ELSEVIER

Journal of Organometallic Chemistry 631 (2001) 181–187

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and crystal structures of chromium and molybdenum complexes containing the 2,4,6-tris(trifluoromethyl)phenyl ligand

Andrei S. Batsanov [a], Keith B. Dillon [a,*], Vernon C. Gibson [b], Judith A.K. Howard [a], Leela J. Sequeira [a], Jing Wen Yao [a,1]

[a] *Chemistry Department, University of Durham, South Road, Durham DH1 3LE, UK*
[b] *Chemistry Department, Imperial College, South Kensington, London SW 7 2AY, UK*

Received 11 May 2001; accepted 10 June 2001

Abstract

Complexes [Cr(NR)$_2$Cl$_2$] react with Li(fmes) to yield [Cr(NR)$_2$(fmes)$_2$], where fmes = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$. X-ray diffraction studies of the newly synthesised complex with R = adamantyl, and the previously known one with R = *tert*-butyl, have revealed tetrahedral coordination of the metal, complemented by two secondary Cr···F interactions with *ortho*-CF$_3$ groups of the fmes ligands. The reaction of [Mo(NC$_6$H$_3{}^i$Pr$_2$-2,6)$_2$Cl$_2$(dme)] with Li(fmes) gave a dimeric complex [Mo(NC$_6$H$_3{}^i$Pr$_2$-2,6)$_2$(fmes)Cl·LiCl(dme)]$_2$. The X-ray structure of the latter (as its pentane solvate) shows a double-ribbon Mo$_2$Li$_2$Cl$_4$ arrangement, with two Cl atoms μ$_2$-bridging between Mo and Li, and two others μ$_3$-bridging between one Mo and two Li atoms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Group VI complexes; Imido ligands; Secondary M–F interactions

1. Introduction

The 2,4,6-tris(trifluoromethyl)phenyl (fmes) ligand first attracted attention for its ability to stabilise, through the combination of steric bulkiness and strong electron-withdrawing ability, compounds of main group elements with low valence and low coordination number [1]. Subsequently, fmes was found also to stabilise complexes, both homoleptic and mixed-ligand, of d-elements, including Co, Ni [2], Re [3], Pd [4] and Au [5]. Until recently, this field was mostly restricted to late- and post-transition metals. However, fmes complexes of earlier transition metals can also be stable. Thus, recently we prepared a number of complexes of V [6], Cr and Mo [7], some of which were characterised by X-ray crystallography. A remarkable feature of some of these complexes is the relatively short distances between the transition metal atom and the fluorine atoms of the *ortho* CF$_3$-groups of fmes. The question arises whether these distances are merely an incidental consequence of steric crowding, or whether they correspond to weak *bonding* interactions ('secondary coordination') [8], which may play an important role in stabilising the structure.

Until recently, a carbon-bonded fluorine atom was regarded as incapable of coordination with a metal. The polarity of the C–F bond is surprisingly low in view of the high formal electronegativity of fluorine [9], and 'organic' fluorine has proved to be a weak nucleophile, e.g. a very poor acceptor of hydrogen bonds [10]. However, the possibility of C–F → M coordination, envisaged by Murray-Rust et al. [11], has now been established experimentally for a number of non- and post-transition metals, although few cases have been reported for transition metals [12]. Such interactions were suggested as being essentially non-bonding in *trans*-[Pd(fmes)$_2$(tht)$_2$] (tht = tetrahydrothiophene) and [Pd(fmes)$_2$(bipy)], where Pd···F distances range from 2.766 to 2.982 Å [4], whereas rather shorter distances were observed in [VCl(fmes)$_2$(thf)] and [V(fmes)$_3$OLi(thf)$_3$] (V···F 2.306(2)–2.668(4) Å) [6] and in [Mo(N^{t}Bu)$_2$(fmes)$_2$] (Mo···F 2.467(3)–2.476(3) Å) [7].

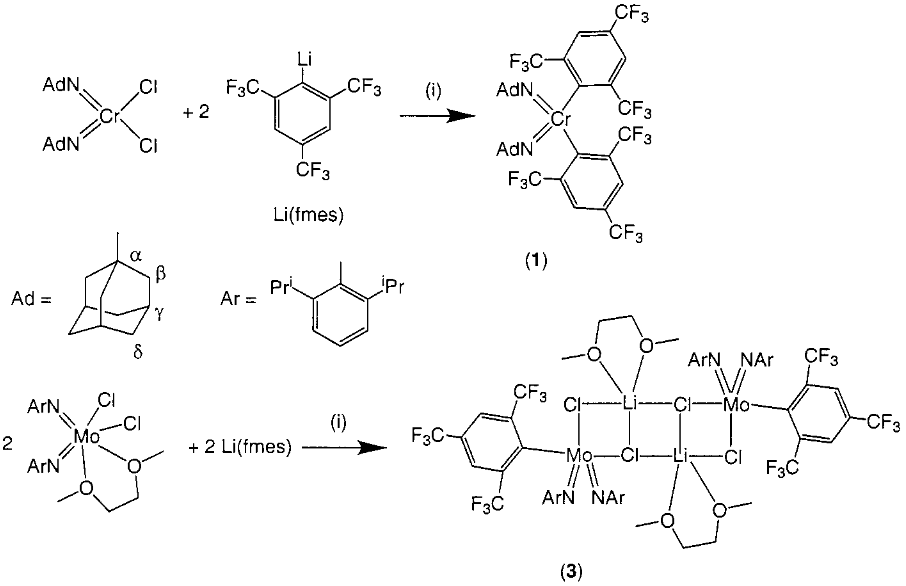
---

[*] Corresponding author. Tel.: +44-191-374-3132; fax: +44-191-384-4737.

E-mail address: k.b.dillon@durham.ac.uk (K.B. Dillon).

[1] Present address: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

PII: S0022-328X(01)01063-4



Scheme 1. Conditions (i): −78 °C, in Et_2O, −2 LiCl.

In order to investigate these interactions further, in the present work we synthesised two new complexes of Group 6 metals with fmes ligands, $[Cr(NAd)_2(fmes)_2]$ (**1**) and $[Mo(NC_6H_3{}^iPr_2\text{-}2,6)_2(fmes)Cl\cdot LiCl(dme)]$ (**3**), and determined their X-ray crystal structures, as well as the structure of the complex $[Cr(N^tBu)_2(fmes)_2]$ (**2**), synthesised earlier [7].

2. Results and discussion

Bright red crystalline complex **1** was obtained in good yield from treatment of $[Cr(NAd)_2Cl_2]$ [13] with two equivalents of Li(fmes), see Scheme 1. The analogous synthesis of complex **2** from $[Cr(N^tBu)_2Cl_2]$ has been described previously [7]. However, the reaction of $[Mo(NC_6H_3^iPr_2\text{-}2,6)_2Cl_2(dme)]$ [14] with Li(fmes) did not result in complete substitution of chloride ligands with fmes, producing instead polynuclear complex **3** (Scheme 1).

The structures of complexes **1**, **2** and **3** were determined by single-crystal X-ray diffraction at 150 K. The molecular structures of **1** and **2** are shown in Figs. 1 and 2, while relevant bond distances and angles are listed in Table 1. The same mode of metal coordination is observed for both complexes as in $[Mo(N^tBu)_2(fmes)_2]$ (**4**) [7], although the crystal packing modes of all three complexes are quite different. It is instructive to compare the structures of **1**, **2** and **4** with those of the non-fluorinated analogues $[Cr(N^tBu)_2(mes)_2]$ (**5**) and $[Mo(N^tBu)_2(2,6\text{-}Me_2C_6H_3)_2]$ (**6**) [15], as shown in Table 2. In each case, two σ-bonded aryl and two imido ligands comprise a distorted tetrahedral environment of the metal atom. The imido ligands are essentially linear, and may be viewed as donating a total of six electrons between them to the metal centre, rather than the usual four each for neutral 1σ,2π ligands. This is a result of the competition between the imido groups

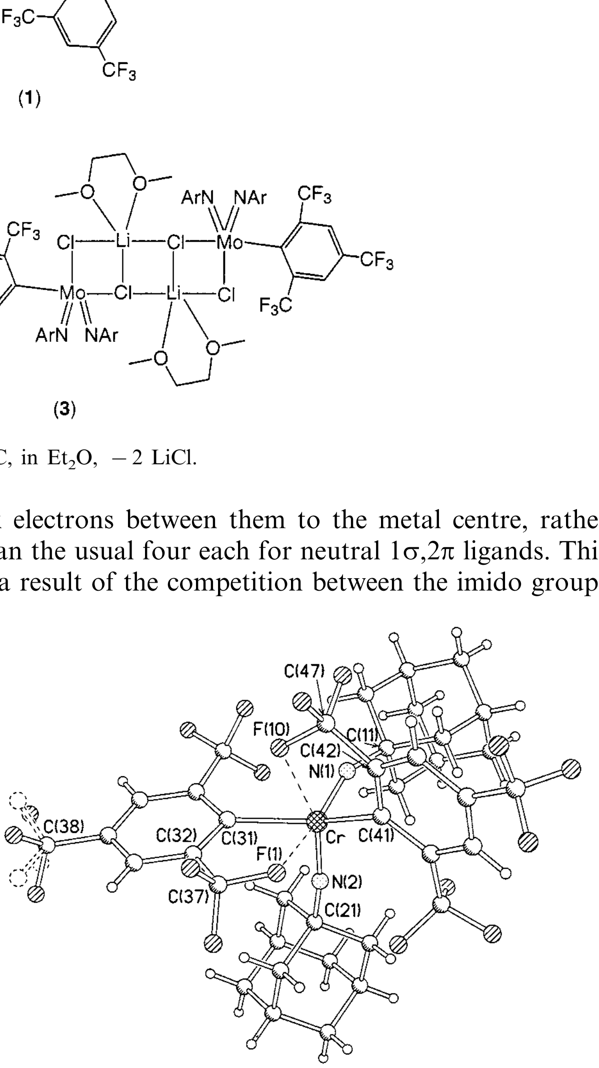


Fig. 1. Molecular structure of $[Cr(NAd)_2(fmes)_2]$ (**1**), showing the disorder of one CF_3 group. H atoms are omitted for clarity.

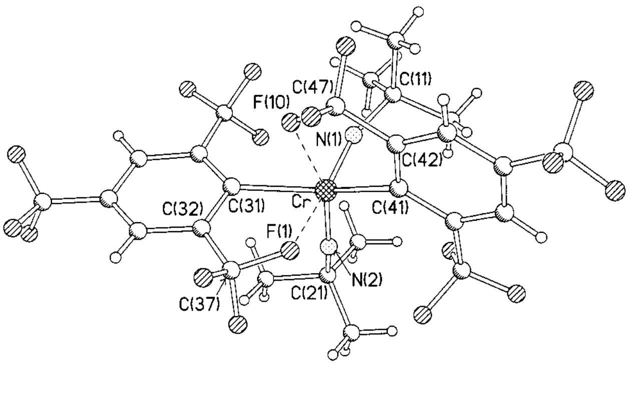


Fig. 2. Molecular structure of $[Cr(N^tBu)_2(fmes)_2]$ (**2**). H atoms are omitted for clarity.

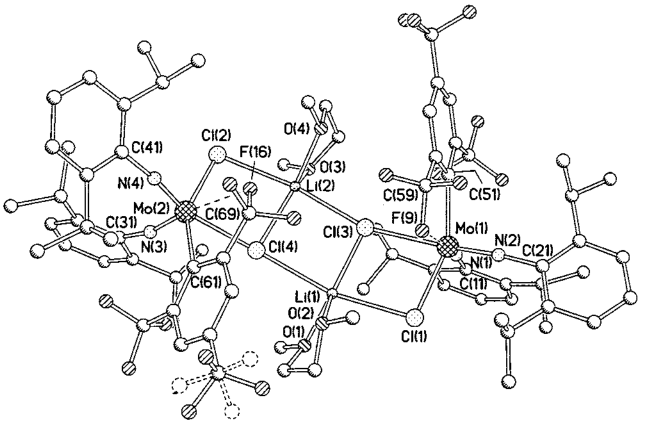


Fig. 3. Molecular structure of [Mo(NC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$(fmes)Cl·LiCl-(dme)]$_2$ (**3**), showing the disorder of one CF$_3$ group. H atoms are omitted for clarity.

for metal dπ orbitals in a tetrahedral coordination environment which allows only three π-bonds (out of the possible four) to be formed. A structural consequence of this is seen in rather long M–N distances which lie at the upper limit of the range usually observed. Although according to VSEPR theory [16], the electron pairs of a multiple bond occupy more space in the coordination sphere than the electron pair of a single bond, in **5** and **6** the C–M–C angle is considerably wider than the N–M–N angle, due to the steric requirements of the mesityl groups. A consequence of the large C–M–C angle is the partial opening up of two additional coordination sites in positions *trans* to the imido ligands. These sites are occupied by one *o*-methyl group of each aryl ligand, one C–H bond of each methyl pointing towards the metal atom. The resulting M···H contacts are far shorter than the sum of the van

Table 1
Bond distances (Å) and bond angles (°) in **1** and **2**

	1	**2**		**1**	**2**
Bond distances					
Cr–N(1)	1.644(2)	1.609(8)	Cr···F(1)	2.443(2)	2.421(5)
Cr–N(2)	1.631(2)	1.612(8)	Cr···F(10)	2.462(2)	2.468(5)
Cr–C(31)	2.133(3)	2.158(9)	Cr–C(41)	2.133(3)	2.129(9)
N(1)–C(11)	1.454(3)	1.48(1)	N(2)–C(21)	1.464(4)	1.47(1)
Bond angles					
N(1)–Cr–N(2)	112.3(1)	112.1(4)	C(31)–Cr–C(41)	138.5(1)	139.9(3)
N(1)–Cr–C(31)	111.4(1)	110.0(4)	N(2)–Cr–C(31)	91.0(1)	92.8(3)
N(1)–Cr–C(41)	92.2(1)	90.1(4)	N(2)–Cr–C(41)	111.7(1)	111.8(4)
N(1)–Cr–F(1)	157.16(9)	156.1(3)	N(2)–Cr–F(1)	89.37(9)	90.7(3)
N(1)–Cr–F(10)	89.25(9)	89.2(3)	N(2)–Cr–F(10)	157.00(9)	157.6(3)
C(31)–Cr–F(1)	73.82(9)	74.5(3)	C(41)–Cr–F(1)	72.25(8)	74.1(3)
C(31)–Cr–F(10)	72.95(8)	72.5(3)	C(41)–Cr–F(10)	73.81(9)	73.6(3)
F(1)–Cr–F(10)	70.66(6)	69.4(2)			
Cr–N(1)–C(11)	155.2(2)	164.0(7)	Cr–N(2)–C(21)	163.2(2)	155.0(7)
Cr–F(1)–C(37)	113.6(2)	111.1(6)	Cr–F(10)–C(47)	109.4(2)	113.9(6)
Cr–C(31)–C(32)	116.6(2)	113.1(7)	Cr–C(41)–C(42)	116.3(2)	117.4(7)
Cr–C(31)–C(36)	129.7(2)	129.7(7)	Cr–C(41)–C(46)	130.0(2)	128.2(6)

Table 2
Average bond distances and angles in [M(NR)$_2$(fmes)$_2$] complexes (**1**, **2**, **4**) and non-fluorinated analogues [M(NR)$_2$R$'_2$] (**5**,**6**)*

	1	**2**	**4**	**5**	**6**
M	Cr	Cr	Mo	Cr	Mo
R	Ad	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu
Bond distances					
M–N	1.638(7)	1.611(8)	1.727(5)	1.626(5)	1.721(13)
M–C	2.133(3)	2.144(15)	2.247(5)	2.034(6)	2.162(7)
M···F	2.453(9)	2.45(2)	2.471(4)		
M···H				2.85	2.60, 2.76
Bond angles					
N–M–N	112.3(1)	112.1(4)	110.6(2)	114.7(3)	112.5(3)
C–M–C	138.5(1)	139.9(3)	138.3(2)	121.2(2)	122.6(3)
M–C–C(R)	116.5(2)	115(2)	116.5(2)	115.1(7)	114.3(5)
M–C–C(H)	129.9(2)	129.0(8)	129.9(2)	127.3(4)	128.1(5)

*R$'$ = 2,4,6-Me$_3$C$_6$H$_2$ (**5**), 2,6-Me$_2$C$_6$H$_3$ (**6**).

der Waals radius of H (1.01 Å) [17] and theoretically calculated [18] radii of isolated atoms of Cr (2.42 Å) and Mo (2.56 Å).

This effect could be explained in terms of the sheer bulkiness of the aryl ligands, which push away the imido ligands and 'wedge' the methyl groups into the coordination sphere. However, the M–C–C angles of each arene ligand are asymmetric, the smaller angle being on the side of the M···H contact, implying attractive M···H interactions (adding to the 16-electron valence shell of the metal atom) rather than forced repulsive contacts. Simple steric repulsion energy calculations failed to reproduce the experimental molecular geometry of **5** and **6** [15], which also supports the existence of specific bonding interactions.

Molecules **1**, **2** and **4** show even stronger distortions of the same type. The C–M–C angles (138–140°) are far wider than in **5** or **6** (121–123°), or in any transition metal complex of this type, available in the Cambridge Crystallographic Database (95–125°, average 111°) [19]. The additional coordination sites are occupied by two fluorine atoms from different fmes ligands, F(1) and F(10) in **1** and **2**. The M···F contacts are even shorter than the M···H contacts in **5** and **6**, even though the van der Waals radius of F exceeds that of H by ca. 0.3 Å [17]. The Cr···F distances of 2.443(2) and 2.462(2) Å in **1**, and 2.421(5) and 2.468(5) Å in **2**, are intermediate between the standard single bond in coordination compounds of 1.870 Å [20] and the sum of the van der Waals radii of ca. 3.7 Å [17,18]. Indeed they are comparable with the axial Cr–F distance of 2.43 Å in CrF_2 [21], and cation–anion contacts of 2.449(5) Å in $[Cr(py)_4](PF_6)_2$ [22] and 2.407(2) Å in $[Cr(NCMe)_4](BF_4)_2$ [23]. It is noteworthy that the latter compound has the cation and anion strongly associated even in solution, as indicated by its low conductivity [23]. These interactions can be regarded as hypervalent bonds (or, in valence bond terms, as a covalent bond↔ion pair resonance) [24]. The order v for the bond length d can be roughly estimated by the formula $v = \exp[(R - d)/0.34]$, where R is the bond-valence parameter (for Cr(VI)–F equal to 1.74 Å) [25], yielding $v = 0.12$ for **1** and **2**. The metal coordination in complexes **1** and **2** can thus be described as 4 + 2, or intermediate between tetrahedral and octahedral, including secondary M–F bonding. The coordination chemistry of the CF unit in fluorocarbons towards metal centres has been extensively reviewed by Plenio [12]. In the first transition series, however, there were considered to be only two convincing reports of such interaction, one being a very short F···Ti distance of 2.151(2) Å in $[Cp_2^*Ti(FPh)][BPh_4]$ [26] and the other in the complex $[VCl(fmes)_2(thf)]$, discussed above [6]. More examples were described for metals in the second transition metal series [12], but none for molybdenum, apart from compound **4** [7] (see above).

The Cr···F interactions in **1** and **2** do not affect the C–F bond lengths significantly. This is not surprising, since the lone electron pairs of fluorine, which interact with the vacant metal d-orbitals, are of essentially p-character and hybridise little with the bonding electrons.

Further evidence of metal–fluorine interaction is provided by NMR spectra. Earlier we have found [7] that both ^1H and ^{19}F spectra of complex **4** in solution indicate a restricted rotation ('locked' conformation) of *ortho*-CF_3 groups of the fmes ligands below 323 K. Although variable-temperature NMR experiments have not been carried out in the present case, similar effects were observed for complexes **1** and **2** even at room temperature, indicating the existence of Cr···F interactions in solution, probably of the same kind as were found in the solid state. In contrast, the *para*-CF_3 groups of fmes must have a very low rotation barrier. Both such groups in molecule **1** are rotationally disordered. For one of them the disorder was approximated by two sets of fluorine atom positions with equal occupancy (50%), for the other we could not find a satisfactory model, while anisotropic refinement of only one orientation left substantial diffuse residual electron density between the fluorine atoms (up to 0.7 e Å^{-3}, compared to 0.2 e Å^{-3} elsewhere in the structure). In structure **2**, both *para*-CF_3 groups also displayed very large and elongated displacement ellipsoids of the fluorine atoms, notwithstanding the low temperature at which both structures were studied.

It is interesting to compare the coordination of the Cr and Mo atoms in **1**, **2** and **4**. The molybdenum atom is larger than chromium, as shown by the covalent radii of 1.27 and 1.10 Å, respectively [27]. In agreement with this, both the M–N and M–C bond lengths in **4** exceed those in **1** and **2** by ca. 0.1 Å. Sterically, there is nothing to prevent the M···F distances elongating proportionally to the covalent bonds, i.e. the whole coordination sphere expanding isotropically. However, the Mo···F distances are only 0.02 Å longer than those for Cr···F, suggesting relatively stronger attractive interactions with Mo ($v = 0.14$, assuming $R = 1.81$ Å [25]). It is noteworthy that Mo···H distances in **6** are shorter than Cr···H in **5**, by an average of 0.17 Å.

M–C distances in complexes **1**, **2** and **4** are longer than in **5** and **6** by ca. 0.1 Å. These σ-bonds are augmented by dπ(M) → pπ(C) back-bonding, which weakens as the C–M–C angle increases, since the two ligands are increasingly competing for the same (occupied) metal d-orbital. All imido-ligands in the complexes under consideration can be described as 'linear', although, as indicated earlier, there is competition between π-donor ligands in a tetrahedral environment, since only three of the possible four π-bonds can be formed between the metal and the *cis*-imido ligands. Their M–N–C angles vary considerably without a cor-

Table 3
Bond distances (Å) and bond angles (°) for **3**

Bond distances			
Mo(1)–N(1)	1.744(7)	Mo(2)–N(3)	1.730(7)
Mo(1)–N(2)	1.754(7)	Mo(2)–N(4)	1.766(7)
Mo(1)–C(51)	2.226(8)	Mo(2)–C(61)	2.221(8)
Mo(1)–Cl(1)	2.434(3)	Mo(2)–Cl(2)	2.433(3)
Mo(1)–Cl(3)	2.614(3)	Mo(2)–Cl(4)	2.598(3)
Mo(1)···F(9)	2.528(5)	Mo(2)···F(16)	2.551(5)
Li(1)–O(1)	1.982(15)	Li(2)–O(2)	1.954(15)
Li(1)–O(2)	2.008(17)	Li(2)–O(4)	2.069(16)
Li(1)–Cl(1)	2.629(15)	Li(2)–Cl(2)	2.623(15)
Li(1)–Cl(3)	2.362(15)	Li(2)–Cl(3)	2.567(14)
Li(1)–Cl(4)	2.730(16)	Li(2)–Cl(4)	2.392(14)
N(1)–C(11)	1.376(11)	N(3)–C(31)	1.405(10)
N(2)–C(21)	1.402(10)	N(4)–C(41)	1.407(11)
Bond angles			
N(1)–Mo(1)–N(2)	109.1(3)	N(3)–Mo(2)–N(4)	108.5(3)
N(1)–Mo(1)–Cl(1)	95.4(1)	N(3)–Mo(2)–Cl(2)	98.0(2)
N(1)–Mo(1)–Cl(3)	98.4(2)	N(3)–Mo(2)–Cl(4)	98.5(2)
N(1)–Mo(1)–C(51)	105.4(3)	N(3)–Mo(2)–C(61)	105.7(3)
N(1)–Mo(1)–F(9)	170.8(2)	N(3)–Mo(2)–F(16)	170.9(2)
N(2)–Mo(1)–Cl(1)	98.2(2)	N(4)–Mo(2)–Cl(2)	98.8(2)
N(2)–Mo(1)–Cl(3)	152.5(2)	N(4)–Mo(2)–Cl(4)	152.8(2)
N(2)–Mo(1)–C(51)	94.8(3)	N(4)–Mo(2)–C(61)	91.4(3)
N(2)–Mo(1)–F(9)	80.1(3)	N(4)–Mo(2)–F(16)	80.4(2)
Cl(1)–Mo(1)–Cl(3)	78.99(8)	Cl(2)–Mo(2)–Cl(4)	80.18(9)
Cl(1)–Mo(1)–C(51)	150.4(2)	Cl(2)–Mo(2)–C(61)	149.7(2)
Cl(1)–Mo(1)–F(9)	83.3(1)	Cl(2)–Mo(2)–F(16)	81.6(1)
Cl(3)–Mo(1)–C(51)	77.3(2)	Cl(4)–Mo(2)–C(61)	77.9(2)
Cl(3)–Mo(1)–F(9)	72.4(2)	Cl(4)–Mo(2)–F(16)	72.5(1)
C(51)–Mo(1)–F(9)	72.9(2)	C(61)–Mo(2)–F(16)	72.1(2)
O(1)–Li(1)–O(2)	85.3(6)	O(3)–Li(2)–O(4)	85.9(6)
O(1)–Li(1)–Cl(1)	99.5(6)	O(3)–Li(2)–Cl(2)	99.3(6)
O(1)–Li(1)–Cl(3)	142.7(8)	O(4)–Li(2)–Cl(4)	146.1(7)
O(1)–Li(1)–Cl(4)	88.8(6)	O(4)–Li(2)–Cl(2)	90.3(5)
O(2)–Li(1)–Cl(1)	92.1(7)	O(4)–Li(2)–Cl(3)	92.9(6)
O(2)–Li(1)–Cl(3)	132.0(7)	O(3)–Li(2)–Cl(4)	127.7(7)
O(2)–Li(1)–Cl(4)	102.9(5)	O(3)–Li(2)–Cl(3)	97.3(6)
Cl(1)–Li(1)–Cl(3)	80.0(4)	Cl(2)–Li(2)–Cl(4)	80.4(4)
Cl(1)–Li(1)–Cl(4)	163.5(7)	Cl(2)–Li(2)–Cl(3)	163.3(6)
Cl(3)–Li(1)–Cl(4)	84.7(5)	Cl(3)–Li(2)–Cl(4)	87.8(4)
Mo(1)–N(1)–C(11)	166.7(6)	Mo(2)–N(3)–C(31)	166.2(6)
Mo(1)–N(2)–C(21)	168.7(6)	Mo(2)–N(4)–C(41)	166.9(6)
Mo(1)–F(9)–C(59)	113.2(5)	Mo(2)–F(16)–C(69)	110.7(4)

responding change in the M–N distance, in agreement with the earlier observation [13] that this angle is relatively 'soft'. The M–N bond lengths approach the upper limit of the usual range (1.58–1.64 Å) for metal–imido bonds [28]. In each of the complexes **1**, **2** and **4** the two M–N–C angles differ by 8–9°, while in **5** and **6** they are virtually equal (159–161°) with the same average value.

The asymmetric unit of structure **3** comprises one dimeric molecule of the complex (Fig. 3, Table 3) and one pentane molecule of crystallisation, which is severely disordered. Molecule **3** contains a double-ribbon $Mo_2Li_2Cl_4$ skeleton, where Cl(1) and Cl(2) are μ_2-bridging between Mo and Li, while Cl(3) and Cl(4) are μ_3-bridging between Mo and two Li atoms. This skeleton has a puckered conformation; the central tetragon of Li(1), Li(2), Cl(3) and Cl(4) is planar, the deviations of other atoms from its plane being as follows: Mo(1) 0.07, Mo(2) 1.32, Cl(1) −0.26, Cl(2) 0.56 Å. The Cl(3) atom is co-planar with the surrounding molybdenum and two lithium atoms within 0.04 Å, while Cl(4) has a pyramidal environment, deviating from the plane of Mo(2), Li(1) and Li(2) by 0.64 Å. The coordination of each Li atom is complemented to distorted trigonal–bipyramidal by a chelating 1,2-(dimethoxy)ethane (dme) ligand. The Mo(1) and Mo(2) atoms have distorted tetragonal-pyramidal coordination (with N(1) and N(3) in apical positions), complemented to distorted octahedral by one weakly coordinated F atom of the fmes ligand, viz. F(9) trans to N(1), and F(16) trans to N(3).

The Mo···F distances are slightly longer than in **4**, in accordance with the higher coordination number of the metal atom. One *para*-CF_3 group of one of the fmes ligands shows a rotational disorder, approximated by two orientations with occupancies of 90 and 10%.

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical service of the Chemistry Department at Durham. NMR spectra were recorded at 25 °C, on a Varian VXR 400 S spectrometer at 400.0 MHz (^1H), 376.32 MHz (^{19}F) or 100.582 MHz (^{13}C); chemical shifts are referenced to the residual protio impurity of the deuterated solvent ($CDCl_3$). 1,3,5-$(CF_3)_3C_6H_3$ (Hfmes) and Li(fmes) were prepared by previously published procedures [7].

3.2. Synthesis of *[Cr(NAd)$_2$(fmes)$_2$]* (*1*)

To $[Cr(NAd)_2Cl_2]$ [13] (250 mg, 0.59 mmol) in Et_2O (20 ml) were added two equivalents of Li(fmes) (1.20 mmol) in Et_2O (20 ml) at −78 °C. The solution was allowed to warm up to room temperature (r.t.), and stirred overnight. After removal of solvent the residue was extracted with pentane (3 × 40 ml); the extracts were reduced in volume to ca. 25 ml and cooled to −78 °C to give deep red crystals of **1**; yield 400 mg (74%), m.p. 158–160 °C. Anal. Found: C, 50.25; H, 3.87; N, 3.49. Calc. for $C_{38}H_{34}CrF_{18}N_2$: C, 50.01; H, 3.75; N, 3.06%. MS: *m*/*e* 913 [M^+]. ^1H-NMR: δ 8.05 (s, 1H, *m*-ArH), 7.82 (s, 1H, *m*-ArH), 2.02 (s, 3H, Ad–H_γ), 1.88 (s, 6H, Ad–H_δ), 1.54 (s, 6H, Ad–H_β). ^{19}F-NMR: δ −56.8 (s, 6F, *o*-CF_3), −59.1 (s, 6F, *o*-CF_3), −62.9 (s, 6F, *p*-CF_3). $^{13}C\{^1H\}$-NMR: δ 175.8 (br, *ipso*-C), 138.5 (q, $^2J_{CF} = 30$ Hz, *o*-CCF_3), 137.2 (q, $^2J_{CF} = 30$ Hz, *o*-CCF_3), 128.7 (q, $^2J_{CF} = 34$ Hz, *p*-CCF_3), 126.7 (q, $^1J_{CF} = 275$ Hz, *p*-CF_3), 123.9 (q, $^1J_{CF} = 273$ Hz, *o*-CF_3), 123.2 (q, $^1J_{CF} = 272$ Hz, *o*-CF_3), 125.0, 124.8 (br s, *m*-C), 82.8 (s, Ad–C_α), 43.7 (s, Ad–C_β), 35.6 (s, Ad–C_δ), 29.5 (s, Ad–C_γ).

3.3. Synthesis of $[Mo(NC_6H_3^iPr_2\text{-}2,6)_2(fmes)Cl\cdot LiCl(dme)]$ (**3**)

To $[Mo(NC_6H_3^iPr_2\text{-}2,6)_2Cl_2\cdot dme]$ (1.0 g, 1.66 mmol), prepared as described earlier [14b], in Et_2O (20 ml) were added two equivalents (3.32 mmol) of Li(fmes) in Et_2O (20 ml) at −78 °C. The solution was allowed to warm up to r.t., and stirred overnight. After removal of solvent the residue was extracted with pentane (3 × 40 ml); the extracts were reduced in volume to ca. 25 ml and cooled to −78 °C to give orange–red crystals of **3**; yield 950 mg (63%). Anal. Found: C, 49.51; H, 5.19; N, 3.56%. Calc. for $C_{37}H_{46}Cl_2F_9LiMoN_2O_2$: C, 49.62; H, 5.17; N, 3.13%. MS: *m*/*e* 763 $[Mo(NC_6H_3^iPr_2\text{-}2,6)_2(fmes)Cl]^+$. ^{1}H-NMR: δ 8.09 (s, 2H, fmes-*H*), 7.09–7.02 (m, 6H, *m*,*p*-C_6H_3), 3.9 (sept, 2H, C*H*Me_2), 3.7 (s, 6H, *Me*OCH_2CH_2O*Me*), 3.5 (s, 4H, MeOC*H*$_2$C*H*$_2$OMe), 2.9 (sept, 2H, $^3J_{CH} = 6.8$ Hz, C*H*Me_2), 1.26 (d, 12H, CH*Me*$_2$), 1.03 (d, 12H, CH*Me*$_2$). ^{19}F-NMR: δ −63.6 (*p*-CF_3). $^{13}C\{^1H\}$-NMR: δ 155–118 (accurate assignment of aryl resonances in this region was hampered by poor resolution and overlap of signals), 71.2 (s, MeOC*H*$_2$C*H*$_2$OMe), 60 (s, *Me*OCH_2CH_2O*Me*), 28.4 (br s, $CHMe_2$), 24.6 (s, CH*Me*$_2$).

Table 4
Crystallographic data and experimental details

Compound	**1**	**2**	**3**
Empirical formula	$C_{38}H_{34}CrF_{18}N_2$	$C_{26}H_{22}CrF_{18}N_2$	$C_{74}H_{92}Cl_4F_{18}Li_2Mo_2N_4O_4\cdot C_5H_{12}$
Formula weight	912.7	756.5	1863.2
T (K)	150	150	150
Symmetry	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (# 2)	$P2_1/n$ (# 14)	$P\bar{1}$ (# 2)
Unit cell dimensions			
a (Å)	12.099(1)	12.760(3)	16.127(11)
b (Å)	12.818(1)	9.451(2)	18.186(10)
c (Å)	14.466(1)	25.330(5)	18.347(8)
α (°)	97.57(1)	90	118.80(5)
β (°)	113.49(1)	99.10(3)	104.26(5)
γ (°)	106.36(1)	90	92.78(4)
V (Å^3)	1896.8(3)	3016(1)	4481(4)
Z	2	4	2
Reflections collected	10 605	4302	14 123
Unique reflections	6167	2810	13 676
R_{int}	0.043	0.116	0.047
Reflections $F^2 > 2\sigma(F^2)$	5185	1795	7062
$R[F^2 > 2\sigma(F^2)]$	0.044	0.077	0.061
$wR(F^2)$, all data	0.116	0.225	0.183

3.4. X-ray crystallography

Crystals of **1** and **2** (deep-red) and **3** (orange-red) of X-ray quality, were grown by slow evaporation of pentane solutions at −20 °C (**1**) and −78 °C (**2** and **3**). The X-ray diffraction data for **2** were collected on a three-circle SMART diffractometer with a 1 K CCD area detector and processed, using SMART and SAINT software [29]. More than a hemisphere of reciprocal space was covered by three sets of ω-scans, each set at different ψ and/or 2θ angles. The data for **1** and **3** were collected on a four-circle Rigaku AFC6S diffractometer with ($2\theta/\omega$ scan mode), using graphite-monochromated Mo–K_α radiation ($\bar{\lambda} = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat, and integrated using TEXSAN programs [30]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software [31]. Crystal data and experimental details are summarized in Table 4.

4. Conclusions

In conclusion, we consider that M···F secondary interactions play a significant role in stabilising the structures of the fmes complexes of Group VI transition metals.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 161590, 161591 and 161592 for compounds **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank EPSRC for a Senior Research Fellowship (J.A.K.H.), EPSRC and Durham University for financial support.

References

[1] (a) H. Grutzmacher, H. Pritzkow, F.T. Edelmann, Organometallics 10 (1991) 23;
(b) S. Brooker, J.-K. Buijink, F.T. Edelmann, Organometallics 10 (1991) 25;
(c) K.H. Whitmire, D. Labahn, H.W. Roesky, M. Noltemeyer, G.M. Sheldrick, J. Organomet. Chem. 402 (1991) 55;
(d) F.T. Edelmann, Comments Inorg. Chem. 12 (1992) 259;
(e) R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, M.R. Bond, C.J. Carrans, J. Am. Chem. Soc. 115 (1993) 2070;
(f) R.D. Schluter, H.S. Isom, A.H. Cowley, D.A. Atwood, R.A. Jones, F. Olbrick, S. Corbelin, R.J. Lagow, Organometallics 13 (1994) 4058;
(g) F.T. Edelmann, Main Group Metal Chem. 17 (1994) 67;
(h) F.T. Edelmann, ACS Symp. Series (Inorg. Fluorine Chem.) 555 (1994) 309.

[2] M. Belay, F.T. Edelmann, J. Organomet. Chem. 479 (1994) C21.

[3] C. de Bellefon, W.A. Herrmann, unpublished results cited in Ref. [1d].

[4] C. Bartolomé, P. Espinet, J. Villafañe, S. Giesa, A. Martin, A.G. Orpen, Organometallics 15 (1996) 2019.

[5] P. Espinet, S. Martin-Barrios, J. Villafañe, P.G. Jones, A.K. Fischer, Organometallics 19 (2000) 290.

[6] V.C. Gibson, C. Redshaw, L.J. Sequeira, K.B. Dillon, W. Clegg, M.R. Elsegood, J. Chem. Soc. Chem. Commun. (1996) 2151.

[7] K.B. Dillon, V.C. Gibson, J.A.K. Howard, C. Redshaw, L. Sequeira, J.W. Yao, J. Organomet. Chem. 528 (1997) 179.

[8] N.W. Alcock, Adv. Inorg. Chem. Radiochem. 15 (1972) 1.

[9] G.V. Bykov, Zh. Fiz. Khim. 33 (1959) 422.

[10] (a) J.A.K. Howard, V.J. Hoy, G.T. Smith, Tetrahedron 38 (1996) 12613;
(b) J.D. Dunitz, R. Taylor, Chem. Eur. J. 3 (1997) 89.

[11] P. Murray-Rust, W.C. Stallings, C.T. Monti, R.K. Preston, J. Glusker, J. Am. Chem. Soc. 105 (1983) 3206.

[12] H. Plenio, Chem. Rev. 97 (1997) 3363.

[13] M.P. Coles, V.C. Gibson, W. Clegg, M.R.J. Elsegood, Polyhedron 17 (1998) 2483.

[14] (a) H.H. Fox, K.B. Yap, J. Robbins, S. Crai, R.R. Schrock, Inorg. Chem. 31 (1992) 2287;
(b) P.W. Dyer, V.C. Gibson, W. Clegg, J. Chem. Soc. Dalton Trans. (1995) 3313.

[15] A.C. Sullivan, G. Wilkinson, M. Motevalli, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1988) 53.

[16] R.J. Gillespie, Molecular Geometry, Van Nostrand Reinhold, London, 1972.

[17] (a) S.C. Nyburg, C.H. Faerman, L. Prasad, Acta Crystallogr. Sect. B 43 (1987) 106;
(b) S.C. Nyburg, C.H. Faerman, Acta Crystallogr. Sect. B 41 (1985) 274.

[18] R. Boyd, J. Phys. B 10 (1977) 2283.

[19] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.

[20] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. Suppl. (1989) 1.

[21] K.H. Jack, R. Maitland, Proc. Chem. Soc. (1957) 232.

[22] G. Fochi, J. Strähle, F. Gingl, Inorg. Chem. 30 (1991) 4669.

[23] R.T. Henriques, E. Herdtweck, F.E. Kühn, A.D. Lopes, J. Mink, C.C. Romão, J. Chem. Soc. Dalton Trans. (1998) 1293.

[24] G. Frenking, N. Fröhlich, Chem. Rev. 100 (2000) 717.

[25] (a) I.D. Brown, D. Altermatt, Acta Crystallogr. Sect. B 41 (1985) 244;
(b) N.E. Brese, M. O'Keeffe, Acta Crystallogr. Sect. B 47 (1991) 192.

[26] J.M. de Wolf, J.M. Gercama, S.I. Troyanov, A. Meetsma, J.H. Teuben, quoted 'in press' in Ref. [12], but to our knowledge not published yet.

[27] P. Pyykkö, Chem. Rev. 88 (1988) 563.

[28] W.A. Nugent, B.L. Haymore, Coord. Chem. Rev. 31 (1980) 123.

[29] SMART, SAINT, Version 4.05. Siemens AXS, Madison, WI, USA, 1995.

[30] TEXSAN, Version 5.1. Molecular Structure Corporation, Woodlands, TX, USA, 1989.

[31] SHELXTL, Version 5.1. Bruker AXS, Madison, WI, USA, 1997.