the DFT method. [d]Averaged over all COs. [e]Averaged over all angles.

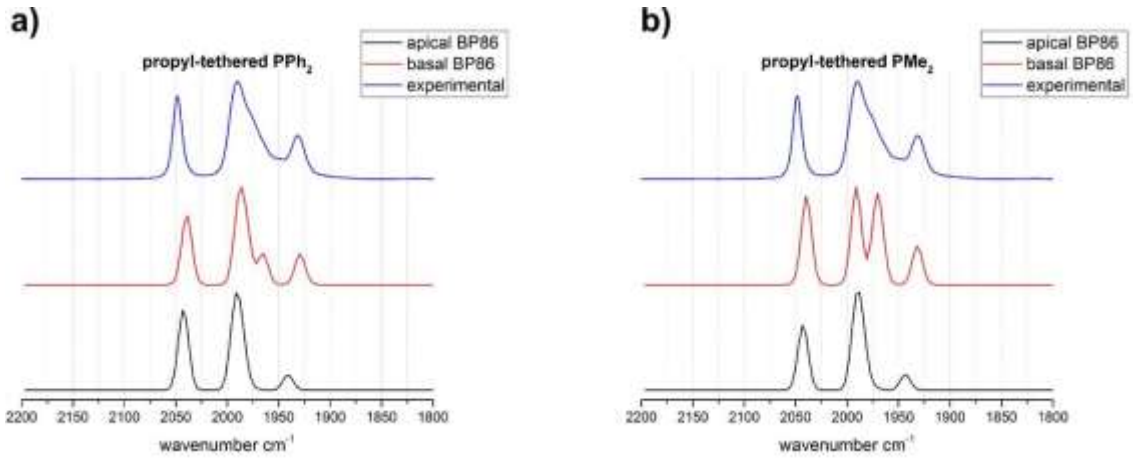


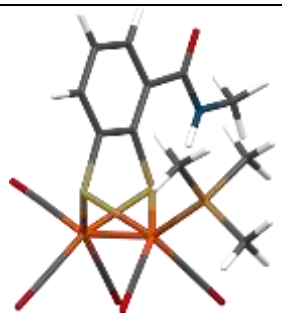
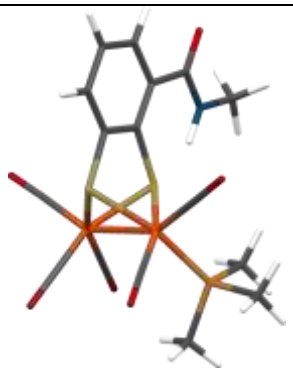
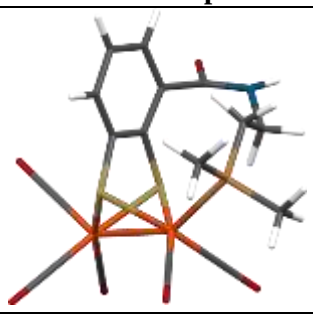
Figure S6. Calculated IR spectra for the propyl tethered complex with a) PPh_2 and b) PMe_2. Black spectra represent the vibrational frequencies for the apical structure, red spectra the basal structure. In blue is the experimental spectrum given for complex 1.

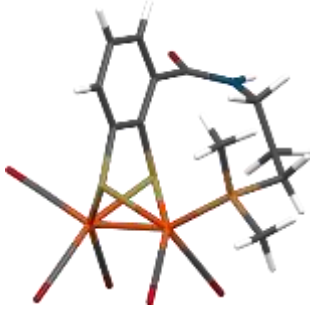
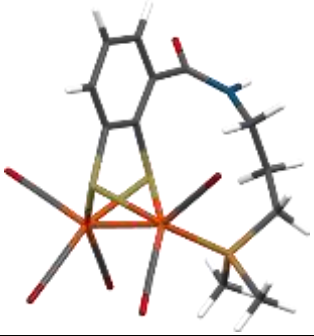
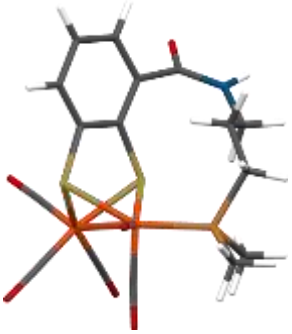
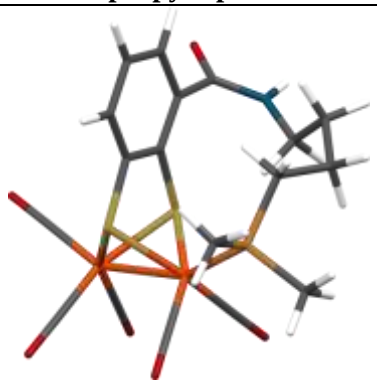
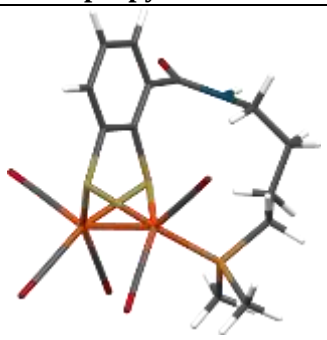
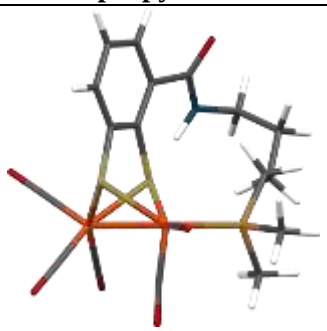
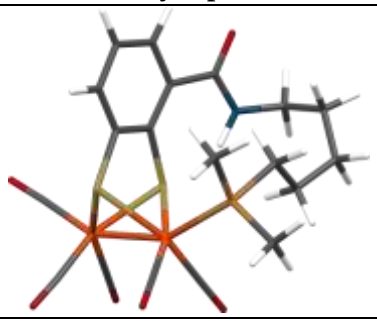
Table S2. Lowest energies for all calculated complexes with PMe_2 (def2-TZVP).

Chain length	functional	substitution	energy (Hartree)
ethyl	BP86	apical	-4790.895878096
		basal	n.a.
	B3LYP	apical	-4789.227840390
		basal	n.a.
	PWPB95	apical	-4789.428088305176
		basal	n.a.
	DLPNO-CCSD(T)	apical	-4785.064883914102
		basal	n.a.
propyl	BP86	apical	-4830.228996212
		basal	-4830.226841589
	B3LYP	apical	-4828.5334390690
		basal	-4828.5285008480
	PWPB95	apical	-4828.732726636371
		basal	-4828.731521479146
	DLPNO-CCSD(T)	apical	-4824.314256716136
		basal	-4824.308893112706
butyl	BP86	apical	-4869.549798348
		basal	-4869.554036785
	B3LYP	apical	-4867.8251102290
		basal	-4867.8282973880
	PWPB95	apical	-4868.023745984527
		basal	-4868.027199833423
	DLPNO-CCSD(T)	apical	-4863.548689363283
		basal	-4863.550183930706
pentyl	BP86	apical	-4908.890972635
		basal	-4908.887348598
	B3LYP	apical	-4907.1382768200
		basal	-4907.1325321590
	PWPB95	apical	-4907.336027496526
		basal	-4907.326278634325
	DLPNO-CCSD(T)	apical	-4902.804389701026
		basal	-4902.795260192346

reference	BP86	apical	-4792.122807997
		basal	-4792.121659707
	B3LYP	apical	-4790.4545319560
		basal	-4790.4515882420
	PWPB95	apical	-4790.640673854177
		basal	-4790.638805425159
	DLPNO-CCSD(T)	apical	-4786.284690443872
		basal	-4786.281398834074
propyl-μ-H	BP86	apical	-4830.593638823
		basal	-4830.592008635
	B3LYP	apical	-4828.912642687
		basal	-4828.910309877
propyl-$H_{term.}$	BP86	apical	-4830.558741527
		basal	-4830.573430899
	B3LYP	apical	-4828.862578903
		basal	--4828.881269625

Table2. Overview calculated structures (BP-86)

		
Reference apical	**Reference basal**	
		

ethyl-apical		
		
propyl-apical	**propyl-basal**	**propyl-TS**
		
butyl-apical	**butyl-basal**	**butyl-TS**
		
pentyl-apical	**Pentyl-basal**	
		
Propyl-basal-μ-H	**Propyl-basal-$H_{term.}$**	