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**Monomeric arylchromium(II) complexes: the crystal structures of [cis-Mes<sub>2</sub>Cr(THF)<sub>2</sub>](THF), [cis-Mes<sub>2</sub>Cr(bipy)](THF), [Mes<sub>4</sub>CrLi<sub>2</sub>(THF)<sub>2</sub>](THF) and Ph<sub>4</sub>CrLi<sub>2</sub>(THF)<sub>4</sub> (Mes = 2,4,6-mesityl; bipy = 2,2'-bipyridine)**

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**Abstract**

The square-planar geometry of the monomeric [Mes<sub>2</sub>Cr(THF)<sub>2</sub>](THF) (**1**) and [Mes<sub>2</sub>Cr(bipy)](THF) (**2**) (Mes = 2,4,6-mesityl; bipy = 2,2'-bipyridine) was determined by X-ray diffraction analysis. Crystal data are as follows. **1**: orthorhombic, *Pccn* with *a* 12.447(3), *b* 14.500(2), *c* 16.593(2) Å, *V* 2994.7(9) Å<sup>3</sup>, *Z* = 4, *R* = 0.121, *R<sub>w</sub>* = 0.121. **2**: Monoclinic, *P2<sub>1</sub>/c* with *a* 14.316(2), *b* 11.071(2), *c* 17.645(3) Å, β 91.24(1)°, *V* 2795.9(3) Å<sup>3</sup>, *Z* = 4, *R* = 0.060, *R<sub>w</sub>* = 0.068. Further reaction of **1** with an excess of MesLi or reaction of CrCl<sub>2</sub>(THF)<sub>2</sub> with 4 equiv. of PhLi, allows the isolation of the monomeric chromates [Mes<sub>4</sub>CrLi<sub>2</sub>(THF)<sub>2</sub>](THF) (**3**) and Ph<sub>4</sub>CrLi<sub>2</sub>(THF)<sub>4</sub> (**4**) in crystalline form. Crystal data for **3** and **4** are as follows. **3**: orthorhombic, *I222* with *a* 8.703(1), *b* 14.129(1), *c* 17.993(1) Å, *V* 2212.6(3) Å<sup>3</sup>, *Z* = 2, *R* = 0.052, *R<sub>w</sub>* = 0.054. **4**: Triclinic, *P1* with *a* 9.187(1), *b* 10.263(1), *c* 10.851(1) Å, α 110.77(1), β 92.16(1), γ 97.48(1)°, *V* 944.7(2) Å<sup>3</sup>, *Z* = 1, *R* = 0.059, *R<sub>w</sub>* = 0.057.

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## Introduction

One of the most characteristic features of the group 6 transition metals (Cr, Mo, W) is the ability to form dinuclear or polynuclear compounds containing intermetallic multiple bonds [1]. In the chemistry of chromium, this ability is well-established for the oxidation state II, where the  $d^4$  electronic configuration allows the formation of “supershort” Cr–Cr quadruple bonds [1b,1c,2]. The occurrence of this interesting functionality, although especially represented in the class of organochromium(II) compounds, remains quite unpredictable. It has been observed in a homogeneous series of Cr<sup>II</sup> compounds, having one or two oxygen donor atoms in the *ortho* positions of the phenyl ring [3], in the tetrakis (dimethylphosphonium)dimethylido complex  $\{[(\text{CH}_3)_2\text{P}(\text{CH}_2)_2]_2\text{Cr}\}_2$  [4], in two homoleptic chromates,  $\text{Me}_8\text{Cr}_2\text{Li}_4(\text{THF})_4$  [5],  $(\text{C}_4\text{H}_8)_4\text{Cr}_2\text{Li}_4(\text{Et}_2\text{O})_4$  [6], in the homoleptic  $(\eta^3\text{-C}_3\text{H}_5)_4\text{Cr}_2$  [7] and the heteroleptic  $[(\text{Me}_3\text{P})(\text{Me}_3\text{SiCH}_2)\text{Cr}(\mu\text{-CH}_2\text{SiMe}_3)]_2$  [8]. However apart from these systems, the square-planar monomeric structure seems to be the most favored in several diversified examples of Cr<sup>II</sup> compounds. Monomeric Cr<sup>II</sup> aryls and alkyls, both *cis* and *trans*, have been obtained by using mono and bidentate phosphines [9]. A monomeric structure has been also suggested for  $\text{Mes}_2\text{Cr}(\text{THF})_2\text{-}(\text{THF})$  (Mes = 2,4,6-Mesityl) on the basis of the magnetic properties [10]. Curiously the less crowded analogue  $\text{Ph}_2\text{Cr}(\text{THF})_x$  cannot be isolated, probably due to a high tendency to rearrange to more stable bis-arene derivatives [11]. Finally, on the basis of magnetic properties, a monomeric, tetrahedral geometry has been indicated for the derivatives  $\text{Ph}_4\text{CrLi}_2(\text{THF})_4$  [12] and  $\text{Mes}_4\text{CrLi}_2(\text{THF})_4$  (Mes = 2,4,6-Mesityl) [13]. However, the recent characterization of one of these complexes showed in fact monomeric Cr<sup>III</sup> species  $\text{Ph}_6\text{CrLi}_3(\text{Et}_2\text{O})_3$ , obtained through an unexplained oxidation reaction [14].

On the other hand the dimeric aggregation between Cr atoms (prerequisite for the formation of Cr–Cr quadruple bonds) is not only affected by the geometry of the ligand [15] and the electronic nature of the donor atom (C,O,N) [5,6,16,17], but also by the alkali cation which, as in the case of anionic Cr<sup>II</sup> chromates  $[(\text{RO})_8\text{Cr}_2\text{Na}_4(\text{THF})_4]$  (R = Ph,  $\beta\text{-C}_{10}\text{H}_8$ , *i*-Pr), can control the molecular complexity through simple solvation/desolvation mechanisms [17]. To try to better understand the role of the alkali cation in determining dimeric aggregation and to gain insights into the real tendency of chromium to form metal–metal bonds, we find it worthwhile to investigate the structural features of both neutral and anionic organochromium(II) complexes. In this paper we describe the characterization of a series of Cr<sup>II</sup> aryls.

## Experimental

All manipulations were carried out under an inert atmosphere ( $\text{N}_2$  or Ar) by using standard Schlenk techniques. Solvents were dried by standard methods,  $\text{CrCl}_2(\text{THF})_2$  [18], Mesityllithium [19a], phenyllithium [19b], MesitylMgBr [20],  $(\text{Mesityl})_2\text{Cr}(\text{THF})_2(\text{THF})$  (1) [10],  $[(\text{Mesityl})_2\text{Cr}(\text{bipy})](\text{THF})$  (2) [20]  $[(\text{Mesityl})_4\text{CrLi}_2(\text{THF})]_2(\text{THF})$  (3) [13] and  $\text{Ph}_4\text{CrLi}_2(\text{THF})_4$  (4) [12] were prepared according to published procedures. Infrared spectra were recorded on a Pye-Unicam Sp-300 spectrophotometer. Elemental analyses were carried out at the Microanalytical Department at the Rijksuniversiteit Groningen. Magnetic susceptibilities were mea-

Table 1  
Crystal data and structural analysis results

Complex	1	2	3	4
Formula	$C_{30}H_{46}O_3Cr$	$C_{32}H_{38}N_2OCr$	$C_{48}H_{68}O_3Li_3Cr$	$C_{40}H_{52}O_4Li_2Cr$
Formula weight (g mol <sup>-1</sup> )	506.69	518.67	758.94	662.73
Crystal system	orthorhombic	monoclinic	orthorhombic	triclinic
Space group	<i>Pccn</i>	<i>P2<sub>1</sub>/c</i>	<i>I222</i>	$P\bar{1}$
Z	4	4	2	1
<i>a</i> (Å)	12.447(3)	14.316(2)	8.703(1)	9.187(1)
<i>b</i> (Å)	14.500(2)	11.071(2)	14.129(1)	10.263(1)
<i>c</i> (Å)	16.593(2)	17.645(3)	17.993(1)	10.851(1)
$\alpha$ (deg)				110.77(1)
$\beta$ (deg)				92.16(1)
$\gamma$ (deg)				97.48(1)
<i>V</i> (Å <sup>3</sup> )	2994.7(9)	2795.9(5)	2212.6(3)	944.7(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.124	1.232	1.139	1.165
<i>F</i> (000)	1096	1104	820	354
$\mu$ <sub>calcd</sub> (cm <sup>-1</sup> )	4.3	4.23	2.9	3.3
Diffractometer	Nicolet R3M	CAD-4F	CAD-4F	CAD-4F
Radiation, $\lambda$ (Å)	Mo-K $\alpha$ (0.71073)	Mo-K $\alpha$ (0.71073)	Mo-K $\alpha$ (0.71073)	Mo-K $\alpha$ (0.71073)
<i>T</i> (K)	298	130	293	293
$\sin \theta / \lambda$ limit (Å <sup>-1</sup> )	0.70	0.594	0.595	0.595
Range of <i>hkl</i>	+ <i>h</i> ; + <i>k</i> ; + <i>l</i>	0:17;0: -13; -20: +20	0:10;0:16;0:21	-10:0; -12:12; -12:12
No. reflections	4839	4880	1128	7230
No. unique refl.	4347	4880	1128	3318
No. refl. used	1472	3336	829	2399
No. parameters	140	390	133	234
<i>R</i> , <i>R</i> <sub>w</sub> , <i>S</i>	0.121,0.121,3.17	0.060, 0.068, 0.48	0.052,0.054,1.38	0.059,0.057,0.52
Largest shift/csd	0.13	0.48	0.027	0.0073
Largest residual peak (e/Å <sup>-3</sup> )	0.59	0.81	0.37	0.36

sured with a MB 4 computerized Gouy balance (Oxford Instruments) in the temperature range 4.2–298 K. Experimental susceptibility data were corrected for the underlying diamagnetism [21].

#### *X-ray crystallographic studies*

A suitable crystal was mounted in a random position on a glass fibre of a goniometric head and placed under the cold nitrogen stream of a locally modified cooling device of an Enraf-Nonius CAD4 diffractometer. The intensities of three standard reflections, which were measured every 3 h, were used to check the drift in the primary beam and in the counting system, and any possible decay of the crystal

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters with esd's in parentheses for 2

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
Cr	0.28232(5)	0.17066(8)	0.05767(4)	1.27(1)
N(1)	0.1978(3)	0.1196(4)	−0.0379(2)	1.47(8)
N(2)	0.3540(3)	0.2456(4)	−0.0364(2)	1.34(8)
C(1)	0.1732(3)	0.1674(5)	0.1378(3)	1.41(9)
C(2)	0.1627(3)	0.0870(4)	0.1986(3)	1.3(9)
C(3)	0.0917(4)	0.1004(5)	0.2512(3)	1.7(1)
C(4)	0.0259(3)	0.1911(5)	0.2447(3)	1.9(1)
C(5)	0.0328(4)	0.2706(5)	0.1835(3)	1.8(1)
C(6)	0.1058(3)	0.2599(5)	0.1317(3)	1.6(1)
C(7)	0.1097(4)	0.3530(5)	0.0683(3)	2.5(1)
C(8)	0.2297(4)	−0.0181(5)	0.2090(3)	1.9(1)
C(9)	−0.0501(4)	0.2056(6)	0.3019(4)	3.1(1)
C(10)	0.4042(3)	0.1718(5)	0.1259(2)	1.45(9)
C(11)	0.4640(3)	0.0713(5)	0.1229(3)	1.5(1)
C(12)	0.5542(4)	0.0735(5)	0.1557(3)	1.8(1)
C(13)	0.5876(3)	0.1753(5)	0.1934(3)	2.1(1)
C(14)	0.5292(4)	0.2753(5)	0.1973(3)	1.7(1)
C(15)	0.4397(3)	0.2747(5)	0.1644(3)	1.5(1)
C(16)	0.3793(4)	0.3861(5)	0.1693(3)	1.8(1)
C(17)	0.4327(4)	−0.0445(5)	0.0838(3)	2.2(1)
C(18)	0.6850(4)	0.1763(6)	0.2286(4)	3.7(2)
C(19)	0.2250(3)	0.1610(5)	−0.1061(3)	1.25(9)
C(20)	0.1780(3)	0.1274(5)	−0.1728(3)	1.7(1)
C(21)	0.1044(4)	0.0476(5)	−0.1692(3)	1.9(1)
C(22)	0.0774(4)	0.0031(5)	−0.0993(3)	2.1(1)
C(23)	0.1257(3)	0.0434(5)	−0.0353(3)	1.8(1)
C(24)	0.3081(3)	0.2391(4)	−0.1047(3)	1.29(9)
C(25)	0.3399(4)	0.3007(4)	−0.1677(3)	1.5(1)
C(26)	0.4203(4)	0.3700(5)	−0.1615(3)	1.7(1)
C(27)	0.4665(4)	0.3772(5)	−0.0916(3)	1.9(1)
C(28)	0.4314(3)	0.3131(5)	−0.0308(3)	1.7(1)
C(29)	0.7291(7)	0.0898(9)	0.5621(4)	6.4(3)
C(30)	0.7399(9)	0.160(1)	0.4386(6)	9.5(4)
O	0.6923(4)	0.0794(7)	0.4882(3)	6.7(2)
C(31)	0.7914(8)	0.244(1)	0.4865(7)	5.1(2) <sup>a</sup>
C(31')	0.8461	0.1923	0.4988	3.1(3) <sup>a</sup>
C(32)	0.809(1)	0.185(2)	0.555(1)	9.9(5) <sup>a</sup>
C(32')	0.8249	0.1188	0.5681	3.0(4) <sup>a</sup>

<sup>a</sup> Isotropically refined.

quality. Scaling factors and Lorentz polarization corrections were applied to the data. Neutral atom scattering factors [22] were corrected for anomalous dispersion [23]. Calculations were performed with SHELX76 [24] and the EUCLID package [25] (geometrical calculations and illustrations) on a MicroVax-II computer. Details on crystal data, structure solution and refinement are given in Table 1. Relevant bond distances and angles for complexes 1–4 are given in Table 6.

*Complex 2.* The data collection was carried out at low temperature (130 K) with Mo- $K_{\alpha}$  radiation ( $\lambda$  0.71073 Å) using  $\omega$ - $2\theta$  scan. 3336 reflections, from a total of 4880 ( $I \geq 3\sigma$ ) were used in the refinement. No absorption correction was applied. The structure was partially solved by direct methods [26]. The position of the remaining atoms could be revealed from succeeding Fourier maps. The interstitial molecule of THF was disordered. Block-diagonal refinement with unit weights converged to a final value of  $R = 0.060$  and  $R_w = 0.068$  using anisotropic temperature factors for the non-hydrogen atoms and isotropic fixed temperature factors ( $B = 5.0 \text{ \AA}^2$ ) for the hydrogen atoms. In the final refinements the positions of the hydrogen atoms were constrained to the corresponding C-atoms at a distance of 0.98 Å. The disorder in the molecule of THF affects mainly the atoms C(31) and C(32). The disorder was solved by dividing the positions of both atoms with an occupancy C/C' of 0.7/0.3. The atoms C(31)-C(31') and C(32)-C(32') were refined with isotropic temperature factors. The hydrogen atoms of the THF molecule were not used in the refinements. Final atomic coordinates are listed in Table 2.

*Complex 3.* Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range  $4.5 < \theta < 11.1^\circ$ . Unit cell parameters were checked for the presence of higher lattice symmetry [27]. Data were corrected for a small linear decay ( $< 1\%$ ) during the 16.5 h of X-ray exposure time but not for absorption. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of two reference reflections:  $\sigma^2(I) = [\sigma_{\text{cs}}^2(I) + (0.012I)^2]$  [28]. Space group  $I222$  was determined from the systematic extinctions:  $hkl: h + k + l = 2n + 1$  and discriminated from  $I2_12_12_1$ ,  $Imm2$ ,  $Im2m$ ,  $I2mm$  and  $Immm$  during the structure determination process. The structure was solved by standard Patterson methods (SHELXS86) [29]. Refinement on  $F$  was carried out by full-matrix least-squares techniques. The THF solvent molecule, which is disordered over a 222 site, was included in the refinement as a rigid-group with isotropic C and O atoms. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters. H-atoms were refined with separate isotropic common thermal parameters for the complex molecule and the solvent molecule respectively ( $U = 0.122(8); 0.14(4) \text{ \AA}^2$ ). Weights based on counting statistics were introduced in the final refinement cycles. Convergence was reached at  $R = 0.052$ . The absolute structure was checked by refinement with opposite  $f''$  anomalous dispersion factors resulting in  $R = 0.057$ ,  $R_w = 0.061$ . Final atomic coordinates are listed in Table 3.

*Complex 4.* Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range  $8.0 < \theta < 13.3^\circ$ . The unit cell parameters were checked for the presence of higher lattice symmetry [27]. Data were corrected for Lp and for a linear decay of 6% during the 114 h of X-ray exposure time but not for absorption. Standard deviations, as obtained from counting statistics, were increased according to an analysis of the excess variance of the two reference reflections:  $\sigma^2(I) = [\sigma_{\text{cs}}^2(I) + (0.032I)^2]$  [28]. The structure was

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters with esd's in parentheses for **3**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$ (Å <sup>2</sup> )
Cr	1/2	1/2	1/2	0.0334(6)
O	1/2	1/2	0.7661(3)	0.069(2)
Li	1/2	1/2	0.6608(6)	0.063(5)
C(1)	0.4732(8)	0.6161(3)	0.5850(3)	0.042(2)
C(2)	0.5826(7)	0.6871(4)	0.5992(3)	0.048(2)
C(3)	0.5517(8)	0.7644(4)	0.6455(4)	0.064(3)
C(4)	0.411(1)	0.7771(5)	0.6785(4)	0.064(3)
C(5)	0.2982(8)	0.7099(4)	0.6649(3)	0.055(2)
C(6)	0.3296(7)	0.6312(4)	0.6207(3)	0.048(2)
C(7)	0.2001(8)	0.5605(4)	0.6112(3)	0.066(2)
C(8)	0.7397(7)	0.6879(5)	0.5621(4)	0.066(3)
C(9)	0.379(1)	0.8621(6)	0.7292(5)	0.098(3)
C(10)	0.5557(9)	0.4249(5)	0.8125(3)	0.083(3)
C(11)	0.507(2)	0.4470(5)	0.8894(3)	0.107(3)

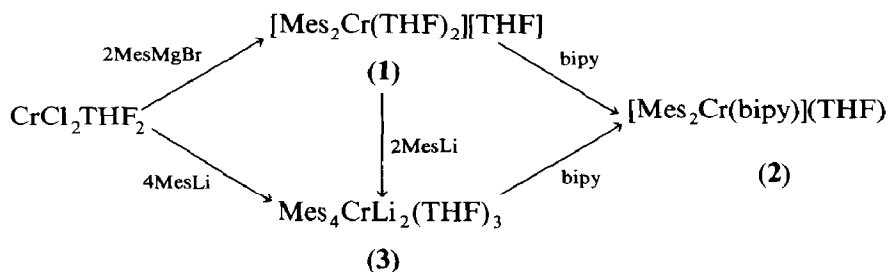
$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j.$$

Table 4

Fractional atomic coordinates and equivalent isotropic thermal parameters with esd's in parentheses for **4**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$ (Å <sup>2</sup> )
Cr	1/2	0	0	0.0635(3)
O(1)	0.3278(3)	0.3238(3)	0.1595(2)	0.088(1)
O(2)	0.3747(3)	0.2606(3)	0.4143(2)	0.091(1)
Li	0.4081(6)	0.1914(6)	0.2289(5)	0.075(2)
C(1)	0.3219(4)	-0.0413(3)	0.1132(3)	0.068(1)
C(2)	0.1797(4)	-0.0082(4)	0.1052(3)	0.085(2)
C(3)	0.0645(5)	-0.0521(5)	0.1690(4)	0.111(2)
C(4)	0.0880(6)	-0.1339(6)	0.2407(5)	0.129(2)
C(5)	0.2231(7)	-0.1728(5)	0.2490(4)	0.128(2)
C(6)	0.3356(4)	-0.1254(4)	0.1882(3)	0.097(2)
C(7)	0.6385(3)	0.1456(4)	0.1757(3)	0.069(1)
C(8)	0.6849(5)	0.0975(4)	0.2719(4)	0.097(2)
C(9)	0.7938(6)	0.1719(6)	0.3744(4)	0.121(2)
C(10)	0.8572(5)	0.3023(7)	0.3872(5)	0.116(2)
C(11)	0.8157(5)	0.3565(5)	0.2951(5)	0.109(2)
C(12)	0.7108(4)	0.2792(4)	0.1918(4)	0.087(2)
C(13)	0.3529(6)	0.3308(5)	0.0336(4)	0.129(2)
C(14)	0.2468(6)	0.4123(6)	0.0059(5)	0.144(3)
C(15)	0.1286(5)	0.4137(5)	0.0940(5)	0.128(2)
C(16)	0.1965(5)	0.3805(5)	0.2013(4)	0.110(2)
C(17) <sup>b</sup>	0.278(2)	0.170(1)	0.4591(7)	0.226(9)
C(18)	0.2785(8)	0.2460(7)	0.6030(5)	0.190(4)
C(19)	0.4304(7)	0.3268(7)	0.6393(4)	0.179(4)
C(20) <sup>b</sup>	0.459(1)	0.3681(8)	0.5215(7)	0.136(5)
<i>Alternative disorder positions (s.o.f. = 0.5)</i>				
C(171)	0.2405(6)	0.261(1)	0.4727(6)	0.155(6)
C(201)	0.4924(7)	0.270(2)	0.5098(6)	0.169(7)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j. \quad ^b \text{Indicates disordered atom (s.o.f. = 0.5).}$$



Scheme 1

solved by direct methods (SHELX86) [29] and subsequent difference Fourier analyses. Refinement on  $F$  was carried out by full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. H-atoms were introduced at calculated positions ( $C-H = 0.98 \text{ \AA}$ ) and included in the refinement riding on their carrier atoms. One of the THF molecules is disordered with two puckering conformations in 1/1 ratio and was refined with a disorder model using geometrical restraints. The disorder model involves short contacts between inversion symmetry-related THF molecules. Attempts to avoid these short contacts by refining the structure with an order model in  $P1$  were unsuccessful. It was therefore concluded that the inversion center is statistical. H-atoms were refined using different isotropic thermal parameters (respectively  $U = 0.40(2)$  in the disordered parts of the molecule, and  $0.157(4) \text{ \AA}^2$  in the rest of the molecule). Weights based on counting statistics, were introduced in the final refinement cycles. Convergence was reached at  $R = 0.059$ . Final atomic coordinate parameters are listed in Table 4.

## Results and discussion

The synthetic procedures are summarized in (Scheme 1).

The labile coordination of the THF molecules allows ligand replacement with a number of nitrogen-containing ligands including pyridine and 2,2'-bipyridine (bipy). In the case of bipy, deep-blue crystals of  $[\text{Mes}_2\text{Cr(bipy)}](\text{THF})$  (2), were isolated in good yield.

Both compounds 1 and 2 are paramagnetic. The values of  $\mu_{\text{eff}}$  ( $\mu_{\text{eff}} = 4.69\mu_{\text{B}}$  and  $\mu_{\text{eff}} = 4.86\mu_{\text{B}}$  for 1 and 2 respectively) are in agreement with the previously reported data and consistent with a high spin  $d^4$  electronic configuration [30]. The high tendency of 1 to lose THF (probably interstitial) frustrated several attempts to obtain a structural characterization. Finally a reasonable data set was obtained from a crystal, sealed in a glass capillary under THF-saturated  $\text{N}_2$  atmosphere.

The monomeric nature of 1 and 2 was confirmed by X-ray diffraction analyses [31\*]. The structure showed the two molecules having a tetrahedrally distorted, square planar geometry (Figs. 1 and 2). The distortion from the planarity is very similar in the two complexes and is probed by the acute angles between the planes  $C(1)-Cr-C(1')/O(1)-Cr-O(1')$  and  $C(10)-Cr-C(1)/N(1)-Cr-N(2)$  ( $27.6(6)$  and

\* Reference number with asterisk indicates a note in the list of references.

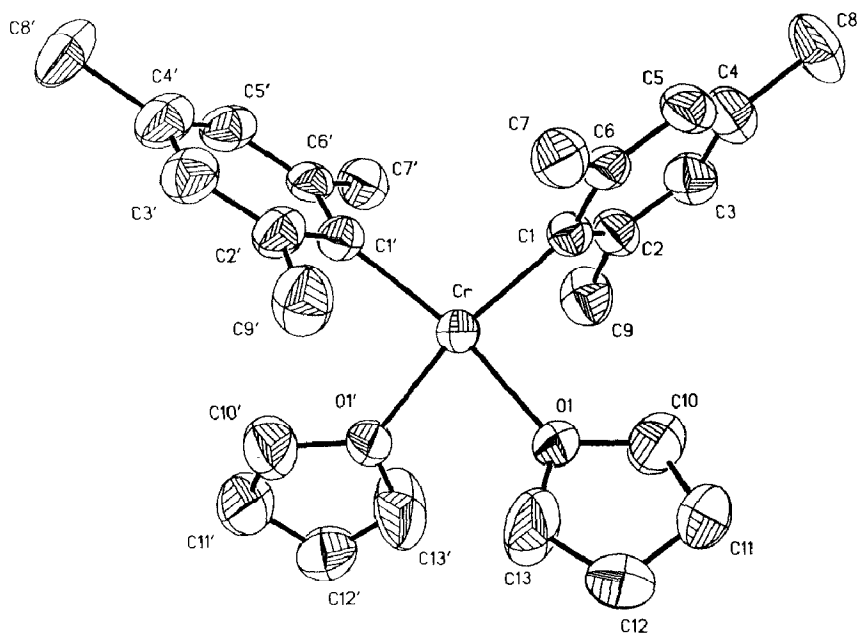


Fig. 1. Thermal motion ellipsoid plot for **1** at 40% probability level with the adopted numbering scheme.

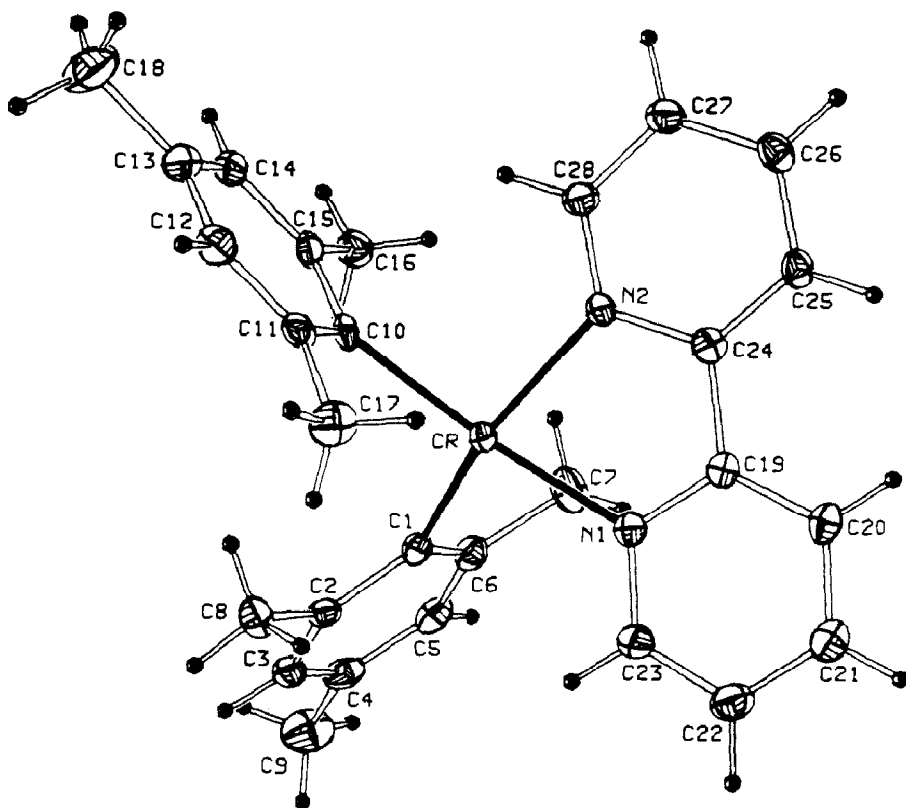


Fig. 2. Thermal motion ellipsoid plot of **2** at 50% probability level, with the adopted numbering scheme.



Table 5

Fractional atomic coordinates and equivalent isotropic thermal parameters with esd's in parentheses for **1**

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cr	0.2500	0.7500	-0.5490(1)	7.1(1)
C(1)	0.2656(10)	0.6405(7)	-0.6294(6)	6.9(4)
C(2)	0.1855(11)	0.5733(9)	-0.6323(7)	8.6(5)
C(3)	0.1918(12)	0.4946(10)	-0.6786(8)	10.1(6)
C(4)	0.2793(12)	0.4778(11)	-0.7289(8)	11.3(7)
C(5)	0.3580(11)	0.5446(10)	-0.7280(7)	9.6(6)
C(6)	0.3512(10)	0.6231(9)	-0.6804(7)	7.6(5)
C(7)	0.4425(10)	0.6889(9)	-0.6831(8)	10.3(6)
C(8)	0.2872(12)	0.3888(10)	-0.7847(9)	13.8(8)
C(9)	0.0874(11)	0.5819(11)	-0.5769(8)	12.2(7)
O(1)	0.3142(7)	0.6700(5)	-0.4542(4)	9.5(3)
C(10)	0.3275(16)	0.5747(10)	-0.4521(10)	17.0(10)
C(11)	0.4222(16)	0.5574(12)	-0.3985(10)	16.4(10)
C(12)	0.4320(15)	0.6400(10)	-0.3509(9)	14.9(9)
C(13)	0.3747(16)	0.7087(11)	-0.3920(11)	20.2(12)
Os	0.2010(23)	0.1854(19)	0.4895(15)	22.1(11)
Os	0.1718(23)	0.2863(20)	0.4827(16)	22.9(11)

31.5(3)° for **1** and **2** respectively). The *cis* arrangement in **2**, probably result of the optimization of the steric hindrance, is sharply in contrast with the *trans*-configuration found in the bulky amide (THF)<sub>2</sub>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> [32], alkoxide [2,6-(<sup>t</sup>Bu)<sub>2</sub>-4-MePhO]<sub>2</sub>Cr(THF)<sub>2</sub> [16b] and aryl Mes<sub>2</sub>Cr(PR<sub>3</sub>)<sub>2</sub> [9].

Table 6

Selected bond distances (Å) and angles (°)

<b>1</b>		<b>2</b>	
Cr-C(1)	2.083(11)	Cr-N(1)	2.131(4)
Cr-O(1)	2.111(8)	Cr-N(2)	2.137(4)
O(1)-Cr-C(1)	91.3(4)	Cr-C(1)	2.130(5)
O(1')-Cr-C(1)	91.3(4)	Cr-C(10)	2.099(5)
		N(1)-Cr-C(10)	155.0(2)
		C(1)-Cr-N(2)	153.3(2)
		N(1)-Cr-N(2)	76.2(2)
		C(1)-Cr-C(10)	103.5(7)
		N(1)-Cr-C(1)	96.2(2)
		N(2)-Cr-C(10)	155.0(2)
<b>3</b>		<b>4</b>	
Cr-C(1)	2.255(5)	Cr-C(1)	2.169(3)
C(1)-Li	2.146(8)	Cr-C(7)	2.188(3)
C(6)-Li	2.481(7)	Li-C(1)	2.283(7)
C(1)-Cr-C(1')	94.6(2)	Li-C(7)	2.279(6)
C(1)-Cr-C(1'')	86.6(2)	Li-O(1)	1.975(7)
C(1)-Cr-C(1''')	168.1(3)	C(1)-Cr-C(7)	93.5(1)
Cr-C(1)-Li	82.2(3)	C(1)-Cr-C(7')	86.5(1)
C(1)-Li-C(1')	101.1(5)	C(1)-Cr-C(1')	180
		Cr-C(1)-Li	78.1(2)
		C(1)-Li-C(7)	88.2(2)
		C(1)-Li-O(2)	116.0(3)

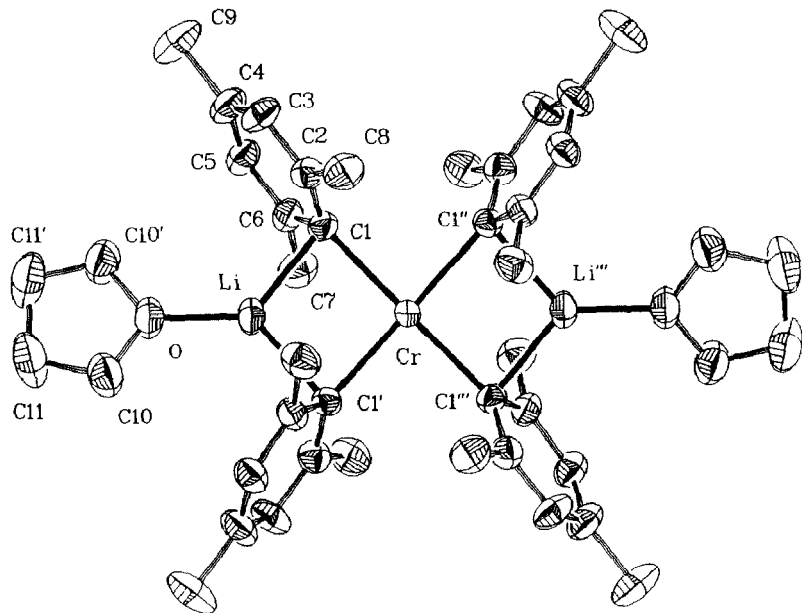


Fig. 3. Thermal motion ellipsoid plot of **3** at 40% probability level, with the adopted numbering scheme.

According to Scheme 1, the reaction of **1** with an excess of  $\text{MeLi}$  yielded yellow-greenish solutions from which brick-red crystals of  $[\text{Me}_4\text{CrLi}_2(\text{THF})_2] \cdot (\text{THF})$  (**3**) were isolated upon cooling at  $-80^\circ\text{C}$ . Compound **3** can also be conveniently synthesized by addition of  $\text{CrCl}_2(\text{THF})_2$  to ethereal solutions of  $\text{MeLi}$  at low temperature ( $\sim 50^\circ\text{C}$ ). Similar results were obtained with  $\text{PhLi}$ , which

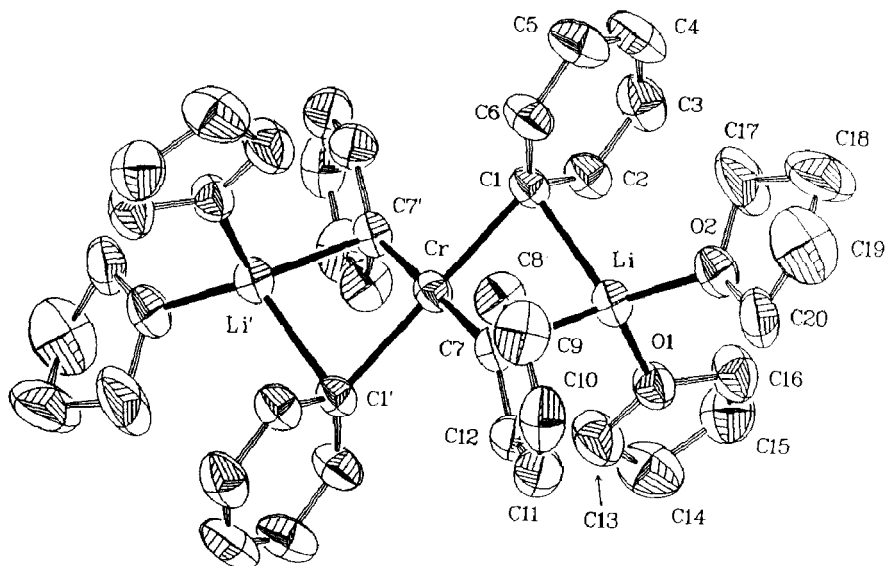
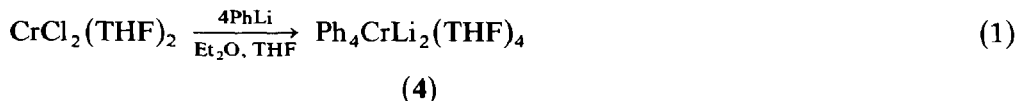


Fig. 4. Thermal motion ellipsoid plot of **4** at 40% probability level, with the adopted numbering scheme.

allowed the isolation of  $\text{Ph}_4\text{CrLi}_2(\text{THF})_4$  (**4**) as yellow crystals (eq. 1).



The chromates **3** and **4** are quite labile since simple coordination of 2,2'-bipyridine is sufficient to remove two molecules of ArLi from the core of the molecule with formation of  $\text{Ar}_2\text{Cr}(\text{bipy})$  (Scheme 1).

Although the values of  $\mu_{\text{eff}}$  ( $\mu_{\text{eff}} = 4.69\mu_{\text{B}}$  and  $\mu_{\text{eff}} = 4.73\mu_{\text{B}}$  for **3** and **4** respectively) exclude in both **3** and **4** the presence of Cr–Cr bonds, dimeric aggregation might be expected in analogy to the case of the paramagnetic alkoxides  $[(\text{RO})_4\text{CrNa}_2(\text{THF})_2]_2$  [16b,17] (isomorphous with the diamagnetic  $\text{R}_8\text{Cr}_2\text{Li}_4(\text{THF})_4$ ) [5,6]. To verify this point we determined the X-ray structures of both **3** and **4**.

The structures of **3** and **4** are rather similar and in both cases consist of discrete mononuclear species (Figs. 3 and 4). The Cr-atom lies in the center of a nearly perfect square-planar coordination geometry (C(1)–Cr–C(1'') 86.6(2), C(1)–Cr–C(1') 94.6(2°) for **3**; C(1)–Cr–C(7) 93.5(1), and C(1)–Cr–C(7') 86.5(1°) for **4**) with the four aromatic rings slightly tilted into a propeller-shaped arrangement. The Cr–C bonding distances (Cr–C(1) 2.255(5) Å (**3**); Cr–C(1) 2.169(3), Cr–C(7) 2.188(3) Å (**4**)) are slightly lengthened with respect to **1** and **2**, probably as a result of an increased steric hindrance. The coordination geometry of the Li atoms in compound **3**, is trigonal. However, one methyl group of each mesityl moiety points towards the fourth and fifth axial coordination sites of the idealized trigonal bipyramid centered on the Li-atom. Although the  $\text{Li} \cdots \text{C}(7)$  2.888(8) Å is too long to reasonably claim any agostic-like interaction, this short proximity may sterically protect lithium, preventing higher coordination numbers. In agreement with this idea, the Li atoms of complex **4** display the more usual tetracoordination, maintaining the square-planar geometry of the main frame  $[\text{Ph}_4\text{Cr}]^{2-}$  (Fig. 4).

Questions arise about which factors disfavor dimeric aggregation which could be expected, at least in the case of  $\text{Mes}_4\text{CrLi}_2(\text{THF})_4$ . In compounds **3** and **4** the Li cations lie almost perpendicularly to the planes of the aromatic rings (Li–C(1)–C(4) 104.7(3)° (**3**); Li–C(1)–C(4) 109.4(2), Li–C(7)–C(10) 112.0(2)° (**4**)). Furthermore the short distance found between the Li-atoms and one of the two C-atoms in the *ortho* positions (Li–C(1) 2.146(8),  $\text{Li} \cdots \text{C}(6)$  2.481(7) Å (**3**); Li–C(1) 2.283(7),  $\text{Li} \cdots \text{C}(2)$  2.668(7) Å (**4**)) suggests a possible interaction of lithium with a portion of the  $\pi$  electron density of the aromatic rings (Fig. 5).

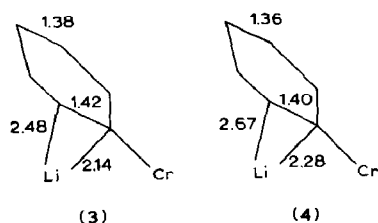


Fig. 5. Relevant bond distances in **3** and **4**.

In complex **4** this feature is less pronounced, probably owing to the higher steric congestion around the Li cation. Although uncommon, this type of interaction is well documented. An allylic-like coordination mode has been observed in the case of benzylolithium [33], fluorenyllithium [34] and triphenylmethylolithium [35], involving the unoccupied  $2s$  and  $2p$  orbitals of the Li cation. This coordination is not affected by the presence of coordinating ligands (THF, Et<sub>2</sub>O, TMEDA), suggesting furthermore that this interaction is strong. On the other hand, the solvation-desolvation processes tune the Lewis acidity of the alkali cation, determining the degree of molecular aggregation (monomeric versus dimeric) [17]. Therefore we suggest that the  $\pi$  interaction with the aromatic rings, resulting in saturation of the coordination sphere and quenching of the Lewis acidity of the lithium atom, is probably the factor which inhibits the dimerization of **3** and **4**.

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*Supplementary material available.* Tables of thermal parameters and extensive lists of bond distances and angles for complexes **2–4** (24 pages). Tables of atomic coordinates, thermal parameters and crystal data for complex **1** (4 pages). List of observed and calculated structure factors for **2–4** (39 pages) are available from the authors\*.

### References

- (a) G. Wilkinson, R.D. Gillard, J.A. McCleverty, *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, Vol. 3, 1987; (b) F.A. Cotton, R.A. Walton, *Multiple Bonds Between Metal Atoms*, J. Wiley, New York, 1982; (c) F.A. Cotton, R.A. Walton, *Metal–Metal Multiple bonds in Dinuclear Clusters in Structure and Bonding*, Vol. 62, Berlin 1985, p. 1.
- F.A. Cotton, X. Feng, P.A. Kibala, M. Matusz, *J. Am. Chem. Soc.* (110) 1988 2807.
- (a) F. Hein, D. Tille, *Z. Anorg. Allg. Chem.*, 329 (1964) 72; (b) F.A. Cotton, S. Koch, M. Millar, *J. Am. Chem. Soc.*, 99 (1977) 7372; (c) F.A. Cotton, S. Koch, *Inorg. Chem.*, 17 (1978) 2021; (d) F.A. Cotton, M. Millar, *Inorg. Chem.*, 17 (1978) 2014.
- F.A. Cotton, B.E. Hanson, W.H. Ilsley, G.W. Rice, *Inorg. Chem.*, 18 (1979) 2713.
- J. Krausse, G. Marx, G. Schodl, *J. Organomet. Chem.*, 21 (1970) 159.
- J. Krausse, G. Schodl, *J. Organomet. Chem.*, 27 (1971) 59.
- T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, K. Tanaka, *Bull. Chem. Soc. Jpn.*, 42 (1969) 545.
- (a) M.B. Hursthouse, K.M.A. Malik, K.D. Sales, *J. Chem. Soc., Dalton Trans.*, (1978) 1314; (b) R.A. Andersen, R.A. Jones, G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1978) 446.
- (a) W. Seidel, G. Stoll, *Z. Chem.*, 12 (1974) 488; (b) G.S. Girolami, J.E. Salt, G. Wilkinson, M. Thornton-Pett, M.B. Hursthouse, *J. Am. Chem. Soc.*, 105 (1983) 5954; (c) A.R. Hermes, J.R. Morris, G.S. Girolami, *Organometallics* 7 (1988) 2372.

\* See NAPS document No. 04761 for 77 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163-3513. Remit in advance, in U.S. Funds only, \$23.85 for photocopies or \$4.00 for microfiche each. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages and \$1.00 for each of 10 pages of material thereafter, or \$1.50 for microfiche postage.

- 10 M. Tsutsui, H. Zeiss, *J. Am. Chem. Soc.*, 82 (1960) 6255.
- 11 (a) F.R. Hein, R. Weiss, B. Heyn, K.H. Barth, D. Tille, *Monatsch. D. Akad. Wiss.*, 1 (1959) 541; (b) F.R. Hein, R. Weiss, *Z. Anorg. Allg. Chem.*, 295 (1958) 145.
- 12 W. Seidel, H. Fischer, K. Schmiedeknecht, *Z. Anorg. Allg. Chem.*, 390 (1972) 273.
- 13 K. Schmiedeknecht, *J. Organomet. Chem.*, 133 (1977) 187.
- 14 M.M. Olmstead, P.P. Power, S.C. Shoner, *Organometallics*, 7 (1988) 1380.
- 15 (a) D.C. Bradley, *Chemistry in Britain*, 11 (1975) 393; (b) R.A. Bartlett, H. Cheng, P.P. Power, *Angew. Chem.* 101 (1989) 325; (c) D.M. Roddick, T.D. Tilley, A.L. Rheingold, S.J. Geib, *J. Am. Chem. Soc.*, 109 (1987) 945; (d) J.E. Salt, G. Wilkinson, M. Motevalli, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1986) 1141; (e) B.D. Murray, H. Hope, P.P. Power, *J. Am. Chem. Soc.*, 107 (1985) 169.
- 16 (a) J.J.H. Edema, S. Gambarotta, F. van Bolhuis, A.L. Spek, W.J.J. Smeets, *Inorg. Chem.*, 28 (1989) 1407; (b) J.J.H. Edema, S. Gambarotta, A.L. Spek, *Inorg. Chem.*, 28 (1989) 811.
- 17 J.J.H. Edema, S. Gambarotta, F. van Bolhuis, A.L. Spek, *J. Am. Chem. Soc.*, 111 (1989) 2142.
- 18 F.H. Kohler, W. Prossdorf, *Z. Naturforsch. B*, 32 (1977) 1026.
- 19 (a) S.D. Rosenberg, *J. Am. Chem. Soc.*, 76 (1954) 4389; (b) J.C.W. Evans, C.F.H. Allen, *Org. Synth. Coll.*, Vol. 2, 518.
- 20 G. Stolze, J. Hahle, *J. Organomet. Chem.*, 7 (1967) 301.
- 21 G. Faese, C.J. Garter, L.J. Smits, *Constantes selectionnées Diamagnetisme Paramagnetisme Relaxation Paramagnetique*, Masson, Paris, 1957.
- 22 D.T. Cromer, J.B. Mann, *Acta Cryst. A* 24 (1968) 321.
- 23 D.T. Cromer, D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
- 24 G.M. Sheldrick, *SHELX-76. A program for crystal structure determination*, Univ. of Cambridge, U.K.
- 25 A.L. Spek, *The Euclid Package in D. Sayre (Ed.), Computational Crystallography*, Clarendon Press, Oxford, 1982, p. 528.
- 26 Computer software: *SDP/PDP Enraf-Nonius & B.A. Frenz & Associates Inc.*
- 27 A.L. Spek, *J. Appl. Cryst.*, 21 (1988) 578.
- 28 L.E. McCandlish, G.H. Stout, L.C. Andrews, *Acta Cryst. A*, 31 (1975) 245.
- 29 G.M. Sheldrick, *SHELXS-86. A program for crystal structure determination*, Univ. of Göttingen, F.R.G.
- 30 F.E. Mabbs, D.J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973.
- 31 X-ray data for **1**. The third molecule of THF (interstitial) in complex **1** is heavily disordered and, regrettably, gave severe calculation problems, preventing the convergence of the X-ray parameters to satisfactory values during the final refinements. Details on crystal data collection and refinement are given in Table 1; atomic coordinates are given in Table 5.
- 32 D.C. Bradley, M.B. Hursthouse, C.W. Newing, A.J. Welch, *J. Chem. Soc., Chem. Commun.*, (1972) 567.
- 33 S.P. Patterman, I.L. Karle, G.D. Stucky, *J. Am. Chem. Soc.*, 92 (1970) 1150.
- 34 J.J. Books, W. Rhine, G.D. Stucky, *J. Am. Chem. Soc.*, 94 (1972) 7339.
- 35 R.A. Bartlett, H.V.R. Diaz, P.P. Power, *J. Organomet. Chem.* 341 (1988) 1.