Supporting information

to the article **The effect of "inert" counter-anions in the deprotonation of the dihydrogen complex *trans*-[FeH(η^2-H_2)(dppe)$_2$]$^+$: Kinetic and theoretical studies**

by

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Experimental Details

The complex *trans*-[FeH(η^2-H_2)(dppe)$_2$](BF_4) was prepared following the literature procedure: Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc*. **1991**, *113*, 4876.

The NMR experiments were carried out using a Varian Inova 400 spectrometer using the standard pulse sequences provided by the manufacturer. The reaction of the starting complex with NEt_3 was monitored in acetone and thf solution at low temperatures using $^{31}P\{^1H\}$ NMR. Both in the absence and in the presence of added salts, the starting complex converts to the final *cis*-dihydride without the appearance of any signal assignable to reaction intermediates. For the case of the $^1H,^{19}F$-HOESY experiments, many attempts were made with different solvents and temperatures using mix times ranging from 10 ms to 1 s. None of these experiments showed NOE contacts between the anion and any of the protons in **1**.

Kinetic experiments were carried out with an Applied Photophysics SX17MV spectrometer. All experiments were carried out under an Ar atmosphere and pseudo first-order conditions of base excess. Solvents were dried and deoxygenated by standard procedures immediately before use. The salts were also dried before use. Similar kinetic results were obtained in thf and acetone solutions.

Computational Details

Calculations were performed with the Gaussian 98 series of programs.[1] Density Functional Theory (DFT) was applied with the B3LYP functional.[2] Effective core potentials (ECPs) were used to represent the innermost electrons of the iron atom as well as the electron core of phosphorus atoms.[3] The basis set for the Fe and P atoms was that associated with the pseudopotential,[3] with a standard double-ξ LANL2DZ contraction,[1] supplemented in the case of P with a set of d-polarization functions.[4] A 6-31G(d,p) basis was used for hydrogen atoms directly bonded to the metal and the nitrogen and fluorine atoms, while a 6-31G basis set was used for the rest of atoms in the system.[5] Solvent effects were taken into account by means of polarized continuum model (PCM) calculations[6] using standard options.[1] Free energies of solvation were calculated with acetone (ε = 20.70) and dichloromethane (ε = 8.93) as solvents, keeping the geometry optimized for the gas phase species (single-point calculations).

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98,* Gaussian, Inc., Pittsburgh PA, **1998**.
2. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
3. (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

4. Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, 208, 237.
5. (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213.
6. (a) Tomasi, J.; Persico, M. *Chem. Rev.* **1994,** *94*, 2027. (b) Amovilli, C.; Barone, V.; Cammi, R.; Cancès, E.; Cossi, M.; Mennucci, B.; Pomelli, C. S.; Tomasi, J. *Adv. Quantum Chem.* **1998**, *32*, 227.

Tables of the optimized geometries (Cartesian coordinates) for the 1b to 4 calculated species

1b

26	.000089	-.000126	.403787
1	.336036	-.227450	2.033460
1	.000289	-.000211	-1.102742
15	1.598238	-1.546675	.039470
1	2.175858	-2.313983	1.092133
1	1.339045	-2.615251	-.859429
15	1.682080	1.514175	.210715
1	1.994423	2.475110	1.212756
1	1.624107	2.399049	-.899433
15	-1.598507	1.546742	.039835
1	-2.176459	2.313583	1.092686
1	-1.339245	2.615702	-.858589
15	-1.682161	-1.514010	.210987
1	-1.623966	-2.399229	-.898877
1	-1.994580	-2.474545	1.213383
6	3.329545	.640827	-.022981
1	3.756240	.492001	.976457
1	4.025483	1.268300	-.587527
6	3.095711	-.715945	-.721320
1	3.977461	-1.359827	-.650092
1	2.869084	-.571379	-1.784024
6	-3.329651	-.640764	-.023132
1	-4.025407	-1.268364	-.587772
1	-3.756568	-.491836	.976210
6	-3.095699	.716018	-.721433
1	-2.868640	.571437	-1.784044
1	-3.977540	1.359813	-.650545
1	-.334736	.227117	2.033561

3

26	0.689754	0.232638	-0.007521
1	-0.012449	-1.049343	-0.828218
1	1.599726	1.292503	0.568513
15	2.420074	0.018129	-1.430734
1	2.375721	-0.829455	-2.576470
1	2.953383	1.169907	-2.069080
15	1.843865	-1.189234	1.323793
1	1.321989	-2.422869	1.806724
1	2.305099	-0.678112	2.567266
15	-0.637098	0.917165	1.673641
1	-1.835854	0.229708	2.012604
1	-0.100678	1.046665	2.983024
15	-0.236324	1.931894	-1.186969
1	0.615969	3.012575	-1.541385
1	-0.870284	1.764075	-2.450487
6	3.428523	-1.748613	0.481040
1	3.192889	-2.673151	-0.060158
1	4.199085	-1.987528	1.219943
6	3.902425	-0.653519	-0.498759
1	4.659604	-1.035159	-1.190307
1	4.338822	0.191585	0.046211
6	-1.587403	2.767688	-0.184754

1	-1.714251	3.810179	-0.491366
1	-2.520059	2.237272	-0.410848
6	-1.251771	2.652811	1.317372
1	-0.439060	3.337373	1.586822
1	-2.116770	2.897261	1.941306
1	-0.658957	-0.776920	-0.425379
7	-2.992238	-1.500068	-0.375782
6	-2.825791	-2.250732	-1.634406
1	-3.688349	-2.903310	-1.857546
1	-2.701692	-1.551579	-2.468176
1	-1.931059	-2.879939	-1.572850
6	-4.173080	-0.620337	-0.463605
1	-4.045176	0.087840	-1.289798
1	-5.109933	-1.179356	-0.636366
1	-4.283730	-0.056268	0.468978
6	-3.138286	-2.436310	0.754725
1	-4.012298	-3.102925	0.646199
1	-2.241415	-3.059954	0.833526
1	-3.253670	-1.874428	1.687711

4

26	0.642778	0.143444	-0.000559
1	-0.899248	-0.273618	0.084028
1	2.134291	0.526735	-0.071000
15	1.270672	-1.339011	-1.542297
1	0.377234	-2.214215	-2.240713
1	2.008686	-0.927852	-2.689128
15	1.302498	-1.383839	1.489455
1	0.472011	-1.961455	2.498572
1	2.391159	-1.062274	2.350599
15	0.606354	1.776263	1.516396
1	-0.530849	2.115640	2.318670
1	1.555615	1.802270	2.578024
15	0.337054	1.767794	-1.501996
1	1.361289	2.006688	-2.463550
1	-0.754635	1.846172	-2.422171
6	1.927870	-2.946582	0.636977
1	1.076054	-3.634216	0.562569
1	2.696861	-3.440061	1.238970
6	2.447920	-2.583867	-0.769695
1	2.560634	-3.471339	-1.400188
1	3.423607	-2.088849	-0.704208
6	0.185759	3.453031	-0.667632
1	0.550916	4.249292	-1.323316
1	-0.883283	3.631722	-0.496398
6	0.944628	3.423419	0.674868
1	2.026758	3.470535	0.507389
1	0.664631	4.264536	1.316618
1	-2.084893	-0.518104	0.060736
7	-3.186330	-0.757781	0.051092
6	-3.424699	-1.655355	-1.123606
1	-4.483898	-1.918058	-1.184167
1	-3.117955	-1.135944	-2.032878
1	-2.824842	-2.559023	-1.004607
6	-3.913337	0.544086	-0.082337
1	-3.608883	1.024928	-1.013455

1	-4.992402	0.370418	-0.091038
1	-3.648022	1.184161	0.760736
6	-3.492689	-1.438828	1.349090
1	-4.554455	-1.693774	1.395302
1	-2.890214	-2.345620	1.422370
1	-3.235470	-0.767296	2.169777

2t

26	0.000007	0.000047	0.000089
1	-0.000387	0.000057	-1.563220
1	0.000376	0.000074	1.563389
15	-1.603957	-1.500267	0.120940
1	-1.925877	-2.382224	-0.961881
1	-1.660365	-2.503085	1.137055
15	-1.604045	1.500312	-0.120450
1	-1.660277	2.503585	-1.136122
1	-1.926467	2.381732	0.962664
15	1.604046	1.500300	0.120580
1	1.926277	2.381857	-0.962476
1	1.660374	2.503453	1.136366
15	1.603960	-1.500286	-0.120802
1	1.926103	-2.382063	0.962095
1	1.660211	-2.503247	-1.136789
6	-3.278617	0.669136	-0.383181
1	-3.375347	0.491791	-1.461365
1	-4.102260	1.320050	-0.071260
6	-3.278735	-0.669196	0.382800
1	-4.102162	-1.320197	0.070493
1	-3.376038	-0.491833	1.460932
6	3.278664	-0.669193	-0.383032
1	4.102168	-1.320178	-0.070899
1	3.375734	-0.491820	-1.461182
6	3.278676	0.669123	0.382977
1	3.375613	0.491742	1.461137
1	4.102258	1.320050	0.070923

2c

26	-0.001248	-0.033881	-0.429507
1	-0.608831	0.699777	-1.622046
1	0.623778	-0.936367	-1.484701
15	-1.800286	-1.212567	-0.756086
1	-2.155312	-1.647898	-2.063766
15	-1.220084	1.308904	0.842486
1	-1.466507	2.663826	0.454240
15	1.771681	1.147767	-0.878243
1	2.287658	1.131444	-2.205767
15	1.244793	-1.217103	0.960931
1	1.226640	-2.645629	1.025039
6	-3.319740	-0.184871	-0.304182
1	-3.509537	0.473793	-1.160296
1	-4.206182	-0.811251	-0.155250
6	-2.996952	0.651350	0.953187
1	-3.714477	1.466896	1.093331
1	-3.038114	0.017011	1.848291
6	3.057495	-0.944166	0.494226

1	3.731187	-1.253330	1.300805
1	3.247588	-1.587828	-0.373030
6	3.266940	0.539108	0.115927
1	3.313573	1.155767	1.023220
1	4.203834	0.687037	-0.432286
1	-2.129415	-2.449768	-0.101517
1	1.922951	2.560166	-0.685555
1	1.338326	-1.033033	2.384460
1	-1.022721	1.616752	2.230738

1b,BF_4^-

26	1.190766	0.113803	-0.263838
1	-0.193662	-0.164356	-1.314289
1	2.130017	0.216874	0.923006
15	-0.085584	1.535680	0.974070
1	-1.335438	2.005680	0.509461
1	-0.404851	1.224176	2.318006
15	2.238756	1.970450	-0.970969
1	2.334972	2.378948	-2.334843
1	3.624776	2.092619	-0.665252
15	2.799900	-1.266482	-0.976179
1	2.753693	-1.992582	-2.206875
1	4.145601	-0.814279	-1.101862
15	0.352876	-1.718940	0.794305
1	0.164507	-1.636709	2.197952
1	-0.856285	-2.334753	0.416144
6	1.511187	3.512147	-0.177669
1	0.729547	3.875890	-0.856594
1	2.264656	4.300811	-0.085856
6	0.897066	3.123894	1.183819
1	0.262079	3.927642	1.572049
1	1.685927	2.930664	1.920653
6	1.564288	-3.160819	0.631866
1	1.579693	-3.762105	1.546714
1	1.177593	-3.802031	-0.170367
6	2.976316	-2.656740	0.267915
1	3.469635	-2.220747	1.144287
1	3.611262	-3.461292	-0.117428
1	0.403927	0.131145	-1.755889
5	-2.842274	-0.298128	-0.216301
9	-2.922898	1.049262	-0.628830
9	-4.087366	-0.874135	-0.036583
9	-2.101915	-0.336979	1.038410
9	-2.066868	-1.031508	-1.170532

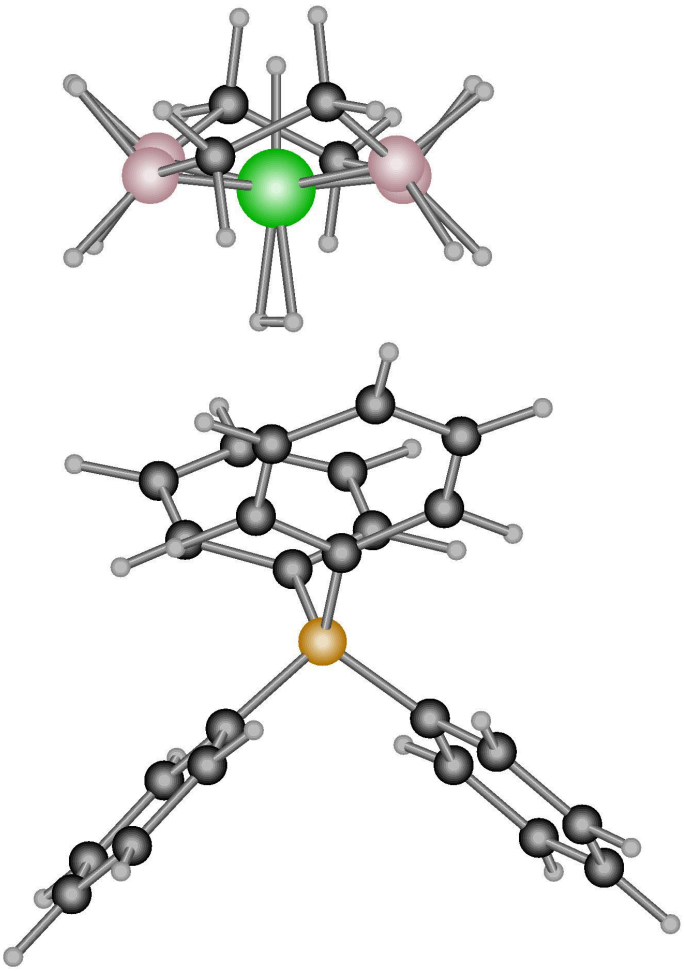
1b,BPh_4^-

26	-3.162550	0.055132	0.015686
1	-1.460500	0.060343	-0.028704
1	-4.642643	0.346572	-0.135930
15	-3.947409	-1.476047	1.447839
1	-3.108456	-2.209946	2.331112
1	-4.946602	-1.100695	2.388902
15	-3.457977	-1.520143	-1.570176
1	-2.426820	-1.955966	-2.445199
1	-4.460885	-1.273972	-2.549910

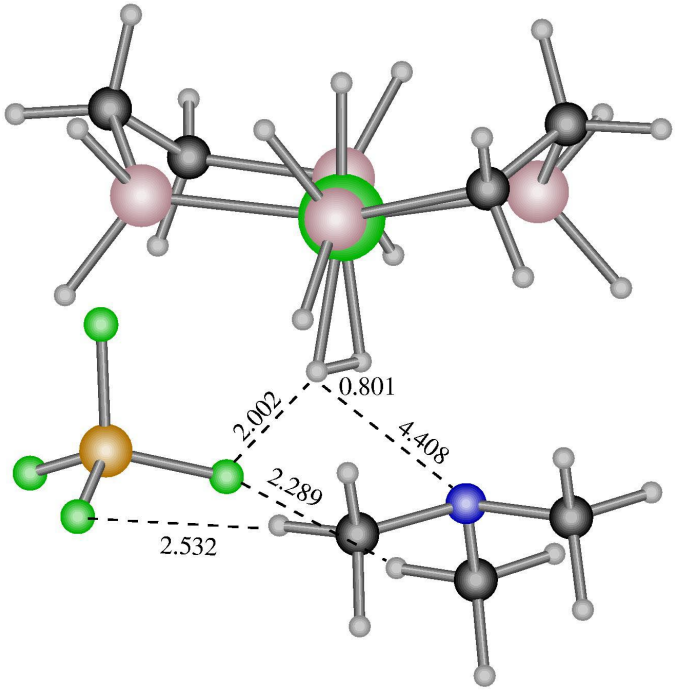
15	-3.006738	1.709160	-1.494124
1	-1.769413	2.071332	-2.092110
1	-3.814043	1.653198	-2.664203
15	-3.172561	1.703052	1.556671
1	-4.346949	1.840817	2.349193
1	-2.219754	1.800470	2.608828
6	-4.028991	-3.136668	-0.801936
1	-3.118063	-3.697483	-0.568543
1	-4.620374	-3.724275	-1.510800
6	-4.820146	-2.836968	0.489657
1	-4.937467	-3.734985	1.104377
1	-5.820909	-2.457595	0.251048
6	-3.013534	3.383348	0.734929
1	-3.510512	4.159230	1.325281
1	-1.940302	3.603640	0.706795
6	-3.569134	3.313541	-0.703234
1	-4.665312	3.300229	-0.701576
1	-3.236512	4.171698	-1.295550
1	-1.637124	-0.600917	0.388793
5	2.557342	-0.076895	0.008585
6	1.734199	1.322849	-0.332960
6	1.330994	2.227077	0.680317
6	0.677465	3.435816	0.397287
6	0.376351	3.784767	-0.927453
6	0.717107	2.891057	-1.953234
6	1.370471	1.686628	-1.653320
1	1.585756	2.001053	1.711665
1	0.448907	4.127442	1.206892
1	-0.080639	4.744480	-1.158029
1	0.512014	3.150667	-2.990280
1	1.654342	1.030155	-2.470461
6	3.575985	-0.510996	-1.221481
6	4.260572	0.451078	-2.001465
6	5.213734	0.099436	-2.965209
6	5.530449	-1.245721	-3.186307
6	4.888980	-2.224773	-2.419424
6	3.937857	-1.858161	-1.458892
1	4.050800	1.505238	-1.843178
1	5.713800	0.876674	-3.538860
1	6.269279	-1.524246	-3.933063
1	5.133807	-3.274804	-2.563774
1	3.472329	-2.642438	-0.868399
6	1.393804	-1.225583	0.284189
6	0.847466	-1.450745	1.572382
6	-0.111492	-2.441487	1.823760
6	-0.581030	-3.251428	0.778948
6	-0.097393	-3.027024	-0.518460
6	0.857426	-2.027033	-0.753607
1	1.221147	-0.863222	2.405540
1	-0.459175	-2.610134	2.841389
1	-1.267202	-4.071233	0.982612
1	-0.425867	-3.662401	-1.339735
1	1.238773	-1.896074	-1.761857
6	3.560074	0.102551	1.313632
6	3.927043	-0.992085	2.131778
6	4.865911	-0.878945	3.164655

6	5.489450	0.347757	3.419570
6	5.166598	1.448476	2.617969
6	4.225311	1.320459	1.588843
1	3.475117	-1.963055	1.948464
1	5.115465	-1.750575	3.765751
1	6.218953	0.441334	4.219683
1	5.652365	2.406534	2.789476
1	4.009374	2.190294	0.974854

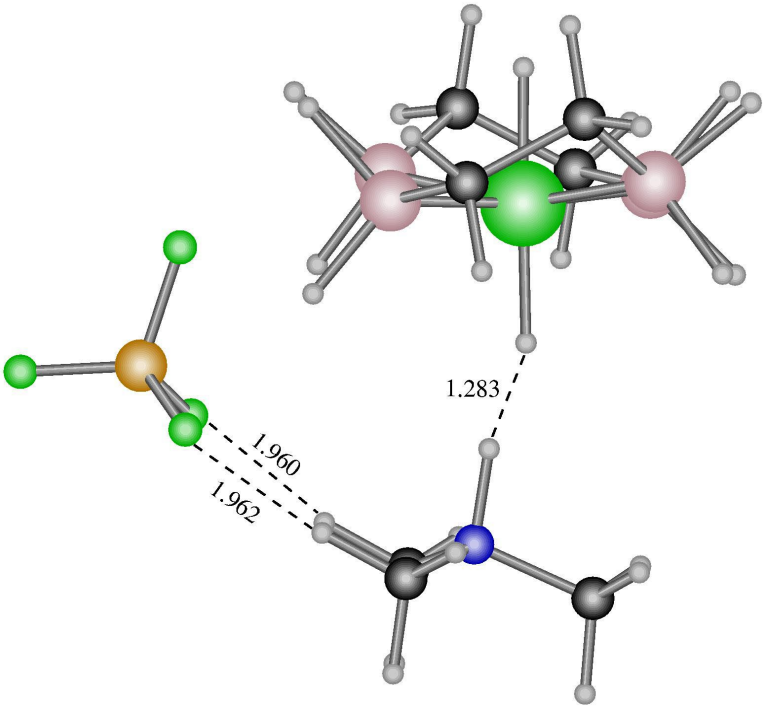
Optimized structure of (1b, BPh_4^-) ion pair



Optimized structures of complexes 5 and 6



5



6