SUPPORTING INFORMATION

Kinetics and Mechanism of the Hydrogenation of the $CpCr(CO)_3$•/ $[CpCr(CO)_3]_2$ Equilibrium to $CpCr(CO)_3H$

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Energy of H_2: UB3LYP/LANL2DZ: -1.1744164 hartree

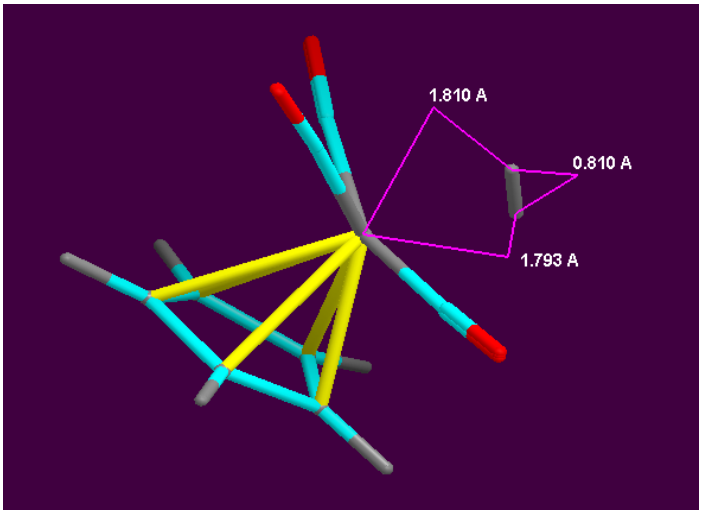

Figure S1. Optimized Structure of $CpCr(CO)_3(H_2)$, UB3LYP/LANL2DZ: –620.89298 hartree

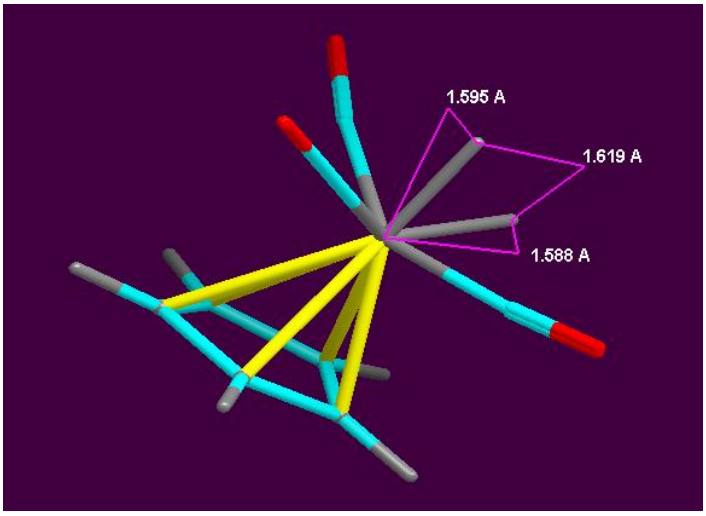

Figure S2. Optimized Structure of $CpCr(CO)_3(H)_2$, UB3LYP/LANL2DZ: –620.880737 hartree

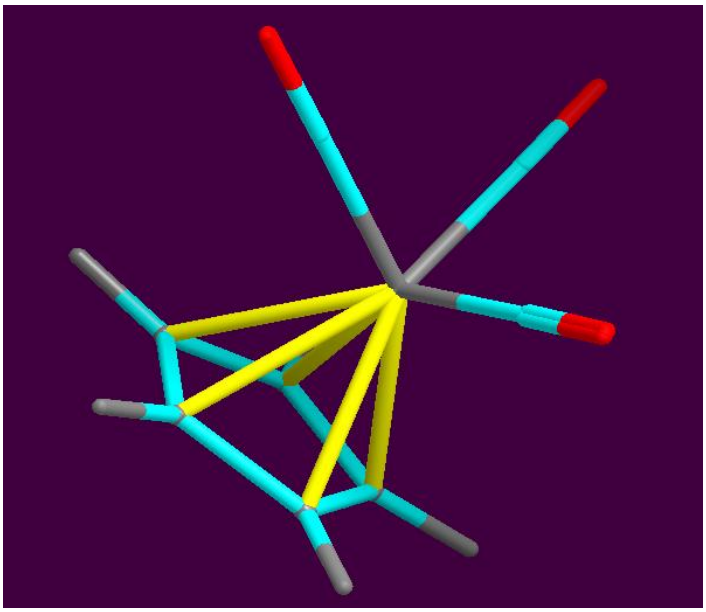

Figure S3. Optimized Structure of $CpCr(CO)_3$• (**1**), UB3LYP/LANL2DZ: –619.770685 hartree

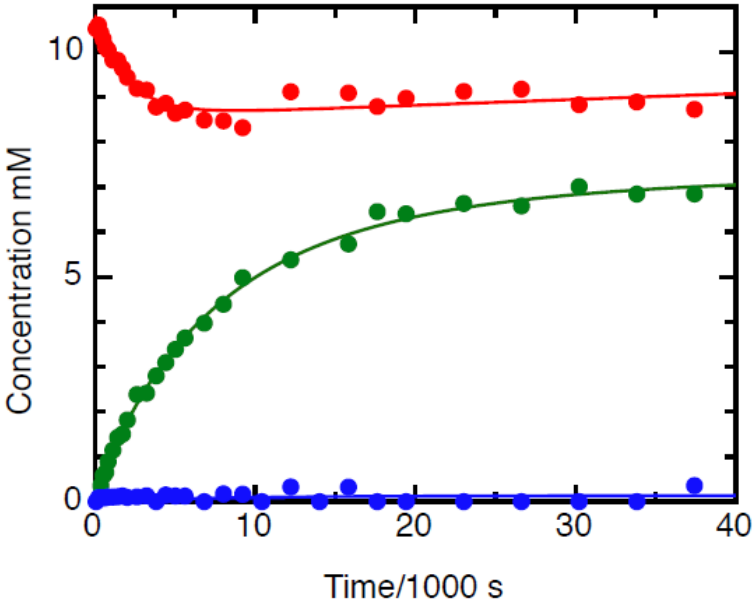

Figure S4. Equilibrating **1** and **2** with 1 atm of H_2 at 25 ^{o}C (run 2).

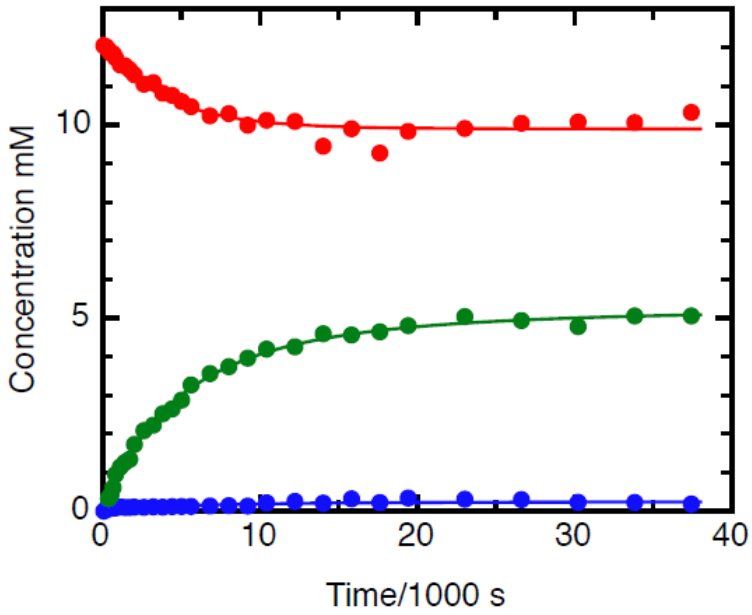

Figure S5. Equilibrating **1** and **2** with 1 atm of H_2 at 25 ^{o}C (run 3).

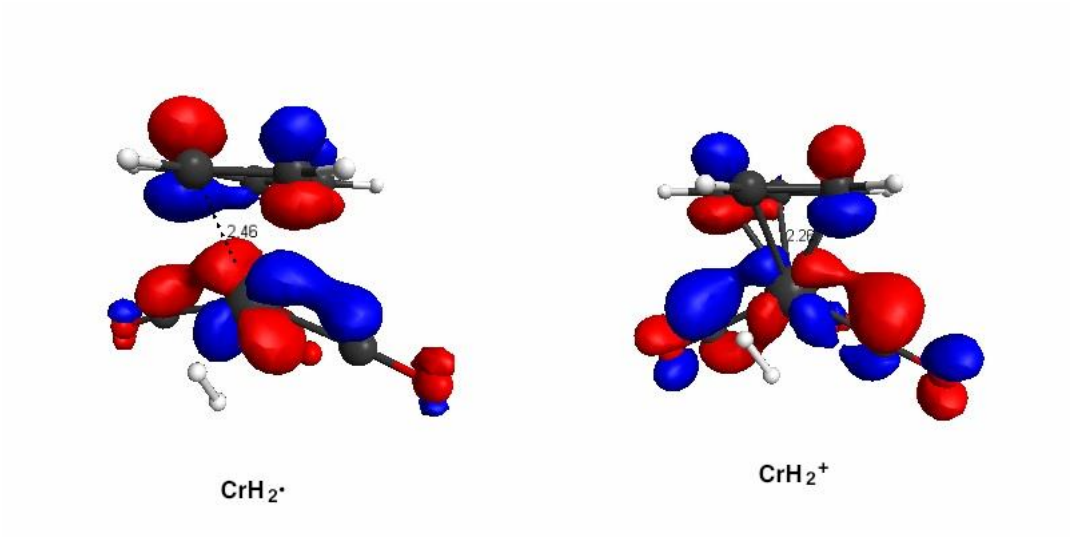

Figure S6. The SOMO for $CpCr(CO)_3(\eta^2\text{-}H_2)\bullet$ (**5**) and the corresponding virtual orbital for $\mathbf{5}^+$, with the Cp–Cr distances indicated

Table S1. Thermochemical data for Mononuclear H_2 Complexes calculated at B3LYP-D3/Ahlrichs polarized VTZ level of theory.

Molecule	E electronic (au)	ZPE (au)	$S°_{298}$ (cal/molK)	$H°_{298}$ (au)	$G°_{298}$ (au)
$CpCr(CO)_3(\eta^1\text{-}H_2)$• (**7**), $<S^2> = 0.779$	-1579.45165	0.10921	129.286	-1579.31500	-1579.37642
H_2	-1.17965	0.01007	31.125	-1.16628	-1.18107
$CpCr(CO)_3$• (**1**) $<S^2> = 0.767$	-1578.27081	0.10921	110.329	-1578.14899	-1578.20141
$CpCr(CO)_3(\eta^2\text{-}H_2)$• (**5**)	-1579.40324	0.12390	114.371	-1579.26532	-1579.31966
$CpCr(CO)_3H_2$• (**6**), $<S^2> = 0.776$	-1579.39481	0.12205	114.502	-1579.25880	-1579.31321

Table S2. Thermochemical data for Mononuclear H_2 Complexes calculated using B3LYP without dispersion correction, with 6-311G** basis on all atoms except SBKJC VDZ ECP basis on Cr.

Molecule	E electronic (au)	$S°_{298}$ (cal/molK)	$H°_{298}$ (au)	$G°_{298}$ (au)
$CpCr(CO)_3(\eta^2\text{-}H_2)$• (**5**)	-621.40337	113.536	-621.26547	-621.31941
H_2	-1.17957	31.126	-1.16620	-1.18099
$CpCr(CO)_3$• (**1**)	-620.27418	108.739	-620.15252	-620.20419
$CpCr(CO)_3H_2$• (**6**), dihyhdride	-621.39502	113.580	-621.25882	-621.31278

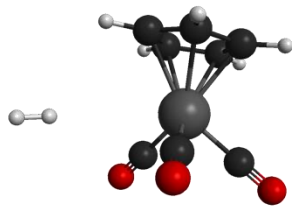

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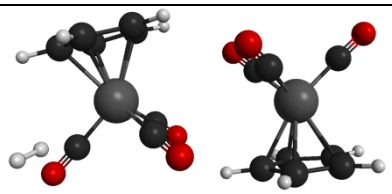
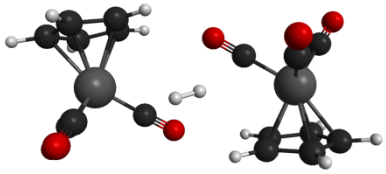
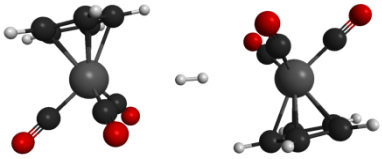
Figure S7. Structure of van der Waals Complex **7**, B3LYP-D3 with Ahlrichs polarized VTZ basis. The change in electronic energy upon forming the complex is –0.11 kcal/mol (including Counterpoise Correction[3] of 0.64 kcal/mol for Basis Set Superposition Error). Thermal correction gives $\Delta H°_{298}$ ~ 0.8 and $\Delta G°_{298}$ = 4.4 kcal/mol.

Table S3. Calculated structures of $2Cr/H_2$ precursor complexes **8**, **9**, **10**, and their energies (kcal/mol) relative to the separated molecules by Grimme's D3 dispersion corrected DFT. The third structure, with a nearly co-linear Cr-H-H-Cr, is close to having C_2 symmetry. From left to right, distances in the structures are (Cr-Cr) 5.3, 6.2 and 6.8 Å, (shortest $Cr-H_2$) 3.26, 3.43 and 3.05 Å, respectively.[a]

 **8**		 **9**	 **10**
ΔE elec	-9.5 (-11.2)[b]	-7.8 (-9.1)[b]	-2.3 (-3.8)[b]
$\Delta H°_{298}$	-6.7	-5.0	+0.5
$\Delta G°_{298}$	-6.9	+8.3	+13.9

[a]B3LYP-D3/DZVP2 except DZVP on Cp hydrogens. [b]Values in parentheses are interaction energy without Counterpoise Correction[3] for Basis Set Superposition Error.

As the structures of the $CpCr(CO)_3$ radicals and H_2 are essentially unchanged in these complexes, the enthalpy and free energy changes were estimated by correcting the electronic energies for changes in the number of rotational, translational and low frequency modes in the complexes. In forming the complexes 6 translational and 5 rotational modes are replaced by 11 low frequency vibrations. Thus, the changes in rotational and translational energies and entropies were calculated using the data in Table S4. For each of the new vibrations, 0.6 kcal/mol of $E_{thermal}$ (0.5 RT) and 4.5 eu (~10 cm-1) for S_{vib} was added. See "Molecular Thermodynamics" by McQuarrie and Simon[1] or the whitepaper on "Thermochemistry in *Gaussian*" by Ochterski

(http://www.gaussian.com/g_whitepap/thermo.htm)[2] for details on the computation of these values.

Table S4. Calculated thermochemical data for structures in Table S3.[a]

Complex or Molecule	E electronic (au)	$I_A I_B I_C$ (au)	E_{298} trans + rot (kcal/mol)	S_{298} trans + rot (cal/molK)
Trimer structure **8** $\langle S^2 \rangle = 1.029$	-3157.29977	8.92674×10^{11}	1.78	79.02
Trimer structure **9** $\langle S^2 \rangle = 1.029$	-3157.29641	1.53092×10^{12}	1.78	79.56
Trimer structure **10** $\langle S^2 \rangle = 1.024$	-3157.28803	2.37313×10^{12}	1.78	79.99
$CpCr(CO)_3$• (**1**) $\langle S^2 \rangle = 0.765$	-1578.05131		1.78	72.45[b]
H_2	-1.17929		1.48	31.13[b]

[a]B3LYP-D3/DZVP2 basis on all atoms except DZVP on Cp hydrogens; rotational entropies are estimated from the product $I_A I_B I_C$ of the moments of inertia, and translational entropies are estimated from molecular weights. [b]Rotational entropies from frequency calculation.

Table S5. The optimized Cartesian coordinates (B3LYP-D3/Alhrichs polarized VTZ) of Structure **7**, the van der Waals complex of H_2 with $CpCr(CO)_3$• (**1**).

Atom	X	Y	Z
Cr	0.00105621	0.08233959	-0.01481906
C	1.49092180	1.11710221	-0.54877558
C	-1.13944712	-1.83121313	-0.31714541
C	0.04400942	-1.90904829	-1.09332476
C	1.15179823	-1.84163896	-0.21150488
C	0.65727555	-1.72363132	1.11162926
C	-0.76744318	-1.71704977	1.04633149
C	-0.05089027	1.16505373	1.51151867
C	-1.43901576	1.12848097	-0.65170009
H	-2.14798874	-1.85870485	-0.69801290
H	0.09321759	-1.98961050	-2.16800781
H	2.19079345	-1.87756276	-0.49823626
H	1.25253696	-1.67029834	2.00869506
H	-1.44175647	-1.65870909	1.88522680

O	2.41941198	1.71444590	-0.85704683
O	-0.08427320	1.82295875	2.45275738
O	-2.33899036	1.73349358	-1.02319021
H	0.08607706	0.46416512	-3.30301607
H	0.08376800	0.56572823	-4.04056796

Table S6. The optimized Cartesian coordinates (B3LYP-D3/Alhrichs polarized VTZ) of $CpCr(CO)_3$• (**1**).

Atom	X	Y	Z
Cr	-0.11687895	0.05920506	0.00000000
C	1.31709707	1.26247190	0.00000000
C	-0.78584888	1.04846821	-1.46530665
C	-0.78584888	1.04846821	1.46530665
O	2.20233693	1.99492176	0.00000000
O	-1.17358121	1.62017216	2.38024979
O	-1.17358121	1.62017216	-2.38024979
C	-0.21094267	-1.87390291	-1.14673419
C	-0.21094267	-1.87390291	1.14673419
C	1.11981590	-1.64974442	0.71306428
C	1.11981590	-1.64974442	-0.71306428
H	1.98111189	-1.52375251	1.34844102
H	1.98111189	-1.52375251	-1.34844102
C	-1.03207609	-2.01343090	0.00000000
H	-2.09748397	-2.18209530	0.00000000
H	-0.54123782	-1.93295540	-2.17141323
H	-0.54123782	-1.93295540	2.17141323

Table S7. The optimized Cartesian coordinates (B3LYP-D3/DZVP2 except DZVP on Cp Hydrogens) of Precursor Complex **8**, $CpCr(CO)_3$ H_2 $CpCr(CO)_3$.

Atom	X	Y	Z
Cr	0.08845046	-2.39935494	0.22584662
C	1.52297059	-3.56977407	-0.11073827
C	0.88662262	-1.13501933	1.36986648
C	0.77600463	-1.40186947	-1.19102312
O	2.38179778	-4.31891167	-0.34457255
O	1.36146078	-0.34249386	2.07849921
O	1.22106409	-0.78644797	-2.07679407
Cr	-0.16361724	2.83474784	-0.09116463
C	-1.03402501	1.87608211	1.26482407
C	-1.02943742	1.67040714	-1.25829403
C	-1.49055375	4.08772132	-0.57319133
O	-1.55683953	1.25615280	2.10213359
O	-1.59342985	0.94748046	-1.98060816
O	-2.28301051	4.87691740	-0.89213511
H	1.68769844	2.54129104	-2.38010240

C	1.68390865	2.83773945	-1.33872278
C	1.86217629	1.96396168	-0.22026742
C	1.49392426	4.15776578	-0.84165387
H	2.05317844	0.90319968	-0.27056432
C	1.78067320	2.75260897	0.96865820
H	1.31768108	5.04473003	-1.43797963
C	1.55503156	4.10691671	0.58437487
H	1.87789181	2.37894231	1.98011872
H	1.42695480	4.94890231	1.25423447
H	-2.24207048	-1.28982906	-1.22558611
C	-1.99779246	-2.06408268	-0.51015928
C	-2.00473539	-1.91942240	0.90392902
C	-1.58359329	-3.39733435	-0.82144550
H	-2.25455590	-1.01987257	1.45108318
C	-1.59453743	-3.16117159	1.47848258
C	-1.33261240	-4.07506699	0.41502847
H	-1.48938563	-3.82058098	-1.81326749
H	-1.48616807	-3.36466521	2.53682465
H	-1.01148115	-5.10405736	0.52282907
H	1.25801394	-3.65503378	3.00007247
H	1.46243879	-3.99042667	3.63156937

Table S8. The optimized Cartesian coordinates (B3LYP-D3/DZVP2 except DZVP on Cp Hydrogens) of Precursor Complex **9**, $CpCr(CO)_3$ H_2 $CpCr(CO)_3$.

Atom	X	Y	Z
Cr	-0.08350183	-3.18785274	-0.02894592
C	-1.00355314	-1.64948508	0.46906587
C	1.91065713	-3.52938786	-0.92698492
C	1.92639418	-2.29270639	-0.20819868
C	1.69608674	-2.58924633	1.17296547
C	1.54062706	-3.99678487	1.30286112
C	1.67294417	-4.58065679	0.00662925
C	-1.43186958	-4.13892438	0.88962941
C	-0.87149435	-2.93232762	-1.71749768
H	2.06191305	-3.64777192	-1.99307999
H	2.10199867	-1.30934929	-0.62232531
H	1.64595623	-1.86155881	1.97155739
H	1.34106611	-4.53349638	2.22232891
H	1.58718908	-5.63529182	-0.22617689
O	-1.58580746	-0.68141052	0.76408690
O	-2.23814985	-4.72674348	1.48678606
O	-1.32323159	-2.74104389	-2.77321821
H	0.13813222	-0.21568430	-1.88869165
Cr	0.05965554	3.00163548	0.05191098
C	0.94906317	1.51691443	0.77840185

C	-1.83856054	3.59119936	-0.93318445
C	-2.04190990	2.31618461	-0.32948554
C	-1.86080490	2.45898145	1.07725423
C	-1.55010603	3.82147870	1.34798933
C	-1.53318024	4.53000744	0.10186388
C	1.35704999	4.03970665	0.90646803
C	1.03898784	3.31169347	-1.52437631
H	-1.90766343	3.81284933	-1.99134131
H	-2.25676882	1.38704923	-0.84139096
H	-1.93217051	1.65875266	1.80163596
H	-1.35672366	4.24747512	2.32459110
H	-1.34165587	5.58712282	-0.03070424
O	1.47115238	0.58682761	1.24813435
O	2.16294603	4.69166812	1.43967044
O	1.61556286	3.53392798	-2.51126283
H	0.32960709	0.43084890	-2.20145228

Table S9. The optimized Cartesian coordinates (B3LYP-D3/DZVP2 except DZVP on Cp Hydrogens) of Precursor Complex **10**, $CpCr(CO)_3$ H_2 $CpCr(CO)_3$.

Atom	X	Y	Z
Cr	-0.07648415	3.41332751	0.00721258
C	0.83445777	2.77523779	1.52994137
C	-1.96490196	3.21192245	-1.14742940
C	-2.16872910	2.59303998	0.12056849
C	-2.01350211	3.59003071	1.12859297
C	-1.71846295	4.82754521	0.48760047
C	-1.68804083	4.59682189	-0.92734367
C	1.19032817	4.78590166	-0.02372172
C	0.92431875	2.65100814	-1.39224390
H	-2.01744745	2.71808041	-2.11013810
H	-2.37747872	1.54389835	0.29132502
H	-2.09714981	3.43024634	2.19668836
H	-1.55207130	5.77571184	0.98325184
H	-1.50710805	5.34074682	-1.69262652
O	1.36849937	2.39340742	2.49056102
O	1.97561854	5.64654658	-0.04794347
O	1.51539210	2.19408840	-2.28486326
H	0.01924554	0.37174151	0.12890121
Cr	0.07628829	-3.41347967	0.00728687
C	-0.83431805	-2.77558295	1.53016608
C	1.96469892	-3.21167513	-1.14729854
C	2.16842496	-2.59284877	0.12063464
C	2.01337305	-3.58982930	1.12856509
C	1.71857915	-4.82728790	0.48757630

C	1.68814384	-4.59654226	-0.92728047
C	-1.19019176	-4.78603021	-0.02384241
C	-0.92430568	-2.65102577	-1.39212511
H	2.01734856	-2.71774077	-2.10990870
H	2.37718052	-1.54376716	0.29143806
H	2.09729843	-3.43008581	2.19661839
H	1.55259299	-5.77550909	0.98317218
H	1.50749605	-5.34049137	-1.69252517
O	-1.36865580	-2.39402966	2.49100267
O	-1.97529896	-5.64710382	-0.04806400
O	-1.51555519	-2.19432719	-2.28492603
H	-0.01958312	-0.37194620	0.12886816

Table S10. Thermodynamic data (kcal/mol) (illustrated in Figure 2) calculated at the UBP86/6-311++G** level of theory for the components of the heterolytic pathway in Scheme 3.

Compound	Total energy	Zero-point energy	Enthalpy (298.15 K)	Entropy J/K
$CpCr(CO)_3$• (**1**) (a) <S2>=0.798	-990484.73	66.85	-990409.99	460.24
$[CpCr(CO)_3]_2$ (a) $<S^2> = 0.000$	-1980983.16	136.09	-1980831.53	686.16
H_2 (a) $<S^2> = 0.000$	-738.81	6.18	-730.55	130.45
Transition State (b) $<S^2> = 0.077$	-1981696.09	142.91	-1981536.72	762.90
Intermediate **11** (c) $<S^2> = 0.000$	-1981706.29	145.78	-1981543.94	775.05
$Cp(CO)_3CrH$ **3** (d) $<S^2> = 0.000$	-990865.59	71.83	-990785.85	450.64

Table S11. The optimized Cartesian coordinates (UBP86/6-311++G**) of the initial monomer **1** ($CpCr(CO)_3$•) in Scheme 3 (part **a** in Figure 2)

Atom	X	Y	Z
Cr	-0.03385100	0.00000400	-0.14192200
C	-1.24306700	0.00001000	1.25731500
C	-1.02953700	1.44935600	-0.76959700
C	-1.02977500	-1.44911600	-0.76970300
O	-2.00380500	0.00003400	2.14093300
O	-1.63368600	2.37468100	-1.13646300
O	-1.63418800	-2.37424200	-1.13663700
H	1.44356500	-1.36067600	2.00317000
C	1.60326700	-0.71876100	1.14050800
C	1.86500400	-1.15564900	-0.19469000
C	1.60329000	0.71689800	1.14164700
C	2.03489800	0.00080700	-1.01384400
H	1.93121400	-2.18874300	-0.52776000
C	1.86505800	1.15593200	-0.19280400
H	1.44354900	1.35743700	2.00532700
H	2.22145000	0.00168900	-2.08606500
H	1.93122400	2.18956300	-0.52421200

Table S12. The optimized Cartesian coordinates (UBP86/6-311++G**) of the initial dimer **2** ($[CpCr(CO)_3]_2$) in Scheme 3 (part **a** in Figure 2)

Atom	X	Y	Z
Cr	1.63628300	-0.05243300	0.00009200
C	1.01587600	-0.91784300	-1.52070600
C	1.01552600	-0.92016600	1.51947200
C	2.70323900	-1.54115900	-0.00082100
O	0.78174500	-1.48861300	-2.51347600
O	0.78106400	-1.49390100	2.51045300
O	3.38989900	-2.48519100	-0.00134400
Cr	-1.63647500	0.05196300	-0.00007100
C	-1.01565600	0.92046100	-1.51901100
C	-1.01610900	0.91802400	1.52042600
C	-2.70378400	1.54034100	0.00085600

O	-0.78092800	1.49626900	-2.50872700
O	-0.78178500	1.49116000	2.51179000
O	-3.38952800	2.48503800	0.00144500
H	-4.13501200	-0.63254700	1.35727400
C	-3.37558900	-1.07509100	0.71705400
C	-2.20689200	-1.76762900	1.15621400
C	-3.37520000	-1.07426100	-0.71939900
H	-1.91043500	-1.94123200	2.18732000
C	-1.49644000	-2.20530600	-0.00130800
H	-4.13427800	-0.63096500	-1.35950900
C	-2.20627200	-1.76631100	-1.15871600
H	-0.56789700	-2.76870600	-0.00135600
H	-1.90921800	-1.93865800	-2.18986200
H	4.13424800	0.62999000	1.35948500
C	3.37528100	1.07343300	0.71934600
C	2.20649800	1.76574600	1.15862300
C	3.37565700	1.07415800	-0.71711000
H	1.90949200	1.93825200	2.18975600
C	1.49675500	2.20481100	0.00118800
C	2.20711000	1.76691800	-1.15631100
H	4.13496700	0.63138600	-1.35730800
H	0.56830500	2.76836500	0.00120500
H	1.91068400	1.94054200	-2.18742200

Table S13. The optimized Cartesian coordinates (UBP86/6-311++G**) calculated for the transition state in Scheme 3 (part **b** in Figure 2)

Atom	X	Y	Z
Cr	-2.85923500	-0.08893900	0.08631400
C	-3.58282100	-0.67899700	1.70632800
C	-1.91405900	-1.46367200	-0.76888500
C	-4.26542400	-1.10202700	-0.54711500
O	-4.08603300	-1.01453100	2.69801800
O	-1.37095100	-2.30743500	-1.35088700
O	-5.15464700	-1.73480800	-0.94968700
Cr	3.05316400	0.05356500	0.11519000
C	1.62605000	0.18851900	1.19512000
C	2.03026600	0.61028700	-1.28670900
C	3.53285800	1.81917100	0.33485700
O	0.67675200	0.30214700	1.92730100
O	1.35351400	0.96808700	-2.18125600
O	3.83534300	2.94096500	0.47035800

H	5.25599100	-0.30409800	-1.82097800
C	4.79229900	-0.79401100	-0.96867100
C	3.71075200	-1.73245600	-1.01822200
C	5.14844100	-0.61491100	0.40631000
H	3.20928100	-2.08118300	-1.91773100
C	3.41451500	-2.14080300	0.31611500
H	5.93252600	0.03774400	0.78266800
C	4.30508600	-1.45135400	1.19726500
H	2.64175800	-2.84623700	0.61210500
H	4.32146400	-1.53364900	2.28162200
H	-3.49719900	1.01800800	-2.54707500
C	-3.17607100	1.32883900	-1.55577500
C	-1.82224000	1.47445000	-1.11811500
C	-4.03602700	1.68015600	-0.46029500
H	-0.92491100	1.29347800	-1.70760100
C	-1.85019000	1.93883200	0.23082000
C	-3.20900500	2.04348800	0.64747700
H	-5.12339700	1.68520800	-0.47430100
H	-0.97811800	2.12921900	0.85289000
H	-3.55430400	2.36748100	1.62647400
H	-1.46265400	-0.57742300	1.26234400
H	-0.73313900	-0.20804500	1.43968500

Table S14. The optimized Cartesian coordinates (UBP86/6-311++G**) calculated for the collinear transition state of homolytic mechanism

Atom	X	Y	Z
Cr	3.109700	-0.043245	0.004144
C	2.386523	-1.139606	-1.320082
C	2.443773	-0.789313	1.580842
C	4.371911	-1.384712	0.142552
O	1.972227	-1.820563	-2.170406
O	2.070967	-1.247578	2.584459
O	5.168821	-2.231386	0.230549
Cr	-3.109698	0.043254	0.004001
C	-2.386539	1.139716	-1.320149
C	-2.443821	0.789235	1.580766
C	-4.371948	1.384677	0.142497
O	-1.972247	1.820716	-2.170440

O	-2.071066	1.247417	2.584439
O	-5.168881	2.231324	0.230545
H	-5.428690	-1.318961	1.183213
C	-4.585541	-1.502126	0.521860
C	-3.295728	-1.975739	0.915789
C	-4.573283	-1.326378	-0.902875
H	-2.982214	-2.210167	1.930337
C	-2.494368	-2.104327	-0.258294
H	-5.405319	-0.985592	-1.513961
C	-3.276645	-1.693091	-1.378638
H	-1.455311	-2.424999	-0.289938
H	-2.945560	-1.673809	-2.414249
H	5.428361	1.318991	1.183958
C	4.585393	1.502137	0.522368
C	3.295457	1.975738	0.915932
C	4.573534	1.326387	-0.902367
H	2.981657	2.210182	1.930388
C	2.494434	2.104323	-0.258385
C	3.277034	1.693096	-1.378500
H	5.405741	0.985600	-1.513220
H	1.455384	2.424991	-0.290331
H	2.946242	1.673797	-2.414204
H	0.383761	-0.017982	0.039776
H	-0.383779	0.018170	0.039691

Table S15: The optimized Cartesian coordinates (UBP86/6-311++G**) calculated for the intermediate $CpCr(CO)_2COH$ (**11**) in Scheme 3 (part **c** in Figure 2)

Atom	X	Y	Z
Cr	-3.03137200	-0.09136100	0.01342200
C	-2.89016100	-0.84458600	1.69130900
C	-2.19521300	-1.15802400	-1.23310700
C	-4.35381100	-1.36627800	-0.15400600
O	-2.79413100	-1.31442400	2.75383100
O	-1.64641700	-1.82141400	-2.01951500
O	-5.17889200	-2.18379500	-0.25709800
Cr	3.17545000	0.06982500	0.04861000
C	1.67133500	0.19777500	0.86508300

C	2.50347200	0.94657500	-1.41374100
C	3.70661400	1.68022100	0.74015300
O	0.58532500	0.34065300	1.53863600
O	2.05418300	1.50568400	-2.34263900
O	4.02519600	2.71072200	1.20264000
H	5.79454600	-0.13984100	-1.33533900
C	5.09596800	-0.73030600	-0.74775100
C	4.01627300	-1.52103000	-1.26049300
C	5.09216000	-0.86309200	0.67928700
H	3.75102300	-1.63496700	-2.30890700
C	3.35988700	-2.14549700	-0.15864700
H	5.78977800	-0.38922800	1.36577300
C	4.02527200	-1.73806500	1.04181500
H	2.50027000	-2.80870600	-0.21838800
H	3.75999400	-2.03940100	2.05237900
H	-4.98328200	1.05816200	-1.85132700
C	-4.24676500	1.35162500	-1.10752300
C	-2.87176900	1.64624100	-1.36030100
C	-4.48571400	1.52545400	0.29637900
H	-2.37699900	1.61523800	-2.32786100
C	-2.26265700	2.00389000	-0.11954000
C	-3.25483800	1.92520100	0.90485200
H	-5.43547300	1.38655200	0.80671000
H	-1.22494600	2.29786800	0.01715700
H	-3.10186800	2.14369200	1.95880900
H	-1.50012000	-0.44784600	0.33612800
H	-0.25321900	0.11530900	1.02662000

Table S16: The optimized Cartesian coordinates (UBP86/6-311++G**) of the product $CpCr(CO)_3H$ (**3**) in Scheme 3 (part **d** in Figure 2)

Atom	X	Y	Z
Cr	0.03925800	-0.00015700	-0.13618400
C	0.95513900	1.47861900	-0.72953700
C	0.95783000	-1.47715300	-0.72999300
C	1.31294100	0.00047800	1.20160300
O	1.51171200	2.41778200	-1.13955000
O	1.51625800	-2.41508800	-1.14026600

O	2.11976000	0.00096800	2.04182400
H	-1.36388500	-1.35997000	2.05685400
C	-1.55080000	-0.71861500	1.19916600
C	-1.85097400	-1.15659000	-0.12732600
C	-1.55144300	0.71590800	1.19968300
H	-1.92634400	-2.18963900	-0.45840800
C	-2.03706000	-0.00076200	-0.94455000
C	-1.85200400	1.15459100	-0.12648600
H	-1.36495800	1.35682800	2.05778800
H	-2.27202900	-0.00050100	-2.00617100
H	-1.92812600	2.18789700	-0.45660000
H	0.42953900	0.00098300	-1.67648400

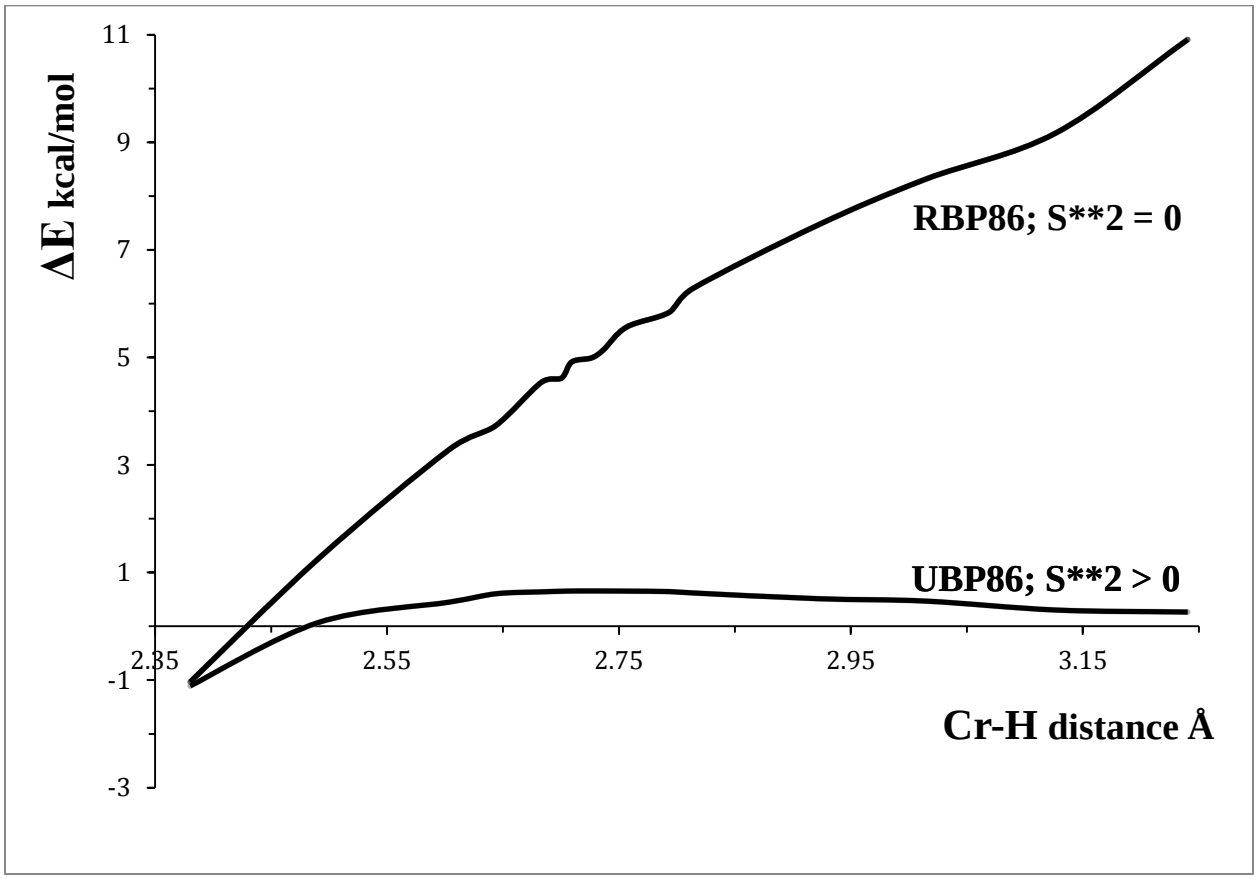


Figure S8. Total {$CpCr(CO)_3$–H_2–$CpCr(CO)_3$} energy in kcal/mol as a Function of Cr-H bond Distance (Å) for homolytic mechanim: RBP86/6-311++G** close shell,(S**2=0); UBP86/6-311++G** open shell (S**2>0). The energy of all curves has been aligned to the total energy of the initial compounds.

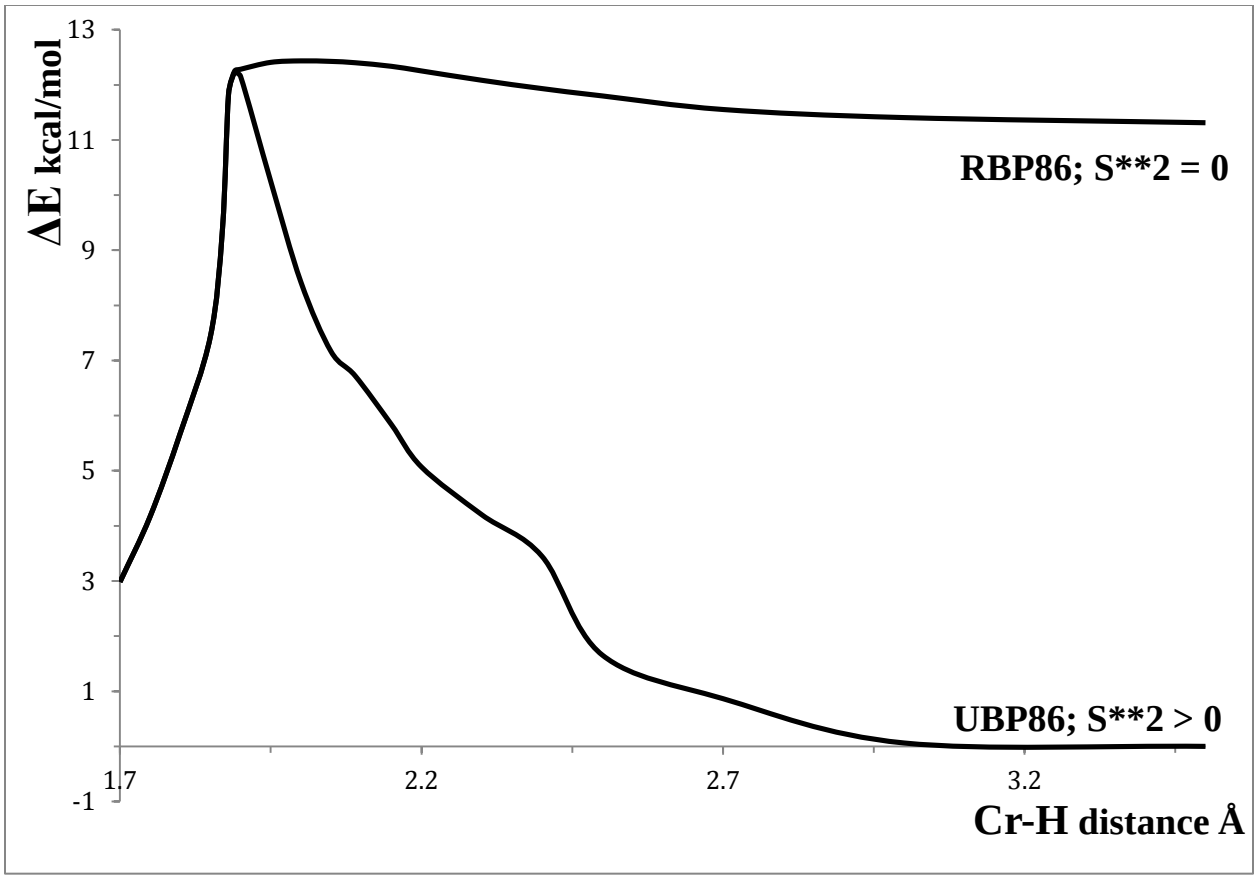


Figure S9. Total{$CpCr(CO)_3$ –H- $CpCr(CO)_3$} Energy in Kcal/mol as a Function of Cr-H bond Distance (Å) for heterolytic mechanim: RBP86/6-311++G** close shell,(S**2=0); UBP86/6-311++G** open shell (S**2>0). The energy of all curves has been aligned to the total energy of the initial compounds. Starting with distances of about 2.2 Å and longer, the S**2 parameter decreases dramatically from about 0.800-0.900 to 0.077 at the maximum point of the S**2>0 curve corresponding to 1.89 Å distance. This is due to the increase of the exchange interaction of hydrogen molecular orbitals with $CpCr(CO)_3$ radical-molecular orbitals. The hydride formation starts immediately after the transition state corresponding to decreasing Cr-H distance with both curves having S**2=0.

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