Supporting information for: Spin-State Effects on the Thermal Dihydrogen Release from Solid-State $[MH(\eta^2\text{-}H_2)dppe_2]^+$ (M = Fe, Ru, Os) Organometallic Complexes for Hydrogen Storage Applications

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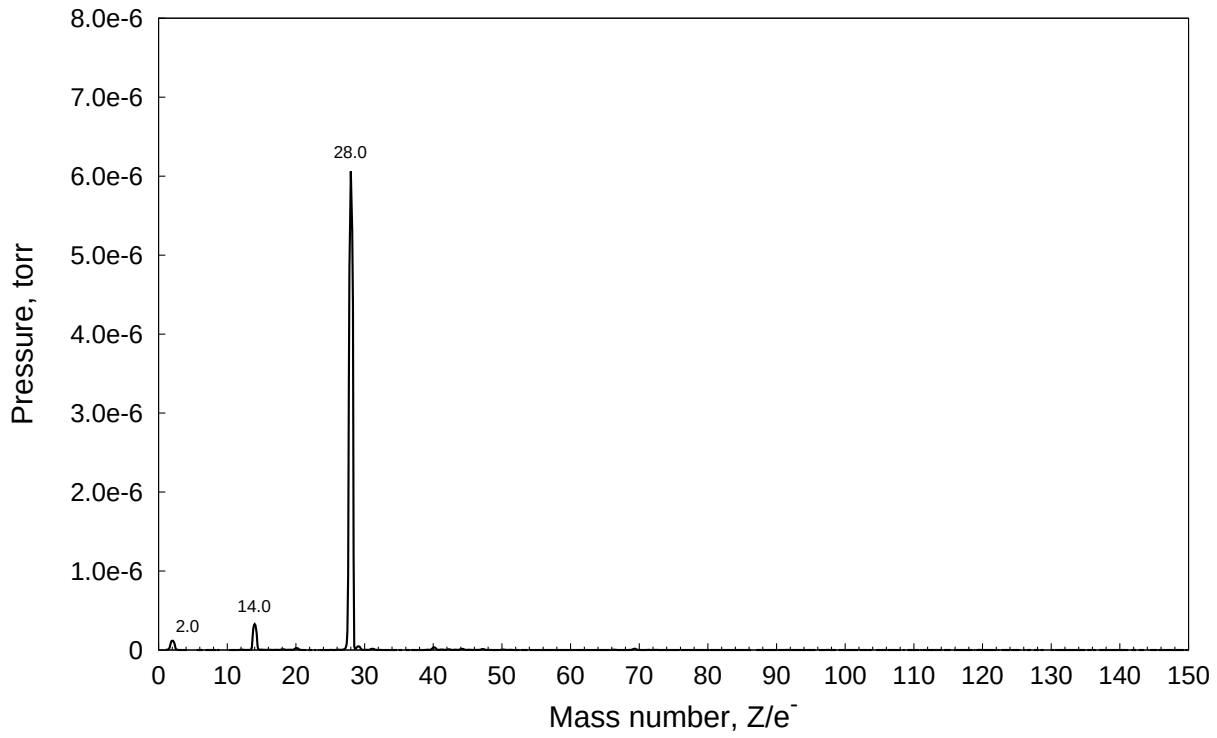

Figure S.1: Residual mass spectrograph of the initial degassing of as-synthesized [FeH(η^2-H_2)dppe$_2$][NTf_2] containing N_2 contamination at the binding site. Degassing occurred from the solid state under vacuum conditions at 393K, and shows the preferential loss of N_2 gas from the species.

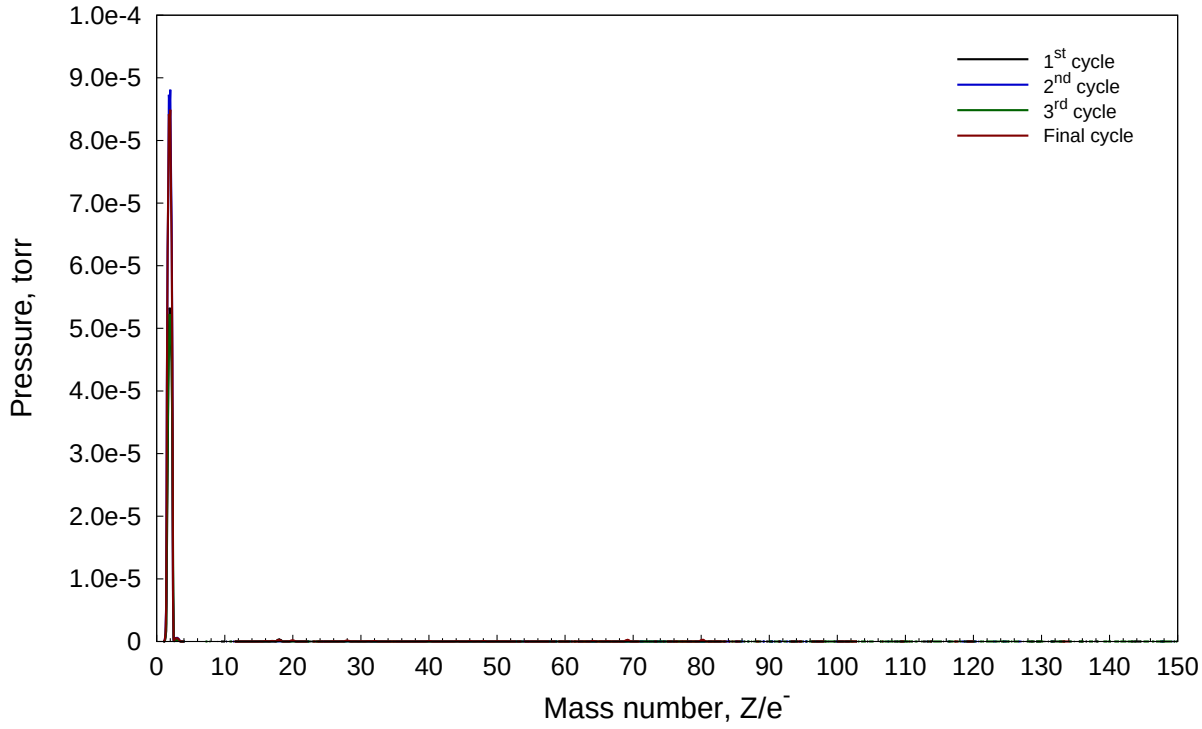

Figure S.2: Residual mass spectrograph of the volatile thermal decomposition products of [FeH(η^2-H_2)dppe$_2$][NTf_2] during hydrogen cycling at 413 K. Hydrogen gas is the only observed decomposition product from the material after for all four hydrogenation/dehydrogenation cycles.

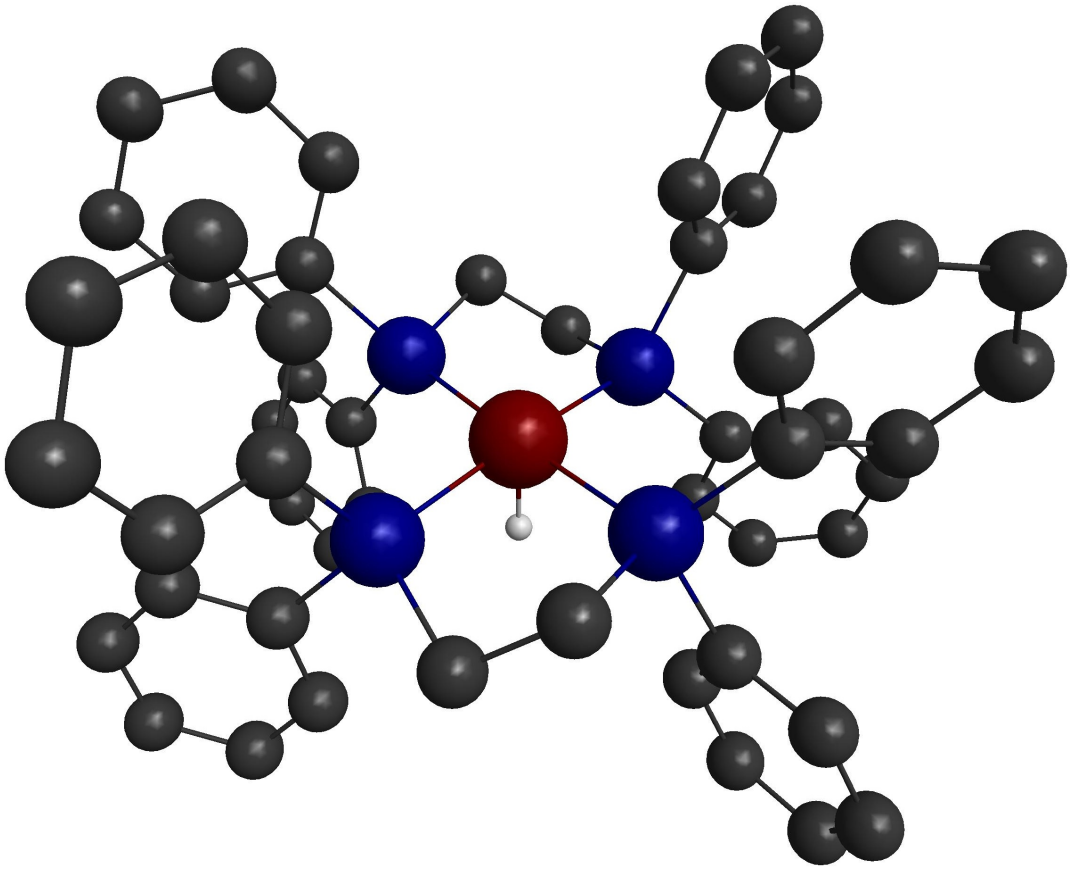

Figure S.3: Optimized structure of the singlet state organometallic fragment $[FeHdppe_2]^+$ using the UHF approximation and LANL2DZ-ECP basis sets, showing typical octahedral geometry. Alkyl and aryl hydrogens have been omitted for clarity.

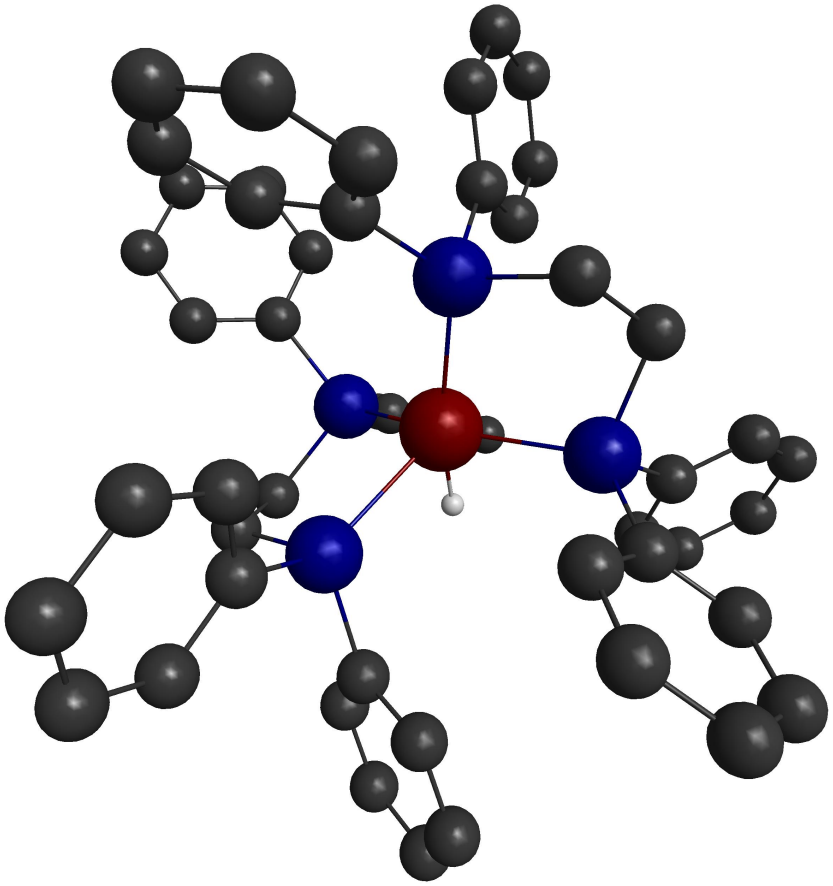

Figure S.4: Optimized structure of the triplet state organometallic $[FeHdppe_2]^+$ using the UHF approximation and LANL2DZ-ECP basis sets. Structure shows the quasi-square pyramidal structure observed by Franke,[1] et al. Alkyl and aryl hydrogens have been omitted for clarity.

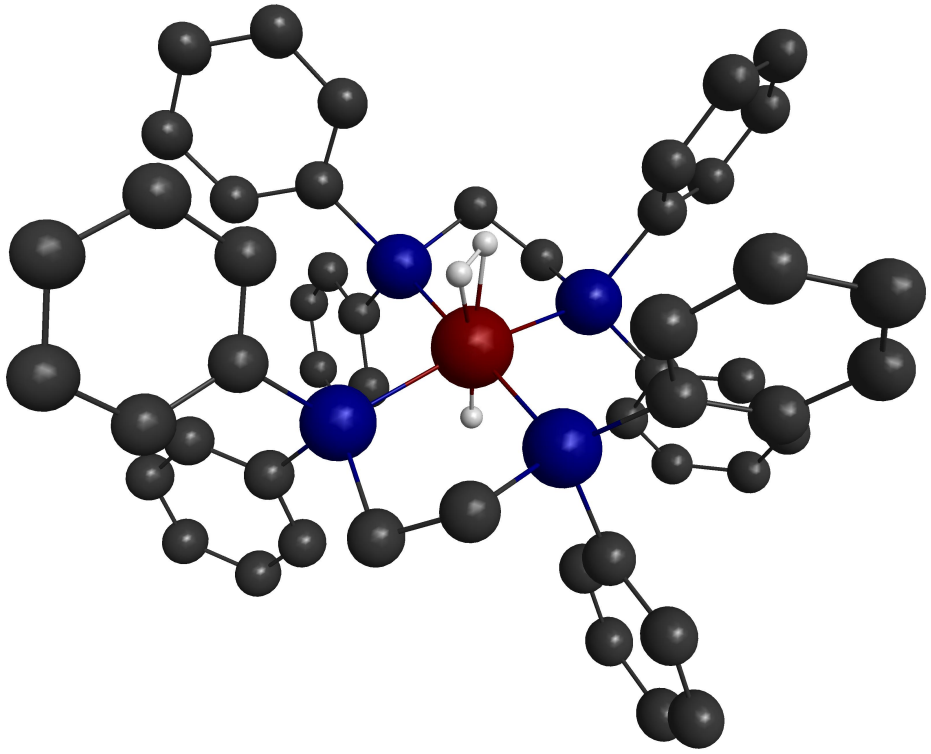

Figure S.5: Optimized structure of $[FeH(\eta^2\text{-}H_2)dppe_2]^+$ using the UHF approximation and LANL2DZ-ECP basis sets, showing the octahedral geometry observed from x-ray diffraction measurements.[2] Alkyl and aryl hydrogens have been omitted for clarity.

Table 1: Calculated values of ground state and vibration energies for molecular fragments as used to calculate the binding energy ΔE. Ground state energies are given using the MP2 level of calculation. Values given are in Hartrees/fragment.

	RHF	ROHF	UHF
H_2			
ε_0	-1.143887	-1.143887	-1.143887
$\varepsilon_{\text{corr}}$ (295K)	0.012077	0.012077	0.012077
$\varepsilon_{\text{corr}}$ (298K)	0.012101	0.012101	0.012101
$\varepsilon_{\text{corr}}$ (300K)	0.012117	0.012117	0.012117
$\varepsilon_{\text{corr}}$ (313K)	0.012220	0.012220	0.012220
$\varepsilon_{\text{corr}}$ (333K)	0.012378	0.012378	0.012378
$\varepsilon_{\text{corr}}$ (343K)	0.012457	0.012457	0.012457
$\varepsilon_{\text{corr}}$ (353K)	0.012536	0.012536	0.012536
$\varepsilon_{\text{corr}}$ (363K)	0.012615	0.012615	0.012615
$\varepsilon_{\text{corr}}$ (373K)	0.012695	0.012695	0.012695
[FeHdppe$_2$]$^+$, singlet			
ε_0	-2149.499647	-2149.478130	-2149.499593
$\varepsilon_{\text{corr}}$ (295K)	0.884147	0.884136	0.884016
$\varepsilon_{\text{corr}}$ (298K)	0.885167	0.885157	0.885036
$\varepsilon_{\text{corr}}$ (300K)	0.885853	0.885842	0.885722
$\varepsilon_{\text{corr}}$ (313K)	0.890418	0.890408	0.890288
$\varepsilon_{\text{corr}}$ (333K)	0.897804	0.897795	0.898047
$\varepsilon_{\text{corr}}$ (343K)	0.901659	0.901650	0.901530
$\varepsilon_{\text{corr}}$ (353K)	0.905621	0.905611	0.905491
$\varepsilon_{\text{corr}}$ (363K)	0.909687	0.909677	0.909557
$\varepsilon_{\text{corr}}$ (373K)	0.913855	0.913846	0.913726
[FeHdppe$_2$]$^+$, triplet			
ε_0	—	-2149.507960	-2149.211701
$\varepsilon_{\text{corr}}$ (295K)	—	0.884384	0.884327
$\varepsilon_{\text{corr}}$ (298K)	—	0.885405	0.884280
$\varepsilon_{\text{corr}}$ (300K)	—	0.886091	0.884960
$\varepsilon_{\text{corr}}$ (313K)	—	0.890659	0.889489
$\varepsilon_{\text{corr}}$ (333K)	—	0.898047	0.896815
$\varepsilon_{\text{corr}}$ (343K)	—	0.901902	0.900639
$\varepsilon_{\text{corr}}$ (353K)	—	0.905863	0.904569
$\varepsilon_{\text{corr}}$ (363K)	—	0.909928	0.908604
$\varepsilon_{\text{corr}}$ (373K)	—	0.914095	0.912741

Table 1 continued

	RHF	ROHF	UHF
[FeH(η^2-H_2)dppe$_2$]$^+$			
ε_0	-2150.671333	-2150.671330	-2150.671332
ε_{corr} (295K)	0.901449	0.901436	0.901443
ε_{corr} (298K)	0.902489	0.902475	0.902482
ε_{corr} (300K)	0.903187	0.903174	0.903181
ε_{corr} (313K)	0.907839	0.907826	0.907833
ε_{corr} (333K)	0.915366	0.915354	0.915360
ε_{corr} (343K)	0.919296	0.919283	0.919290
ε_{corr} (353K)	0.923333	0.923321	0.923328
ε_{corr} (363K)	0.927478	0.927466	0.927472
ε_{corr} (373K)	0.931728	0.931716	0.931723
[RuHdppe$_2$]$^+$, singlet			
ε_0	-2120.162390	—	—
ε_{corr} (295K)	0.884338	—	—
ε_{corr} (298K)	0.885284	—	—
ε_{corr} (300K)	0.886047	—	—
ε_{corr} (313K)	0.890622	—	—
ε_{corr} (333K)	0.898020	—	—
ε_{corr} (343K)	0.901880	—	—
ε_{corr} (353K)	0.905847	—	—
ε_{corr} (363K)	0.909918	—	—
ε_{corr} (373K)	0.914092	—	—
[RuH(η^2-H_2)dppe$_2$]$^+$			
ε_0	-2121.328628	—	—
ε_{corr} (295K)	0.900999	—	—
ε_{corr} (298K)	0.902042	—	—
ε_{corr} (300K)	0.902743	—	—
ε_{corr} (313K)	0.907410	—	—
ε_{corr} (333K)	0.914960	—	—
ε_{corr} (343K)	0.918901	—	—
ε_{corr} (353K)	0.922949	—	—
ε_{corr} (363K)	0.927105	—	—
ε_{corr} (373K)	0.931365	—	—

Table 1 continued

	RHF	ROHF	UHF
[OsHdppe$_2$]$^+$, singlet			
ε_0	-2117.324594	—	—
ε_{corr} (295K)	0.884733	—	—
ε_{corr} (298K)	0.885755	—	—
ε_{corr} (300K)	0.886442	—	—
ε_{corr} (313K)	0.891014	—	—
ε_{corr} (333K)	0.898409	—	—
ε_{corr} (343K)	0.902268	—	—
ε_{corr} (353K)	0.906233	—	—
ε_{corr} (363K)	0.910302	—	—
ε_{corr} (373K)	0.914474	—	—
[OsH(η^2-H$_2$)dppe$_2$]$^+$			
ε_0	-2118.506051	—	—
ε_{corr} (295K)	0.899768	—	—
ε_{corr} (298K)	0.900799	—	—
ε_{corr} (300K)	0.901493	—	—
ε_{corr} (313K)	0.906110	—	—
ε_{corr} (333K)	0.913583	—	—
ε_{corr} (343K)	0.917484	—	—
ε_{corr} (353K)	0.921493	—	—
ε_{corr} (363K)	0.925609	—	—
ε_{corr} (373K)	0.929830	—	—

Table 2: SCS-MP2 calculated values of ground state energies for molecular fragments as used to calculate the binding energy ΔE. Calculations were available for the RHF approximation only. Values given are in Hartrees/fragment.

H_2	-1.147356
[FeHdppe$_2$]$^+$, singlet	-2149.376507
[FeH(η^2-H$_2$)dppe$_2$]$^+$	-2150.544791
[RuHdppe$_2$]$^+$, singlet	-2120.037432
[RuH(η^2-H$_2$)dppe$_2$]$^+$	-2121.202370
[OsHdppe$_2$]$^+$, singlet	-2117.197672
[OsH(η^2-H$_2$)dppe$_2$]$^+$	-2118.377019

References

(1) Franke, O.; Wiesler, B.E.; Lehnert, N.; Peters, G.; Burger, P.; Tuczek, F. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1247.

(2) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.