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Electronic Supplementary Information for:

N-Heterocyclic Carbene and Cyclic (Alkyl)(amino)carbene ligated Half-sandwich Complexes of Chromium(I) and Chromium(II)

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1. Crystallographic Details

General Informations

Crystals suitable for single crystal X-Ray diffraction analysis were immersed in a film of perfluoropolyether oil mounted on a custom-made polyimide microloop and transferred to a low temperature stream of nitrogen at 100 K.

The data were collected on a Rigaku Oxford Diffraction XtaLAB Synergy-DW diffractometer with a Hy-Pix-6000HE detector and monochromated Cu-Kα or Mo-Kα radiation equipped with an Oxford Cryo 800 cooling unit. The data were collected at 100 K. The images were processed, corrected for Lorentz-polarization effects and absorption with the implemented CrysAlisPro software packages from Rigaku Oxford Diffraction. The structures were solved using Fourier expansion technique and the intrinsic phasing method provided by SHELXT[1]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were usually assigned to idealized 'riding' positions by full-matrix least squares against F2 of all data and were included in structure factors calculations. The Diamond software package was used for graphical visualization of the structures.[2] Full structural information as also been deposited at Cambridge Crystallographic Data Centre (CCDC-Numbers see Tables S1 – S5).

Experimental Crystal Data Collection Parameter

Table S1 Crystallographic data of compounds **1** -**3**.

	[{Cr (I*i*Pr^{Me})(THF)Cl(μ-Cl) }$_2$] **1**	[{Cr(cAAC^{Me})Cl(μ-Cl)}$_2$] **2**	[CpCr(IMe^{Me})Cl] **3**
Chemical formula	$C_{30}H_{56}Cl_4Cr_2N_4O_2$	$C_{40}H_{62}Cl_4Cr_2N_2$	$C_{12}H_{17}ClCrN_2$
Formula Mass [g·mol^{-1}]	750.58	816.71	276.72
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	1.54184	1.54184	1.54184
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$
a [Å]	9.7853(2)	10.41860(10)	9.76230(10)
b [Å]	9.8595(2)	9.81210(10)	19.7090(2)
c [Å]	10.5749(2)	20.0881(2)	13.40020(10)
α [°]	104.3170(10)	90	90
β [°]	108.8080(10)	90.9570(10)°	98.2380(10)
γ [°]	100.6240(10)	90	90
Unit cell volume [Å^3]	896.15(3)	2053.29(4)	2551.66(4)
No. of formula units per unit cell	1	2	8
Density (calc) [g·cm^{-3}]	1.391	1.321	1.441
Absorption coefficient [mm^{-1}]	7.989	6.969	9.085
F (000)	396	864	1152
Theta range *ϑ* [°]	4.679 to 74.473	4.244 to 77.600	4.018 to 72.125
hkl	-11<=h<=12, -12<=k<=12, -13<=l<=13	-12<=h<=13, -12<=k<=10, -23<=l<=25	-11<=h<=12, -24<=k<=24, -15<=l<=16
Reflections collected	18361	21657	26247
Independent reflections	3651	4304	5019
Completeness to theta [%]	99.9	100	100
R_{int}	0.0420	0.0523	0.0340
Data	3651	4304	5019
Restraints	0	0	0
Parameter	196	225	297
*R*1 and *wR*2 for [$I > 2\sigma(I)$]	0.0317, 0.0873	0.0432, 0.1185	0.0400, 0.1029
*R*1 and *wR*2 (all data)	0.0323, 0.0878	0.0456, 0.1204	0.0420, 0.1041
Largest diff. peak and hole [eÅ^{-3}]	0.469 / -0.745	0.765 / -0.825	1.409 / -565
GooF	1.049	1.062	1.073
CCDC number	2279734	2279739	2279747

Table S2 Crystallographic data of compounds **4** -**6**.

	[CpCr(I*i*Pr^{Me})Cl] **4**	[CpCr(IMes)Cl] **5**	[CpCr(IDipp)Cl] **6**
Chemical formula	$C_{16}H_{25}ClCrN_2$	$C_{26}H_{29}ClCrN_2$	$C_{44}H_{53}ClCrN_2$
Formula Mass [g·mol^{-1}]	332.83	456.96	697.33
Temperature [K]	100(2)	100(2)	100.00(10)
Wavelength [Å]	1.54184	1.54184	1.54184
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	C2/c	$P2_1/c$
a [Å]	9.7164(2)	32.9527(2)	12.78010(10)
b [Å]	13.4856(2)	8.58380(10)	21.8107(2)
c [Å]	26.2318(4	33.4485(2)	14.6278(2)
α [°]	90	90	90
β [°]	90	92.0050(10)	102.9610(10)
γ [°]	90	90	90
Unit cell volume [Å^3]	3437.19(10)	9455.43(14)	3973.52(7)
No. of formula units per unit cell	8	16	4
Density (calc) [g·cm^{-3}]	1.286	1.284	1.166
Absorption coefficient [mm^{-1}]	6.829	5.117	3.209
F (000)	1408	3840	1488
Theta range *ϑ* [°]	3.370 to 72.102	2.644 to 72.128	3.549 to 72.128°.
hkl	-11<=h<=11, -16<=k<=16, -12<=l<=32	-40<=h<=40, -10<=k<=10, -29<=l<=41	-15<=h<=15, -26<=k<=24, -18<=l<=17
Reflections collected	18250	48886	41187
Independent reflections	3382	9231	7815
Completeness to theta [%]	99.9	99.1	99.9
R_{int}	0.0397	0.0329	0.0315
Data	3382	9231	7815
Restraints	120	0	0
Parameter	233	533	441
*R*1 and *wR*2 for [$I > 2\sigma(I)$]	0.0371, 0.0903	0.0373, 0.0992	0.0341, 0.0888
*R*1 and *wR*2 (all data)	0.0408, 0.0924	0.0403, 0.1009	0.0395, 0.0919
Largest diff. peak and hole [eÅ^{-3}]	0.564 / -0.377	0.371 / -0.467	0.261 / -0.422
GooF	1.051	1.080	1.070
CCDC number	2279743	2279746	2279741

Table S3 Crystallographic data of compounds **7** -**9**.

	[CpCr(cAAC^{Me})Cl] **7**	[Cp*Cr(IMe^{Me})Cl] **8**	[FlCr(cAAC^{Me})Cl] **9**
Chemical formula	$C_{25}H_{36}ClCrN$	$C_{17}H_{27}ClCrN_2$	$C_{40}H_{48}ClCrN$
Formula Mass [g·mol^{-1}]	438.00	488.05	630.24
Temperature [K]	100.00(10)	100(2)	100(2)
Wavelength [Å]	1.54184	1.54184	1.54184
Crystal system	tetragonal	monoclinic	trigonal
Space group	$P4_1$	$P2_1/c$	P
a [Å]	10.70621(4)	8.3556(2)	23.8746(4)
b [Å]	10.70621(4)	15.6072(4)	23.8746(4)
c [Å]	20.09860(10)	27.4722(6)	10.3635(2)
α [°]	90	90	90
β [°]	90	91.100(2)°.	90
γ [°]	90	90	120
Unit cell volume [Å^3]	2303.76(2)	3581.92(15)	5115.7(2)
No. of formula units per unit cell	4	8	6
Density (calc) [g·cm^{-3}]	1.263	1.286	1.227
Absorption coefficient [mm^{-1}]	5.206	6.573	3.676
F (000)	936	1472	2016
Theta range *ϑ* [°]	4.129 to 80.341	3.218 to 66.997	3.703 to 72.091
hkl	-13<=h<=13, -13<=k<=13, -25<=l<=25	-8<=h<=9, -18<=k<=18, -32<=l<=32	-29<=h<=29, -29<=k<=29, 0<=l<=12
Reflections collected	48084	32738	38450
Independent reflections	4990	6366	6687
Completeness to theta [%]	100	99.7	99.8
R_{int}	0.0512	0.1037	0.0578
Data	4990	6366	6688
Restraints	215	0	318
Parameter	307	397	456
*R*1 and *wR*2 for [$I > 2\sigma(I)$]	0.0374, 0.0992	0.0708, 0.1855	0.0585, 0.1306
*R*1 and *wR*2 (all data)	0.0379, 0.0995	0.0758/ 0.1900	0.0797, 0.1375
Largest diff. peak and hole [eÅ^{-3}]	0.281 / -0.512	1.230 / -1.354	0.395 / -0.416
GooF	1.109	1.040	1.156
CCDC number	2279737	2279744	2279735

Table S4 Crystallographic data of compounds **10** - **12**.

	[IndCr(cAAC^{Me})Cl] **10**	[CpCr(cAAC^{Me})(NPh$_2$)]**11**	[CpCr(IMe^{Me})(η^3-C$_3$H$_5$)] **12**
Chemical formula	$C_{29}H_{38}ClCrN$	$C_{37}H_{46}CrN_2$	$C_{15}H_{22}CrN_2$
Formula Mass [g·mol^{-1}]	488.05	570.76	282.34
Temperature [K]	100(2)	100.00(10)	100(2)
Wavelength [Å]	1.54184	1.54184	1.54184
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P	$P2_1/c$
a [Å]	10.77400(10)	9.9514(2)	12.67350(10)
b [Å]	14.56590(10)	10.4567(2)	10.56340(10)
c [Å]	17.1932(2)	16.9742(2)	21.8451(2)
α [°]	90	100.5140(10).	90.
β [°]	107.7990(10)	96.1890(10)	101.5660(10)
γ [°]	90	111.365(2)	90
Unit cell volume [Å^3]	2569.03(4)	1587.74(5)	2865.13(5)
No. of formula units per unit cell	4	2	8
Density (calc) [g·cm^{-3}]	1.262	1.194	1.309
Absorption coefficient [mm^{-1}]	4.725	3.149	6.425
F (000)	1040	612	1200
Theta range *ϑ* [°]	4.062 to 67.080	2.697 to 72.129.	3.560 to 77.759.
hkl	-12<=h<=11, -17<=k<=13, -20<=l<=19	-11<=h<=12, -12<=k<=12, -20<=l<=20	-16<=h<=13, -12<=k<=13, -27<=l<=27
Reflections collected	17093	32289	28895
Independent reflections	4449	6246	5981
Completeness to theta [%]	96.9	99.9	99.8
R_{int}	0.0241	0.0313	0.0403
Data	4449	6246	5981
Restraints	0	0	0
Parameter	297	369	333
*R*1 and *wR*2 for [$I > 2\sigma(I)$]	0.0281, 0.0728	0.0325, 0.0794	0.0361, 0.0927
*R*1 and *wR*2 (all data)	0.0306 / 0.0739	0.0340, 0.0802	0.0407, 0.0958
Largest diff. peak and hole [eÅ^{-3}]	0.277 / -0.299	0.364/ -0.374	0.392/ -0.437
GooF	1.067	1.061	1.051
CCDC number	2279745	2279742	2279736

Table S5 Crystallographic data of compounds **13** and **14**.

	[Cp*Cr(IMe^{Me})(CO)$_2$] **13**	[Cr(IMe^{Me})(THF)Cl$_2$]
Chemical formula	$C_{19}H_{27}CrN_2O_2$	$C_{52}H_{96}Cr_5N_8O_6Cl_{10}$
Formula Mass [g·mol^{-1}]	367.42	1543.86
Temperature [K]	100(2)	100(2)
Wavelength [Å]	1.54184	1.54184
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P -1
a [Å]	16.8832(2)	9.44530(10)
b [Å]	8.39770(10)	11.66530(10)
c [Å]	14.6843(2)	16.9234(2)
α [°]	90	108.0530(10)
β [°]	114.2490(10)	90.2920(10)
γ [°]	90	98.8250(10)
Unit cell volume [Å^3]	1898.25(4)	1749.12(3)
No. of formula units per unit cell	4	1
Density (calc) [g·cm^{-3}]	1.286	1.466
Absorption coefficient [mm^{-1}]	5.053	10.111
F (000)	780	802
Theta range *ϑ* [°]	2.871 to 67.037	2.751 to 77.708
hkl	-20<=h<=20, -10<=k<=10, -17<=l<=16	-11<=h<=11, -14<=k<=15, -20<=l<=21
Reflections collected	32635	35798
Independent reflections	3388	7330
Completeness to theta [%]	100	99.9
R_{int}	0.0366	0.0358
Data	3388	7330
Restraints	0	49
Parameter	226	343
*R*1 and *wR*2 for [$I > 2\sigma(I)$]	0.0267, 0.0652	0.0550, 0.1378
*R*1 and *wR*2 (all data)	0.0276, 0.0657	0.00550, 0.01394
Largest diff. peak and hole [eÅ^{-3}]	0.245 / -0.282	1.395 / -1.396
GooF	1.062	1.056
CCDC number	2279738	2279740

2. Molecular Structures of Compounds 1 – 13 and of [Cr(IMe^{Me})(THF)Cl$_2$]

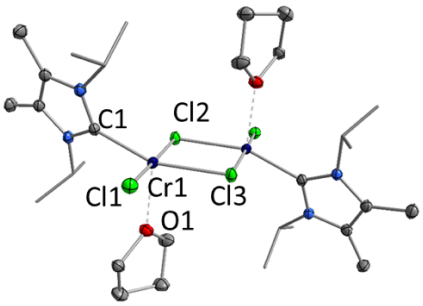

Figure S1: The molecular structure of [{Cr(I*i*Pr^{Me})(THF)Cl(μ-Cl)}$_2$] **1** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **1**: Cr–C1 2.1396(16), Cr–Cl1 2.3505(5), Cr–Cl2 2.4161(5), Cr–Cl3 2.4601(4), Cr1–O1 2.3237(11), C1-Cr-Cl1 93.51(4), C1-Cr-Cl2 87.21(4), C1-Cr-Cl3 159.30(4), C1-Cr1-O1 108.89(5), Cl1-Cr-Cl2 174.239(16), Cl1-Cr-Cl3 93.637(14), Cl1-Cr-O1 92.49(3), O1-Cr1-Cl2 92.68(3), O1-Cr1-Cl3 90.17(3).

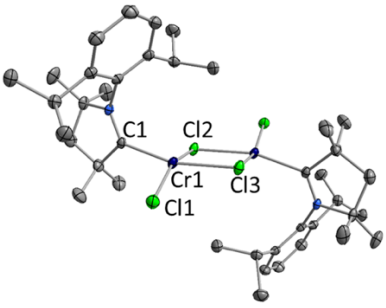

Figure S2: The molecular structure of [{Cr(cAAC^{Me})Cl(μ-Cl)}$_2$] **2** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **2**: Cr–C1 2.1311(20), Cr–Cl1 2.2992(7), Cr–Cl2 2.3951(7), Cr–Cl3 2.4155(7), C1-Cr-Cl1 100.39(6), C1-Cr-Cl2 87.09(6), C1-Cr-Cl3 163.31(6), Cl1-Cr-Cl2 159.28(3), Cl1-Cr-Cl3 92.29(2).

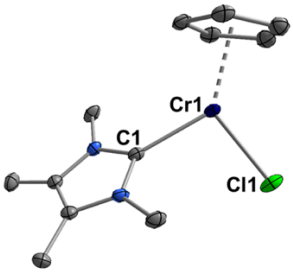

Figure S3: The molecular structure of [(η^5-C_5H_5)Cr(IMe)Cl] **3** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **3**: Cr1–C1 2.1213(24), Cr1–Cl1 2.3309(7), Cr–Cp$_{Centroid}$ 1.9869(4), C1-Cr1-Cl1 100.16(6), C1-Cr1-Cp$_{Centroid}$ 130.239(65), Cl1-Cr1-Cp$_{Centroid}$ 129.507(23).

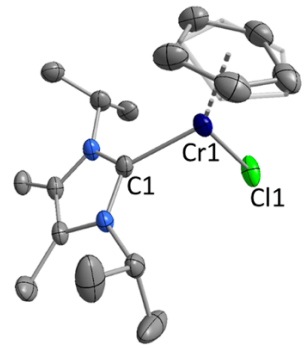

Figure S4: The molecular structure of [(η^5-C_5H_5)Cr(I*i*Pr^{Me})Cl] **4** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability (the disordered part of the cyclopentadienyl ring is also depicted). Selected bond lengths [Å] and angles [°] for **4**: Cr–C1 2.1072(19), Cr–Cl1 2.2915(7), Cr–$Cp_{Centroid}$ 2.0027(5), C1-Cr-Cl1 95.79(6), C1-Cr-$Cp_{Centroid}$ 131.245(57), Cl1-Cr-$Cp_{Centroid}$ 132.893(24).

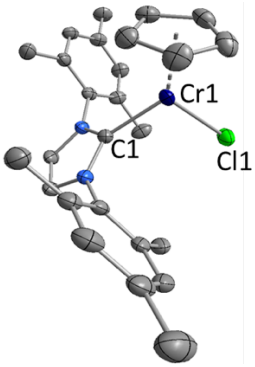

Figure S5: The molecular structure of [(η^5-C_5H_5)Cr(IMes)Cl] **5** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **5**: Cr–C1 2.1096(18), Cr–Cl1 2.2988(9), Cr–$Cp_{Centroid}$ 1.98671(6), C1-Cr-Cl1 98.70(5), C1-Cr-$Cp_{Centroid}$ 133.283(53), Cl1-Cr-$Cp_{Centroid}$ 128.014(36).

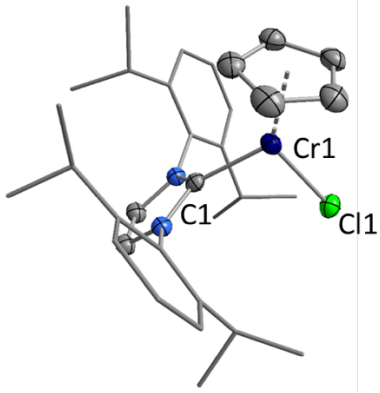

Figure S6: The molecular structure of [(η^5-C_5H_5)Cr(IDipp)Cl] **6** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability (the di*iso*propylphenyl-groups are represented in wire-stick model). Selected bond lengths [Å] and angles [°] for **5**: Cr–C1 2.1014(14), Cr–Cl1 2.3076(5), Cr–$Cp_{Centroid}$ 1.9867(3), C1-Cr-Cl1 94.83(4), C1-Cr-$Cp_{Centroid}$ 132.358(41), Cl1-Cr-$Cp_{Centroid}$ 132.718(17).

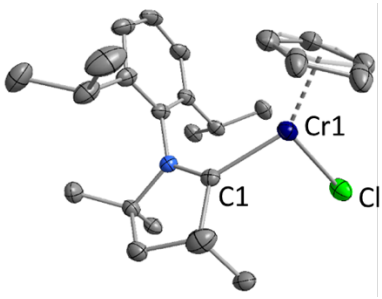

Figure S7: Molecular structure of [(η^5-C_5H_5)CrC(cAAC^{Me})Cl] **7** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability (the disordered part of the cyclopentadienyl-ring is also shown in wirestick model representation). Selected bond lengths [Å] and angles [°] for **7**: Cr–C1 2.1332(33), Cr–Cl1 2.299(1), Cr–$Cp_{Centroid}$ 1.9576(5), C1-Cr-Cl1 97.38(8), C1-Cr-$Cp_{Centroid}$ 140.286(91), Cl1-Cr-$Cp_{Centroid}$ 122.275(33).

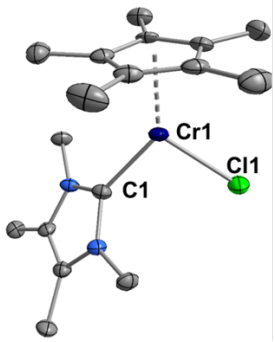

Figure S8: Molecular structure of [(η^5-C_5Me_5)Cr(IMe^{Me})Cl] **10** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **10**: Cr1–C1 2.1204(33), Cr1–Cl1 2.3162(12), Cr1–Cp*$_{Centroid}$ 1.9637(6), C1-Cr1-Cl1 97.81(10), C1-Cr1-Cp*$_{Centroid}$ 135.764(91), Cp*$_{Centroid}$-Cr1-Cl1 126.213(37).

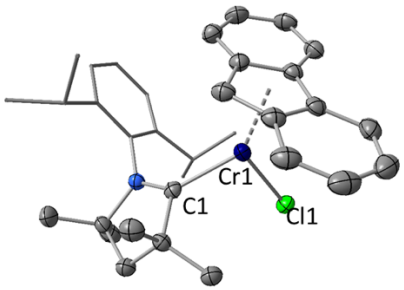

Figure S9: Molecular structure of [(η^5-$C_{13}H_9$)Cr(cAAC^{Me})Cl] **8** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability (the di*iso*propylphenyl-group is represented in wire-stick model). Selected bond lengths [Å] and angles [°] for **8:** Cr–C1 2.0933(32), Cr–Cl1 2.3122(7), Cr–$Fl_{Centroid}$ 2.0243(5), C1-Cr-Cl1 98.29(6), C1-Cr-$Fl_{Centroid}$ 131.799(69), Cl1-Cr-$Fl_{Centroid}$ 129.072(25).

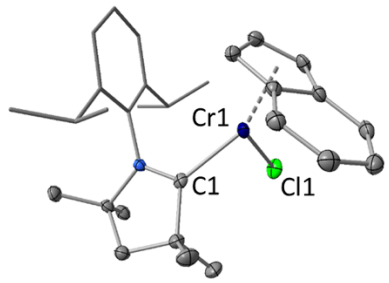

Figure S10: Molecular structure of [(η^5-C_8H_7)Cr(cAAC^{Me})Cl] **9** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability (the di*iso*propylphenyl-group is represented in wire-stick model). Selected bond lengths [Å] and angles [°] for **9**: Cr–C1 2.1311(17), Cr–Cl1 2.2994(4), Cr–Ind$_{Centroid}$ 2.0075(3), C1-Cr-Cl1 93.12(4), C1-Cr-Ind$_{Centroid}$ 140.811(45), Cl1-Cr-Ind$_{Centroid}$ 125.863(17).

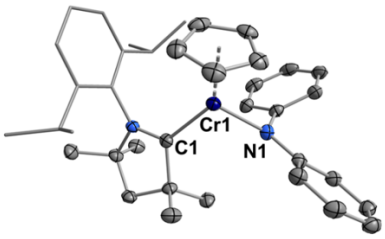

Figure S11: Molecular structure of [(η^5-C_5Me_5)Cr(IMe)$(CO)_2$] **11** in the solid state. Hydrogen atoms are omitted for clarity (the di*iso*propylphenyl-group is represented in wire-stick model). Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **11**: Cr1–C1 2.1329(14), Cr1–C_5H_5 $_{Centroid}$ 2.0056(2), Cr1–N1 2.0270(13), C1-Cr1-N1 97.76(5), C1-Cr1-C_5H_5 $_{Centroid}$ 140.586(44), N1-Cr1-C_5H_5 $_{Centroid}$ 121.419(38).

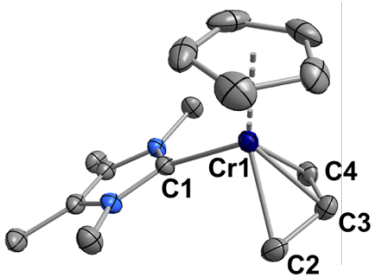

Figure S12: Molecular structure of [(η^5-C_5H_5)Cr(IMe^{Me})(η^3-C_3H_5)] **12** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **12**: Cr1–C1 2.0834(17), Cr1–C2 2.1240(21), Cr1–C3 2.03080(22), Cr1–C4 2.1342(17), Cr–Cp$_{Centroid}$ 1.8707(4), C2–C3 1.4326(26), C3–C4 1.4329(27), C1-Cr1-C2 92.93(7), C1-Cr1-C3 114.06(7), C1-Cr1-C4 93.35(7), C1-Cr1-Cp$_{Centroid}$ 121.952(49), C2-Cr1-Cp$_{Centroid}$ 130.455(56), C3-Cr1-Cp$_{Centroid}$ 123.967(58), C4-Cr1-Cp$_{Centroid}$ 132.197(52).

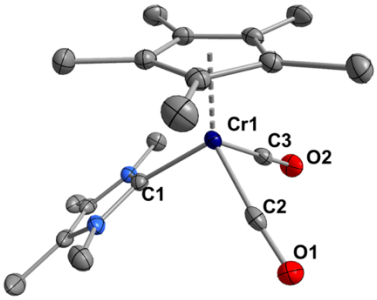

Figure S13: Molecular structure of [(η^5-C_5Me_5)Cr(IMe)($CO)_2$] **13** in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **13**: Cr1–C1 2.0767(19), Cr1–$C_5Me_{5\ Centroid}$ 1.8599(3), Cr1–C2 1.8298(14), Cr1–C3 1.8268(17), C2–O1 1.1697(17), C3–O2 1.1686(20), C1-Cr1-C2 97.41(6), C1-Cr1-C3 95.92(6), C1-Cr1-$C_5Me_{5\ Centroid}$ 124.408(49), C2-Cr-C3 97.46(7), C2-Cr1-$C_5Me_{5\ Centroid}$ 123.853(57), C3-Cr1-$C_5Me_{5\ Centroid}$ 124.485(57).

The attempts to isolate [{Cr(IMe^{Me})(THF)Cl(μ-Cl)}$_2$], which in principle defied isolation, lead to formation of small amounts of a number of single crystals suitable for X-ray diffraction. The resulting molecular structures crystal structures reveal that the situation here is more complicated as different isomers have been characterized by X-ray crystallography, which consists of isolated molecules [{Cr(IMe^{Me})(THF)Cl(μ-Cl)}$_2$] (Figure S14), one dimensional strands of [{Cr(IMe^{Me})Cl(μ-Cl)}$_2$] and [Cr(THF)$_2$Cl$_2$], in which each [{Cr(IMe^{Me})Cl(μ-Cl)}$_2$] molecule is bridged by two μ-chloride ligands of [Cr(THF)$_2$(Cl$_2$], i.e., $^1_\infty$[{Cr(IMe^{Me})Cl(μ-Cl)}$_2$][Cr(THF)$_2$(μ-Cl)$_2$] (Figure S15) or a mixture thereof (Figure S16).

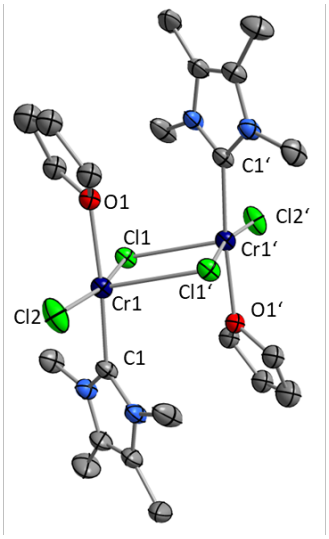

Figure S14: The molecular structure of [{Cr(IMe^{Me})(THF)Cl(μ-Cl)}$_2$] in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: Cr1–C1 2.1377(37), Cr1–O1 2.1636(58), Cr1–Cl1 2.3960(8), Cr1–Cl2 2.3546(10), Cr1–Cl1' 2.6816(10), C1-Cr1-O1 171.72(15), Cl1-Cr1-Cl2 169.19(4), Cl1-Cr1-Cl1' 89.41(3), Cl1-Cr1'-Cl2' 100.21(3).

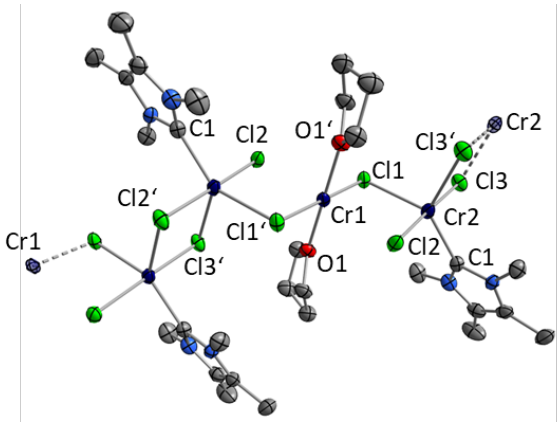

Figure S15: The molecular structure of $^{1}_{\infty}$[{Cr(IMe^{Me})Cl(μ-Cl)}$_2$][Cr(THF)$_2$(μ-Cl)$_2$] in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: Cr1–O1/O1' 2.0673(28), Cr–Cl1/Cl1' 2.4093(8), Cr2–Cl2 2.3746(9), Cr2–Cl3 2.3899(9), Cr2–Cl3' 2.5361(11), O1-Cr1-O1' 180.000, Cl1-Cr1-Cl1' 180.000, Cr1-Cl1-Cr2 93.30(3), Cl1-Cr2-C1134.08(9), Cl1-Cr2-Cl3 89.79(3), Cl1-Cr-Cl3' 100.68(3), C1-Cr2-Cl2 93.13(9), Cr1-Cr2-Cl3 86.08(9), C1-Cr2-Cl3' 124.88(9), Cr1-Cl3/Cl3'-Cr2 91.15(3).

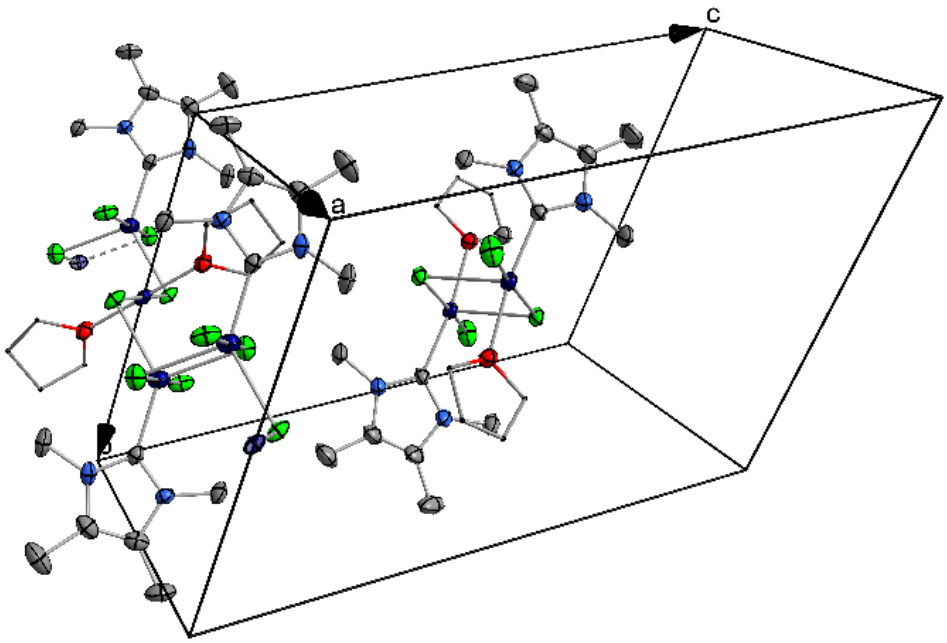

Figure S16: The molecular structure of "[Cr(IMe^{Me})(THF)Cl$_2$]" in the solid state.

3. High Resolution Mass Spectrometry Data

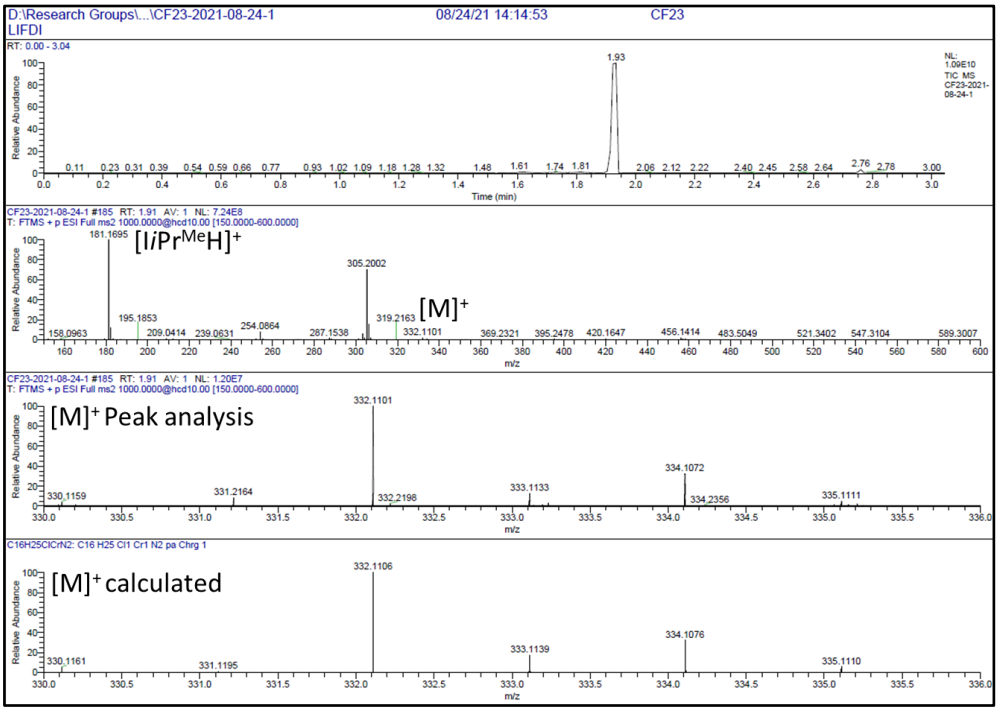

Figure S17: Mass spectrometric data obtained for [(η^5-C_5H_5)Cr(I*i*Pr^{Me})Cl] **4**.

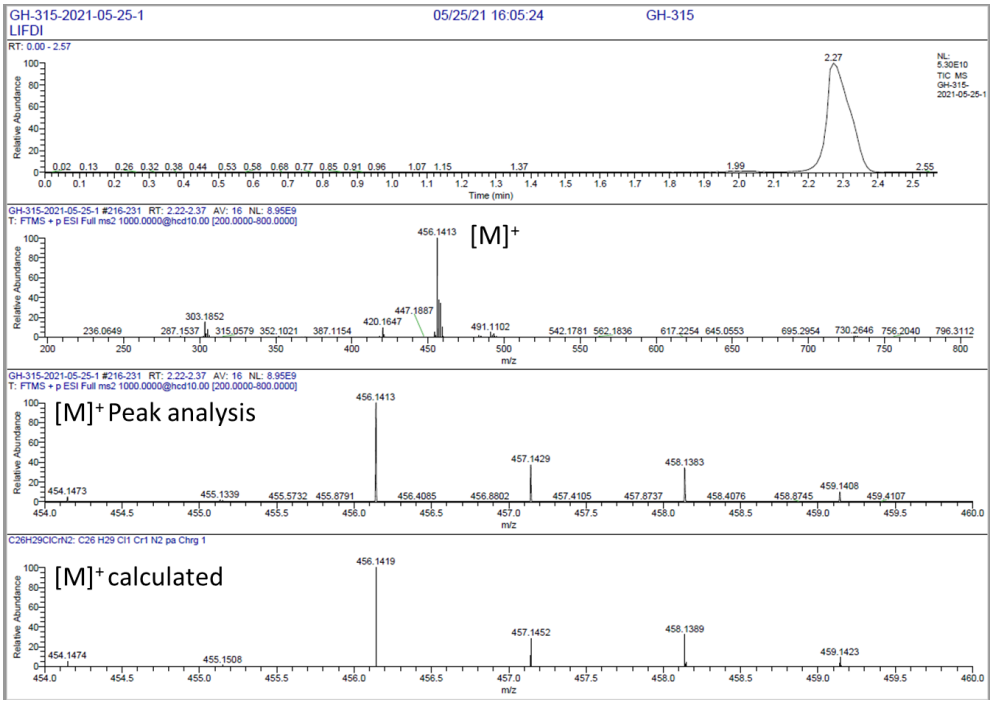

Figure S18: Mass spectrometric data obtained for [(η^5-C_5H_5)Cr(IMes)Cl] **5**.

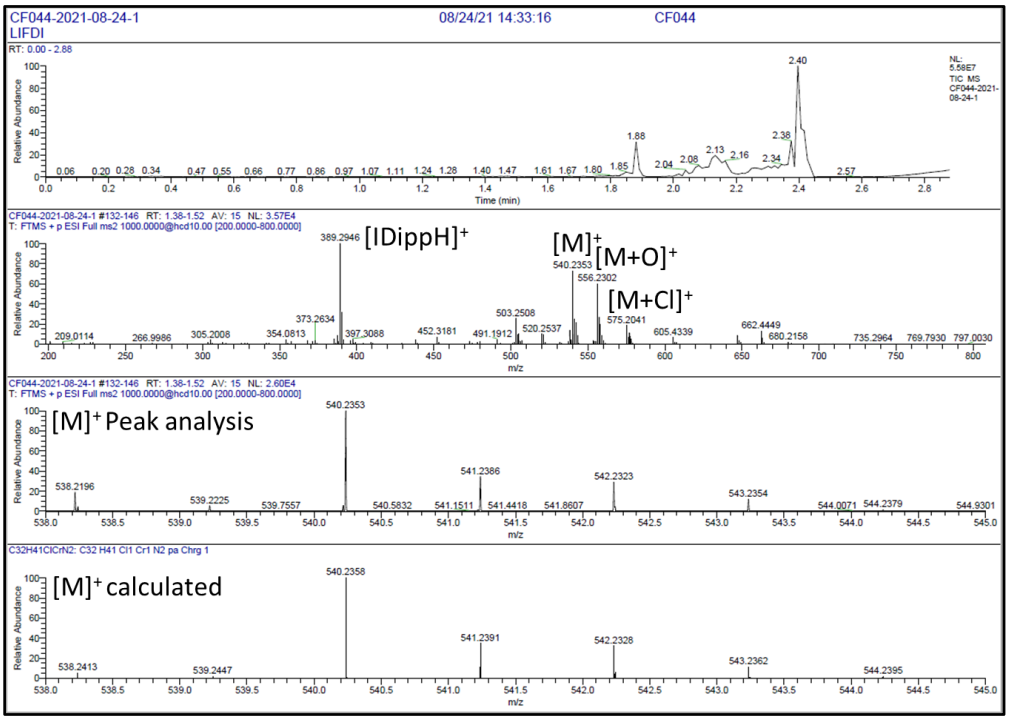

Figure S19: Mass spectrometric data obtained for [(η^5-C_5H_5)Cr(IDipp)Cl] **6**. Due to its high sensitivity towards ambient air and moisture, additional peaks were observed and assigned to the oxidation products [(η^5-C_5H_5)Cr(O)(IDipp)Cl] (m/z = 556.2302) and [(η^5-C_5H_5)Cr(IDipp)Cl_2] (m/z = 575.2041) as well as the protonated ligand $IDippH^+$ (m/z = 389.2946).

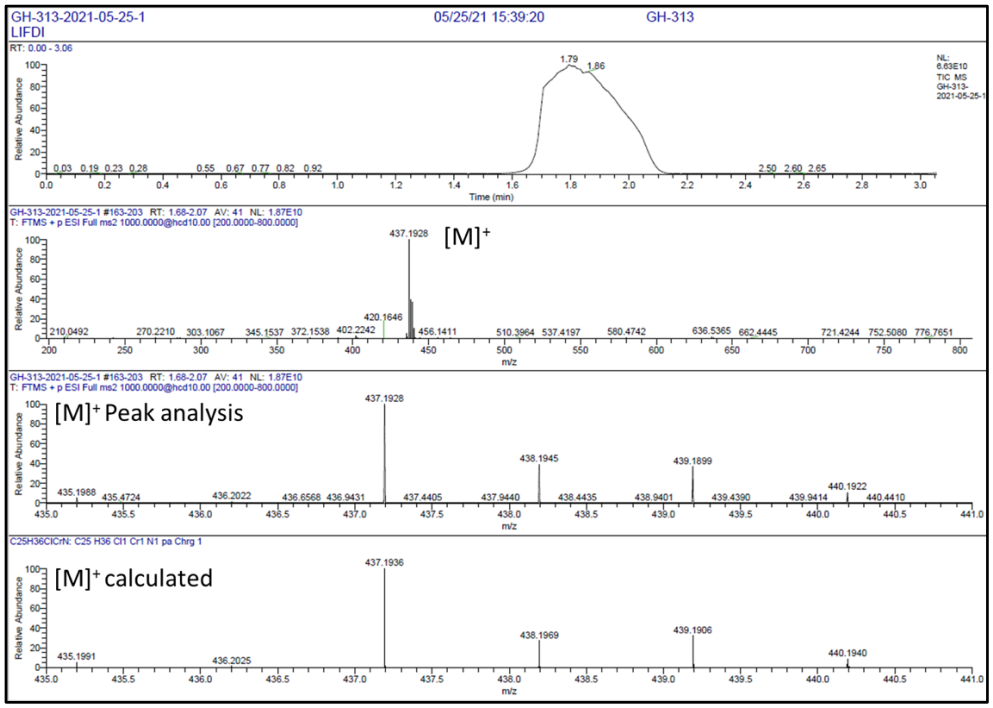

Figure S20: Mass spectrometric data obtained for [(η^5-C_5H_5)Cr($cAAC^{Me}$)Cl] **7**.

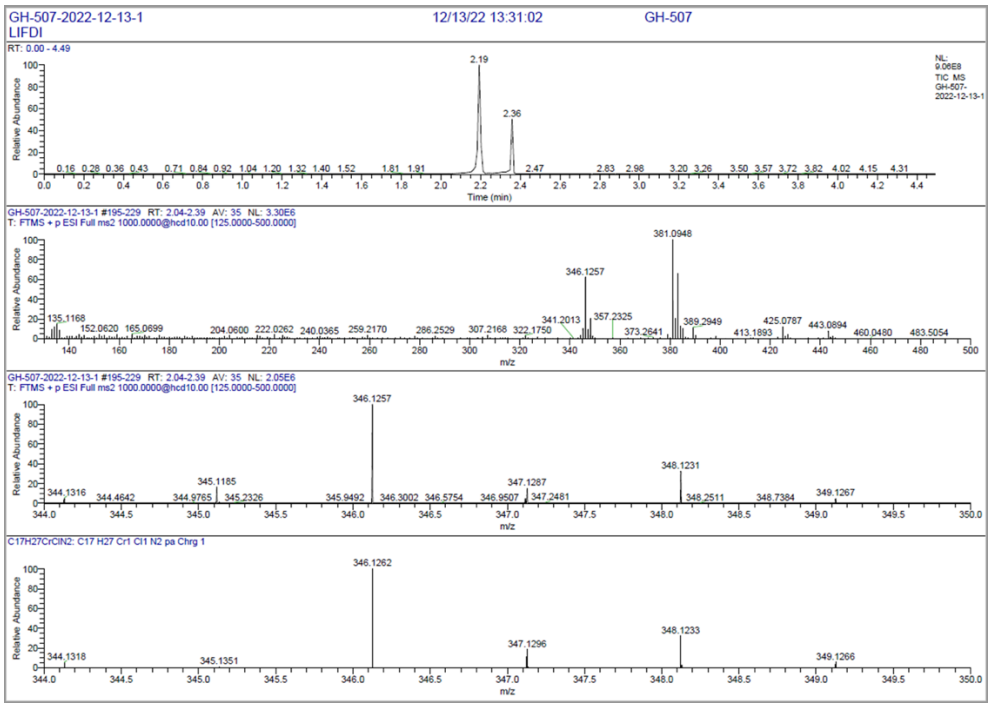

Figure S21: Mass spectrometric data obtained for [(η^5-C_5Me_5)Cr(IMe^{Me})] **8**

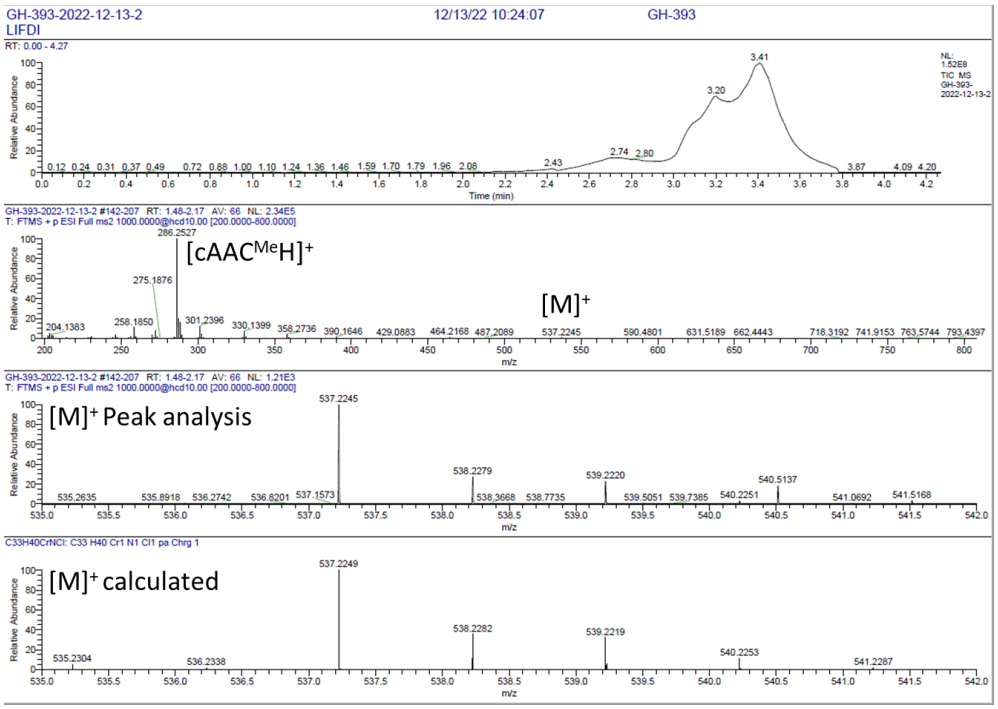

Figure S22: Mass spectrometric data obtained for [(η^5-$C_{13}H_9$)Cr(cAAC^{Me})Cl] **9.**

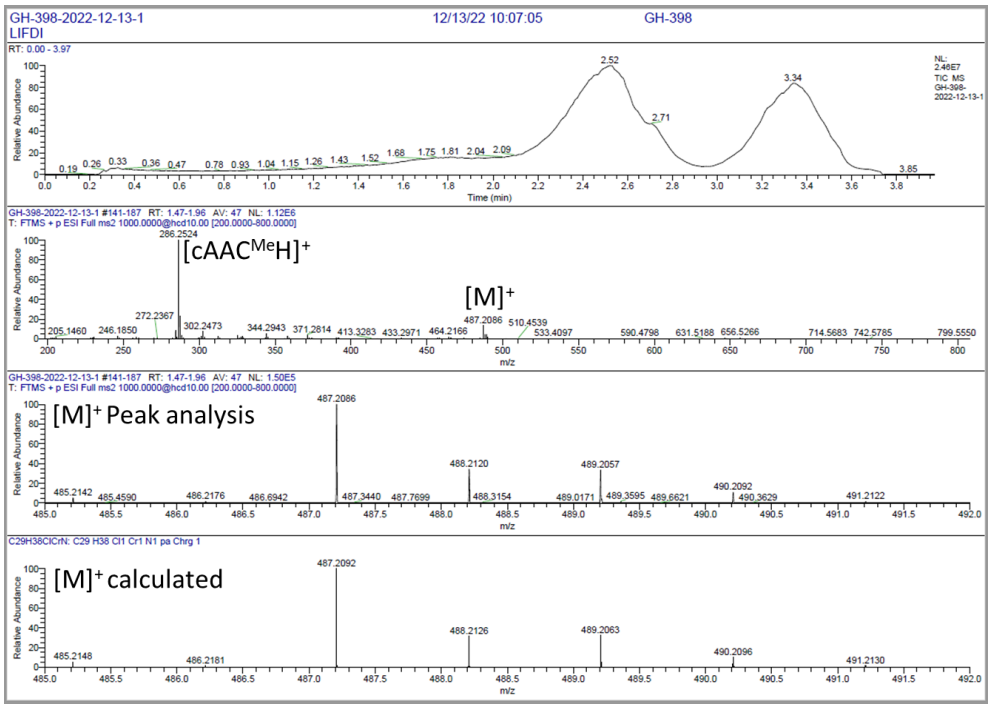

Figure S23: Mass spectrometric data obtained for $[(\eta^5\text{-}C_9H_7)Cr(cAAC^{Me})Cl]$ **10.**

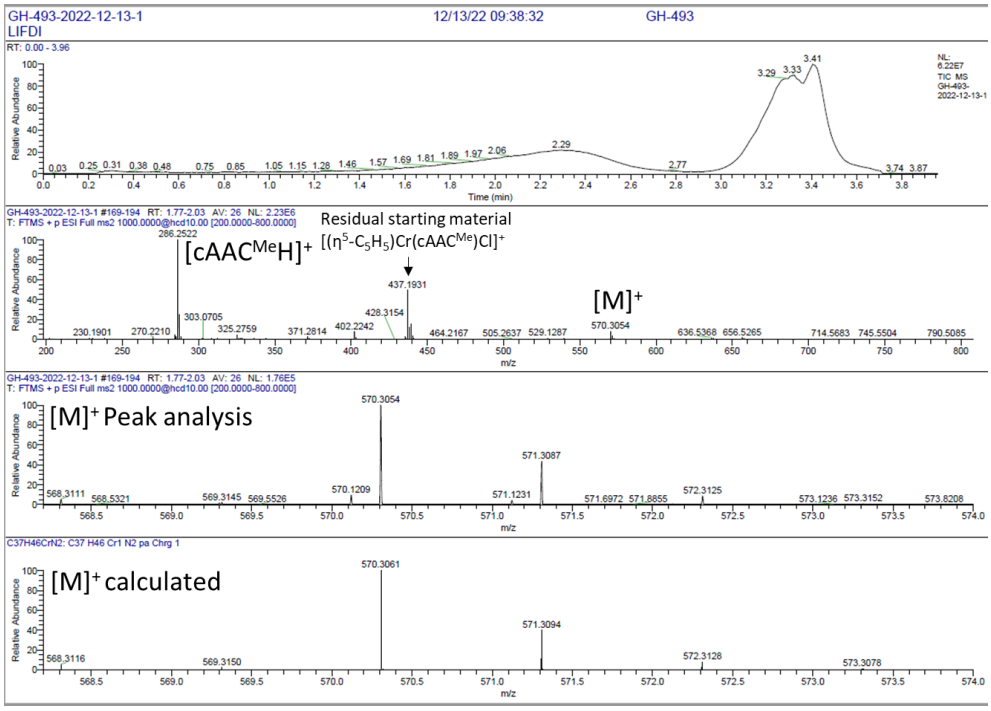

Figure S24: Mass spectrometric data obtained for $[(\eta^5\text{-}C_5H_5)Cr(cAAC^{Me})(NPh_2)]$ **11.**

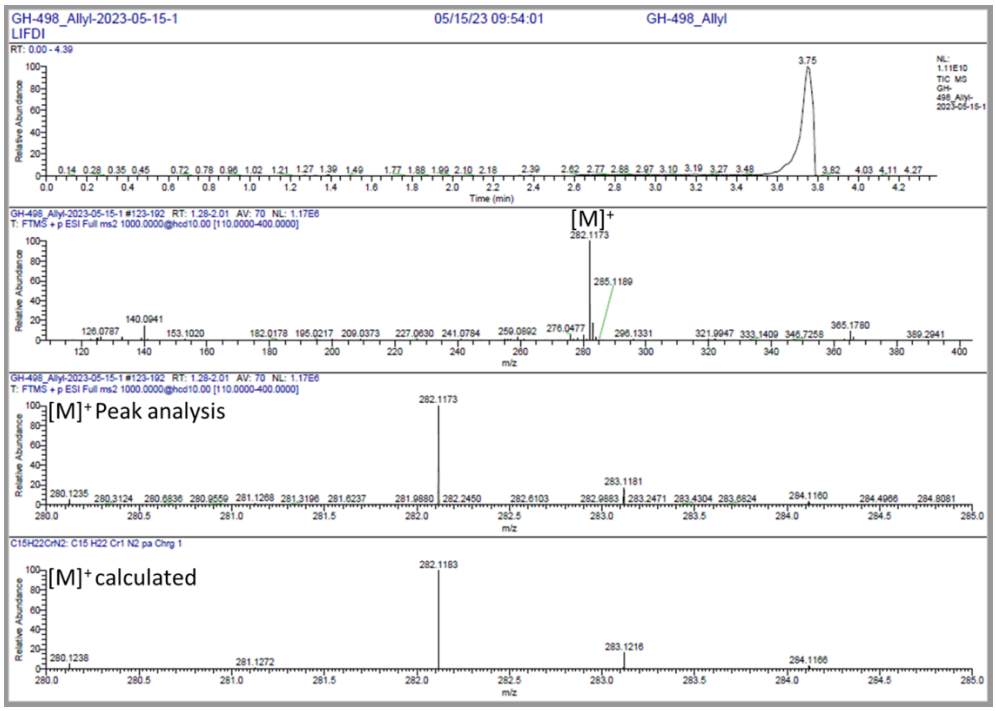

Figure S25: Mass spectrometric Data obtained for $[(\eta^5\text{-}C_5H_5)Cr(IMe^{Me})(\eta^5\text{-}C_3H_5)]$ **12**.

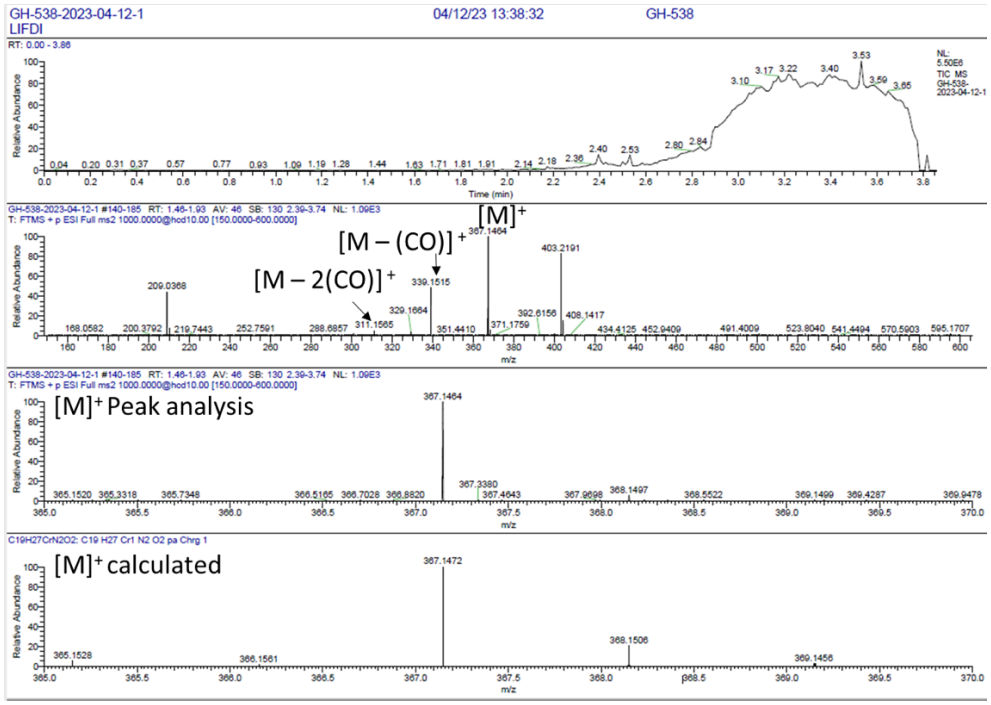

Figure S26: Mass spectrometric Data obtained for $[(\eta^5\text{-}C_5Me_5)Cr(IMe^{Me})(CO)_2]$ **13**.

4. IR-Spectrum of $[(\eta^5\text{-}C_5Me_5)Cr(IMe^{Me})(CO)_2]$ 13

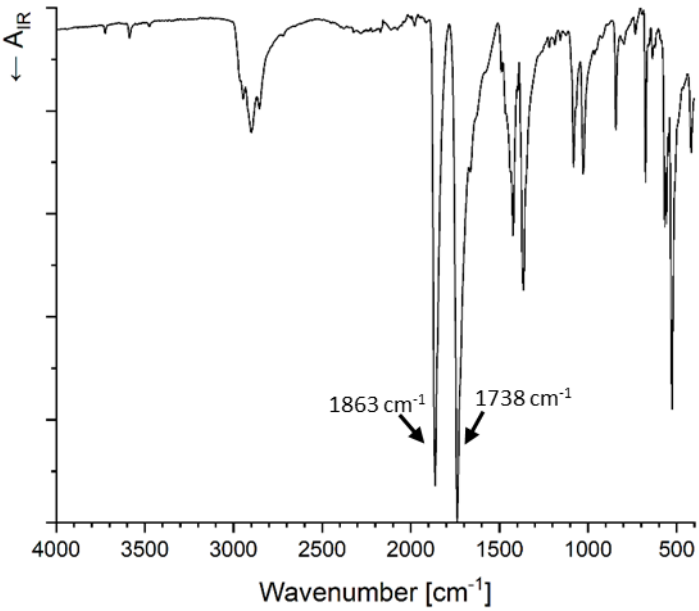

Figure S27: IR spectrum obtained for $[(\eta^5\text{-}C_5Me_5)Cr(CO)_2(IMe^{Me})]$ **13**. The bands at 1738 cm^{-1} and 1863 cm^{-1} can be assigned to the $\nu_{CO\ symm}$ and $\nu_{CO\ asymm}$ stretching modes of CO.

5. UV-Vis Spectra of Compounds

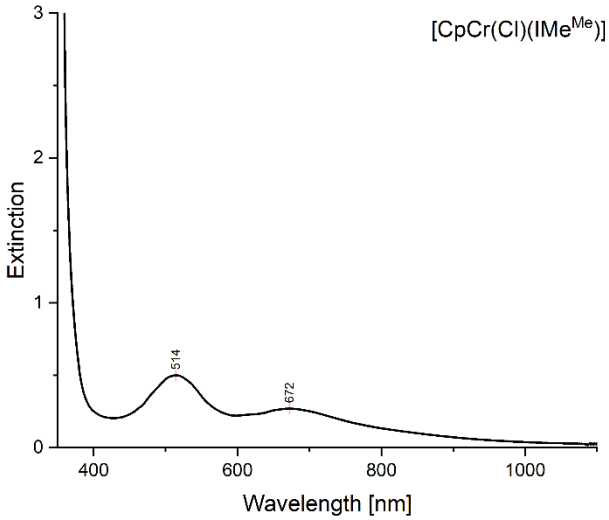

Figure S28: UV-Vis spectrum of [(η^5-C_5H_5)Cr(IMe^{Me})Cl] **3** in toluene. Molar extinction coefficients of **3**: 514 nm (ε = 105 L mol^{-1} cm^{-1}), 672 nm (ε = 55 L mol^{-1} cm^{-1}).

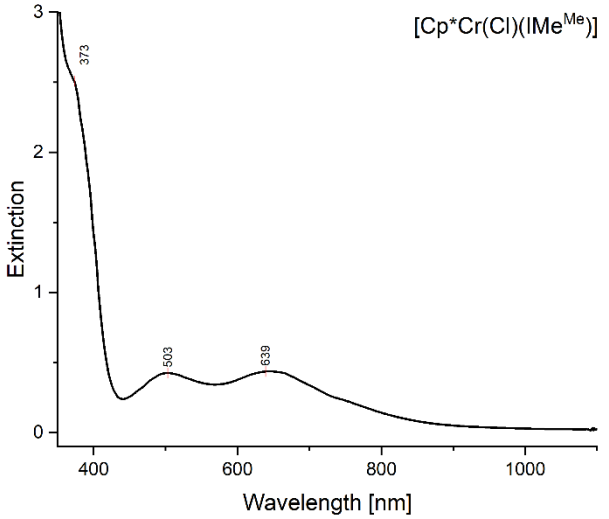

Figure S29: UV-Vis spectrum of [(η^5-C_5Me_5)Cr(IMe^{Me})Cl] **8** in toluene. Molar extinction coefficients of **8**: 373 (ε = 667 L mol^{-1} cm^{-1}), 503 (ε = 126 L mol^{-1} cm^{-1}), 639(ε = 122 L mol^{-1} cm^{-1}).

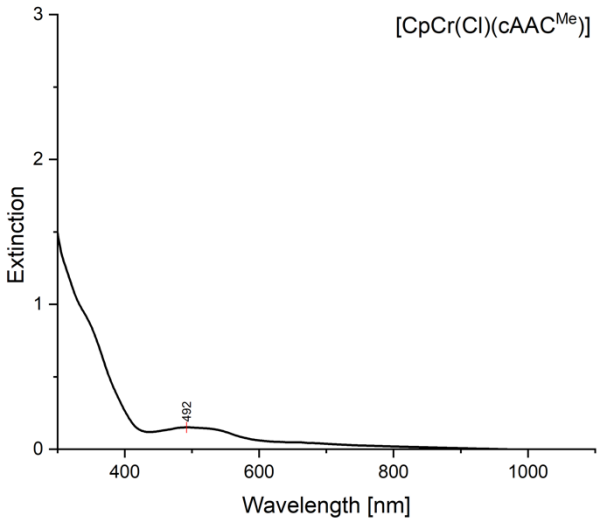

Figure S30: UV-Vis spectrum of [(η^5-C_5H_5)Cr(cAAC^{Me})Cl] **7** in toluene. Molar extinction coefficients of **7**: 492 nm (ε = 248 L mol^{-1} cm^{-1}).

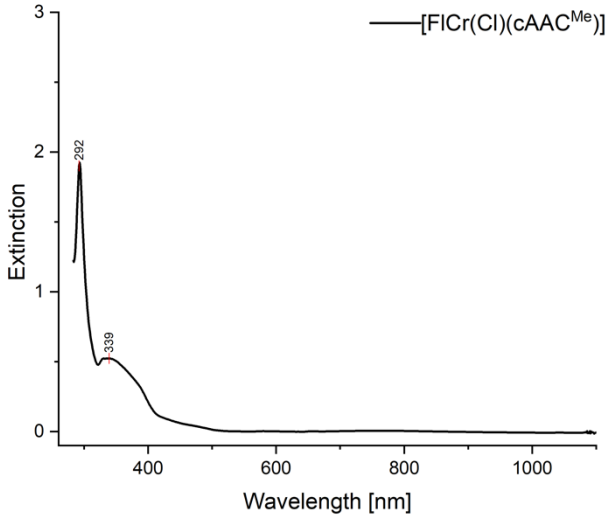

Figure S31: UV-Vis spectrum of [(η^5-$C_{13}H_9$)Cr(cAAC^{Me})Cl] **9** in toluene. Molar extinction coefficients of **9:** 292 nm (ε = 7603 L mol^{-1} cm^{-1}), 339 nm (ε = 2600 L mol^{-1} cm^{-1}), 745 nm (ε = 166 L mol^{-1} cm^{-1}).

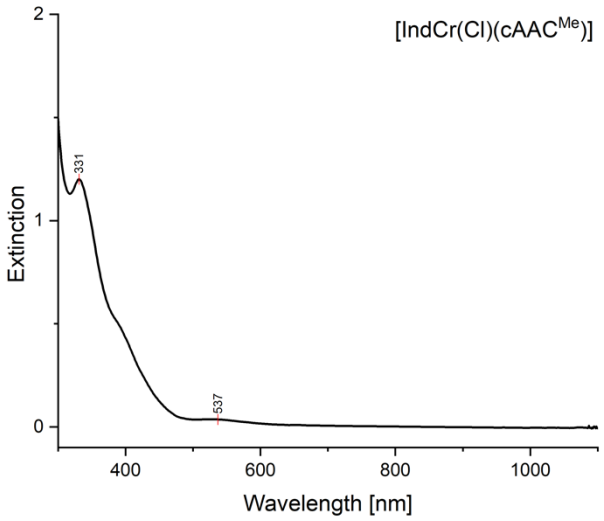

Figure S32: UV-Vis spectrum of [(η^5-C_9H_7)Cr(cAAC^{Me})Cl] **10** in toluene. Molar extinction coefficients of **10:** 331 nm (ε = 3881 L mol^{-1} cm^{-1}), 537 nm (ε = 168 L mol^{-1} cm^{-1}).

5. Computational Details – Optimized Geometries

General Considerations

Calculations have been performed using the TURBOMOLE V7.2 program suite, a development of University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.[3] Geometry optimizations were performed using (RI-)DFT calculations[4] on a m4 grid employing the BP86[5] functional and a def2-TZVP basis set for chromium and for all other atoms the def2-SVP basis sets.[6] Vibrational frequencies were calculated at the same level with the AOFORCE[7] module and the optimized structure represents a true minimum without imaginary frequencies.

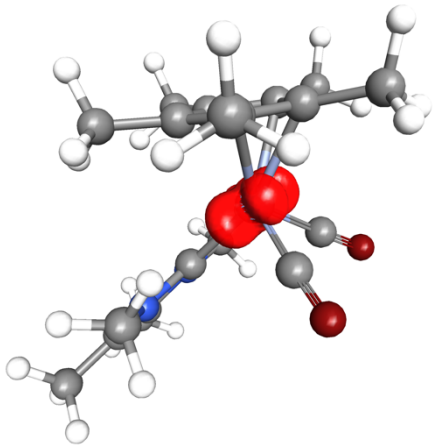

Figure S33: Spin-density of [(η^5-C_5Me_5)Cr(IMe^{Me})(CO)$_2$] **13** at the DFT/def2-SVP,def2-TZVP(Cr)/BP86 level of theory.

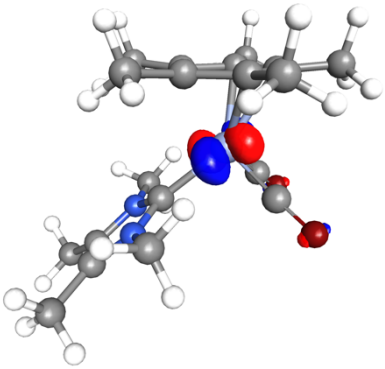

Figure S34: Calculated SOMO of [(η^5-C_5Me_5)Cr(IMe^{Me})$(CO)_2$] **13** at the DFT/def2-SVP,def2-TZVP(Cr)/BP86 level of theory.

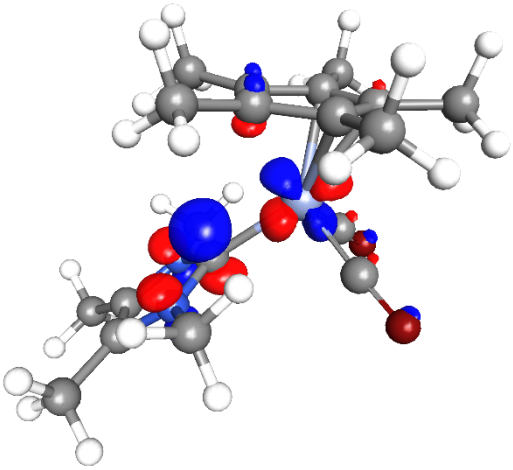

Figure S35: Calculated LUMO of [(η^5-C_5Me_5)Cr(IMe^{Me})$(CO)_2$] **13** at the DFT/def2-SVP,def2-TZVP(Cr)/BP86 level of theory.

Cartesian coordinated of the optimized complex [(η^5-C_5Me_5)Cr(IMe^{Me})$(CO)_2$] 13

Energy = -2044.166647395

C	2.7490976	3.8520007	6.0874196
N	3.6096341	2.7881859	6.2635443
N	3.3654682	4.5918907	5.0994175
Cr	1.0005429	4.2579536	7.0852213
C	4.7380732	2.8751959	5.4345935
C	3.4116369	1.7296808	7.2398690
C	4.5824102	4.0245806	4.6925076
C	2.8539394	5.8494575	4.5798516
C	1.4069531	5.9823119	7.4992540
C	1.6789131	4.0379287	8.7582059
C	-0.2583699	2.6369631	6.1444316
C	-0.4472554	3.8550683	5.3969633
C	-0.9899297	4.8461420	6.2883265
C	-1.1403984	4.2425380	7.5924235

C	-0.6847899	2.8734766	7.4989263
C	5.8300048	1.8563281	5.4405693
C	5.4529364	4.6370623	3.6450700
O	1.6327624	7.0984718	7.8135066
O	2.0744914	3.9277455	9.8658946
C	0.1814419	1.3240954	5.5579968
C	-0.2313731	4.0018881	3.9163621
C	-1.4578823	6.2239579	5.9052514
C	-1.7810645	4.8806736	8.7940960
C	-0.7861044	1.8443310	8.5920584
H	0.5303775	0.6177236	6.3363199
H	-0.6574222	0.8243331	5.0234694
H	1.0032660	1.4498558	4.8245736
H	0.6870729	3.4825021	3.5756863
H	-1.0809482	3.5666866	3.3435018
H	-0.1506558	5.0636103	3.6118043
H	-0.9069673	6.6211091	5.0297140
H	-2.5378790	6.2179464	5.6381227
H	-1.3246732	6.9489128	6.7314022
H	-1.6146988	5.9755003	8.8132316
H	-2.8815707	4.7120587	8.8064734
H	-1.3738526	4.4730612	9.7399645
H	-0.6001513	2.2841689	9.5910507
H	-1.7989188	1.3842480	8.6141165
H	-0.0573728	1.0206948	8.4559670
H	4.1188850	1.8278122	8.0890780
H	2.3832205	1.8196009	7.6324521
H	3.5448409	0.7341305	6.7718486
H	6.2998509	1.7528757	6.4419182
H	5.4678411	0.8479486	5.1446402
H	6.6276270	2.1413173	4.7286801
H	6.3703652	4.0347214	3.5055454
H	4.9453004	4.6997547	2.6581393
H	5.7694167	5.6673228	3.9144379
H	2.8459186	5.8423493	3.4717881
H	1.8234163	5.9767191	4.9563412
H	3.4626738	6.7076089	4.9317741

6. References

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