Electronic Supplementary Information for:

Revisiting the structure and properties of mid-valent monopentamethylcyclopentadienylchromium complexes

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Table S1. Experimental Data for the X-ray Diffraction Studies on **2**–**5**.

	2	**3**·2C_6H_5F	**4**	**5**
Formula	$C_{32}H_{40}Cl_2Cr_2N_2$	$C_{44}H_{52}Cl_2Cr_2F_2N_2$	$C_{40}H_{64}Cr_4$	$C_{17}H_{23}Cr$
M_r	627.56	821.77	752.91	279.35
T [K]	150(2)	150(2)	150(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	orthorhombic	triclinic	orthorhombic
space group	*P*–1	*Pbca*	*P*–1	*Pnma*
a [Å]; α [º]	8.863(1); 76.80(1)	11.895(1)	10.644(1); 83.35(1)	10.578(1)
b [Å]; β [º]	9.910(1); 67.60(1)	17.283(1)	10.847(1); 82.63(1)	12.283(1)
c [Å]; γ [º]	9.933(1); 67.74(1)	19.370(2)	17.792(1); 67.66(1)	10.954(1)
V [Å^3]	742.9(1)	3982.1(6)	1879.3(2)	1423.2(1)
Z	1	4	2	4
ρ_{calcd} [g cm^{-3}]	1.403	1.371	1.331	1.304
$\mu_{MoK\alpha}$ [mm^{-1}]	0.935	0.723	1.151	0.784
F(000)	328	1720	800	596
crystal size [mm^3]	0.05×0.08×0.18	0.11×0.11×0.20	0.17×0.24×0.25	0.17×0.24×0.31
θ range [deg]	3.00 to 27.51	2.71 to 26.43	2.04 to 27.56	3.32 to 27.51
index ranges	–11 to 11, –12 to 12, –12 to 12	–14 to 14, –21 to 21, –24 to 24	–13 to 13, –14 to 14, –23 to 23	–13 to 13, –15 to 15, –14 to 14
Reflections collected	25589	112624	77282	59888
Unique data	3403 [R_{int} = 0.077]	4088 [R_{int} = 0.145]	8644 [R_{int} = 0.042]	1705 [R_{int} = 0.043]
obsd data [I>2σ(I)]	2694	2988	7947	1588
Goodness-of-fit on F^2	1.263	1.040	1.290	1.259
final R[a] indices [I>2σ(I)]	R1 = 0.069, wR2 = 0.217	R1 = 0.054, wR2 = 0.146	R1 = 0.058, wR2 = 0.167	R1 = 0.027, wR2 = 0.093
R[a] indices (all data)	R1 = 0.084, wR2 = 0.224	R1 = 0.081, wR2 = 0.170	R1 = 0.070, wR2 = 0.186	R1 = 0.042, wR2 = 0.118
largest diff. peak/hole [e Å^{-3}]	1.274/–0.515	2.164/–0.726	0.877/–1.710	0.544/–0.814

[a] $R1 = \Sigma||F_0|-|F_c|| / [\Sigma|F_0|]$, $wR2 = \{[\Sigma w(F_0^2-F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

Table S2. Experimental Data for the X-ray Diffraction Studies on **6**, **7**, **9**, and **10**.

	6	**7**	**9**·1.5C_7H_8	**10**·C_6H_6
Formula	$C_{20}H_{38}B_2Cr_2$	$C_{10}H_{23}B_2Cr$	$C_{50.5}H_{88}Al_4Cr_4$	$C_{66}H_{112}Al_4Cr_6$
M_r	404.12	216.90	1011.12	1325.47
T [K]	150(2)	150(2)	150(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pnnm$
a [Å]; α [º]	11.149(1)	8.346(1)	14.146(1)	14.025(1)
b [Å]; β [º]	13.752(1); 101.49(1)	13.551(1); 109.87(1)	21.574(1); 103.10(1)	13.961(1)
c [Å]; γ [º]	14.763(1)	12.171(1)	18.360(1)	17.422(1)
V [Å^3]	2218.1(2)	1294.6(1)	5457.3(3)	3411.3(3)
Z	4	4	4	2
ρ_{calcd} [g cm^{-3}]	1.210	1.113	1.231	1.290
$\mu_{MoK\alpha}$ [mm^{-1}]	0.979	0.841	0.870	1.010
F(000)	864	468	2156	1408
crystal size [mm^3]	0.10×0.16×0.26	0.09×0.17×0.21	0.21×0.25×0.31	0.12×0.18×0.19
θ range [deg)]	2.04 to 26.45	2.33 to 27.52	1.90 to 27.50	1.86 to 27.50
index ranges	–13 to 13, –17 to 17, –18 to 18	–10 to 10, –17 to 17, –15 to 15	–18 to 18, –28 to 28, –21 to 23	–18 to 18, –18 to 18, –21 to 22
Reflections collected	59339	36653	152986	95713
Unique data	4542 [R_{int} = 0.082]	2966 [R_{int} = 0.038]	12518 [R_{int} = 0.049]	4056 [R_{int} = 0.036]
obsd data [I>2σ(I)]	3648	2702	10934	3838
Goodness-of-fit on F^2	1.142	1.193	1.140	1.390
final R[a] indices [I>2σ(I)]	R1 = 0.044, wR2 = 0.117	R1 = 0.028, wR2 = 0.083	R1 = 0.037, wR2 = 0.123	R1 = 0.029, wR2 = 0.103
R^a indices (all data)	R1 = 0.067, wR2 = 0.137	R1 = 0.033, wR2 = 0.096	R1 = 0.048, wR2 = 0.138	R1 = 0.046, wR2 = 0.137
largest diff. peak/hole [e Å^{-3}]	0.526/–1.193	0.563/–0.469	0.833/–0.758	0.900/–1.414

[a] $R1 = \Sigma||F_0|-|F_c|| / [\Sigma|F_0|]$, $wR2 = \{[\Sigma w(F_0^2-F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

Table S3. Selected Lengths (Å) and Angles (º) for **4**.

Cr(1)–H(2)	2.07(5)	Cr(1)–H(3)	1.72(6)
Cr(1)–H(4)	1.79(6)	Cr(2)–H(1)	1.93(4)
Cr(2)–H(3)	1.85(6)	Cr(2)–H(4)	1.95(6)
Cr(3)–H(1)	1.80(4)	Cr(3)–H(2)	1.91(5)
Cr(3)–H(4)	1.74(6)	Cr(4)–H(1)	1.76(4)
Cr(4)–H(2)	1.88(5)	Cr(4)–H(3)	1.78(6)
Cr(1)···Cr(2)	2.509(1)	Cr(1)···Cr(3)	2.753(1)
Cr(1)···Cr(4)	2.586(1)	Cr(2)···Cr(3)	2.591(1)
Cr(2)···Cr(4)	2.745(1)	Cr(3)···Cr(4)	2.532(1)
Cr(1)–Cm(1)[a]	1.924	Cr(2)–Cm(2)[a]	1.922
Cr(3)–Cm(3)[a]	1.918	Cr(4)–Cm(4)[a]	1.917
H(2)–Cr(1)–H(3)	89(2)	H(2)–Cr(1)–H(4)	80(2)
H(3)–Cr(1)–H(4)	96(3)	H(1)–Cr(2)–H(3)	79(2)
H(1)–Cr(2)–H(4)	86(2)	H(3)–Cr(2)–H(4)	87(3)
H(1)–Cr(3)–H(2)	92(2)	H(1)–Cr(3)–H(4)	96(2)
H(2)–Cr(3)–H(4)	86(2)	H(1)–Cr(4)–H(2)	94(2)
H(1)–Cr(4)–H(3)	86(2)	H(2)–Cr(4)–H(3)	94(2)
Cr(2)–H(1)–Cr(3)	88(2)	Cr(2)–H(1)–Cr(4)	96(2)
Cr(3)–H(1)–Cr(4)	90(2)	Cr(1)–H(2)–Cr(3)	88(2)
Cr(1)–H(2)–Cr(4)	82(2)	Cr(3)–H(2)–Cr(4)	84(2)
Cr(1)–H(3)–Cr(2)	89(3)	Cr(1)–H(3)–Cr(4)	95(3)
Cr(2)–H(3)–Cr(4)	98(3)	Cr(1)–H(4)–Cr(2)	84(3)
Cr(1)–H(4)–Cr(3)	103(3)	Cr(2)–H(4)–Cr(3)	89(3)
Cr(2)–Cr(1)–Cr(3)	58.8(1)	Cr(2)–Cr(1)–Cr(4)	65.2(1)
Cr(3)–Cr(1)–Cr(4)	56.5(1)	Cr(1)–Cr(2) –Cr(3)	65.3(1)
Cr(1)–Cr(2) –Cr(4)	58.8(1)	Cr(3)–Cr(2)–Cr(4)	56.6(1)
Cr(1)–Cr(3)–Cr(2)	55.9(1)	Cr(1)–Cr(3)–Cr(4)	58.4(1)
Cr(2)–Cr(3)–Cr(4)	64.8(1)	Cr(1)–Cr(4)–Cr(2)	56.1(1)
Cr(1)–Cr(4)–Cr(3)	65.1(1)	Cr(2)–Cr(4)–Cr(3)	58.7(1)

[a] Cm(1) = Centroid of the η^5-C_5Me_5 ring linked to Cr(1). Cm(2) = Centroid of the η^5-C_5Me_5 ring linked to Cr(2). Cm(3) = Centroid of the η^5-C_5Me_5 ring linked to Cr(3). Cm(4) = Centroid of the η^5-C_5Me_5 ring linked to Cr(4).

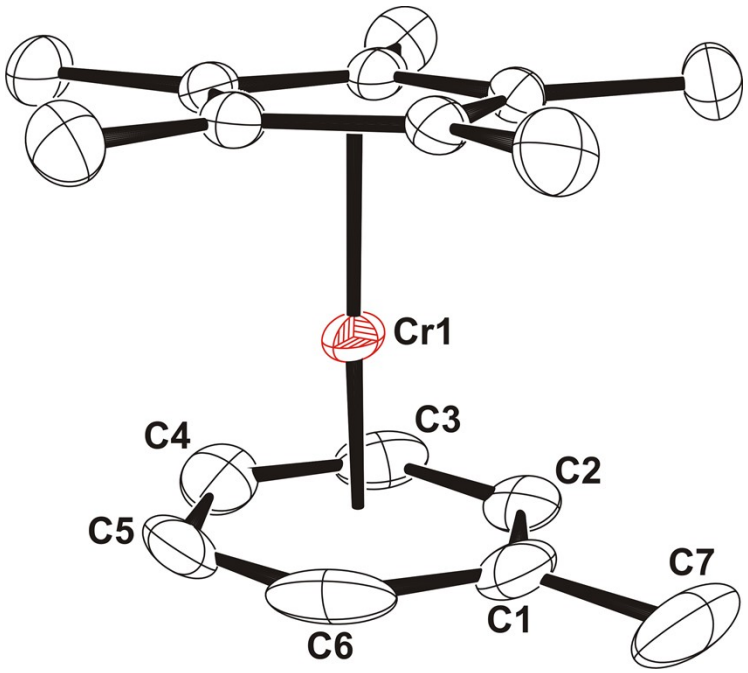

Figure S1. Perspective view of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Selected Lengths (Å) and Angles (º) for **5**.

Cr(1)–C(1)	2.101(2)	Cr(1)–C(2)	2.201(7)
Cr(1)–C(3)	2.207(4)	Cr(1)–C(4)	2.111(8)
Cr(1)–C(5)	2.036(7)	Cr(1)–C(6)	1.992(8)
Cr(1)–Cm(1)[a]	1.569	Cr(1)–Cm(2)[a]	1.787
C(1)–Cr(1)–Cm(2)[a]	140.2	C(2)–Cr(1)–Cm(2)[a]	135.5
C(3)–Cr(1)–Cm(2)[a]	132.3	C(4)–Cr(1)–Cm(2)[a]	134.3
C(5)–Cr(1)–Cm(2)[a]	139.4	C(6)–Cr(1)–Cm(2)[a]	144.2
Cm(1)–Cr(1)–Cm(2)[a]	171.3		

[a] Cm(1) = Centroid of the η^6-C_6H_5Me ring. Cm(2) = Centroid of the η^5-C_5Me_5 ring.

Table S5. Selected Lengths (Å) and Angles (º) for **6**.

Cr(1)–Cr(2)	2.586(1)	Cr(1)···B(1)	2.368(4)
Cr(1)···B(2)	2.365(3)	Cr(2)···B(1)	2.369(4)
Cr(2)···B(2)	2.370(3)	Cr(1)–H(11)	2.12(3)
Cr(1)–H(13)	1.86(4)	Cr(1)–H(21)	2.06(4)
Cr(1)–H(23)	1.96(3)	Cr(2)–H(11)	2.07(4)
Cr(2)–H(12)	1.95(3)	Cr(2)–H(21)	1.97(4)
Cr(2)–H(22)	2.01(3)	Cr(1)–Cm(1)[a]	1.897
Cr(2)–Cm(2)[a]	1.904		
H(11)–Cr(1)–H(13)	56(1)	H(11)–Cr(1)–H(21)	99(2)
H(11)–Cr(1)–H(23)	117(1)	H(13)–Cr(1)–H(21)	113(2)
H(13)–Cr(1)–H(23)	81(2)	H(21)–Cr(1)–H(23)	55(2)
H(11)–Cr(2)–H(12)	56(1)	H(11)–Cr(2)–H(21)	104(2)
H(11)–Cr(2)–H(22)	114(1)	H(12)–Cr(2)–H(21)	113(2)
H(12)–Cr(2)–H(22)	76(1)	H(21)–Cr(2)–H(22)	55(1)
Cr(1)–H(11)–Cr(2)	76(1)	Cr(1)–H(21)–Cr(2)	80(1)
Cr(1)–H(11)–B(1)	89(2)	Cr(2)–H(11)–B(1)	92(2)
Cr(1)–H(13)–B(1)	99(2)	Cr(2)–H(12)–B(1)	95(2)
Cr(1)–H(21)–B(2)	91(2)	Cr(2)–H(21)–B(2)	96(2)
Cr(1)–H(23)–B(2)	96(2)	Cr(2)–H(22)–B(2)	94(2)
Cr(1)–B(1)–Cr(2)	66.2(1)	Cr(1)–B(2)–Cr(2)	66.2(1)

[a] Cm(1) = Centroid of the η^5-C_5Me_5 ring linked to Cr(1). Cm(2) = Centroid of the η^5-C_5Me_5 ring linked to Cr(2).

Table S6. Selected Lengths (Å) and Angles (º) for **7**.

Cr(1)···B(1)	2.312(2)	Cr(1)···B(2)	2.322(2)
Cr(1)–H(11)	1.82(3)	Cr(1)–H(12)	1.86(3)
Cr(1)–H(21)	1.91(3)	Cr(1)–H(22)	1.89(3)
Cr(1)–Cm(1)[a]	1.838		
H(11)–Cr(1)–H(12)	62(1)	H(11)–Cr(1)–H(21)	82(1)
H(11)–Cr(1)–H(22)	112(1)	H(12)–Cr(1)–H(21)	114(1)
H(12)–Cr(1)–H(22)	85(1)	H(21)–Cr(1)–H(22)	59(1)
Cr(1)–H(11)–B(1)	97(1)	Cr(1)–H(12)–B(1)	96(2)
Cr(2)–H(21)–B(2)	95(1)	Cr(2)–H(22)–B(2)	98(2)

[a] Cm(1) = Centroid of the η^5-C_5Me_5 ring.

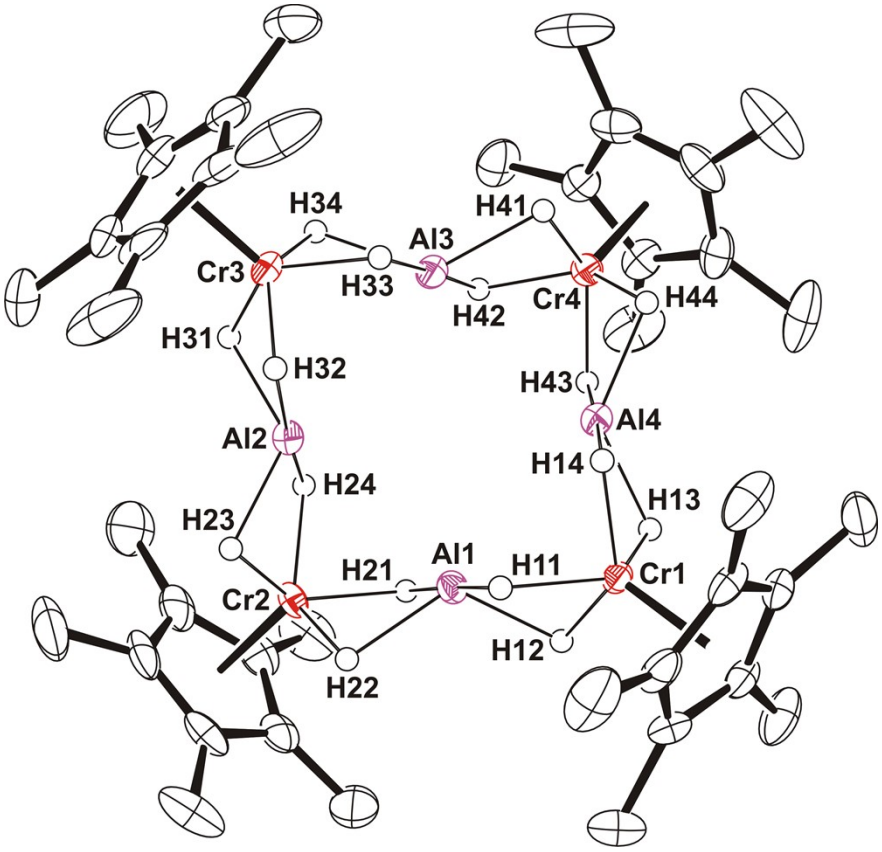

Figure S2. Perspective view of **9** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

Table S7. Selected Lengths (Å) and Angles (º) for **9**.

Cr(1)–H av.	1.65(6)	Cr(2)–H av.	1.68(4)
Cr(3)–H av.	1.59(4)	Cr(4)–H av.	1.60(2)
Al(1)–H av.	1.71(3)	Al(2)–H av.	1.71(3)
Al(3)–H av.	1.72(2)	Al(4)–H av.	1.72(2)
Cr(1)–Al(1)	2.374(1)	Cr(1)–Al(4)	2.376(1)
Cr(2)–Al(1)	2.375(1)	Cr(2)–Al(2)	2.378(1)
Cr(3)–Al(2)	2.374(1)	Cr(3)–Al(3)	2.374(1)
Cr(4)–Al(3)	2.380(1)	Cr(4)–Al(4)	2.374(1)
Cr(1)–Cm(1)[a]	1.807	Cr(2)–Cm(2)[a]	1.806
Cr(3)–Cm(3)[a]	1.811	Cr(4)–Cm(4)[a]	1.808
Cr(1)···Cr(2)	4.749(1)	Cr(1)···Cr(3)	6.209(1)
Cr(1)···Cr(4)	4.747(1)	Cr(2)···Cr(3)	4.746(1)
Cr(2)···Cr(4)	6.119(1)	Cr(3)···Cr(4)	4.752(1)
Al(1)···Al(2)	3.002(1)	Al(1)···Al(4)	2.997(1)
Al(2)···Al(3)	2.978(1)	Al(3)···Al(4)	3.000(1)
Cr(1)–Al(1)–Cr(2)	178.7(1)	Cr(2)–Al(2)–Cr(3)	174.4(1)
Cr(3)–Al(3)–Cr(4)	176.4(1)	Cr(1)–Al(4)–Cr(4)	176.4(1)
Al(1)–Cr(1)–Al(4)	78.2(1)	Al(1)–Cr(2)–Al(2)	78.4(1)
Al(2)–Cr(3)–Al(3)	77.7(1)	Al(3)–Cr(4)–Al(4)	78.3(1)
H–Cr(1)–H	73(2)-134(2)	H–Cr(2)–H	73(2)-136(2)
H–Cr(3)–H	72(2)-135(2)	H–Cr(4)–H	72(2)-134(2)
H–Al(1)–H	81(2)-178(2)	H–Al(2)–H	79(2)-172(2)
H–Al(3)–H	80(2)-178(2)	H–Al(4)–H	80(2)-178(1)
Cr–H–Al av.	90(2)		

[a] Cm(1) = Centroid of the η^5-C_5Me_5 ring linked to Cr(1). Cm(2) = Centroid of the η^5-C_5Me_5 ring linked to Cr(2). Cm(3) = Centroid of the η^5-C_5Me_5 ring linked to Cr(3). Cm(4) = Centroid of the η^5-C_5Me_5 ring linked to Cr(4).

Table S8. Averaged experimental vs. calculated lengths (Å) and angles (º) for complex **9**.

	X-ray	**DFT**
Cr–Al	2.376(2)	2.386(3)
Al···Al	2.994(11)	2.992(2)
Cr–H	1.63(5)	1.66(1)
Al–H	1.72(2)	1.79(1)
Cr–Al–Cr	176(2)	177.0(1)
Al–Cr–Al	78.2(3)	77.6(1)
H–Cr–H	72(2)-136(2)	74-138
H–Al–H	79(2)-178(2)	81-180
Cr–H–Al	90(2)	87(1)

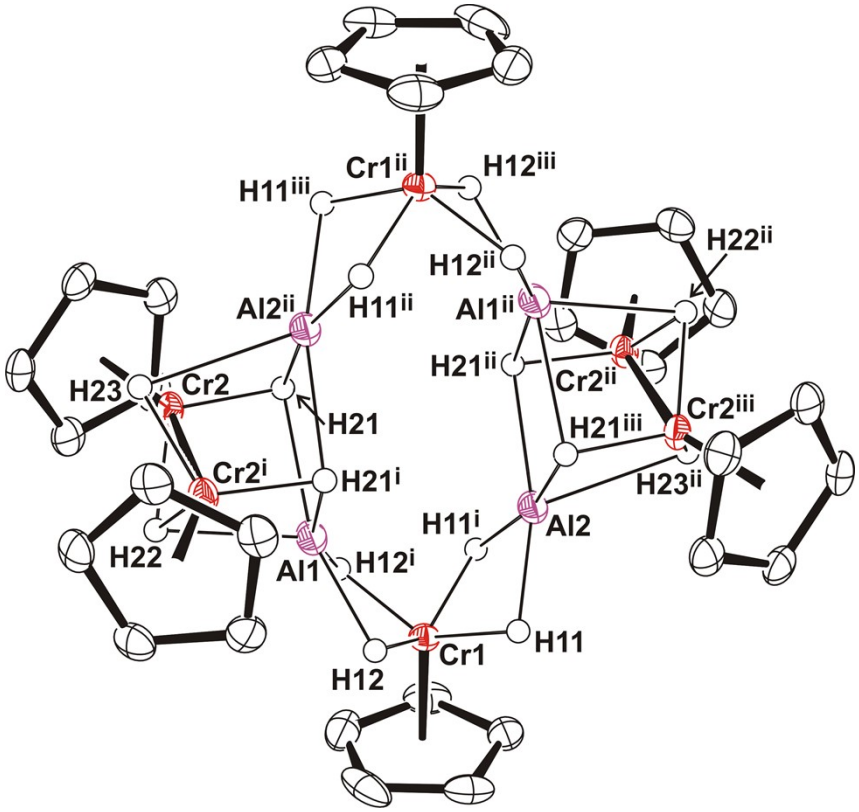

Figure S3. Perspective view of **10** with thermal ellipsoids at the 50% probability level. Methyl groups of the η^5-C_5Me_5 ligands are omitted for clarity. Symmetry code: (i) *x*, *y*, 1 – *z*; (ii) 1 – *x*, 1 – *y*, *z*; (iii) 1 – *x*, 1 – *y*, 1 – *z*.

Table S9. Selected Lengths (Å) and Angles (º) for **10**.

Cr(1)–H(11)	1.54(3)	Cr(1)–H(12)	1.62(3)
Cr(2)–H(21)	1.55(3)	Cr(2)–H(22)	1.65(3)
Cr(2)–H(23)	1.68(3)	Cr(2)–Cr(2)^{i}	2.324(1)
Al(1)–H(12)	1.71(3)	Al(1)–H(21)	1.97(3)
Al(1)–H(22)	2.24(4)	Al(2)–H(11)	1.72(3)
Al(2)–H(21)^{ii}	2.05(3)	Al(2)–H(23)^{ii}	2.12(4)
Cr(1)–Al(1)	2.387(1)	Cr(1)–Al(2)	2.394(1)
Cr(2)–Al(1)	2.531(1)	Cr(2)–Al(2)^{ii}	2.534(1)
Cr(1)–Cm(1)^{a}	1.812	Cr(2)–Cm(2)^{a}	1.837
H(11)–Cr(1)–H(12)	77(2)	H(11)–Cr(1)–H(12)^{i}	134(1)
H(11)–Cr(1)–H(11)^{i}	87(2)	H(12)–Cr(1)–H(12)^{i}	85(1)
H(21)–Cr(2)–H(22)	111(2)	H(21)–Cr(2)–H(23)	110(2)
H(22)–Cr(2)–H(23)	81(2)	H(21)–Cr(2)–Cr(2)^{i}	94(1)
H(22)–Cr(2)–Cr(2)^{i}	45(1)	H(23)–Cr(2)–Cr(2)^{i}	46(1)
H(12)–Al(1)–H(12)^{i}	79(1)	H(12)–Al(1)–H(21)	165(1)
H(12)–Al(1)–H(21)^{i}	99(1)	H(21)–Al(1)–H(21)^{i}	80(1)
H(12)–Al(1)–H(22)	117(1)	H(21)–Al(1)–H(22)	78(1)
H(11)–Al(2)–H(11)^{i}	76(1)	H(11)–Al(2)–H(21)^{ii}	162(1)
H(11)–Al(2)–H(21)^{iii}	101(1)	H(21)^{ii}–Al(2)–H(21)^{iii}	76(1)
H(11)–Al(2)–H(23)^{ii}	119(1)	H(21)^{ii}–Al(2)–H(23)^{ii}	79(1)
Cr(1)–H(11)–Al(2)	94(1)	Cr(1)–H(12)–Al(1)	92(1)
Cr(2)–H(21)–Al(1)	91(1)	Cr(2)–H(21)–Al(2)^{ii}	88(1)
Al(1)–H(21)–Al(2)^{ii}	102(1)	Cr(2)–H(22)–Al(1)	80(1)
Cr(2)–H(22)–Cr(2)^{i}	90(1)	Cr(2)–H(23)–Cr(2)^{i}	88(1)
Cr(2)–H(23)–Al(2)^{ii}	83(1)	Al(1)–Cr(1)–Al(2)	79.4(1)

^{a} Cm(1) = Centroid of the η^5-C_5Me_5 ring linked to Cr(1). Cm(2) = Centroid of the η^5-C_5Me_5 ring linked to Cr(2). Symmetry code: (i) x, y, $1 - z$; (ii) $1 - x$, $1 - y$, z; (iii) $1 - x$, $1 - y$, $1 - z$.

Table S10. Experimental vs. calculated lengths (Å) and angles (º) for complex **10**.

	X-ray	**DFT**
Cr(1)–H av.	1.58(5)	1.65(1)
Cr(2)–Cr(2)^{i}	2.324(1)	2.307
Cr(2)–H(21)	1.55(3)	1.66
Cr(2)–H(22)/H(23) av.	1.66(2)	1.72(1)
Al–H(Cr(1)) av.	1.72(1)	1.81(1)
Al–H(21) av.	2.01(4)	2.02(2)
Al–H(22)/H(23) av.	2.18(7)	2.30(1)
Cr(1)–Al av.	2.390(5)	2.424(8)
Cr(2)–Al av.	2.532(2)	2.552(1)
H–Cr(1)–H(*cis*) av.	82(5)	82(9)
H–Cr(1)–H(*trans*) av.	134(1)	138(1)
H(21)–Cr(2)–H(22)/H(23) av.	110(1)	114(1)
H(22)–Cr(2)–H(23)	81(2)	81
H(21)–Cr(2)–Cr(2)^{i}	94(1)	94
H(22)/H(23)–Cr(2)–Cr(2)^{i} av.	46(1)	48(1)
H–Al–H	76(1)-165(1)	77-162
Cr–H–Cr av.	89(1)	84(1)
Al–H–Al	102(1)	103
Cr–H–Al	80(1)-94(1)	77-89
Al(1)–Cr(1)–Al(2)	79.4(1)	80.6

Symmetry code: (i) x, y, $1 - z$.

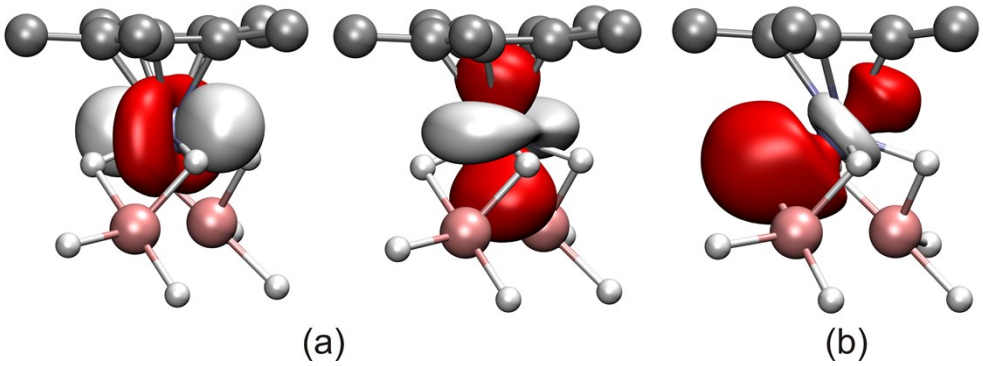

Figure S4. Computed NBO orbitals for compound **9**, (a) doubly occupied Cr orbitals, (b) one of the four Cr–H bonding orbital (color code: C = gray, H = white, Cr = iceblue, Al = pink). Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

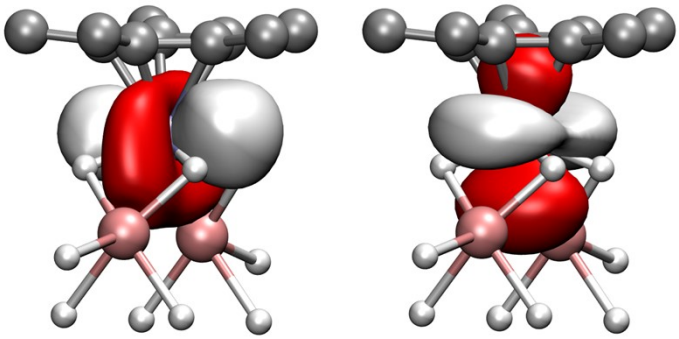

Figure S5. Computed NBO doubly occupied orbitals for the isolated Cr atoms in compound **10**. Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

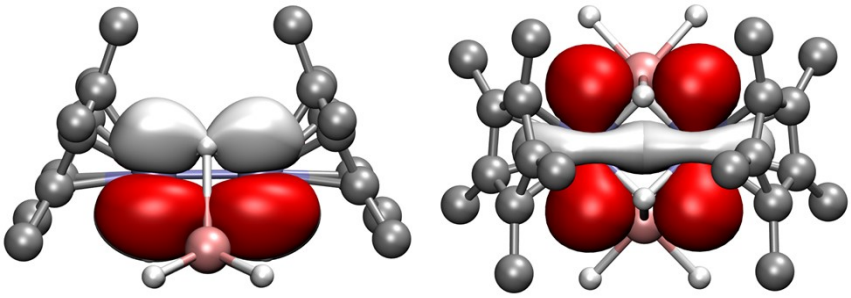

Figure S6. Computed semioccupied Cr NBO orbitals for the dinuclear Cr units in compound **10**. Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

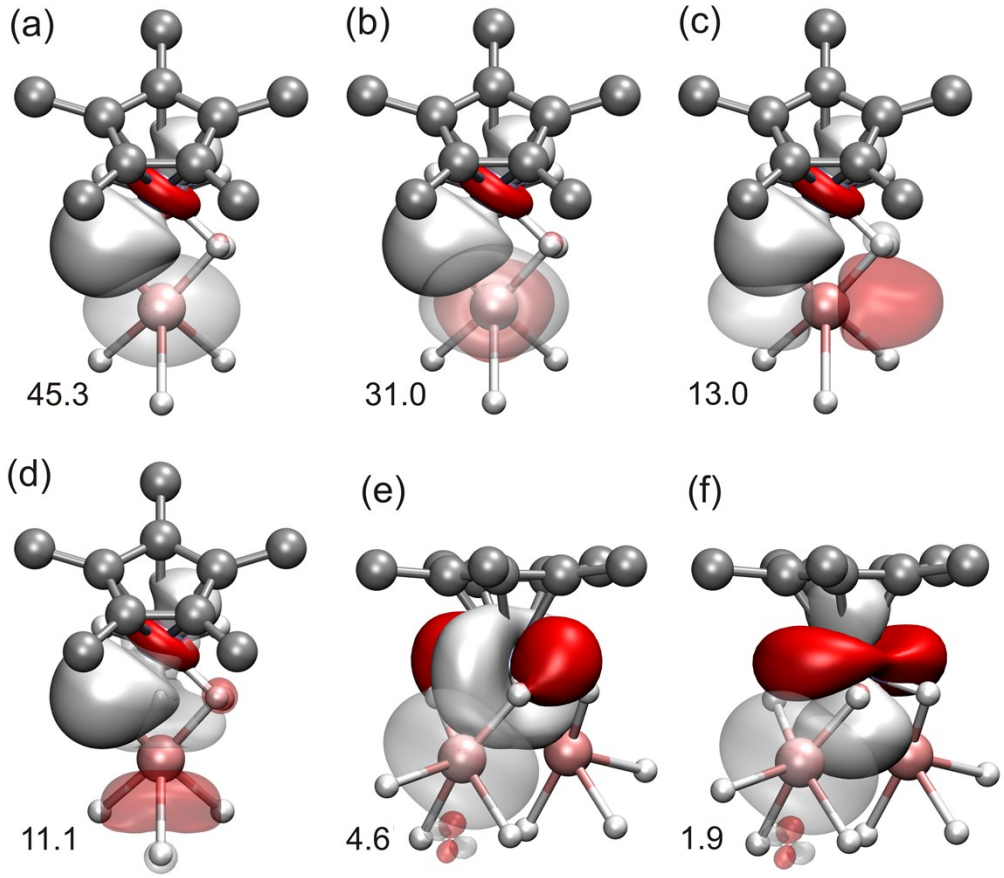

Figure S7. Donor/acceptor (a-d) Cr–H→Al and (e-f) Cr→Al interactions within the mononuclear Cr units in compound **10**. Solid and transparent orbitals represent electron donor (full) and acceptor (empty) orbitals, respectively. The number near each representation corresponds to the NBO donor/acceptor stabilization energy in kcal/mol. Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

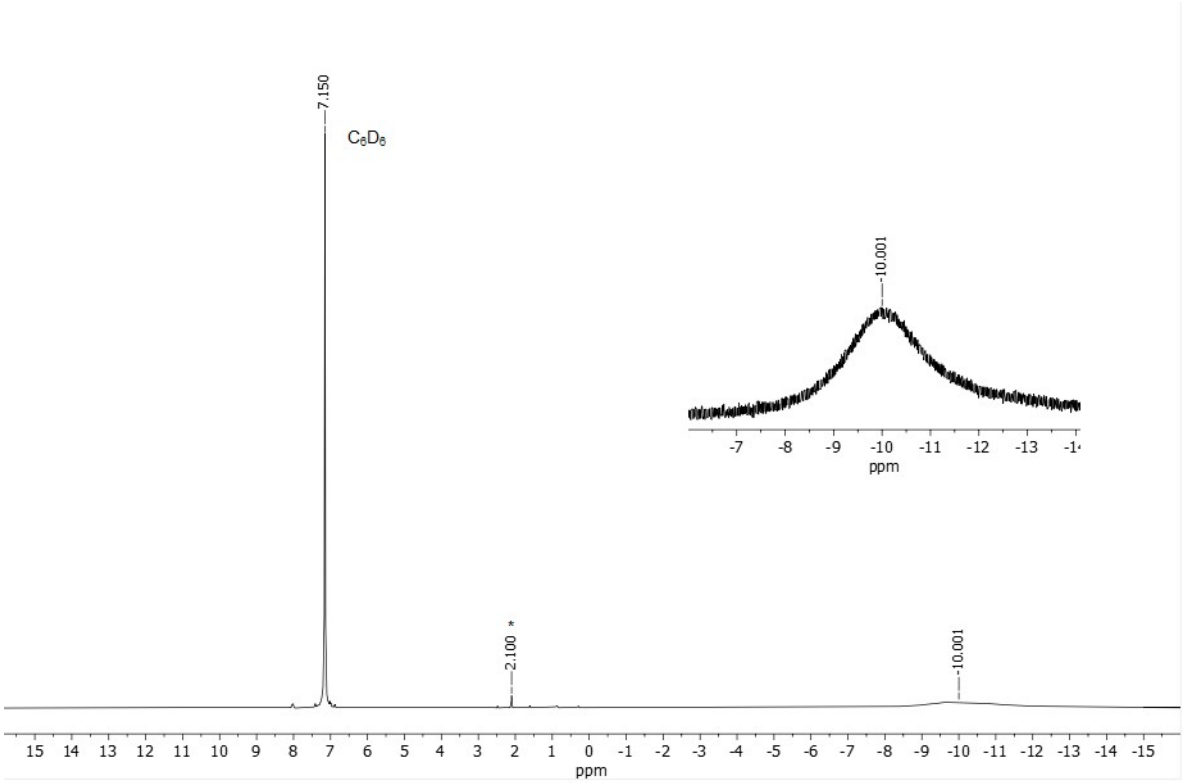

Figure S8. ^{1}H NMR spectrum (300 MHz, C_6D_6, 20 ºC) of [{CrCp*Cl(μ-NPh)}$_2$] (**2**). *Toluene.

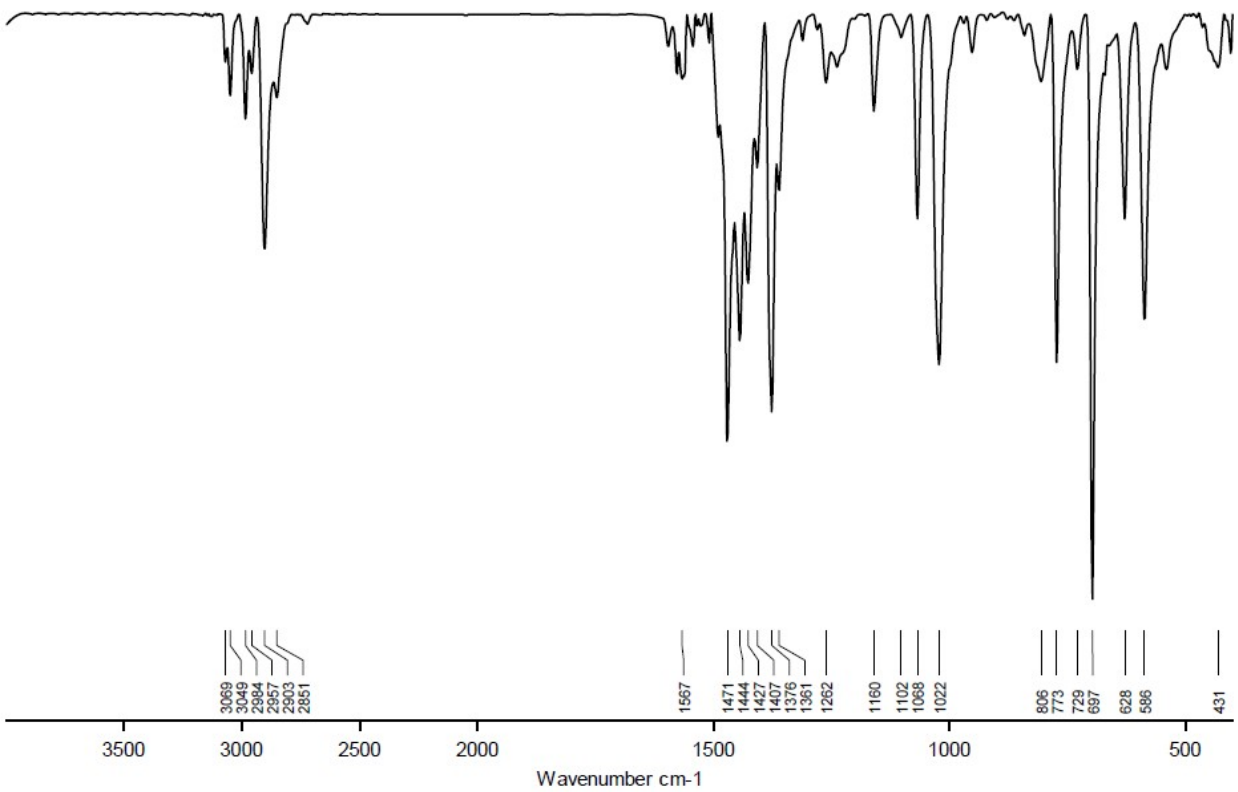

Figure S9. IR spectrum (KBr, cm^{-1}) of [{CrCp*Cl(μ-NPh)}$_2$] (**2**).

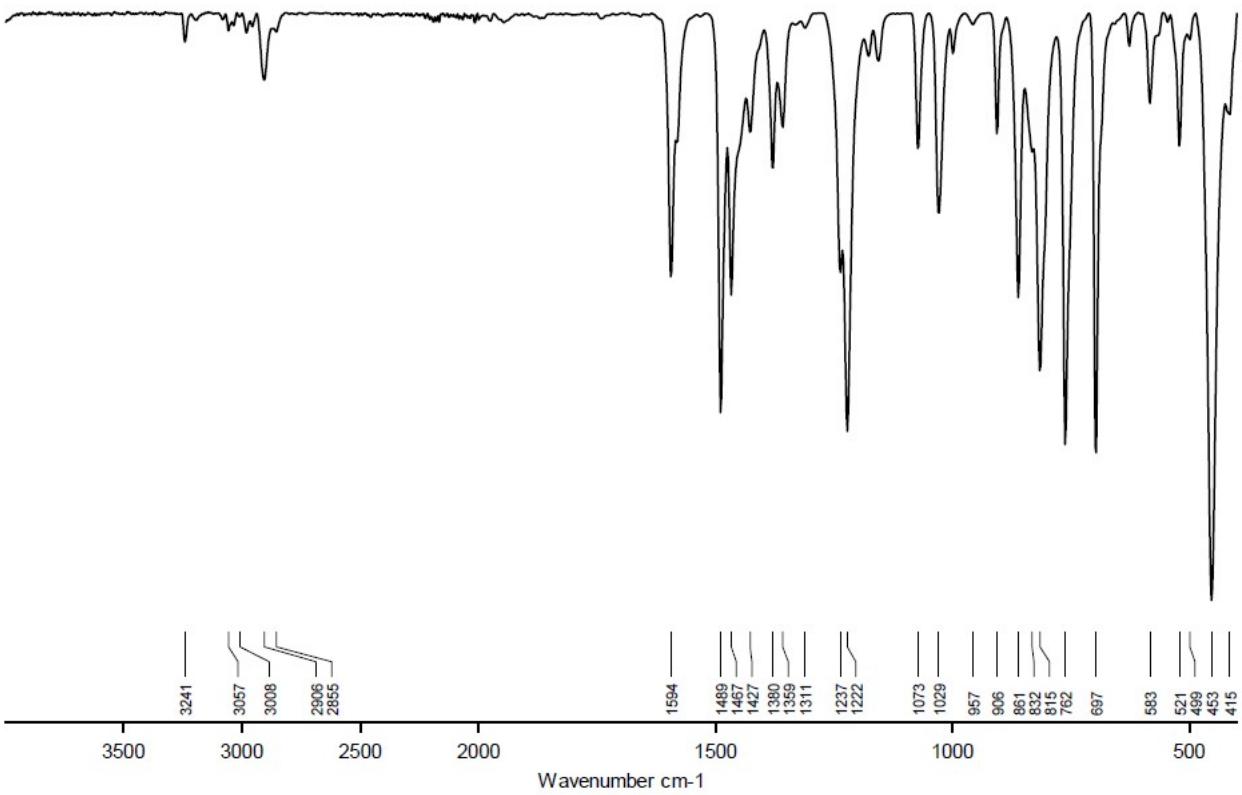

Figure S10. IR spectrum (ATR, cm^{-1}) of $[\{CrCp^*Cl(\mu\text{-}NHPh)\}_2]$ (**3**).

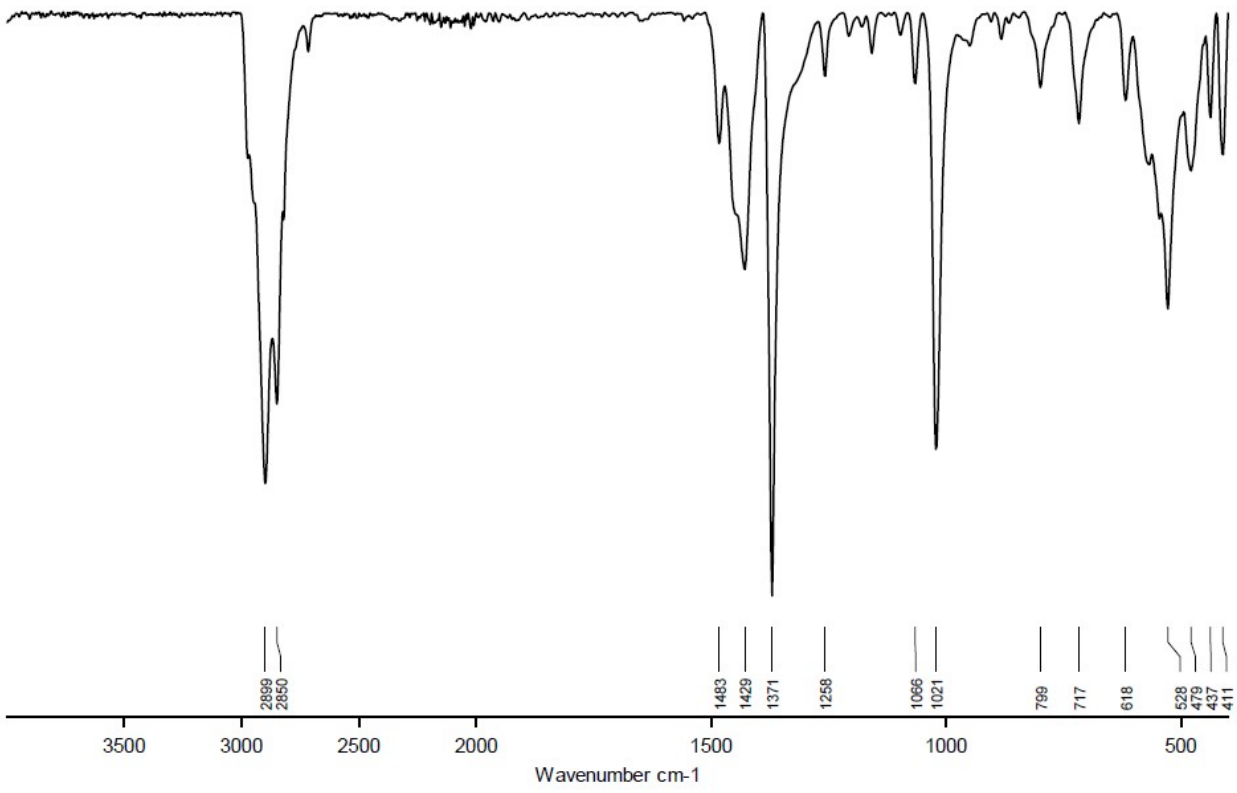

Figure S11. IR spectrum (ATR, cm^{-1}) of $[\{CrCp^*(\mu_3\text{-}H)\}_4]$ (**4**).

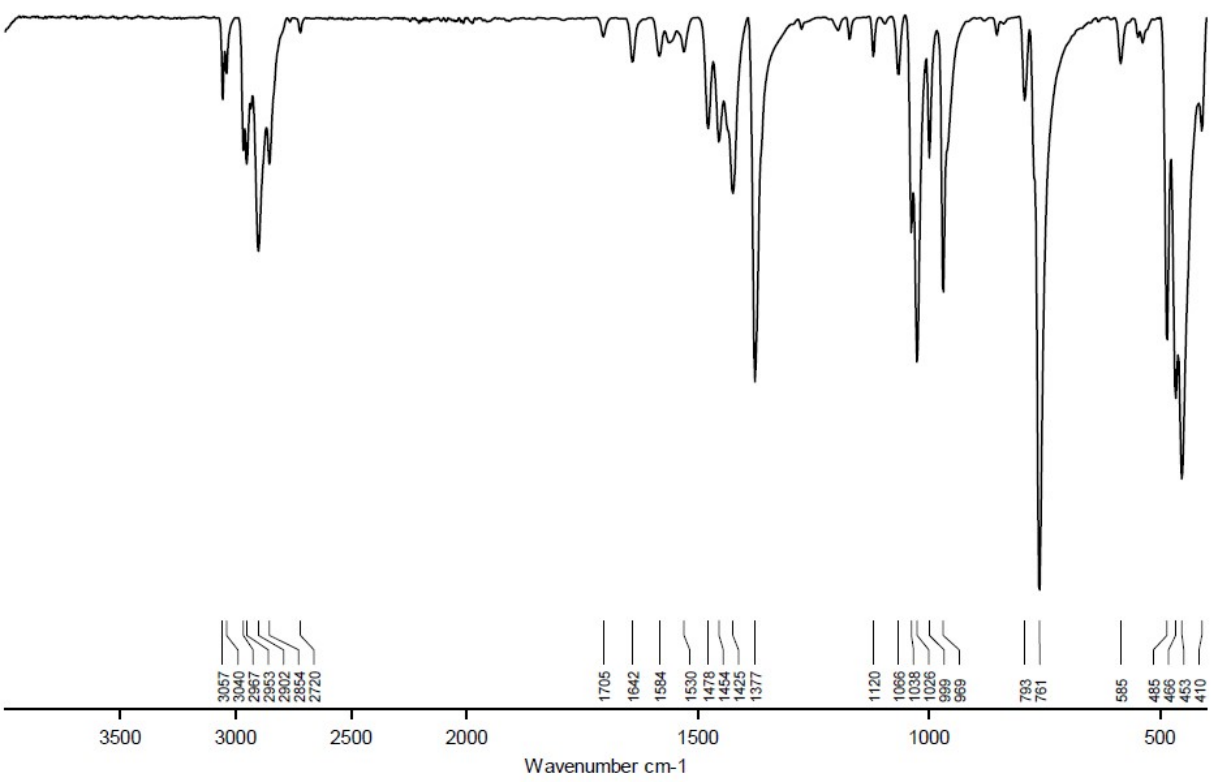

Figure S12. IR spectrum (ATR, cm^{-1}) of [CrCp*(η^6-C_6H_5Me)] (**5**).

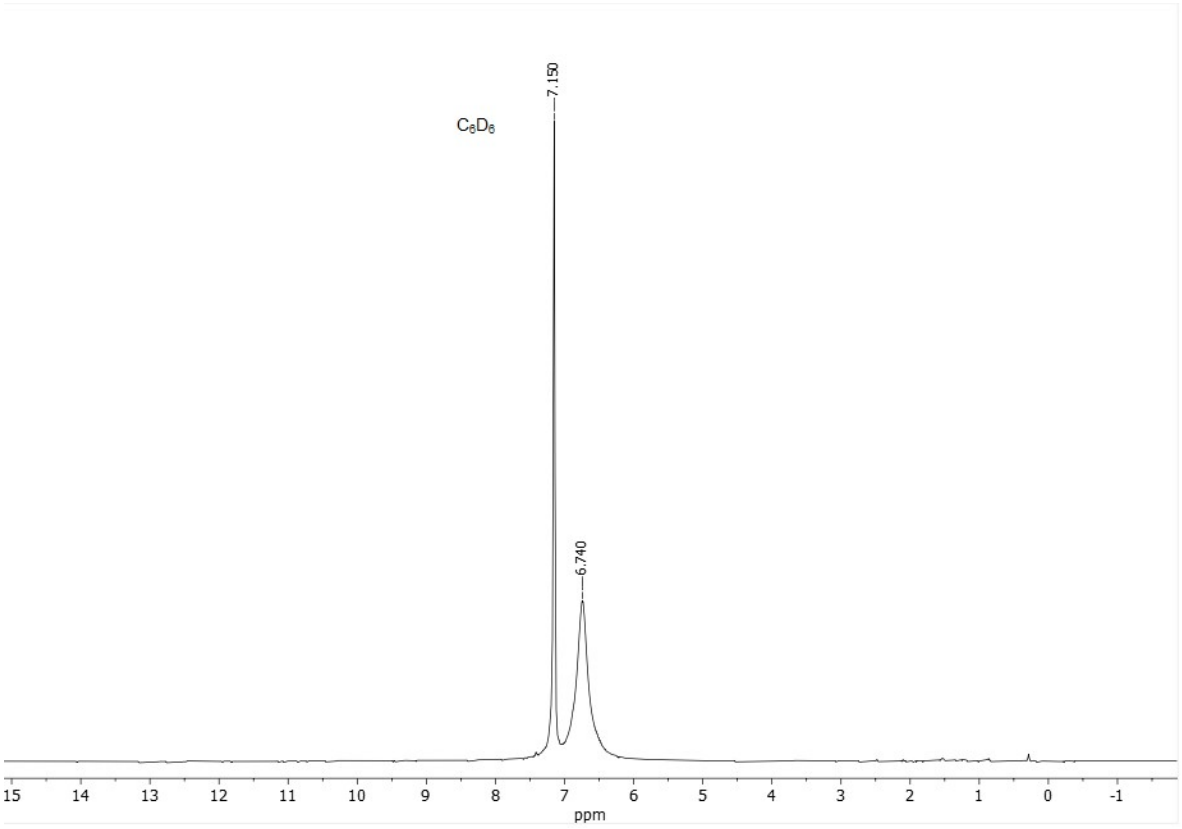

Figure S13. ^1H NMR spectrum (300 MHz, C_6D_6, 20 ºC) of [{CrCp*(μ-κ^3-BH_4)}$_2$] (**6**).

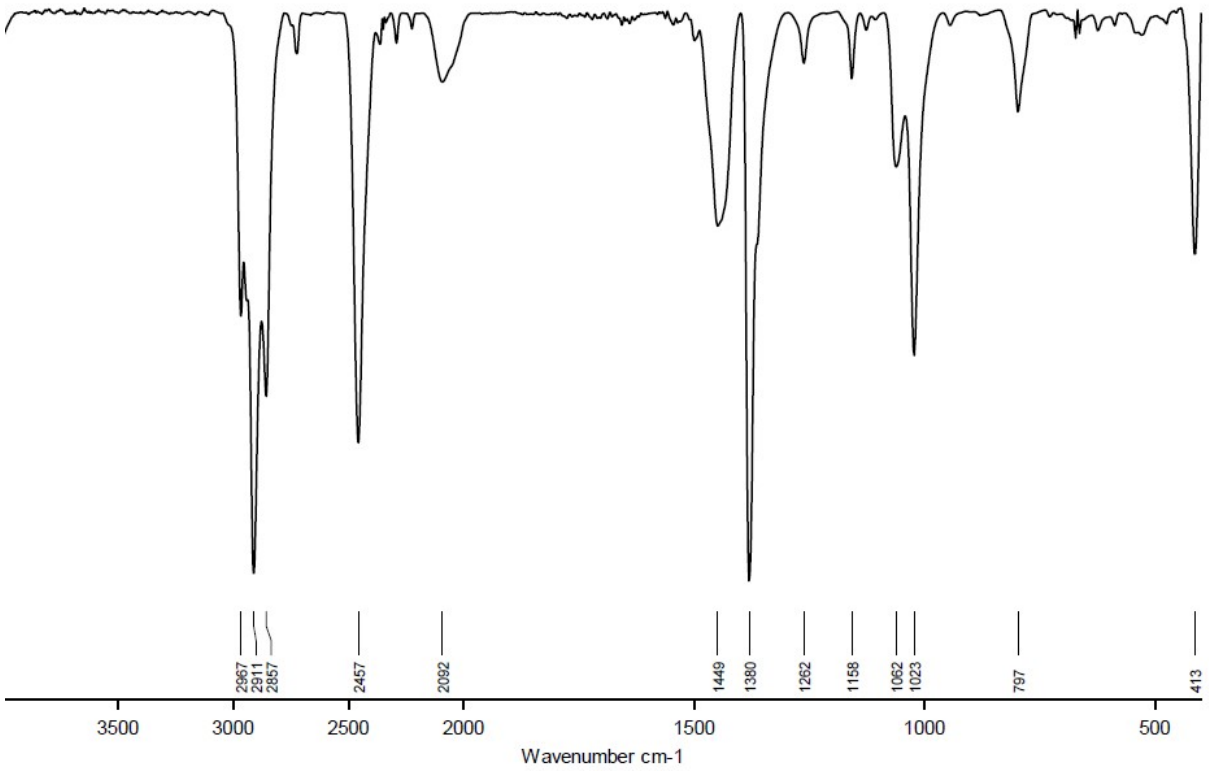

Figure S14. IR spectrum (ATR, cm^{-1}) of $[\{CrCp^*(\mu\text{-}\kappa^3\text{-}BH_4)\}_2]$ (**6**).

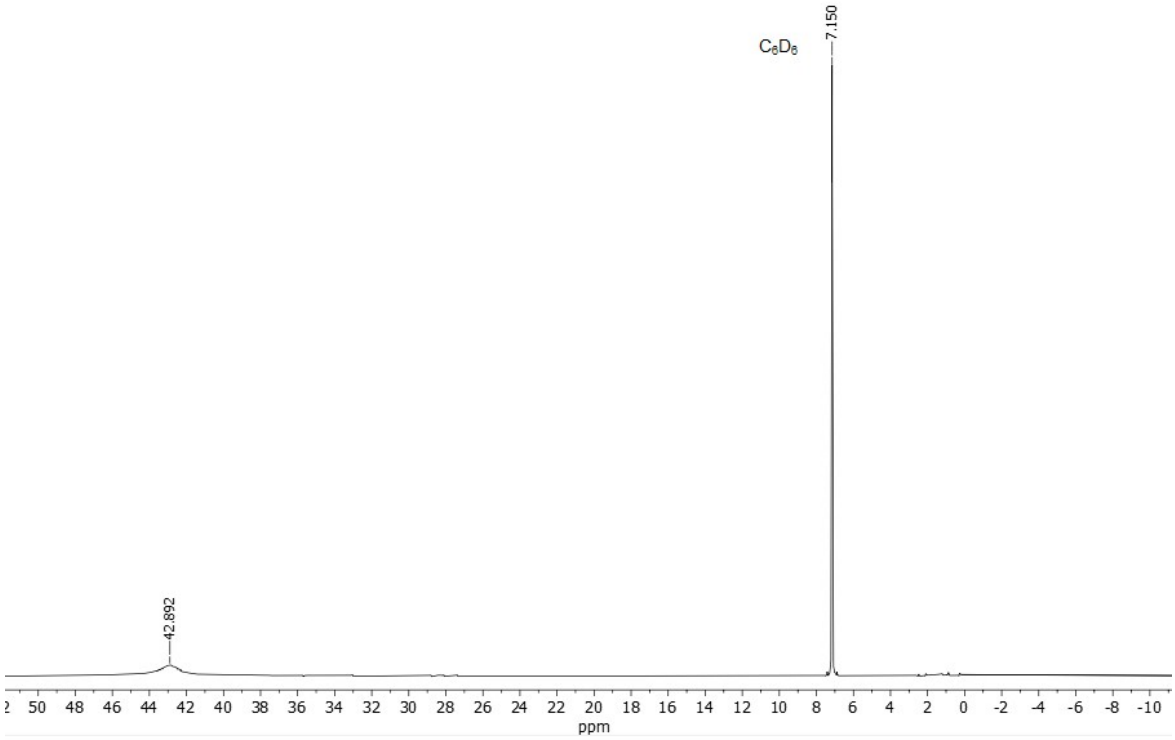

Figure S15. ^1H NMR spectrum (300 MHz, C_6D_6, 20 ºC) of $[CrCp^*(\kappa^2\text{-}BH_4)_2]$ (**7**).

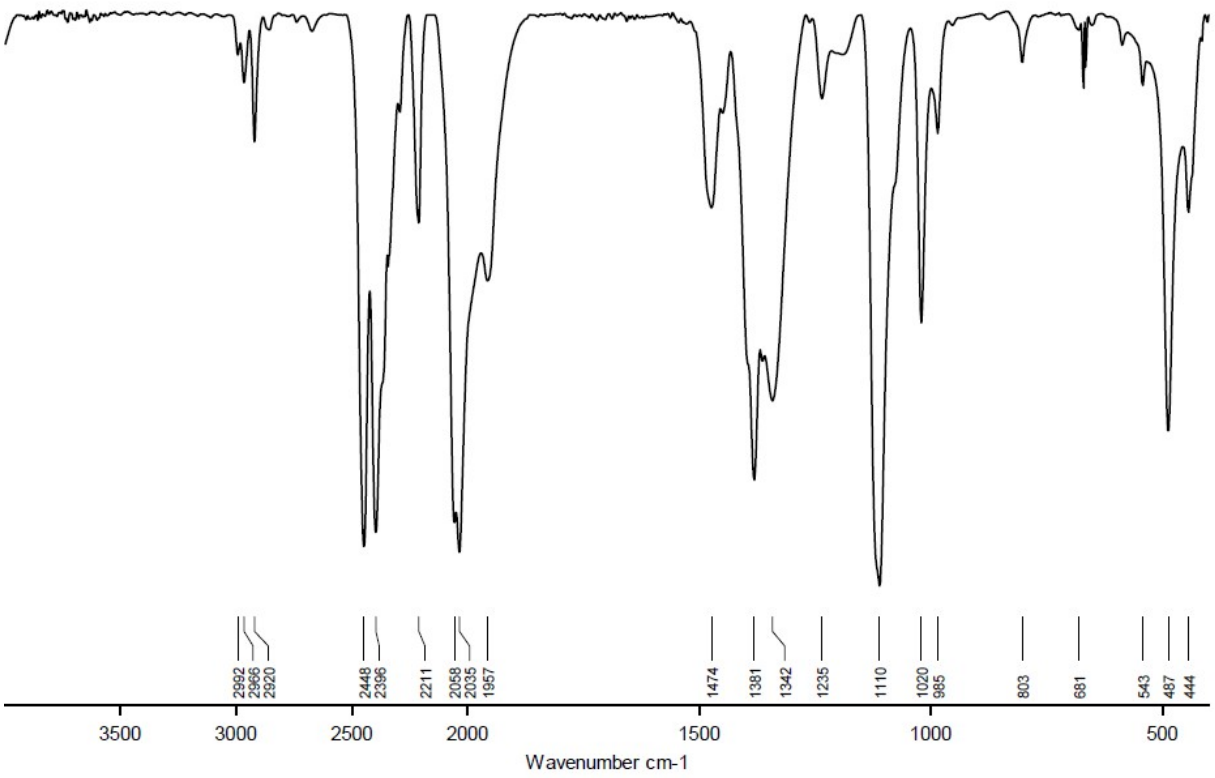

Figure S16. IR spectrum (ATR, cm^{-1}) of [$CrCp^*(\kappa^2\text{-}BH_4)_2$] (**7**).

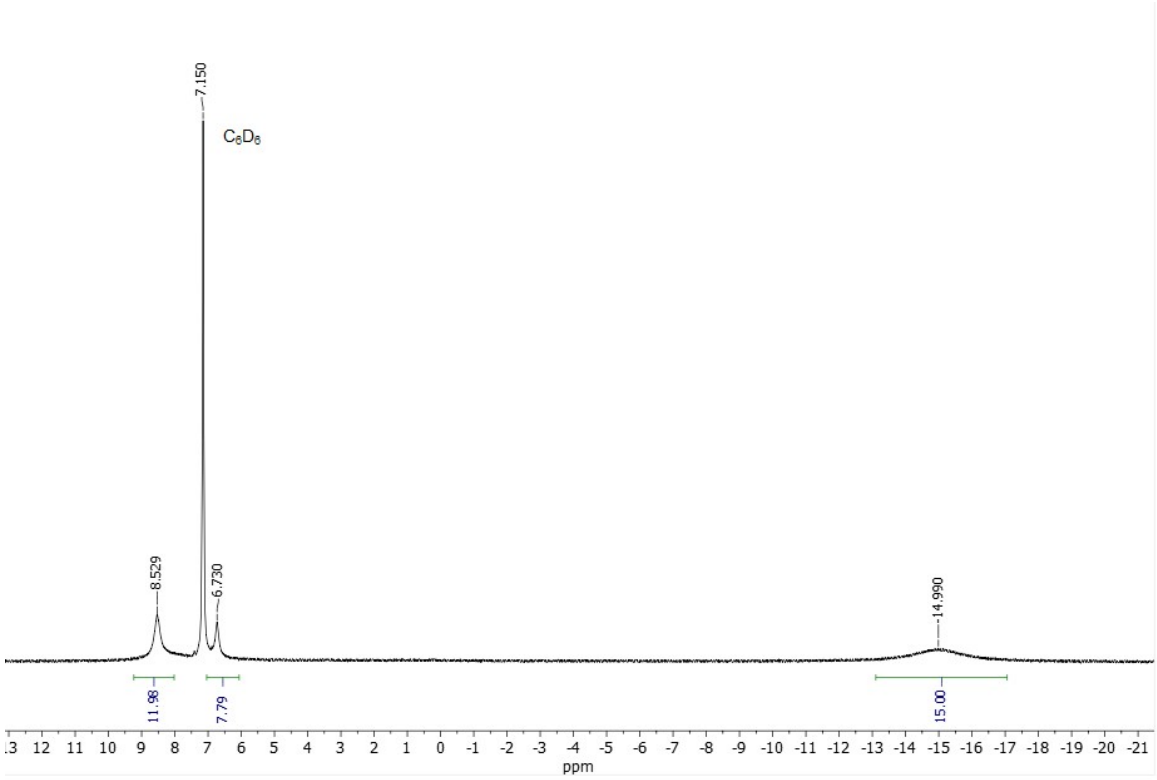

Figure S17. ^1H NMR spectrum (300 MHz, C_6D_6, 20 ºC) of [$CrCp^*(\eta^6\text{-}C_6H_5\text{-}BPh_3)$] (**8**).

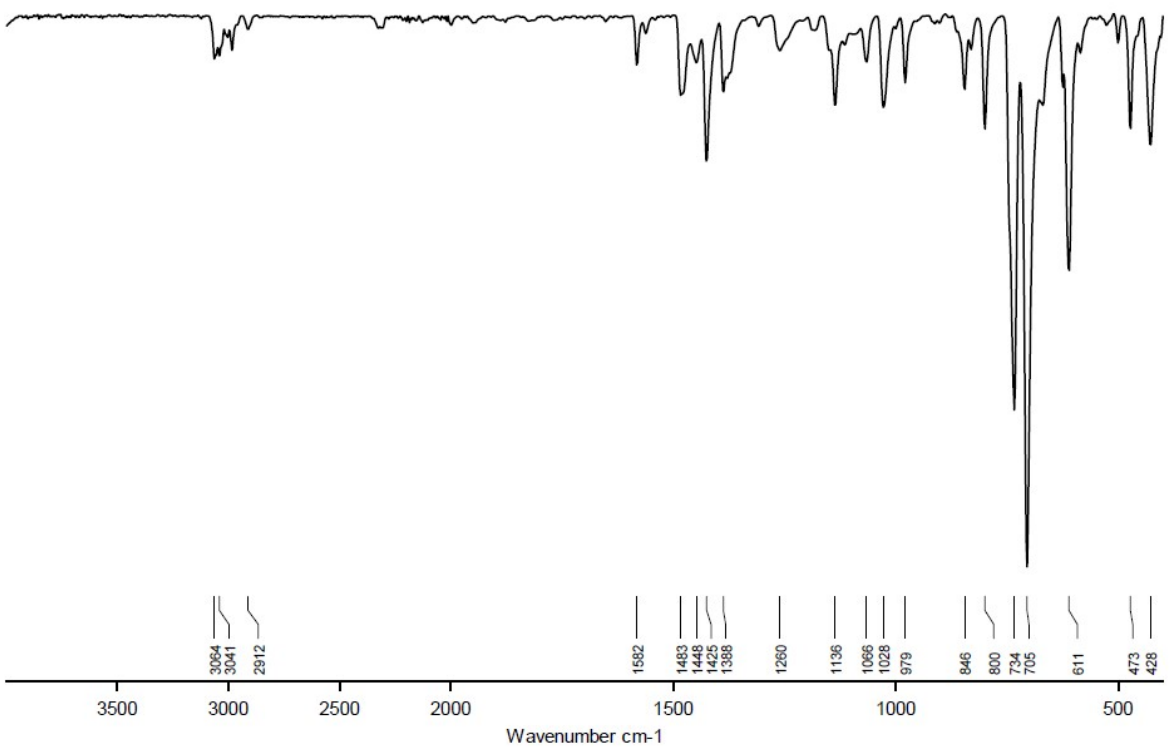

Figure S18. IR spectrum (ATR, cm^{-1}) of [CrCp*(η^6-C_6H_5-BPh_3)] (**8**).

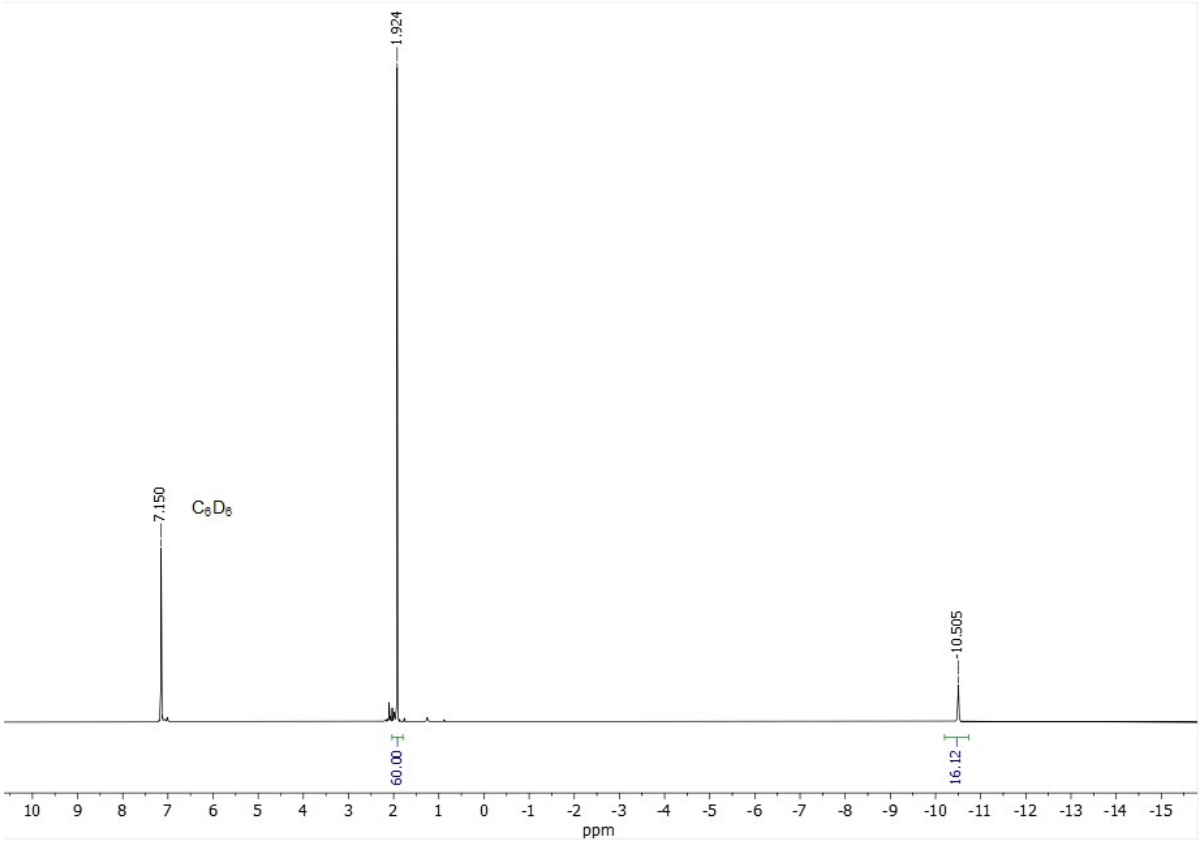

Figure S19. ^1H NMR spectrum (400 MHz, C_6D_6, 20 ºC) of [(Al{(μ-H)$_4$CrCp*})$_4$] (**9**).

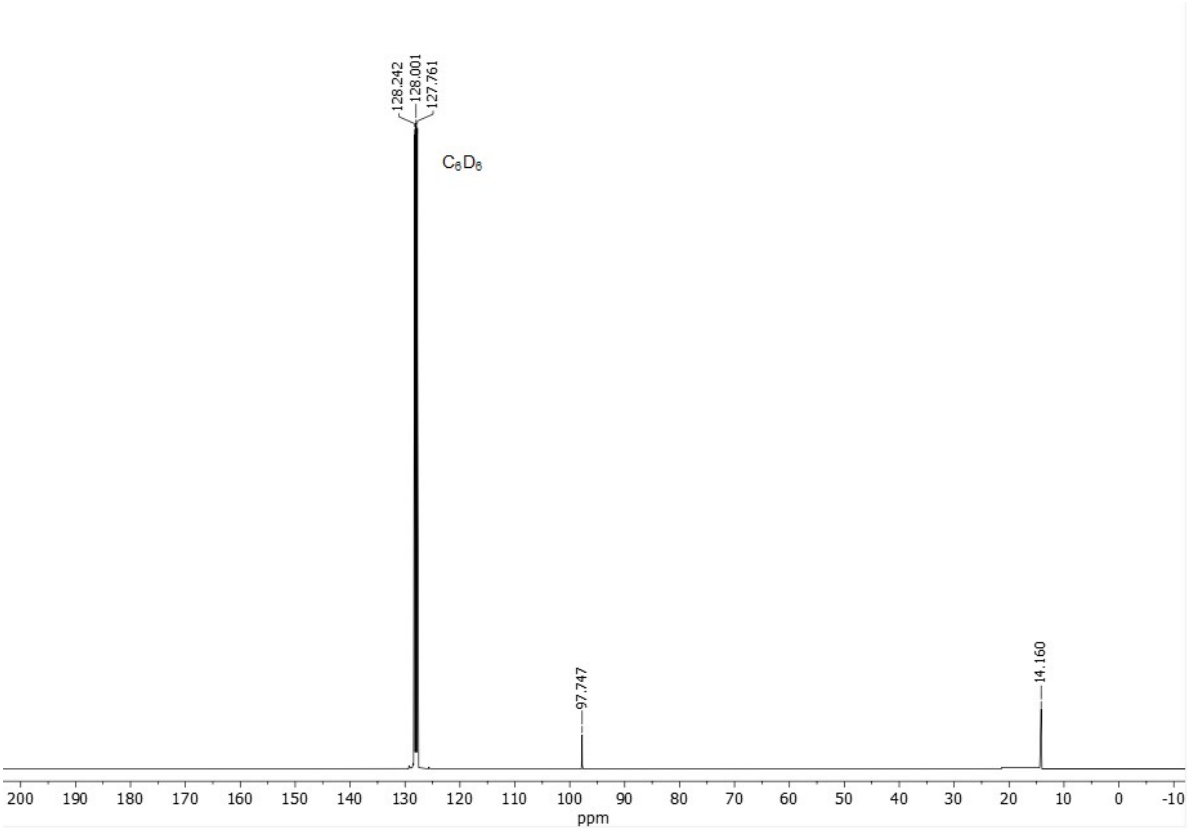

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6, 20 ºC) of $[(Al\{(\mu\text{-}H)_4CrCp^*\})_4]$ (**9**).

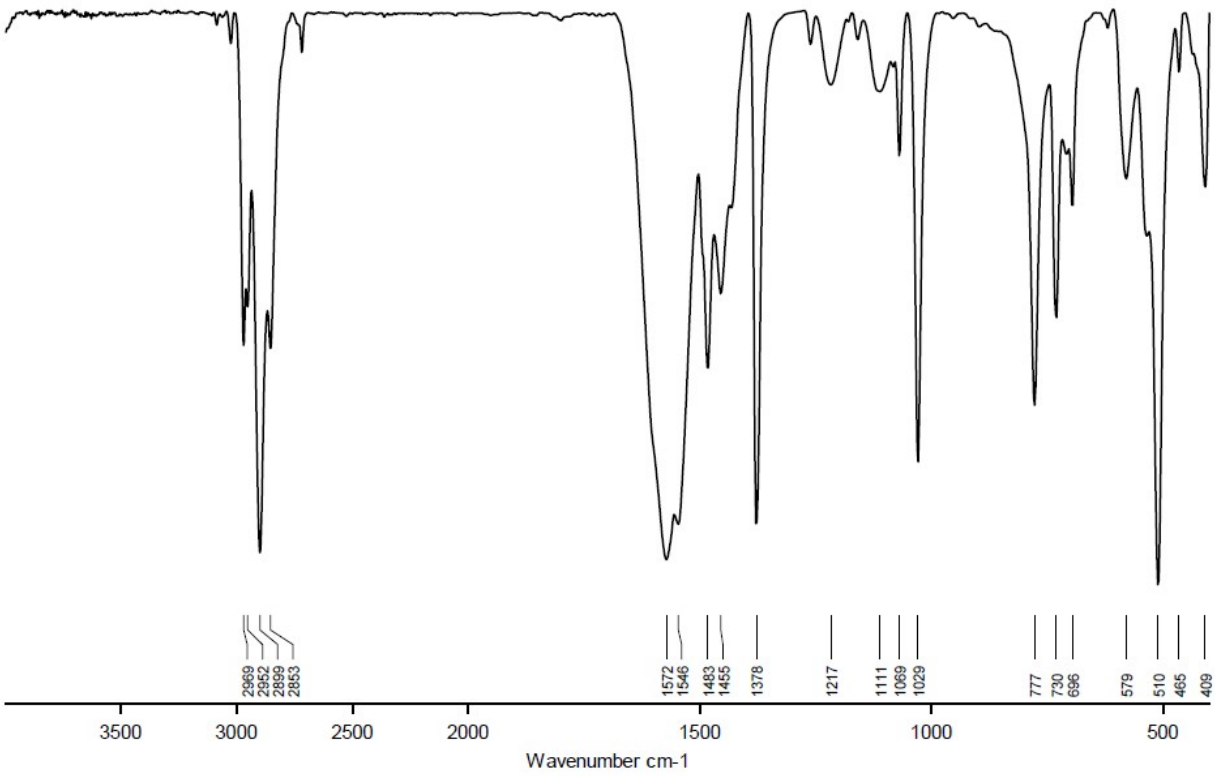

Figure S21. IR spectrum (ATR, cm^{-1}) of $[(Al\{(\mu\text{-}H)_4CrCp^*\})_4]$ (**9**).

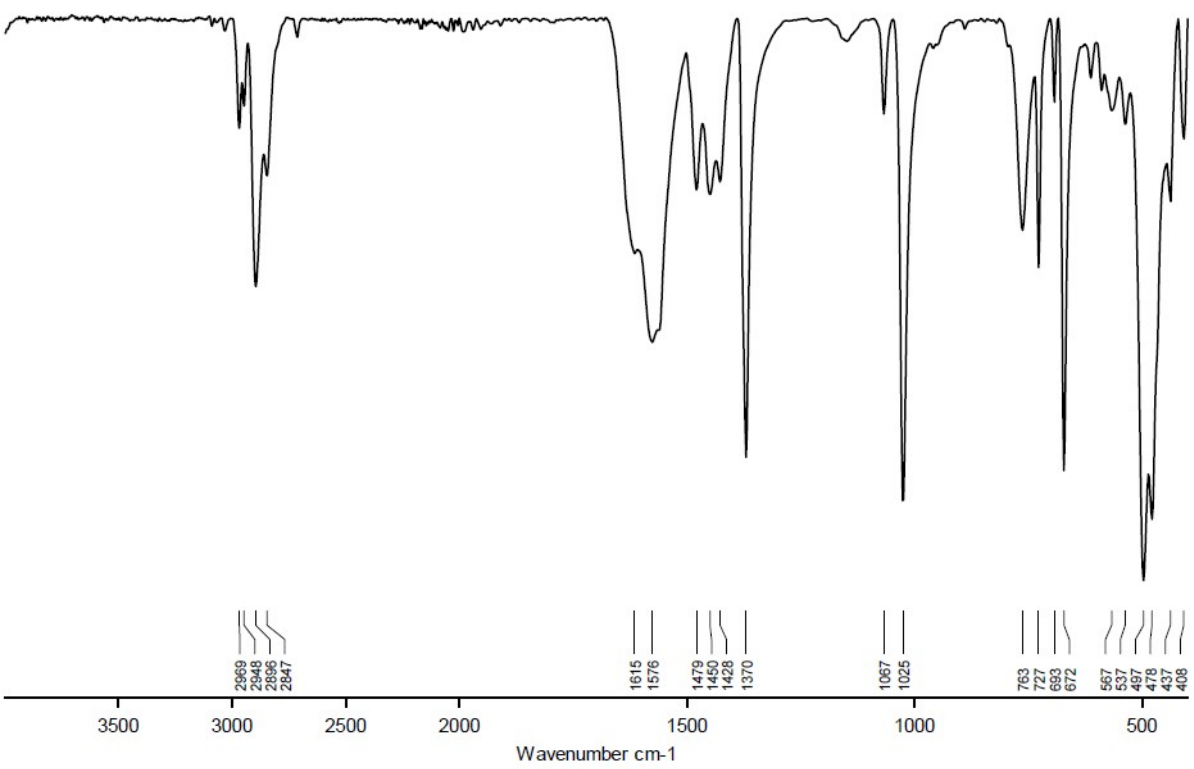

Figure S22. IR spectrum (ATR, cm^{-1}) of $[(Al_2\{(\mu\text{-}H)_4CrCp^*\}\{(\mu_3\text{-}H)_4Cr_2Cp^*_2\})_2]\cdot 0.5C_6H_6$ (**10**$\cdot 0.5C_6H_6$).