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An *ab initio* multireference study of reductive eliminations from organoferrates(III): It is all about the spin state

—Supporting Information—

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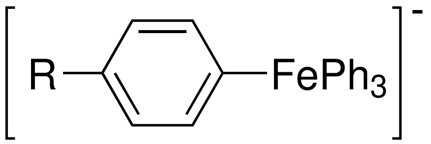
The List of Investigated Arylferrates(III)



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R = NMe_2	**(a)**
OMe	**(b)**
Me	**(c)**
Ph	**(d)**
H	**(e)**
F	**(f)**
CF_3	**(g)**
Cl	**(h)**

Calculated Energies From Single-Reference Methods

Table S1: Calculated free energies at room temperature (298 K) in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant $^{4}\mathbf{1}$ obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	$^{4}\mathbf{1}$	$^{6}\mathbf{1}$	$^{4}\mathbf{TS}_{\mathbf{cross}}$	$^{4}\mathbf{TS}_{\mathbf{homo}}$	$^{6}\mathbf{TS}_{\mathbf{cross1}}$	$^{6}\mathbf{TS}_{\mathbf{homo1}}$	$^{6}\mathbf{TS}_{\mathbf{cross2}}$	$^{6}\mathbf{TS}_{\mathbf{homo2}}$
a	0.0	1.28	13.73	13.57	34.50	34.11	33.14	33.60
b	0.0	0.84	13.79	12.93	33.99	32.67	33.32	32.83
c	0.0	1.40	13.85	13.23	33.25	32.93	33.07	32.77
d	0.0	0.85	12.15	12.28	29.39	33.44	32.67	32.61
e	0.0	0.50	12.93		32.81		32.28	
f	0.0	0.47	14.52	14.72	34.36	32.95	33.69	32.75
g	0.0	0.15	13.47	11.87	29.97	32.56	34.17	32.73
h	0.0	0.08	13.42	11.94	32.24	32.00	33.47	32.65

Table S2: Calculated free energies at room temperature (298 K) in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant $^{4}\mathbf{1}$ obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	$^{2}\mathbf{2}_{\mathbf{cross/near}}$	$^{2}\mathbf{2}_{\mathbf{cross/far}}$	$^{2}\mathbf{2}_{\mathbf{homo}}$
a	-9.53	-7.54	-7.25
b	-9.18	-7.22	-5.39
c	-9.20	-7.70	-6.51
d	-10.84	-7.96	-9.13
e	6.92		
f	-6.33	-5.71	-7.28
g	-10.14	-8.38	-9.50
h	-6.43	-8.32	-10.01

Table S3: Calculated free energies at 400 K in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	^{4}**1**	^{6}**1**	^{4}**TS**$_{\text{cross}}$	^{4}**TS**$_{\text{homo}}$	^{2}**2**$_{\text{cross/near}}$	^{2}**2**$_{\text{cross/far}}$	^{2}**2**$_{\text{homo}}$
a	0.0	1.43	14.38	14.23	-7.67	-5.52	-5.51
b	0.0	0.84	14.26	13.37	-7.61	-5.33	-3.18
c	0.0	1.70	14.75	13.81	-7.07	-5.75	-4.15
d	0.0	0.73	12.56	12.69	-8.85	-6.19	-7.30
e	0.0	0.40	13.43		-4.60		
f	0.0	0.36	15.02	15.14	-4.84	-3.38	-5.31
g	0.0	-0.09	14.22	12.30	-8.80	-7.17	-7.36
h	0.0	-0.15	13.75	12.25	-4.59	-7.09	-8.77

Table S4: Calculated free energies at 700 K in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	^{4}**1**	^{6}**1**	^{4}**TS**$_{\text{cross}}$	^{4}**TS**$_{\text{homo}}$	^{2}**2**$_{\text{cross/near}}$	^{2}**2**$_{\text{cross/far}}$	^{2}**2**$_{\text{homo}}$
a	0.0	1.94	16.33	16.24	-4.32	-1.56	-2.51
b	0.0	0.88	15.70	14.75	-5.11	-1.75	1.55
c	0.0	2.77	17.58	15.56	-2.87	-1.99	0.94
d	0.0	0.40	13.86	14.00	-5.00	-2.93	-3.87
e	0.0	0.17	14.96		0.38		
f	0.0	0.08	16.54	16.46	-2.58	1.64	-1.53
g	0.0	-0.75	16.61	13.65	-6.93	-5.74	-2.89
h	0.0	-0.75	14.80	13.22	-1.14	-5.59	-7.24

Table S5: Calculated electronic energies in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	$^{4}\mathbf{1}$	$^{6}\mathbf{1}$	$^{2}\mathbf{1}$	$^{4}\mathbf{TS}_{\mathbf{cross}}$	$^{4}\mathbf{TS}_{\mathbf{homo}}$	$^{6}\mathbf{TS}_{\mathbf{cross1}}$	$^{6}\mathbf{TS}_{\mathbf{homo1}}$	$^{6}\mathbf{TS}_{\mathbf{cross2}}$	$^{6}\mathbf{TS}_{\mathbf{homo2}}$
a	0.0	1.16	6.95	12.95	12.7	35.04	33.94	34.02	33.9
b	0.0	1.15	7.14	13.44	12.61	35.72	33.8	34.26	34.02
c	0.0	1.2	7.2	12.45	12.47	34	33.9	33.84	33.81
d	0.0	1.62	7.27	11.86	12.04	30.17	34.03	34.16	33.88
e	0.0	1.13	6.72	12.42	0	33.89	0	33.87	0
f	0.0	1.1	7.65	13.92	14.56	35.5	33.99	34.82	34.02
g	0.0	1.38	7.42	12.47	11.55	30.74	34.13	34.83	34.2
h	0.0	1.2	7.44	13.43	12.02	33.67	34.23	34.86	34.13

Table S6: Calculated electronic energies in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the B3LYP/def2-TZVPD level of theory.

Derivative	$^{2}\mathbf{2}_{\mathbf{cross/near}}$	$^{2}\mathbf{2}_{\mathbf{cross/far}}$	$^{2}\mathbf{2}_{\mathbf{homo}}$	$^{4}\mathbf{2}_{\mathbf{cross/near}}$	$^{4}\mathbf{2}_{\mathbf{cross/far}}$	$^{4}\mathbf{2}_{\mathbf{homo}}$
a	-13.75	-11.49	-10.67	-22.31	-14.59	-14.7
b	-12.42	-10.82	-9.24	-18.61	-13.53	-14.8
c	-13.68	-11.52	-11.22	-14.89	-14.91	-14.95
d	-14.43	-11.19	-12.48	-18.34	-15.03	-15.03
e	-11.4			-14.42		
f	-9.06	-10.29	-11.34	-10.2	-13.22	-15.06
g	-12.32	-10.27	-13.49	-16.37	-14.56	-15.14
h	-9.75	-10.23	-12.14	-13.86	-12.8	-15.77

Table S7: Calculated electronic energies in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the DLPNO-CCSD(T)/aug-cc-PVTZ level of theory.

Derivative	$^{4}\mathbf{1}$	$^{6}\mathbf{1}$	$^{4}\mathbf{TS}_{\mathbf{cross}}$	$^{4}\mathbf{TS}_{\mathbf{homo}}$	$^{6}\mathbf{TS}_{\mathbf{cross1}}$	$^{6}\mathbf{TS}_{\mathbf{cross2}}$	$^{6}\mathbf{TS}_{\mathbf{homo1}}$	$^{6}\mathbf{TS}_{\mathbf{homo2}}$
a	0.00	-10.77	0.04	–	16.79	24.03	22.47	20.82
b	0.00	-10.37	4.69	–	35.06	29.29	32.39	30.99
c	0.00	-8.95	22.84	9.35	33.23	37.12	23.37	39.01
d	0.00	-5.73	42.75	45.51	40.23	63.50	42.13	63.37
e^{a}	–	–	–	–	–	–	–	–
f	0.00	-8.45	21.91	19.99	37.11	30.37	27.77	36.77
g	0.00	-3.49	14.73	23.76	46.22	53.43	43.69	65.22
h	0.00	-18.88	37.98	16.98	33.28	25.59	59.48	30.44

^{a} The CC calculation of ^{4}**1e** did not converge. Hence, no relative energies could be obtained for this derivative.

Table S8: Calculated electronic energies in kcal mol^{-1} for different isomers relative to the electronic ground state of the reactant ^{4}**1** obtained on the DLPNO-CCSD(T)/aug-cc-PVTZ level of theory.

Derivative	^{4}**1**	^{6}**1**	^{4}**TS**$_{\textbf{cross}}$	^{4}**TS**$_{\textbf{homo}}$	^{2}**2**$_{\textbf{cross/near}}$	^{2}**2**$_{\textbf{cross/far}}$	^{2}**2**$_{\textbf{homo}}$	^{4}**2**$_{\textbf{cross/near}}$	^{4}**2**$_{\textbf{cross/far}}$	^{4}**2**$_{\textbf{homo}}$
a	0.0	-7.9	15.9	17.7	-25.9	-22.3	-21.2	-19.3	-9.6	-7.1
e	0.0	-7.9	16.81			-23.25			-9.34	
g	0.0	-5.1	17.2	17.6	-22.0	-17.4	-21.7	-12.1	-1.3	-7.8

Structural parameters of the optimized transition state geometries for ^{4}TS and ^{6}TS

Table S9: Iron-Carbon distances in Angstrom for different isomers ^{4}**TS**

Derivative	^{4}**TS**$_{\textbf{cross}}$		^{4}**TS**$_{\textbf{homo}}$	
	Fe-C1	Fe-C2	Fe-C1	Fe-C2
a	2.019	2.008	2.013	2.012
b	2.023	2.005	2.013	2.012
c	2.016	2.011	2.012	2.008
d	2.002	2.021	2.009	2.008
e	2.009	2.009	2.009	2.009
f	2.02	2.012	2.029	2.007
g	2.007	2.038	2.012	2.011
h	2.011	2.015	2.009	2.01

Table S10: Iron-Carbon distances in Angstrom for different isomers ^{6}**TS**

Derivative	^{6}**TS**$_{\textbf{cross1}}$		^{6}**TS**$_{\textbf{homo1}}$		^{6}**TS**$_{\textbf{cross2}}$		^{6}**TS**$_{\textbf{homo2}}$	
	Fe-C1	Fe-C2	Fe-C1	Fe-C2	Fe-C1	Fe-C2	Fe-C1	Fe-C2
a	2.061	2.354	2.069	2.316	2.304	2.065	2.308	2.068
b	2.066	2.351	2.067	2.33	2.317	2.067	2.315	2.068
c	2.062	2.334	2.068	2.317	2.311	2.07	2.314	2.07
d	2.054	2.247	2.066	2.321	2.312	2.068	2.314	2.066
e	2.064	2.325	2.064	2.325	2.313	2.067	2.313	2.067
f	2.064	2.341	2.064	2.313	2.324	2.067	2.318	2.071
g	2.063	2.262	2.067	2.321	2.33	2.066	2.318	2.068
h	2.064	2.307	2.063	2.319	2.329	2.068	2.314	2.067

Table S11: Natural orbital occupation numbers (NOONs) for DMRG-SCF(25,25) for $^{4}\mathbf{TS_f}$ and $^{4}\mathbf{TS_h}$

Derivative	Occupation numbers				
$^{4}\mathbf{TS_{cross,f}}$	1.975	1.966	1.948	1.945	1.944
	1.943	1.941	1.939	1.937	1.937
	1.729	1.001	1.000	0.999	0.276
	0.079	0.065	0.062	0.062	0.060
	0.059	0.059	0.042	0.021	0.010
$^{4}\mathbf{TS_{homo,f}}$	1.968	1.962	1.949	1.943	1.943
	1.941	1.939	1.937	1.911	1.906
	1.718	1.001	1.000	1.000	0.283
	0.108	0.094	0.063	0.061	0.061
	0.059	0.057	0.052	0.034	0.010
$^{4}\mathbf{TS_{cross,h}}$	1.968	1.963	1.944	1.943	1.943
	1.941	1.940	1.940	1.913	1.91
	1.712	1.001	1.000	0.999	0.29
	0.105	0.093	0.062	0.060	0.059
	0.058	0.058	0.054	0.034	0.01
$^{4}\mathbf{TS_{homo,h}}$	1.975	1.968	1.947	1.945	1.945
	1.942	1.940	1.939	1.938	1.937
	1.733	1.001	1.000	0.999	0.274
	0.076	0.064	0.062	0.062	0.060
	0.060	0.059	0.042	0.020	0.009

Reactant Sextet Structure

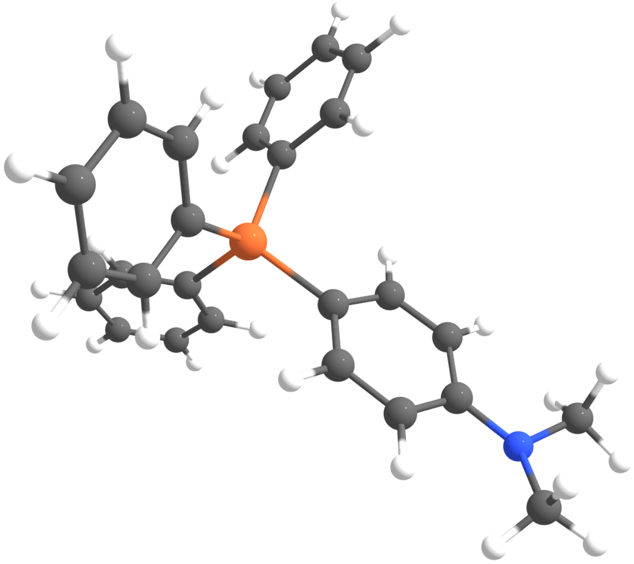

Figure S1: Ball and stick representation of the structure of ^{6}**1a**. The structure features an almost perfectly tetrahedral coordination environment for the Fe center.

Transition State Sextet Structure

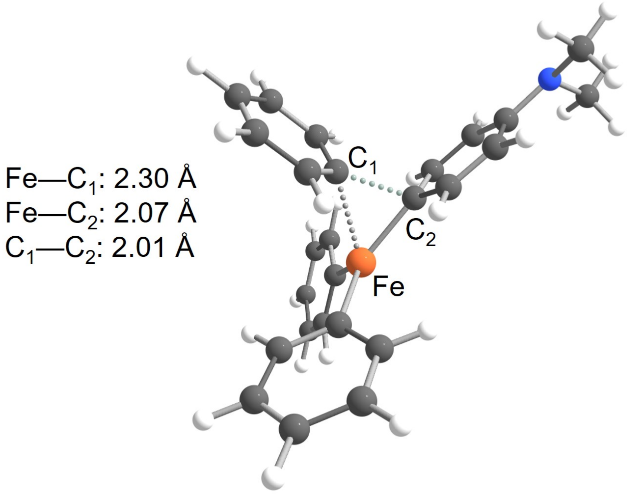

Figure S2: Ball and stick representation of the structure of ^{6}**TSa**. One Fe–C bond is significantly longer than the other indicating different partial charges.

Product Sextet Structure

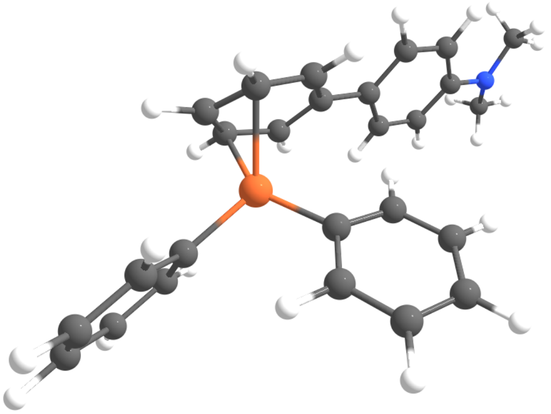

Figure S3: Ball and stick representation of the structure of $^{4}\mathbf{2}_{\mathbf{cross/far}}$. The aryl ring is bound to the Fe center in an η^3 fashion.

Relaxed Potential Energy Surface Scan Between ^{4}TSe And $^{4/2}$MECPe

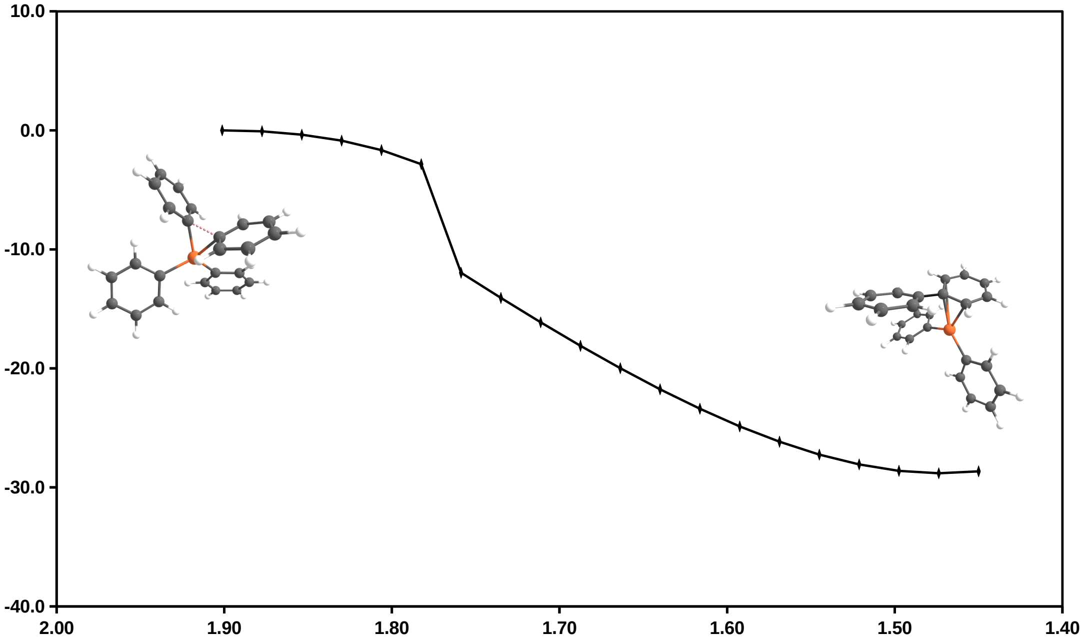

Figure S4: Energy profile of the relaxed potential energy surface scan between **^{4}TSe** and **$^{4/2}$MECPe** on the DFT level of theory. The minimum energy crossing point is reached barrierlessly. The C–C bond distance of the newly formed bond is taken as scanned parameter.

Active Orbitals of ^{4}TSa

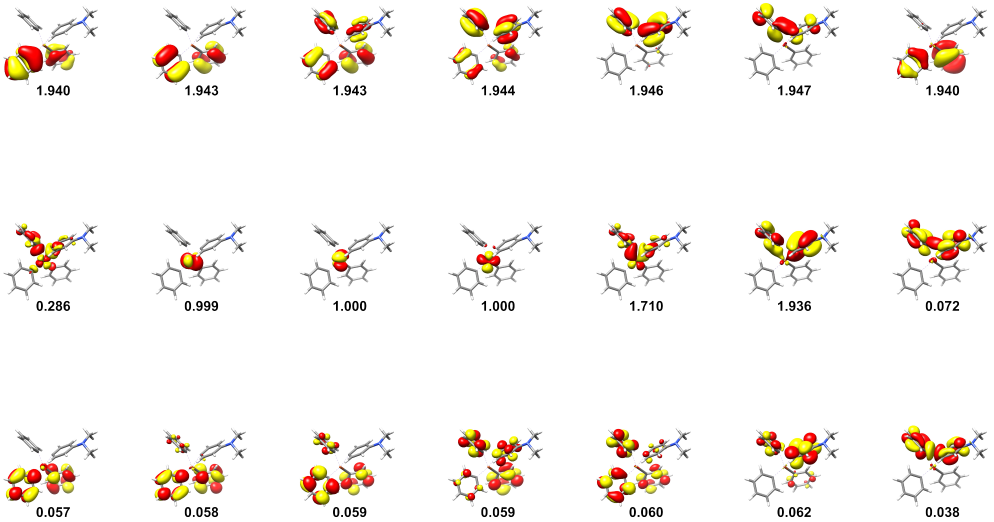

Figure S5: Surface plots of the 21 active orbitals of ^{4}**TSa** together with their corresponding occupation numbers at an isovalue of 0.03.

Active Orbitals of $^{2}\mathbf{2a}_{\mathbf{cross/near}}$

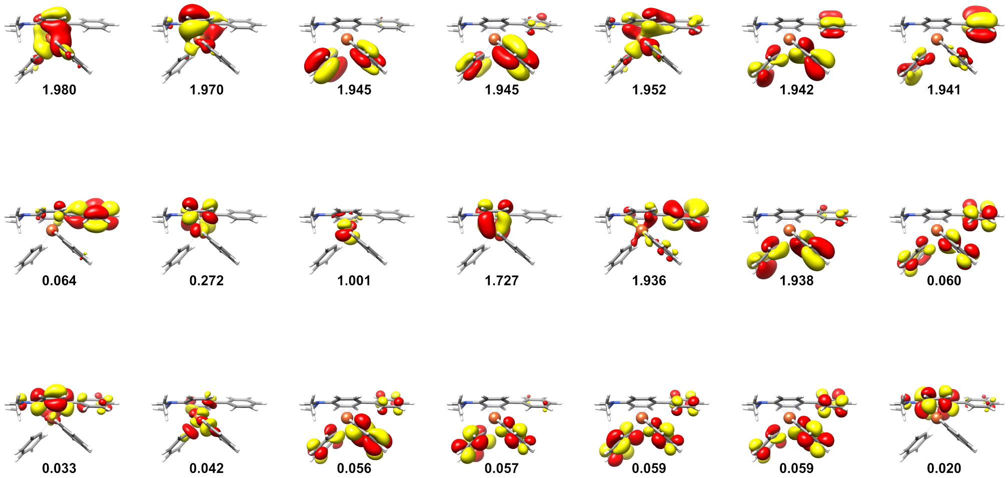

Figure S6: Surface plots of the 21 active orbitals of $^{2}\mathbf{2a}_{\mathbf{cross/near}}$ together with their corresponding occupation numbers at an isovalue of 0.03.