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Supporting Information

Shape and Spin State in Four Coordinate Transition-Metal Complexes: The Case of the d^6 Configuration

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Supporting Information

Table S1. B3LYP-calculated energies for the different spin states of the compounds studied in their optimized geometries.

S	Total Energy (a.u.)	Rel. Energy (kcal·mol^{-1})	S(T_d)	S(D4h)
$[FeMe_4]^{2-}$				
2	- 1423.268815	0.0	0.07	31.86
1	- 1423.254410	9.0	33.34	0.01
0	- 1423.196027	45.7	12.02	8.42
$[FeCl_4]^{2-}$				
2	- 3104.931412	0.0	0.10	31.88
1	- 3104.882727	30.6	0.16	29.72
0	- 3104.797517	84.0	1.52	28.44
$[NiBr(norbornyl)_3]$(experimental structure)				
2	- 4902.462120	80.4	2.40	31.16
1	- 4902.533628	35.6	2.40	31.16
0	- 4902.590298	0.0	2.40	31.16
$[NiBrMe_3]$				
2	- 4202.062634	59.0	0.34	33.06
1	- 4202.119737	23.1	2.81	25.10
0	- 4202.156586	0.0	4.96	32.54
$[Fe(2,6\text{-xylyl})_2(PH_3)_2]$				
2	- 2570.724332	0.0	26.62	3.19
1	- 2570.722589	1.1	33.11	0.40

Table S2. Atomic coordinates for the optimized geometries of the dtudied compounds.

$[FeMe_4]^{2-}$(S = 2)

Fe	0.000000	0.000000	0.000000
C	-1.815587	0.787037	1.074661
C	1.709307	-0.282608	1.438032
C	-0.405716	-2.015740	-0.917848
C	0.506112	1.508930	-1.592471
H	-1.654865	1.762681	1.567532
H	-2.702268	0.911185	0.427403
H	-2.111947	0.083244	1.872537
H	1.946352	0.676272	1.932081
H	1.494425	-1.002540	2.248045
H	2.645843	-0.624690	0.962198
H	-0.694036	-2.791118	-0.185608
H	-1.244256	-1.938817	-1.632468
H	0.446718	-2.430012	-1.485683
H	0.746865	2.513315	-1.200368
H	1.396205	1.175414	-2.154838
H	-0.295061	1.653438	-2.339359

$[FeMe_4]^{2-}$(S = 1)

Fe	0.000000	0.000000	0.000000
C	-0.989196	0.471405	1.806791
C	1.227375	-1.412694	0.981621
C	0.989253	-0.471301	-1.806784
C	-1.227400	1.412688	-0.981617
H	-0.444032	1.360146	2.181143
H	-2.043861	0.780647	1.697019
H	-0.942049	-0.290011	2.604296
H	2.138734	-0.837607	1.238464
H	0.833854	-1.823898	1.926854
H	1.562779	-2.260101	0.357558
H	2.043884	-0.780653	-1.697000
H	0.444017	-1.359950	-2.181253
H	0.942210	0.290200	-2.604211
H	-1.562849	2.260056	-0.357525
H	-0.833865	1.823952	-1.926818
H	-2.138735	0.837590	-1.238521

$[FeMe_4]^{2-}$(S = 0)

Fe	0.000329	0.019483	0.336260
C	-2.112530	0.033168	0.562314
C	2.113571	0.032995	0.558812
C	-0.000490	-1.841850	-0.442959
C	-0.000527	1.776355	-0.657315
H	-2.519834	0.948760	1.041869
H	-2.588185	-0.027930	-0.436922
H	-2.521583	-0.815853	1.150557
H	2.521731	0.948691	1.037441
H	2.523533	-0.815887	1.146631
H	2.587622	-0.028422	-0.441169
H	0.000406	-2.454075	0.490362
H	-0.895669	-2.150487	-1.011447
H	0.893548	-2.150564	-1.013205
H	0.000203	2.494376	0.197304
H	0.893579	2.015751	-1.259954
H	-0.895703	2.015689	-1.258380

$[FeCl_4]^{2-}$(S = 2)

Fe	0.000000	0.000000	0.000000
Cl	-1.929798	0.448225	1.385206
Cl	1.930216	0.426069	1.391498
Cl	-0.008282	-2.281769	-0.801393
Cl	0.007552	1.396733	-1.973105

$[FeCl_4]^{2-}$(S = 1)

Fe	0.000000	0.000000	0.000000
Cl	-1.286713	0.900018	1.797120
Cl	2.290159	-0.070717	0.730383
Cl	-0.596792	-2.204948	-0.692959
Cl	-0.307724	1.445048	-1.897605

$[FeCl_4]^{2-}$(S = 0)

Fe	0.000000	0.000000	0.000000
Cl	-1.728038	0.000095	1.575540
Cl	1.728249	-0.000105	1.575256
Cl	0.000063	-1.728202	-1.575332
Cl	-0.000283	1.728210	-1.575356

$[Fe(2,6\text{-xylyl})_2(PH_3)_2]$ (S = 1)

Fe	0.006962	-0.037181	-0.004852
C	-1.532377	1.327233	0.091739
C	1.559602	-1.363082	-0.095790
C	-2.879929	0.906704	0.109157
C	2.901530	-0.928370	-0.106120
C	-3.921472	1.832517	0.212048
C	3.953206	-1.844579	-0.194012
C	-3.656482	3.193302	0.289655
C	3.703085	-3.208537	-0.266229
C	-2.338322	3.628771	0.262981
C	2.389023	-3.656860	-0.249394
C	-1.285509	2.715741	0.161473
C	1.326801	-2.753081	-0.162568
C	-3.223923	-0.561912	-0.010975
C	3.226837	0.545419	-0.002017
C	-0.086267	-3.292128	-0.123818
C	0.130261	3.246400	0.104124
H	-4.949240	1.483698	0.234107
H	4.977659	-1.485614	-0.207452
H	-2.123027	4.690904	0.325120
H	2.184787	-4.721530	-0.306048
H	-3.160203	-0.910033	-1.046939
H	3.031991	0.933492	1.003282
H	-4.238950	-0.770283	0.330778
H	4.276282	0.746269	-0.222400
H	-2.547659	-1.190534	0.574487
H	2.628960	1.145281	-0.694411
H	-0.122271	-4.355744	-0.364184
H	0.189714	4.278651	0.452445
H	-0.739890	-2.777303	-0.834511
H	0.815682	2.656105	0.717558
H	-0.539645	-3.174283	0.866124
H	0.528692	3.232596	-0.915303
P	-0.111258	0.122417	-2.304997
P	-0.015328	-0.080441	2.306027
H	-4.468006	3.906071	0.375774
H	4.522625	-3.913596	-0.338931

H	-1.373651	-0.142477	-2.927944
H	0.124575	1.408178	-2.890530
H	-1.251325	-0.395419	2.957997
H	0.846774	-0.931732	3.072970
H	0.717759	-0.654890	-3.179627
H	0.252727	1.150360	2.988103

$[Fe(2,6\text{-xylyl})_2(PH_3)_2]$ (S = 2)

Fe	-0.093671	-0.133343	-0.011768
C	-1.535792	1.375898	0.094027
C	1.609634	-1.334018	-0.098065
C	-2.898846	1.007852	0.113884
C	2.930245	-0.834819	-0.102478
C	-3.907381	1.971700	0.202283
C	4.024784	-1.699804	-0.178604
C	-3.587005	3.320613	0.262535
C	3.837476	-3.074391	-0.246169
C	-2.252855	3.708351	0.236838
C	2.548253	-3.589636	-0.237362
C	-1.235623	2.755341	0.151980
C	1.445220	-2.735606	-0.160530
C	-3.300296	-0.447840	0.009477
C	3.187578	0.652309	-0.008283
C	0.060381	-3.345155	-0.120630
C	0.199497	3.229214	0.108563
H	-4.948210	1.665063	0.226008
H	5.031958	-1.296223	-0.189120
H	-2.001840	4.762810	0.287558
H	2.398985	-4.663173	-0.292683
H	-3.323838	-0.785399	-1.031317
H	2.965875	1.034587	0.992542
H	-4.292717	-0.629344	0.425235
H	4.228421	0.898675	-0.222600
H	-2.602874	-1.101093	0.543515
H	2.565814	1.214976	-0.708844
H	0.059032	-4.378197	-0.471745
H	0.284853	4.288755	0.354351
H	-0.644831	-2.790802	-0.747443
H	0.828237	2.677481	0.810857
H	-0.347793	-3.352292	0.894766
H	0.637472	3.094024	-0.884856
P	-0.366551	-0.155791	-2.843182
P	-0.257008	-0.416577	2.827468
H	-4.370327	4.065784	0.335742
H	4.690734	-3.739217	-0.311372
H	-1.604621	0.060678	-3.542548
H	0.332622	0.964164	-3.409528
H	-1.478477	-0.255503	3.569667
H	0.286295	-1.486534	3.621718
H	0.165824	-1.146865	-3.739129
H	0.462167	0.643847	3.476143

Table S3. Structurally characterized four-coordinate d^6 complexes that fall along the tetrahedron-square interconversion path (within a 15%) for which structural magnetic data have been reported.

Metal	$\varphi_Q(T_d \rightarrow D_{4h})$	μ_{eff}	S	Refcode	Ref.
Fe	9.1	5.10	2	IMSPFE10	[1]
Fe	9.9	4.50	2	GIJGIP	[2]
Fe	14.8	5.10	2	PTHPFE10	[3]
Fe	16.0	4.60	2	TATWAM	[4]
Fe	18.0	4.60	2	TATWEQ	[4]
Fe	19.0	5.00	2	YEWSOI	[5]
Fe	22.2	4.70	2	FIHRET	[6]
Fe	28.7	5.30	2	SOQLUF	[7]
Fe	31.2	4.40	2		[8]
Fe	48.7	5.19	2	CIWQUU	[9]
Co	72.9	3.60	1	NINBUH	[10]
Fe	96.5	2.90	1		[8]
Fe	97.6	4.40	1	TPORFE	[11]
Co	98.5	3.10	1	NINBOB	[10]
Fe	99.8	3.60	1	QATQUX	[12]
Fe	100.3	2.70	1		[8]
Fe	100.0	3.50	1	BUYKUB10	[13]
Fe	100.0	4.60	1	DEDWUE	[13]
Fe	100.4	2.80	1	OAZNFE	[14]

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