ELECTRONIC SUPPLEMENTARY INFORMATION

DEC. 28, 2017

Transition States of Spin-Forbidden Reactions

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3. Optimized structures on the lowest mixed-spin PES for the α-H elimination reaction of the model W Complex

Energies are in hartrees. DFT calculations performed with the unrestricted Kohn-Sham theory suing the of M06-L exchange-correlation functional. In section 2, the def2-TZVPP basis set is used for C, O, and Fe atoms. In section 3, the 6-31G* basis set is used for C, H, O atoms, and the def2-TZVP basis set is used for the W atoms. Enthalpy (*H*) and Gibbs free energy (*G*) were computed at 298.15 Kelvin and 1 atmosphere pressure.

1. Coupling constants χ

The coupling constant χ was determined for each system by the following procedure:

(a) Initial saddle point geometry optimization is performed by employing the *TSSMM* Perl script along with the *Gaussian* program as described in the main text. An initial guess for the coupling constant χ is provided, which was determined based on parametrization to an atom or monoatomic ion;

(b) A reaction coordinate scan was performed along the minimum energy path is using the optimized saddle point geometry from step (a) to locate a representative geometry along the reaction coordinate where the low- and high-spin surfaces are close in energy;

(c) Singlet-triplet excitation energies are computed at the representative geometry using the *ADF2016.103* program package. The spin-orbit coupling is included by employing the spin-orbit ZORA Hamiltonian. The M06-L exchange-correlation functional is used with a Slater-type ZORA/QZ4P basis set.

(d) The singlet–triplet splitting of the representative geometry is determined by averaging the corresponding singlet–triplet excitation energies as calculated in step (c). The value of coupling constant χ is adjusted so that the difference between the eigenvalues of the following 2 × 2 matrix reproduces the singlet-triplet splitting.

$$\begin{pmatrix} E_1 & \chi \\ \chi & E_2 \end{pmatrix}$$

where E_1 and E_2 are the energies of low- and high-spin states computed from the single-point calculations using *Gaussian* for the representative geometry.

(e) Steps (a) to (d) are repeated until the value of the coupling constant χ converges to the desired precision.

Table S1: Calculated single-point energies, singlet–triplet excitation energies, and the coupling constant χ for the $Fe(CO)_n$ and model W representative geometries at the final iteration. All energies are given in hartrees. The corresponding representative geometries are provided below Figs. S1 and S2.

	W model complex	$Fe(CO)_n$
E_1	-377.17345	-1830.55724
E_2	-377.17352	-1830.55782
	0.58562	0.46338
$E_{excitation}$	0.59541	0.46343
	0.63180	0.46387
Coupling constant χ	0.011103	0.008513

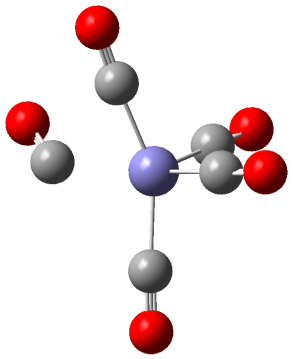

Fig. S1: The representative geometry of the $Fe(CO)_4$ + CO system.

Fe	0.178049000000	0.009280000000	-0.195510000000
C	-2.144052000000	0.815201000000	-0.494665000000
C	0.802900000000	1.720906000000	-0.633644000000
C	1.854855000000	-0.738539000000	-0.148327000000
C	-0.086581000000	0.136956000000	1.607737000000
C	-0.649950000000	-1.606451000000	-0.598403000000
O	-3.204639000000	0.589052000000	-0.161325000000
O	1.204884000000	2.769030000000	-0.846106000000
O	2.897081000000	-1.207209000000	-0.065615000000
O	-0.218539000000	0.196606000000	2.743749000000
O	-1.134408000000	-2.625993000000	-0.786450000000

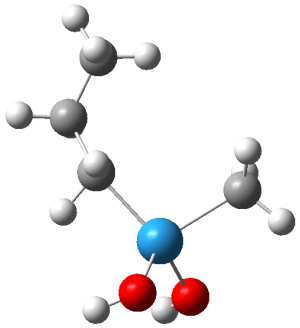

Fig. S2: The representative geometry of the model W system.

C	2.915106000000	-0.460781000000	0.678123000000
H	2.820323000000	0.008037000000	1.667776000000
H	3.393703000000	-1.437088000000	0.855271000000
C	1.546643000000	-0.685420000000	0.087061000000
H	1.640453000000	-1.098729000000	-0.946800000000
W	-0.374630000000	-0.020996000000	-0.009772000000
H	1.076289000000	-1.514110000000	0.695179000000
C	3.816112000000	0.368450000000	-0.213198000000
H	3.415218000000	1.379260000000	-0.358326000000
H	4.821108000000	0.462101000000	0.213296000000
H	3.918386000000	-0.088947000000	-1.205617000000
O	-1.281740000000	-1.463951000000	-0.893137000000
H	-1.247778000000	-2.330947000000	-0.449669000000
O	-1.668286000000	0.695078000000	1.231325000000
H	-1.653141000000	0.452794000000	2.166417000000
C	-0.109694000000	1.900851000000	-0.837373000000
H	0.273115000000	2.527215000000	-0.010182000000
H	0.573449000000	1.997851000000	-1.689247000000
H	-1.090655000000	2.305011000000	-1.123577000000

2. Optimized structures on the lowest mixed-spin PES for the CO association reaction of the $Fe(CO)_4$ Complex

O atoms are shown in red; C in grey; Fe in purple.

$Fe(CO)_4$ + CO (reactant)

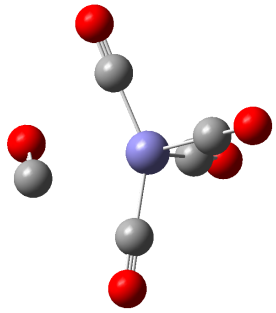

Fig. S3: Fe(CO)4 + CO complex (reactant).

SCF	E_{ZP}	H	G
-1830.565360	-1830.528169	-1830.512874	-1830.575159

Fe	0.35482600	-0.00961700	-0.22614000
C	-2.80001800	0.79962600	-0.45695300
C	0.54818300	1.80229800	-0.64214200
C	2.11602300	-0.50733700	-0.08845600
C	-0.01026500	0.07321000	1.56871400
C	-0.40619400	-1.65115900	-0.66321600
O	-3.54622000	0.10266800	0.02416400
O	0.68128800	2.91169100	-0.87461300
O	3.21270900	-0.81884200	0.01192300
O	-0.22961700	0.12095600	2.69131000
O	-0.85714200	-2.67269500	-0.90628800

$Fe(CO)_4$ + CO (transition structure)

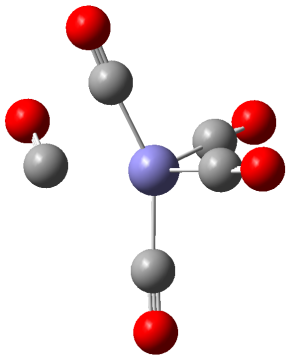

Fig. S4: Fe(CO)4 + CO complex (transition structure).

SCF	E_{ZP}	H	G
-1830.564540	-1830.527409	-1830.513150	-1830.570728

Fe	0.22263800	-0.00566200	-0.20503200
C	-2.27341700	0.91969500	-0.55807600
C	0.79742800	1.73086500	-0.62779100
C	1.90083700	-0.75682600	-0.12781600
C	-0.06714800	0.13003000	1.60010700
C	-0.66247400	-1.60038800	-0.59393400
O	-3.26184800	0.56528200	-0.13521800
O	1.19508700	2.77745200	-0.84906300
O	2.94286200	-1.22538000	-0.06156500
O	-0.22363600	0.20055100	2.73224600
O	-1.14745700	-2.61703500	-0.78941200

$Fe(CO)_5$ (product)

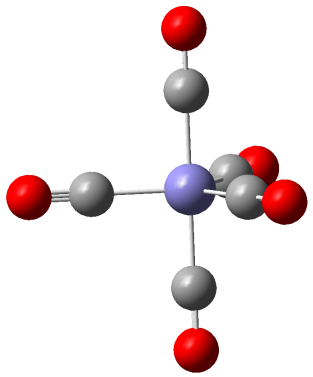

Fig. S5: $Fe(CO)_5$ complex (product).

SCF	E_{ZP}	H	G
-1830.616960	-1830.574884	-1830.562145	-1830.615675

Fe	0.00000600	0.00033600	-0.00029500
C	1.81586600	0.00060800	-0.00045400
C	-0.00002200	-1.21961500	-1.34021000
C	-1.81585400	0.00075400	-0.00050300
C	-0.00003800	-0.55301600	1.72513200
C	0.00007900	1.77147100	-0.38416500
O	2.95693200	0.00065900	-0.00039100
O	-0.00006800	-1.99023800	-2.18660200
O	-2.95691900	0.00082500	-0.00045500
O	-0.00010000	-0.90264900	2.81509700
O	0.00011200	2.89016000	-0.62653900

3. Optimized structures on the lowest mixed-spin PES for the α-H elimination reaction of the model W Complex

O atoms are shown in red; H in light gray, C in dark Grey; W in Blue.

$W(CH_3)(C_3H_7)(OH)_2$ (reactant)

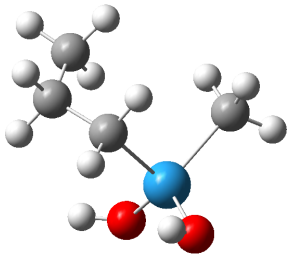

Fig. S6: $W(CH_3)(C_3H_7)(OH)_2$ complex (reactant).

SCF	E_{ZP}	H	G
-377.214384	-377.060080	-377.046863	-377.099766

C	-2.50599000	0.80875000	0.27831700
H	-2.42978000	0.87169600	1.37614800
H	-3.29329400	1.52978300	0.00369300
C	-1.17932200	1.22962500	-0.35262900
H	-1.30089800	1.27432600	-1.45149600
W	0.49596700	-0.04848100	0.05050100
H	-0.94880200	2.26591700	-0.04284700
C	-2.96148400	-0.58790000	-0.11445500
H	-2.28153800	-1.36238600	0.26893400
H	-3.96244500	-0.81403100	0.27115200
H	-2.98974600	-0.70153100	-1.20640700
O	1.64397700	1.44403300	-0.35823300
H	1.22595200	2.31740600	-0.43846900
O	0.49410200	-0.94895200	1.73966100
H	-0.19914300	-0.83307900	2.40480100
C	0.26970600	-1.43014300	-1.54486300
H	-0.59187900	-2.09433400	-1.38019500
H	0.07131900	-0.88842400	-2.48170400
H	1.15657400	-2.06035000	-1.71035900

W(···H)(CH_3)(=C_3H_6)($OH)_2$ (transition structure)

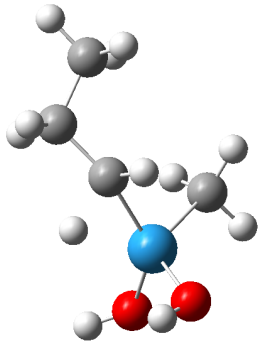

Fig. S7: W(···H)(CH_3)(=C_3H_6)($OH)_2$ complex (transition structure).

SCF	E_{ZP}	H	G
-377.169256	-377.018825	-377.006386	-377.056746

C	2.75476500	-0.49692100	0.66265200
H	2.66846800	-0.03811600	1.65776400
H	3.19563100	-1.49505600	0.81976100
C	1.39220000	-0.59199800	0.03929900
H	1.40125200	-1.14322200	-0.93707500
W	-0.48542700	-0.04574900	-0.00978200
H	0.62772500	-0.92650400	1.07995600
C	3.68608400	0.33536600	-0.20966500
H	3.29355400	1.35035000	-0.34119700
H	4.68482600	0.40829800	0.23538400
H	3.79640600	-0.10658300	-1.20747300
O	-1.41339700	-1.47110300	-0.89277200
H	-1.32731100	-2.36616000	-0.52320400
O	-1.79388100	0.67727500	1.22320500
H	-1.75031500	0.44148600	2.15765700
C	-0.22357400	1.89123400	-0.83239900
H	0.11804400	2.54791300	-0.01489800
H	0.44852800	2.01363400	-1.68618700
H	-1.23385200	2.22393900	-1.11944000

$W(H)(CH_3)(=C_3H_6)(OH)_2$ (product)

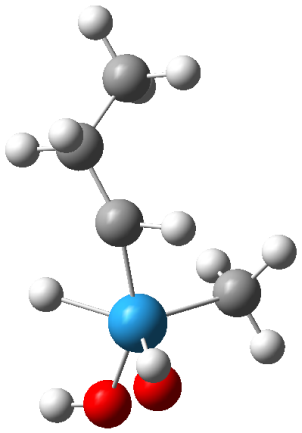

Fig. S8: $W(H)(CH_3)(=C_3H_6)(OH)_2$ complex (product).

SCF	E_{ZP}	H	G
-377.209233	-377.056625	-377.044223	-377.094628

W	-0.42387000	-0.03021600	0.04243900
O	-0.54695900	-1.59597800	-1.06031400
H	-1.38476400	-2.05907900	-0.89227700
O	-2.07683400	-0.36779800	1.01946300
H	-2.09920000	-0.45365300	1.97932500
C	-1.19429700	1.74966400	-0.81144000
H	-1.16507500	2.46066600	0.03099700
H	-0.64596000	2.20075800	-1.64296300
H	-2.24817300	1.61217900	-1.08859500
H	0.10061200	0.01381000	1.68243000
C	1.39659000	0.37442700	-0.02642700
H	1.22850000	0.24599300	-1.14781000
C	2.78803600	0.62890000	0.40356700
H	2.79144700	0.71717400	1.49877400
H	3.12713400	1.60782200	0.02677600
C	3.77244700	-0.45270200	-0.03426000
H	4.78897300	-0.22737400	0.30879300
H	3.48486900	-1.42988500	0.36906600
H	3.80168700	-0.54392400	-1.12680400