

Group 6 transition metal complexes containing the σ -bonded 2,4,6-tris(trifluoromethyl)phenyl (“fluoromes”) ligand¹

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Abstract

Group 6 transition metal complexes containing the σ -bonded 2,4,6-tris(trifluoromethyl)phenyl (“fluoromes” or “fmes”) ligand are described. Treatment of $\text{CrCl}_2(\text{thf})$ with two equivalents of Li(fmes) in the presence of PMe_3 affords divalent $[\text{Cr(PMe}_3)_2(\text{fmes})_2]$ (**1**), whereas reaction of $\text{Cr(N}^i\text{Bu)}_2\text{Cl}_2$ with two equivalents of Li(fmes) in diethylether gives the hexavalent bis(imido)chromium complex $[\text{Cr(N}^i\text{Bu)}_2(\text{fmes})_2]$ (**2a**). The molybdenum analogue, $[\text{Mo(N}^i\text{Bu)}_2(\text{fmes})_2]$ (**2b**), is obtained upon treatment of $\text{Mo(N}^i\text{Bu)}_2\text{Cl}_2(\text{dme})$ ($\text{dme} = 1,2\text{-dimethoxyethane}$) with Li(fmes) under similar conditions.

Keywords: Chromium; Molybdenum; Mesityl; Imido; Phosphine; Fluorine

1. Introduction

Recent years have witnessed increasing interest in the bulky, highly electron-withdrawing 2,4,6-tris(trifluoromethyl)phenyl (“fluoromes”) ligand, particularly for its ability to stabilise low valent, low coordinate main group compounds. Examples include derivatives of Ga [1], Sn [2], Pb [3] and Bi [4], X-ray structures of which show weak intramolecular interactions between the main group element centres and the CF_3 fluorine substituents. By contrast, examples of transition metal compounds containing this ligand are relatively rare and, until recently, were restricted to late transition metal derivatives [5–7]. In a recent communication, we have described the first early transition metal complexes containing the σ -bonded fluoromes group, the vanadium complexes $[\text{V(fluoromes)}_2\text{Cl(thf)}]$ and $[\text{V(fluoromes)}_3\text{-OLi(thf)}_3]$ [8], both of which reveal multiple $\text{M} \cdots \text{F}$ interactions. In the expectation that such interactions are likely to have an important influence upon the derivative chemistry of transition metal fluoromes complexes,

we have extended our investigations to other early and mid transition metal systems.

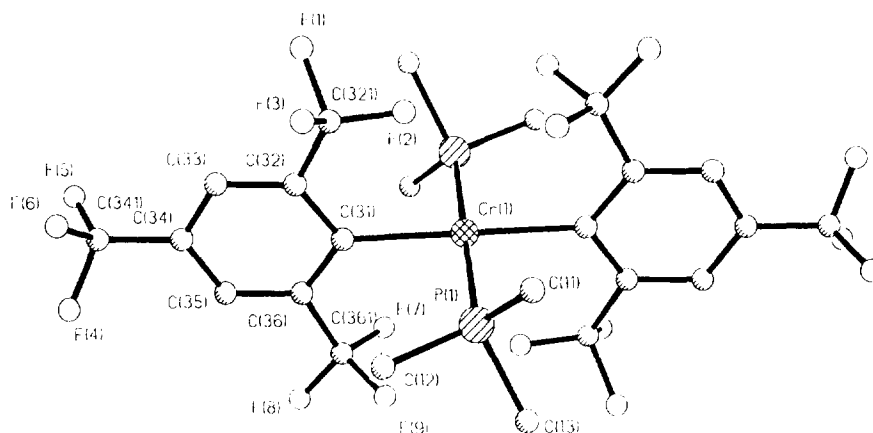
Here, we report the structures of two Group 6 σ -bonded transition metal fluoromes derivatives, namely divalent $[\text{Cr(PMe}_3)_2(\text{fmes})_2]$ (**1**) and a hexavalent molybdenum complex from the bis(imido) Group 6 metal derivatives, $[\text{M(N}^i\text{Bu)}_2(\text{fmes})_2]$ [$\text{M} = \text{Cr}$ (**2a**), Mo (**2b**)].

2. Results and discussion

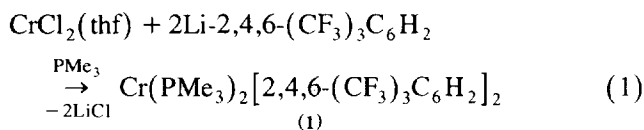
Orange–red **1** is obtained as an air and moisture sensitive compound in moderate yield (40–50%) upon treatment of $\text{CrCl}_2(\text{thf})$ with two equivalents of Li(fluoromes) in the presence of excess PMe_3 (Eq. (1)). Crystals just suitable for an X-ray crystallographic study were grown from pentane solution and the molecular structure is shown in Fig. 1. [The CF_3 groups in **1** show very high thermal vibrations despite reduced temperature X-ray data collection. The nature of the crystal precluded any further reduction below 220 K. A complex model of partial occupancy over a variety of atomic sites was refined for these groups and is reported herein. This model gives rise to an unusual CF_3 geometry, adding little to the knowledge base, but the funda-

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¹ Dedicated to Professor Malcolm Green on the occasion of his 60th birthday.

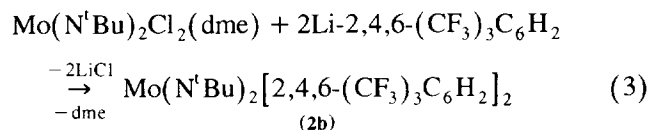
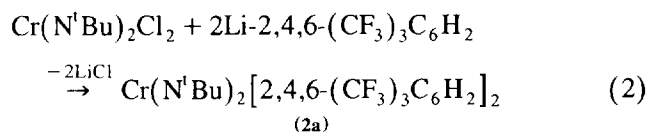
Fig. 1. Molecular structure of **1**.

mental molecular structure and connectivities are correct. An alternative model was tried, the centre of symmetry at Cr was removed. This required a large increase in least-square parameters and resulted in a worse fit of the entire molecule to the recorded data. The space group $P2_1/c$ was retained and the reported molecular geometry corresponds thereto. The methyl C atoms of the PMe_3 ligands also show partial disorder. The sites in Fig. 1 are those with 75% occupancy.] Selected bond distances and angles are collected in Table 1 and crystal data are given in Table 2. **1** possesses a square planar geometry with the two bulky fluoromes groups positioned mutually *trans*. The Cr–P and Cr–C bond distances [2.519(1) and 2.184(4) Å] are somewhat longer than those found in $[\text{Cr}(\text{PMe}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2]$ [2.462(2) and 2.130(6) Å] [10], a consequence of the increased steric congestion around the metal centre in **1**.



The ^1H NMR spectrum of **1** shows broad contact-shifted resonances for the PMe_3 and aryl hydrogens at $\delta = -33.4$ and 21.3 ppm respectively, which compare

with shifts of $\delta = -26.2$ and 33.8 ppm for its protio-mesityl analogue [10]. In the ^{19}F NMR spectrum, the *para*- CF_3 group appears at $\delta = -63$ ppm while the *ortho*- CF_3 signal is broadened into the baseline.



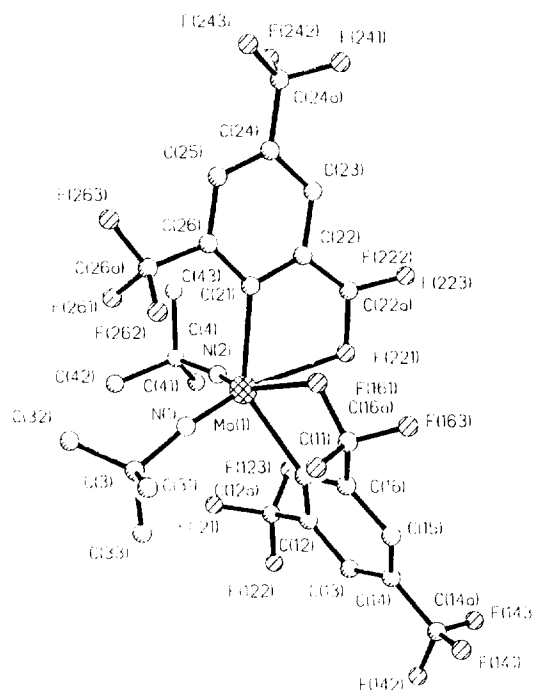
The hexavalent bis(imido) complexes **2a** and **2b** may be obtained by treatment of $\text{Cr}(\text{N}^t\text{Bu})_2\text{Cl}_2$ and $\text{Mo}(\text{N}^t\text{Bu})_2\text{Cl}_2(\text{dme})$ ($\text{dme} = 1,2\text{-dimethoxyethane}$) with two equivalents of Li(fluoromes) (Eqs. (2) and (3)). Both **2a** and **2b** are relatively air stable (days) and are readily soluble in hydrocarbon solvents. Crystals of **2b** suitable for an X-ray diffraction study were grown by slow cooling of a pentane solution to -20°C . The molecular structure is shown in Fig. 2 and key bond distances and angles are given in Table 3. The crystal data are collected in Table 2. **2b** possesses a pseudo-tetrahedral geometry with N–Mo–N and C–Mo–C angles

Table 1
Selected bond lengths (Å) and angles ($^\circ$) for compound **1**

Cr(1)–C(31)	2.184(4)	C(321)–F(1)	1.393(12)
Cr(1)–P(1)	2.519(1)	C(321)–F(2)	1.288(9)
P(1)–C(11)	1.782(9)	C(321)–F(3)	1.304(12)
P(1)–C(12)	1.842(8)	C(341)–F(4)	1.311(12)
P(1)–C(13)	1.872(8)	C(341)–F(5)	1.270(19)
C(32)–C(321)	1.486(8)	C(341)–F(6)	1.358(9)
C(34)–C(341)	1.493(8)	C(361)–F(7)	1.338(7)
C(36)–C(361)	1.502(7)	C(361)–F(8)	1.342(7)
		C(361)–F(9)	1.324(7)
C(31)#1–Cr(1)–C(31)	180.0	C(31)–Cr(1)–P(1)	90.6(1)
C(31)–C(32)–C(321)	120.4(4)	C(33)–C(34)–C(341)	120.6(6)
C(35)–C(36)–C(361)	119.3(4)		

#1 – x, – y, – z.

of 110.6° and 138.3° respectively. The latter is considerably larger than that observed for the mesityl analogue $[\text{Mo}(\text{N}^i\text{Bu})_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2]$ (122.6°) [11], a consequence of the larger size of the fluoromes group. Additionally, however, fluorines on two of the *ortho*- CF_3 groups lie in close contact with the molybdenum centre, with $\text{Mo} \cdots \text{F}$ distances of 2.467(3) and 2.476(3) Å. Such $\text{M} \cdots \text{F}$ interactions, although believed to be quite weak, are also observed widely throughout main group derivatives [1–4]. To minimize steric congestion and electrostatic $\text{F} \cdots \text{F}$ repulsions, the two aromatic rings are twisted by $99.0(2)^\circ$ relative to one another. There is some disorder in the fluorine atom positions for one of the *para*- CF_3 groups [those attached to C(14a)]; the lower occupancy sites (43%) are omitted from Fig. 2 for clarity. For the imido groups, the $\text{Mo}=\text{n}$ distances 1.724(5) and 1.729(4) Å and the $\text{Mo}-\text{N}-\text{C}$ angles $165.0(4)^\circ$ and $156.1(4)^\circ$ lie within the range of bond lengths and angles found for ‘linear’ imido units in bis(imido)molybdenum compounds [12]. The ^{19}F and ^1H NMR data show that the *ortho*- CF_3 and *meta*-aryl hydrogens of each fluoromes ligand are inequivalent in room temperature spectra due to restricted rotation about

Fig. 2. Molecular structure of **2b**.Table 2
Crystallographic experimental details

Compound	1	2b
Chemical formula	$\text{CrP}_2\text{F}_{18}\text{C}_{24}\text{H}_{22}$	$\text{MoN}_2\text{F}_{18}\text{C}_{26}\text{H}_{22}$
M_r	766.34	800.40
Crystal size (mm^3)	$0.34 \times 0.25 \times 0.20$	$0.40 \times 0.30 \times 0.20$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	10.674(2)	18.721(7)
b (Å)	14.493(2)	18.622(8)
c (Å)	10.2410(10)	17.652(6)
β ($^\circ$)	98.130(10)	92.66(3)
D_c (g cm^{-3})	1.623	1.730
Volume ($\text{\AA}^3$)	1568.3(4)	6147(4)
$F(000)$	764	3168
Radiation, Mo $K\alpha\lambda$ (Å)	0.71073	0.71073
(graphite monochromated)		
Absorption coefficient μ (mm^{-1})	0.589	0.557
Diffractometer	Siemens P4	AFC6S
Scan method	$2\theta/\omega$	ω
$2\theta_{\text{max}}$ ($^\circ$)	45	50
Temperature (K)	220(2)	150(2)
Reflections collected	2684	6388
Independent reflections	2051	5422
$(h, k, l)_{\text{min}}$	$-11, -15, -1$	$-1, -1, -20$
$(h, k, l)_{\text{max}}$	11, 1, 11	22, 22, 20
Absorption correction	none	empirical
$T_{\text{min}}/T_{\text{max}}$ transmission		0.948, 1.000
Refinement method ^a	F^2	F^2
Data/restraints/parameters	2051/0/314	5387/0/506
Goodness-of-fit on F^2	0.920	1.032
$R(wR)\%$ [$I > 2\sigma(I)$]	4.68 (11.48)	4.38 (11.21)
$R\%$ (all data)	7.20 (12.36)	8.82 (19.57)
Largest difference peak/hole ($\text{e \AA}^{-3}$)	0.44, -0.39	0.89, -0.80
Anisotropic atoms	All non-H	All non-H

^a SHELXL-93 [9].

Table 3
Selected bond lengths (Å) and angles (°) for compound **2b**

Mo(1)–N(1)	1.724(5)	C(12A)–F(121)	1.346(6)
Mo(1)–N(2)	1.729(4)	C(12A)–F(122)	1.349(6)
Mo(1)–C(11)	2.252(5)	C(12A)–F(123)	1.337(6)
Mo(1)–C(21)	2.241(5)	C(24)–C(24A)	1.498(9)
Mo(1)–F(161)	2.467(3)	C(24A)–F(241)	1.344(11)
Mo(1)–F(221)	2.476(3)	C(24A)–F(242)	1.283(10)
N(1)–C(3)	1.474(7)	C(24A)–F(243)	1.315(10)
N(2)–C(4)	1.476(7)	C(3)–C(31)	1.547(10)
C(12)–C(12A)	1.505(8)	C(3)–C(32)	1.498(9)
C(4)–C(41)	1.523(9)	C(3)–C(33)	1.532(11)
N(1)–Mo(1)–N(2)	110.6(2)	F(123)–C(12A)–F(122)	106.1(4)
N(1)–Mo(1)–C(21)	111.0(2)	F(121)–C(12A)–F(122)	105.6(5)
N(1)–Mo(1)–C(11)	93.6(2)	C(23)–C(24)–C(24A)	119.9(7)
C(21)–Mo(1)–C(11)	138.3(2)	F(242)–C(24A)–F(243)	111.3(8)
N(1)–Mo(1)–F(161)	92.2(2)	F(242)–C(24A)–F(241)	105.2(8)
N(1)–Mo(1)–F(221)	159.0(2)	F(243)–C(24A)–F(241)	101.2(8)
F(161)–Mo(1)–F(221)	68.01(12)	C(32)–C(3)–C(33)	113.9(7)
C(13)–C(12)–C(12A)	115.7(5)	C(32)–C(3)–C(31)	110.4(7)
F(123)–C(12A)–F(121)	106.7(4)	C(33)–C(3)–C(31)	106.7(6)

the metal–carbon bond. As the temperature is raised the resonances for the *ortho*-CF₃ and *meta*-aryl hydrogens coalesce ($T_c = 323$ K), affording a free energy of activation ($\Delta G^\ddagger$) for aryl ring rotation of 64 kJ mol^{-1} .

The potential of the “fluoromes” ligand to stabilize novel transition metal environments through its size, electron-withdrawing capacity and ability to form weak $\text{M} \cdots \text{F}$ interactions is under further investigation.

3. Experimental details

3.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz (¹H) and 376.3 MHz (¹⁹F); chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (Nujol mulls, CsI windows), Perkin-Elmer 577 and 457 grating spectrophotometers. 1,3,5-(CF₃)₃C₆H₃ and Li(fmes) were prepared by previously published procedures [5]. CrCl₂ · thf [13], Mo(N^tBu)₂Cl₂ · dme [14,15] and Cr(N^tBu)₂Cl₂ [16] were synthesised via the literature methods. All other chemicals were obtained commercially and used as received unless stated otherwise.

3.2. Synthesis of Cr(PMe₃)₂(2,4,6-(CF₃)₃C₆H₂)₂ (**1**)

To CrCl₂ · thf (0.85 g, 4.36 mmol) in Et₂O (30 cm³) was added PMe₃ (0.69 g, 9.07 mmol) to give a deep

blue solution. Li(fmes) (9.15 mmol) in Et₂O (30 cm³) was then added. After stirring for 3 h, the solution was filtered and reduced in volume (to ca. 30 cm³). Cooling of this solution to ca. –20 °C afforded large red prisms. Yield 1.43 g, ca. 43%. Anal. Found: C, 37.70; H, 2.92. C₂₄H₂₂P₂F₁₈Cr Calc.: C, 37.61; H, 2.89%.

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 21.3 (s, br, $\nu_{1/2}$ ca. 500 Hz, 4H, *m*-ArH), –33.4 (s, br, $\nu_{1/2}$ ca. 1600 Hz, 18H, PMe₃). ¹⁹F NMR (C₆D₆, 376.32 MHz, 298 K): δ –63 (s, 6F, *p*-CF₃).

3.3. Synthesis of Cr(N^tBu)₂(2,4,6-(CF₃)₃C₆H₂)₂ (**2a**)

To Cr(N^tBu)₂Cl₂ (400 mg, 1.51 mmol) in Et₂O (20 cm³) was added 2 equiv. of Li(fmes) (3.0 mmol) in Et₂O (20 cm³) at –78 °C. This solution was allowed to warm to room temperature and stirred overnight. After removal of solvent, the residue was extracted with pentane (3 × 40 cm³) which was then reduced in volume (to ca. 25 cm³) and cooled to –78 °C to give deep red crystals. Yield 635 mg, ca 84%. Anal. Found: C, 40.84; H, 3.20; N, 3.67. C₂₆H₂₂N₂F₁₈Cr Calc.: C, 41.28; H, 2.91; N, 3.70%.

Mass spectrum: m/e 757 [M]⁺, 701 [M – CF₃]⁺, 476 [M – fmes]⁺.

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 8.00 (s, 2H, ArH), 7.74 (s, 2H, ArH), 1.06 (s, 18H, NCMe₃). ¹⁹F NMR (C₆D₆, 376.32 MHz, 298 K): –57.0 (s, 6F, *o*-CF₃), –59.3 (s, 6F, *o*-CF₃), –62.7 (s, 6F, *p*-CF₃). ¹³C{¹H} NMR (C₆D₆, 100.582 MHz, 298 K): 176.0 (br, *ipso*-C), 138.7 (q, ²J_{CF} 30 Hz, *o*-CCF₃), 137.4 (q, ²J_{CF} 32 Hz, *o*-CCF₃), 129.2 (q, ¹J_{CF} 34 Hz, *p*-CCF₃), 127.4 (q, ¹J_{CF} 275 Hz, *p*-CF₃), 124.4 (q, ¹J_{CF} 273 Hz, *o*-CF₃), 123.6 (q, ¹J_{CF} 272 Hz, *o*-CF₃), 125.5, 125.1 (s, br, *m*-C), 80.5 (s, NCMe₃), 31.1 (s, NCMe₃). IR (Nujol, CsI,

cm^{-1}): 1621(s), 1567(s), 1280(s), 1125(br), 684(s), 434(s).

3.4. Synthesis of $\text{Mo}(\text{N}^i\text{Bu})_2(2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2)_2$ (**2b**)

To $\text{Mo}(\text{N}^i\text{Bu})_2\text{Cl}_2 \cdot \text{dme}$ (500 mg, 1.25 mmol) in Et_2O (20 cm^3) was added 2.4 equiv. of $\text{Li}(\text{fmes})$ (3.0 mmol) in Et_2O (20 cm^3) at -78°C . This mixture was allowed to warm to room temperature and stirred overnight. After removal of solvent, the residue was extracted with pentane ($3 \times 40\text{ cm}^3$) which was then reduced in volume (to ca. 25 cm^3) and cooled to -78°C to give pale yellow crystals. Yield 600 mg, ca. 75%. Anal. Found: C, 38.71; H, 2.86; N, 3.62. $\text{C}_{26}\text{H}_{22}\text{N}_2\text{F}_{18}\text{Mo}$ Calc.: C, 39.00; H, 2.75; N, 3.50%.

Mass spectrum: m/e ^{98}Mo : 802 $[\text{M}]^+$.

^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 8.00 (s, 2H, *m*-ArH), 7.68 (s, 2H, *m*-ArH), 1.13 (18H, s, NCMe_3). ^{19}F NMR (C_6D_6 , 376.32 MHz, 298 K): δ -58.6 (s, 6F, *o*- CF_3), -59.0 (s, 6F, *o*- CF_3), -62.8 (s, 6F, *p*- CF_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.582 MHz, 298 K): 172.7 (br, *ipso*-C), 140.7 (M, br, *o*- CF_3), 137.5 (M, br, *o*- CF_3), 130.3 (q, $^2J_{\text{CF}}$ 34 Hz, CCF_3), 125.1, 124.8 (s, br, *m*-C), 123.4 (q, $^1J_{\text{CF}}$ 272 Hz, *p*- CF_3), 73.8 (s, NCMe_3). IR (Nujol, CsI , cm^{-1}): 1620(s), 1569(s), 1290(s), 1123(br), 1080(s), 1010(s), 909(d), 843(d), 685(s), 435(s).

Acknowledgements

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References

- [1] R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, M.R. Bond and C.J. Carrano, *J. Am. Chem. Soc.*, **115** (1993) 2070; R.D. Schluter, H.S. Isom, A.H. Cowley, D.A. Atwood, R.A. Jones, F. Olbrich, S. Corbelin and R.J. Lagow, *Organometallics*, **13** (1994) 4058.
- [2] H. Grützmacher, H. Pritzkow and F.T. Edelman, *Organometallics*, **10** (1991) 23.
- [3] S. Brooker, J.-K. Buijink and F.T. Edelman, *Organometallics*, **10** (1991) 25.
- [4] K.H. Whitmire, D. Labahn, H.W. Roesky, M. Noltemeyer and G.M. Sheldrick, *J. Organomet. Chem.*, **402** (1991) 55.
- [5] G.E. Carr, R.D. Chambers, T.F. Holmes and D.G. Parker, *J. Organomet. Chem.*, **325** (1987) 13.
- [6] M. Belay and F.T. Edelman, *J. Organomet. Chem.*, **479** (1994) C21.
- [7] C. Bartolomé, P. Espinet, F. Villafane, S. Giesa, A. Martín and A.G. Orpen, *Organometallics*, **15** (1996) 2019.
- [8] V.C. Gibson, C. Redshaw, L. Sequeira, K.B. Dillon, W. Clegg and M.R.J. Elsegood, *J. Chem. Soc., Chem. Commun.*, (1996) 2151.
- [9] G.M. Sheldrick, SHELXL-93, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.
- [10] A.R. Hermes, R.J. Morris and G.S. Girolami, *Organometallics*, **7** (1988) 2372.
- [11] M.B. Hursthouse, M. Motevalli, A.C. Sullivan and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, (1986) 1398.
- [12] A. Bell, W. Clegg, P.W. Dyer, M.R.J. Elsegood, V.C. Gibson and E.L. Marshall, *J. Chem. Soc., Chem. Commun.*, (1994) 2247.
- [13] L.F. Larkworthy and M.H.O. Nelson-Richardson, *Chem. Ind. (London)*, (1974) 164.
- [14] H.H. Fox, K.B. Yap, J. Robbins, S. Cai and R.R. Schrock, *Inorg. Chem.*, **31** (1992) 2287.
- [15] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle and C. Wilson, *Polyhedron*, **14** (1995) 103.
- [16] A.A. Danopoulos, Wa-Hung Leung, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *Polyhedron*, **21** (1990) 2625.