

Polyhedron Vol. 15, No. 5-6, pp. 873-879, 1996 Copyright € 1995 Elsevier Science Ltd Printed in Great Britain. All rights reserved 0277-5387/96 515.00+0.00

0277-5387(95)00324-X

# REACTIONS OF BIS(MESITYLIMIDO)BIS(ARYLTHIOLATO)CHROMIUM(VI) COMPOUNDS

## ANDREAS A. DANOPOULOS AND GEOFFREY WILKINSON<sup>†</sup>

Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, U.K.

and

### TRACY K. N. SWEET and MICHAEL B. HURSTHOUSE†

Department of Chemistry, University of Wales Cardiff, P.O. Box 912, Cardiff CF1 3TB, U.K.

(Received 26 May 1995; accepted 29 June 1995)

Abstract—The chromium(VI) imidothiolato complex,  $Cr(Nmes)_2(Smes)_2$  (1),  $mes = 2,4,6-Me_3C_6H_2$ , reacts with 2,6-xylylisocyanide (xylNC) to form the five-coordinate chromium(IV) complex  $Cr(Nmes)_2(xylNC)_2(2)$ . A similar interaction of  $Cr(Nmes)_2$  ( $SC_6H_2-2,4,6-Pr_3)_2$  gives only the disulfide adduct  $Cr(Nmes)_2(SC_6H_2-2,4,6-Pr_3)_2 \cdot (2,4,6-Pr_3C_6H_2S)_2(3)$ . Interaction of 1 and PMePh<sub>2</sub> gives  $Cr_4(Nmes)_2(\mu-Nmes)_4(Smes)_2(O)_2(\mu-O)_2(4)$ , where the oxygen atoms arise from adventious oxygen during work up. The X-ray crystal structures of 2–4 have been determined. In 2 the  $Cr^{IV}$  centre has trigonal bipyramidal geometry with axial isocyanides. The  $Cr^{VI}$  centre in 3 is tetrahedral and 4 is a centro-symmetric tetramer in which the outer  $Cr^{V}$  centres are tetrahedral and the inner  $Cr^{IV}$  centres are square-pyramidal.

The first arylimido compounds of chromium(VI),  $Cr(NAr)_2Cl_2$ , Ar = mes, xyl and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, together with derivatives made by replacing Cl with carbon, oxygen and sulfur ligands have been described.<sup>1</sup> This paper reports some reactions of the thiolato compound,  $Cr(Nmes)_2(Smes)_2(1)$ .

## **RESULTS AND DISCUSSION**

The interaction of 1 with 3 equivalents of 2,6xylylisocyanide (xylNC) in refluxing toluene for 0.5 h affords high yields of the monomeric, diamagnetic and pentacoordinate chromium(IV) complex  $Cr(Nmes)(Smes)_2(xylNC)_2(2)$ . After isolation of 2 the carbodiimide, mesN=C=Nxyl, found in the of  $(\text{mesS})_2$  were also detected. The structure of the molecule,  $Cr(Nmes)(Smes)_2(xylNC)_2$  is shown in Fig. 1; selected bond lengths and angles are in Table 1. The chromium(IV) geometry is close to trigonal bipyramidal with axial arylisocyanide ligands, for which the Cr—C distances are equal within experimental error. In the equator, for which the angle sum is close to  $360^\circ$ , the S—Cr—S angle is the largest. This may be ascribed to steric effects involving the packing of the thiolato mesityl and isocyanide *o*-xylyl groups. The imido function coordinates in the usual 6e manner, with Cr—N—C geometry close to linear. Distances are similar to those in other  $Cr^{IV}$  imido complexes.<sup>1</sup>

supernatent was characterized by GC/MS; traces

In analytical and spectroscopic data for 2 are in accord with the structure. The <sup>1</sup>H NMR spectrum has three types of mesityl groups in a 2:1 ratio corresponding to Smes and Nmes, respectively, plus

<sup>†</sup> Authors to who correspondence should be addressed.



Fig. 1. Diagram of the molecule Cr(Nmes)(Smes)<sub>2</sub>(CNxyl)<sub>2</sub> (2).

xylNC bands. Although 2 is five-coordinate, the <sup>1</sup>H NMR spectrum is temperature independent from -40 to 60°C, suggesting rigidity. The xylNC group shows a typical isocyanide<sup>2</sup> band at 2150 cm<sup>-1</sup>. The formation of **2** and the carbodiimide could occur as in eq. (1).

Spectroscopic identification of  $\eta^2$ -carbodiimide species formed in reactions of Cp\*Ir(NBu<sup>t</sup>)<sup>3a</sup> and Cp<sub>2</sub>Zr(NBu<sup>t</sup>)(THF)<sup>3b</sup> with isocyanides has been made and some  $\eta^2$ -carbodiimide complexes have been structurally characterized.<sup>4</sup>

By contrast, the reaction of the more sterically



875

Table 1. Selected bond lengths (Å) and angles (°) for Cr(Nmes)(Smes)<sub>2</sub>(CNxyl)<sub>2</sub>,
(2) with estimated standard deviations in parentheses

CrS(1)	2.275(3)
Cr—S(2)	2.271(3)
Cr-C(1)	1.909(7)
Cr-C(2)	1.924(7)
Cr-N(3)	1.656(5)
S(1)-C(101)	1.745(7)
S(2)—C(201)	1.773(7)
N(1) - C(1)	1.212(7)
N(1) - C(11)	1.439(9)
N(2) - C(2)	1.194(7)
N(2) - C(21)	1.431(9)
N(3)—C(31)	1.379(9)
S(1) - Cr - C(1)	91.0(2)
S(1)— $Cr$ — $C(2)$	82.0(2)
S(1)— $Cr$ — $N(3)$	115.6(2)
S(1)Cr $S(2)$	127.4(1)
S(2) - Cr - C(1)	82.1(2)
S(2)—Cr—C(2)	91.4(2)
S(2)— $Cr$ — $N(3)$	116.9(2)
C(1)— $Cr$ — $C(2)$	164.8(3)
C(1)— $Cr$ — $N(3)$	97.4(3)
C(2)—Cr—N(3)	97.8(3)
Cr-C(1)-N(1)	173.7(6)
Cr-C(2)-N(2)	173.9(6)
Cr - S(1) - C(101)	107.9(2)
Cr—S(2)—C(201)	107.8(2)
Cr—N(3)—C(31)	175.(5)
C(1) - N(1) - C(11)	174.7(7)
C(2) - N(2) - C(21)	175.0(7)

hindered  $Cr(Nmes)_2(SC_6H_2-2,4,6-Pr^i_3)_2$  with xylNC in refluxing toluene gives a solution from which no well defined products could be isolated. However, removal of volatiles and sublimation of the residue onto a dry-ice probe gave a low yield of red crystals, **3**.

The structure of these crystals contains the two neutral, molecular species Cr(Nmes)<sub>2</sub>(SC<sub>6</sub>H<sub>2</sub>-2,4,6- $Pr_{3}^{i}_{2}$  and the disulphide  $(2,4,6-Pr_{3}^{i}C_{6}H_{2}S)_{2}$ , as shown in Fig. 2; selected bond lengths and angles are in Table 2. In the complex molecule the  $Cr^{VI}$ centre has tetrahedral geometry and is bonded to two arylimido and two arylthiolato ligands. The L—Cr—L angles vary from 102.7(2) to  $117.8(1)^{\circ}$ , with the largest again involving S-Cr-S. Here it is difficult to ascribe a direct steric rationalization involving the bulky aryl groups since they adopt distal arrangements. We presume therefore that the size of the S atoms is effective, and it is pertinent to note that in (Bu'N)<sub>2</sub>CrCl<sub>2</sub>,<sup>1</sup> the Cl—Cr—Cr angles were also the largest. The two imido functions are bonding in the normal 6e mode with Cr-N-C angles close to linear; we are unable to rationalize the apparently significant difference between what are essentially equivalent Cr-N bonds [1.647(4) and 1.673(5) Å]. The Cr–S bonds to the thiolates are equal, and, as expected ca 0.03 Å shorter than those in 2.

The alkoxide  $Cr(Nmes)_2(Omes)_2^{-1}$  does not react with xylNC even under forcing conditions, while interaction of **2** with Bu'NC or C<sub>6</sub>H<sub>11</sub>NC gave only intractable mixtures.



Fig. 2. Diagram of the asymmetric unit of  $Cr(Nmes)_2(SC_6H_2-2,4,6-Pr_3)_2$  and  $(2,4,6-Pr_3C_6H_2S)_2$  (3).

Table 2. Selected bond lengths (Å) and angles (°) for  $Cr(Nmes)_2(SC_6H_2-2,4,6-Pr_{3})_2 \cdot (2,4,6-Pr_{3}C_6H_2S)_2$  (3) with estimated standard deviations in parentheses

Cr—S(1)	2.235(2)	
Cr—S(2)	2.246(4)	
Cr—N(1)	1.673(5)	
Cr—N(2)	1.647(4)	
S(1)C(11)	1.802(5)	
S(2)C(21)	1.788(6)	
N(1)—C(111)	1.370(6)	
N(2)—C(211)	1.387(6)	
S(3)—S(4)	2.071(3)	
S(3)—C(31)	1.800(6)	
S(4)—C(41)	1.798(4)	
S(1)—Cr—N(1)	111.0(2)	
S(1)— $Cr$ — $N(2)$	102.7(2)	
S(1)— $Cr$ — $S(2)$	117.8(1)	
S(2) - Cr - N(1)	103.7(2)	
S(2) - Cr - N(2)	104.8(2)	
N(1)— $Cr$ — $N(2)$	117.3(2)	
Cr - S(1) - C(11)	111.8(2)	
Cr-S(2)-C(21)	106.1(2)	
Cr - N(1) - C(111)	162.1(3)	
Cr—N(2)—C(211)	166.8(4)	
C(31) - S(3) - S(4)	102.8(2)	
C(41) - S(4) - S(3)	103.6(2)	

The interaction of 1 with tertiary phosphines gives complex mixtures and only when using  $PMePh_2$  low yields of a crystalline product 4 were isolated on refluxing toluene solutions (2 h) followed by work up in which adventious oxygen was present. Its structure is shown in Scheme I.

Table 3. The tetramer is centrosymmetric and contains two distinctly different Cr atoms. Cr(1) is tetrahedrally coordinated to one terminal arylimido, one arylthiolato and two bridging arylimido groups. The terminal imido is a normal, almost linear 6e ligand. The five-coordinate Cr(2) atom is bonded to two bridging oxygens, two bridging arylimido ligands and one terminal oxo function. The distribution of ligands gives a formal assignment of oxidation states V and VI for Cr(1) and Cr(2), respectively. This result could explain the asymmetry in the bridging arylimido groups. In the  $Cr_2N_2$  ring the angles at N are smaller than those at Cr [85.6(3) and 86.3(2)° versus 89.2(2) and 95.7(2)°], and are implying some  $Cr \cdots Cr$  interaction, as we have discussed previously.<sup>1</sup> Indeed, the  $Cr(1) \cdots Cr(2)$  distance is 2.487(4) Å.<sup>1</sup> However. on further analysis and recognizing the fact that only one electron is available to support this proposed metal ··· metal interaction, which is therefore not likely to be strong, we also now suggest that the  $Cr_2N_2$  ring geometry, and the  $Cr \cdots Cr$  distance in particular, may in part derive from the presence of the tetrahedral Cr(1) atom (for which N-Cr-N would preferably be closer to 109°) and the short Cr-N bridge bonds, i.e. a purely geometrical feature. The distance between the two Cr<sup>VI</sup> atoms is much longer, at 3.15 Å, which is not unexpected in view of the oxidation states of these two, and the fact that the O-Cr-O feature in this central ring involves two cis sites of a square-pyramidal coordination of Cr(2).

In train with these interpretations, we propose that the diamagnetism found for the compound involves coupling through a combination of the  $Cr(1)\cdots Cr(2)$  interactions and the Cr(2)—O—Cr(2') [and even Cr(1)—N—Cr(2)] bridges. The



A diagram of the  $Cr_4N_6O_4S_2$  core of  $[Cr_2(Nmes)(Smes)(\mu-Nmes)_2(O)(\mu-O)]_2$ , is shown as Fig. 3 and selected bond lengths and angles are in

<sup>1</sup>H NMR spectrum shows mesityl groups corresponding to terminal and bridging Nmes groups and to terminal Smes groups. The loss of Smes

groups is probably due to formation of  $(mesS)_2$ and of Nmes to mesN= $PMePh_2$ .

#### **EXPERIMENTAL**

Analyses were by the Imperial College microanalytical laboratory. All operations were carried out under purified  $N_2$  or Ar, under vacuum, or in a Vacuum Atmospheres box. All solvents were degassed and distilled before use.

NMR data were obtained using JEOL EX-270 or Bruker Avance DRX-300 spectrometers operating at 270 and 300 MHz (<sup>1</sup>H), respectively, and referenced to residual H impurity in the solvent ( $\delta$  7.15 C<sub>6</sub>D<sub>6</sub>, 7.26 CDCl<sub>3</sub>, 5.2 CD<sub>2</sub>Cl<sub>2</sub>). Mass spectra were obtained on a VG-7070E (EI) or VG Autospec (FAB and GC/MS).

The starting materials were prepared as in ref. 1. Commercial chemicals are from Aldrich and Avocado Chemicals.

(2,4,6 - Trimethylphenylimido)bis(2,6 - dimethyl - phenylisocyanide)bis(2,4,6 - trimethylthiophenolato) chromium(IV) (2)

A mixture of  $Cr(Nmes)_2(Smes)_2$  (1.0 g, 1.6 mmol) and 2,6-xylylisocyanide (0.7 g, 5.3 mmol) in toluene (50 cm<sup>3</sup>) was refluxed for *ca* 1 h. After concentrating to *ca* 10 cm<sup>3</sup> (or when crystallization started) the mixture was cooled at  $-20^{\circ}$ C for 12 h giving redorange crystals of **2**, m.p. 180–185°C. A second crop can be obtained by addition of petroleum to the supernatent solution after isolation of the first crop. Yield: 0.75 g, *ca* 80%. Mass spectrum (FAB): *m*/*z* 749(M<sup>+</sup>), 618(M<sup>+</sup>-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC), 487(M<sup>+</sup>-2Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC). Found (calc.): C, 72.5 (72.7); H, 6.7 (6.7); N, 5.6 (5.6)%. NMR (CDCl<sub>3</sub>). <sup>1</sup>H:  $\delta$  7.01 (s, 4H, Smes), 6.75 (s, 2H, Nmes), 6.59 (br, 6H, xylNC), 2.58 (s, 6H, *o*-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N), 2.44 (s, 3H, *p*-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N), 2.20 (s, 12H, *o*-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>S), 2.08 (s, 6H, *p*-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>S), 1.72 (s, 12H. *Me*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC).

 $Cr(Nmes)_2(SC_6H_2 - 2,4,6 - Pr^i_3)_2 \cdot (2,4,6 - Pr^i_3C_6H_2S)_2$ (3)

A mixture of Cr(Nmes)<sub>2</sub> (SC<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup><sub>3</sub>)<sub>2</sub> (0.3 g, 0.42 mmol) and 2,6-xylylisocyanide (0.21 g, 1.6 mmol) in toluene was refluxed for 5 h. After removal of the volatiles under reduced pressure, the red-brown residue was heated to *ca* 120°C under high vacuum when red crystals formed on a dry-ice cooled probe located *ca* 0.5 mm from the surface of the residue. NMR (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H:  $\delta$  7.04 [s, 4H, (Pr<sup>i</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>S)<sub>2</sub>], 7.11 and 6.39 (s, 4H each, aromatic), 4.50 and 2.80 (sept. 4H and 2H, *o*- and *p*-CHCMe<sub>2</sub> of disulphide), 2.30 (s, 12H, *o*-Me), 2.00 (s, 6H, *p*-Me), 1.50 and 1.35 (d, 24H and 12H *o*- and *p*-CHC*Me*<sub>2</sub> of thiophenoxide), 1.30 and 1.20 (d, 24H and 12H *o*- and *p*-CHCMe<sub>2</sub> of disulphide). The



Fig. 3. Diagram of the coordination sphere of  $[Cr_2(Nmes)(Smes)(\mu-Nmes)_2(O)(\mu-O)]_2$  (4), with only the  $\alpha$ -carbons of the mesityl groups included for clarity.

NMR spectrum of the residue shows the presence of unreacted starting material.

Table	3.	Select	ed bo	nd	lengths	(Á)	and
angles	(°)	for [	$Cr_2(N)$	mes)	)(Smes)(	μ-Nn	nes) <sub>2</sub>
$(O)(\mu$ -	O)]	<sub>2</sub> ( <b>4</b> )	with	est	timated	stan	dard
deviations in parentheses							

Cr(1)— $Cr(2)$	2.491(4)
Cr(2)—Cr(2')	3.150(4)
Cr(1) - N(1)	1.654(5)
Cr(1)—N(2)	1.778(6)
Cr(1)—N(3)	1.774(5)
Cr(1)—S	2.245(4)
Cr(2)—O(1)	1.952(5)
Cr(2)—O(1')	1.948(5)
Cr(2)O(2)	1.574(5)
Cr(2) - N(2)	1.886(5)
Cr(2)—N(3)	1.867(6)
Cr(2')—O(1)	1.948(5)
<b>S</b> — <b>C</b> (1)	1.778(7)
N(1) - C(11)	1.372(8)
N(2)—C(21)	1.409(8)
N(3)—C(31)	1.403(8)
N(1)— $Cr(1)$ — $N(2)$	118.8(3)
N(1)— $Cr(1)$ — $N(3)$	117.5(3)
N(1)— $Cr(1)$ — $S$	105.9(2)
N(2)— $Cr(1)$ — $N(3)$	95.7(2)
N(2)— $Cr(1)$ — $S$	108.5(2)
N(3) - Cr(1) - S	110.0(2)
O(1)— $Cr(2)$ — $O(1')$	72.2(2)
O(1)— $Cr(2)$ — $O(2)$	106.5(3)
O(1) - Cr(2) - N(2)	88.6(2)
O(1)— $Cr(2)$ — $N(3)$	143.0(2)
O(2)— $Cr(2)$ — $O(1')$	107.9(2)
O(2) - Cr(2) - N(2)	108.2(3)
O(2) - Cr(2) - N(3)	109.2(3)
N(2)— $Cr(2)$ — $O(1')$	142.7(2)
N(2)— $Cr(2)$ — $N(3)$	89.2(2)
N(3)— $Cr(2)$ — $O(1')$	87.9(2)
Cr(1)— $S$ — $C(1)$	110.1(3)
Cr(2) - O(1) - Cr(2')	107.8(2)
Cr(1) - N(1) - C(11)	167.2(5)
Cr(1) - N(2) - C(21)	145.8(4)
Cr(2) - N(2) - C(21)	128.4(4)
Cr(1) - N(2) - Cr(2)	85.6(3)
Cr(1) - N(3) - C(31)	142.4(5)
Cr(2) - N(3) - C(31)	131.2(5)
Cr(1) - N(3) - Cr(2)	86.3(2)

The	symmetry	transformation,	rep-
resented	as '. is $-x$ -	+0.5 v + 1.5	z

The tetramer  $Cr_4(NMes)_2(\mu-Nmes)_4(Smes)_2(O)_2(\mu-O)_2$  (4)

To a solution of Cr(Nmes)<sub>2</sub>(Smes)<sub>2</sub> in toluene (0.5 g, 0.8 mmol in 30 cm<sup>3</sup>) was added PMe- $Ph_2$  (0.65 g, 3.2 mmol, excess) and the red mixture refluxed for 3 h. During the first 0.5 h the colour became green-brown and after 2 h, brown. After removing the volatiles under reduced pressure, excess of unreacted PMePh, was condensed on a dry-ice cooled probe (120°C) and the red-brown residue washed with petroleum and extracted into ether  $(2 \times 20 \text{ cm}^3)$ . The filtered extracts were concentrated slowly to  $ca 5 \text{ cm}^3$ and cooled slowly to  $-20^{\circ}$ C to give small quantity of red-brown prisms. NMR ( $CD_2Cl_2$ ): <sup>1</sup>H:  $\delta 6.80$ (s, 8H, bridging Nmes, aromatic), 6.58 (s, 8H) and 6.40 (s, 4H aromatic terminal Nmes and Smes, but not assigned), 2.32 (s, 12H, o-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>S), 2.12 (s, 24H, o-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N, bridging), 2.08 (s, 6H,  $p-Me_3C_6H_2S$ ), 2.02 and 1.92 (two singlets,  $Me_{3}C_{6}H_{2}N$ , terminal) 1.88 (s, 12H, *p*-Me\_{3}C\_{6}H\_{2}N, bridging).

#### X-ray crystallography

X-ray data were collected at 140 K (2) and at 120 K (3 and 4) using a FAST TV area detector diffractometer with Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71069$ Å), as previously described.<sup>5</sup> The structures of 2and 3 were solved via application of the Patterson instruction of SHELXS-866 and the structure of 4 was solved using direct methods in the same program. Refinement was by full-matrix least-squares on  $F^2$  using the program SHELXL-93.<sup>7</sup> The data for all compounds were corrected for absorption using the program DIFABS<sup>8</sup> with maximum and minimum correction factors listed in Table 4. The non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions, except for those of the isopropyl groups of 3, which were experimentally located from the difference map. The crystal data and refinement details for the structures are summarized in Table 4. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Compound	2	3	4
Formula	$C_{45}H_{51}CrN_3S_2$	$C_{78}H_{114}CrN_{2}S_{4}$	$C_{72}H_{88}Cr_4N_6O_4S_2$
М.	750.01	1259.95	1373.6
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	РĪ	РĪ	C2/c
a (Å)	10.300(7)	10.938(9)	31.82(4)
b (Å)	10.322(9)	17.58(2)	15.169(14)
<i>c</i> (Å)	19.645(9)	19.79(3)	15.04(3)
$\alpha$ (**)	79.79(3)	83.2(2)	90
$\beta$ ( )	84.49(4)	85.02(4)	101.36(8)
$\gamma$ ( )	87.38(3)	87.58(4)	90
$U(\text{\AA}^3)$	2045(2)	3762(7)	7116(18)
Ζ	2	2	4
$D_c ({\rm Mg}{\rm m}^{-3})$	1.218	1.112	1.282
F(000)	796	1368	2888
Crystal size (mm)	$0.15 \times 0.045 \times 0.04$	$0.35 \times 0.06 \times 0.05$	$0.14 \times 0.12 \times 0.06$
$\mu (Mo-K_{x}) (mm^{-1})$	0.416	0.304	0.703
Collection temperature (K)	140	120	120
Reflections collected	6616	14,966	10,742
Independent reflections $(R_{int})$	5123(0.0749)	9903(0.0749)	5016(0.1028)
Maximum, minimum correction factors	1.215, 0.720	1.053, 0.877	1.072, 0.783
Data, restraints, parameters	5120, 6, 473	9898, 0, 832	5016, 6, 409
Goodness of fit, $F^2$	0.726	0.540	0.479
Final R indices			
<i>R</i> 1, w <i>R</i> 2	0.0634, 0.1298	0.0446, 0.0764	0.0438, 0.0688
$[I > 2\sigma(I)]$			
(all data)	0.1359, 0.1508	0.1267, 0.0922	0.1802, 0.0878
Largest difference peak and hole (e $Å^{-3}$ )	0.496, -0.375	0.234, -0.237	0.301, -0.344

	Table 4. Crystal of	data and structure re	finement details f	for compounds	s 2, 3 and 4
--	---------------------	-----------------------	--------------------	---------------	--------------

 $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}; R_1 = \Sigma [(F_o - F_c)] / \Sigma F_o; wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}; w = 1 / [\sigma^2 (F_o^2 + (xP)^2)];$  $P = [\max (F_o^2) + 2(F_c^2)] / 3, \text{ where } n = \text{number of reflections and } p = \text{total number of parameters. } x = 0.0428, 0.0000 \text{ and } 0.0000 \text{ for compounds } 2, 3 \text{ and } 4 \text{ respectively.}$ 

Acknowledgement—We thank the EPSRC for support (A.A.D.) and provision of X-ray facilities.

#### REFERENCES

- A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, J. Chem. Soc., Dalton Trans. 1995, 2111.
- K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edn. Wiley-Interscience, NY (1986).
- (a) D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, J. Am. Chem. Soc. 1991, 113, 2041; (b)

P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics* 1993, **12**, 3705.

- 4. G. Hörlin, N. Mahr and H. Werner, *Organometallics* 1993, **12**, 1775, and refs therein.
- A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, J. Chem. Soc., Dalton Trans. 1991, 1855.
- 6. G. M. Sheldrick, SHELXS-86, Acta. Crystallogr. 1990, A46, 467.
- 7. G. M. Sheldrick, University of Göttingen, Germany (1993).
- N. P. C. Walker and D. Stuart, *Acta Crystallogr.* 1983, A39, 158 (adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, 1991).