Selective Trimerisation and Polymerisation of Ethylene: Halogenated Chromium Triazacyclohexane Complexes as Probes for an Internal 'Halogen Effect'

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Dedicated to Prof. John Bercaw on the occasion of his 70th birthday.

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ABSTRACT

A range of triazacyclohexane (R_3TAC) complexes of $CrCl_3$ with unsaturated N-substituents R have been prepared. The complexes with R = allyl (**3f**) and $CH_2CH(CH_2CH{=}CH_2)_2$ (**3h**) have been characterised by X-ray crystallography. Addition of HX or X_2 (X=Cl or Br) across the double bonds of the complexed ligand gives access to β- and γ-branched N-substituents containing three to twelve organic halogen atoms. The complexes with R = $CH_2CHBrCH_2Br$ (**3k**), $CH_2CH_2CX(^nC_5H_{11})_2$ (X=Cl (**3n**) and Br (**3o**)) have been characterised by X-ray crystallography. N-substituent chlorinated complexes can also be prepared via alkyl chloride containing amines as demonstrated for a crystal structure of a complex with R = $(CH_2)_3Cl$ (**3e**). Complexes with β-branched N-substituents give high selectivity for ethylene trimerisation to 1-hexene while complexes with γ-branched N-substituents are good ethylene polymerisation catalysts. The halogenated polymerisation catalysts give higher activities than their hydrogenated analogues, especially chlorine containing species. Chlorinated trimerisation catalysts demonstrated significantly improved 1-hexene selectivities, though activity was similar to hydrogenated alternatives. This lends support to the concept of a positive 'halogen effect' on the catalysis.

1. Introduction

The rapid expansion of oil and gas extraction from shale deposits in the USA and around the world has led to a significant increase in the availability of feed-stock gases [1]. Of significant commercial interest is therefore the conversion of light linear α-olefins, accessed via direct isolation, dehydrogenation or oligomerisation, into value-added products such as co-monomers, polymers and high performance fuels. Trimerisation and polymerisation are highly efficient synthetic routes to these higher molecular weight products and they are often based on chromium catalysts [2].

We have previously reported that triazacyclohexane complexes of $CrCl_3$ can be activated with MAO to produce effective ethylene polymerisation, [3] ethylene trimerisation [4] or α-olefin trimerisation [5] catalysts depending on the ligand design. Polyethylene produced by these species shows a similar branching and end group distribution to that of the Phillips catalyst [6]. $R_3TACCrCl_3$ catalysts can therefore be considered a good model for its investigation using a more defined system. This reactivity is attributed to the proposed ability of these species to form chromacyclic intermediates that

lead to highly selective trimerisation of ethylene to 1-hexene, which is then incorporated into the polymer.

Previous results have shown that the catalyst activity is correlated to the solubility of the $R_3TACCrCl_3$ complexes, which can be increased by introduction of branching into the N-substituent. As such, the readily available 2-ethylhexyl and 2-propylheptyl [4] substituents gave good solubility and activity for ethylene trimerisation.

Chlorinated and brominated additives have been used in ethylene trimerisation experiments with (1,3,5-tribenzyl-1,3,5-triazacyclohexane)$CrCl_3$ activated with 2,5-dimethylpyrrole and triethylaluminium [4]. It was found that addition of *n*-butyl bromide (*n*-BuBr) enhanced the selectivity for C_6 and the productivity of the system. Further improvements were found when ethylaluminium dichloride (EADC) was added, giving even greater productivity and selectivity for C_6. This demonstrated that halogenated organic additives are beneficial to catalysis in much the same way as halides. This suggests that what is sometimes referred to as the 'halide effect' is better described as the 'halogen effect'. Similar 'halogen effects' have been observed for numerous other systems, yet its origin is still only poorly understood [7].

This publication explores the effect of both branching and halogen incorporation into the N-substituent of ethylene oligo/polymerisation catalysts based on $R_3TACCrCl_3$. Triazacyclohexanes are synthesised with unsaturated N-substituents symmetrically branched at the β or γ position, coordinated to $CrCl_3$ and subsequently halogenated by the addition of HCl, HBr, Cl_2 or Br_2 to the double bonds. Non-halogenated complexes of similar structures have been included in this study to allow an assessment of an internal 'halogen effect' on the catalysis.

2. Experimental

2.1. Materials

All manipulations of air/moisture sensitive compounds were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques or in an argon atmosphere in a Saffron glove box. All reagents were obtained from major suppliers. Complexes **3a-d** have been described previously [5, 8]. Fluorobenzene and 1,2-difluorobenzene were distilled under N_2 from CaH_2 and stored over molecular sieves in the glove box. Other dry solvents were obtained from the Innovative Technology Solvent Purification System (SPS).

2.2. Instrumentation and Characterization Procedures

NMR spectra were obtained on either a Bruker DRX500 MHz FT-NMR spectrometer [500MHz (^{1}H), 125MHz (^{13}C), 50MHz (^{15}N)], or a Bruker DRX400 MHz FT-NMR spectrometer [400MHz (^{1}H), 100MHz (^{13}C)] at 298K. All ^{13}C spectra are H decoupled unless otherwise stated. Shift values are quoted in ppm relative to TMS or set internal solvent signals [16]. Coupling constants and line widths are quoted in Hz. J-coupling is J_{H-H} for ^{1}H NMR spectra and J_{C-H} for coupled ^{13}C NMR spectra unless otherwise stated. Line widths at half height (W) are given in Hz for paramagnetic NMR spectra. NMR spectra are often taken without the use of deuterated solvent and referenced to the solvent signal externally referenced to TMS. The shift of 1,2-difluorobenzene (PhF_2) was set to 6.976 (^{1}H) and 117.98 (^{13}C) ppm determined for neat solvent relative an added trace of TMS. Effective magnetic moments were measured using the Evans method and corrected for the diamagnetic contribution. [9]

Mass spectra were obtained using a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik) using acetonitrile as a solvent collecting data in positive mode. The peaks quoted correspond to the calculated exact mass, the correct isotope patterns are present where the peak is quoted. For metal complexes a small amount of Me_3N.HCl or $^nPrNH_2$.HCl was added to obtain a predictable ion formation ($M+C_3H_{10}N^+$) unless otherwise stated.

Elemental analysis was performed on an Exeter Analytical CE440 Elemental Analyzer by Mr. A. K. Carver in the University of Bath, Department of Chemistry, or externally by London Metropolitan University Elemental Analysis Service, UK.

2.3. X-ray Crystallographic Analysis

Intensity data for all structures were collected at 150(2) K on a Nonius KappaCCD diffractometer or an Agilent Xcalibur (for **3k**, **3o**) equipped with an Oxford Cryostream, using graphite monochromated MoKα radiation (λ= 0.71073 Å). Data were processed using the Nonius Software. [10] and Agilent Software [11]. For all structures a symmetry-related (multi-scan) absorption correction had been applied. Crystal parameters and details on data collection, solution and refinement for the complexes are provided in Table 2. Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-1.80 suite of programs throughout [12].

2.4. Preparation

2.4.1. $CrCl_3(THF)_3$ [13]

9.5 g of anhydrous $CrCl_3$ (60 mmol) and 270 mg Zn dust (4 mmol) are placed into a 250 mL flask and thoroughly dried under high vacuum and heating with a heat gun. 100 mL of dry and degassed THF is added and the suspension stirred for one day until a thick paste has formed. 100 mL of dry dichloromethane is added to give a deep-purple solution with some solid remaining. The solution is filtered off (some residual Zn and $CrCl_2(THF)$ remains on filter). The solvent is pumped off and the residue is washed with three 50 mL portions of dry Et_2O and dried *in vacuo* yielding 20 g (90%) of purple $CrCl_3(THF)_3$. Analysis corresponds to literature data.

2.4.2. Characterisation of [(2-ethylhexyl)$_3$TACCrCl_3] (**3c**)

^{13}C NMR, CH_2Cl_2: δ = 44.3 (W = 104, -CH**C**H_2Me), 38.0 (W = 101, -CH**C**H_2Pr), 27.7 (W = 42, -CH**C**H_2Pr), 21.7 (W = 25, -CHCH$_2$**C**H_2Et), 12.2 (W = 20, -CHCH$_2$CH$_2$CH$_2$**C**H_3), 11.1 (W = 53, -CHCH$_2$**C**H_3), -42 (W = 930, -**C**H).

2.4.3. Characterisation of [(2-propylheptyl)$_3$TACCrCl_3] (**3d**)

^{13}C NMR (CH_3CN, CN set to 116.4 (W = 5.5)): δ = 46.7 (W = 94.4, -CH**C**H_2Et), 44.2 (W = 92.3, -CH**C**H_2Bu), 31.6 (W = 7.7, -CHCH$_2$CH$_2$**C**H_2Et), 25.1 (W = 14.2, -CHCH$_2$**C**H_2Pr), 21.9 (W = 3.9, -CHCH$_2$CH$_2$CH$_2$**C**H_2Me), 18.9 (W = 14.7, -CHCH$_2$**C**H_2Me), 13.6 (W = 8.6, -CHCH$_2$CH$_2$**C**H_3), 12.9 (W = 3.0, -CHCH$_2$CH$_2$CH$_2$CH$_2$**C**H_3), -55 (W = 3050, **C**H). ESI-MS (m/z) of $[C_{33}H_{69}Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 724.4775, found 724.4792. *Anal.* Calc. for $C_{33}H_{69}Cl_3CrN_3$ (%): C, 59.49; H, 10.44; N, 6.31. Found: C, 59.30; H, 10.41; N, 6.24.

2.4.4. Synthesis of [(ClCH$_2$CH$_2$CH$_2$)$_3$TACCrCl_3] (**3e**)

2.4.4.1. Synthesis of (ClCH$_2$CH$_2$CH$_2$)$_3$TAC (**2e**)

3-Chloropropylamine hydrochloride (1.85 g, 14.2 mmol) is suspended in toluene (20 mL). 1.0 mL of 37w% formaldehyde solution (13.4 mmol) is added, then once the solids have dissolved KOH (930 mg, 14.1 mmol based on 85% purity) is also added. The mixture is stirred for 5 hrs. The clear toluene phase is taken from the white paste and filtered through $MgSO_4$. The solids are extracted with a further 1 mL of toluene. The combined solutions are pumped down and the residue is dried under high vacuum for 1hr to leave a colourless oil (1.298 g, 4.1 mmol, 93%) which turns cloudy within a few hours. ^{1}H NMR (m-PhF set to 7.072): δ = 3.39 (6H, t, J = 6.4, -C**H**$_2$Cl), 3.12 (6H, s, NC**H**$_2$N), 2.38 (6H, t, J = 6.6, TACC**H**$_2$-), 1.64 (6H, quintet, J = 6.5, -C**H**$_2$CH$_2$Cl). ^{13}C NMR – ^{1}H-coupled, (m-PhF

set to 130.476): δ = 74.6 (t of quintets, J = 143 / 4.6, N**C**H_2N), 49.6 (t, J = 133, TAC-**C**H_2-), 43.3 (t of quintets, J = 151 / 4.2, -**C**H_2Cl), 31.1 (t of t, J = 128 / 2.8, -**C**H_2CH_2Cl).

2.4.4.2. Synthesis of [$(ClCH_2CH_2CH_2)_3$TACCrCl_3] (**3e**)

2e (1.267 g, 4 mmol) and $CrCl_3(THF)_3$ (1.68 g, 4.5 mmol) is suspended in dry DCM (50 mL). The mixture is left standing for 1 day, filtered under N_2 and washed with dry DCM. The purple residue is washed with dilute HCl, water and DCM then dried *in vacuo*. The solid was extracted with 3 x 50 mL portions of hot 1:1 MeCN/$CHCl_3$ mixture until all purple solid is dissolved, leaving some white solid behind, giving a total of 1.60g (3.4 mmol, 75%) of purple **3e**. ^{13}C NMR – ^{1}H-coupled, $CDCl_3$: δ = 71.1 (W = 243, **C**H_2Cl), -69.9 (W = 2712, -**C**H_2CH_2Cl). ESI-MS (m/z) of $[C_{12}H_{24}Cl_6CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 532.0320; found: 532.0328. *Anal.* Calc. for $C_{12}H_{24}Cl_6CrN_3$ (%): C, 30.34; H, 5.09; N, 8.85. Found: C, 30.47; H, 5.27; N, 8.86. Magnetic Moment (MeCN:$CDCl_3$ 50:50w%) = 3.70BM.

2.4.5. Synthesis of [Allyl$_3$TACCrCl_3] (**3f**)

2.4.5.1. Synthesis of Allyl$_3$TAC (**2f**)

Allylamine (7.61 g, 133 mmol) and paraformaldehyde (3.30 g, 111 mmol) were stirred overnight in toluene (100 mL). The solvent was removed *in vacuo* to give an oil. Further toluene (50 mL) was added and then reduced *in vacuo* to take off any remaining water. The pale yellow oil was vacuum transferred to give a clear viscous oil (5.79 g, 107mmol, 96%). ^{1}H NMR, $CDCl_3$: δ = 5.82 (3H, m, -CH_2C**H**=CH_2), 5.17 (6H, m, -CH=C**H**$_2$), 3.34 (6H, broad s, NC**H**$_2$N), 3.10 (6H, d, J = 6.4, TAC-C**H**$_2$). ^{13}C NMR, $CDCl_3$: δ = 134.76 (CH_2**C**H=CH_2), 116.93 (-CH=**C**H_2), 73.13 (N**C**H_2N), 55.33 (TAC-**C**H_2).

2.4.5.2. Synthesis of [Allyl$_3$TACCrCl_3] (**3f**)

$CrCl_3(THF)_3$ (0.2g, 0.5mmol) was added to Allyl$_3$TAC (0.224g, 1.1mmol) in a Schlenk tube under argon. Dry THF (30ml) was added and the solution stirred until all solids had dissolved. The resulting solution was left to stand for 24h. The purple crystals of Allyl$_3$TACCrCl_3 that formed were isolated by decanting off the remaining solution and dried under vacuum at 40˚C. ^{13}C NMR (MeCN, Me set to 1.79): δ = 138.5 (W = 210, -CH=**C**H_2), 32.8 (W = 530, -**C**H=CH_2). ESI-MS (m/z) of $[C_{12}H_{21}Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 424.1014, found: 424.1020 . *Anal*. Calc. for $C_{12}H_{21}Cl_3CrN_3$ (%): C, 39.4; H, 5.8; N, 11.5. Found: C, 39.67; H, 5.84; N, 11.03.

2.4.6. Synthesis of [$(Hexyl_2CH^*CH_2)_3$TACCrCl_3] (**3g**) (*60% Deuterated)

2.4.6.1. Synthesis of Hexyl$_2$C(CN)COOMe (**4g**)

Sodium methoxide (6.16 g, 114 mmol) was dissolved in 40 mL of methanol in an addition funnel. 20 mL of this solution was added to the flask. Ethyl cyanoacetate (6.50 g, 57.5 mmol) was added to the flask and stirred for 5 minutes. Hexyl bromide (9.41 g, 57.3 mmol) was added and the reaction mixture heated to 75˚C for 20 minutes. After cooling to room temperature the remaining sodium methoxide solution was added and stirred for 5 minutes. A further portion of hexyl bromide (9.02 g, 55.0 mmol) was added and the reaction mixture once again heated to 70 ºC for 20 minutes. After cooling to room temperature water (100 mL) was added. The product was obtained via separation with ethyl acetate (6x 50 mL). The combined organic layers were dried with $MgSO_4$ and the solvent removed under reduced pressure yielding 14.01g (87%) of **4g** as a colourless liquid. ^{1}H NMR, $CDCl_3$: δ = 1.85 (2H, m, -CHC**H**$_2$Pe), 1.73 (2H, m, -CHC**H**$_2$Pe), 1.26 (19H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me and -OC**H**$_3$), 0.846 (6H, t, J = 7.06, -C**H**$_3$), ^{13}C NMR, $CDCl_3$: δ = 169.84 (**C**=O), 119.37 (-**C**N), 53.09 (**C**-

CN), 37.51 (-**C**H_2Et), 31.33 (-**C**H_2Pe), 28.82 (-**C**H_2Pr), 25.34 (-**C**H_2Bu), 22.40 (-**C**H_2Me), 14.11 (-O**C**H_3), 13.89 (-CH_2**C**H_3).

2.4.6.2. Synthesis of Hexyl$_2$CH*CN (**5g**) (*60% Deuterated)

4g (14.01 g, 49.0 mmol) was dissolved in dry DMSO (100 mL), lithium chloride (5.29 g, 124 mmol) and D_2O (0.980 g, 49.0 mmol) were added. The reaction mixture was stirred overnight at 150˚C under nitrogen. The product was obtained via separation with water and ethyl acetate (6 x 50 ml). The combined organic layers were dried with $MgSO_4$ and the solvent removed under reduced pressure. The resulting yellow oil was vacuum transferred yielding 8.34 g (81%) of a clear oil of **5g** (~60% Hexyl$_2$CDCN as determined by NMR spectroscopy). ^{1}H NMR (no solvent, Me set to 0.846): δ = 2.25 (~0.4H, q, -C**H**CN). 1.26-1.47 (20H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.846 (6H, t, J = 7.25, -C**H**$_3$). ^{2}H NMR (no solvent): δ = 2.25 (~0.6D, -C**D**). ^{13}C NMR (no solvent, Me set to 13.89): δ = 121.33 (-**C**N), 32.48 (CH**C**H$_2$Pe), 32.37 (-CD**C**H$_2$Pe), 31.72 (-**C**H$_2$Et), 31.50 (-**C**HCN), 31.17 (t, J_{C-D} = 21.1, -**C**DCN), 28.95 (-**C**H$_2$Pr), 27.21 (-**C**H$_2$Bu), 22.63 (-**C**H$_2$Me), 13.89 (-**C**H$_3$).

2.4.6.3. Synthesis of Hexyl$_2$CH*CH$_2$NH$_2$ (**1g**) (*60% Deuterated)

Whilst cooling with ice, aluminium trichloride (4.94 g, 37.0 mmol) was dissolved in dry diethyl ether (100 mL). Solid lithium aluminium hydride (4.19 g, 111 mmol) was added in portions to this solution whilst still cooling with ice. **5g** (7.76 g, 37.1 mmol) in dry diethyl ether (30 mL) was added drop wise to the reaction mixture and stirred overnight. THF (50 mL) containing water (2.64 g, 147 mmol) was added drop wise to the ether reaction mixture. The solvent was removed under reduced pressure and the product washed from the remaining solid with petroleum ether (3x 50 mL) and diethyl ether (3x 50 mL). The collected organic fractions were dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. The resulting yellow oil was vacuum transferred with slight heating yielding 1.93g (24%) of **1g** (~60% Hexyl$_2$CDCH$_2$NH$_2$ by NMR spectroscopy) as a clear oil. ^{1}H NMR (no solvent, Me set to 0.846): δ = 2.49 (2H, m, -C**H**$_2$NH$_2$), 1.72 (~0.4H, m, -C**H**CH$_2$NH$_2$), 1.24 (20H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me, 1.43 (2H, s, -CH$_2$N**H**$_2$), 0.846 (6H, t, J = 6.84, -C**H**$_3$). ^{2}H NMR (no solvent): δ = 1.72 (~0.6D, -C**D**CH$_2$NH$_2$). ^{13}C NMR ($CDCl_3$): δ = 44.32 (-CH**C**H$_2$NH$_2$), 44.23 (-CD**C**H$_2$NH$_2$), 39.44 (-**C**HCH$_2$NH$_2$), 38.88 (t, J_{C-D} = 18.7, -**C**DCH$_2$NH$_2$), 31.69 (-**C**H$_2$Et), 31.18 (-CH**C**H$_2$Pe), 31.06 (-CD**C**H$_2$Pe), 29.51 (-**C**H$_2$Pr),), 26.37 (-CHCH$_2$**C**H$_2$Bu), 26.33 (-CDCH$_2$**C**H$_2$Bu), 22.47 (-**C**H$_2$Me), 13.88 (-**C**H$_3$).

2.4.6.4. Synthesis of (Hexyl$_2$CH*CH$_2$)$_3$TAC (**2g**) (*60% Deuterated)

1g (1.77 g, 7.80 mmol) was dissolved in toluene (100 ml) and then paraformaldehyde (0.23 g, 7.80 mmol) was added and left stirring overnight. The solvent was removed under reduced pressure. After further washing with toluene 1.80 g (97%) of **2g** was collected as a pale yellow oil. ^{1}H NMR (no solvent, Me set to 0.846ppm): δ = 3.18 (6H, broad s, NC**H**$_2$N), 2.19-2.22 (6H, m, -CHC**H**$_2$TAC and -CDC**H**$_2$TAC), 2.01 (3H, m, -C**H**CH$_2$TAC), 1.23-1.34 (62H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.846 (18H, t, J= 6.71, -C**H**$_3$). ^{2}H NMR (no solvent): δ = 2.01 (C**D**). ^{13}C NMR (no solvent, Me set to 13.95): δ = 75.28 (N**C**H$_2$N), 56.86 (-CH**C**H$_2$TAC), 56.76 (-CD**C**H$_2$TAC), 36.16 (-**C**HCH$_2$TAC), 35.29 (br, -**C**DCH$_2$TAC), 32.36 (-CH**C**H$_2$Pe), 32.24 (-CD**C**H$_2$Pe), 31.88 (-**C**H$_2$Et), 29.85 (-**C**H$_2$Pr), 26.58 / 26.54 (-C(H/D)CH$_2$**C**H$_2$Bu), 22.58 (-**C**H$_2$Me), 13.95 (-**C**H$_3$).

2.4.6.4. Synthesis of [(Hexyl$_2$CH*CH$_2$)$_3$TACCrCl$_3$] (**3g**) (*60% Deuterated)

2g (1.80 g, 2.67 mmol) was dissolved in dry DCM (40 mL) and an excess of $CrCl_3(THF_3)$ (1.11 g, 2.93 mmol) was added. The reaction mixture was stirred overnight. The resulting purple solution was separated by column chromatography with DCM. The solvent of the purple fractions was removed under reduced pressure and the resulting solid dried under vacuum, yielding a purple solid, **2g** (1.10 g, 49%). ^{2}H-NMR (DCM, peak set to 5.30) δ = 7.63 (-C**D**CH$_2$TAC). ^{13}C-NMR (DCM, set to 54.00, W = 3.4) δ = 44.66 (W = 115.6, -**C**H$_2$Pe), 30.41 (W = 11.1, -**C**H$_2$Et), 28.65 (W = 19.1, -**C**H$_2$Pr), 25.24 (W = 38.0, -**C**H$_2$Bu), 12.35 (W = 4.8, -**C**H$_3$), 21.18 (W = 7.1, -**C**H$_2$Me), -43.46 (very br, -

C(H/D)CH_2TAC). ESI-MS (m/z) of $[C_{45}H_{91}D_2Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 892.67, found 892.6753. *Anal.* Calc. for $C_{45}H_{91.5}D_{1.5}Cl_3CrN_3$ (%): C, 64.64; H, 11.21; N, 5.02. Found: C, 64.30; H, 11.30; N, 5.05. Magnetic moment (DCM) = 3.88BM.

2.4.7. Synthesis of [(Allyl$_2$CH*CH$_2$)$_3$TACCrCl$_3$] (**3h**) (*60% Deuterated)

2.4.7.1. Synthesis of Allyl$_2$C(CN)COOMe (**4h**).

4h (9.27 g, 90%) was obtained as a colourless liquid by reaction of allyl bromide (5.00mL, 57.4 mmol) with ethyl cyanoacetate (6.51 g, 57.6 mmol) and sodium methoxide (6.16 g, 114 mmol) in a manner analogous to the procedure for the synthesis of **4g**. ^{1}H NMR (MeOH, Me set to 3.49): δ = 5.52 (2H, m, -C**H**=CH$_2$), 4.95–5.00 (4H, m, -CH=C**H**$_2$), 2.35 (4H, m, -C**H**$_2$CH=CH$_2$), 0.944 (3H, t, J = 7.19, -OC**H**$_3$). ^{13}C NMR (MeOH, Me set to 50.41): δ = 171.04 (**C**=O). 132.04 (-**C**H=CH$_2$), 121.48 (-CH=**C**H$_2$), 119.03 (-**C**N), 41.46 (-**C**H$_2$-CH=CH$_2$), 37.99 (**C**-CN), 14.86 (-O**C**H$_3$).

2.4.7.2. Synthesis of Allyl$_2$CH*CN (**5h**) (*60% Deuterated)

5h was obtained as a clear oil (4.73 g, 75%) by reaction of **4h** (9.27 g, 51.8 mmol) with LiCl (6.61 g, 156 mmol) and D_2O (1.21 g, 60 mmol) in dry DMSO (100 mL) in a manner analogous to the procedure for the synthesis of **5g.** ^{1}H NMR (m-PhF set to 7.072): δ = 5.62 (2H, m, -C**H**=CH$_2$). 4.99 – 5.02 (4H, m, -CH=C**H**$_2$), 2.25 (0.4H, m, -C**H**CH$_2$CH=CH$_2$), 2.01 (4H, m, -C(H/D)C**H**$_2$CH=CH$_2$). ^{2}H NMR (m-PhF set to 7.072): δ = 2.18 (C**D**CH$_2$CH=CH$_2$). ^{13}C NMR (No solvent, Allyl CH set to 132.04): δ = 132.04 (-**C**H=CH$_2$). 119.35 (-**C**N), 116.82 (-CH=**C**H$_2$), 33.90 (CH**C**H$_2$CH=CH$_2$), 33.81 (CD**C**H$_2$CH=CH$_2$), 29.22 (-**C**HCN), 28.92 (t, J_{C-D} = 20.9, -**C**DCN).

2.4.7.3. Synthesis of Allyl$_2$CH*CH$_2$NH$_2$ (**1h**) (*60% Deuterated)

1h was obtained as a clear oil (2.20 g, 45%) by the reaction of **5h** with lithium aluminium hydride (4.44 g, 117 mmol) and aluminium trichloride (5.21 g, 39 mmol) in diethyl ether (130 mL) in a manner analogous to the procedure for the synthesis of **1g**. ^{1}H NMR (neat, CH$_2$-CH=C**H**$_2$ set to 4.99): δ = 5.79 (2H, m, -C**H**=CH$_2$). 4.99 - 5.05 (4H, m, -CH=C**H**$_2$), 2.57 (2H, s, -C**H**$_2$NH$_2$), 2.03 - 2.12 (4H, m, -C**H**$_2$CH=CH$_2$), 1.90 (2H, s, -N**H**$_2$), 1.51 (0.4H, septet, J = 6.54, -C**H**CH$_2$NH$_2$). ^{2}H NMR (neat): δ = 1.51 (-C**D**CH$_2$NH$_2$). ^{13}C NMR (neat, Allyl CH set to 132.04): δ = 30.79 (-**C**H$_2$CH=CH$_2$), 35.22 (t, J_{C-D} = 19.6, -**C**DCH$_2$NH$_2$), 35.75 (-**C**HCH$_2$NH$_2$), 39.42 (-CD**C**H$_2$NH$_2$), 39.56 (CH**C**H$_2$NH$_2$), 110.78 (-CH=**C**H$_2$), 132.04 (-**C**H=CH$_2$).

2.4.7.4. Synthesis of (Allyl$_2$CH*CH$_2$)$_3$TAC (**2h**) (*60% Deuterated)

2h was obtained as a clear oil (2.32 g, 94%) by the reaction of **1h** (2.20 g, 17.5 mmol) with paraformaldehyde (0.5276 g, 18 mmol) in toluene (100 mL) in a manner analogous to the procedure for the synthesis of **2g**. ^{1}H NMR (toluene, *meta*-CH set to 7.25): δ = 5.86 (6H, m, -C**H**=CH$_2$), 5.11–5.14 (12H, m, -CH=C**H**$_2$), 3.35 (6H, broad s, NC**H**$_2$N), 2.37 / 2.39 (6H, s, CDC**H**$_2$TAC / CHC**H**$_2$TAC), 2.14-2.23 (12H, m, CHC**H**$_2$CH=CH$_2$ and CDC**H**$_2$CH=CH$_2$), 1.69 (1.2H, septet, J = 6.47, -C**H**CH$_2$TAC). ^{2}H NMR (no solvent): δ = 1.69 (-C**D**CH$_2$TAC). ^{13}C NMR (toluene, *meta*-CH set to 129.07): δ = 136.94 (-**C**H=CH$_2$), 116.21 (-CH=**C**H$_2$), 75.10 (N**C**H$_2$N), 55.85 (-CH**C**H$_2$TAC), 55.76 (-CD**C**H$_2$TAC), 36.32 (CH**C**H$_2$CH=CH$_2$), 36.24 (-**C**HCH$_2$TAC), 36.21 (-CD**C**H$_2$CH=CH$_2$), 35.76 (t, J_{C-D} = 18.2, -**C**DCH$_2$CH=CH$_2$).

2.4.7.5. Synthesis of [(Allyl$_2$CH*CH$_2$)$_3$TACCrCl$_3$] (**3h**) (*60% Deuterated)

Purple solid **3h** (2.46 g, 79%) was synthesised by the reaction of **2h** (2.32 g, 5.45 mmol) with $CrCl_3(THF_3)$ (2.25 g, 6.0 mmol) in dichloromethane (40 mL) in a manner analogous to the procedure

for the synthesis of **3g** and purified by column chromatography on silica with acetonitrile as eluent. ^{2}H NMR (DCM, set to 1.72) δ = 4.51 (-C**D**$CH_2CH{=}CH_2$). ^{13}C NMR (DCM set to 54.0 (W = 5)) δ = 138.20 (W = 58, -**C**$H{=}CH_2$), 118.17 (W = 36, -$CH{=}$**C**H_2), 52.44 (W = 124, -**C**$H_2CH{=}CH_2$), -50.87 (W = 831, -**C**(H/D)CH_2TAC). ESI-MS (m/z) [$C_{27}H_{43}D_2Cl_3CrN_3.C_3H_{10}N$]: Calculated exact mass 628.29, found 628.2958. *Anal.* Calc. for $C_{27}H_{43}D_2Cl_3CrN_3$ (%): C, 56.69; H, 7.93; N, 7.34. Found: C, 56.60; H, 7.95; N, 7.31. Magnetic moment (DCM) = 3.55BM.

2.4.8. Synthesis of [(Pentyl$_2$C=CHCH_2)$_3$TACCrCl_3] (**3i**)

2.4.8.1. Synthesis of Pentyl$_2$C=CHCN (**6**)

Sodium methoxide (4.72 g, 87.5 mmol) was dissolved in dry methanol (100 mL) and stirred for 5 minutes under N_2. Diethylcyanomethylphosphonate (12.33 g, 11.5 mL, 70.4 mmol) was pipetted into the solution and stirred for a further 5 minutes. 6-undecanone (10.0 g, 12.0 mL, 58.7 mmol) in 50 mL of dry methanol was added slowly by dropping funnel. The mixture was then heated at 70˚C for 4 days. The solvent was removed under reduced pressure and the product extracted from the remaining salts by washing with petroleum ether (3 x 50 mL) and then diethyl ether (50 mL). The combined fractions were reduced under vacuum. The resulting yellow oil was vacuum transferred to yield 10.48 g (92%) of a clear oil. ^{1}H NMR (MeOH, Me set to 3.31): δ = 5.18 (1H, s, J = 1.3, =C**H**CN), 2.36 (2H, t, J = 7.8, -*trans*-C**H**$_2$Bu), 2.17 (2H, t of d, J = 7.7 / 1.3, -*cis*-C**H**$_2$Bu), 1.45 (4H, m, -C**H**$_2$Me), 1.30 (8H, m, -C**H**$_2$C**H**$_2$Et), 0.88 (6H, m, -C**H**$_3$). ^{13}C NMR (MeOH, set to 49.0): δ = 169.9 (-**C**=CHCN), 116.9 (-**C**N), 94.6 (=**C**HCN), 35.8 (-*trans*-**C**H_2Bu), 34.6 (-*cis*-**C**H_2Bu), 31.5/31.4 (-**C**H_2Et), 27.6/27.0 (-**C**H_2Pr), 22.42/22.37 (-**C**H_2Me), 13.53/13.52 (-**C**H_3).

2.4.8.2. Synthesis of Pentyl$_2$C=CHCH_2NH_2 (**1i**)

$AlCl_3$ (8.352 g, 62.5 mmol) was carefully dissolved into 400 mL of ice-cooled dry Et_2O under a nitrogen atmosphere. $LiAlH_4$ (7.513 g, 197.9 mmol) was then slowly added to avoid excessive boiling of the solvent during the highly exothermic reaction. The grey suspension was stirred for an hour at ambient temperature. A solution of **6** (11.6058 g, 59.6 mmol) in dry Et_2O (50 mL) was added drop-wise over 30 minutes and left to stir for half an hour. Significant bubbling was observed on addition of each drop due to the highly exothermic nature of the reaction. After complete addition the mixture was cooled in an ice bath and hydrolysed by the careful addition of 7.5 mL of water, 7.5 mL of 20% NaOH in water, 30 mL water and another 1 5mL of 20% NaOH solution, in that order. The mixture was stirred vigourously for an hour to ensure complete hydrolysis. The suspension became white over this period. The suspension was left to settle before decanting off the clear Et_2O solution, followed by extractions with Et_2O (3 x 150 mL). The solvent was removed from the combined extracts under reduced pressure to give a viscous clear liquid. Vacuum transfer at 10^{-2} mbar and ~300 ˚C yielded 9.6786 g (44 mmol, 82%) of unsaturated amine **1i**. ^{1}H NMR, $CDCl_3$: δ = 5.13 (1H, t, J = 6.9, =C**H**CH_2NH_2), 3.17 (2H, d, J = 6.8, -C**H**$_2NH_2$), 1.89 (4H, m, J = 6.6, -C**H**$_2$Bu), 1.15-1.33 (12H, m, -C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.99 (2H, broad s, -N**H**$_2$), 0.81 (6H, t, J = 6.5, -C**H**$_3$). ^{13}C NMR, $CDCl_3$: δ = 141.0 (-**C**=$CHCH_2NH_2$), 125.9 (=**C**HCH_2NH_2), 39.4 (-**C**H_2NH_2), 36.7 (-*trans*-**C**H_2Bu), 31.9/31.6 (-**C**H_2Et), 30.1 (-*cis*-**C**H_2Bu), 28.4/27.7 (-**C**H_2Pr), 22.5 (-**C**H_2Me), 14.0 (-**C**H_3).

2.4.8.3. Synthesis of (Pentyl$_2$C=CHCH_2)$_3$TAC (**2i**)

2i (2.11 g, 96%) was synthesised as a clear oil by reaction of **1i** (2.07 g, 10.5 mmol) with paraformaldehyde (0.31 g, 10.4 mmol) in toluene (100 mL) in a manner analogous to the procedure for the synthesis of **2g**. The oil was then kept for 12 hours at 110˚C under vacuum (10^{-2} mbar) to remove any water or other volatile impurities. ^{1}H NMR, CDCl3: δ = 5.12 (3H, t, J = 6.6, =C**H**CH_2TAC), 3.22 (6H, broad s, NC**H**$_2$N), 2.99 (6H, d, J = 6.5, -C**H**$_2$TAC), 1.93 (12H, m,-C**H**$_2$Bu), 1.17-1.34 (36H, m, -C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.81 (18H, m, -C**H**$_3$). ^{13}C NMR, CDCl3: δ = 143.0 (-**C**=$CHCH_2$TAC), 121.5 (=**C**HCH_2TAC), 77.2 (N**C**H_2N), 50.2 (-**C**H_2TAC), 36.8 (-*trans*-**C**H_2Bu), 32.0/31.7 (-**C**H_2Et), 30.3 (-*cis*-**C**H_2Bu), 28.2/27.8 (-**C**H_2Pr), 22.6 (-**C**H_2Me), 14.0 (-**C**H_3).

2.4.8.4. Synthesis of [(Pentyl$_2$C=CHCH$_2$)$_3$TACCrCl$_3$] (**3i**)

Purple solid **3i** (4.316 g, 90%) was synthesised by the reaction of **2i** (4.037 g, 6.40 mmol) with $CrCl_3(THF_3)$ (2.55 g, 6.80 mmol) in dichloromethane (20 mL) in a manner analogous to the procedure for the synthesis of **2h**. ^{13}C NMR (DCM set to 54.0 (W = 10)): δ = 165.1 (W = 131, -**C**=CHCH$_2$TAC), 30.2 (W = 19, -**C**H$_2$Pr), 29.9 (W = 15, -**C**H$_2$Et), 28.3 (W = 36, -**C**H$_2$Bu), 27.8 (W = 19, -**C**H$_2$Pr), 25.6 (W = 42, -**C**H$_2$Bu), 21.02 (W = 13, -**C**H$_2$Me), 20.78 (W = 8, -**C**H$_2$Me), 12.16 (W = 11, -**C**H$_3$), -4 (W = 720, =**C**HCH$_2$TAC). ESI-MS (m/z) $[C_{42}H_{81}Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 844.5714, found 844.5719. *Anal.* Calc. for $C_{42}H_{81}Cl_3CrN_3$ (%): C, 64.14; H, 10.38; N, 5.34. Found: C, 64.10; H, 10.40; N, 5.29. Magnetic moment (DCM) = 3.68BM.

2.4.9. Chlorine Addition to Complexes

2.4.9.1. Synthesis of [(ClCH$_2$CH(Cl)CH$_2$)$_3$TACCrCl$_3$] (**3j**)

A purple suspension of **3f** was prepared *in situ* by stirring **2f** (277 mg, 1.336 mmol) and $CrCl_3(THF)_3$ (523 mg, 1.396mmol) in 10 mL of dry DCM for 2hrs. The atmosphere in the flask was replaced by an atmosphere of Cl_2 gas for several hours and left standing for 2 days. The solvent was allowed to evaporate to dryness in a stream of nitrogen. The purple residue was dissolved in 20 mL of MeCN, filtered and allowed to evaporate. The residue was dissolved in DCM and washed with dilute HCl and water until the aqueous phase was no longer green. The remaining deep purple DCM solution was filtered through $MgSO_4$ to dry. The solvent was removed *in vacuo* and the residue washed with dry toluene followed by dry Et_2O. The resulting purple solid **3j** (398 mg, 85%) was dried under reduced pressure. ^{13}C NMR ($SOCl_2$, TMS set to 0.0): 70-85 (m, -CHCl**C**H$_2$Cl), -16 (m, -**C**HClCH$_2$Cl). ESI-MS (m/z) $[C_{12}H_{21}Cl_9CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 633.9151; found: 633.9135. *Anal.* Calc. for $C_{12}H_{21}Cl_9CrN_3$ (%): C, 24.92; H, 3.66; N, 7.27. Found: C, 26.5; H, 3.82; N, 6.90.

2.4.9.2. Synthesis of [((ClCH$_2$CH(Cl)CH$_2$)$_2$CH*CH$_2$)$_3$TACCrCl$_3$] (**3l**) (*60% Deuterated)

3h (0.528 g, 0.928 mmol) was dissolved in dry dichloromethane (60 mL). The solution was cooled whilst Cl_2 gas was bubbled through it in a closed system, occasionally venting the pressure. Cl_2 gas was generated by addition of concentrated hydrochloric acid (20.0 mL, 635 mmol) to potassium permanganate (3.33 g, 21.1 mmol). The solution was stirred overnight and the ice bath allowed to warm to room temperature. Argon was bubbled through the solution to reduce the volume and the residue was purified by column chromatography (eluting with 3:1, $CHCl_3$: MeCN). The solvent was removed under reduced pressure to yield a purple oil. This was dissolved in dichloromethane and an equal volume of methanol added. The dichloromethane was removed under reduced pressure, the methanol decanted and the resulting purple solid, **3l**, dried under vacuum for 12 hours (777 mg, 84% yield). ^{2}H NMR ($CHCl_3$, set to 7.26): δ = 8.62 (-C**D**CH$_2$CHClCH$_2$Cl). ^{13}C NMR (MeCN, Me set to 1.89): δ = 46 – 63 (m, -C(H/D)**C**H$_2$**C**HCl**C**H$_2$Cl), -50 (-**C**(H/D)CH$_2$TAC). ESI-MS (m/z) $[C_{27}H_{42}D_3Cl_{15}CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 1050.9343, found 1050.9372. *Anal.* Calc. for $C_{27}H_{43}D_2Cl_{15}CrN_3$ (%): C, 32.51; H, 4.55; N, 4.22. Found: C, 33.50; H, 4.70; N, 4.15. Magnetic moment (MeCN) = 3.32BM.

2.4.10. Bromine Addition to Complexes

2.4.10.1. Synthesis of [(BrCH$_2$CH(Br)CH$_2$)$_3$TACCrCl$_3$] (**3k**)

A purple suspension of **3f** is prepared in situ by stirring **2f** (169 mg, 0.815 mmol) and $CrCl_3(THF)_3$ (304 mg, 0.811 mmol) in 10 mL of dry DCM for 2 hrs. The suspension is cooled in an ice bath and a solution of Br_2 (650 mg, 4.1mmol) in DCM (10 mL) is slowly added over 1 hr. After stirring for another hour at RT, most of the suspension was dissolved to form a deep purple solution. Further stirring overnight resulted in a purple precipitate. The purple solids were dissolved in in several portions of 1:1, DCM:MeCN and the combined solutions were left to evaporate yielding a purple solid **3k** (290 mg, 42%). ^{13}C NMR ($SOCl_2$,TMS set to 0.0): δ = 55-80 (m, -**C**H$_2$Br), -20 (m, -**C**HBrCH$_2$Br). ESI-MS (m/z) $[C_{12}H_{21}Cl_3Br_6CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 897.6123, found:

897.6094. *Anal.* Calc. for $C_{12}H_{21}Cl_3Br_6CrN_3$ (%): C, 17.05; H, 2.50; N, 4.97. Found: C, 16.0; H, 2.59; N, 4.88.

2.4.10.2. Synthesis of [((BrCH$_2$CH(Br)CH$_2$)$_2$CH*CH$_2$)$_3$TACCrCl$_3$] (**3m**) (*60% Deuterated)

3h (0.522 g, 0.917 mmol) was dissolved in dry dichloromethane (60 mL). Bromine (3.00 mL, 9.30 g, 58.3 mmol) was added drop wise. The solution was stirred overnight and then purified by column chromatography (eluting with 3:1, $CHCl_3$: MeCN). The solvent and remaining bromine were removed under pressure to yield a brown oil. This was dissolved in dichloromethane and an equal volume of methanol added. The dichloromethane was removed under reduced pressure, the methanol decanted. The resulting purple solid, **3m**, was dried under vacuum (0.927 g, 66% yield). ^{2}H NMR ($CHCl_3$, set to 7.26): δ = 9.40 (-C**D**CH$_2$CHBrCH$_2$Br). ^{13}C NMR (MeCN, Me set to 1.89): δ = 39.71 – 55.57 (m, -C(H/D)**C**H$_2$**C**HBr**C**H$_2$Br), -80 – -60 (-**C**(H/D)CH$_2$TAC). ESI-MS (m/z) $[C_{27}H_{43}D_2Cl_3Br_{12}CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 1577.3223, isotopic abundance too low to be observed. Calculated max abundance peak: 1591.3066, found 1591.3237. *Anal.* Calc. for $C_{27}H_{43}D_2Cl_3Br_{12}CrN_3$ (%): C, 21.18; H, 2.97; N, 2.75. Found: C, 21.60; H, 3.02; N, 2.77. Magnetic moment (MeCN) = 3.47BM.

2.4.11. HCl addition to **3i**: Synthesis of [(Pentyl$_2$ClCCH$_2$CH$_2$)$_3$TACCrCl$_3$] (**3n**)

3i (1.786 g, 2.27 mmol) was dissolved in a mixture of acetyl chloride (12 mL, 169 mmol) and dichloromethane (10 mL) and cooled in an ice bath. Methanol (6.60 mL, 163 mmol) dissolved in 10 mL of dry DCM was added drop wise to the reaction mixture followed by stirring for 12 hours while warming to room temperature. Excess HCl was removed by bubbling N_2 through the solution. The resulting purple solution was passed through a short silica column eluting with DCM. The solvent of the purple fractions was removed under reduced pressure yielding a purple solid **3n,** which was further dried by heating the solid to 40 ˚C at 10^{-2} mbar overnight (0.33 g, 77%). ^{13}C NMR (DCM, set to 54.0 (W= 10)): δ = 102.3 (W = 188, -**C**ClCH$_2$CH$_2$TAC), 39.1 (W = 60, -**C**H$_2$Bu), 30.8 (W = 30, -**C**H$_2$Et), 24.7 (W = 52, -**C**H$_2$Pr), 21.8 (W = 26, -**C**H$_2$Me), 13.8 (W = 23, -**C**H$_3$), -26 (W = 930, -**C**H$_2$Bu). ESI-MS $[C_{42}H_{84}Cl_6CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 952.5015, found 952.4977. *Anal.* Calc. for $C_{42}H_{84}Cl_6CrN_3$ (%): C, 56.31; H, 9.45; N, 4.69. Found: C, 56.16; H, 9.65; N, 4.81. Magnetic moment (DCM) = 3.79BM.

2.4.12. HBr addition to **3i**: Synthesis of [(Pentyl$_2$BrCCH$_2$CH$_2$)$_3$TACCrCl$_3$] (**3o**)

3i (0.643 g, 0.82 mmol) was dissolved in a mixture of acetyl bromide (5 mL, 68 mmol) and dichloromethane (6 mL) and cooled in an ice bath. Methanol (2.60 mL, 64 mmol) dissolved in 3 mL of dry DCM was carefully added drop wise to the reaction mixture followed by stirring for 12 hours while warming to room temperature. The resulting purple solution was passed through a short silica column eluting with DCM. The solvent of the purple fractions was removed under reduced pressure yielding a purple solid **3o** which was further dried by heating the solid to 40 ˚C at 10^{-2} mbar overnight (603 mg, 69%). ^{13}C NMR (DCM, set to 54.0 (W= 10)) δ = 102.9 (W = 168, -**C**BrCH$_2$CH$_2$TAC), 40.4 (W = 59, -**C**H$_2$Bu), 30.7 (W = 28, -**C**H$_2$Et), 25.5 (W = 52, -**C**H$_2$Pr), 21.8 (W = 22, -**C**H$_2$Me), 13.2 (W = 20, -**C**H$_3$), -25 (W=810, -**C**H$_2$CH$_2$TAC). ESI-MS (m/z) $[C_{42}H_{87}Br_3Cl_3CrN_3.C_3H_{10}N]^+$: Calculated exact mass: 1084.3499, found 1084.3526. *Anal.* Calc. for $C_{42}H_{87}Br_3Cl_3CrN_3$ (%): C, 49.01; H, 8.23; N, 4.08. Found: C, 49.15; H, 8.32; N, 4.27.
Magnetic moment (DCM) = 3.85BM.

2.4.13. Hydrogenated Complex [(Pentyl$_2$CHCH$_2$CH$_2$)$_3$TACCrCl$_3$] (**3o**)

2.4.13.1. Synthesis of 3-pentyloctylamine, Pentyl$_2$CHCH$_2$CH$_2$NH$_2$ (**1o**)

10.8714 g of saturated/unsaturated amine mix produced from unselective nitrile reduction attempts was diluted into MeOH (120 mL). 10% Pd/C (430 mg) was added to form a black suspension. A large excess of hydrogen was generated by the drop-wise addition of water (2 mL) to a suspension of

CaH_2 (1.636 g, 39 mmol) in THF (20 mL). This was performed in a separate flask, connected to the reaction flask via a glass bridge, after evacuation of the whole system to the solvent vapour pressure. An oil bubbler was used to gauge the rate of H_2 produced. After the water addition the system was left stirring under hydrogen overnight. The solvent was removed under reduced pressure and the remaining liquid vacuum transferred off the Pd/C catalyst yielding 8.7760 of clear liquid (80% yield). ^{1}H NMR, $CDCl_3$: δ = 2.48 (2H, t, J = 6.8, -C**H**$_2$NH$_2$), 1.19 (2H, m, J = 6.5, -C**H**$_2$CH$_2$NH$_2$), 1.10 (1H, m, J = 6.8, -C**H**CH$_2$CH$_2$NH$_2$), 1.06 (16H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.89 (2H, s, -N**H**$_2$), 0.69 (6H, t, J = 7.1, -C**H**$_3$). ^{13}C NMR, $CDCl_3$: δ = 39.81 (-**C**H$_2$NH$_2$), 37.98 (-**C**HCH$_2$CH$_2$NH$_2$), 35.02 (-**C**H$_2$CH$_2$NH$_2$), 33.47 (-**C**H$_2$Bu), 32.08 (-**C**H$_2$Et), 26.03 (-**C**H$_2$Pr), 22.43 (-**C**H$_2$Me), 13.78 (-**C**H$_3$). ^{15}N NMR, $CDCl_3$: δ = 23.1.

2.4.13.2. Synthesis of (Pentyl$_2$CHCH$_2$CH$_2$)$_3$TAC (**2o**)

2o was obtained as a viscous liquid (3.880 g, 79%) by the reaction of **1o** (4.67 g, 23.4 mmol) with paraformaldehyde (0.634 g, 21.1 mmol) in toluene (15 mL) in a manner analogous to the procedure for the synthesis of **2g**. ^{1}H NMR, $CDCl_3$: δ = 3.30 (6H, broad s, NC**H**$_2$N), 2.39 (6H, t, J = 7.6, -C**H**$_2$TAC), 1.41 (6H, t, J = 6.6, -C**H**$_2$CH$_2$TAC), 1.29 (3H, m, J = 6.8, -C**H**CH$_2$CH$_2$TAC), 1.25 (48H, m, -C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$Me), 0.88 (18H, t, J = 7.1, -C**H**$_3$). ^{13}C NMR – ^{1}H-coupled, $CDCl_3$: δ = 74.65 (t, J=140.3, N**C**H2N), 50.44 (t, J = 130.9, -**C**H$_2$TAC), 35.62 (d, J = 126.5, -**C**HCH$_2$CH$_2$TAC), 33.48 (t, J = 124.8, -**C**H$_2$Bu), 32.11 (t, J = 127.2, -**C**H$_2$Et), 31.33 (t, J = 123.4, -**C**H$_2$CH$_2$TAC), 26.06 (t, J = 125.8, -**C**H$_2$Pr), 22.46 (t, J = 124.9, -**C**H$_2$Me), 13.83 (q, J = 124.4, -**C**H$_3$). ^{15}N NMR, $CDCl_3$: δ = 48.2.

2.4.13.3. Synthesis of [(Pentyl$_2$CHCH$_2$CH$_2$)$_3$TACCrCl$_3$] (**3o**)

3o was obtained as a purple solid (2.039 g, 93%) by the reaction of **2o** (3.880 g, 6.1 mmol) with $CrCl_3(THF)_3$ (2.192 g, 5.9 mmol) in DCM (20 mL) in a manner analogous to the procedure for the synthesis of **3g**. ^{13}C NMR, $CDCl_3$: δ = 62.1 (W = 142, -**C**HCH$_2$CH$_2$TAC), 34.8 (W = 67, -**C**H$_2$Bu), 29.2 (W = 43, -**C**H$_2$Pr), 33.7 (W = 29, -**C**H$_2$Et), 24.3 (W = 19, -**C**H$_2$Me), 15.9 (W = 15, -**C**H$_3$), -30.9 (W = 470, -**C**H$_2$CH$_2$TAC). ESI-MS (m/z) [$C_{42}H_{87}Cl_3CrN_3.C_3H_{10}N$]$^+$: Calculated exact mass: 850.6184, found 850.6193. *Anal.* Calc. for $C_{42}H_{87}Cl_3CrN_3$ (%): C, 63.65; H, 11.07; N, 5.30. Found: C, 63.83; H, 11.14; N, 5.47. Magnetic moment ($CDCl_3$) = 3.80BM.

2.5. General procedure for ethylene oligo/polymerisation

2.5.1. Ambient Pressure Tests

A 1 L four-necked flask, the reaction vessel, was dried by heating at 120ºC for at least 30 minutes before each run whilst flushing with argon at 40 L/min. Meanwhile, 20 μmol of the complex to be tested was weighed into a Schlenk tube whilst under argon. 500 equivalents of MAO were then added, in the form of 4.75 M toluene solution, to the complex and stirred for 15 minutes at 300 rpm. The common observation on activation of the catalyst is that the purple $R_3TACCrCl_3$ solid dissolves and forms a green solution.

Dry toluene (250 mL) was added to the reaction vessel and degassed by bubbling argon through and stirring vigourously while the temperature was increased to 40˚C. Once the temperature had stabilised the activated catalyst solution was injected into the reaction vessel, resulting in a pale yellow/green solution. The argon flow was turned off and the oligo/polymerisation reaction carried out by bubbling ethylene (40 L/minute) through the toluene solution for 10 minutes, whilst stirring at 300 rpm. The temperature was maintained between 38-42ºC for the duration of the reaction with the use of an ice bath. After 10 minutes the ethylene flow was turned off and replaced with a flow of argon for 10 minutes to remove any residual ethylene.

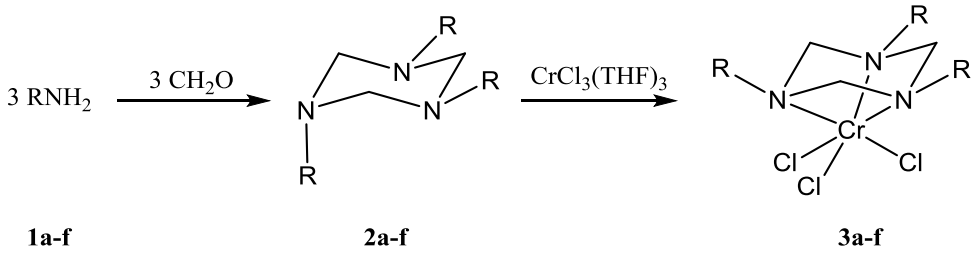
The system was then opened and a 1mL sample of the reaction mixture taken immediately by syringe and injected into a GCMS Headspace vial. Gas-phase GCMS analysis at this stage allowed quantitive analysis of 1-hexene production in conjunction with external calibration.

Methanol (50 mL) was then added to the bulk solution and stirred for 30 minutes to precipitate any polymer produced. If polymer precipitated, MeOH:HCl (4:1, 50 mL) was added to hydrolyse and solubilise the MAO. Further MeOH (200 mL) was added and stirred for 30 minutes before filtration and washing with more MeOH. The extracted polymer was dried at 70˚C and the weight recorded before submitting for analysis by GPC, DSC and IR.

3. Results and Discussion

3.1. Synthesis and Characterisation

Triazacyclohexane complexes $R_3TACCrCl_3$ were prepared in analogy to previously described complexes by condensation of primary amines with paraformaldehyde, followed by reaction with $CrCl_3(THF)_3$ in dichloromethane as shown in Scheme 1[5]. We also report here a convenient modification [13] for the synthesis of $CrCl_3(THF)_3$ which avoids Soxhlet extraction and is easily scaled up. The complexes are inert to air and moisture and can be further purified by column chromatography on silica.



1a-f **2a-f** **3a-f**

R = n-octyl (**a**) [5], n-dodecyl (**b**) [5], 2-ethylhexyl (**c**) [4], 2-propylheptyl (**d**) [4], $(CH_2)_3Cl$ (**e**) or allyl (**f**).

Scheme 1. Synthesis of triazacyclohexanes and their $CrCl_3$ complexes.

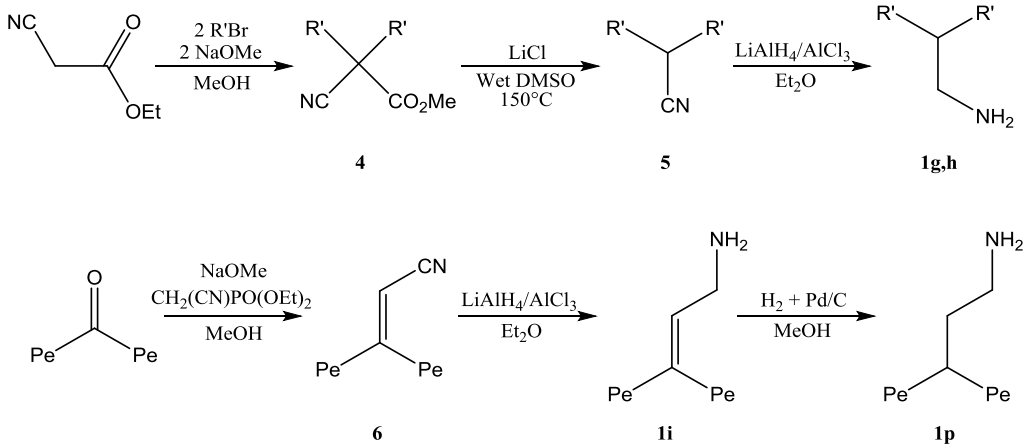
This procedure is limited by the functionality of the R groups, however, which restricts the versatility of the catalysts. In relation to this study, the synthesis of triazacyclohexanes incorporating aliphatic organohalides is hindered by quarternisation reactions with the amine. Nevertheless, these catalysts can be synthesised, as demonstrated for **3e**, by rapid complexation of **2e** because the chromium coordination acts as a protecting group for the amines.

The free 3-chloropropylamine is obtained in situ from the hydrochloride salt with NaOH followed by paraformaldehyde reaction, water removal by azeotropic distillation of the toluene solvent and immediate reaction with $CrCl_3(THF)_3$. Once formed, the complex **3e** is just as inert as other triazacyclohexane complexes. The bromide analogue of **2e** was too reactive in our hands to allow the synthesis of an analogous bromide complex. Therefore, the ability of the chromium centre to act as a protecting group for the amine led us to investigate the introduction of halides into the ligand after coordination.

We have developed a general synthetic route to halogenated triazacyclohexane catalysts based on addition of X_2 or HX (X = Cl or Br) to complexes with unsaturated N-substituents. The allyl substituted complex **3f** displays very limited solubility in most common solvents; therefore it was necessary to use larger unsaturated amines to achieve compatibility with the catalytic procedure. A range of branched unsaturated amines were prepared by modified literature procedures as shown in Scheme 2.

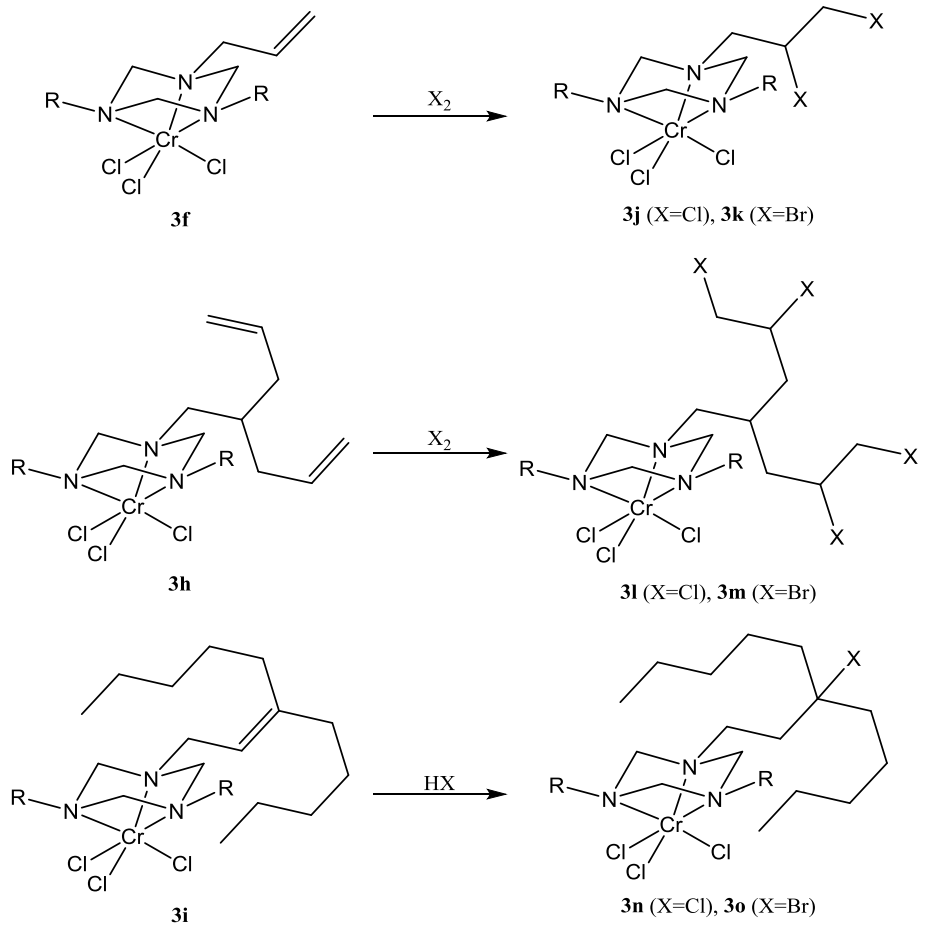
When the decarboxylation of **4** to **5** was performed in D_2O/DMSO, deuterium enriched analogues of compounds **1,3,5g,h** were obtained. Labelling of the β position in this way gave access to ^2H NMR as

an analytical tool for the characterisation of the paramagnetic chromium complexes. The selective reduction of the nitrile of **6** with $LiAlH_4$ was prevented due to significant reduction of the alkene, irrespective of variations to the stoichiometry, rate or order of addition. However, addition of an excess of a 3:1 mixture of solid $LiAlH_4$ and $AlCl_3$ ("AlH_3") gave selective reduction of the nitrile.



Scheme 2. Synthesis of branched amines. R' = n-hexyl (**g**) or allyl (**h**). Pe = Pentyl.

Chlorine and bromine have been added to complexes **3f** and **3h** while HCl and HBr have been reacted with **3i** as shown in Scheme 3. The clean addition to the olefinic groups demonstrates the inertness of the bonds to chromium against these aggressive reagents. Many attempts were also made at the addition of hydrogen iodide to **3i** but all proved incomplete. ESI-MS showed variable levels of HI addition and attempts at further purification ultimately led to HI loss. Thus, there appears to be an equilibrium between HI addition and elimination. In order to assess the 'halogen effect' of **3n,o** relative to a closely related halogen-free complex, **1i** was hydrogenated to **1p** before conversion to triazacyclohexane **2p** and subsequent complexation to form **3p**.



Scheme 3. Introduction of halogens into complexes **3f,h,i**.

All organic ligands and precursors were fully characterised by NMR spectroscopy. The triazacyclohexane complexes have been characterised by elemental analysis and ESI-MS. Mass Spectrometry was performed with the addition of ammonium salts which generates cations via Cr-Cl..H-N bridges [15]. Correct exact mass and isotope patterns for the adducts were found in all cases. NMR spectroscopy of the paramagnetic complexes was also performed and well resolved ^{13}C signals were observed at separations of three bonds or more from the TAC ring. This analysis also allowed calculation of the magnetic moments of the catalysts via the Evans method. In each case they were found to be around 3.6 μ_B, which is typical for Cr(III) complexes.

The observed ^{13}C shifts are listed in Table 1 along with their line widths, corresponding free ligand shifts and approximate isotropic shift due to the paramagnetism, calculated as the difference between the shifts of coordinated and free ligands. ^{1}H NMR spectra only show severely overlapping signals of little use in characterisation of these complexes, but ^{13}C NMR spectra give well resolved signals with characteristic paramagnetic shifts and line broadening depending on the spin delocalisation through bonds and the through-space distance from the paramagnetic centre, respectively [17]. The spectrum of **3i** and its HCl adduct **3n** and HBr adduct **3o** are included in the supplementary material. They show the changes in the ligand with a characteristic upfield shift of the olefinic ^{13}C signals and merging of the cis/trans pentyl branches. In the case of halogenated ligands the free ligand shifts were not available and predicted ^{13}C shifts [14] have been used. Previously unpublished NMR data of the known complexes **3a-d** have been included for comparison. The line widths, given in parentheses, depend strongly on the solvent and concentration used, but the relative width within one sample is a good indication for the distance from the paramagnetic chromium centre.

Comparison of this data demonstrates that the ^{13}C shifts follow simple rules which are useful in characterising the HX and X_2 addition reactions. While the ring and α-carbon positions were too

broad to be detected, the β-carbon position is observed as a significantly broadened peak (line width between 400 and 3100 Hz) shifted up-field by about 80ppm. The γ-carbon position is broadened to a width of around 100 Hz and shifted down-field by approximately 20ppm. Carbon positions with greater separation from the paramagnetic centre are only shifted by a few ppm and are slightly broadened. The influence of the paramagnetism, in terms of both peak shift and line broadening, decreases with increasing distance from the chromium.

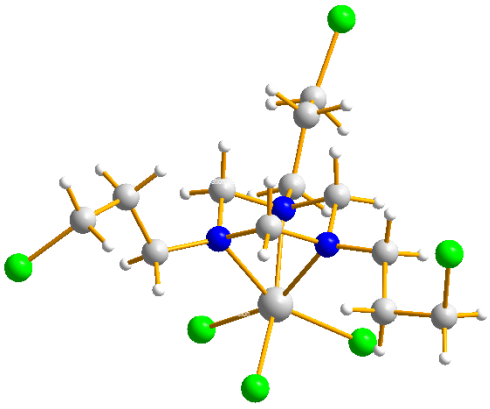
These rules allow the "diamagnetic" shift of the ligands to be accurately predicted, enabling assignment of olefinic, chlorinated, brominated and aliphatic carbon atoms and therefore confirmation of the reaction products. Cl_2 and Br_2 addition leads to mixtures of diastereomers with complex signal patterns in the ^{13}C NMR spectrum, which prevented measurement of the line width. However, the range of these signals matches those expected and it is significantly different from olefinic ^{13}C signals, giving good analytical evidence for complete halogenation. Complexes **3c,d** also contain racemic chiral carbon centres and should occur as a mixture of diastereomers. However, any differences in their NMR chemical shifts are not resolved for the chromium complexes.

Table 1. ^{13}C NMR shifts in complexes **3** compared to those in the free ligand **2** (line widths for **3**). Predicted shifts are used for the ligands **2d,j,k,l,m,n,o** and are shown in italics. Line widths have been omitted where severe broadening or overlapping peaks prevented reliable measurement. *The remaining, increasingly more distant peaks of **3b**: 26.8 (7), 29.4 (4), 20.1 (3), 11.5 (3).
2b: 29-32 (2C), 22.5, 13.9. Δ: ~ -4, ~ -1, -3, -2.

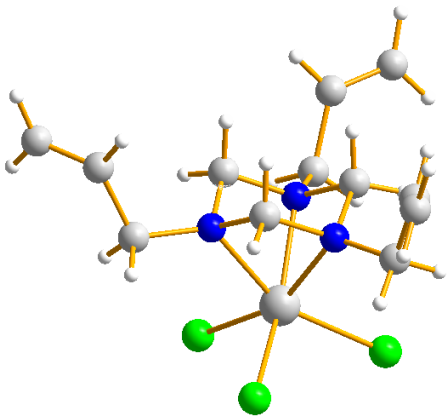
	Carbon Position						
Compound	β	γ	δ	ε	ζ	η	θ
3a	-70.5 (1650)	46.4 (150)	23.3 (33)	22.4 (21)	25.4 (15)	16.2 (12)	7.7 (11)
2a	27.4	27.3	29.1	29.3	31.7	22.5	13.9
Δ	-98	+19	-6	-7	-7	-7	-6
3b*	-70.0 (2450)	50.0 (220)	26.4 (15)	27.1	27.1	27.1	27.1
2b*	27.5	27.4	29.3	29-32	29-32	29-32	29-32
Δ	-98	+23	-3	~ -4	~ -4	~ -4	~ -4
3c	-42 (930)	(**C**H_2Pr)	(**C**H_2Et)	(**C**H_2Me)	(**C**H_3)		
		38.0 (101)	27.7 (42)	21.7 (25)	12.2 (20)		
		(**C**H_2Me)	(**C**H_3)				
		44.3 (104)	11.1 (53)				
2c	37.7	29.38	25.01				
		31.84	11.20	23.58	14.54		
Δ	-80	+9	+3				
		+12	0	-2	-3		
3d	-55 (3050)	(**C**H_2Bu)	(**C**H_2Pr)	(**C**H_2Et)	(**C**H_2Me)	(**C**H_3)	
		44.2 (92)	25.1 (14)	31.6 (8)	21.9 (4)	12.9 (3)	
		(**C**H_2Et)	(**C**H_2Me)	(**C**H_3)			
		46.7 (94)	18.9 (15)	13.6 (9)			
2d	*35.4*	*30.5*	*26.2*	*32.1*	*22.7*	*14.1*	
		30.5	*21.4*	*14.2*			
Δ	-90	+13	-1	0	-1	-1	
		+16	-2	0			
3e	-69.9 (2712)	71.1 (243)					
2e	31.1	43.3					
Δ	-101	+28					
3f	32.8 (530)	138.5 (210)					
2f	136.4	116.9					
Δ	-104	+22					
3j	-16	78					
2j	*59.5*	*46.2*					
Δ	-76	~ +30					
3k	-20	55-80					
2k	*53.7*	*34.5*					

Δ	-74	~ +30					
3g	-43.5	44.7 (116)	25.2 (38)	28.7 (19)	30.4 (11)	21.2 (7)	12.4 (5)
2g	36.2	32.4	26.6	29.9	31.9	22.6	13.9
Δ	-80	+12	-1	-1	-2	-2	-2
3h	-50.9 (831)	52.4 (124)	138.2 (58)	118.2 (36)			
2h	36.2	36.3	136.9	116.2			
Δ	-87	+16	+1	+2			
3l	-50	46-63	46-63	46-63			
2l	*37.9*	*44.9*	*60.1*	*47.6*			
Δ	-88	~ +10	~ -5	~ +7			
3m	-70	40-56	40-56	40-56			
2m	*37.9*	*48.2*	*52.1*	*35.9*			
Δ	-108	~ 0	~ -4	~ +12			
3i	-4 (1000)	165.1 (131)	cis/trans				
			25.6 (42)	27.8 (19)	29.9 (15)	20.8 (8)	12.2 (11)
			28.3 (36)	30.2 (19)	29.9 (15)	21.0 (13)	
2i	122.0	143.3	30.7	28.3	32.1	23.0	14.3
			37.3	28.7	32.4		
Δ	-124	+22	-4	0	-2	-2	-2
			-9	+1	-2		
3n	-27 (930)	102.3 188)	39.0 (59)	24.7 (52)	30.8 (30)	21.8 (26)	13.2 (23)
2n	*34.4*	*72.8*	*37.1*	*20.7*	*31.9*	*22.7*	*14.1*
Δ	-61	+30	+2	+4	-1	-1	-1
3o	-25 (810)	102.9 (168)	40.4 (59)	25.5 (52)	30.7 (28)	21.8 (22)	13.2 (20)
2o	*34.2*	*70.9*	*34.0*	*29.0*	*31.9*	*22.7*	*14.1*
Δ	-59	+32	+6	-3	-1	-1	-1
3p	-30.9 (470)	62.1 (142)	34.8 (67)	29.2 (43)	33.7 (29)	24.3 (19)	15.9 (15)
2p	31.3	35.6	33.5	26.1	32.1	22.5	13.8
Δ	-62	+25	+1	+3	+2	+1	+2

The complexes **3e,f,h,k,n,o** gave crystals of sufficient quality for X-ray diffraction and their structures are shown in Figure 1 along with selected average bond distances and angles in Table 2. The structures of **3k,n,o** have some disorder in one of the N-substituents. Crystals of **3p** were poor and showed severe disorder. Nevertheless, the connectivity of atoms confirmed the complex and details are given in the supplementary information.



3e



3f

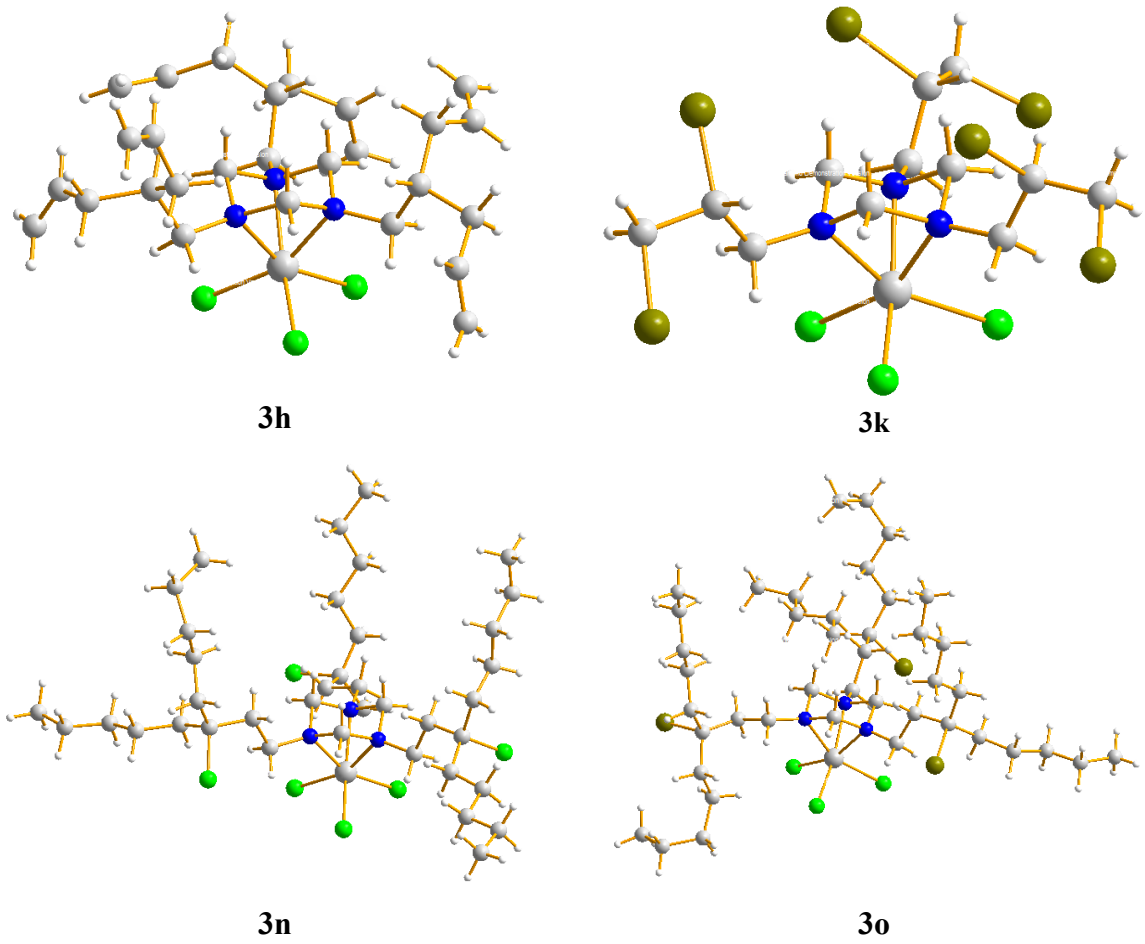


Fig. 1. The molecular structures of **3e,f,h,k,n,o**. A disorder in one of the N-substituents for **3k,n,o** and one of the pentyl groups in **3n** have been removed for clarity. Grey = C and Cr, White = H, Blue = N, Green = Cl, Brown = Br.

Table 2. Summary of X-ray Crystallography for **3e,f,h,k,n,o** with selected average bond distances and angles (*indicates range of values or SD, if greater, as a measure of confidence).

Empirical Formula	$C_{12}H_{24}Cl_6Cr\ N_3$ **3e**	$C_{12}H_{21}Cl_3CrN_3$ **3f**	$C_{28}H_{47}Cl_5CrN_3$ **3h**.CH_2Cl_2	$C_{12}H_{21}Br_6Cl_3CrN_3$ **3k**	$C_{42}H_{84}Cl_6CrN_3$ **3n**	$C_{42}H_{84}Br_3Cl_3CrN_3$ **3o**
Formula Weight	475.04	365.67	654.94	845.13	895.82	1029.20
Crystal System	Monoclinic	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P $2_1/c$	P 6_3	P $2_1/a$	C c	P $2_1/n$	P $2_1/n$
Unit Cell Dimensions						
a (Å)	11.01510(10)	11.8914(3)	13.7501(5)	14.621(4)	13.9670(18)	13.9501(8)
b (Å)	12.9310(2)	11.8914(3)	18.6094(4)	19.236(7)	13.9827(4)	14.1189(7)
c (Å)	14.2340(2)	6.93060(10)	13.8611(4)	9.154(2)	24.8449(4)	25.0564(12)
α (°)	90	90	90	90	90	90
β (°)	105.2230(10)	90	102.3530(10)	109.04(3)	91.149(2)	91.458(4)
γ (°)	90	120	90	90	90	90
V ($Å^3$)	1956.30(4)	848.73(3)	3464.68(18)	2433.8(12)	4851.1(6)	4933.5(4)
Z	4	2	4	4	4	4
μ (Mo Ka) (mm^{-1})	1.403	1.137	0.737	10.654	0.597	2.855
Total Reflections	45014	15247	55540	8198	39684	30961
Independent Reflections (R_{int})	5696 (0.0594)	1273 (0.0520)	6092 (0.1683)	4241 (0.0972)	8494 (0.1271)	10700 (0.0575)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0329, 0.0665	0.0228, 0.0568	0.0563, 0.1043	0.0803, 0.1874	0.0862, 0.2206	0.0459, 0.1020
Goodness-of-fit (GOF) on F^2	1.050	1.129	1.045	0.883	1.026	0.847
Largest Difference in Peak and Hole (e/$Å^3$)	0.402, -0.703	0.180, -0.362	0.344, -0.465	1.406, -0.807	1.228, -1.206	1.272, -1.042

Selected Structural Data						
Av. Cr-N (Å)*	2.115(8)	2.0985(14)	2.092(3)	2.08(2)	2.115(10)	2.128(5)
Av. Cr-Cl (Å)*	2.287(8)	2.2849(4)	2.292(4)	2.34(3)	2.275(2)	2.285(5)
Av. N-Cr-N (°)*	65.6(3)	66.01(6)	66.2(2)	66.7(7)	65.5(2)	65.73(13)
Av. Cl-Cr-Cl (°)*	99(2)	99.38(2)	99.6(5)	100.2(3)	98.14(70)	98.3(7)
Av. Cr-N-C(R) (°)*	129(6)	127.55(11)	124.4(11)	126(2)	127(3)	128(4)

$R_1 = \Sigma ||Fo|-|Fc|| / \Sigma |Fo|$. $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$.

$GOF = S = \{\Sigma[w(Fo^2 - Fc^2)^2]] / (n-p)\}^{1/2}$.

The structural parameters of all the crystallised complexes are very similar to typical triazacyclohexane complexes of chromium. Each features a large Cr-N-R angle of 124-129° due to the ring strain of the triazacyclohexane resulting in bend-bonding coordination of the nitrogen donors to the chromium centre [15]. As observed previously, the N-substituents mostly adopt an *anti*-conformation, but the *syn*-conformation is accessible and observed in the structures for **3e,n,o** leading to slightly longer Cr-N bonds. Thus, the organic halogen atoms should be able to interact with any coordinatively unsaturated chromium species during catalysis. The crystal structure of **3k** shows the racemate of the most likely RRS/SSR diastereomer. The similarity of these structures shows that halogenation does not affect the bonding in these complexes.

3.2. Catalysis of Ethylene Oligo- or Polymerisation

The catalysts were tested for their ethylene oligomerisation and trimerisation activities after MAO activation under ambient pressure conditions and at 40˚C. The results for the new complexes along with data on previously described analogous complexes **3a-d** are listed in Table 3.

Table 3. Oligomerisation and polymerisation activities at ambient pressure. Activities given in Kg mol(Cr)$^{-1}$ h^{-1} while (~) denotes negligible yields which could not be reliably quantified.

Catalyst	Conditions	1-Hexene Activity	C_{10} Activity	Polymer Activity
3a	a	~	~	717
3b	b	21	~	495
3c	a	213	309	16
	b	600	291	~
3d	a	308	373	15
	b	626	203	~
3e	b	54	~	405
3g	b	821	227	~
3h	b	86	11	~
3j	b	4	~	~
3l	b	536	80	~
3m	b	164	15	~
3n	b	83	15	1002
3o	b	45	~	740
3p	b	36	~	562

Conditions: a) Al:Cr = 320; T = 40 °C; t = 60 min; solvent toluene;
b) Al:Cr = 500; T = 40 °C; t = 10 min; solvent toluene [4].

Generally, branching at the β-carbon leads to high trimerisation activity and selectivity (**3c,d,g,h,l,m**) whereas no branching (**3a,b,e**) or branching at the γ position (**3n,o,p**) leads to mostly polyethylene production. This agrees with previously published results [4,8] and halogenation does not appear to alter this trend. **3j** (and to a lesser degree **3e**) has poor solubility and low catalytic activity, indicating that linear halogenated N-substituted complexes are unsuitable catalysts. Complex **3h** with six vinyl groups in the substituents shows unusually low activity compared to other β-branched complexes (**3c,d,g**). The olefinic groups seem to interfere with catalysis, potentially by coordination and/or co-insertion. This prevents effective comparison with the associated halogenated species.

Analysis of the 'halogen effect' must therefore be based on a comparison of halogenated complexes with similar non-halogenated saturated complexes. Thus, suitable comparisons for trimerization selective catalysts are the non-halogenated complexes **3c,d,g** versus chlorinated **3l** and brominated **3m**. The activity for the chlorinated complex is slightly lower than the non-halogenated alternatives while the activity for the brominated complex is significantly lower. This suggests that halogen incorporation into the ligand has a negative impact on ethylene trimerisation activities.

However, the selectivity for C_6 over C_{10} after 10 minutes shows a significant improvement for the halogenated complexes **3l** (87 wt%) and **3m** (92) relative to the non-halogenated β-branched complexes **3c** (67), **3d** (76) and **3g** (78). The quantity of C_{10} produced increases for longer reaction periods (60 min vs. 10 min for **3c,d**) as would be expected when decenes are formed as co-trimers of hexene and ethylene.

On the other hand, the trend observed for polymerisation activities shows halogenation to have a strongly beneficial effect. The non-halogenated catalysts, unbranched **3a,b** and γ-branched **3p**, gave activities of around 500 Kg mol(Cr)$^{-1}$ hr^{-1}. This is considerably lower than both the brominated, **3o** (740), and the chlorinated complex, **3n** (1002). Thus, incorporation of halogens into the N-substituents, especially in the form of chloroalkyls, results in improved polymerisation activities under ambient pressure conditions.

4. Conclusions

A novel range of triazacyclohexane chromium trichloride complexes with unbranched, β- and γ-branched N-substituents have been synthesised. It has been demonstrated that halogens can be incorporated into unsaturated coordinated ligands by the facile addition of X_2 or HX (X = Cl or Br) to unsaturated N-substituents. All catalysts have been shown to be active in relation to oligomerisation and/or polymerisation of ethylene. They have all been fully characterised by paramagnetic NMR spectroscopy and six structures have been identified using X-ray crystallography.

The 'halogen effect' has been investigated by comparison of chlorine and bromine containing catalysts with their saturated non-halogenated analogues. The presence of halogens in the ligand does not change the selectivity of the catalyst for trimerisation versus polymerisation, which remains determined by branching points. In regards to selective trimerisation catalysts, the presence of chloroalkyls showed a limited negative effect while bromoalkyls led to significantly lower activity. However, selectivity for 1-hexene relative to higher oligomers improves upon halogenation.

For polymerisation catalysts, considerable improvements were observed for bromoalkyl substituents while almost two-fold increases in activity were seen when chlorine was incorporated into the ligand. This suggests that incorporating halogens into the ligand at positions capable of interaction with the chromium centre can give similar improvements to additives more typically associated with 'halogen effects'. The intelligent design of halogen containing polymerisation catalysts may therefore remove the need for additives in the future.

Investigations into these novel complexes as catalysts in variable pressure and temperature studies, as well as for α-olefin trimerisation, are being prepared for publication elsewhere.

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Appendix A. Supplementary Data

CCDC 994535-994540 contain the supplementary crystallographic data for **3e**, **3f**, **3h**, **3k**, **3n** and **3o**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html,or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.
A picture and some crystal data for the poor structure of **3p** and the ^{13}C NMR spectrum of **3i** is provided as supplementary material.

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