Supplementary Information for:

Systematic Variation of Metal-Metal Bond Order in Metal-Chromium Complexes

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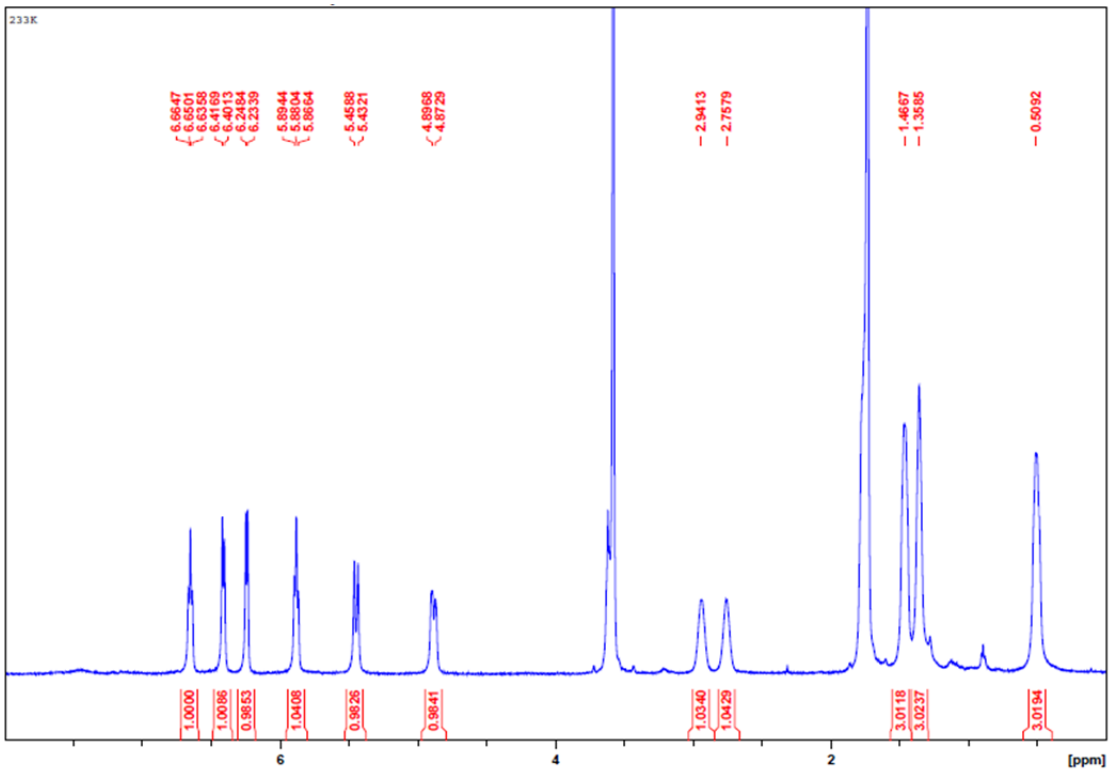
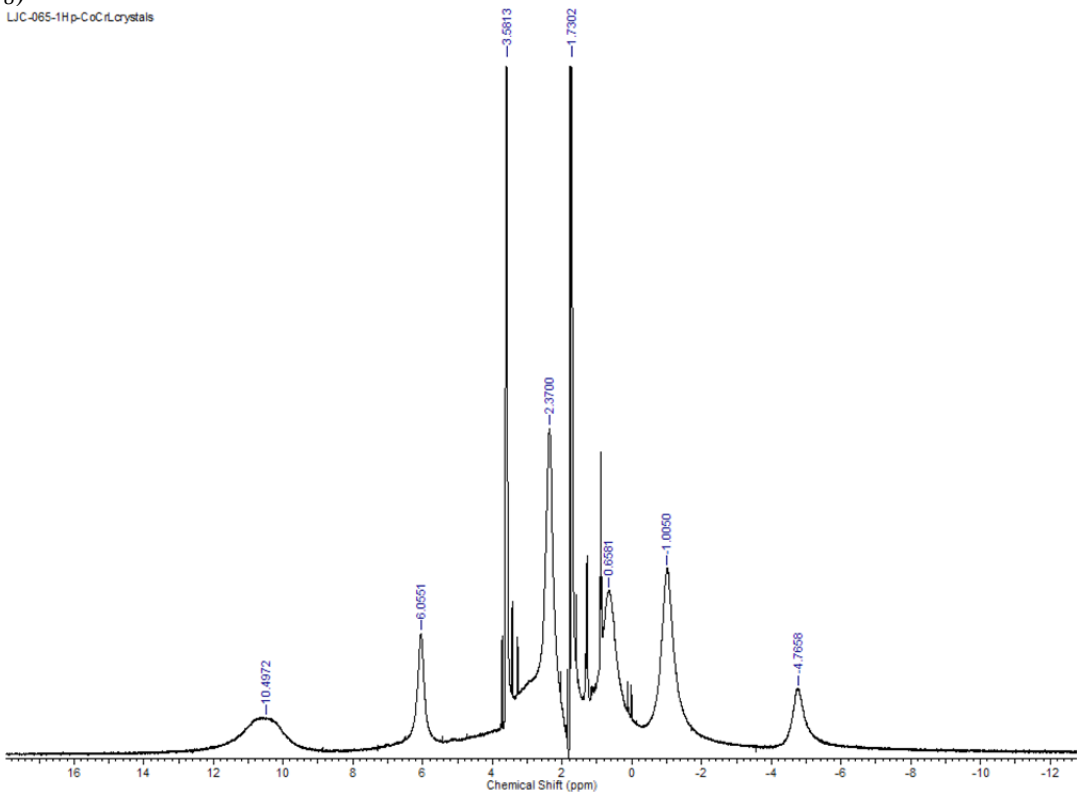
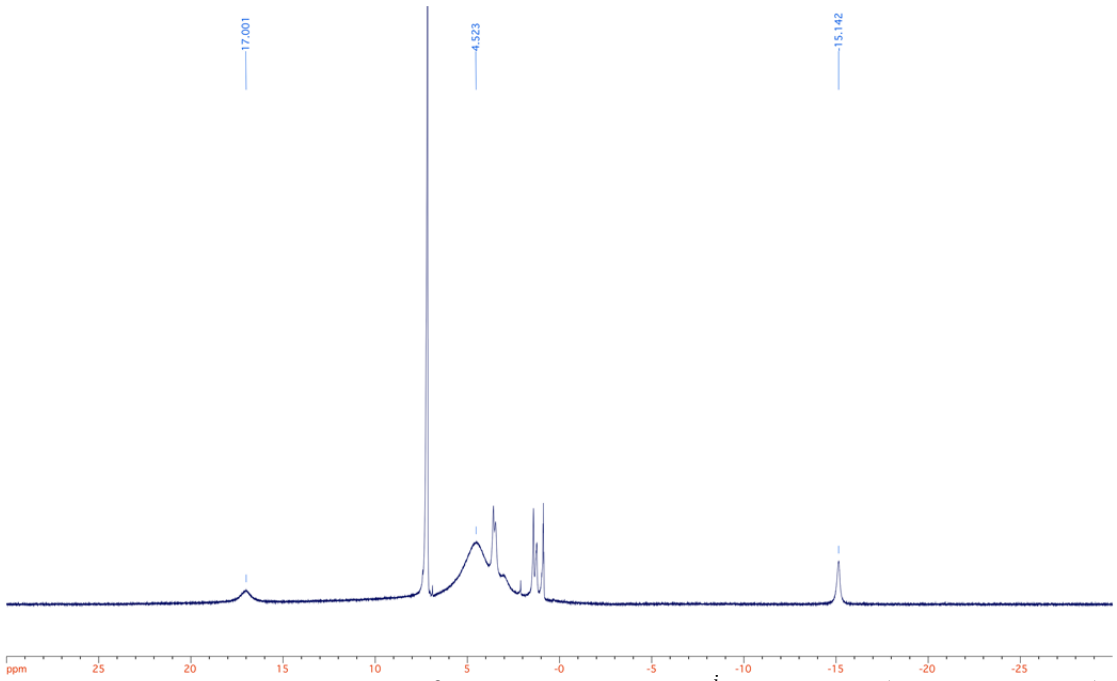


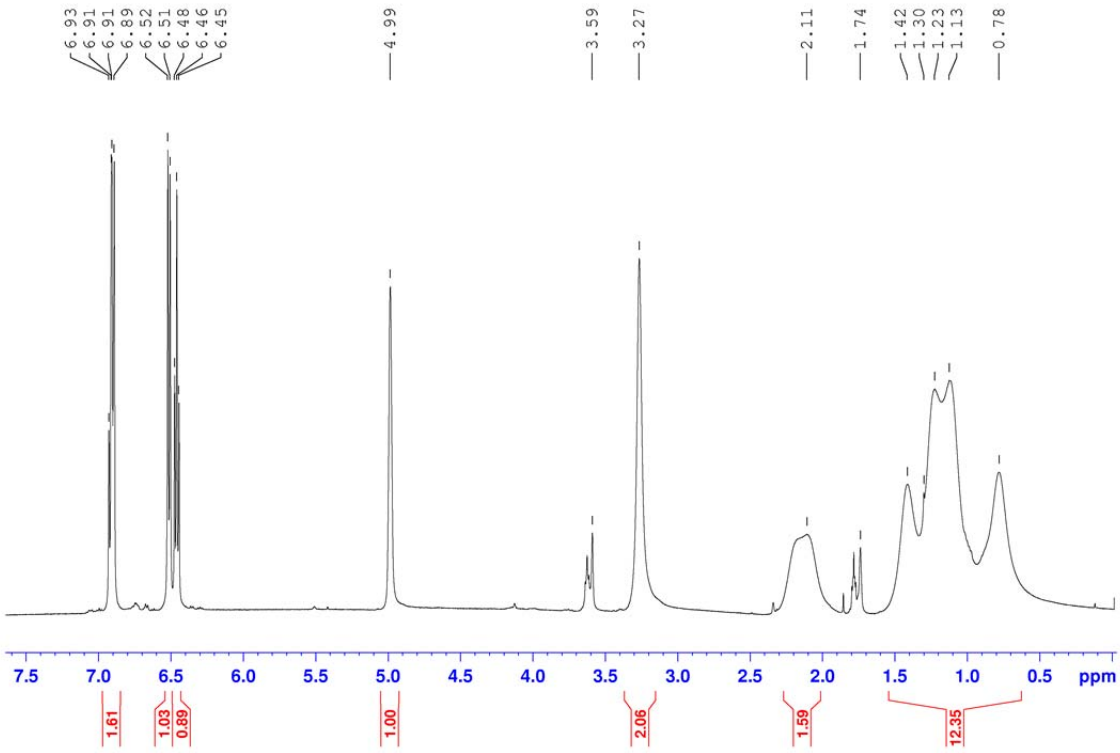
SI Figure 1. Proton NMR spectrum of **1**, *MnCr(N(o-(NCH$_2$P^{i}Pr$_2$)C$_6$H$_4$)$_3$)*at 233K (500 MHz, THF-d_8)



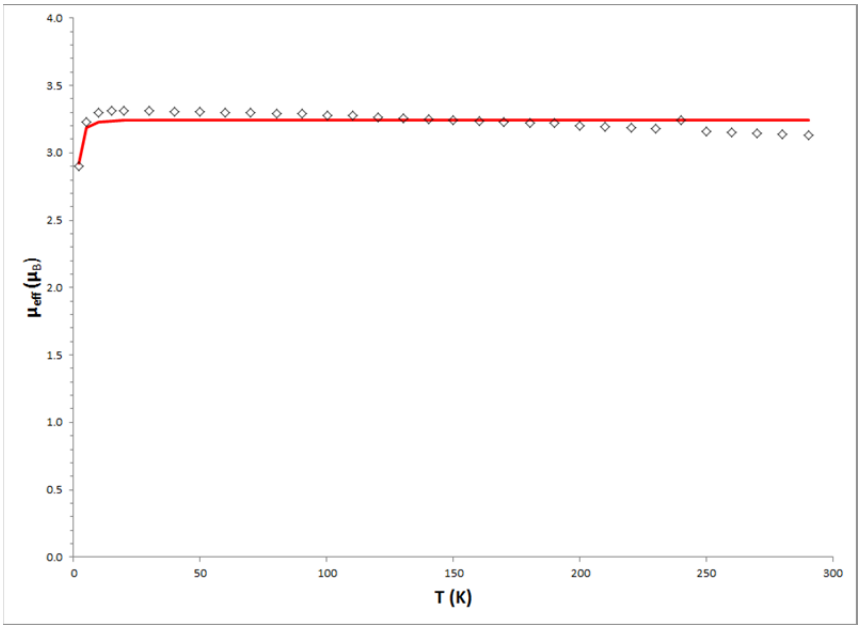
SI Figure 2. Proton NMR spectrum of **3** *CoCr[o-(NCH$_2$P^{i}Pr$_2$)C$_6$H$_4$)$_3$]* (500 MHz, THF-d_8)



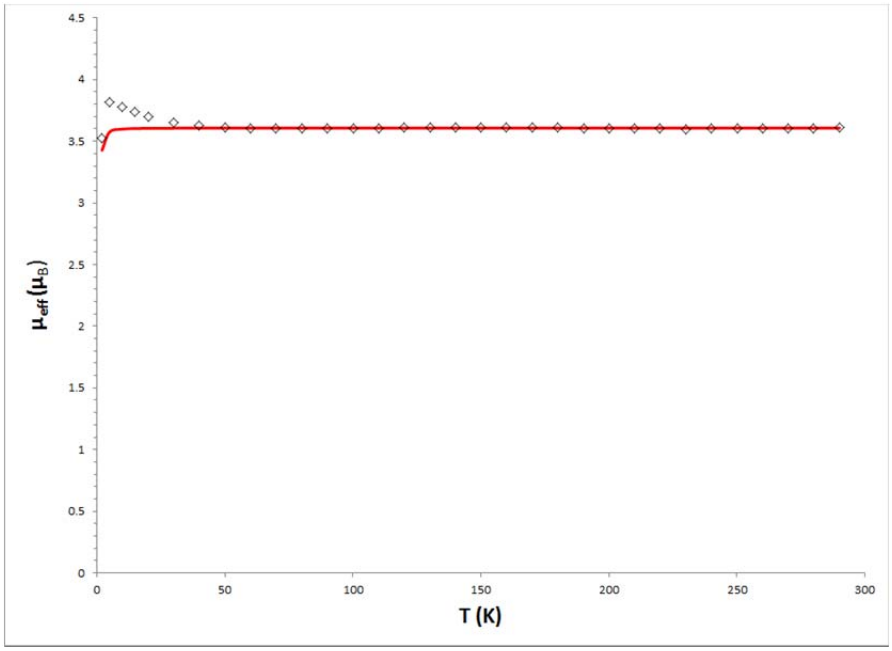
SI Figure 3. Proton NMR spectrum of **4** *NiCr[N(o-(NCH$_2$P^{i}Pr$_2$)C$_6$H$_4$)$_3$]* (300 MHz, C_6D_6)



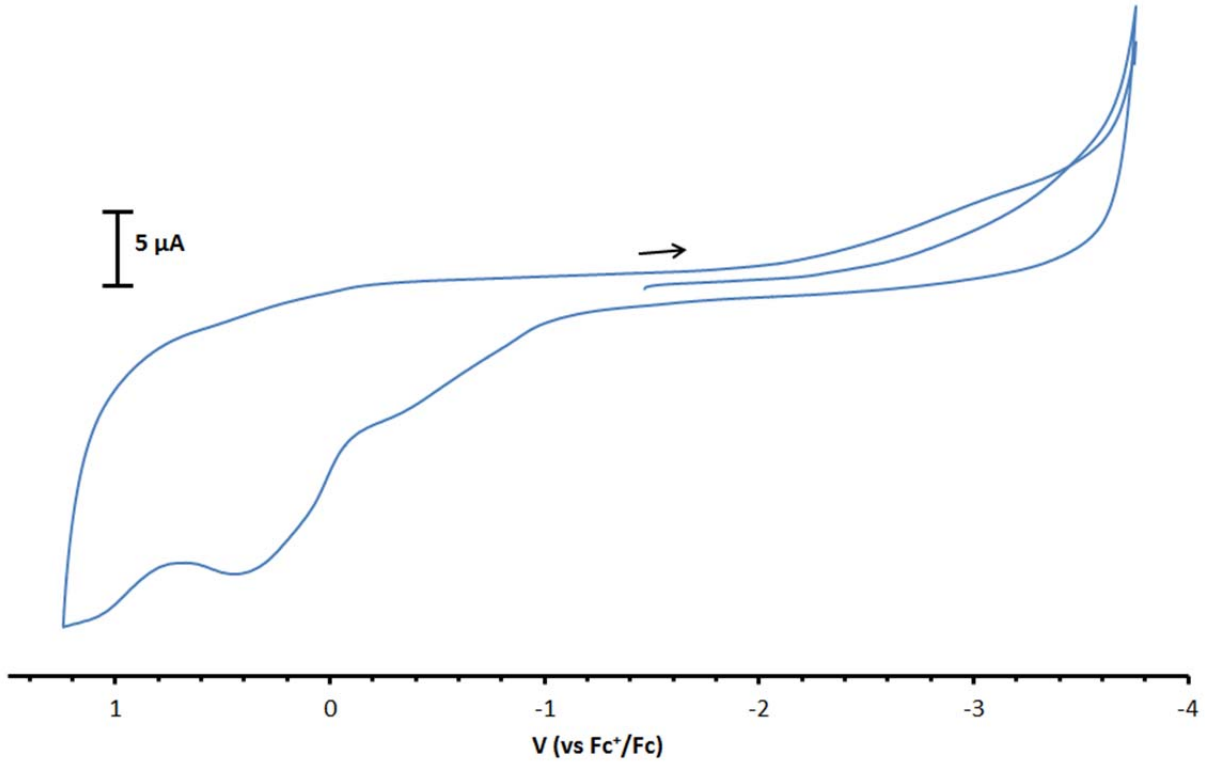
SI Figure 4. Proton NMR spectrum of **5** *Ni[N(o-(NHCH$_2$P^{i}Pr$_2$)C$_6$H$_4$)$_3$)]* (500 MHz, THF-d_8)



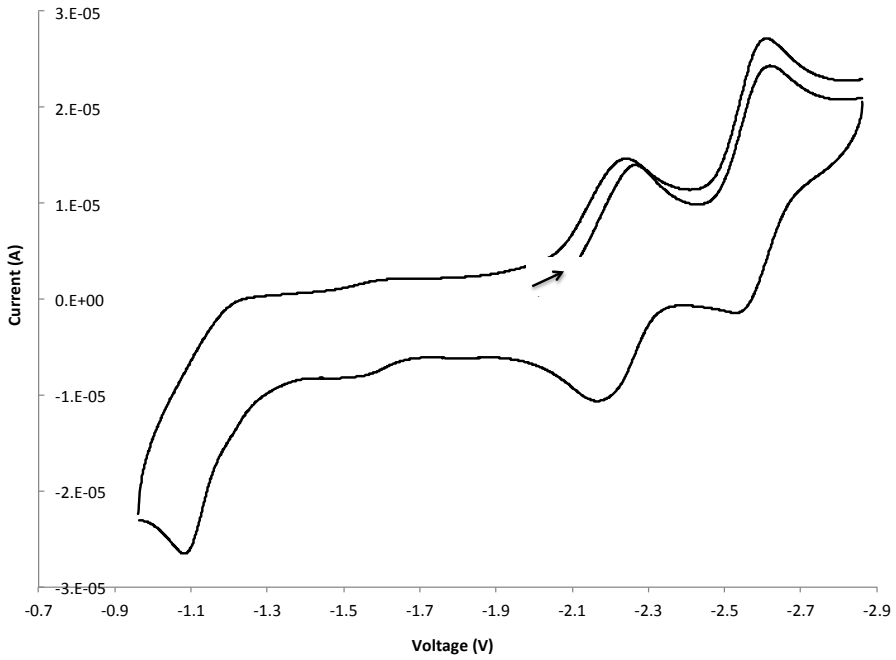
SI Figure 5. Temperature dependence of the effective magnetic moment, μ_{eff}, of **3**-CoCr (shown as diamonds, 1 Tesla, 2–290 K). The red solid line represents the spin-Hamiltonian simulation. The parameters used for the fitting are: $S_{tot} = 1$, $g = 2.293$, with a correction for the underlying diamagnetism of -423×10^{-6} cm^3/mol.



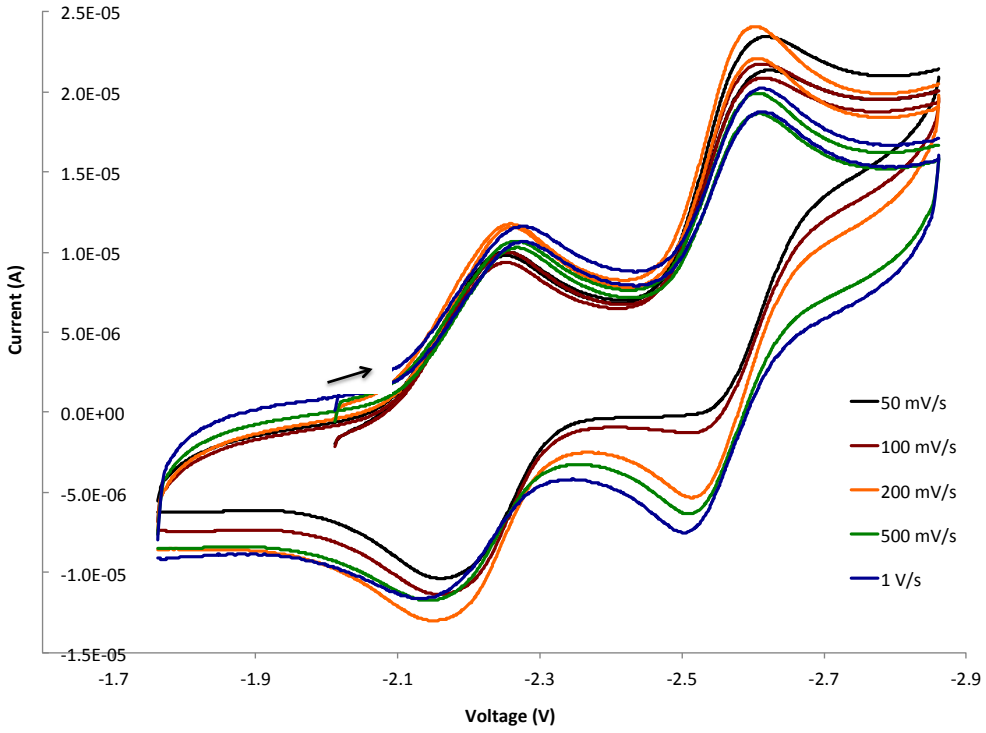
SI Figure 6. Temperature dependence of the effective magnetic moment, μ_{eff}, of **4**-NiCr (shown as diamonds, 1 Tesla, 2–290 K). The red solid line represents the spin-Hamiltonian simulation. The parameters used for the fitting are: $S_{tot} = 1.5$, $g = 1.862$, with a correction for the underlying diamagnetism of -406×10^{-6} cm^3/mol. We caution readers that this g-value is too low to be accurate. A low μ_{eff} may result from diamagnetic impurities in the bulk sample.



SI Figure 7. Cyclic voltammogram of chromium monometallic complex in 0.1 M $[^{n}NBu_4]PF_6$ in THF solution (scan rate of 100 V/s).



SI Figure 8. Cyclic voltammogram of **1** (1.5 mM) in 0.4 M $[Bu_4N][PF_6]$ THF at 100 mV/s.



SI Figure 9. Cyclic voltammogram studies of **1** demonstrating a scan speed dependence between 50 – 1000 mV/s (1.5 mM **1**, 0.4 M $[Bu_4N][PF_6]$ in THF). Current values were normalized by dividing the measured current by the square root of the scan speed.

Structural parameters of DFT optimized species

SI Table 1. Selected Bond Lengths (Å) and Angles (deg) for the DFT Calculated Structures of **1**, **3**, and **4** (with comparison to experimental structures)

M-Cr pair	1-Mn-Cr		3-Co-Cr			4-Ni-Cr	
	Exp	Theo	Exp		Theo	Exp	Theo
M-Cr, Angstrom	1.819	1.811	2.145	2.135	2.218	2.4105	2.432
Cr-Nax, Angstrom	2.38	2.368	2.226	2.216	2.231	2.085	2.266
M-P, Angstrom	2.379	2.259	2.208	2.209	2.179	2.2176	2.18
	2.379	2.26	2.221	2.213	2.179	2.222	2.177
	2.379	2.259	2.217	2.218	2.178	2.236	2.17
Cr-Neq, Angstrom	2.009	1.95	1.915	1.924	1.925	1.95	1.92
	2.009	1.95	1.921	1.925	1.925	1.949	1.915
	2.009	1.95	1.925	1.926	1.924	1.969	1.9
P-M-P, deg	119.4	118.1	119.1	117.9	120	118.5	118.6
	119.4	117.9	121	120.6	119.8	121.1	120.6
	119.4	118	119.7	121.4	120.2	119.7	120
Neq-Cr-Neq, deg	114.2	115.7	113.5	115.1	116.9	111.1	115.2
	114.2	115.6	117.8	116.5	117.2	126	119.7
	114.2	115.4	117.2	118	116.9	117	118.5
M-Cr-Nax, deg	180	179.9	179.6	178.7	179.9	179.5	179.3

Energies of optimized species

SI Table 2. Calculated relative energies of **1**-MnCr for various possible spin states at DFT, CASSCF, and CASPT2 levels of theory.

Spin state	DFT (PBE) (kcal/mol)	CASSCF (kcal/mol)	CASPT2 (kcal/mol)	Percent of main configuration
singlet	0	0	0	54 %
triplet	8.50	6.932	17.130	59 %
quintet	18.81	19.851	44.864	73 %
septet	32.31	19.337	66.782	88 %

SI Table 3. Calculated relative energies of **3**-CoCr for various possible spin states at DFT, CASSCF, and CASPT2 levels of theory.

Spin state	DFT (PBE) (kcal/mol)	CASSCF (kcal/mol)	CASPT2 (kcal/mol)	Percent of main configuration
singlet	23.2	23.1	32.4	60 %
triplet	0	0	0	64%
quintet	14.9	-	-	-

SI Table 4. Calculated relative energies of **4**-NiCr for various possible spin states at DFT, CASSCF, and CASPT2 levels of theory.

Spin state	DFT (PBE) (kcal/mol)	CASSCF (kcal/mol)	CASPT2 (kcal/mol)	Percent of main configuration
doublet	7.4	-	-	-
quartet	0	0	0	86%
sextet	28.4	34.4	37.7	94%

Population and charge Analysis

S Table 5. Calculated charges at the metal centers of the ground spin state of **1**, **3**, and **4**.

	1			
	Mn		**Cr**	
	Mulliken	**LoProp**	**Mulliken**	**LoProp**
CASSCF	-0.3531	0.5209	1.9322	1.0840
CASPT2	-0.3713	N/A	1.9137	N/A
DFT	0.1439	N/A	0.1940	N/A
	3			
	Co		**Cr**	
	Mulliken	**LoProp**	**Mulliken**	**LoProp**
CASSCF	-0.0405	0.3672	1.9163	1.1914
CASPT2	-0.0124	N/A	1.8774	N/A
DFT	0.0097	N/A	0.26374	N/A
	4			
	Ni		**Cr**	
	Mulliken	**LoProp**	**Mulliken**	**LoProp**
CASSCF	-0.6005	0.2383	2.1472	1.4369
CASPT2	-0.5562	N/A	2.0935	N/A
DFT	-0.0499	N/A	0.3493	N/A

SI Table 6. CASSCF Mulliken spin densities at the metal centers of the ground spin state of **1**, **3**, and **4**.

	Spin density from CASSCF		**Spin density from DFT**	
	M	**Cr**	**M**	**Cr**
1-MnCr	0	0	0	0
3-CoCr	-0.3	2.22	0.20	2.22
4-NiCr	-0.07	2.96	0.34	2.83

CASSCF molecular orbital analysis of the ground spin state

SI Table 7. Detailed CASSCF orbital analysis of **1**-MnCr.

	orbital type	%Mn	%Cr	total electrons	Electron Mn	Electron Cr
orbital 156	sigma	58,8	41,2	1,789	1,052	0,736
orbital 157	pi	61,9	38,1	1,797	1,112	0,685
orbital 158	pi	61,9	38,1	1,798	1,112	0,685
orbital 159	delta	67,8	32,2	1,708	1,158	0,550
orbital 160	delta	67,7	32,3	1,709	1,157	0,551
orbital 161	4d Mn	63,2	36,8	0,007	0,004	0,003
orbital 162	4d mn	72,0	28,0	0,011	0,008	0,003
orbital 163	pi*	40,2	59,8	0,188	0,075	0,112
orbital 164	pi*	40,4	59,6	0,188	0,076	0,112
orbital 165	sigma*	40,6	59,4	0,202	0,082	0,120
orbital 166	4d Mn	87,1	12,9	0,023	0,020	0,003
orbital 167	delta*	34,3	65,7	0,274	0,094	0,180
orbital 168	delta*	34,2	65,8	0,275	0,094	0,181
orbital 169	4d Mn	74,2	25,8	0,011	0,008	0,003
orbital 170	4d Mn	87,1	12,9	0,023	0,020	0,003
			totals=	10,00	6,07	3,93

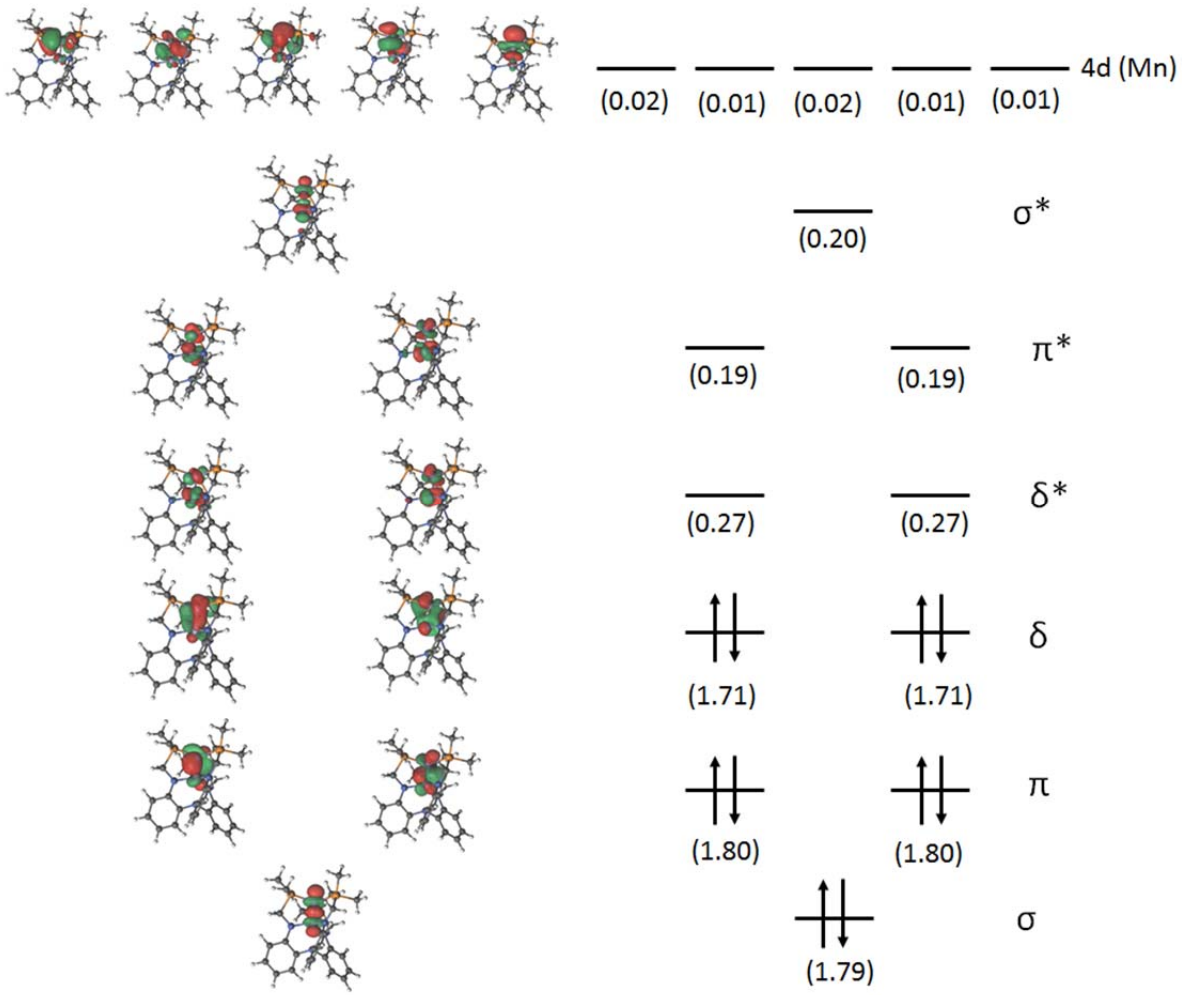
SI Table 8. Detailed CASSCF orbital analysis of **3**-CoCr.

	orbital type	%Cr	%Co	total electrons	Electron Co	Electron Cr
orbital 156	pi*	94,2	5,8	0,995	0,058	0,937
orbital 157	3d Co	0,0	100,0	1,953	1,953	0,000
orbital 158	pi	15,2	84,8	1,789	1,517	0,272
orbital 159	sigma	31,0	69,0	1,770	1,221	0,549
orbital 160	3d Co	0,0	100,0	1,953	1,953	0,000
orbital 161	pi	15,6	84,4	1,792	1,513	0,279
orbital 162	pi*	95,6	4,4	0,994	0,044	0,950
orbital 163	sigma*	68,1	31,9	0,220	0,070	0,150
orbital 164	4d Co	0,0	100,0	0,042	0,042	0,000
orbital 165	4d Co	24,7	75,3	0,042	0,031	0,010
orbital 166	4d Co	6,4	93,6	0,022	0,000	0,000
orbital 167	4d Co	17,5	82,5	0,022	0,000	0,000
orbital 168	4d Co	33,4	66,6	0,017	0,092	0,046
orbital 169	3d Cr	85,0	15,0	0,193	0,036	0,206
orbital 170	3d Cr	83,8	16,2	0,196	0,031	0,162
			totals=	12,00	8,51	3,49

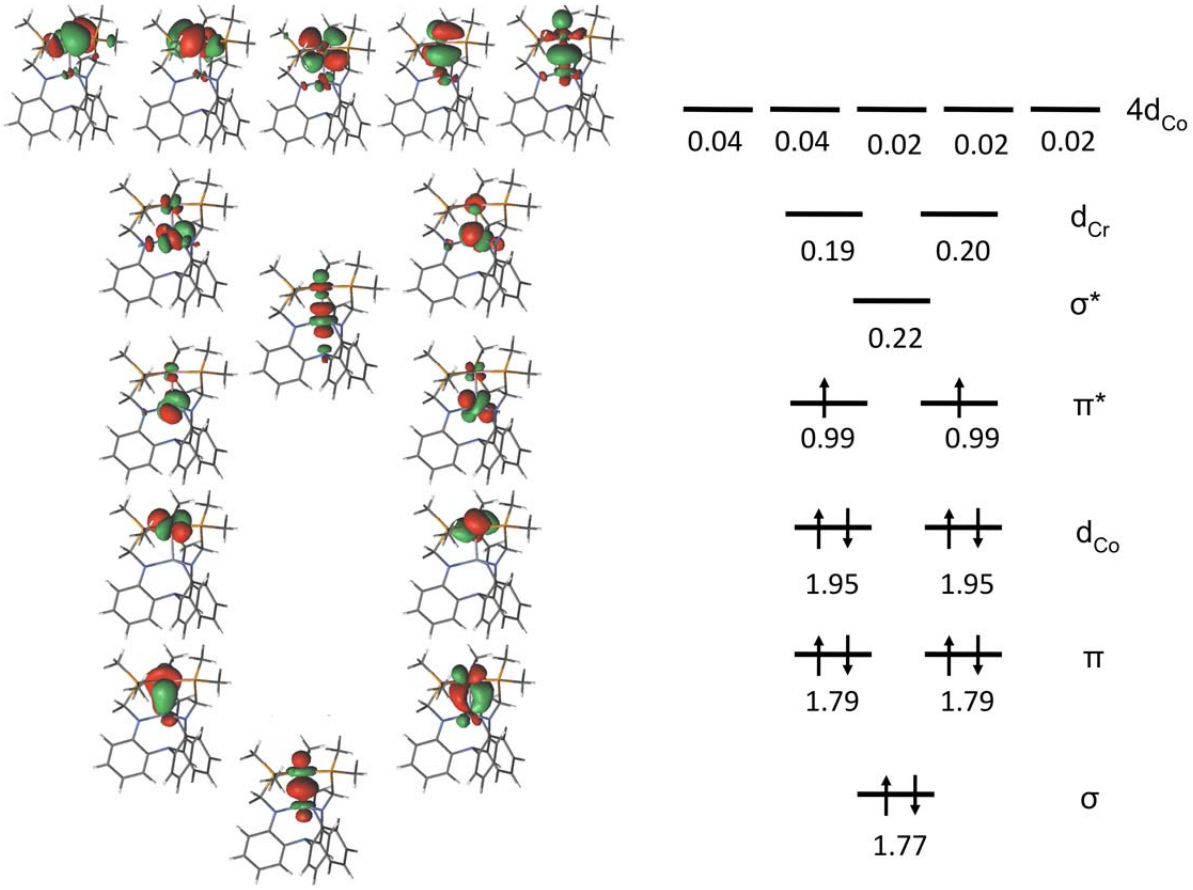
SI Table 9. Detailed CASSCF orbital analysis of **4**-NiCr.

	orbital type	**%Ni**	**%Cr**	**total electrons**	**Electron Ni**	**Electron Cr**
orbital 156	3d Ni	100,0	0,0	1,970	1,970	0,000
orbital 157	3d Ni	100,0	0,0	1,970	1,970	0,000
orbital 158	3d Ni	100,0	0,0	1,950	1,950	0,000
orbital 159	3d Ni	100,0	0,0	1,960	1,960	0,000
orbital 160	sigma	86,4	13,6	1,866	1,612	0,254
orbital 161	sigma*	38,8	61,2	0,130	0,050	0,080
orbital 162	3d Cr	0,0	100,0	1,000	0,000	1,000
orbital 163	3d Cr	0,0	100,0	1,003	0,000	1,003
orbital 164	3d Cr	0,0	100,0	1,002	0,000	1,002
orbital 165	4d/4s Ni	90,3	9,7	0,003	0,002	0,000
orbital 166	4d/4s Ni	100,0	0,0	0,046	0,046	0,000
orbital 167	4d/4s Ni	100,0	0,0	0,038	0,038	0,000
orbital 168	4d/4s Ni	100,0	0,0	0,027	0,027	0,000
orbital 169	4d/4s Ni	64,7	35,3	0,006	0,004	0,002
orbital 168	4d/4s Ni	100,0	0,0	0,030	0,030	0,000
			totals=	13,00	9,66	3,34

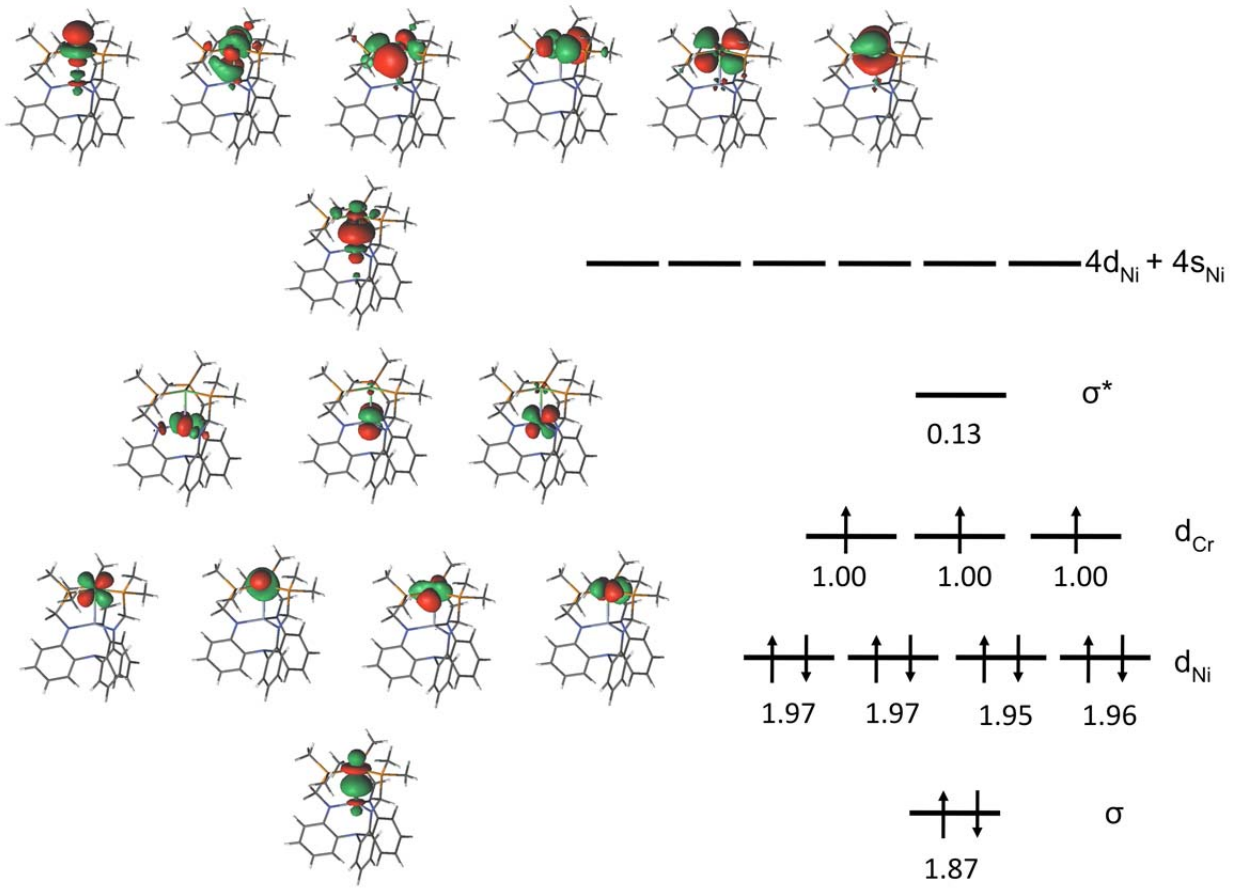
CASSCF Active space



SI Figure 10. Qualitative MO diagram showing the natural orbitals for **1** resulting from CASSCF calculations. The complete active space of 10 d-electrons in 15 orbitals is shown, with the occupancies per MO. Only the dominating electronic configuration (54 %) is shown. Effective bond order (computed by (bonding occupancies – antibonding occupancies)/2) is 3.94.



SI Figure 11. Qualitative MO diagram showing the natural orbitals for **3** resulting from CASSCF calculations. The complete active space of 12 d-electrons in 15 orbitals is shown, with the occupancies per MO. Only the dominating electronic configuration (60%) is shown. Effective bond order (computed by (bonding occupancies – antibonding occupancies)/2) is 1.58.



SI Figure 12. Qualitative MO diagram showing the natural orbitals for **4** resulting from CASSCF calculations. The complete active space of 13 d-electrons in 15 orbitals is shown, with the occupancies per MO. Only the dominating electronic configuration (86%) is shown. Effective bond order (computed by (bonding occupancies – antibonding occupancies)/2) is 0.87.

XYZ Coordinates of DFT optimized ground Spin state

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DFT, **1** MnCr, singlet,

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Mn	15.975720	-0.006686	-0.756394
Cr	15.979560	0.000141	1.054133
N	15.986615	0.006048	3.421867
N	16.654576	-1.780577	1.474811
P	15.960765	-2.243561	-1.072358
C	16.966454	-1.021220	3.750105
C	17.619623	-1.087387	4.983952
H	17.431780	-0.301320	5.732221
C	18.518785	-2.134491	5.266393
H	19.029249	-2.177944	6.241602
C	18.746712	-3.115915	4.291811
H	19.439625	-3.948944	4.498164
C	18.119725	-3.044281	3.037147
H	18.344523	-3.812510	2.282735
C	17.232794	-1.980406	2.724637
C	16.918494	-2.771352	0.452271
H	16.611850	-3.799030	0.771445
H	18.003220	-2.819268	0.171537
C	14.415055	-3.277521	-0.930180
H	13.750657	-3.070497	-1.797187
C	16.849829	-3.149110	-2.434309
H	16.906853	-4.242688	-2.233801
N	17.183759	1.478138	1.464412
P	17.917771	1.100918	-1.085541
C	16.385731	1.369505	3.745263
C	16.122649	1.968749	4.979978
H	15.543953	1.411263	5.733428
C	16.573602	3.274318	5.256127
H	16.360018	3.739182	6.231784
C	17.296055	3.965640	4.273944
H	17.664034	4.986039	4.474624
C	17.542095	3.385740	3.018899
H	18.083726	3.968077	2.258608
C	17.071470	2.081510	2.713237
C	17.899092	2.201545	0.434017
H	18.942778	2.458661	0.745819
H	17.390496	3.160692	0.151763
C	19.590811	0.287776	-0.947260
H	19.749948	-0.384813	-1.818239
C	18.247593	2.318580	-2.454899
H	19.163517	2.920712	-2.259942
N	14.101504	0.311284	1.475795
P	14.044544	1.120414	-1.079430
C	14.607378	-0.327597	3.753440
C	14.226673	-0.857898	4.989151

H	15.003340	-1.085932	5.736025
C	12.871301	-1.113932	5.274659
H	12.580526	-1.532900	6.251108
C	11.905262	-0.824005	4.301338
H	10.837807	-1.008090	4.509976
C	12.277739	-0.319802	3.044619
H	11.498646	-0.132744	2.291071
C	13.641616	-0.083580	2.728760
C	13.109916	0.566913	0.450883
H	12.371810	1.348005	0.762788
H	12.528072	-0.352770	0.178506
C	13.915971	2.977419	-0.954579
H	14.426889	3.443614	-1.825288
C	12.815835	0.789126	-2.438240
H	11.838332	1.284167	-2.240630
H	18.378392	1.771093	-3.413148
H	17.373564	2.995662	-2.558091
H	19.596343	-0.331600	-0.025066
H	20.421301	1.029011	-0.898869
H	13.218487	1.168719	-3.402001
H	12.664408	-0.306925	-2.531900
H	12.859566	3.329294	-0.917125
H	14.443581	3.297737	-0.030661
H	16.314326	-2.991335	-3.395413
H	17.875782	-2.736512	-2.535878
H	14.634695	-4.368742	-0.886732
H	13.882694	-2.971724	-0.004231

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DFT, **3** CoCr, triplet,

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Co	-0.85860000	-0.80530000	-2.11130000
Cr	-0.07090000	-0.06910000	-0.17350000
P	-2.12630000	-2.20330000	-1.02300000
P	1.16300000	-1.39080000	-2.67240000
P	-1.57270000	1.20560000	-2.55280000
N	-0.42230000	-1.60000000	0.93920000
N	0.71930000	0.67580000	1.77540000
N	1.76370000	0.25370000	-0.65600000
N	-1.19190000	1.47590000	0.07700000
C	-1.17180000	-2.75910000	0.48660000
H	-1.85610000	-3.15410000	1.28040000
H	-0.50100000	-3.60110000	0.17380000
C	1.89490000	1.47330000	1.40550000
C	2.44190000	2.47020000	2.21480000
H	1.94840000	2.72930000	3.16480000
C	3.60700000	3.15220000	1.80970000
H	4.03410000	3.94210000	2.44760000
C	4.21000000	2.81150000	0.59060000
H	5.12660000	3.33170000	0.26490000
C	3.64990000	1.82960000	-0.24350000

H	4.12380000	1.60430000	-1.21090000
C	2.46000000	1.15810000	0.13500000
C	2.33000000	-0.12660000	-1.93810000
H	3.36600000	-0.53880000	-1.83470000
H	2.38470000	0.73800000	-2.65000000
C	-0.38620000	1.46180000	2.33650000
C	-1.33480000	1.93130000	1.38110000
C	-2.11440000	1.96590000	-0.93210000
H	-2.12050000	3.08410000	-0.98900000
H	-3.16790000	1.63570000	-0.73740000
C	-2.37440000	2.77750000	1.84330000
H	-3.11830000	3.17060000	1.13420000
C	-2.48550000	3.08940000	3.20860000
H	-3.31230000	3.73750000	3.54470000
C	-1.57890000	2.56940000	4.14350000
H	-1.68510000	2.79460000	5.21640000
C	-0.52160000	1.75200000	3.69510000
H	0.19620000	1.32780000	4.41470000
C	1.03190000	-0.54480000	2.52870000
C	0.34070000	-1.71370000	2.09390000
C	0.52700000	-2.90630000	2.83770000
H	0.00300000	-3.82650000	2.53940000
C	1.40650000	-2.93280000	3.93290000
H	1.54570000	-3.87700000	4.48570000
C	2.12290000	-1.78810000	4.31120000
H	2.83130000	-1.82060000	5.15410000
C	1.92640000	-0.58750000	3.59940000
H	2.48640000	0.32000000	3.87520000
C	-0.44830000	2.54040000	-3.21210000
H	-0.95860000	3.52720000	-3.28960000
H	0.42250000	2.63090000	-2.52780000
H	-0.07280000	2.24080000	-4.21460000
C	-3.07960000	1.49370000	-3.61530000
H	-2.85170000	1.20840000	-4.66500000
H	-3.91240000	0.85360000	-3.25420000
H	-3.39840000	2.56030000	-3.59680000
C	1.71520000	-1.40530000	-4.45490000
H	1.43850000	-0.44180000	-4.93340000
H	2.81440000	-1.55950000	-4.54450000
H	1.19540000	-2.22450000	-4.99680000
C	1.94190000	-2.97810000	-2.07640000
H	1.36520000	-3.84220000	-2.47300000
H	3.00710000	-3.07350000	-2.38790000
H	1.88190000	-2.99910000	-0.96690000
C	-2.62100000	-3.83960000	-1.77190000
H	-3.30550000	-3.66180000	-2.62910000
H	-1.71580000	-4.35860000	-2.15310000
H	-3.13730000	-4.49210000	-1.03200000
C	-3.74390000	-1.69310000	-0.24630000
H	-4.44480000	-1.35640000	-1.04080000
H	-4.21540000	-2.51850000	0.33410000

H	-3.54650000	-0.83470000	0.43090000

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DFT, **4** NiCr, quartet,

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Ni	0.000000000	0.000000000	0.000000000
Cr	-0.000000000	0.000000000	2.431970874
P	-2.148612542	-0.267277016	0.138928946
P	1.321582537	-1.725847296	0.114137539
P	0.878476858	1.993278545	0.091882058
N	-1.648170340	-0.893470927	2.740142809
N	0.021602838	0.019962196	4.697633966
N	1.630517100	-0.966825138	2.706835786
N	0.117962445	1.897428982	2.701026797
C	-2.569474137	-1.265784977	1.677574890
H	-3.634705504	-1.088123384	1.972297749
H	-2.477540727	-2.349069943	1.408117896
C	1.429774518	-0.244155055	5.008523475
C	1.991606011	0.041327992	6.255380188
H	1.370859097	0.526387229	7.025373159
C	3.341805798	-0.259356285	6.522224580
H	3.777245487	-0.023672571	7.506220497
C	4.117362208	-0.854891184	5.518561590
H	5.175227092	-1.101281232	5.710525472
C	3.572509516	-1.123781012	4.252182443
H	4.212839375	-1.561584822	3.471647988
C	2.222123254	-0.807130558	3.958154666
C	2.413153757	-1.560258836	1.633844337
H	2.820083079	-2.561781414	1.924500598
H	3.289645123	-0.921040878	1.350303639
C	-0.438298490	1.375358432	5.000655338
C	-0.301864965	2.343935715	3.954130230
C	0.251882962	2.871705338	1.628088902
H	0.944174888	3.706012077	1.906930729
H	-0.732526331	3.338366593	1.365211539
C	-0.667150382	3.682573468	4.246726029
H	-0.564144041	4.457846258	3.472863784
C	-1.193172081	4.029263286	5.501911908
H	-1.476454858	5.077677439	5.694268797
C	-1.381428712	3.057125756	6.494308000
H	-1.818438255	3.323874140	7.469623743
C	-0.997841868	1.727583897	6.232282489
H	-1.144971107	0.948899643	6.997178587
C	-0.913805904	-1.052504885	5.042300026
C	-1.816918331	-1.454971446	4.008870400
C	-2.785934814	-2.439382967	4.323074386
H	-3.501489610	-2.766680849	3.554210848
C	-2.820050325	-3.033244278	5.595728139
H	-3.576506788	-3.807274016	5.807024625
C	-1.891221863	-2.671371443	6.580986353
H	-1.902171580	-3.156302412	7.570048540

C	-0.938675210	-1.674208949	6.293784727
H	-0.194549276	-1.386487551	7.052962092
C	2.718570727	2.176258420	0.325149137
H	3.027833521	3.240854975	0.426984057
H	3.012589977	1.622234319	1.241935478
H	3.245497356	1.722503154	-0.541956840
C	0.579150703	3.320890714	-1.186737667
H	1.050397265	3.011346680	-2.144383692
H	-0.513612151	3.422727468	-1.358801376
H	0.998524770	4.306117157	-0.880403570
C	2.616233996	-2.120979509	-1.171478680
H	3.221454827	-1.211324319	-1.373255690
H	3.289833076	-2.948688214	-0.851894968
H	2.109414621	-2.413254955	-2.116206977
C	0.609311528	-3.425672181	0.393737183
H	-0.044388332	-3.694935245	-0.464450410
H	1.398625955	-4.202186843	0.511399949
H	-0.014791893	-3.397875876	1.312815887
C	-3.136621085	-1.213303244	-1.130651518
H	-3.128526550	-0.648656193	-2.087698798
H	-2.655498144	-2.198591653	-1.309278156
H	-4.192155688	-1.368869237	-0.810457914
C	-3.256563869	1.211037663	0.385469214
H	-3.155570834	1.893154432	-0.486286659
H	-4.325888317	0.924462855	0.505735230
H	-2.919309408	1.754233962	1.294162864