

Activation of $[\text{CrCl}_3\{\text{PPh}_2\text{N}(\text{iPr})\text{PPh}_2\}]$ for the selective oligomerisation of ethene: a Cr K-edge XAFS study

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Supporting Information

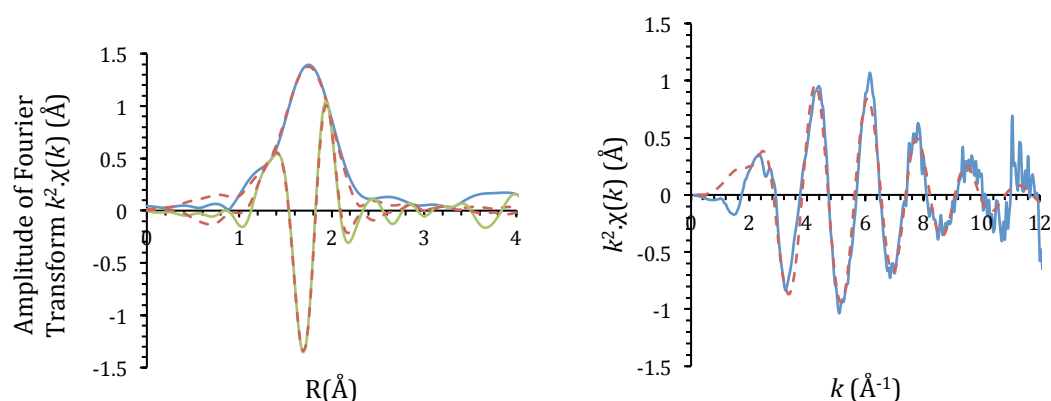


Fig. S1 Cr K-edge k^2 -weighted a) Fourier transform EXAFS and b) EXAFS data for $[\text{CrCl}_3\{\text{PPh}_2\text{N}(\text{R})\text{PPh}_2\}(\text{THF})]$ **1a** ($\text{R}=\text{iPr}$) in BN. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S1 Cr K-edge EXAFS powder data analyses for $[\text{CrCl}_3\{\text{PPh}_2\text{N}(\text{R})\text{PPh}_2\}(\text{THF})]$ **1a** ($\text{R}=\text{iPr}$) in BN [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^2)$	Fitting Factors
3 Cr-Cl	2.28(1)	0.003(1)	$E_0 = 4(2)$, $R = 0.0047$
2 Cr-P	2.48(2)	0.002(2)	
1 Cr...N	2.96(8)	0.000(8)	
1 Cr-O	2.05 ^a	0.003 ^a	

$S_0^2 = 0.9^a$, $k\text{-weight} = 1, 2, 3$.

^aFixed parameters.

Table S2. Comparison of the theoretical models for predicting the bond lengths as observable by Cr K-edge EXAFS calibrated against the X-ray structure of $[\text{CrCl}_3(\text{PPh}_2\text{N}(\text{Cy})\text{PPh}_2)(\text{NCMe})]$ (Cy = cyclohexyl).

	Mean bond lengths ($\text{\AA}$)		
	Cr-N	Cr-Cl	Cr-P
$[\text{CrCl}_3(\text{PPh}_2\text{N}(\text{Cy})\text{PPh}_2)(\text{NCMe})]^a$	2.05	2.29	2.49
$[\text{CrCl}_3(\text{PPh}_2\text{N}(\text{iPr})\text{PPh}_2)(\text{NCMe})]$			
Density functional model			
B3LYP/6-31G*	2.15	2.32	2.59
B3LYP/6-31G**	2.12	2.31	2.55
B3LYP/6-31+G*	2.12	2.31	2.55
EDF2/6-31G*	2.11	2.30	2.55
EDF2/6-31G**	2.12	2.31	2.55
EDF2/6-31+G*	2.12	2.31	2.55
$\omega\text{B97X-D}/6\text{-}31\text{G}^*$	2.14	2.30	2.53
$\omega\text{B97X-D}/6\text{-}31\text{G}^{**}$	2.13	2.30	2.53
$\omega\text{B97X-D}/6\text{-}31\text{+G}^*$	2.11	2.31	2.55

^a S. Teo, Z. Weng, and T. S. A. Hor, *Organometallics*, 2008, **27**, 4188-4192

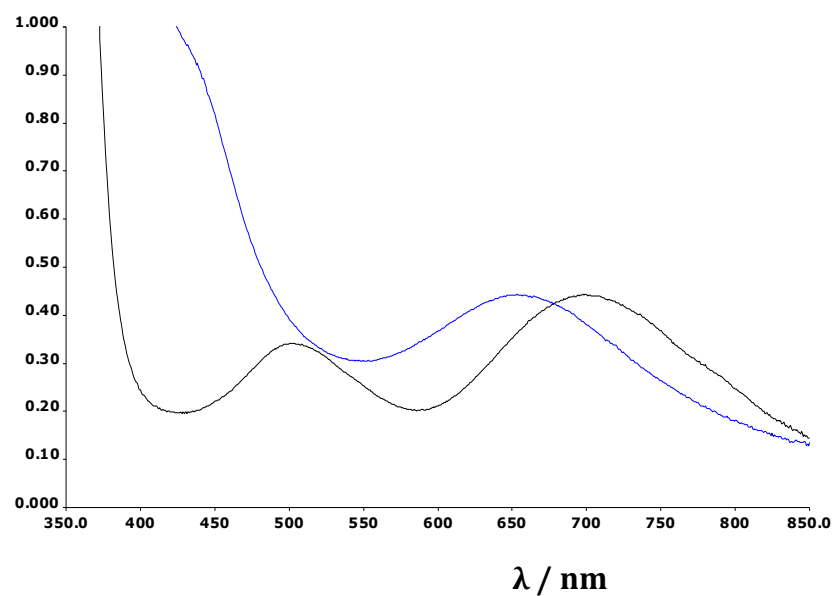


Fig. S2. UV/visible spectra of a 5 mM toluene solution 1a before (black) and after (blue) treatment with 5 equivalents of Me_3Al .

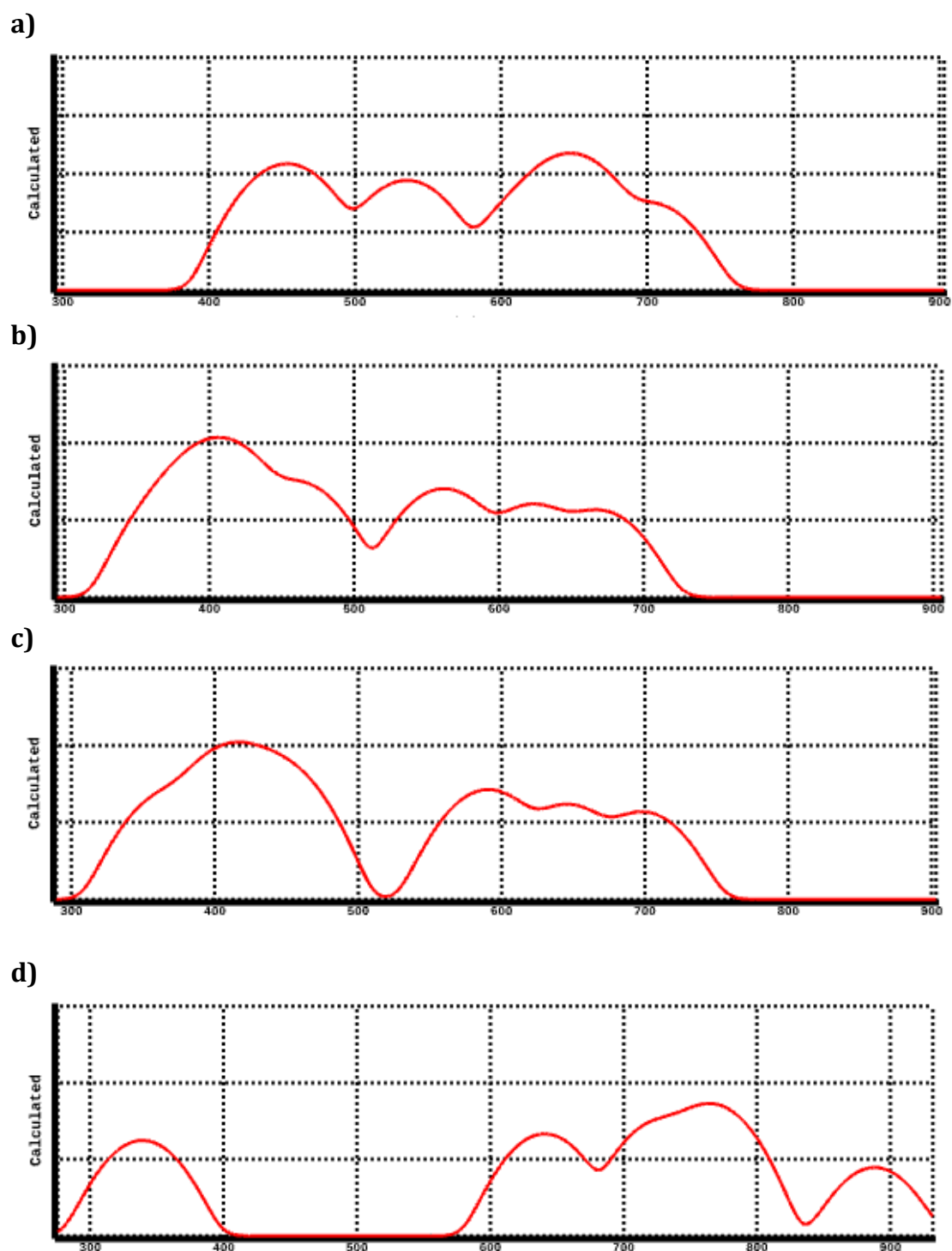
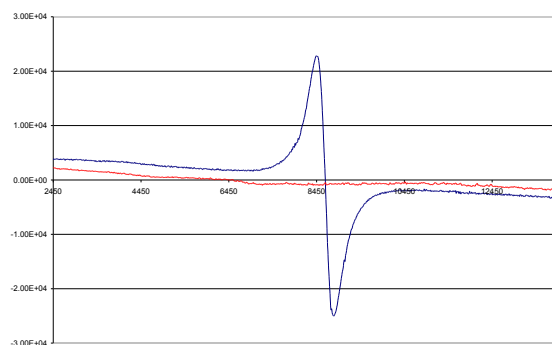


Fig. S3. Calculate UV/visible by TDDF using ω B97X-D/6-31G** parameters for complexes a) **1b**, b) **3b**, c) **4b**, d) **8b**.



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Fig. S4. EPR spectrum (Q-band) for a toluene/CH₂Cl₂ solution of **1a** (blue) treated with 3 equivalents of Me₃Al (red); recorded as a frozen glass at T = 115 K, after ~ 10 minutes reaction time. $g = 1.99$

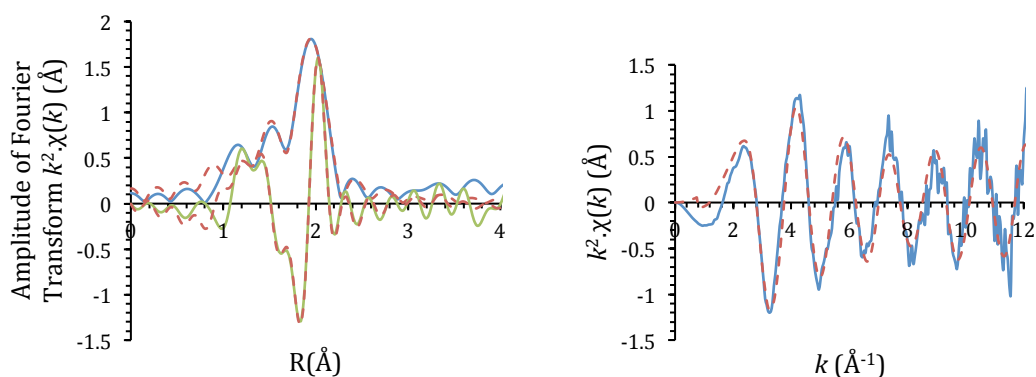


Fig. S5 Cr K-edge k^2 -weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 AlMe₃ frozen after 1 minute in toluene. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S3 Cr K-edge EXAFS solution data analyses for **1a** + 20 AlMe₃ frozen after 1 minute reaction time in toluene. [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^2)$	Fitting Factors
2 Cr-C/O	2.03(4)	0.001(3)	2.0 < k < 12.0, 1.1 < R < 2.6 $E_0 = 2(2)$, $R = 0.0045$
2 Cr-Cl	2.37(1)	0.0003(11)	
2 Cr-P	2.54(6)	0.006(8)	

$S_0^2 = 0.9^a$, k -weight = 1,2,3.

^aFixed parameters.

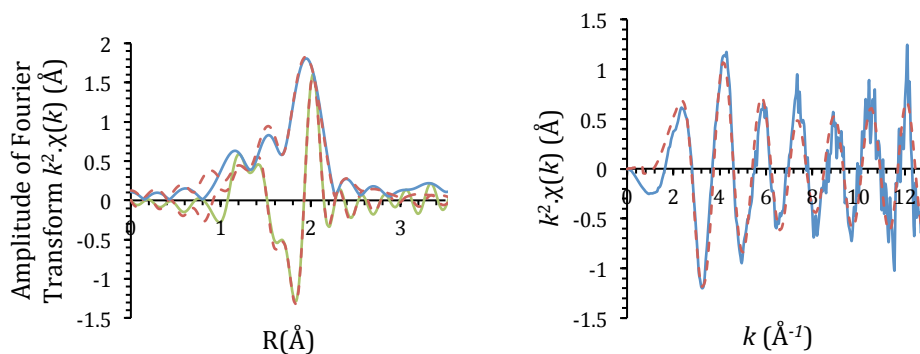


Fig. S6 Cr K-edge k^2 -weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 AlMe₃ frozen after 1 minute **4a** with split Cr-P fitting. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S4 Cr K-edge EXAFS solution data analyses for **1a** + 20 AlMe₃ frozen after 1 minute (**4a**) with split Cr-P fitting. [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^2)$	Fitting Factors
2 Cr-C/O	2.04 ^a	0.001 ^a	$2.3 < k < 12.0$, $1.1 < R < 2.95$ $E_0 = 1.7(8)$, $R = 0.0046$
2 Cr-Cl	2.37 ^a	0.0001(13)	
1 Cr-P	2.45(6)	0.0004(17)	
1 Cr-P'	2.60(2)	0.0005(15)	

$S_0^2 = 0.9^a$, k -weight = 1,2,3. ^aFixed parameters.

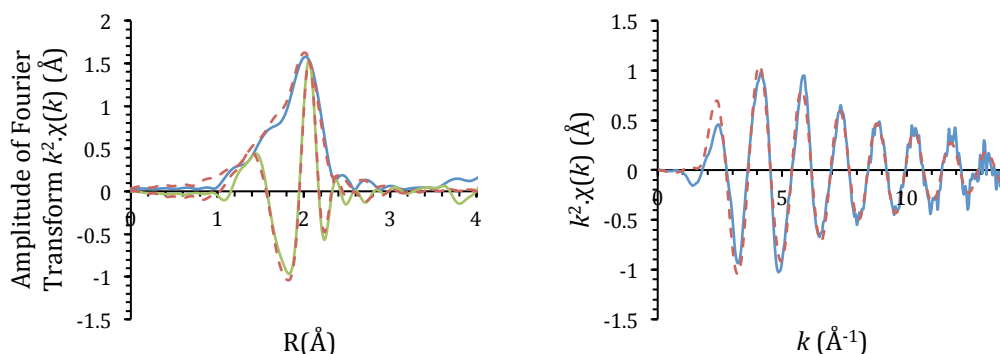


Fig. S7 Cr K-edge k^2 -weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 AlMe₃ frozen after 5 minutes (**3**) in toluene. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S5 Cr K-edge EXAFS powder data analyses for **1a** + 20 AlMe₃ frozen after 5 minutes in toluene. [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^2)$	Fitting Factors
1 Cr-C	2.10(5)	0.002(5)	$2.0 < k < 14.0$, $1.1 < R < 2.6$ $E_0 = 3(2)$, $R = 0.009$
2 Cr-Cl	2.37(3)	0.0003(12)	
2 Cr-P	2.49(2)	0.0004(12)	

$S_0^2 = 0.9^a$, k -weight = 1,2,3. ^aFixed parameters.

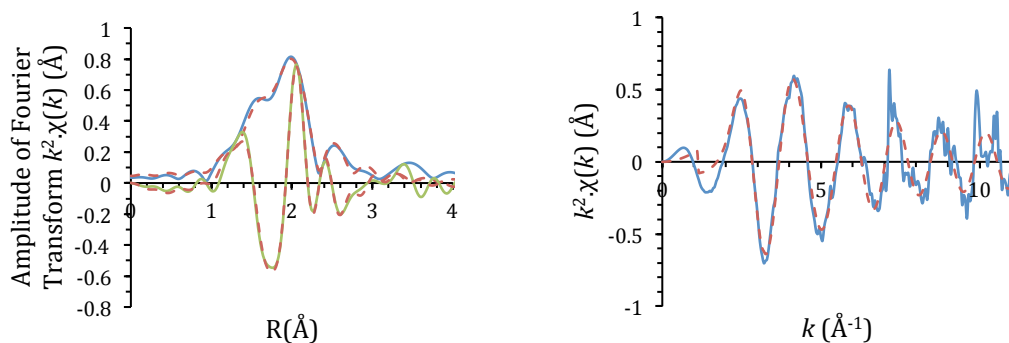


Fig. S8 Cr K-edge k^2 -weighted a) Fourier transform EXAFS and b) EXAFS data for room temperature reaction of **1a** + AlMe₃ in toluene. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S6 Cr K-edge EXAFS powder data analyses for room temperature reaction of **1a** + AlMe₃ in toluene (proposed [(PNP)CrMe(ClAlMe₃)] structure) [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})^a$	$2\sigma^2/(\text{\AA}^{-2})$	Fitting Factors
2 Cr-P	2.49(1)	0.0043(8)	2.0 < k < 11.0, 1.2 < R < 3.5 $E_0 = 4.8(9)$, $R = 0.007$
1 Cr-Cl-Al	2.73(3)	0.013(5)	
1 Cr-C	2.14(2)	0.003(2)	

$S_0^2 = 1^a$, k -weight = 1,2. ^aFixed parameters.

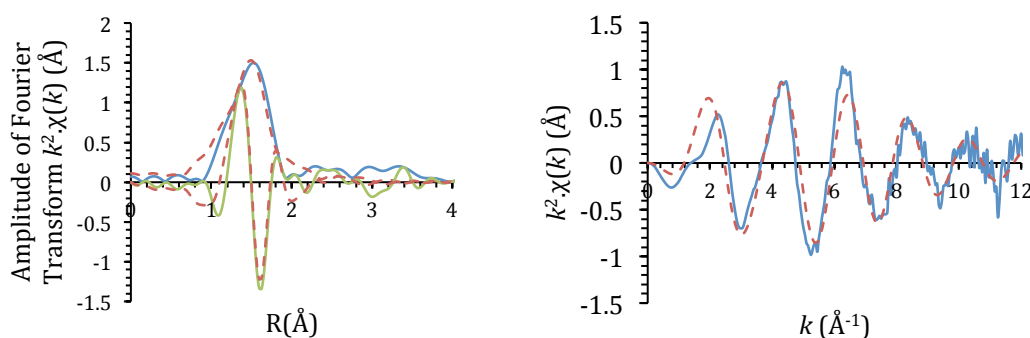


Fig. S9 Cr K-edge k^3 -weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 30 AlMe₃ + 1 [Ph₃C][Al{OC(^tBu^F)₃}₄]. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S7 Cr K-edge EXAFS analyses for **1a** + 30 AlMe₃ + 1 [Ph₃C][Al{OC(^tBu^F)₃}₄]. [Standard deviations in brackets].

Absorber - Scatterer	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^{-2})$	Fitting Factors
1 ^a Cr-Cr	2.01(2)	0.002(1)	1.0 < k < 12.0; 1.2 < R < 2.5 $E_0 = -1(2)$, $R = 0.025$
3.3(7) Cr-C	2.14(4)	0.003 ^a	

$S_0^2 = 1^a$, k -weight = 1,2,3. ^aFixed parameters.

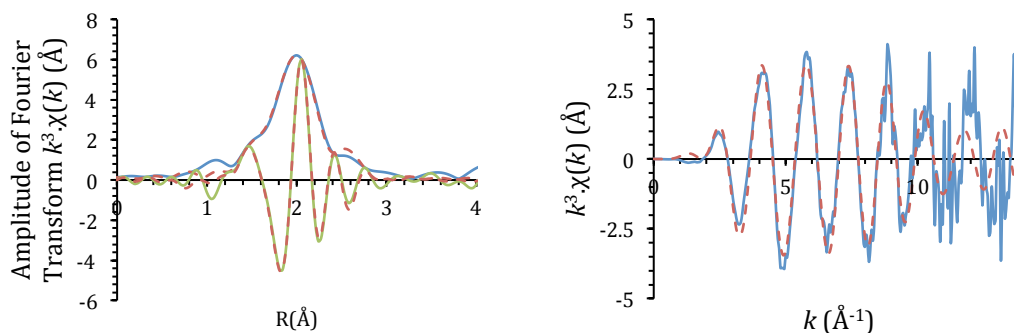


Fig. S10 Cr K-edge k^3 -weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 AlMe₃ + 1 B(C₆F₅)₃. **Blue** = Experimental EXAFS data (**Green** = Imaginary part of FT); **Red dashed** = Fit data.

Table S8 Cr K-edge EXAFS analyses for **1a** + 20 AlMe₃ + 1 B(C₆F₅)₃. [Standard deviations in brackets].

Absorber - Scatterer ^a	$R/(\text{\AA})$	$2\sigma^2/(\text{\AA}^{-2})$	Fitting Factors
2 Cr-Cl	2.36(2)	0.013(3)	2.0 < k < 11.0, 1.2 < R < 3.5 $E_0 = 1(1)$, $R = 0.0002$
2 Cr-P	2.472(8)	0.004(7)	
1 Cr-C	3.04(1)	0.001(2)	

$S_0^2 = 1^a$, k -weight = 3. ^aFixed parameters.

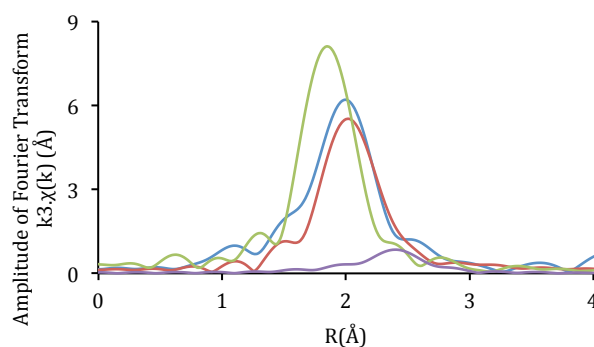


Fig. S11. Cr K-edge k^3 -weighted Fourier transform EXAFS data for **1a** + 30 AlMe₃ + 1 B(C₆F₅)₃. **Blue** = Experimental data; **Red** = Cr-P fitted pathway; **Green** = Cr-Cl fitted pathway; **Purple** = Cr-C fitted pathway.

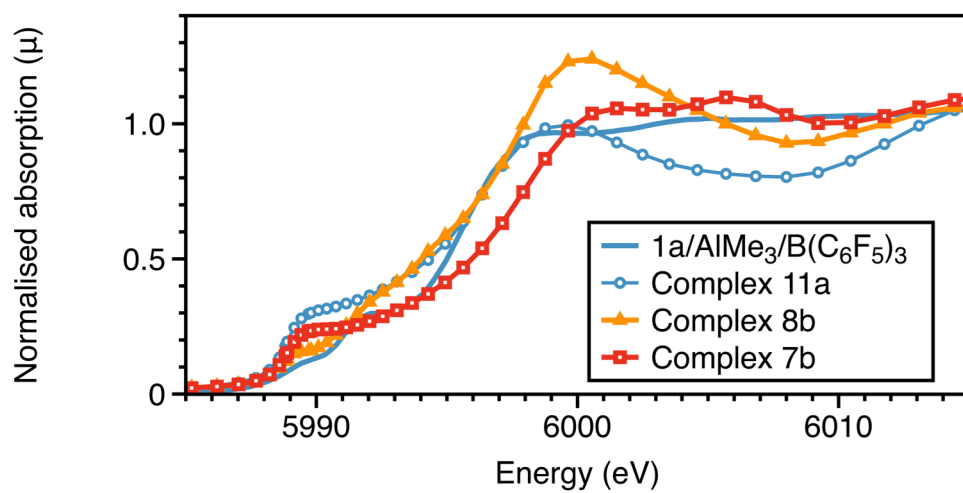


Fig. S12. Cr K edge XANES of the reaction product of complex **1a**, AlMe₃ and B(C₆F₅)₃ with the calculated XANES of alternative structural models