Electronic Supplementary Information

Electrochemical and theoretical investigations of the reduction of $[Fe_2(CO)_5L\{\mu\text{-}SCH_2XCH_2S\}]$ complexes related to [FeFe]Hydrogenase.

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Figure S1 : Cyclic voltammetry of $[Fe_2(CO)_6\{\mu\text{-}SCH_2N(^iPr)CH_2S\}]$ **1b** (1 mM) under Ar in MeCN-$[NBu_4][PF_6]$ (v = 0.2 V s^{-1}; vitreous carbon electrode; potentials are in V vs Fc^+/Fc).

Figure S2 : Scan rate dependence of the current function for the reduction of $[Fe_2(CO)_6\{\mu\text{-}S(CH_2)_3S\}]$ **2** (1.4 mM) under Ar and under CO in MeCN-$[NBu_4][PF_6]$ (vitreous carbon electrode).

Figure S3 : Cyclic voltammetry of $[Fe_2(CO)_6\{\mu\text{-}SCH_2N(^iPr)CH_2S\}]$ **1b** (1 mM) at different scan rates under Ar in MeCN-$[NBu_4][PF_6]$ (vitreous carbon electrode; potentials are in V vs Fc^+/Fc).

Figure S4 : Cyclic voltammetry of complexes a) **1a** and b) **2** in MeCN-$[NBu_4][PF_6]$ under CO at different scan rates (vitreous carbon electrode; potentials are in V vs Fc^+/Fc).

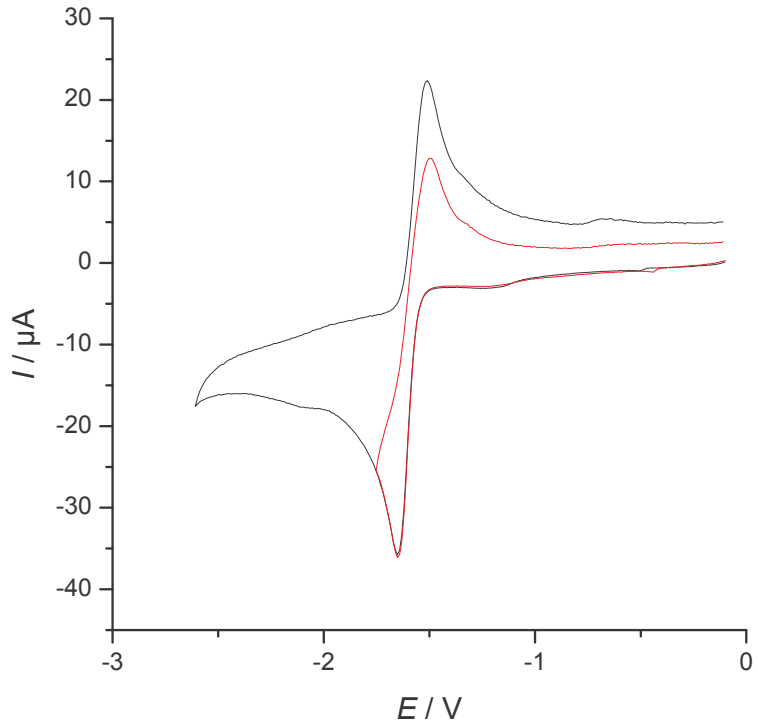
Figure S5 : Cyclic voltammetry of **3a** (a) under Ar, and (b) under CO in thf-$[NBu_4][PF_6]$ (vitreous carbon electrode; v = 0.2 Vs^{-1}; potentials are in V vs Fc^+/Fc).

Figure S6 : Cyclic voltammetry of **3a** (a) under Ar, and (b) under CO in CH_2Cl_2-$[NBu_4][PF_6]$ (vitreous carbon electrode; v = 0.2 Vs^{-1}; potentials are in V vs Fc^+/Fc).

Table S1 Average lengths and angles (Å & °) in $Fe_2(CO)_6\{\mu\text{-}SCH_2N(R)CH_2S\}$ molecules**.**

Figure S7 NR Conformations. Plot of mean S-C-N-R torsion angles against deformation parameter 360-SUMN.

Table S2 : Optimised cartesian coordinates and total energies of all species reported



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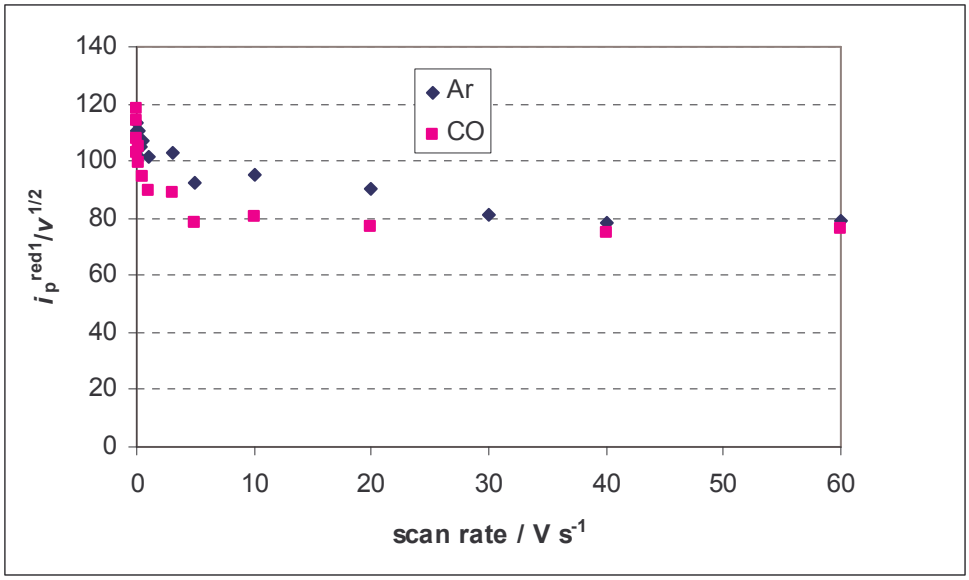

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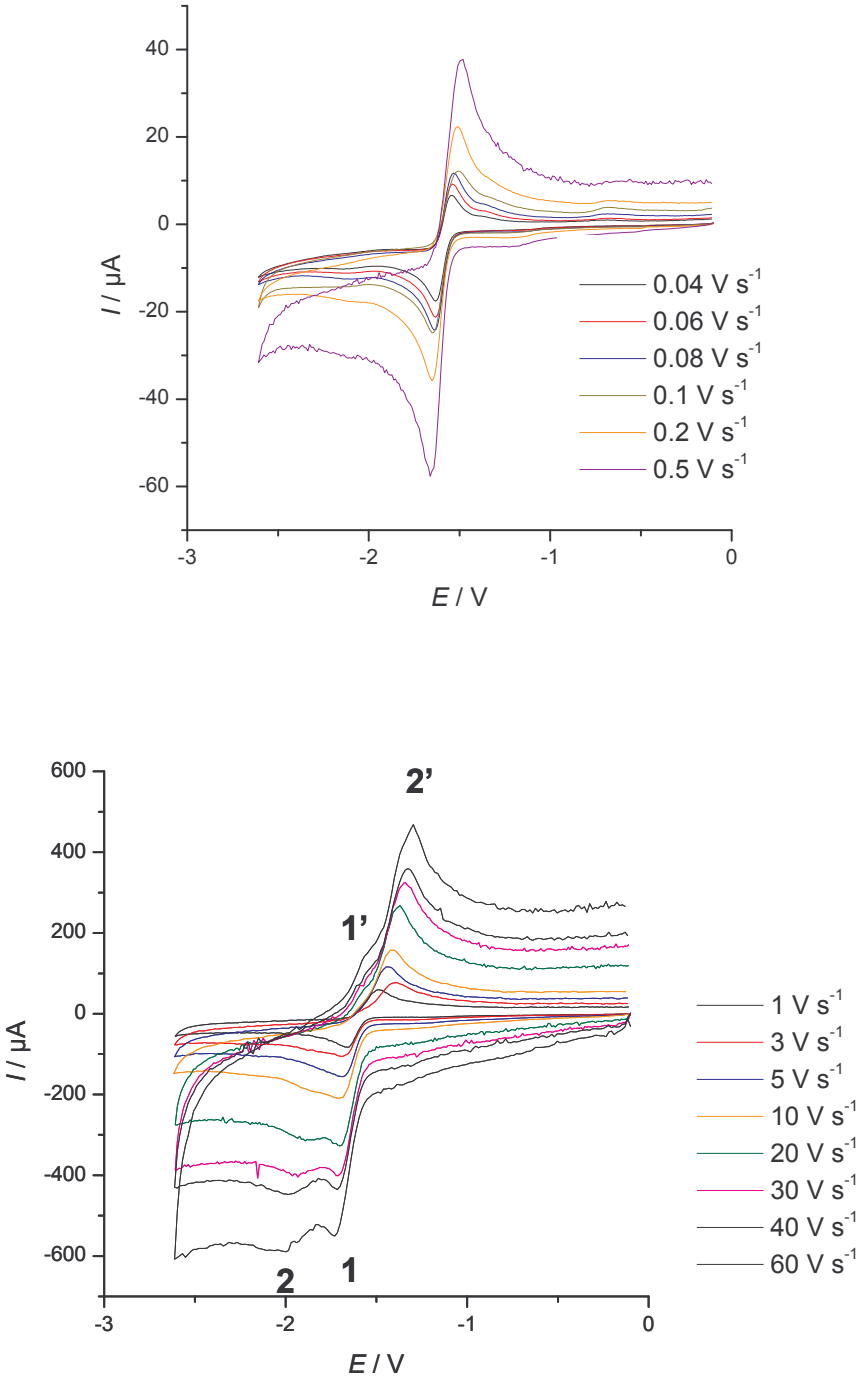
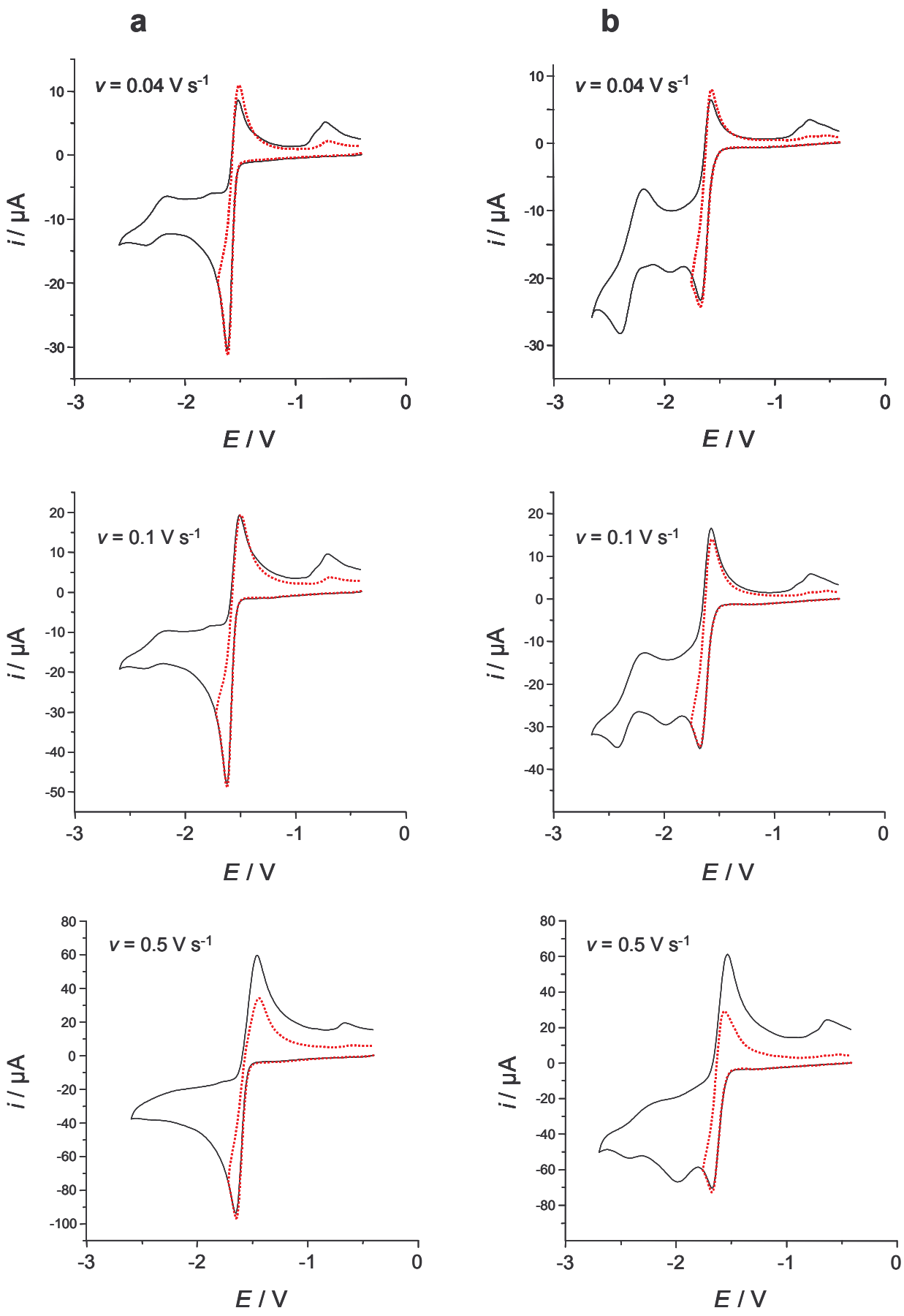


Figure S3 : Cyclic voltammetry of $[Fe_2(CO)_6\{\mu\text{-}SCH_2N(^iPr)CH_2S\}]$ **1b** (1 mM) at different scan rates under Ar in MeCN-$[NBu_4][PF_6]$ (vitreous carbon electrode; potentials are in V vs Fc^+/Fc).



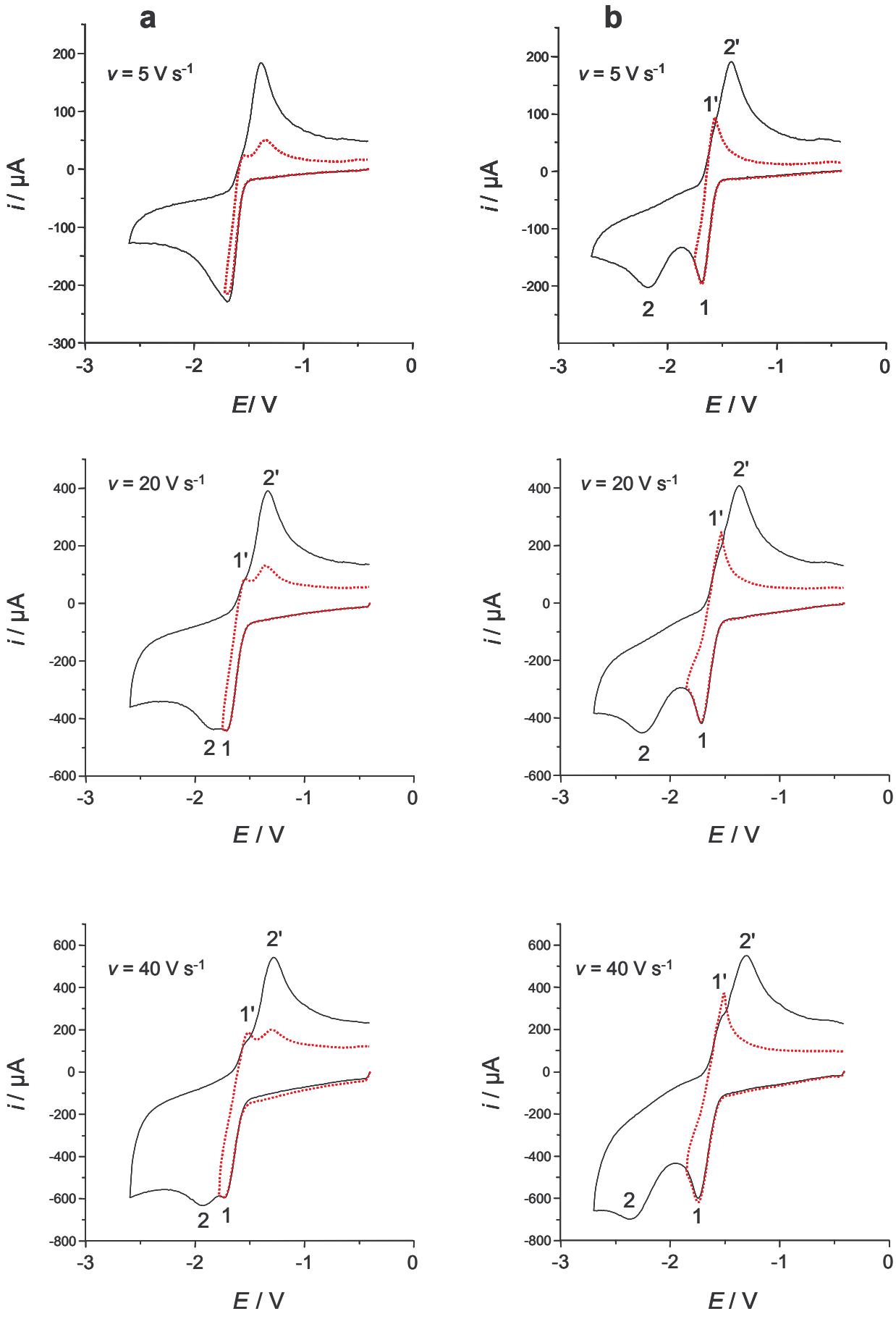


Figure S4 : Cyclic voltammetry of complexes a) **1a** and b) **2** in MeCN-$[NBu_4][PF_6]$ under CO at different scan rates (vitreous carbon electrode; potentials are in V vs Fc^+/Fc).

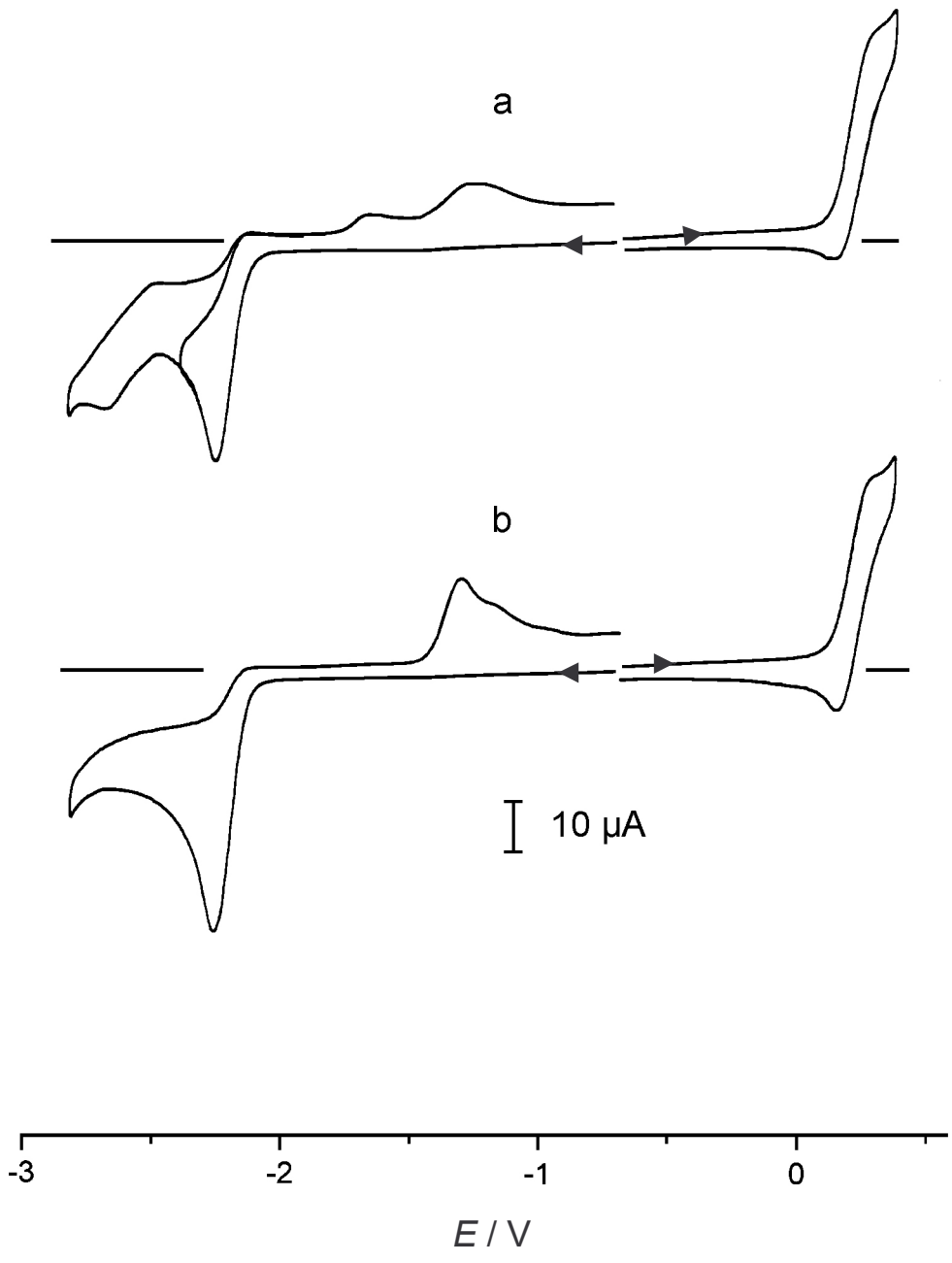


Figure S5 : Cyclic voltammetry of **3a** (a) under Ar and (b) under CO in thf-[NBu_4][PF_6] (vitreous carbon electrode; v = 0.2 Vs^{-1}; potentials are in V vs Fc^+/Fc).

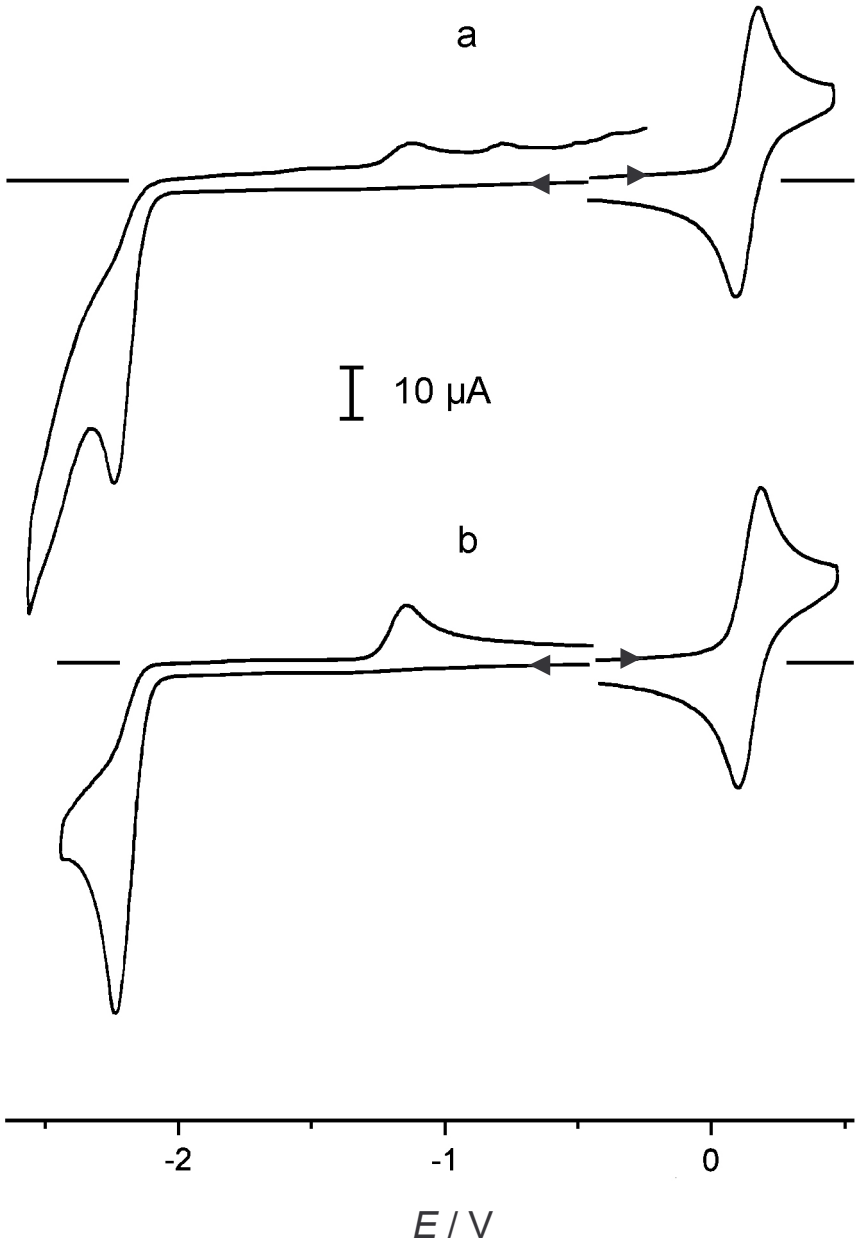


Figure S6 : Cyclic voltammetry of **3a** (a) under Ar, and (b) under CO in CH_2Cl_2-[NBu_4][PF_6] (vitreous carbon electrode; v = 0.2 Vs^{-1}; potentials are in V vs Fc^+/Fc).

Table S1 Average lengths and angles (Å & °) in $Fe_2(CO)_6\{\mu\text{-}SCH_2N(R)CH_2S\}$ molecules.

(a) **<Fe-S>, <S-C>** and **<N-C>** are the mean distances in the Fe-S-CH_2-N-CH_2-S rings.

(b) **N-R** is the exocyclic N-C bond length.

(c) **360-SUMN** is the sum of the three C-N-C bond angles subtracted from 360° and measures the departure of the central N atom from trigonal planar coordination.

(d) **SCNC** is the mean of the absolute values of the two S-CH_2-N-R torsion angles.

(e) **Type** defines the axial or equatorial conformation of the N(R) substituent.

(f) **Hybrid.** is the hybridisation type of the C atom in the exocyclic N-C bond.

(g) **Δ** is the difference between the exocyclic and mean endocyclic N-C bond lengths i.e. **N-R** minus **<N-C>**.

Ref.	*Refcode*	Fe-Fe	< >	<S-C>	<N-C>	N-R	360-SUMN	SCNC	Type	Hybrid.	Δ
8b	BIHHEG	2.500	2.264	1.854	1.428	1.387	2.3	93.2	ax	sp2	-0.041
8a	ITAJIW	2.508	2.252	1.827	1.433	1.477	19.0	157.8	eq	sp3	0.044
5j	KAPXEF	2.533	2.258	1.865	1.418	1.462	2.1	100.9	ax	sp3	0.044
9a	OCEQUJ	2.513	2.247	1.822	1.443	1.472	25.8	164.4	eq	sp3	0.029
5k	OKACEI	2.499	2.261	1.855	1.422	1.404	4.0	90.9	ax	sp2	-0.018
5k	OKACIM	2.506	2.260	1.851	1.428	1.402	5.1	88.2	ax	sp	-0.026
12b	PEFYIJ	2.496	2.251	1.842	1.428	1.386	3.2	90.6	ax	sp2	-0.042
12b	PEFYOP	2.500	2.260	1.848	1.421	1.413	4.7	88.0	ax	sp2	-0.008
5c	QOZQOL	2.492	2.259	1.875	1.401	1.418	8.2	86.2	disordered	sp3	0.017
8c	SECVAY	2.515	2.248	1.831	1.428	1.450	10.1	146.1	eq	sp3	0.022
8c	SECVEC	2.506	2.268	1.878	1.420	1.466	11.5	82.7	ax	sp3	0.047
5d	YOBVEQ	2.505	2.266	1.862	1.429	1.409	5.0	88.9	ax	sp2	-0.020
	This work	2.513	2.249	1.832	1.445	1.478	23.5	161.4	eq	sp3	0.033
8e	1	2.513	2.247	1.822	1.443	1.472	25.8	164.5	eq	sp3	0.029
8e	2	2.513	2.25	1.823	1.441	1.477	27.9	168.3	eq	sp3	0.036
8e	3	2.504	2.252	1.818	1.437	1.472	19.9	159.5	eq	sp3	0.035
9b	1	2.501	2.265	1.871	1.410	1.455	7.1	89.1	ax	sp3	0.045
9b	2	2.503	2.254	1.864	1.415	1.456	9.0	85.9	ax	sp3	0.041
	Mean	**2.507**	**2.256**	**1.847**	**1.427**	**1.442**	**11.9**	**117.0**			
	Maximum	**2.533**	**2.268**	**1.878**	**1.445**	**1.478**	**27.9**	**168.3**			
	Minimum	**2.492**	**2.247**	**1.818**	**1.401**	**1.386**	**2.1**	**82.7**			

A plot of 360-SUMN versus SCNC (Figure S7 below) clearly shows that equatorial conformations are characterised by mean S-CH_2-N-R torsion angles of typically 157 - 168° and pyramidal N atoms with **360-SUMN** between 19 and 26°. Axial conformations have S-CH_2-N-R torsion angles of typically 83 - 101° and much flatter N coordination with **360-SUMN** between 2 and 12°. SECVAY (ref 8c) is the only exception to this classification.

Figure S7

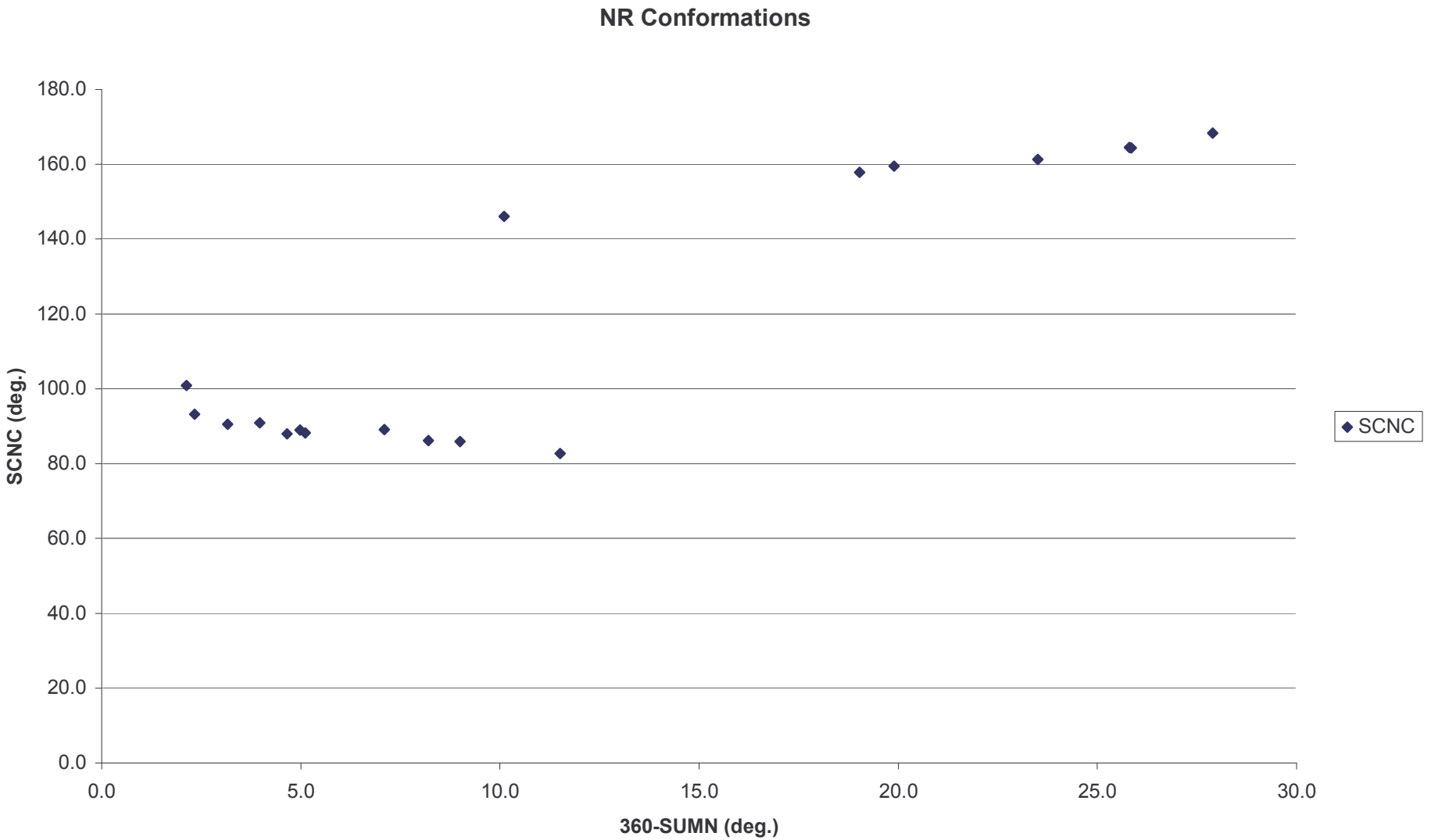


Table S2 Optimised cartesian coordinates and total energies of all species reported:

$Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)$ (compound **1a-A**)

E = -2051.45861834 au

26	1.963464000	-0.357376000	-0.042421000
26	0.133018000	1.354101000	0.171628000
16	0.154929000	-0.276486000	-1.471510000
16	0.389491000	-0.409151000	1.642062000
6	2.414191000	-2.089858000	-0.162513000
6	3.151147000	0.196358000	1.200953000
6	2.952338000	0.330880000	-1.388099000
6	0.575195000	2.539721000	-1.112475000
6	-1.627878000	1.699380000	0.326281000
6	0.779412000	2.422509000	1.471545000
8	1.194818000	3.101096000	2.302236000
8	3.903817000	0.547224000	1.996528000
8	3.576549000	0.769691000	-2.248628000
8	2.683021000	-3.206924000	-0.239999000
8	0.859367000	3.295326000	-1.931890000
8	-2.745001000	1.955291000	0.428068000
6	-0.911990000	-1.696807000	1.336123000
1	-1.527828000	-1.687102000	2.238358000
1	-0.381611000	-2.664380000	1.288084000
6	-1.062062000	-1.615325000	-1.064720000
1	-0.510309000	-2.569775000	-1.123685000
1	-1.787042000	-1.591930000	-1.880380000
7	-1.757476000	-1.449896000	0.191425000
6	-3.048577000	-2.156634000	0.232196000
1	-3.330012000	-2.304192000	1.279159000
1	-2.990676000	-3.158300000	-0.225067000
6	-4.160161000	-1.355082000	-0.446144000
1	-3.897107000	-1.111679000	-1.490387000
1	-4.303718000	-0.400207000	0.083202000
8	-5.327114000	-2.147933000	-0.402902000

6	-6.449495000	-1.506011000	-0.970711000
1	-6.697078000	-0.573410000	-0.439211000
1	-6.285864000	-1.265949000	-2.033743000
1	-7.291963000	-2.197447000	-0.888368000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)$ (compound **1a-B**)

E = -2051.42331142 au

6	0.627048000	-2.493632000	2.062720000
8	1.318515000	-2.976806000	2.843310000
26	-0.473031000	-1.751504000	0.832243000
6	-1.658080000	-0.988471000	1.998133000
8	-2.392295000	-0.542398000	2.761969000
6	0.468656000	-2.228329000	-0.651416000
8	1.097170000	-2.561767000	-1.555958000
6	-1.675682000	-3.039030000	0.476908000
8	-2.442616000	-3.866325000	0.249086000
26	-1.241908000	0.118677000	-0.841058000
16	-0.362845000	0.956357000	-2.633881000
6	1.387633000	1.635481000	-2.405019000
7	1.962195000	1.816065000	-1.104891000
6	2.028668000	0.671179000	-0.259715000
16	0.396064000	0.425392000	0.688989000
6	-2.504912000	-0.751347000	-1.789235000
8	-3.305945000	-1.341515000	-2.366438000
6	-2.400791000	1.138598000	0.017691000
8	-3.130366000	1.892395000	0.495705000
1	2.244141000	-0.220696000	-0.849631000
1	2.779373000	0.816718000	0.515616000
1	1.409784000	2.588104000	-2.937492000
1	1.988485000	0.915641000	-2.973034000
6	1.841318000	3.127997000	-0.459026000
6	3.170827000	3.668618000	0.060160000
8	3.591292000	2.900516000	1.172592000
6	4.818637000	3.343133000	1.715327000

1	5.044382000	2.700273000	2.569676000
1	5.637787000	3.269328000	0.982559000
1	4.753349000	4.387250000	2.060075000
1	1.456334000	3.834972000	-1.199747000
1	1.119978000	3.105163000	0.368866000
1	3.927875000	3.636583000	-0.740886000
1	3.035960000	4.723633000	0.357190000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)$ (compound **1a-C**)
E = -2051.35949648 au

6	-0.416465000	-2.354885000	-1.663233000
8	0.015403000	-3.120935000	-2.400871000
26	-1.204227000	-1.163442000	-0.556080000
8	1.926220000	-0.786483000	1.357712000
6	3.101365000	-1.201183000	0.668036000
6	3.203641000	-0.468624000	-0.664258000
7	3.568025000	0.962824000	-0.537961000
6	4.918334000	1.364807000	-1.069443000
16	6.159797000	0.561662000	-0.056102000
26	-2.008468000	1.151094000	-0.123129000
6	-2.920192000	-1.472879000	-0.777152000
8	-4.026790000	-1.706313000	-1.005424000
16	-0.645686000	0.598179000	-1.693573000
6	2.808020000	1.788121000	0.095745000
6	-1.133872000	-2.177916000	0.943940000
8	-1.041104000	-2.803391000	1.902784000
6	-3.770945000	1.276406000	0.244883000
8	-4.905867000	1.342042000	0.408041000
6	-1.623420000	0.726852000	1.545943000
8	-1.319084000	0.535815000	2.644304000
6	-1.725040000	2.927370000	-0.255952000
8	-1.489371000	4.050801000	-0.283561000
1	1.917798000	1.426927000	0.594405000
1	3.108392000	2.828675000	0.158770000
1	4.916955000	1.041603000	-2.118908000

1	4.928415000	2.460786000	-1.047999000
1	3.994981000	-0.935130000	-1.251797000
1	2.249861000	-0.512792000	-1.200208000
1	3.061498000	-2.283650000	0.464795000
1	4.003363000	-0.986613000	1.254451000
6	1.923631000	-1.199602000	2.719155000
1	2.792184000	-0.792538000	3.255145000
1	1.005901000	-0.816454000	3.168993000
1	1.937285000	-2.295924000	2.803470000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^-$ (compound **1a**$^-$**-A**)

E = -2051.51769699 au

26	-1.848040000	-0.974159000	0.087104000
26	-0.399099000	1.433088000	-0.036645000
16	-0.034168000	-0.370378000	1.465472000
16	-0.431405000	-0.267010000	-1.666767000
6	-1.670464000	-2.767928000	0.146517000
6	-3.196032000	-0.816328000	-1.061000000
6	-2.910759000	-0.570004000	1.457074000
6	-0.900196000	2.395327000	1.373435000
6	1.261369000	2.115930000	-0.336313000
6	-1.463273000	2.372943000	-1.116056000
8	-2.133378000	3.000013000	-1.827724000
8	-4.070281000	-0.736622000	-1.821758000
8	-3.602448000	-0.334536000	2.361222000
8	-1.678141000	-3.928340000	0.240123000
8	-1.203676000	3.030473000	2.296547000
8	2.269401000	2.650152000	-0.555853000
6	1.151696000	-1.221221000	-1.543146000
1	1.715356000	-0.985260000	-2.450709000
1	0.873722000	-2.291392000	-1.574262000
6	1.426780000	-1.334410000	0.866984000
1	1.123939000	-2.397343000	0.835817000
1	2.193165000	-1.224502000	1.638549000
7	1.990483000	-0.903376000	-0.401086000

6	3.387701000	-1.309607000	-0.562658000
1	3.634729000	-1.300509000	-1.629479000
1	3.579231000	-2.337797000	-0.203193000
6	4.338358000	-0.344061000	0.145191000
1	4.097007000	-0.264107000	1.218029000
1	4.232331000	0.661001000	-0.288848000
8	5.661643000	-0.834891000	-0.020365000
6	6.623969000	-0.000120000	0.575335000
1	6.616279000	1.013360000	0.140409000
1	6.467543000	0.096852000	1.663398000
1	7.605072000	-0.453042000	0.399704000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^-$ (compound **1a**$^-$**-B**)

E = -2051.51636115 au

6	-0.643479000	-2.980463000	1.903128000
8	-0.487887000	-3.594632000	2.875642000
26	-0.835260000	-2.046894000	0.402418000
6	-2.403525000	-1.005961000	0.647068000
8	-3.517921000	-0.953647000	1.018692000
6	0.522713000	-2.258951000	-0.769678000
8	1.407279000	-2.436456000	-1.499300000
6	-1.816563000	-3.263836000	-0.434061000
8	-2.453483000	-4.070113000	-0.969793000
26	-1.120689000	0.351675000	-0.439755000
16	0.463867000	1.411790000	-1.809095000
6	2.177428000	1.046098000	-1.181640000
7	2.449788000	1.149235000	0.240091000
6	2.061942000	0.016468000	1.018428000
16	0.211657000	-0.172157000	1.412190000
6	-2.149286000	0.236615000	-1.882244000
8	-2.821994000	0.143051000	-2.821103000
6	-1.989145000	1.720604000	0.362297000
8	-2.451991000	2.675026000	0.829755000
1	2.399566000	-0.897553000	0.527365000
1	2.526416000	0.080979000	2.007935000

1	2.839648000	1.739987000	-1.708909000
1	2.454643000	0.034774000	-1.489923000
6	2.173797000	2.436161000	0.871557000
6	2.806850000	3.626926000	0.167471000
8	4.218826000	3.490245000	0.127323000
6	4.841060000	4.565395000	-0.528429000
1	5.918596000	4.372385000	-0.525907000
1	4.501340000	4.665353000	-1.573405000
1	4.652854000	5.527439000	-0.018744000
1	1.092502000	2.640171000	0.927978000
1	2.558219000	2.386811000	1.898651000
1	2.399314000	3.733744000	-0.849318000
1	2.529918000	4.539986000	0.724704000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^-$ (compound **1a**$^-$**-C**)

E = -2051.47806287 au

6	0.055678000	2.078726000	-1.777109000
8	-0.747494000	2.622173000	-2.420027000
26	1.254334000	1.231857000	-0.798968000
8	-2.969963000	1.780785000	1.298143000
6	-4.058461000	1.344845000	0.497853000
6	-3.531131000	0.516437000	-0.665345000
7	-3.033538000	-0.813801000	-0.262724000
6	-3.807478000	-2.001721000	-0.774693000
16	-5.506291000	-1.983390000	-0.172457000
26	2.531556000	-0.722992000	0.344520000
6	3.332091000	-0.505208000	-1.261782000
8	3.851113000	-0.381814000	-2.290688000
16	0.548205000	-0.858332000	-0.989893000
6	-2.009322000	-0.937085000	0.512893000
6	2.218767000	2.651640000	-0.325864000
8	2.850941000	3.576352000	-0.011168000
6	3.975985000	-0.194916000	1.240132000
8	4.917033000	0.135073000	1.828107000
6	1.404338000	-0.050159000	1.574661000

8	0.665874000	0.351578000	2.378036000
6	2.556538000	-2.489884000	0.637079000
8	2.567193000	-3.629999000	0.828367000
1	-1.564911000	-0.066511000	0.971078000
1	-1.685726000	-1.931867000	0.793105000
1	-3.735150000	-1.929306000	-1.869023000
1	-3.224172000	-2.874399000	-0.459248000
1	-4.359327000	0.335003000	-1.352317000
1	-2.719173000	1.045409000	-1.174364000
1	-4.600847000	2.214693000	0.088242000
1	-4.764252000	0.733012000	1.076200000
6	-3.382063000	2.442107000	2.473584000
1	-4.005670000	1.792545000	3.108056000
1	-2.477463000	2.718550000	3.021160000
1	-3.956007000	3.355400000	2.244183000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^{2-}$ (compound **1a**$^{2-}$-**A**)
E = -2051.44120846 au

26	2.265818000	-0.701832000	0.115541000
26	-0.286912000	1.673976000	0.024269000
16	0.513547000	-0.131610000	-1.428594000
16	0.493886000	0.027991000	1.614280000
6	2.367200000	-2.350224000	-0.475240000
6	3.312963000	-1.013231000	1.487474000
6	3.349363000	0.474555000	-0.630789000
6	-0.808589000	2.606170000	-1.363820000
6	-1.880825000	1.713020000	0.752247000
6	0.919060000	2.843452000	0.572918000
8	1.575334000	3.721095000	0.997602000
8	3.990812000	-1.221906000	2.422041000
8	4.150292000	1.128877000	-1.189101000
8	2.556324000	-3.418203000	-0.944462000
8	-1.159629000	3.205979000	-2.309958000
8	-2.923833000	1.826865000	1.297166000
6	-0.711001000	-1.371380000	1.388902000

1	-1.436309000	-1.315135000	2.209572000
1	-0.120674000	-2.298078000	1.502392000
6	-0.734211000	-1.459899000	-1.092990000
1	-0.205237000	-2.427838000	-1.158122000
1	-1.467159000	-1.420050000	-1.907214000
7	-1.473523000	-1.335620000	0.153701000
6	-2.721127000	-2.078896000	0.164145000
1	-2.984204000	-2.333585000	1.197885000
1	-2.657925000	-3.039198000	-0.385391000
6	-3.860633000	-1.239719000	-0.417642000
1	-3.613775000	-0.903191000	-1.436992000
1	-4.004382000	-0.343076000	0.200442000
8	-5.053327000	-2.033167000	-0.445154000
6	-6.158162000	-1.305264000	-0.905906000
1	-6.372043000	-0.427336000	-0.271586000
1	-6.015515000	-0.940491000	-1.939272000
1	-7.029345000	-1.972161000	-0.888733000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^{2-}$ (compound **1a^{2-}-B**)
E = -2051.45281393 au

6	1.985145000	0.185267000	-0.767552000
8	1.916354000	-0.571261000	0.127917000
26	2.125116000	1.233041000	-2.173522000
6	0.502424000	2.454729000	-1.879123000
8	-0.592327000	2.284772000	-1.418640000
6	3.613952000	0.873100000	-3.078285000
8	4.590193000	0.563001000	-3.652705000
6	1.093514000	0.378564000	-3.298195000
8	0.406759000	-0.219002000	-4.037103000
26	1.584388000	3.728689000	-2.719455000
16	3.269996000	4.759487000	-4.262850000
6	4.950525000	4.273465000	-3.678469000
7	5.274823000	4.466242000	-2.258317000
6	4.884664000	3.378080000	-1.403103000
16	3.053212000	3.089929000	-1.006614000

6	0.585942000	3.694518000	-4.166236000
8	-0.076120000	3.687634000	-5.127619000
6	0.948084000	5.189965000	-2.024050000
8	0.467909000	6.149142000	-1.549503000
1	5.269674000	2.446682000	-1.821827000
1	5.343854000	3.533810000	-0.418543000
1	5.675435000	4.854898000	-4.264905000
1	5.134339000	3.217679000	-3.894530000
6	4.946097000	5.774513000	-1.706698000
6	5.556553000	6.943077000	-2.463588000
8	6.983879000	6.920699000	-2.387554000
6	7.565457000	7.945006000	-3.140341000
1	8.654455000	7.851300000	-3.048588000
1	7.295851000	7.883176000	-4.209669000
1	7.270628000	8.951263000	-2.782945000
1	3.858441000	5.947832000	-1.688583000
1	5.308419000	5.800271000	-0.668901000
1	5.226754000	6.926274000	-3.511542000
1	5.183976000	7.883096000	-2.015839000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)]^{2-}$ (compound **1a^{2-}-C**)
E = -2051.44603218 au

6	0.300831000	2.002085000	-1.889268000
8	-0.097384000	2.598176000	-2.813527000
26	1.017684000	1.092774000	-0.587710000
8	-2.872585000	2.042306000	1.175184000
6	-3.917600000	1.460947000	0.394787000
6	-3.360326000	0.442619000	-0.591251000
7	-2.893506000	-0.779035000	0.043091000
6	-3.445956000	-2.055400000	-0.489800000
16	-5.275845000	-2.147925000	-0.533711000
26	1.992410000	-0.960049000	0.353905000
6	2.547811000	0.263647000	-1.186088000
8	3.412889000	0.362950000	-1.994355000
16	-0.108729000	-0.888658000	-0.767547000

6	-1.597113000	-0.783915000	0.563380000
6	1.858038000	2.455986000	0.126332000
8	2.376699000	3.361889000	0.652247000
6	3.617168000	-0.707915000	0.967791000
8	4.700694000	-0.559401000	1.376711000
6	1.249846000	-0.697645000	1.951705000
8	0.829072000	-0.542504000	3.030477000
6	2.219648000	-2.653674000	-0.111658000
8	2.369221000	-3.780983000	-0.374795000
1	-1.387703000	0.120166000	1.131219000
1	-1.415798000	-1.675393000	1.168467000
1	-3.030058000	-2.233261000	-1.496796000
1	-3.028654000	-2.833496000	0.164241000
1	-4.196478000	0.154445000	-1.238841000
1	-2.571805000	0.912569000	-1.200656000
1	-4.442794000	2.265434000	-0.156095000
1	-4.644327000	0.954625000	1.046753000
6	-3.352807000	2.897557000	2.173587000
1	-4.016907000	2.374133000	2.884288000
1	-2.487317000	3.287313000	2.719493000
1	-3.919129000	3.750381000	1.752845000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)$ (compound 2-**A**)
E = -1842.30104824 au

26	-1.150089000	-0.609425000	0.000000000
26	1.280343000	0.018397000	0.000000000
16	-0.230394000	0.810933000	-1.571508000
16	-0.230394000	0.810933000	1.571508000
6	-2.853209000	-0.050514000	0.000000000
6	-1.223299000	-1.861302000	1.301486000
6	-1.223299000	-1.861302000	-1.301486000
6	1.903013000	-1.067378000	-1.298473000
6	2.584534000	1.253074000	0.000000000
6	1.903013000	-1.067378000	1.298473000
8	2.295788000	-1.759379000	2.128702000

8	-1.271336000	-2.652779000	2.134335000
8	-1.271336000	-2.652779000	-2.134335000
8	-3.937677000	0.337671000	0.000000000
8	2.295788000	-1.759379000	-2.128702000
8	3.434125000	2.030524000	0.000000000
6	-0.742522000	2.565635000	1.283634000
1	-0.364330000	3.114098000	2.152171000
1	-1.836896000	2.579792000	1.335953000
6	-0.742522000	2.565635000	-1.283634000
1	-1.836896000	2.579792000	-1.335953000
1	-0.364330000	3.114098000	-2.152171000
6	-0.250672000	3.224398000	0.000000000
1	-0.601286000	4.267022000	0.000000000
1	0.843361000	3.267667000	0.000000000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)$ (compound **2-B**)
E = -1842.26007560 au

26	0.045956000	-1.329059000	0.776244000
6	1.173015000	-2.292093000	1.816169000
8	1.884234000	-2.910395000	2.473400000
6	0.777394000	-1.736200000	-0.841944000
8	1.264366000	-2.045417000	-1.837219000
8	-2.921033000	-0.299729000	-2.142155000
6	-1.299430000	-2.471764000	0.424981000
8	-2.156467000	-3.204965000	0.198763000
6	-2.025209000	0.146810000	-1.576113000
26	-0.619506000	0.782294000	-0.637001000
16	1.131750000	0.745864000	0.783632000
6	-1.618428000	1.803161000	0.406590000
8	-2.241389000	2.561087000	1.011016000
6	-0.973163000	-0.594383000	2.105891000
8	-1.616075000	-0.173615000	2.960567000
16	0.234244000	1.730827000	-2.377158000
6	2.667172000	0.881669000	-0.227741000
1	2.717201000	0.093517000	-0.983324000

1	3.504543000	0.754719000	0.464509000
6	1.950169000	2.402788000	-2.199091000
1	1.896043000	3.458325000	-2.484985000
1	2.513162000	1.888427000	-2.987716000
6	2.698302000	2.277460000	-0.868382000
1	2.317093000	3.014136000	-0.150703000
1	3.746565000	2.548604000	-1.058863000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)$ (compound **2-C**)
E = -1842.14867080 au

6	0.704985000	1.478058000	-2.757455000
26	-0.102779000	2.842238000	-3.620168000
6	1.143827000	2.992513000	-4.929900000
8	1.935453000	3.081631000	-5.757080000
8	1.235988000	0.664838000	-2.143156000
26	-1.923213000	4.512737000	-3.847795000
6	-3.662604000	4.999965000	-3.878377000
8	-4.771215000	5.279107000	-3.985572000
6	0.409443000	4.298626000	-2.769097000
8	0.873646000	5.161009000	-2.150842000
16	-2.073045000	2.692838000	-2.474599000
6	-2.973258000	1.213912000	-3.196154000
6	-4.261099000	0.900045000	-2.424678000
6	-5.386280000	1.913084000	-2.663371000
16	-6.915886000	1.446086000	-1.815688000
1	-4.050828000	0.825171000	-1.352111000
6	-1.294673000	6.089271000	-4.488938000
8	-0.887865000	7.087220000	-4.884068000
6	-1.662060000	3.631969000	-5.348357000
8	-1.695259000	3.128608000	-6.394322000
1	-2.270553000	0.376613000	-3.128403000
1	-3.170409000	1.413011000	-4.252759000
1	-5.090169000	2.904666000	-2.286372000
1	-5.568715000	2.033933000	-3.740824000
1	-4.599884000	-0.094879000	-2.745680000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^-$ (compound **2**$^-$-**A**)
E = -1842.35964817 au

26	-0.265518000	-1.410253000	0.095914000
26	-0.321935000	1.390430000	-0.077872000
16	0.777063000	0.116438000	1.583248000
16	0.735715000	-0.116594000	-1.600823000
6	0.846532000	-2.826806000	-0.023464000
6	-1.593274000	-1.726865000	-1.055462000
6	-1.255997000	-1.936047000	1.477909000
6	-1.732669000	1.449556000	1.018390000
6	0.598174000	2.918946000	0.173576000
6	-1.293455000	1.933341000	-1.462329000
8	-1.908643000	2.299259000	-2.376050000
8	-2.443725000	-1.956617000	-1.813063000
8	-1.878897000	-2.298949000	2.387813000
8	1.486109000	-3.789866000	-0.158411000
8	-2.642025000	1.532297000	1.737645000
8	1.089805000	3.944312000	0.424996000
6	2.563721000	-0.163667000	-1.316515000
1	3.018949000	0.260419000	-2.219696000
1	2.855704000	-1.219770000	-1.263880000
6	2.599419000	0.064331000	1.257217000
1	2.907105000	-0.980969000	1.385659000
1	3.069004000	0.647897000	2.058359000
6	3.081247000	0.592078000	-0.094087000
1	4.182960000	0.537956000	-0.101699000
1	2.819272000	1.650965000	-0.187373000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^-$ (compound **2**$^-$**-B**)
E = -1842.35202178 au

26	0.164404000	-1.473152000	0.590378000
6	0.995745000	-2.181655000	1.990170000
8	1.565277000	-2.653824000	2.885454000
6	1.000424000	-1.785388000	-0.983279000

8	1.561467000	-2.028383000	-1.968178000
8	-3.200486000	0.140501000	-1.668952000
6	-0.936814000	-2.838191000	0.332321000
8	-1.647316000	-3.740051000	0.172860000
6	-2.215222000	0.411307000	-1.123125000
26	-0.706357000	0.790081000	-0.259331000
16	1.283159000	0.578047000	0.898071000
6	-1.314653000	2.203128000	0.693488000
8	-1.647621000	3.186888000	1.207499000
6	-1.306917000	-0.497750000	1.322018000
8	-2.191277000	-0.501117000	2.100290000
16	0.079346000	1.679272000	-2.247869000
6	2.708123000	0.880855000	-0.230523000
1	2.781896000	0.088215000	-0.979311000
1	3.600036000	0.831506000	0.403933000
6	1.842561000	2.240623000	-2.236261000
1	1.852123000	3.255327000	-2.653527000
1	2.386591000	1.600837000	-2.944288000
6	2.607733000	2.254034000	-0.911441000
1	2.159117000	2.979066000	-0.220131000
1	3.629171000	2.611892000	-1.120898000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^-$ (compound **2**$^-$**-C**)

E = -1842.29130535 au

6	0.236219000	1.818331000	-2.028244000
26	-0.333479000	2.820371000	-3.352340000
6	1.147813000	2.691475000	-4.304326000
8	2.092386000	2.578665000	-4.970746000
8	0.632675000	1.221315000	-1.112126000
26	-1.669782000	4.662895000	-4.242722000
6	-2.974718000	5.794495000	-3.807137000
8	-3.858020000	6.508321000	-3.562336000
6	-0.094338000	4.613741000	-2.911169000
8	0.586282000	5.354886000	-2.297931000
16	-2.558542000	3.020912000	-2.789707000

6	-3.367344000	1.651102000	-3.752482000
6	-4.075533000	0.641144000	-2.839846000
6	-5.300336000	1.221227000	-2.123019000
16	-6.209625000	0.024026000	-1.093275000
1	-3.371431000	0.246934000	-2.097535000
6	-0.727395000	5.870571000	-5.126421000
8	-0.119948000	6.670199000	-5.707337000
6	-1.920596000	3.665404000	-5.691946000
8	-2.106147000	3.046554000	-6.661624000
1	-2.604853000	1.143965000	-4.352968000
1	-4.077736000	2.111284000	-4.448727000
1	-4.992622000	2.040821000	-1.458416000
1	-5.995914000	1.665763000	-2.848144000
1	-4.393468000	-0.212133000	-3.455239000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^{2-}$ (compound **2^{2-}-A**)

E = -1842.28168760 au

26	-0.273671000	-1.749903000	0.182474000
26	-0.279721000	1.724116000	-0.194372000
16	0.482939000	0.162394000	1.483847000
16	0.364347000	-0.211405000	-1.557924000
6	0.847054000	-2.978789000	-0.370464000
6	-1.917565000	-1.834468000	-0.454069000
6	-0.654759000	-2.601563000	1.666973000
6	-1.978062000	1.597351000	0.289747000
6	0.580725000	3.035107000	0.585279000
6	-0.504397000	2.668225000	-1.653984000
8	-0.639812000	3.282224000	-2.646300000
8	-2.972297000	-2.047221000	-0.928423000
8	-0.891910000	-3.152940000	2.675575000
8	1.491544000	-3.873439000	-0.797725000
8	-3.089564000	1.725953000	0.645668000
8	1.055583000	3.949942000	1.164406000
6	2.214308000	-0.228454000	-1.424020000
1	2.609502000	0.259197000	-2.327181000

1	2.530848000	-1.277320000	-1.447071000
6	2.315542000	0.049098000	1.183511000
1	2.595442000	-0.992348000	1.380366000
1	2.815369000	0.681229000	1.932232000
6	2.802534000	0.490196000	-0.203511000
1	3.902077000	0.368218000	-0.232456000
1	2.592122000	1.559606000	-0.310102000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^{2-}$ (compound **2^{2-}-B**)

E = -1842.28358172 au

26	3.128172000	0.551641000	-0.544037000
6	3.744404000	-0.326608000	0.848491000
8	4.174248000	-0.970078000	1.732899000
6	4.184421000	0.318849000	-1.956537000
8	4.900852000	0.096185000	-2.860290000
8	-0.472560000	2.314366000	-2.457549000
6	1.913649000	-0.572234000	-1.109491000
8	1.115033000	-1.349914000	-1.474707000
6	0.504889000	2.526347000	-1.855203000
26	1.972767000	2.868516000	-0.949013000
16	4.072555000	2.651810000	0.048469000
6	1.424617000	4.297852000	-0.123969000
8	1.025476000	5.236917000	0.453214000
6	1.551550000	1.551332000	0.314444000
8	0.768669000	1.273061000	1.180972000
16	2.684343000	3.970292000	-3.065434000
6	5.535758000	3.118895000	-0.993747000
1	5.923724000	2.209888000	-1.464153000
1	6.292074000	3.457472000	-0.272200000
6	4.500377000	3.787802000	-3.273527000
1	4.780532000	4.424091000	-4.126393000
1	4.754253000	2.756618000	-3.550912000
6	5.350092000	4.202361000	-2.061006000
1	4.922756000	5.109442000	-1.613365000
1	6.366463000	4.466428000	-2.412665000

$[Fe_2(CO)_6(\mu\text{-}SCH_2\{CH_2\}CH_2S)]^{2-}$ (compound **2^{2-}-C**)

E = -1842.27689845 au

6	0.315875000	1.860986000	-2.046746000
26	-0.292359000	2.850883000	-3.348494000
6	1.141791000	2.707977000	-4.347856000
8	2.065861000	2.578636000	-5.050681000
8	0.771553000	1.275441000	-1.143917000
26	-1.647959000	4.675842000	-4.247177000
6	-2.884200000	5.839003000	-3.734755000
8	-3.715085000	6.603925000	-3.444943000
6	-0.043114000	4.626326000	-2.951123000
8	0.650883000	5.376609000	-2.349301000
16	-2.501118000	3.048759000	-2.736532000
6	-3.316505000	1.636929000	-3.646131000
6	-4.081805000	0.657753000	-2.735780000
6	-5.437426000	1.156209000	-2.205349000
16	-6.426216000	-0.154469000	-1.361206000
1	-3.449026000	0.347497000	-1.894005000
6	-0.696158000	5.829431000	-5.170119000
8	-0.078099000	6.605246000	-5.784106000
6	-2.057477000	3.708232000	-5.680125000
8	-2.325507000	3.123522000	-6.654779000
1	-2.529196000	1.114116000	-4.203497000
1	-3.994155000	2.085861000	-4.381601000
1	-5.258251000	2.005472000	-1.528431000
1	-5.999615000	1.564074000	-3.063507000
1	-4.269145000	-0.251989000	-3.325602000

$Fe_2(CO)_5(\mu\text{-}SCH_2\{N(CH_2)_2OMe\}CH_2S)$ (compound **1a-CO**)

E = -1938.11169725 au

6	-2.478198000	-0.786230000	-1.204124000
26	-1.608085000	0.181566000	0.038132000
6	-2.624734000	1.663585000	0.059118000
8	-3.257831000	2.627061000	0.075439000

8	-3.030593000	-1.404140000	-2.003452000
6	-2.341407000	-0.760021000	1.384836000
8	-2.804379000	-1.364560000	2.248838000
26	0.661851000	-0.819610000	-0.038859000
6	0.481915000	-2.090797000	-1.280334000
8	0.325804000	-2.914285000	-2.074481000
16	0.057719000	0.792123000	1.560711000
6	0.773854000	2.466650000	1.084175000
7	1.501697000	2.527554000	-0.143334000
6	2.886137000	2.078501000	-0.136065000
6	3.262360000	0.727411000	0.486710000
8	2.739237000	-0.397016000	-0.249450000
6	3.600701000	-1.543063000	-0.181117000
16	-0.076496000	0.695226000	-1.648773000
6	0.720271000	2.364585000	-1.330911000
6	0.657219000	-2.009219000	1.294378000
8	0.614275000	-2.780263000	2.153244000
1	4.605629000	-1.267956000	-0.522648000
1	3.184422000	-2.297812000	-0.847382000
1	3.650678000	-1.935859000	0.842081000
1	-0.066731000	3.166999000	1.050627000
1	1.427587000	2.749451000	1.915079000
1	3.481244000	2.816455000	0.426229000
1	3.248589000	2.098773000	-1.168829000
1	1.347542000	2.550036000	-2.206579000
1	-0.095064000	3.096130000	-1.327763000
1	2.937899000	0.651068000	1.530551000
1	4.358611000	0.666155000	0.463527000

$Fe_2(CO)_6(\mu\text{-}SCH_2\{N(CH_2)_2SMe\}CH_2S)$ (compound **1aS**)
E = -2374.44073499 au

6	-1.961440000	-2.681491000	0.163179000
8	-1.905863000	-3.831464000	0.183675000
26	-2.014322000	-0.888233000	0.128862000
6	-3.051704000	-0.565124000	1.571919000

8	-3.706993000	-0.357638000	2.493925000
26	-0.744975000	1.273020000	-0.081950000
6	-1.755723000	2.178251000	-1.268847000
8	-2.402641000	2.752259000	-2.027114000
16	-0.196393000	-0.372574000	1.451107000
6	1.308864000	-1.297308000	0.887113000
7	1.835052000	-0.885076000	-0.394103000
6	3.266493000	-1.199030000	-0.560482000
6	4.158726000	-0.165626000	0.135295000
16	5.919898000	-0.636993000	-0.086675000
6	6.712569000	0.795862000	0.721749000
16	-0.617212000	-0.422676000	-1.645417000
6	1.007894000	-1.307916000	-1.500770000
6	-3.397874000	-0.631707000	-1.004326000
8	-4.274945000	-0.469019000	-1.730040000
6	-1.395859000	2.230004000	1.300481000
8	-1.812381000	2.839067000	2.182859000
6	0.838009000	2.098196000	-0.319332000
8	1.833011000	2.655933000	-0.470856000
1	1.527758000	-1.085353000	-2.435573000
1	0.770749000	-2.386397000	-1.483670000
1	1.048563000	-2.369742000	0.915864000
1	2.057419000	-1.109342000	1.659008000
1	3.489660000	-1.185144000	-1.631764000
1	3.504095000	-2.214477000	-0.199703000
1	3.939050000	-0.108767000	1.207561000
1	3.979390000	0.821533000	-0.301426000
1	6.458737000	1.729204000	0.210270000
1	6.429363000	0.863675000	1.776663000
1	7.792443000	0.639646000	0.656665000

$Fe_2(CO)_5(\mu\text{-}SCH_2\{N(CH_2)_2SMe\}CH_2S)$ (compound **1aS-CO**)
E = -2261.10631876 au

6	-2.635935000	-0.798354000	-1.167318000
8	-3.209807000	-1.392476000	-1.969591000

26	-1.737356000	0.138616000	0.079731000
6	-2.382175000	-0.884609000	1.411172000
8	-2.788944000	-1.539976000	2.266817000
26	0.555459000	-0.815517000	-0.102833000
16	-0.031295000	0.744558000	1.551174000
6	0.553332000	2.482512000	1.112119000
7	1.247638000	2.637519000	-0.124306000
6	0.469369000	2.438389000	-1.306578000
16	-0.267756000	0.735428000	-1.630452000
6	-2.790231000	1.586968000	0.202180000
8	-3.452215000	2.527617000	0.288508000
6	0.661254000	-2.019723000	1.209158000
8	0.721843000	-2.796019000	2.062483000
16	2.783020000	-0.369163000	-0.517771000
6	3.256191000	1.122213000	0.447502000
6	2.686192000	2.429374000	-0.137126000
6	0.323747000	-2.076220000	-1.345830000
8	0.148856000	-2.897350000	-2.138036000
6	3.826212000	-1.601831000	0.342911000
1	4.881655000	-1.349915000	0.206952000
1	3.624620000	-2.570821000	-0.119762000
1	3.579156000	-1.650521000	1.406465000
1	-0.342789000	3.111944000	1.119388000
1	1.199430000	2.791873000	1.939004000
1	3.154603000	3.238137000	0.444989000
1	3.031390000	2.547283000	-1.169339000
1	1.079960000	2.656144000	-2.186251000
1	-0.386416000	3.123306000	-1.300127000
1	2.940180000	0.977968000	1.484835000
1	4.350912000	1.187971000	0.423585000