Pentacyanoiron(II) as an Electron Donor Group for Nonlinear Optics: Medium-Responsive Properties and Comparisons with Related Pentaammineruthenium(II) Complexes

Benjamin J. Coe, Josephine L. Harries, Madeleine Helliwell, Lathe A. Jones, Inge Asselberghs, Koen Clays, Bruce S. Brunschwig, James A. Harris, Javier Garín, and Jesús Orduna

Supporting Information

Table S1. Crystallographic Data and Refinement Details for Salt **1**•$9H_2O$

Formula	$C_{16}H_{29}FeN_7Na_2O_9$
M	565.29
Crystal system	Triclinic
Space group	$P\,\overline{1}$
a/Å	8.5761(12)
b/Å	8.9830(12)
c/Å	17.030(2)
α/°	100.830(2)
β/°	95.083(2)
γ/°	99.411(2)
U/Å^3	1261.6(3)
Z	2
T/K	100(2)
μ/mm^{-1}	0.690
Reflections collected	10089
Independent reflections (R_{int})	5084 (0.0248)
Goodness-of-fit on F^2	1.059
Final $R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0292, 0.0761
(all data)	0.0320, 0.0812

[a] The structure was refined on F_o^2 using all data; the value of $R1$ is given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$.

Table S2. Selected Interatomic Distances (Å) and Angles (°) for Salt **1**•9H_2O

Fe(1)–C(16)	1.8927(16)	N(5)–C(14)	1.165(2)
Fe(1)–C(15)	1.9179(16)	N(6)–C(15)	1.160(2)
Fe(1)–C(14)	1.9209(16)	N(7)–C(16)	1.166(2)
Fe(1)–C(12)	1.9211(16)	C(1)–C(2)	1.380(2)
Fe(1)–C(13)	1.9216(16)	C(2)–C(3)	1.397(2)
Fe(1)–N(1)	2.0257(13)	C(3)–C(4)	1.401(2)
N(1)–C(5)	1.348(2)	C(3)–C(6)	1.480(2)
N(1)–C(1)	1.350(2)	C(4)–C(5)	1.384(2)
N(2)–C(9)	1.347(2)	C(6)–C(10)	1.397(2)
N(2)–C(8)	1.348(2)	C(6)–C(7)	1.402(2)
N(2)–C(11)	1.4829(19)	C(7)–C(8)	1.377(2)
N(3)–C(12)	1.169(2)	C(9)–C(10)	1.372(2)
N(4)–C(13)	1.162(2)		
C(16)–Fe(1)–C(15)	89.58(7)	C(14)–Fe(1)–C(13)	91.64(6)
C(16)–Fe(1)–C(14)	86.74(6)	C(12)–Fe(1)–C(13)	89.63(6)
C(15)–Fe(1)–C(14)	90.01(7)	C(16)–Fe(1)–N(1)	175.86(6)
C(16)–Fe(1)–C(12)	92.04(7)	C(15)–Fe(1)–N(1)	89.38(6)
C(15)–Fe(1)–C(12)	88.72(7)	C(14)–Fe(1)–N(1)	89.25(6)
C(14)–Fe(1)–C(12)	178.24(6)	C(12)–Fe(1)–N(1)	91.94(6)
C(16)–Fe(1)–C(13)	89.99(6)	C(13)–Fe(1)–N(1)	91.18(6)
C(15)–Fe(1)–C(13)	178.27(6)		

Table S3. Results of Theoretical Calculations on the Complex Anions in **1** and **5**

parent salt	model chemistry	E_{max} (eV)	μ_{12} (D)	f_{os}	$\Delta\mu_{12}$[a] (D)	$\Delta\mu_{12}$[b] (D)	β_0[c] (10^{-30} esu)	β_0[d] (10^{-30} esu)
1	B3P86/6-311+G*[e]	1.75	10.2	0.69	1.2	2.1	46	84
	PCM-B3P86/6-311+G*[e]	1.82	9.7	0.65	16.7	8.5	553	284
	PCM-B3P86/6-311+G*[f]	1.82	6.7	0.31	24.7	17.0	391	269
5	B3P86/6-311+G*[e]	1.64	12.3	0.94	1.4	2.3	93	155
	PCM-B3P86/6-311+G*[e]	1.65	11.7	0.86	19.5	6.3	1155	371
	PCM-B3P86/6-311+G*[f]	1.71	7.4	0.35	28.3	23.2	613	503

[a] Calculated by using the RhoCI density. [b] Calculated by using the FF approach. [c] Calculated from eq 5 by using the RhoCI $\Delta\mu_{12}$ value. [d] Calculated from eq 5 by using the FF $\Delta\mu_{12}$ value. [e] Geometry optimized in vacuum by using B3P86/6-31G*. [f] Geometry optimized in water by using PCM-B3P86/6-31G*.

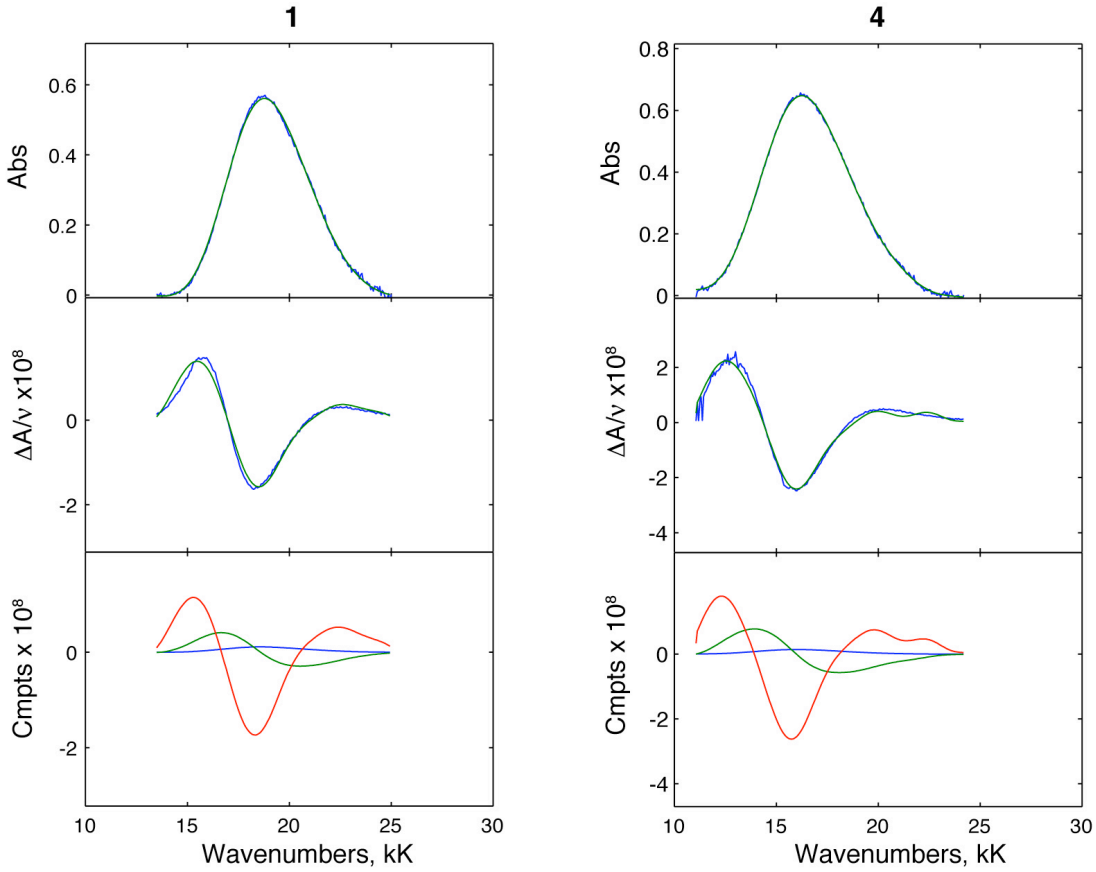

Figure S1. MLCT absorption and electroabsorption spectra and calculated fits for the salts **1** and **4** in external electric fields of 2.79 and 2.80 × 10^7 V m^{-1}, respectively. Top panel: absorption spectrum; middle panel: electroabsorption spectrum, experimental (blue) and fits (green) according to the Liptay equation; bottom panel: contribution of 0th (blue), 1st (green) and 2nd (red) derivatives of the absorption spectrum to the calculated fits.

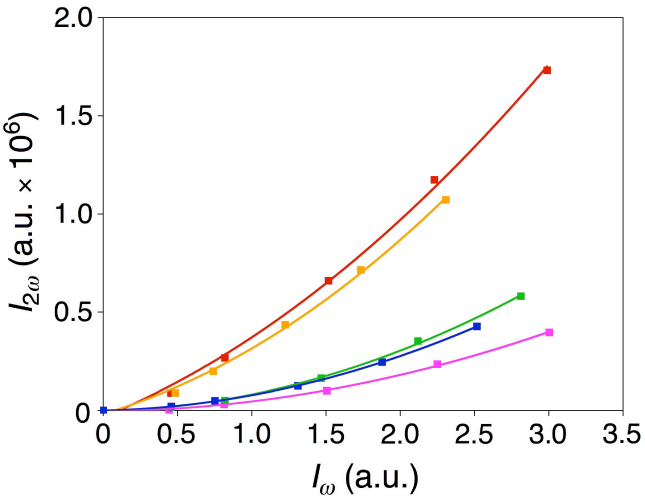

Figure S2. Quadratic fits to HRS data recorded using a 800 nm laser for salt **4** and its protonated form **4**H_2; solvent (purple), untreated sample 1 (red), once-acidified sample 2 (green), neutralized sample 3 (gold), twice-acidified sample 4 (blue).

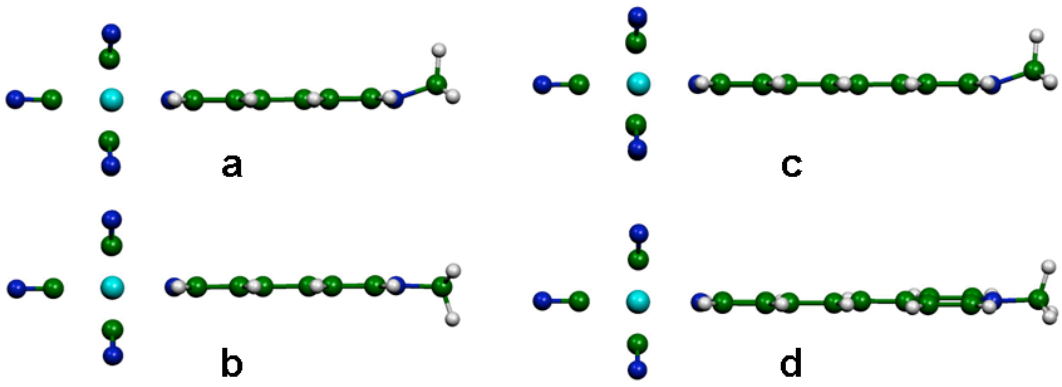

Figure S3. Side views of the optimized geometries of the complex anion in **1** in vacuum (a) and water (b), and of the complex anion in **5** in vacuum (c) and water (d).

Cartesian coordinates of optimized geometries used in theoretical calculations (B3P86/6-31G*)

Complex in 1 in gas phase (vacuum).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.524935	1.185260	-0.082555
2	6	0	-4.173145	1.203675	-0.079884
3	6	0	-3.376061	0.000004	-0.074861
4	6	0	-4.173104	-1.203697	-0.079323
5	6	0	-5.524895	-1.185330	-0.081990
6	1	0	-6.121144	2.092490	-0.089548
7	1	0	-3.689354	2.173637	-0.090892
8	1	0	-3.689280	-2.173647	-0.089866
9	1	0	-6.121071	-2.092584	-0.088531
10	6	0	-1.968520	0.000027	-0.062724
11	6	0	-1.185757	-1.195774	-0.054717
12	6	0	-1.185782	1.195849	-0.055285
13	6	0	0.178728	-1.157881	-0.035613
14	1	0	-1.657297	-2.173183	-0.061422
15	6	0	0.178706	1.158002	-0.036171
16	1	0	-1.657346	2.173243	-0.062531
17	1	0	0.768995	-2.064962	-0.028169
18	1	0	0.768927	2.065120	-0.029680
19	6	0	-7.625255	0.000037	0.322792
20	1	0	-8.138191	-0.886373	-0.065236
21	1	0	-8.138268	0.886144	-0.065832
22	1	0	-7.722663	0.000403	1.422281
23	26	0	2.789018	0.000014	0.015428
24	6	0	2.892897	1.407079	-1.306084
25	7	0	2.850489	2.267694	-2.099631
26	6	0	2.893640	-1.403379	-1.309816
27	7	0	2.851760	-2.261728	-2.105839
28	6	0	2.835262	-1.407942	1.339652
29	7	0	2.758620	-2.268673	2.130483
30	6	0	4.703282	-0.000138	0.059783
31	7	0	5.873837	-0.000380	0.086331
32	6	0	2.836206	1.404283	1.343411
33	7	0	2.760252	2.262916	2.136581
34	7	0	0.904281	0.000069	-0.022885
35	7	0	-6.257150	-0.000058	-0.123809

Complex in 1 in water (PCM).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.561300	-1.170589	-0.009508
2	6	0	4.186867	-1.194756	-0.010068
3	6	0	3.443442	0.000710	-0.008325
4	6	0	4.188708	1.195165	-0.006933
5	6	0	5.563097	1.168835	-0.006540
6	1	0	6.158002	-2.081047	-0.010500
7	1	0	3.710345	-2.171287	-0.015122
8	1	0	3.713982	2.172496	-0.009057
9	1	0	6.161204	2.078371	-0.005052
10	6	0	1.976381	0.001086	-0.009537
11	6	0	1.230764	1.189921	-0.010233
12	6	0	1.231263	-1.187972	-0.008299
13	6	0	-0.150787	1.145796	-0.008434
14	1	0	1.701868	2.169681	-0.011867
15	6	0	-0.150353	-1.144419	-0.006449
16	1	0	1.703104	-2.167465	-0.007996
17	1	0	-0.726045	2.064115	-0.008742
18	1	0	-0.725308	-2.062951	-0.005124
19	6	0	7.706111	-0.002583	0.035691
20	1	0	8.076992	0.889355	-0.470106
21	1	0	8.075719	-0.893404	-0.473013
22	1	0	8.037670	-0.004481	1.077276
23	26	0	-2.847779	0.000997	0.001316
24	6	0	-2.863585	-1.355658	-1.346628
25	7	0	-2.859581	-2.191538	-2.174965
26	6	0	-2.862401	1.352650	-1.352081
27	7	0	-2.853908	2.185616	-2.183372
28	6	0	-2.851442	1.357014	1.350569
29	7	0	-2.839568	2.192316	2.179435
30	6	0	-4.738264	-0.001511	0.010975
31	7	0	-5.915418	-0.005194	0.020589
32	6	0	-2.851837	-1.351726	1.354274
33	7	0	-2.841119	-2.184842	2.185389
34	7	0	-0.865958	0.000601	-0.005927
35	7	0	6.238287	-0.001399	-0.007683

Complex in 5 in gas phase (vacuum).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.866024	-1.124816	-0.086298
2	6	0	5.519801	-1.029341	-0.080726
3	6	0	5.738189	1.377421	-0.058387
4	6	0	7.081939	1.240165	-0.064108
5	1	0	7.381464	-2.080590	-0.099121
6	1	0	4.944977	-1.948908	-0.100470
7	1	0	5.322510	2.381673	-0.056398
8	1	0	7.759920	2.087824	-0.062673
9	6	0	1.088298	-0.394998	-0.044108
10	6	0	0.430690	0.871733	-0.038073
11	6	0	0.203510	-1.513579	-0.036231
12	6	0	-0.932399	0.957841	-0.023335
13	1	0	1.002023	1.794533	-0.044373
14	6	0	-1.152692	-1.352744	-0.021080
15	1	0	0.613463	-2.520632	-0.040624
16	1	0	-1.439065	1.914281	-0.018433
17	1	0	-1.827161	-2.199220	-0.014749
18	6	0	9.063190	-0.138016	0.330021
19	1	0	9.660700	0.689846	-0.066558
20	1	0	9.488562	-1.073558	-0.047650
21	1	0	9.158911	-0.135174	1.429444
22	26	0	-3.645037	0.053716	0.015511
23	6	0	-3.610984	1.463480	-1.302799
24	7	0	-3.490106	2.315377	-2.097163
25	6	0	-3.579832	1.460030	1.338695
26	7	0	-3.441477	2.310781	2.131413
27	6	0	-5.547978	0.237212	0.020463
28	7	0	-6.713232	0.348987	0.026352
29	6	0	-3.880663	-1.345119	-1.293090
30	7	0	-3.922770	-2.209827	-2.081705
31	6	0	-3.848770	-1.328701	1.348794
32	7	0	-3.872362	-2.183029	2.149379
33	7	0	-1.759814	-0.129630	-0.012640
34	7	0	7.701714	-0.010515	-0.120993
35	6	0	3.459361	0.416901	-0.058181
36	6	0	2.477993	-0.584939	-0.054628
37	1	0	3.114773	1.450597	-0.052602
38	1	0	2.806756	-1.624151	-0.056351
39	6	0	4.835901	0.249446	-0.066137

Complex in 5 in water (PCM).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.886922	-1.120643	-0.045698
2	6	0	5.518881	-1.015430	-0.052519
3	6	0	5.756155	1.369584	0.028111
4	6	0	7.120641	1.211605	0.034386
5	1	0	7.396035	-2.082199	-0.076349
6	1	0	4.942073	-1.936334	-0.095171
7	1	0	5.348507	2.378729	0.054518
8	1	0	7.807370	2.055605	0.067863
9	6	0	1.101748	-0.343225	-0.020408
10	6	0	0.457581	0.905225	-0.059001
11	6	0	0.265525	-1.469394	0.020362
12	6	0	-0.921935	0.967885	-0.053003
13	1	0	1.019132	1.836327	-0.096832
14	6	0	-1.109541	-1.317804	0.026435
15	1	0	0.690762	-2.471740	0.049919
16	1	0	-1.427747	1.925970	-0.083265
17	1	0	-1.759836	-2.184235	0.059570
18	6	0	9.134638	-0.169762	0.055313
19	1	0	9.600050	0.691036	-0.426072
20	1	0	9.420833	-1.081241	-0.470540
21	1	0	9.454362	-0.228442	1.099206
22	26	0	-3.715588	0.047271	0.005400
23	6	0	-3.625265	1.324379	-1.415601
24	7	0	-3.561857	2.107540	-2.292102
25	6	0	-3.595395	1.463455	1.285496
26	7	0	-3.514732	2.336220	2.071254
27	6	0	-5.595459	0.204282	0.020021
28	7	0	-6.769153	0.301412	0.028689
29	6	0	-3.849735	-1.369078	-1.272214
30	7	0	-3.922260	-2.246507	-2.053519
31	6	0	-3.812587	-1.232264	1.423337
32	7	0	-3.859488	-2.021688	2.295169
33	7	0	-1.725662	-0.118648	-0.008995
34	7	0	7.676381	-0.020843	-0.002757
35	6	0	3.468319	0.460166	-0.017791
36	6	0	2.539860	-0.525580	-0.020434
37	1	0	3.155740	1.504979	-0.010693
38	1	0	2.863073	-1.568734	-0.016151
39	6	0	4.898373	0.251404	-0.013553

Complex in 1H in water (PCM).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.641733	-1.165131	-0.036847
2	6	0	4.266631	-1.192137	-0.036211
3	6	0	3.525489	0.001605	-0.000211
4	6	0	4.262624	1.195172	0.038005
5	6	0	5.639878	1.172336	0.034462
6	1	0	6.242467	-2.073029	-0.063478
7	1	0	3.791264	-2.168824	-0.071513
8	1	0	3.785254	2.170920	0.072544
9	1	0	6.234862	2.083466	0.065635
10	6	0	2.050332	0.000449	-0.000823
11	6	0	1.309825	1.187357	-0.037053
12	6	0	1.309518	-1.186263	0.035156
13	6	0	-0.074956	1.142374	-0.034874
14	1	0	1.780924	2.166597	-0.072124
15	6	0	-0.075361	-1.140932	0.033161
16	1	0	1.779848	-2.165810	0.070967
17	1	0	-0.649936	2.060327	-0.063675
18	1	0	-0.650462	-2.058748	0.061722
19	6	0	7.783105	-0.010594	0.005991
20	1	0	8.149381	1.008801	-0.111963
21	1	0	8.138705	-0.628985	-0.820292
22	1	0	8.131117	-0.422181	0.956359
23	26	0	-2.862007	0.001948	-0.000746
24	6	0	-2.813752	-0.092545	-1.914402
25	7	0	-2.777669	-0.149238	-3.087316
26	6	0	-2.911274	1.912606	-0.089417
27	7	0	-2.979156	3.084897	-0.143523
28	6	0	-2.810918	0.083106	1.912970
29	7	0	-2.780221	0.132564	3.086408
30	6	0	-4.646898	0.003623	0.001446
31	7	0	-5.822887	-0.001025	0.008694
32	6	0	-2.915229	-1.909174	0.087894
33	7	0	-2.986419	-3.081285	0.140783
34	7	0	-0.786020	0.000805	-0.001016
35	7	0	6.314097	0.005496	-0.004051
36	1	0	-6.837792	0.020218	-0.000125

Complex in $1H_2$ in water (PCM).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.608553	1.115697	0.359061
2	6	0	-4.231095	1.139630	0.375715
3	6	0	-3.502866	0.001662	0.002996
4	6	0	-4.228344	-1.135675	-0.377786
5	6	0	-5.605610	-1.109018	-0.380092
6	1	0	-6.210653	1.976141	0.646810
7	1	0	-3.737296	2.053013	0.701620
8	1	0	-3.732007	-2.047655	-0.703661
9	1	0	-6.205479	-1.967680	-0.677847
10	6	0	-2.029911	0.001849	0.006384
11	6	0	-1.303304	-1.155033	0.301395
12	6	0	-1.301849	1.157596	-0.289209
13	6	0	0.081629	-1.110629	0.291138
14	1	0	-1.795613	-2.089403	0.564570
15	6	0	0.083301	1.112356	-0.283518
16	1	0	-1.793926	2.091485	-0.554643
17	1	0	0.655526	-2.003670	0.514082
18	1	0	0.661554	1.998128	-0.519638
19	6	0	-7.745775	-0.009021	0.013325
20	1	0	-8.109478	-0.682962	-0.762830
21	1	0	-8.113215	1.000316	-0.172824
22	1	0	-8.081245	-0.353960	0.994650
23	26	0	2.825777	0.001939	-0.006247
24	6	0	2.848567	-0.822251	1.630324
25	7	0	2.865205	-1.341046	2.679695
26	6	0	4.627349	0.024634	-0.070611
27	7	0	5.797180	0.039151	-0.123380
28	6	0	2.817529	1.716141	0.854854
29	7	0	2.805796	2.762207	1.385620
30	6	0	2.802326	-1.689612	-0.909487
31	7	0	2.781380	-2.723601	-1.463158
32	6	0	2.774574	0.876431	-1.720564
33	7	0	2.733158	1.404274	-2.766813
34	7	0	0.782159	0.000129	0.002704
35	7	0	-6.275840	0.004297	-0.016068
36	1	0	6.813661	0.060468	-0.175620
37	1	0	2.886909	-1.791062	3.593996

Complex in $1H_5$ in water (PCM).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.657041	1.136296	0.285397
2	6	0	-4.278753	1.162427	0.298659
3	6	0	-3.554929	0.001474	0.001688
4	6	0	-4.275599	-1.159835	-0.301934
5	6	0	-5.653834	-1.133105	-0.305396
6	1	0	-6.259590	2.013793	0.515683
7	1	0	-3.783814	2.095647	0.561738
8	1	0	-3.777899	-2.091492	-0.565292
9	1	0	-6.253868	-2.009935	-0.544550
10	6	0	-2.079848	0.002219	0.004326
11	6	0	-1.354542	-1.116927	0.418642
12	6	0	-1.353965	1.121436	-0.408726
13	6	0	0.029355	-1.076023	0.408079
14	1	0	-1.845997	-2.020415	0.776004
15	6	0	0.029925	1.079801	-0.397789
16	1	0	-1.844848	2.025030	-0.766563
17	1	0	0.590934	-1.944946	0.738927
18	1	0	0.591934	1.948347	-0.728970
19	6	0	-7.793106	-0.008646	0.016010
20	1	0	-8.156948	-0.738162	-0.707893
21	1	0	-8.159796	0.984621	-0.243676
22	1	0	-8.126477	-0.280119	1.020828
23	26	0	2.763211	-0.000135	0.000471
24	6	0	2.771875	-0.757291	1.715537
25	7	0	2.781476	-1.210771	2.782435
26	6	0	4.612778	-0.002325	-0.005740
27	7	0	5.772598	-0.005607	-0.012323
28	6	0	2.768540	1.698043	0.794686
29	7	0	2.770438	2.742117	1.298596
30	6	0	2.761856	-1.698405	-0.793562
31	7	0	2.761574	-2.742317	-1.297802
32	6	0	2.764432	0.757435	-1.714505
33	7	0	2.769502	1.211070	-2.781366
34	7	0	0.728737	0.001536	0.004612
35	7	0	-6.322322	0.001995	-0.014951
36	1	0	2.781020	1.613692	-3.727595
37	1	0	6.799747	-0.005055	-0.016762
38	1	0	2.797128	-1.612816	3.728841
39	1	0	2.768172	-3.668991	-1.744859
40	1	0	2.779920	3.668709	1.745253

Complete References 3d, 3j, 24 and 38b:

(3) (d) Malaun, M.; Kowallick, R.; McDonagh, A. M.; Marcaccio, M.; Paul, R. L.; Asselberghs, I.; Clays, K.; Persoons, A.; Bildstein, B.; Fiorini, C.; Nunzi, J.-M.; Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2001**, 3025–3038. (j) Sporer, C.; Ratera, I.; Ruiz-Molina, D.; Zhao, Y.-X.; Vidal-Gancedo, J.; Wurst, K.; Jaitner, P.; Clays, K.; Persoons, A.; Rovira, C.; Veciana, J. *Angew. Chem. Int. Ed.* **2004**, *43*, 5266–5268.

(24) Gaussian 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, V. G.; Montgomery, J. A., Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Pittsburgh PA, 2003.

(38) (b) Hurst, S. K.; Cifuentes, M. P.; Morrall, J. P. L.; Lucas, N. T.; Whittall, I. R.; Humphrey, M. G.; Asselberghs, I.; Persoons, A.; Samoc, M.; Luther-Davies, B.; Willis, A. C. *Organometallics* **2001**, *20*, 4664–4675.