Supporting Information for: Scalar relativistic computations and localized orbital analysis of electron paramagnetic resonance hyperfine coupling and paramagnetic NMR chemical shifts

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January 2, 2012

Table S1: HFCC calculated with NWChem using the non-hybrid PBE functional, the global hybrid PBE0, and the range-separated CAM-B3LYP hybrid (CAM). Unscaled scalar ZORA, Gaussian nucleus model. pcJ4 basis for all atoms with the exception of Hg, Ti and Np where we used an uncontracted ANO basis set, and F in NpF_6 (IGLO-III).

		PBE			PBE0			CAM			Exp
Molecule	Atom	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	
CH_2	C	211.1	-0.2728	210.8	225.4	-0.2691	225.2	219.0	-0.2792	218.7	
CH_2	H	-18.72	0.0080	-18.71	-24.62	0.0078	-24.61	-14.41	0.0081	-14.41	
CH_3	C	70.72	-0.2470	70.47	84.80	-0.2495	84.55	76.20	-0.2574	75.94	108[a]
CH_3	H	-64.43	0.0159	-64.42	-72.75	0.0151	-72.74	-65.76	0.0158	-65.74	-64.46[a]
CHO	C	379.0	-0.5175	378.5	387.6	-0.5369	387.1	390.1	-0.5676	389.5	365[b]
CHO	H	371.6	-0.0773	371.5	374.9	-0.0791	374.8	394.8	-0.0810	394.7	354[b]
CHO	O	-24.39	0.5841	-23.81	-34.21	0.5628	-33.64	-35.16	0.5710	-34.59	
HSiO	Si	-531.6	1.125	-530.5	-547.0	1.100	-545.9	-588.7	1.124	-587.6	-630[c]
HSiO	H	428.6	-0.0261	428.6	432.5	-0.0265	432.4	477.1	-0.0276	477.1	450[c]
HSiO	O	-6.759	0.2069	-6.552	-11.06	0.1569	-10.90	-11.09	0.1169	-10.97	
HSiS	Si	-496.4	1.923	-494.5	-507.5	1.991	-505.5	-522.5	2.162	-520.4	
HSiS	H	327.3	-0.0641	327.3	328.5	-0.0667	328.4	356.3	-0.0717	356.3	
HSiS	S	0.4332	-0.1961	0.2371	1.305	-0.0660	1.239	-1.515	0.2178	-1.297	
SiOH	O	-21.45	0.6916	-20.75	-21.25	0.6995	-20.55	-21.16	0.9825	-20.18	
SiOH	Si	33.66	7.003	40.66	19.44	7.388	26.83	12.84	10.36	23.20	
SiOH	H	54.39	-0.1406	54.25	51.57	-0.1371	51.44	52.53	-0.1834	52.35	
SiSH	S	24.15	-0.1319	24.02	20.00	-0.1238	19.88	21.28	-0.1427	21.14	
SiSH	Si	30.70	5.214	35.91	15.03	5.507	20.54	9.385	6.946	16.33	
SiSH	H	129.0	-0.0595	128.9	120.4	-0.0577	120.3	122.3	-0.0640	122.3	
HgH	Hg	6814	-199.1	6615	7247	-200.8	7047	7378	-205.4	7173	7002[d]
HgH	H	747.2	-1.863	745.4	728.3	-1.699	726.6	771.8	-1.723	770.0	710[d]
HgF	Hg	17752	-20.67	17732	19033	-33.86	18999	19917	-28.19	19889	22163[e]
HgF	F	238.8	-149.1	89.70	284.0	-107.8	176.2	270.3	-103.3	167.0	670[e]
TiF_3	Ti	-231.4	2.283	-229.1	-198.5	3.051	-195.4	-203.5	3.252	-200.2	184.8[f]
TiF_3	F	2.700	0.7282	3.428	-15.41	0.7867	-14.62	-10.22	0.9565	-9.264	-23.6[f]
NpF_6	Np	-495.1	-1632	-2127	-232.4	-2106	-2338	-239.6	-2105	-2345	-1994[g]
NpF_6	F	-26.20	-1.494	-27.69	-38.01	-14.88	-52.89	-38.01	-14.88	-52.89	-72.67[g]

[a] Reference 1
[b] Reference 2
[c] Reference 3. Sign was not reported and changed by us to match the sign of the calculated HFCC.
[d] Reference 4
[e] Reference 5
[f] Reference 6
[g] Reference 7

Table S2: HFCC calculated with NWChem using the non-hybrid PBE functional, the global hybrid PBE0, and the range-separated CAM-B3LYP hybrid (CAM). Unscaled scalar ZORA, point-size nucleus model. pcJ4 basis for all atoms with the exception of Hg, Ti and Np where we used an uncontracted ANO basis set, and F in NpF_6 (IGLO-III).

		PBE			PBE0			CAM			Exp
Molecule	Atom	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	
CH_2	C	211.1	-0.2728	210.8	225.4	-0.2691	225.2	219.0	-0.2792	218.7	
CH_2	H	-18.72	0.0080	-18.71	-24.62	0.0078	-24.61	-14.41	0.0081	-14.41	
CH_3	C	70.72	-0.2470	70.47	84.80	-0.2495	84.56	76.20	-0.2574	75.95	108[a]
CH_3	H	-64.43	0.0159	-64.42	-72.75	0.0151	-72.74	-65.76	0.0158	-65.74	-64.46[a]
CHO	C	379.0	-0.5175	378.5	387.7	-0.5369	387.1	390.1	-0.5676	389.5	365[b]
CHO	H	371.6	-0.0773	371.5	374.9	-0.0791	374.8	394.8	-0.0810	394.7	354[b]
CHO	O	-24.39	0.5841	-23.81	-34.21	0.5628	-33.65	-35.16	0.5710	-34.59	
HSiO	Si	-531.7	1.125	-530.6	-547.1	1.100	-546.0	-588.7	1.124	-587.6	-630[c]
HSiO	H	428.6	-0.0261	428.6	432.5	-0.0265	432.4	477.1	-0.0276	477.1	450[c]
HSiO	O	-6.759	0.2069	-6.552	-11.06	0.1569	-10.90	-11.09	0.1169	-10.97	
HSiS	Si	-496.5	1.923	-494.6	-507.5	1.991	-505.5	-522.6	2.162	-520.4	
HSiS	H	327.3	-0.0641	327.3	328.5	-0.0667	328.4	356.3	-0.0717	356.3	
HSiS	S	0.4333	-0.1961	0.2372	1.305	-0.0660	1.239	-1.515	0.2178	-1.297	
SiOH	O	-21.45	0.6916	-20.76	-21.25	0.6995	-20.55	-21.16	0.9825	-20.18	
SiOH	Si	33.66	7.003	40.66	19.44	7.388	26.83	12.84	10.36	23.20	
SiOH	H	54.39	-0.1406	54.25	51.57	-0.1371	51.44	52.53	-0.1834	52.35	
SiSH	S	24.16	-0.1319	24.02	20.01	-0.1238	19.88	21.28	-0.1427	21.14	
SiSH	Si	30.70	5.214	35.91	15.03	5.507	20.54	9.386	6.946	16.33	
SiSH	H	129.0	-0.0595	128.9	120.4	-0.0577	120.3	122.3	-0.0640	122.3	
HgH	Hg	7013	-199.2	6813	7458	-200.9	7258	7593	-205.4	7388	7002[d]
HgH	H	747.3	-1.863	745.4	728.4	-1.699	726.7	771.8	-1.723	770.1	710[d]
HgF	Hg	18272	-20.66	18251	19591	-33.86	19557	20501	-28.18	20473	22163[e]
HgF	F	238.8	-149.1	89.70	284.0	-107.8	176.2	270.3	-103.3	167.0	670[e]
TiF_3	Ti	-231.4	2.283	-229.1	-198.5	3.051	-195.5	-203.5	3.252	-200.2	184.8[f]
TiF_3	F	2.690	0.7282	3.419	-15.40	0.7867	-14.62	-10.22	0.9564	-9.264	-23.6[f]
NpF_6	Np	-513.5	-1632	-2146	-230.8	-2138	-2370	-239.6	-2105	-2345	-1994[g]
NpF_6	F	-26.20	-1.494	-27.69	-41.69	-19.94	-61.63	-38.01	-14.88	-52.89	-72.67[g]

[a] Reference 1
[b] Reference 2
[c] Reference 3. Sign was not reported and changed by us to match the sign of the calculated HFCC.
[d] Reference 4
[e] Reference 5
[f] Reference 6
[g] Reference 7

Table S3: HFCC calculated with NWChem using the non-hybrid PBE functional, the global hybrid PBE0, and the range-separated CAM-B3LYP hybrid (CAM). Scaled scalar ZORA, point-size nucleus model. pcJ4 basis for all atoms with the exception of Hg, Ti and Np where we used an uncontracted ANO basis set, and F in NpF_6 (IGLO-III).

		PBE			PBE0			CAM			Exp
Molecule	Atom	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	FC+SD	PSOSO	Total	
CH_2	C	211.2	-0.2728	210.9	225.5	-0.2691	225.3	219.1	-0.2792	218.8	
CH_2	H	-18.72	0.0080	-18.71	-24.62	0.0078	-24.61	-14.42	0.0081	-14.41	
CH_3	C	70.80	-0.2470	70.56	84.90	-0.2495	84.65	76.29	-0.2574	76.04	108[a]
CH_3	H	-64.43	0.0159	-64.42	-72.75	0.0151	-72.74	-65.76	0.0158	-65.74	-64.46[a]
CHO	C	379.1	-0.5174	378.5	387.7	-0.5369	387.1	390.1	-0.5676	389.5	365[b]
CHO	H	371.6	-0.0773	371.5	374.8	-0.0791	374.8	394.8	-0.0810	394.7	354[b]
CHO	O	-24.45	0.5841	-23.86	-34.28	0.5628	-33.71	-35.23	0.5710	-34.66	
HSiO	Si	-531.7	1.125	-530.6	-547.1	1.100	-546.0	-588.7	1.124	-587.6	-630[c]
HSiO	H	428.6	-0.0261	428.6	432.4	-0.0265	432.4	477.1	-0.0276	477.1	450[c]
HSiO	O	-6.805	0.2069	-6.598	-11.11	0.1569	-10.96	-11.14	0.1169	-11.03	
HSiS	Si	-496.5	1.923	-494.6	-507.5	1.991	-505.5	-522.6	2.162	-520.4	
HSiS	H	327.3	-0.0641	327.3	328.4	-0.0667	328.4	356.3	-0.0717	356.2	
HSiS	S	0.4939	-0.1963	0.2976	1.380	-0.0662	1.314	-1.435	0.2176	-1.218	
SiOH	O	-21.45	0.6915	-20.76	-21.26	0.6995	-20.56	-21.17	0.9825	-20.19	
SiOH	Si	33.50	7.003	40.50	19.25	7.388	26.64	12.65	10.36	23.01	
SiOH	H	54.39	-0.1406	54.25	51.57	-0.1371	51.44	52.53	-0.1834	52.35	
SiSH	S	24.15	-0.1318	24.02	20.00	-0.1238	19.87	21.28	-0.1427	21.14	
SiSH	Si	30.53	5.214	35.74	14.83	5.507	20.33	9.180	6.946	16.13	
SiSH	H	129.0	-0.0595	128.9	120.4	-0.0577	120.3	122.3	-0.0640	122.3	
HgH	Hg	7011	-200.7	6810	7454	-202.3	7252	7589	-206.9	7383	7002[d]
HgH	H	747.2	-1.864	745.4	728.3	-1.700	726.6	771.7	-1.724	770.0	710[d]
HgF	Hg	18264	-21.25	18242	19574	-34.30	19540	20486	-28.63	20457	22163[e]
HgF	F	239.5	-149.1	90.47	284.9	-107.8	177.1	271.1	-103.3	167.8	670[e]
TiF_3	Ti	-231.4	2.283	-229.1	-198.5	3.051	-195.5	-203.5	3.253	-200.3	184.8[f]
TiF_3	F	2.651	0.7282	3.380	-15.42	0.7866	-14.64	-10.23	0.9563	-9.269	-23.6[f]
NpF_6	Np	-497.5	-1631	-2128	-212.0	-2137	-2349	-221.5	-2104	-2326	-1994[g]
MpF_6	F	-26.36	-1.493	-27.86	-41.92	-19.94	-61.86	-38.22	-14.88	-53.10	-72.67[g]

[a] Reference 1
[b] Reference 2
[c] Reference 3. Sign was not reported and changed by us to match the sign of the calculated HFCC.
[d] Reference 4
[e] Reference 5
[f] Reference 6
[g] Reference 7

Table S4: Comparison of HFCCs calculated with NWChem (see Section 2 of the main article) and a recent ZORA implementation in ADF.[8] BP functional, unscaled ZORA, Gaussian nucleus model.

		NW[a]		ADF[b]	
Molecule	Atom	FC+SD	PSOSO	FC+SD	PSOSO
CH_2	C	207.4	-0.2764	200.3	-0.2540
CH_2	H	-16.65	0.0082	-20.07	0.0090
CH_3	C	61.26	-0.2516	59.13	-0.2270
CH_3	H	-62.83	0.0158	-68.22	0.0170
CHO	C	377.1	-0.5167	370.8	-0.5260
CHO	H	373.0	-0.0766	374.0	-0.0820
CHO	O	-21.66	0.5790	-21.72	0.5380
HSiO	Si	-552.8	1.149	-545.7	1.091
HSiO	H	428.6	-0.0262	436.7	-0.0270
HSiO	O	-4.511	0.1983	-4.225	0.1450
HSiS	Si	-513.0	1.954	-507.5	1.892
HSiS	H	327.2	-0.0642	333.2	-0.0650
HSiS	S	1.451	-0.1650	0.0470	-0.1110
SiOH	O	-22.30	0.7055	-21.34	0.6960
SiOH	Si	12.55	7.246	17.19	7.055
SiOH	H	54.77	-0.1435	54.41	-0.1450
SiSH	S	25.51	-0.1384	24.75	-0.1450
SiSH	Si	10.74	5.363	15.76	5.205
SiSH	H	129.1	-0.0595	130.7	-0.0610
HgH	Hg	6943	-203.2	6551	-201.3
HgH	H	743.2	-1.885	758.7	-1.873
HgF	Hg	17631	-20.28	16904	-21.43
HgF	F	205.3	-152.2	209.3	-146.9
TiF_3	Ti	-237.6	2.295	-229.7	2.480
TiF_3	F	7.867	0.6801	6.1800	0.6030
NpF_6	Np	-524.7	-1626	-524.7	-2551
NpF_6	F	-23.40	-1.080	-27.24	-12.51

[a] pcJ4 basis for all atoms except Hg, Ti and Np where an uncontracted ANO basis set was used. Also, for NpF_6 we used IGLO-III for fluorine.

[b] QZ4P basis set for all atoms.

Table S5: Comparison of HFCCs calculated with NWChem (see Section 2 of the main article) and a recent ZORA implementation in ADF.[8] PBE functional, unscaled ZORA, Gaussian nucleus model.

		NW[a]		ADF[b]	
Molecule	Atom	FC+SD	PSOSO	FC+SD	PSOSO
CH_2	C	211.1	-0.2728	208.0	-0.2490
CH_2	H	-18.72	0.0080	-18.72	0.0090
CH_3	C	70.72	-0.2470	68.80	-0.2200
CH_3	H	-64.43	0.0159	-64.24	0.0170
CHO	C	379.0	-0.5175	372.8	-0.5290
CHO	H	371.6	-0.0773	368.4	-0.0830
CHO	O	-24.39	0.5841	-23.38	0.5450
HSiO	Si	-531.6	1.125	-522.9	1.055
HSiO	H	428.6	-0.0261	430.8	-0.0270
HSiO	O	-6.759	0.2069	-5.685	0.1450
HSiS	Si	-496.4	1.923	-490.4	1.851
HSiS	H	327.3	-0.0641	329.3	-0.0650
HSiS	S	0.4332	-0.1961	-0.1620	-0.1230
SiOH	O	-21.45	0.6916	-20.83	0.7040
SiOH	Si	33.66	7.003	34.95	6.984
SiOH	H	54.39	-0.1406	53.80	-0.1460
SiSH	S	24.15	-0.1319	24.31	-0.1450
SiSH	Si	30.70	5.214	38.00	5.097
SiSH	H	129.0	-0.0595	129.4	-0.0620
HgH	Hg	6814	-199.1	6563	-199.1
HgH	H	747.2	-1.863	753.1	-1.865
HgF	Hg	17752	-20.67	17024	-21.15
HgF	F	238.8	-149.1	230.6	-145.9
TiF_3	Ti	-231.4	2.283	-225.4	2.490
TiF_3	F	2.700	0.7282	3.573	0.6990
NpF_6	Np	-495.1	-1632	-463.7	-2563
NpF_6	F	-26.20	-1.494	-28.85	-12.47

[a] pcJ4 basis for all atoms except Hg, Ti and Np where an uncontracted ANO basis set was used. Also, for NpF_6 we used IGLO-III for fluorine.

[b] QZ4P basis set for all atoms.

Table S6: Mercury HFCCs calculated with a non-hybrid DFT formalism and with a point nucleus model (PN) and a finite Gaussian nucleus model (FN). Comparison with published DKH2 data ('Ref' column) and with nonrelativistic point-nucleus data (NR).

		NW[a]		ADF[b]		Ref[c]
		BP	PBE	BP	PBE	BP
Molecule	Method	A_{iso}	A_{iso}	A_{iso}	A_{iso}	A_{iso}
HgH	NR	3851	3800			3810
	PN	7434	7302	7140	7222	8647
	FN	6465	6339	6439	6418	7505
	PN-FN	969	963	701	804	1142
	Exp	7002	7002			
HgF	NR	8530	8476			8548
	PN	19464	19550	19189	19542	23062
	FN	16967	17028	17325	17626	19469
	PN-FN	2497	2522	1863	1917	3593
	Exp	22127	22127			
HgCN	NR	7196	7151			7205
	PN	16146	16244	16065	16448	19555
	FN	14056	14132	14514	14799	16218
	PN-FN	2090	2112	1551	1650	3337
	Exp	15850	15850			
HgAg	NR	2228	2259			2203
	PN	3820	3876	3748	3896	4770
	FN	3366	3412	3396	3516	3886
	PN-FN	454	464	352	379	884
	Exp	2723	2723			

[a] Un-scaled scalar ZORA with uncontracted Gaussian basis designed for point nuclei used for NR and PN calculations. Finite nucleus Hirao basis set for FN calculations. See Section 2 of main article.

[b] Un-scaled scalar ZORA with modified TZ2P Hg basis set from reference 9. See text for details.

[c] Scalar relativistic DKH2 data from Malkin et al., Reference 10.

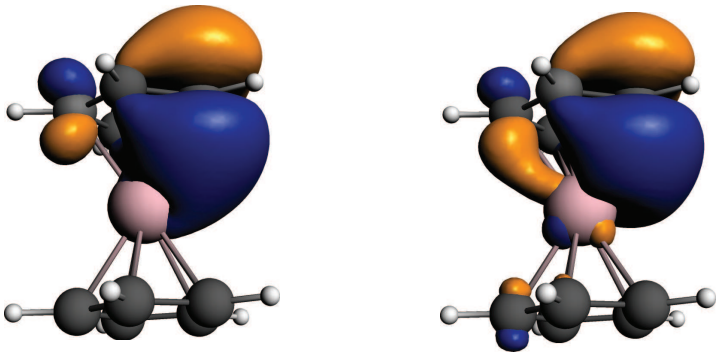

Figure S1: Two nickelocene localized orbitals representing delocalized Cp π bonding. Left: an α spin-orbital. Right: the corresponding β spin-orbital. The β orbital has a large contribution from a formally unoccupied Ni d_{π}^{β} orbital.

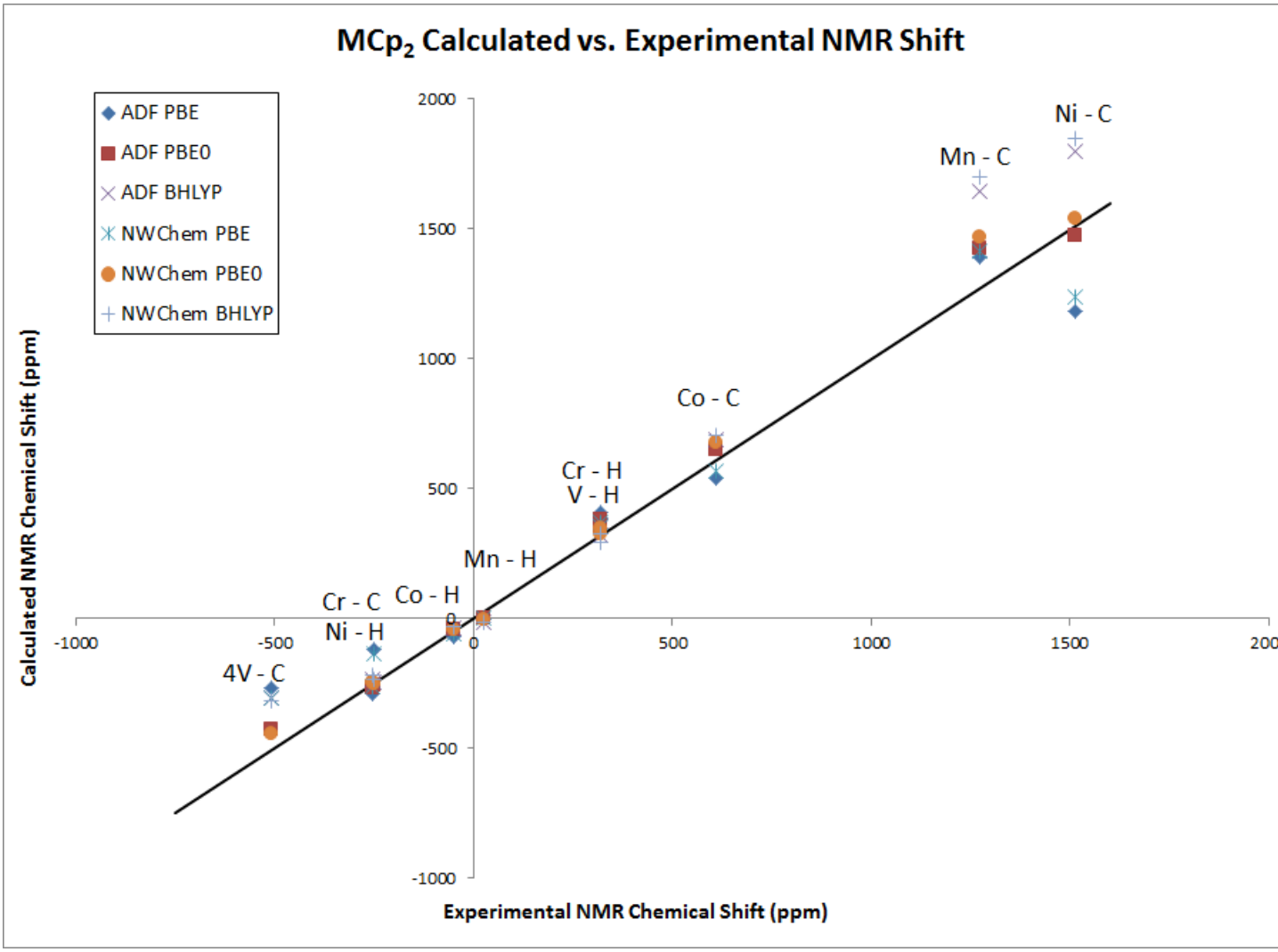

Figure S2: Metallocene pNMR chemical shifts calculated with NWChem and ADF using different functionals, versus experiment. ADF 'jcpl' basis set, see reference 11. NWChem calculations employed the basis set combination described in Section 3 of the main article.

Table S7: Orbital, contact, and PC contributions to the metallocene shielding constants calculated with NWChem, PBE0 functional. For Co and Cr the Cp rings in the optimized geometries are not perfectly parallel. The corresponding shielding constants were averaged.

		Orb	Contact (C)	PC	C + PC	Total Shielding
CoCp2						
	13C	97.5	-594.5	10.2	-584.3	-486.8
	1H	27.4	45.4	0.5	45.9	73.3
CrCp2						
	13C	74.6	362.3	2.3	364.7	439.3
	1H	26.0	-320.4	-0.9	-321.2	-295.2
NiCp2						
	13C	90.7	-1471.9	29.8	-1442.1	-1351.4
	1H	26.3	249.6	0.2	249.8	276.1
VCp2						
	13C	82.6	550.8	-0.9	549.9	632.5
	1H	26.2	-342.5	-0.2	-342.7	-316.5
MnCp2						
	13C	69.0	-1351.2	-0.1	-1351.3	-1282.3
	1H	25.1	8.8	0.0	8.8	33.9

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[3] Van Zee, R. J.; Ferrante, R. F.; Weltner, Jr., W. *J. Chem. Phys.* **1985,** *83,* 6181–6187.

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