Activation of *[CrCl$_3${PPh$_2$N(^{i}Pr)PPh$_2$}]* for the selective oligomerisation of ethene: a Cr K-edge XAFS study

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Supporting Information

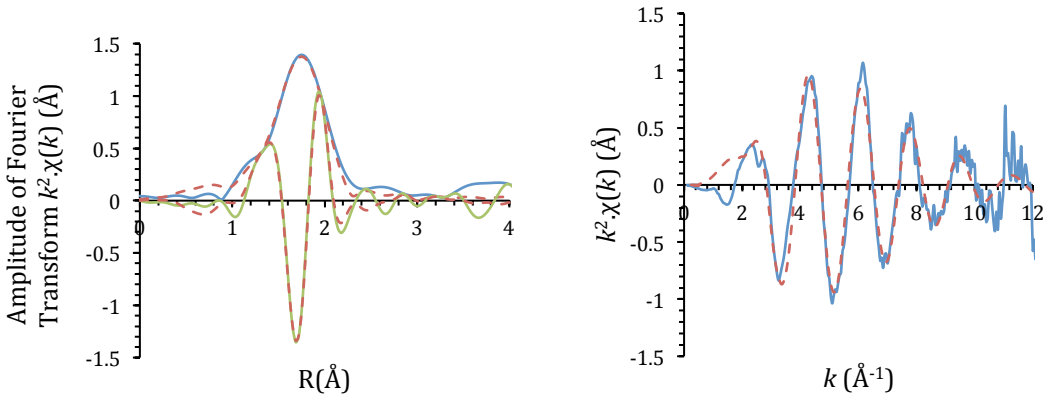

Fig. S1 Cr K-edge k^2-weighted a) Fourier transform EXAFS and b) EXAFS data for [CrCl$_3${PPh$_2$N(R)PPh$_2$}(THF)] **1a** (R=^{i}Pr) in BN. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

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

Absorber - Scatterer[a]	***R*/(Å)**	**$2\sigma^2$/(Å^{-2})**	**Fitting Factors**
3 Cr-Cl	2.28(1)	0.003(1)	2.0<*k*<12.0, 1.1<R<3.5 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-weight = 1,2,3.
[a]Fixed 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 $[CrCl_3(PPh_2N(Cy)PPh_2)(NCMe)]$ (Cy = cyclohexyl).

	Mean bond lengths (Å)		
	Cr-N	**Cr-Cl**	**Cr-P**
$[CrCl_3(PPh_2N(Cy)PPh_2)(NCMe)]$[a]	2.05	2.29	2.49
$[CrCl_3(PPh_2N(^iPr)PPh_2)(NCMe)]$			
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
ωB97X-D/6-31G*	2.14	2.30	2.53
ωB97X-D/6-31G**	2.13	2.30	2.53
ωB97X-D/6-31+G*	2.11	2.31	2.55

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

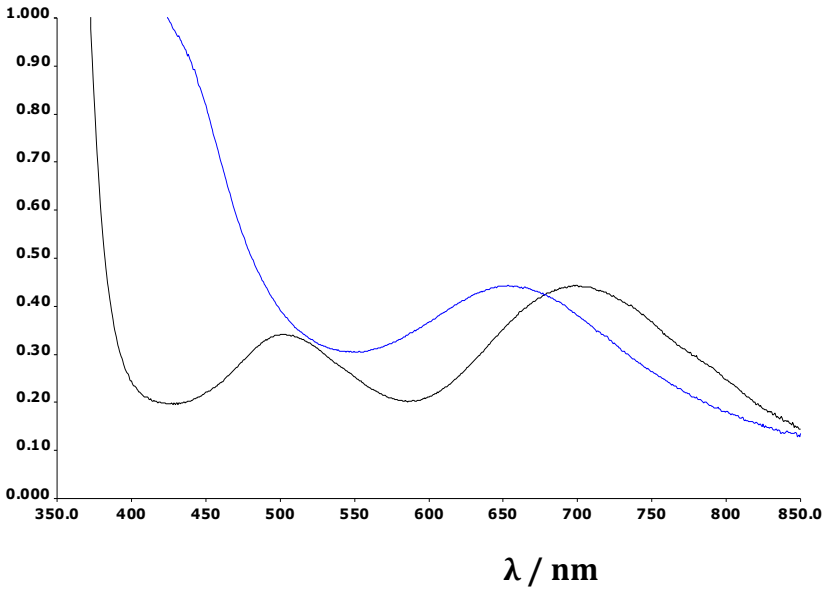

Fig. S2. UV/visible spectra of a 5 mM toluene solution 1a before (black) and after (blue) treatment with 5 equivalents of Me_3Al.

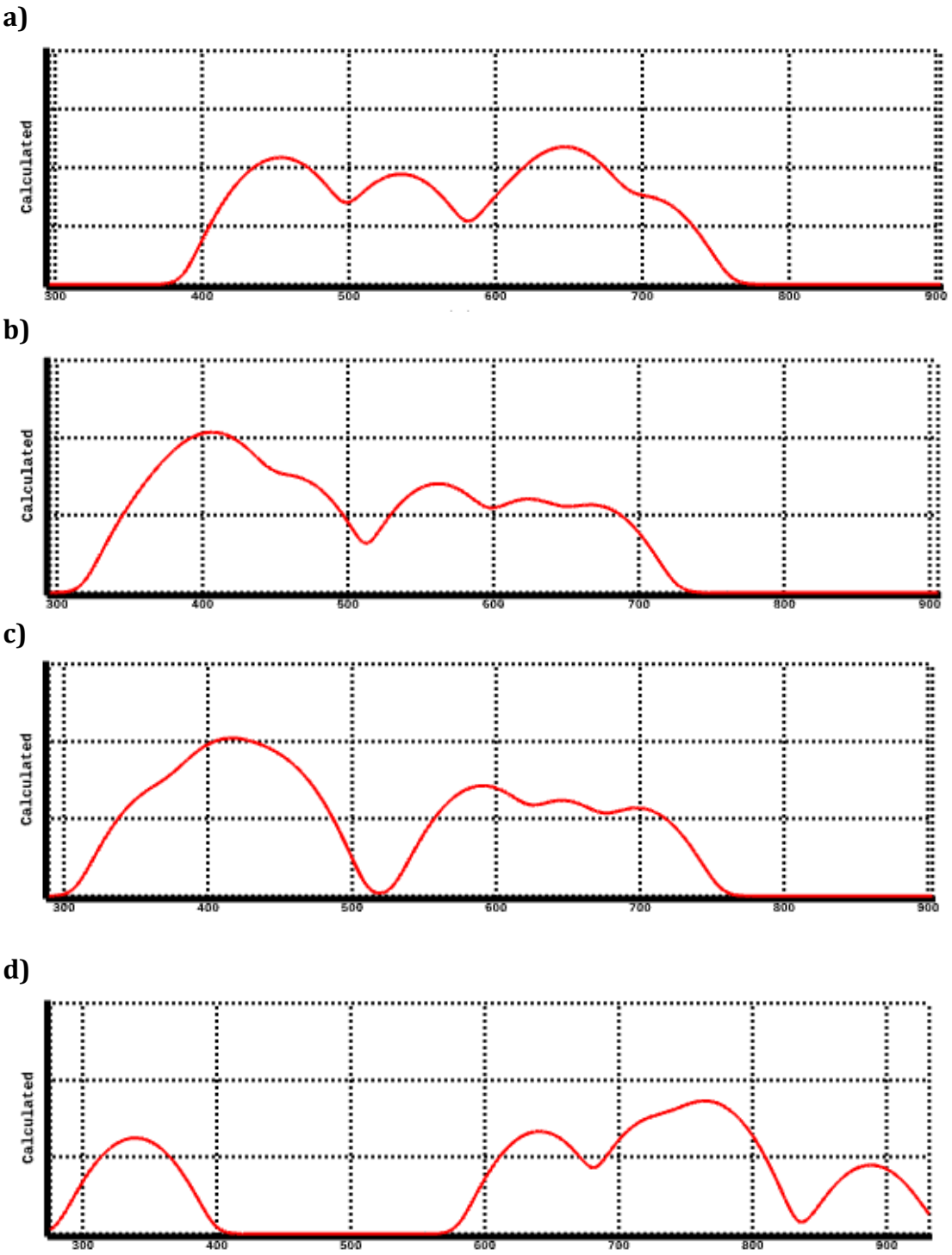

Fig. S3. Calculate UV/visible by TDDF using ωB97X-D/6-31G** parameters for complexes a) **1b**, b) **3b**, c) **4b**, d) **8b**.

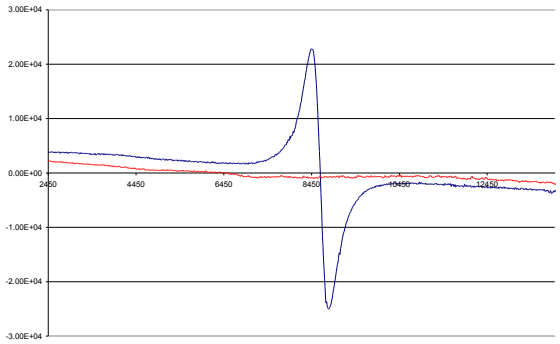

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Fig. S4. EPR spectrum (Q-band) for a toluene/CH_2Cl_2 solution of **1a** (blue) treated with 3 equivalents of Me_3Al (red); recorded as a frozen glass at T = 115 K, after ~ 10 minutes reaction time. ***g*** = 1.99

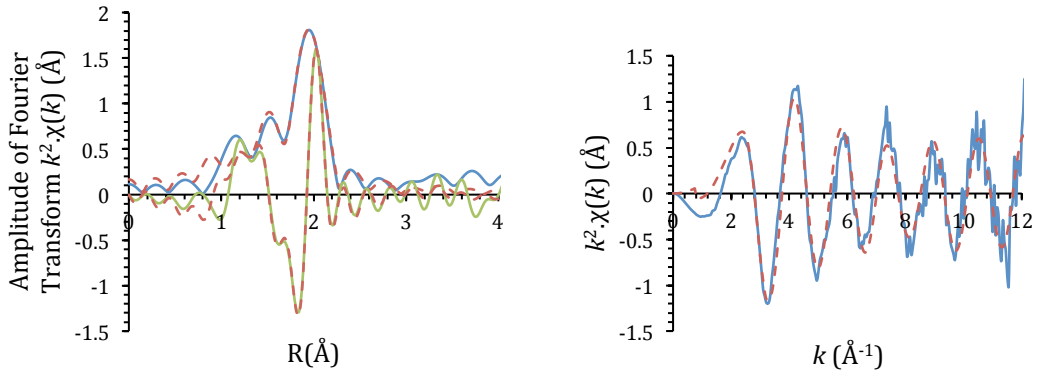

Fig. S5 Cr K-edge k^2-weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 $AlMe_3$ frozen after 1 minute in toluene. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S3 Cr K-edge EXAFS solution data analyses for **1a** + 20 $AlMe_3$ frozen after 1 minute reaction time in toluene. [Standard deviations in brackets].

Absorber - Scatterer[a]	***R*/(Å)**	**$2\sigma^2$/(Å^{-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.
[a]Fixed parameters.

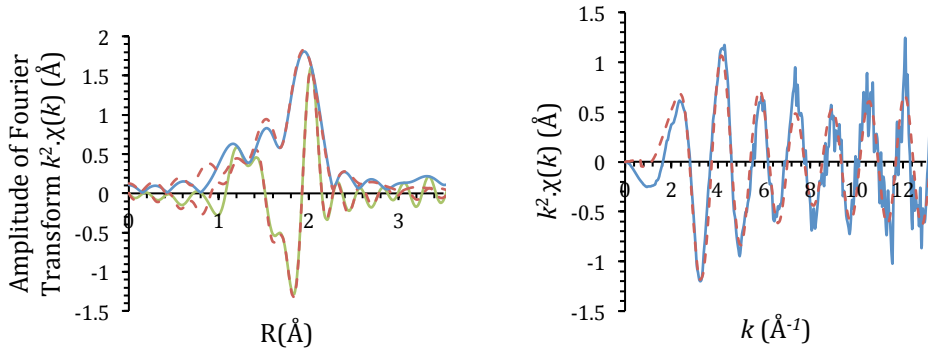

Fig. S6 Cr K-edge k^2-weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 $AlMe_3$ frozen after 1 minute **4a** with split Cr-P fitting. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S4 Cr K-edge EXAFS solution data analyses for **1a** + 20 $AlMe_3$ frozen after 1 minute (**4a**) with split Cr-P fitting. [Standard deviations in brackets].

Absorber - Scatterer[a]	***R*/(Å)**	**$2\sigma^2$/(Å^{-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. [a]Fixed parameters.

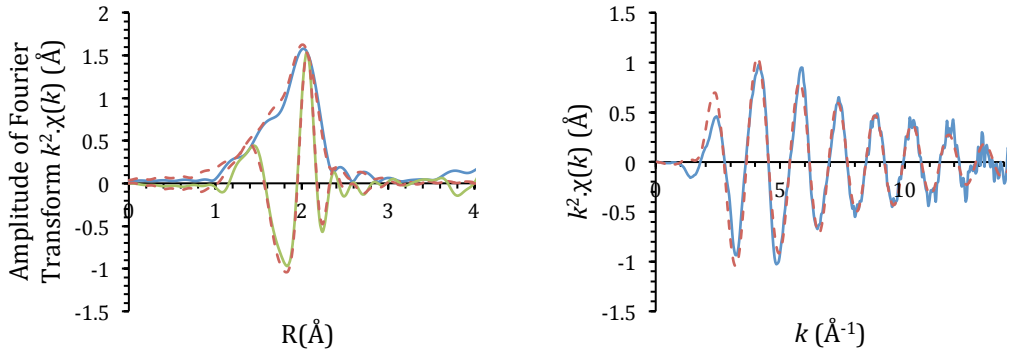

Fig. S7 Cr K-edge k^2-weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 $AlMe_3$ frozen after 5 minutes (**3**) in toluene. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S5 Cr K-edge EXAFS powder data analyses for **1a** + 20 $AlMe_3$ frozen after 5 minutes in toluene. [Standard deviations in brackets].

Absorber - Scatterer[a]	***R*/(Å)**	**$2\sigma^2$/(Å^{-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. [a]Fixed parameters.

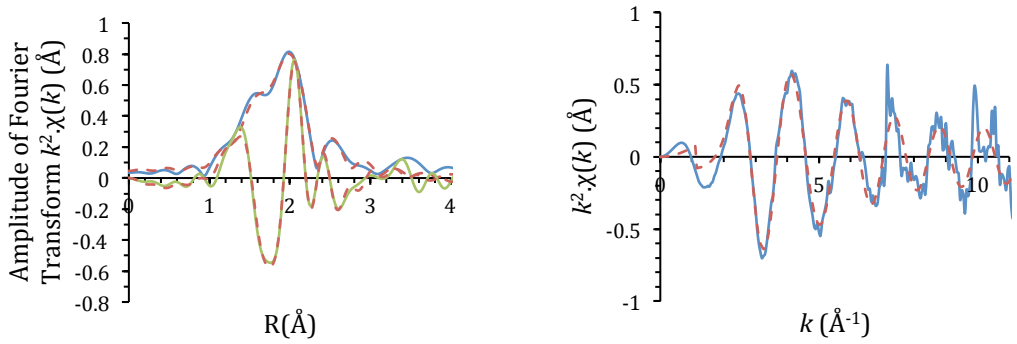

Fig. S8 Cr K-edge k^2-weighted a) Fourier transform EXAFS and b) EXAFS data for room temperature reaction of **1a** + $AlMe_3$ in toluene. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S6 Cr K-edge EXAFS powder data analyses for room temperature reaction of **1a** + $AlMe_3$ in toluene (proposed [(PNP)CrMe($ClAlMe_3$)] structure) [Standard deviations in brackets].

Absorber - Scatterer[a]	***R*/(Å)**[a]	**$2\sigma^2$/(Å^{-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. [a]Fixed parameters.

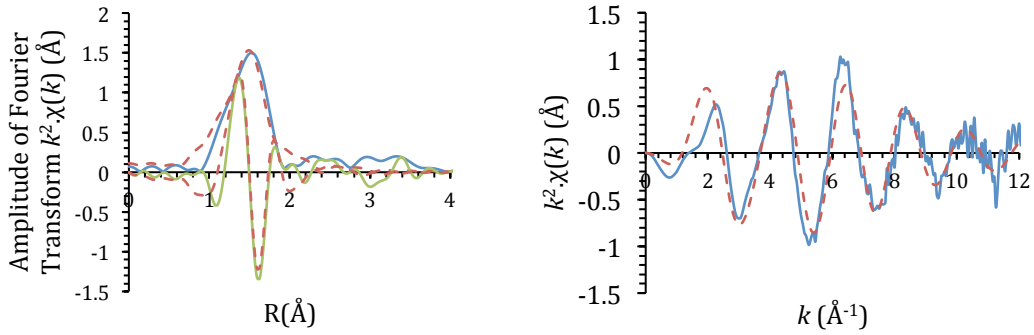

Fig. S9 Cr K-edge k^3-weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 30 $AlMe_3$ + 1 [Ph_3C][Al{OC(^{t}Bu^F)$_3$}$_4$]. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S7 Cr K-edge EXAFS analyses for **1a** + 30 $AlMe_3$ + 1 [Ph_3C][Al{OC(^{t}Bu^F)$_3$}$_4$]. [Standard deviations in brackets].

Absorber - Scatterer	***R*/(Å)**	**$2\sigma^2$/(Å^{-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. [a]Fixed parameters.

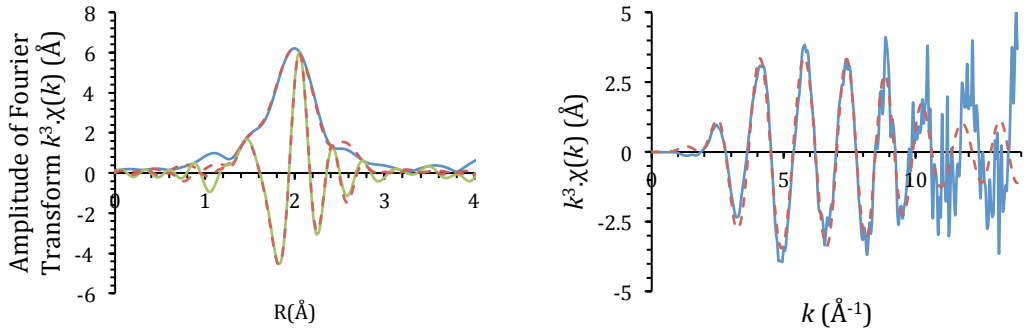

Fig. S10 Cr K-edge k^3-weighted a) Fourier transform EXAFS and b) EXAFS data for **1a** + 20 $AlMe_3$ + 1 $B(C_6F_5)_3$. Blue = Experimental EXAFS data (Green = Imaginary part of FT); Red dashed = Fit data.

Table S8 Cr K-edge EXAFS analyses for **1a** + 20 $AlMe_3$ + 1 $B(C_6F_5)_3$.. [Standard deviations in brackets].

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

S_0^2 = 1[a], k-weight = 3. [a]Fixed parameters.

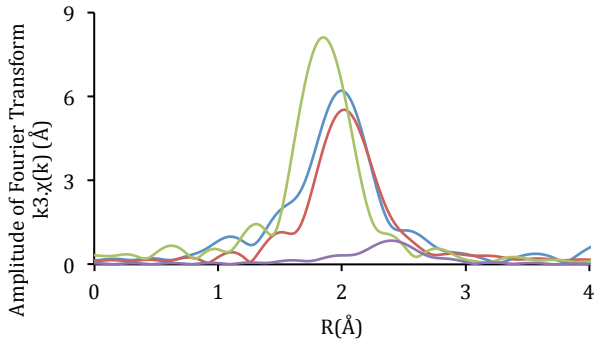

Fig. S11. Cr K-edge k^3-weighted Fourier transform EXAFS data for **1a** + 30 $AlMe_3$ + 1 $B(C_6F_5)_3$. Blue = Experimental data; Red = Cr-P fitted pathway; Green = Cr-Cl fitted pathway; Purple = Cr-C fitted pathway.

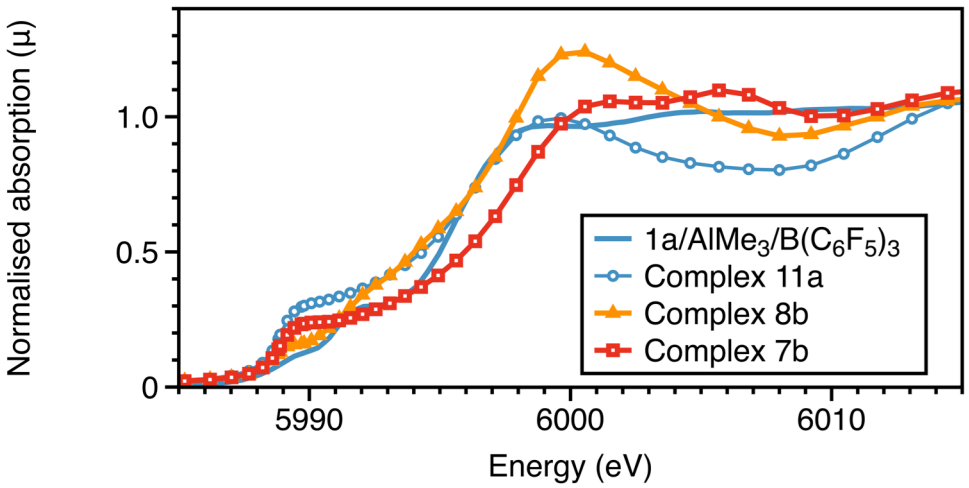

Fig. S12. Cr K edge XANES of the reaction product of complex **1a**, $AlMe_3$ and $B(C_6F_5)_3$ with the calculated XANES of alternative structural models