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Interaction of xylylisocyanide with $Cr^{VI}(Nmesityl)_2(SC_6F_5)_2$

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Abstract—The interaction of 2,6-dimethylphenylisocyanide (xylNC) with $Cr(Nmes)_2(SC_6F_5)_2$ in refluxing toluene gives *mer*-$Cr(SC_6F_5)_3(xylNC)_3$ **1** and minor amounts of *trans*-$Cr(SC_6F_5)_2(xylNC)_4$ **2**. Compound **2** is best made by interaction of either $Cr(mes)_2(THF)_3$ or $CrCl_2$ with C_6F_5SH or C_6F_5SNa, respectively, in the presence of xylNC. The X-ray crystal structures of **1** and **2** have been determined. The similar imido thiolates of molybdenum(VI) are inert towards xylNC. © 1997 Published by Elsevier Science Ltd

Keywords: chromium; imido; thiolate; isocyanide; crystal structure.

The reduction of $Cr(Nmes)_2(Smes)_2$, mes = 2,4,6-trimethylphenyl on interaction with xylNC, xyl = 2,6-dimethylphenyl, in refluxing toluene gave the five-coordinate chromium(IV) complex, $Cr(Nmes)(Smes)_2(xylNC)_2$ together with the carbodiimide, xylN=C=Nmes [1]. Related imido transfer reactions to xylNC from $Cr(Nmes)_2(SC_6F_5)_2$ are now described. Although similar imido thiolates of molybdenum(VI) were made these are unaffected by xylylisocyanide.

RESULTS AND DISCUSSION

The interaction of $Cr(Nmes)_2(SC_6F_5)_2$ [2] with xylylisocyanide in refluxing toluene led to a mixture of the crystalline, paramagnetic complexes, orange-brown *mer*-$Cr(SC_6F_5)_3(xylNC)_3$ **1** and yellow *trans*-$Cr(SC_6F_5)_2(xylNC)_4$ **2**. The Cr^{III} complex is the main product and can be separated from **2** by repeated crystallisation from diethylether. The Cr^{II} complex can be separated with difficulty and is more conveniently made in high yield from $Cr(mes)_2(THF)_3$ or powdered $CrCl_2$ as in eqs (1) and (2).

$$Cr(mes)_2(THF)_3 + 2C_6F_5SH + 4xylNC \xrightarrow{THF} Cr(SC_6F_5)_2(xylNC)_4 + 2mesH \quad (1)$$

$$CrCl_{2(s)} + 2NaSC_6F_5 + 4xylNC \xrightarrow{THF} Cr(SC_6F_5)_2(xylNC)_4 + 2NaCl \quad (2)$$

From the reaction as in eq. (1) a small quantity of material, believed to be $Cr(SC_6F_5)(xylNC)_5$ **3**, was isolated.

These new compounds are rare examples of chromium thiolates in oxidation states I–III [3]. It may be noted that the interaction of $Cr(mes)_2(THF)_3$ and $CrCl_2$ with C_6F_5SH or $NaSC_6F_5$ respectively in the absence of xylylisocyanide gives only intractable materials. If 2,4,6-$Pr^i_3C_6H_2SH$ is used transient colours are observed but no identifiable products could be isolated. The structures of **1** and **2** have been determined by X-ray diffraction and are shown in Figs 1 and 2; selected bond lengths and angles are given in Tables 1 and 2. We have not been successful in obtaining good single crystals of **3** but a reasonable image obtained from a rather poor set of data pointed quite clearly to a confirmation of the formulation as the Cr^{I} species.

The coordination geometry of compound **1** is slightly distorted octahedral, with *cis* and *trans* angles

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[✠] Deceased 26 September 1996.

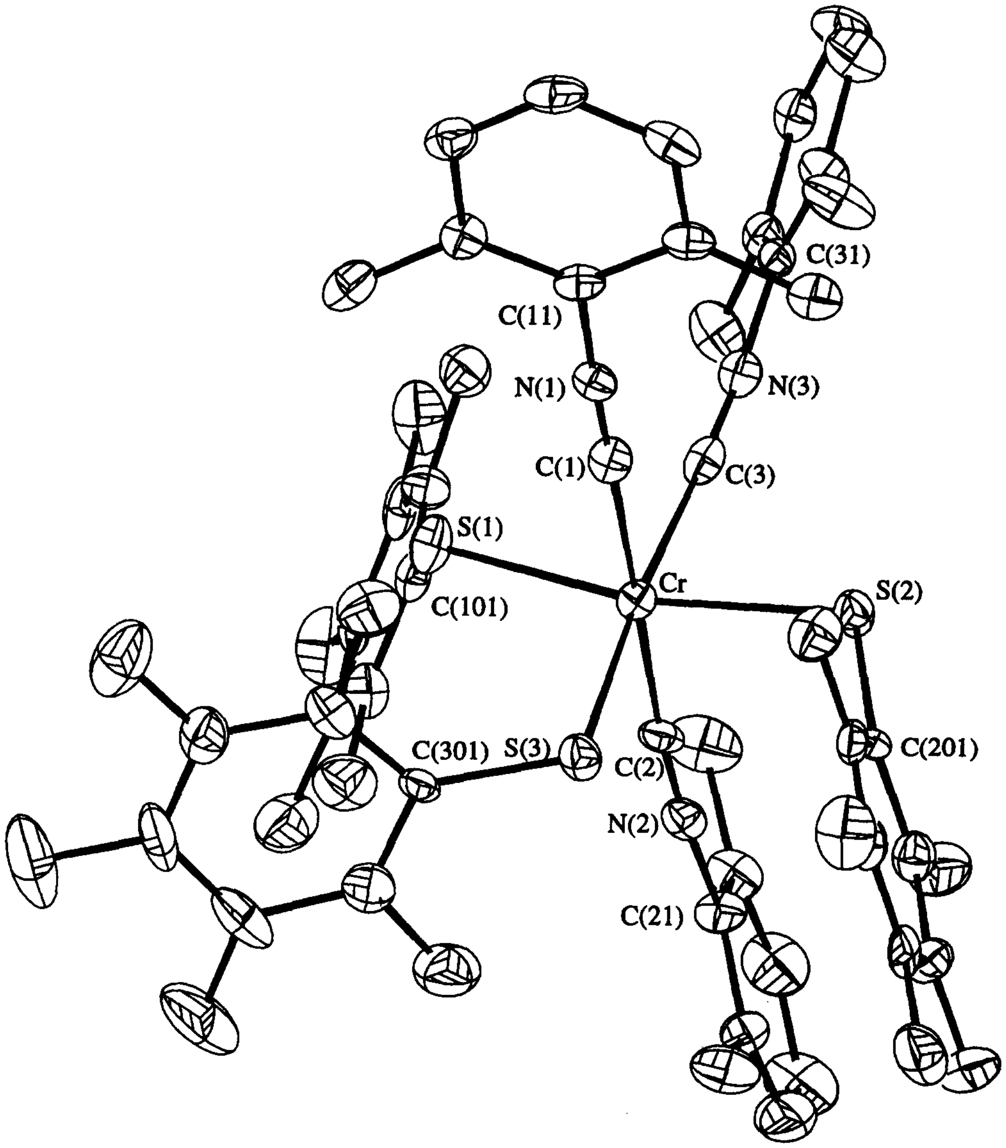

Fig. 1. The structure of *mer*Cr(SC_6F_5)$_3$(xylNC)$_3$.

in the ranges 81.7(2)–95.6(2)° and 168.98(7)–179.4(2)° respectively. For each of the two sets of Cr-ligand bonds, Cr—C and Cr—S, one distance is slightly, but significantly, different from the other two; i.e. Cr—C(2) is shorter than Cr—C(1), Cr—C(3), and Cr—S(2) is longer than Cr—S(1), Cr—S(3). However, in neither case is the unique bond the central bond in the *mer* grouping, and there is no obvious explanation for these features. The ligand geometries are as expected,with approximately linear geometry for the Cr—C—N—C isocyanide bonding, and approximately tetrahedral bond angles at the thiol sulfur atoms.

In compound **2** the *trans* molecule lies in a general position in the unit cell. The two Cr—S distances are similar in length, and longer than those in compound **1** whereas the four Cr—C distances show three equal values [2.002–2.007(4) Å] and one slightly longer [2.032(4) Å]. All, however, are shorter than in **1**. We ascribe these features to steric effects between the bulky ligands since the Cr^{II} species is low spin (μ_{eff} = 2.57 at 20°C), and therefore it is unlikely that electronic effects are involved.

The mechanism of the formation of **1** and **2** by interaction of xylNC with $Cr^{VI}(Nmes)_2(SC_6F_5)_2$ is not clear and the reaction is probably complex since the yields are rather low; attempts to characterise the other intractable products were unsuccessful. It is possible that the initial reaction is similar to that proposed before [1] producing (mesN)$Cr^{IV}(SC_6F_5)_2$

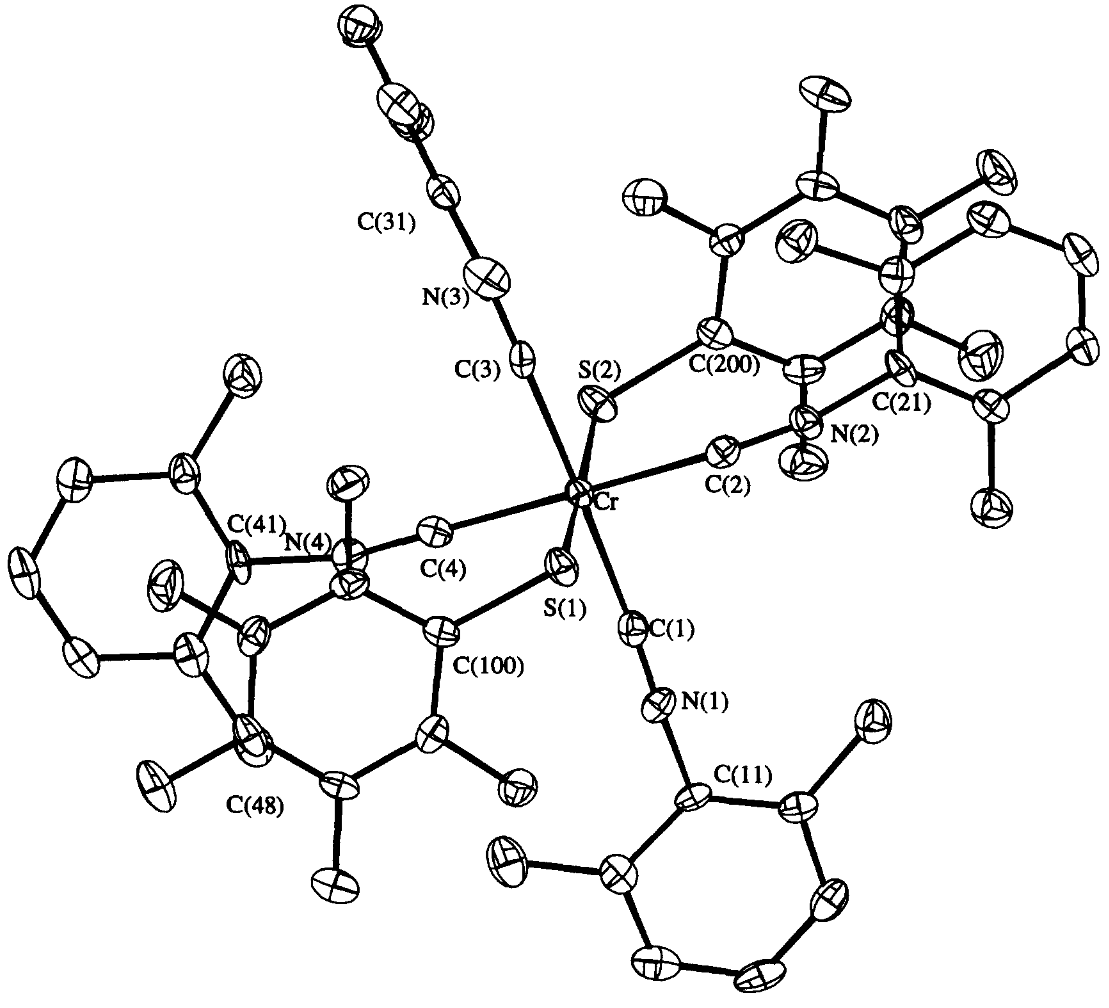

Fig. 2. The structure of *trans* $Cr(SC_6F_5)_2(xylNC)_4$.

Table 1. Selected bond lengths (Å) and angles (°) for compound **1**

Cr—C(1)	2.067(6)	Cr—C(2)	2.041(6)
Cr—C(3)	2.055(6)	Cr—S(1)	2.370(2)
Cr—S(2)	2.391(1)	Cr—S(3)	2.366(2)
S(1)—C(101)	1.751(5)	S(2)—C(201)	1.766(5)
S(3)—C(301)	1.731(6)	N(1)—C(1)	1.154(6)
N(1)—C(11)	1.433(6)	N(2)—C(2)	1.161(6)
N(2)—C(21)	1.424(6)	N(3)—C(3)	1.160(6)
N(3)—C(31)	1.430(6)		
C(2)—Cr—C(1)	179.3(2)	C(3)—Cr—C(1)	87.4(2)
C(1)—Cr—S(3)	92.2(2)	C(1)—Cr—S(1)	84.1(2)
C(1)—Cr—S(2)	89.8(2)	C(2)—Cr—S(3)	87.6(2)
C(2)—Cr—C(3)	93.0(2)	C(2)—Cr—S(1)	95.2(2)
C(2)—Cr—S(2)	90.9(2)	C(3)—Cr—S(3)	174.1(2)
C(3)—Cr—S(1)	88.8(2)	C(3)—Cr—S(2)	81.7(2)
S(3)—Cr—S(1)	97.00(8)	S(3)—Cr—S(2)	92.39(8)
S(1)—Cr—S(2)	168.99(7)	C(101)—S(1)—Cr	109.3(2)
C(201)—S(2)—Cr	107.6(2)	C(301)—S(3)—Cr	110.9(2)
C(1)—N(1)—C(11)	177.1(6)	C(2)—N(2)—C(21)	173.7(6)
C(3)—N(3)—C(31)	170.6(6)	N(1)—C(1)—Cr	178.9(6)
N(2)—C(2)—Cr	171.6(5)	N(3)—C(3)—Cr	172.3(5)

Table 2. Selected bond lengths (Å) and angles (°) for compound **2**

Cr—C(2)	2.002(4)	Cr—C(3)	2.002(4)
Cr—C(4)	2.007(4)	Cr—C(1)	2.032(4)
Cr—S(1)	2.4187(13)	Cr—S(2)	2.4225(14)
S(1)—C(100)	1.763(4)	S(2)—C(200)	1.769(4)
N(1)—C(1)	1.156(4)	N(1)—C(11)	1.409(5)
N(2)—C(2)	1.161(5)	N(2)—C(21)	1.413(5)
N(3)—C(3)	1.162(4)	N(3)—C(31)	1.406(5)
N(4)—C(4)	1.160(5)	N(4)—C(41)	1.420(5)
C(2)—Cr—C(3)	90.5(2)	C(2)—Cr—C(4)	179.7(2)
C(3)—Cr—C(4)	89.2(2)	C(2)—Cr—C(1)	91.1(2)
C(3)—Cr—C(1)	178.2(2)	C(4)—Cr—C(1)	89.1(2)
C(2)—Cr—S(1)	86.25(11)	C(3)—Cr—S(1)	87.64(10)
C(4)—Cr—S(1)	93.92(11)	C(1)—Cr—S(1)	93.05(11)
C(2)—Cr—S(2)	91.75(12)	C(3)—Cr—S(2)	87.98(10)
C(4)—Cr—S(2)	88.06(12)	C(1)—Cr—S(2)	91.39(11)
S(1)—Cr—S(2)	175.17(5)	C(100)—S(1)—Cr	105.71(12)
C(200)—S(2)—Cr	107.75(12)	C(1)—N(1)—C(11)	177.4(4)
C(2)—N(2)—C(21)	169.3(4)	C(3)—N(3)—C(31)	176.2(4)
C(4)—N(4)—C(41)	162.0(4)	N(1)—C(1)—Cr	177.0(4)
N(2)—C(2)—Cr	173.9(3)	N(3)—C(3)—Cr	179.0(4)
N(4)—C(4)—Cr	174.3(4)		

$(\mathrm{xylNC})_2$ but proceeds further by a second mesN transfer, as in eq. (3):

$$\mathrm{Cr^{VI}(Nmes)_2(SC_6F_5)_2} \xrightarrow{\mathrm{xylNC}} \mathrm{2MesN{=}C{=}Nxyl} + \text{“}\mathrm{Cr^{II}(SC_6F_5)_2}\text{”} \qquad (3)$$

While this would account for presence of the $\mathrm{Cr^{II}}$ species and the formation of the carbodiimide (characterised by GC/MS) it is not clear how the $\mathrm{Cr^{III}}$ species is formed. Oxidation of the $\mathrm{Cr^{II}}$ species by the $\mathrm{Cr^{VI}}$ complex with transfer of an $\mathrm{SC_6F_5}$ group is possible but radical reactions could also be involved as could a comproportionation reaction in the presence of xylNC:

$$2\text{“}\mathrm{Cr^{II}(SC_6F_5)_2}\text{”} \xrightarrow{\mathrm{xylNC}} \mathrm{Cr(SC_6F_5)_3(xylNC)_3} + \mathrm{Cr(SC_6F_5)(xylNC)_5}$$

The $\mathrm{Cr^{I}}$ complex was detected only in the reactions starting with $\mathrm{Cr^{VI}}$ species, however.

Attempts to prepare the molybdenum(VI) compounds $\mathrm{(Ar^*N)_2Mo(SAr)_2}$, Ar* = mes, $\mathrm{2,6\text{-}Pr^i_2C_6H_2}$; Ar = mes, $\mathrm{C_6F_5}$, $\mathrm{2,4,6\text{-}Pr^i_3C_6H_2}$ were made, but crystalline products were obtained only for $\mathrm{Mo(NAr^*)_2(S2,4,6\text{-}Pr^i_3C_6H_2)_2}$ Ar* = mes, **4**, $\mathrm{2,6\text{-}Pr^i_2C_6H_3}$, **5**, from the interaction of $\mathrm{(Ar^*N)_2MoCl_2(dme)}$ with NaSAr. The other reactions gave intractable mixtures even when TlSAr was used as the thiolate source.

However, neither **4** nor **5** reacted with xylNC even after refluxing in toluene for 7 days; this inertness may be due to the bulky ligands preventing initial coordination of xylylisocyanide.

EXPERIMENTAL

Analyses were by the Imperial College microanalytical laboratory. All operations were carried out under purified Ar or N_2, or in a Vacuum Atmospheres glove box. All solvents were degassed and distilled before use. The petroleum used throughout had a boiling point 40–60°C.

NMR data were obtained using a JEOL EX-270 or Bruker Avance DRX-300 spectrometer operating at 270 or 300 MHz (^{1}H), respectively, and referenced to the residual proton impurity in the solvent (δ 7.15 $\mathrm{C_6D_6}$). Mass spectra were obtained on a VG Autospec spectrometer. Magnetic susceptibility measurements in the solid state at room temperature were carried out on an Evans' balance (Sherwood Scientific, Cambridge, U.K.).

The starting materials were prepared according to literature procedures: $\mathrm{Cr(Nmes)_2(SC_6F_5)_2}$ [1], $\mathrm{Cr(mes_2)(THF)_3}$ [4], $\mathrm{Mo(Nmes)_2Cl_2(dme)}$ [5], $\mathrm{Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2Cl_2(dme)}$ [5].

Sodium arylthiolates were prepared by interaction of sodium with arylthiol in ether. All commercial chemicals were Aldrich, Avocado or Fluka.

Tris(pentafluorothiophenolato)tris(2,6-dimethylphenylisocyanide)chromium(III) 1

A mixture of $\mathrm{Cr(Nmes)_2(SC_6F_5)_2}$ (0.7 g, *ca* 1 mmol) and 2,6-xylylisocyanide (0.67 g, 5 mmol) in toluene (50 cm^3) was refluxed for 3 h. After removal of volatiles under reduced pressure, washing the residue with petroleum (3 × 10 cm^3), extraction with $\mathrm{Et_2O}$

(2 × 100 cm^3), filtering, concentration of the filtrates and cooling (−20°C) for 12 h gave orange crystals. Yield 0.36 g *ca* 35%. Found (calc.): C, 52.8 (51.8), H, 2.9 (2.6), N 4.3 (4.0)%. IR (Nujol mull) cm^{-1}. 2358, 2330, 2183. The ether insoluble residue was extracted with toluene (*ca* 10 cm^3) filtered, and concentrated to *ca* 2 cm^3. After cooling (−20°C) yellow crystals of *trans*-$Cr(SC_6F_5)_2(xylNC)_4$ were obtained. Yield: 0.08 g, (*ca* 8%).

Bis(pentafluorothiophenolato)tetrakis(2,6-*dimethylphenylisocyanide)chromium(II)* **2**

(i) *From Crmes*$_2$*(THF)*$_3$. To a solution of $Crmes_2(THF)_3$ in THF (0.7 g, 0.39 mmol, in 70 cm^3) at −78°C was added a solution of C_6F_5SH in THF (0.56 g, 2.8 mmol in 20 cm^3). The green reaction mixture was stirred at −60°C for 2 h; on addition of xylylisocyanide (1.1 g, 8.4 mmol) the solution became brown and then orange. Removal of volatiles under reduced pressure, washing of the residue with a small quantity of petroleum, extraction into toluene (30 cm^3), filtration, concentration and cooling of the extracts (−20°C) gave yellow crystals. Yield: 1.0 g, 75%, m.p. *ca* 183°C. From the petroleum washings after concentration and cooling, yellow crystals were obtained in low yield.

(ii) *From CrCl*$_2$. To a suspension of $CrCl_2$ in THF (0.25 g, 2.0 mmol in 50 cm^3) at −78°C was added a solution of $NaSC_6F_5$ (0.9 g, 4.0 mmol) in THF. To the green-blue reaction mixture at room temperature was added xylylisocyanide (1.58 g, 12 mmol). The orange-brown reaction mixture was worked-up as above giving yellow crystals identical with those from method (i). Yield: 1.27 g, 65%, m.p. *ca* 185°C. Found (calc.): C 59.0 (59.2), H 3.7 (3.7), N 5.5 (5.7)%. IR (Nujol mull), cm^{-1}: 2086 (C≡N).

Bis(mesitylimido)bis(2,4,6-*triisopropylphenylthiolato)molybdenum(VI)* **4**

To a solution of $Mo(Nmes)_2Cl_2dme$ in Et_2O (0.55 g, 1 mmol in 30 cm^3) at −78°C was added a suspension of $Na(SC_6H_2\text{-}Pr^i_3)$ in Et_2O (0.54 g, 2.1 mmol in 30 cm^3). After warming to room temperature the reaction mixture was stirred for 12 h. Evaporation of volatiles under reduced pressure afforded an orange-red oil which, after extraction in hexamethyldisiloxane, concentration and cooling (−20°C) gave orange crystals. Yield: 0.54 g, 65%, m.p. 142–145°C. M.S. (E.I.): *m/z*, 834 (M^+), 599 ($M^+\text{-}SC_6H_2Pr^i_3$). NMR (C_6D_6). ^{1}H: δ 7.1 (s, 4H, $SC_6\mathit{H}_2Pr^i_3$), 6.6 (s, 4H, $NC_6\mathit{H}_2Me_3$), 4.3 [sept., 4H, $SC_6H_2(o\text{-}\mathit{Pr}^i_2)Pr^i$], 2.8 [sept., 2H, $SC_6H_2(p\text{-}\mathit{Pr}^i)Pr^i_2$], 2.2 [s, 12H, $NC_6H_2(o\text{-}\mathit{Me})_2Me$], 2.0 [s, 6H, $NC_6H_2(p\text{-}\mathit{Me})Me_2$], 1.3 [d, 24H, $SC_6H_2(o\text{-}\mathit{Pr}^i_2)Pr^i$], 1.2 [d, 12H, $SC_6H_2(p\text{-}\mathit{Pr}^i)Pr^i_2$].

Bis(2,6-*diisopropylphenylimido)bis*(2,4,6-*triisopropylphenylthiolato)molybdenum(VI)* **5**

This was obtained following a method similar to that described for **3** from $Mo(NC_6H_2Pr^i_2)_2Cl_2dme$ and

Table 3. Crystal data and structure refinement details for compounds **1**–**2**

Compound	**1**	**2**
Formula	$C_{45}H_{27}CrF_{15}N_3S_3$	$C_{48}H_{36}CrF_{10}N_4S_2$
M_r	1042.88	974.93
Temperature (K)	150	293
Crystal system	$P2_1/n$	$P\bar{1}$
Space group	Monoclinic	Triclinic
a (Å)	11.128(10)	7.643(2)
b (Å)	21.512(9)	14.139(6)
c (Å)	18.631(8)	20.726(4)
α(°)		83.20(2)
β(°)	98.27(4)	89.190(10)
γ(°)		81.22(3)
V (Å^3)	4414(5)	2197.9(12)
Z	4	2
D_c (Mg m^{-3})	1.569	1.473
F(000)	2100	996
Crystal dimensions (mm)	0.15 × 0.12 × 0.09	0.42 × 0.12 × 0.03
μ/(Mo-K_α) (mm^{-1})	0.502	0.438
Collected reflections	16710	7368
Independent reflections (R_{int})	6618(0.0938)	5681(0.0464)
Correction factors	1.087, 0.873	
Data, restraints, parameters	6617, 0, 610	5680, 0, 642
Goodness of fit, F^2	0.485	0.874
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0389, 0.0601	0.0427, 0.0932
$R1$, $wR2$ (all data)	0.1612, 0.0757	0.0667, 0.0994
Largest difference peak and hole (eÅ^{-3})	0.264, −0.230	0.355, −0.266

$Na(SC_6H_2\text{-}Pr^i_3)$ in Et_2O as orange crystals from petroleum. Yield: *ca* 75%, m.p. 217°C. Found (calc.): C 70.3 (70.7), H 8.8 (8.7), N 2.9 (3.0)%. M.S. (E.I.): *m/z* 918 (M^+), 682 ($M^+\text{-}SC_6H_2Pr^i_3$). NMR (C_6D_6), ^1H: δ 7.2 (s, 4H, $SC_6\mathit{H}_2Pr^i_3$), 6.9 (s, 6H $NC_6\mathit{H}_3Pr^i_2$), 4.3 [sept., 4H, $SC_6H_2(o\text{-}\mathit{Pr}^i_2)Pr^i$], 3.6 (sept., 4H, $NC_6H_3\mathit{Pr}^i_2$), 2.8 [sept., 2H, $SC_6H_2(p\text{-}\mathit{Pr}^i)Pr^i_2$], 1.5 [d, 24H, $NC_6H_3\mathit{Pr}^i_2$], 1.3 [d, 12H, $SC_6H_2(p\text{-}\mathit{Pr}^i)Pr^i_2$], 1.2 [d, 24H, $SC_6H_2(o\text{-}\mathit{Pr}^i_2)Pr^i$].

X-ray crystallography

X-ray data for compounds **1** and **2** were collected at low temperature using a FAST TV area detector diffractometer with Mo-K_α radiation ($\lambda = 0.71069$ Å), as previously described [6]. The structures were solved *via* direct methods procedures of SHELXS 86 [7] and refined by full-matrix least-squares on F_o^2 using the program SHELXL 93 [8]. All unique data used were corrected for Lorentz polarisation factors and for absorption using the program DIFABS [9]. The non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were included in idealised positions. Crystal data and refinement details are summarized in Table 3.

Additional material available from the Cambridge Crystallographic Data comprises fractional atomic co-ordinates, thermal parameters and remaining bond lengths and angles.

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REFERENCES

1. Danopoulos, A. A., Wilkinson, G., Sweet, T. K. N. and Hursthouse, M. B., *Polyhedron* 1996, **15,** 873.
2. Danopoulos, A. A., Wilkinson, G., Sweet, T. K. N. and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* 1995, 2111.
3. (a) Larkworthy, L. F., Noland, K. B. and O'Brien, P. in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), p. 876. Pergamon, Oxford (1987); (b) Eremenko, I. L., Berke, H., Kolobkov, B. and Novotortsev, V. M., *Organometallics* 1994, **13,** 244 and references cited therein; (c) Goh, L. C., Tay, M. S., Mak, T. G. W. and Wang, R.-J., *Organometallics* 1992, **11,** 1711; (d) Springs, J., Janzen, C. P., Darensbourg, M. Y., Calabrese, J. C., Konsic, P. J., Verpeaux, J.-N. and Amatore, C., *J. Am. Chem. Soc.* 1990, **112,** 5787.
4. Stolze G. and Hüble, J., *J. Organomet. Chem.* 1967, **7,** 301.
5. Fox, H. H., Yap, K. B., Robbins, J., Cai, S. and Schrock, R. R., *Inorg. Chem.* 1992, **31,** 2287.
6. Danopoulos, A. S., Wilkinson, G., Hussain-Bates, B. and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* 1991, 1855.
7. Sheldrick, G. M., *SHELX* 86, *Acta Cryst. Sect. A* 1990, **46,** 467.
8. Sheldrick, G. M., *SHELX* 93, *Program for Crystal Structure Refinement.* University of Göttingen, Germany (1993).
9. Walker, N. P. C. and Stuart, D., *Acta Cryst. Sect. A* 1983, **39,** 158 (adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff (1991).