Metallocene Derivatives of Early Transition Elements. Part 1. Niobium(IV) Chlorides, Chloroalkyls, and Dialkyls $[Nb(\eta\text{-}C_5H_4X)_2RR']$, and the Crystal and Molecular Structure of $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ †, ‡

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Reaction of $[NbCl_4(thf)_2]$ with $Li[C_5H_4X]$ (X = H, Me, or $SiMe_3$) in tetrahydrofuran (thf) gives a high yield of the volatile $[Nb(\eta\text{-}C_5H_4X)_2Cl_2]$, (1). Treatment of (1) with $2Li[CH_2SiMe_3]$ provides $[Nb(\eta\text{-}C_5H_4X)_2(CH_2SiMe_3)_2]$, (2a)—(2c), whereas $2Mg(R)Cl$ ($R = CH_2SiMe_3$ or CH_2CMe_3) affords the chloroalkyls $[Nb(\eta\text{-}C_5H_4X)_2ClR]$, (3a)—(3e); using the less bulky Grignard reagent $Mg(Me)I$ or $Mg(CH_2Ph)Cl$ yields the dialkyls $[Nb(\eta\text{-}C_5H_4X)_2R'_2]$, (2e)—(2h). The solution e.s.r. spectra of compounds (1)—(3) have been recorded and show a ten-line spectrum due to hyperfine coupling to ^{93}Nb but not α hydrogens. The $g_{av.}$ values are in the range 1.97—2.00 [(1) < (3) < (2)] and $a(^{93}Nb)$ (8.6—11.7 mT) decrease in the reverse sequence and in the order X = H > Me > $SiMe_3$. An *X*-ray crystal-structure determination (to $R = 0.045$, $R' = 0.064$) of $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ shows it to possess roughly tetrahedral geometry, taking each C_5H_5 ring as unidentate, Nb–C(benzyl)$_{av.}$ 2.304(3) Å, Nb–C$(C_5H_5)_{av.}$ 2.410(28) Å, Nb–C–Ph$_{av.}$ 120.0(5)°, and C–Nb–C$_{av.}$ (C = benzyl C) 79.0(4)°. There is a relationship between $a(^{93}Nb)$ and (*a*) electronic configuration of M, $d^0 > d^1$, (*b*) electronegativity of ligand L, $Cl^- > R^-$, and (*c*) steric effects, X = H > Me > $SiMe_3$; *X*-ray data establish that L–M–L (*e.g.* C–Nb–C) also correlates with (*a*) and (*b*).

A MAJOR objective in our studies on metal alkyls was the search for kinetically stable compounds in unusual oxidation states; emphasis was first on homoleptic neutral complexes, like $[Cr\{CH(SiMe_3)_2\}_3]$,[1] and was then extended to cationic heteroleptic complexes, such as $[M(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2][SbF_6]$ (M = Nb or Ta).[2] Success was largely determined by the choice of suitable alkyl ligands which made normal decomposition pathways energetically costly. A significant feature of ligands such as CH_2SiMe_3 and $CH(SiMe_3)_2$ is their ability to render many derived metal complexes soluble in nonpolar (including hydrocarbon) solvents, often important for manipulative and spectroscopic purposes. A further extension, using the same principle, was to alkylmetal complexes in which the alkyl ligand may be regarded as providing a stable host environment for an unusual guest ligand, as exemplified by the complex $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}(\eta^2\text{-}N_2)]$.[3]

The present series has a similar aim (and indeed there is some overlap), but it is the two η-cyclopentadienyl, or substituted η-cyclopentadienyl, groups which are chosen as forming the essence of the metal host environment. Among the substituents in the $C_5H_5^-$ ring, the trimethylsilyl group as in $\eta\text{-}C_5H_4SiMe_3^-$, $\eta\text{-}C_5H_3(SiMe_3)_2^-$, and $\eta\text{-}C_5H_2(SiMe_3)_3^-$ will feature prominently in some later parts. The choice of such groups may be seen as an alternative approach to that which is based on the $C_5Me_5^-$ ligand.[4] Five of our earlier full papers are related to the present series; they concern $[M(\eta\text{-}C_5H_5)_2RR']$ (M = Ti, Zr, Hf, or Nb; $R = R' = CH_2SiMe_3$),[5] $[Ti(\eta\text{-}C_5H_5)_2(CH_2GeMe_3)_2]$,[5a] $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)Cl]$,[5a] $[M(\eta\text{-}C_5H_5)_2R]$[M = Ti and R = $CHPh_2$ or $CH(SiMe_3)_2$; or M = V and R = $CH(SiMe_3)_2$],[6] $[M(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$ (M = Zr or Hg),[6] $[M(\eta\text{-}C_5H_5)_2(CHPh_2)_2]$ (M = Zr or Hf),[6] $[Zr(\eta\text{-}C_5H_5)_2Bu^n\{CH(SiMe_3)_2\}]$,[6] $[Zr(\eta\text{-}C_5H_4X)_2\{CH(SiMe_3)_2\}(\eta^2\text{-}N_2)]$ (X = H or Me),[3] $[Zr(\eta\text{-}C_5H_4X)_2\{CH(SiMe_3)_2\}]$ (X = Et, Pr^i, Bu^t, or $SiMe_3$),[3] $[\{Zr(\eta\text{-}C_5H_4X)_2[CH(SiMe_3)_2]\}_2N_2]$ (X = H or Me),[3] $[M(\eta\text{-}C_5H_5)_2(\mu\text{-}R)_2(AlR_2)]$ (M = Sc, Y, Gd, Dy, Ho, Er, Tm, Yb, or Ti, R = Me; or M = Sc, Y, or Ho, R = Et; or M = Ti, R = H),[7] $[\{M(\eta\text{-}C_5H_5)_2Me\}_2]$ (M = Y, Dy, Ho, Er, Tm, or Yb),[8] and $[Sc(\eta\text{-}C_5H_5)_2MeL]$ ($L = NC_5H_5$ or thf, tetrahydrofuran).[8]

Prior to this work few compounds of the type $[M(\eta\text{-}C_5H_4X)_2R_2]$ (M = V, Nb, or Ta; X = H or alkyl; R = alkyl or aryl) had been prepared. These were the complexes in which (*i*) M = V, X = H, R = Me or CH_2SiMe_3;[9] (*ii*) M = Nb, X = H, R = Me,[10] Ph[11] (not isolated),[10b] or CH_2SiMe_3;[5b] (*iii*) M = Nb, X = Me,[10] or (not isolated)[12] Pr^i, Bu^t, CH_2Ph, or CMe_2Ph, and R = Me; and (*iv*) (not isolated) M = Ta, X = Me, R = Me or Ph.[10b] We now present (*a*) the synthesis and characterisation of some new dialkyl-, chloroalkyl-, and dichloro-bis(cyclopentadienyl)niobium(IV) compounds, (*b*) e.s.r. spectroscopic data, and (*c*) the molecular structure of crystalline $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$. An important objective is the correlation between e.s.r. parameters, structural data, and molecular-orbital theory.

RESULTS AND DISCUSSION

Synthesis of the Bis(η-cyclopentadienyl)niobium(IV) *Dialkyls and Chloroalkyls*.—Although a good route for the preparation of $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ has been described,[13] we now report a general method for the preparation of the analogous substituted cyclopentadienyl complexes (1); this is from $[NbCl_4(thf)_2]$,[10a] equation (1).

$$[NbCl_4(thf)_2] + 2Li[C_5H_4X] \longrightarrow [Nb(\eta\text{-}C_5H_4X)_2Cl_2] + 2LiCl \quad (1)$$

(1a) X = H
(1b) X = Me
(1c) X = $SiMe_3$

Thus $[NbCl_4(thf)_2]$ reacts smoothly with 2 mol of $Li[C_5H_4X]$ (X = H,

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† Dibenzylbis(cyclopentadienyl)niobium(IV).

‡ No reprints available.

Me, or $SiMe_3$) in thf as solvent, to give, on sublimation of the reaction mixture, high yields (70—80%) of the metallocene dichloride. One of these compounds (1) is new, (1c), $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$.

Alkylation of $[Nb(\eta\text{-}C_5H_4X)_2Cl_2]$ according to equation (2) in hexane at room temperature gave the appropriate bis(trimethylsilylmethyl)niobium(IV) compound, (2). Use of more polar solvents such as diethyl ether or thf often

$$[Nb(\eta\text{-}C_5H_4X)_2Cl_2] + 2Li[CH_2SiMe_3] \longrightarrow [Nb(\eta\text{-}C_5H_4X)_2(CH_2SiMe_3)_2] + 2LiCl \quad (2)$$

(2a) $X = H$
(2b) $X = Me$
(2c) $X = SiMe_3$

caused the formation of paramagnetic purple-blue solids which have not yet been characterised. In an analogous fashion $[Nb(C_5H_4SiMe_3)_2(CH_2CMe_3)_2]$, (2d), was prepared from $[Nb(C_5H_4SiMe_3)_2Cl_2]$ and 2 mol of $Li[CH_2CMe_3]$ in hexane as solvent. The Grignard reagent Mg(R)Cl ($R = CH_2SiMe_3$ or CH_2CMe_3) gave only mono-alkyl-(chloro)metal complexes, (3), even if an excess of the Grignard reagent was employed, equation (3). It had likewise been found that $Mg(CH_2SiMe_3)Cl$ was unsatisfactory as a reagent for obtaining $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$, but excellent for $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)Cl]$.[5]

$$[Nb(\eta\text{-}C_5H_4X)_2Cl_2] + 2Mg(R)Cl \longrightarrow [Nb(\eta\text{-}C_5H_4X)_2RCl] \quad (3)$$

(3a) $X = H, R = CH_2SiMe_3$
(3b) $X = Me, R = CH_2SiMe_3$
(3c) $X = SiMe_3, R = CH_2SiMe_3$
(3d) $X = Me, R = CH_2CMe_3$
(3e) $X = SiMe_3, R = CH_2CMe_3$

In contrast, the less bulky Grignard reagents Mg(Me)I or $Mg(CH_2Ph)Cl$ induced dialkylation, equation (4).

$$[Nb(\eta\text{-}C_5H_4X)_2Cl_2] + 2Mg(R)Y \longrightarrow [Nb(\eta\text{-}C_5H_4X)_2R_2] + 2MgY_2 \quad (4)$$

(2e) $X = H, R = Me$
(2f) $X = SiMe_3, R = Me$
(2g) $X = H, R = CH_2Ph$
(2h) $X = SiMe_3, R = CH_2Ph$

TABLE 1

Some physical data for compounds of the type $[Nb(\eta\text{-}C_5H_4X)_2RR']$

Compound	X	R	R′	M.p. (θ_c/°C)	Colour	Analysis (%) * C	Analysis (%) * H
(1c)	$SiMe_3$	Cl	Cl	233—240	Green-brown	44.0 (44.1)	5.90 (5.95)
(2c)	$SiMe_3$	CH_2SiMe_3	CH_2SiMe_3	46—48	Brown	51.9 (53.3)	8.35 (8.85)
(2d)	$SiMe_3$	CH_2CMe_3	CH_2CMe_3	78—81	Red	59.7 (61.3)	8.65 (9.50)
(2f)	$SiMe_3$	Me	Me	50—51	Red	(54.4)	(8.05)
(2h)	$SiMe_3$	CH_2Ph	CH_2Ph	122—124	Deep red	65.4 (65.5)	6.30 (7.35)
(3c)	$SiMe_3$	CH_2SiMe_3	Cl	100—102	Brown	49.1 (49.0)	7.55 (7.60)
(3e)	$SiMe_3$	CH_2CMe_3	Cl		Copper	See text	
(2a)	H	CH_2SiMe_3	CH_2SiMe_3	128—130	Brown	54.8 (54.4)	8.50 (8.05)
(2g)	H	CH_2Ph	CH_2Ph	140—142	Deep red	69.1 (69.1)	5.50 (5.95)
(3a)	H	CH_2SiMe_3	Cl		Green	48.3 (48.6)	6.10 (6.10)
(2b)	Me	CH_2SiMe_3	CH_2SiMe_3	100—101	Brown	56.1 (56.4)	9.30 (8.55)
(3b)	Me	CH_2SiMe_3	Cl	111—114	Green	(51.4)	(6.75)
(3d)	Me	CH_2CMe_3	Cl		Russet	(57.1)	(7.05)

* Calculated values are given in parentheses.

Properties of the Bis(η-cyclopentadienyl)niobium(IV) *Chloroalkyls and Dialkyls,* (2) *and* (3).—The new compounds are dark brown to red crystalline solids, with two exceptions, the dark green chloro(alkyl)metal complexes (3a) and (3b) (see Table 1). They are very air-sensitive, decomposing to yellow residues on exposure to air. The trimethylsilylcyclopentadienyl derivatives, in particular, are exceedingly soluble in pentane and considerable difficulty was encountered in obtaining analytically pure crystals. The neopentyl derivative $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(CH_2CMe_3)Cl]$,[3] (3e), was always contaminated with some reduction product (as shown by e.s.r. spectroscopy) and satisfactory analyses were not obtained. Some data for the other new compounds are shown in Table 1.

The e.s.r. spectra of these d^1 paramagnetic compounds were run as pentane, toluene, or thf solutions. At room temperature in each case a ten-line spectrum was observed due to hyperfine coupling to ^{93}Nb ($I = \frac{9}{2}$). Even on cooling to −80 °C no coupling to the α-hydrogen atoms of the alkyl ligands was observed. The line width of the signals was of the order of 1.5 mT. The $g_{av.}$ values of the new compounds ranged over 1.97—2.0 in keeping with earlier data on related compounds.[2,5b,10-12] The value of the hyperfine coupling to ^{93}Nb varied monotonically with the degree of alkyl substitution from *ca.* 11.5 mT for $[Nb(C_5H_4X)_2Cl_2]$, through *ca.* 10.0 mT for $[Nb(C_5H_4X)_2RCl]$, to *ca.* 9.0 mT for $[Nb(C_5H_4X)_2R_2]$. The magnitude of $a(^{93}Nb)$ decreased in the order $X = H > X = Me > X = SiMe_3$ within each of the three series of compounds (1), (2), and (3).

Electron spin resonance data for the new compounds and for previously determined related compounds are presented in Table 2.

The Crystal and Molecular Structure of $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$, (2g).—The final atomic co-ordinates are in Table 3. The conformations and atom-numbering schemes of the two independent molecules are shown in Figure 1, and their bond lengths and angles are listed in Table 4. If the cyclopentadienyl rings are regarded as unidentate, then both molecules have roughly tetrahedral geometry. As viewed in Figure 1, the two rings are half-way between the eclipsed and staggered forms and the two molecules have close to enantiomeric configurations taking into account the orientations of the cyclopentadienyl rings about their normals and the rotations of the phenyl groups about the CH_2–Ph bonds. The two molecules are related approximately by the transformation $(x, \frac{1}{2} - y, \frac{3}{4} + z)$.

TABLE 2

Electron spin resonance parameters [a] for bis(cyclopentadienyl)niobium dichlorides, dialkyls, and chloroalkyls of the type $[Nb(\eta\text{-}C_5H_4X)_2RR']$

Compound	X	R	R′	$a(^{93}Nb)$/mT	$g_{av.}$	$a(^1H)$/mT	Ref.
	H	Cl	Cl	11.65	1.977 0		10*b*
	Me	Cl	Cl				12
(1c)	$SiMe_3$	Cl	Cl	11.51	1.977 6		*b*
	CH_2Ph	Cl	Cl	11.31	1.977 9		12
	$CHMe_2$	Cl	Cl	11.23	1.978 0		12
	CMe_2Ph	Cl	Cl	10.96	1.978 4		12
	CMe_3	Cl	Cl	10.94	1.977 4		12
(3a)	H	CH_2SiMe_3	Cl	10.66	1.983 9		*b*
(3b)	Me	CH_2SiMe_3	Cl	10 52	1.985 1		*b*
(3c)	$SiMe_3$	CH_2SiMe_3	Cl	9.80	1.991 2		*b*
(3d)	Me	CH_2CMe_3	Cl	9.97	1.996 6		*b*
(3e)	$SiMe_3$	CH_2CMe_3	Cl	9.82	2.006 7		*b*
(2a)	H	CH_2SiMe_3	CH_2SiMe_3	9.50	1.996 1		*b*
(2b)	Me	CH_2SiMe_3	CH_2SiMe_3	9.42	1.994 8		*b*
(2c)	$SiMe_3$	CH_2SiMe_3	CH_2SiMe_3	9.05	1.991 3		*b*
(2d)	$SiMe_3$	CH_2CMe_3	CH_2CMe_3	8.71	2.000 1		*b*
(2g)	H	CH_2Ph	CH_2Ph	8.76	1.995 6		*b*
(2h)	$SiMe_3$	CH_2Ph	CH_2Ph	8.61	1.991 2		*b*
	H	Me	Me	8.88	1.998 4	0.65	10*b*
	Me	Me	Me	8.58	1.998 1	0.65	12
(2f)	$SiMe_3$	Me	Me				*b*
	CH_2Ph	Me	Me	8.56	1.999 2	0.64	12
	$CHMe_2$	Me	Me	8.54	1.998 1	0.62	12
	CMe_2Ph	Me	Me	8.08	2.000 6	0.56	12
	CMe_3	Me	Me	8.04	1.999 6	0.59	12

[a] Hyperfine coupling constants and isotropic *g* factors are all corrected to second order using the Breit–Rabi equation. [b] This work.

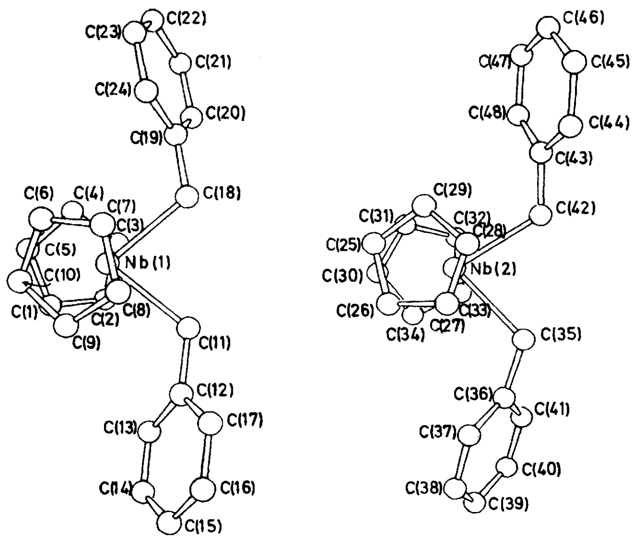


FIGURE 1 Diagram of the molecule showing the numbering system used

Chemically equivalent bond lengths and angles in both of the two molecules show good internal consistency. The Nb–C(benzyl) bonds average 2.304(3) Å, not significantly different from the values of 2.316(8) Å for the Nb–C(ethyl) bond in $[Nb(\eta\text{-}C_5H_5)_2(C_2H_5)(C_2H_4)]$ [14] and 2.309(31) Å for the Nb–C(σ-allyl) bond in $[Nb(\eta\text{-}C_5H_5)_2(C_3H_4)(CS_2)]$.[15] The Nb–C–C(phenyl) angles average 120.0(5)° again close to the value of 118.6(7)° for the ethyl group in $[Nb(\eta\text{-}C_5H_5)_2(C_2H_5)(C_2H_4)]$. Each of the phenyl and cyclopentadienyl groups is planar within experimental error (Table 5) and the angles between the normals to the two cyclopentadienyl groups in each of the two molecules are 133.1° and 133.2°, similar to those in $[Nb(\eta\text{-}C_5H_5)_2(C_2H_5)(C_2H_4)]$ (132.3°), $[Nb(\eta\text{-}C_5H_5)_2(C_3H_4)(CS_2)]$ (132.4° and 131.6°), $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$, (130.9° and 129.6°),[16] and $[\{Nb(\eta\text{-}C_5H_5)_2Cl\}_2O]^{2+}$ (129.7°).[16] The average Nb–C(η-C_5H_5) distance, 2.410(28), and C–C(η-C_5H_5) distance, 1.402(20) Å, are similar to those elsewhere, *e.g.* 2.402(5) and 1.383(7) Å respectively in $[Nb(\eta\text{-}C_5H_5)_2(C_2H_5)(C_2H_4)]$, but the spread of values for each is larger than might be expected from the estimated standard deviations of individual values. A plot of Nb–C against C–C bond lengths for the cyclopentadienyl rings is shown in Figure 2. Although there are some anomalies, there does seem to be a trend of shorter Nb–C bonds associated with longer C–C bonds for those carbon atoms farthest away from the benzyl groups and closest to the mean Nb–benzyl plane as viewed in Figure 1, *e.g.* C(1), C(5), C(4), C(6), C(10), C(25), and C(26).

Discussion of Trends.—We have shown that a large variety of alkyl ligands form thermally robust compounds with a paramagnetic niobium centre. The structure of $[Nb(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ suggests that the Nb–alkyl bond is not inherently weak. Thus the Nb–C(benzyl) distance, 2.305(7) Å, is not significantly longer than those of isoleptic diamagnetic complexes of zirconium [Zr(η-C_5H_5)$_2$$R_2$], [R = CH_2SiMe_3, 2.279(4) Å;[17] R = $CHPh_2$, 2.379(6) Å].[6] The major difference between the structure of [Nb(η-C_5H_5)$_2$(CH_2Ph)$_2$] and its zirconium bis(alkyl) counterparts is the value of the alkyl–M–alkyl angle. The former has an angle of 79.0(4)°, the latter about 95°.[6] This is consistent with the findings of Prout *et al.*[16] on a series of d^0—d^2 metallocene dichlorides, [M(η-C_5H_5)$_2$$Cl_2$]; they reported angles for d^0 complexes in the range 94—97°, d^1 85—88°, and d^2 76—82°. Their findings have a theoretical basis.[18-21] It has been shown that the h.o.m.o. (highest occupied molecular orbital) [corresponding to the l.u.m.o. (lowest unoccupied molecular orbital) for a d^0 analogous complex] for a d^1 complex [M(η-C_5H_5)$_2$$L_2$] is an a_1 orbital (primarily metal-centred) the energy and degree of metal character of which is related to the L–M–L angle. The result of adding *d* electrons to a d^0 system is to decrease the L–M–L angle and to decrease the degree of metal character in the a_1 orbital (which is populated by the non-bonding electron of a d^1 system).

TABLE 3

Final atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Nb(1)	2 484.6(7)	1 009.0(2)	2 819.4(3)
Nb(2)	2 314.0(7)	3 925.2(3)	10 301.8(3)
C(1)	4 835(11)	1 542(4)	2 689(5)
C(2)	4 935(9)	1 260(4)	3 337(5)
C(3)	3 805(10)	1 519(4)	3 757(4)
C(4)	3 031(11)	1 974(4)	3 393(5)
C(5)	3 667(12)	2 005(4)	2 720(6)
C(6)	626(12)	1 355(5)	1 980(6)
C(7)	102(10)	785(5)	2 223(4)
C(8)	1 158(10)	326(4)	2 034(4)
C(9)	2 356(11)	606(4)	1 675(4)
C(10)	2 035(12)	1 238(4)	1 642(4)
C(11)	3 350(9)	40(3)	3 135(4)
C(12)	4 267(8)	−338(3)	2 639(4)
C(13)	5 762(9)	−192(4)	2 466(4)
C(14)	6 578(10)	−554(4)	2 014(4)
C(15)	5 956(10)	−1 076(4)	1 730(5)
C(16)	4 524(10)	−1 234(4)	1 886(4)
C(17)	3 665(9)	−881(4)	2 343(4)
C(18)	937(8)	801(3)	3 752(4)
C(19)	64(8)	1 306(3)	4 074(4)
C(20)	485(9)	1 540(4)	4 735(4)
C(21)	−300(10)	2 023(4)	5 038(4)
C(22)	−1 525(9)	2 293(4)	4 699(4)
C(23)	−1 960(10)	2 066(4)	4 059(4)
C(24)	−1 162(9)	1 585(3)	3 751(4)
C(25)	3 531(14)	2 949(4)	10 168(6)
C(26)	4 698(13)	3 401(5)	10 176(5)
C(27)	4 746(11)	3 653(4)	10 839(5)
C(28)	3 617(11)	3 372(4)	11 222(5)
C(29)	2 852(11)	2 943(4)	10 842(6)
C(30)	1 818(15)	3 724(5)	9 110(5)
C(31)	470(13)	3 603(4)	9 469(5)
C(32)	−69(10)	4 162(5)	9 723(5)
C(33)	983(11)	4 635(4)	9 535(5)
C(34)	2 146(11)	4 351(4)	9 165(4)
C(35)	3 160(10)	4 889(3)	10 643(4)
C(36)	4 107(8)	5 269(3)	10 148(4)
C(37)	5 585(10)	5 106(4)	9 965(4)
C(38)	6 445(9)	5 477(4)	9 527(4)
C(39)	5 841(10)	6 014(4)	9 254(5)
C(40)	4 390(10)	6 179(4)	9 426(4)
C(41)	3 543(9)	5 818(4)	9 869(4)
C(42)	786(9)	4 118(4)	11 240(4)
C(43)	−74(9)	3 611(3)	11 574(4)
C(44)	316(9)	3 390(4)	12 228(4)
C(45)	−531(9)	2 929(4)	12 547(4)
C(46)	−1 805(9)	2 657(4)	12 231(4)
C(47)	−2 226(10)	2 901(4)	11 594(4)
C(48)	−1 370(9)	3 357(4)	11 269(4)

TABLE 4

Intramolecular distances and angles with estimated standard deviations in parentheses and selected torsion angles

(*a*) Bonds (Å)

Nb(1)–C(1)	2.387(9)	Nb(2)–C(25)	2.376(10)
Nb(1)–C(2)	2.447(8)	Nb(2)–C(26)	2.404(11)
Nb(1)–C(3)	2.420(8)	Nb(2)–C(27)	2.460(10)
Nb(1)–C(4)	2.404(9)	Nb(2)–C(28)	2.432(9)
Nb(1)–C(5)	2.394(9)	Nb(2)–C(29)	2.406(9)
Nb(1)–C(6)	2.426(11)	Nb(2)–C(30)	2.386(10)
Nb(1)–C(7)	2.450(9)	Nb(2)–C(31)	2.395(10)
Nb(1)–C(8)	2.418(8)	Nb(2)–C(32)	2.441(9)
Nb(1)–C(9)	2.379(8)	Nb(2)–C(33)	2.432(9)
Nb(1)–C(10)	2.362(8)	Nb(2)–C(34)	2.387(8)
Nb(1)–C(11)	2.305(7)	Nb(2)–C(35)	2.303(7)
Nb(1)–C(18)	2.307(7)	Nb(2)–C(42)	2.300(8)
C(1)–C(2)	1.394(13)	C(25)–C(26)	1.419(16)
C(1)–C(5)	1.437(13)	C(25)–C(29)	1 436(16)
C(2)–C(3)	1 402(12)	C(26)–C(27)	1.393(14)
C(3)–C(4)	1.387(12)	C(27)–C(28)	1.382(13)
C(4)–C(5)	1.420(15)	C(28)–C(29)	1.361(13)
C(6)–C(7)	1.393(15)	C(30)–C(31)	1.404(17)
C(6)–C(10)	1.429(15)	C(30)–C(34)	1.385(14)
C(7)–C(8)	1.408(13)	C(31)–C(32)	1.385(14)
C(8)–C(9)	1.402(12)	C(32)–C(33)	1.425(14)
C(9)–C(10)	1.390(12)	C(33)–C(34)	1.394(13)
C(11)–C(12)	1.496(10)	C(35)–C(36)	1.512(11)
C(12)–C(13)	1.399(11)	C(36)–C(37)	1.399(11)
C(12)–C(17)	1.406(11)	C(36)–C(41)	1.393(11)
C(13)–C(14)	1.376(12)	C(37)–C(38)	1.390(12)
C(14)–C(15)	1.366(12)	C(38)–C(39)	1.378(12)
C(15)–C(16)	1.345(12)	C(38)–C(40)	1.373(12)
C(16)–C(17)	1.392(12)	C(40)–C(41)	1.378(12)
C(18)–C(19)	1.471(10)	C(42)–C(43)	1.479(11)
C(19)–C(20)	1.424(11)	C(43)–C(44)	1.395(11)
C(19)–C(24)	1.388(10)	C(43)–C(48)	1.400(11)
C(20)–C(21)	1.380(12)	C(44)–C(45)	1.387(12)
C(21)–C(22)	1.393(12)	C(45)–C(46)	1.384(11)
C(22)–C(23)	1.385(11)	C(46)–C(47)	1.365(11)
C(23)–C(24)	1.387(11)	C(47)–C(48)	1.391(12)

(*b*) Angles (°)

C(18)–Nb(1)–C(11)	79.3(3)	C(42)–Nb(2)–C(35)	78.6(3)
C(12)–C(11)–Nb(1)	120.2(5)	C(36)–C(35)–Nb(2)	119.1(5)
C(19)–C(18)–Nb(1)	119.9(4)	C(43)–C(42)–Nb(2)	120.9(5)
C(5)–C(1)–C(2)	108.1(9)	C(29)–C(25)–C(26)	107.5(11)
C(3)–C(2)–C(1)	107.7(9)	C(27)–C(26)–C(25)	107.4(10)
C(4)–C(5)–C(1)	106.8(11)	C(28)–C(29)–C(25)	106.0(9)
C(4)–C(3)–C(2)	109.7(9)	C(28)–C(27)–C(26)	107.5(10)
C(5)–C(4)–C(3)	107.7(10)	C(29)–C(25)–C(27)	111.5(10)
C(10)–C(6)–C(7)	106.8(10)	C(34)–C(30)–C(31)	108.7(10)
C(8)–C(7)–C(6)	108.1(9)	C(32)–C(31)–C(30)	107.9(9)
C(9)–C(10)–C(6)	109.2(9)	C(33)–C(34)–C(30)	108.2(10)
C(9)–C(8)–C(7)	109.1(9)	C(33)–C(32)–C(31)	107.7(10)
C(10)–C(9)–C(5)	106.9(9)	C(34)–C(33)–C(32)	107.5(9)
C(13)–C(12)–C(11)	122.9(7)	C(37)–C(36)–C(35)	122.9(7)
C(17)–C(12)–C(11)	120.5(7)	C(41)–C(36)–C(35)	120.4(7)
C(17)–C(12)–C(13)	116.6(7)	C(41)–C(36)–C(37)	116.7(7)
C(14)–C(13)–C(12)	121.4(8)	C(38)–C(37)–C(36)	121.5(5)
C(16)–C(17)–C(12)	120.4(8)	C(40)–C(41)–C(36)	121.6(8)
C(15)–C(14)–C(13)	120.6(9)	C(39)–C(38)–C(37)	120.2(8)
C(16)–C(15)–C(14)	119.8(9)	C(40)–C(39)–C(38)	119.2(9)
C(17)–C(16)–C(15)	121.2(9)	C(41)–C(40)–C(39)	120.8(9)
C(20)–C(19)–C(18)	120.3(7)	C(44)–C(43)–C(42)	121.4(7)
C(24)–C(19)–C(18)	122.7(7)	C(48)–C(43)–C(42)	121.7(7)
C(24)–C(19)–C(20)	117.0(7)	C(48)–C(43)–C(44)	116.8(8)
C(21)–C(20)–C(19)	121.1(8)	C(45)–C(44)–C(43)	120.9(8)
C(23)–C(24)–C(19)	121.8(8)	C(47)–C(48)–C(43)	122.1(8)
C(22)–C(21)–C(20)	120.3(8)	C(46)–C(45)–C(44)	120.8(8)
C(23)–C(22)–C(21)	119.3(8)	C(47)–C(46)–C(45)	119.5(8)
C(24)–C(23)–C(22)	120.4(9)	C(48)–C(47)–C(46)	119.8(9)

It is interesting that the L–M–L angle is less for [Nb(η-

TABLE 4 (*continued*)

(*c*) Torsion angles (°)

C(18)–Nb(1)–C(11)–C(12)	162.5(6)
C(11)–Nb(1)–C(18)–C(19)	165.2(6)
Nb(1)–C(11)–C(12)–C(13)	71.9(8)
Nb(1)–C(11)–C(12)–C(17)	–110.8(7)
Nb(1)–C(18)–C(19)–C(20)	–107.6(7)
Nb(1)–C(18)–C(19)–C(24)	70.8(8)
C(42)–Nb(2)–C(35)–C(36)	–164.0(6)
C(35)–Nb(2)–C(42)–C(43)	–164.0(7)
Nb(2)–C(35)–C(36)–C(37)	–69.4(9)
Nb(2)–C(35)–C(36)–C(41)	112.9(7)
Nb(2)–C(42)–C(43)–C(44)	109.1(8)
Nb(2)–C(42)–C(43)–(C48)	–74.8(9)

$C_5H_5)_2(CH_2Ph)_2]$ (79°) than for $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ (85°).[16] This implies that there is more *d*-electron density on the metal for the former, as is consistent with the different electronegativities of CH_2Ph and Cl^-. The h.o.m.o. in the former should also have less metal character than in the latter, leading to a smaller value of the ^{93}Nb hyperfine coupling constant.[20] This expectation is verified by the e.s.r. data on niobocene dichlorides, (1), and dialkyls, (2). From similar e.s.r. results on the niobocene chloroalkyls, (3), we predict that the alkyl–Nb–Cl angle in compound (3) will prove to lie in the range 82—83°. Work is in progress on this aspect.

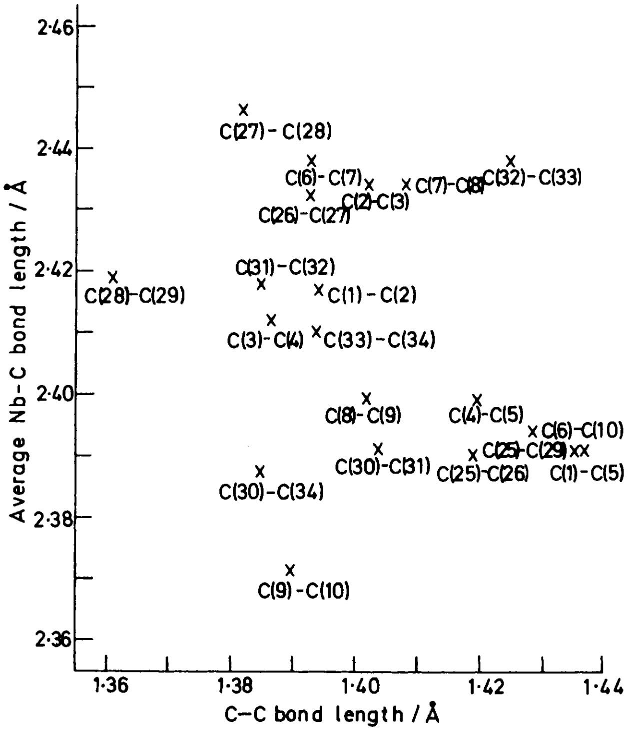
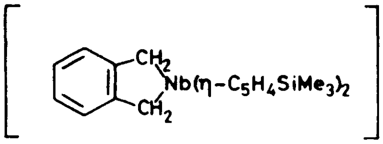


FIGURE 2 Plot of Nb–C bond lengths against C–C bond lengths for the cyclopentadienyl rings for (2g)

As the contribution from the cyclopentadienyl rings to the h.o.m.o. is small (*ca.* 5%), the electronic effect of a substituent on the ring should have little influence on bond angles and hence hyperfine coupling constants. Steric interactions, however, may be important, and we suggest that the sequential lowering of $a(^{93}Nb)$ in the series $C_5H_5 > C_5H_4Me > C_5H_4SiMe_3$ is due to the progressive decrease in the L–M–L angle and hence the extent of metal character of the a_1 orbital, due to the repulsion between the cyclopentadienyl ring substituents and the alkyl(chloro)-ligands. The e.s.r. results of Broussier *et al.*[12] on other substituted niobocene dichlorides and dialkyls show similar evidence of steric effects (Table 2). Recently we have reported on the niobium(IV) metallocycle (4), in which C–Nb–C is 72.4(2), and $a(^{93}Nb) = 7.72$ mT.[22]



(4)

EXPERIMENTAL

Materials.—Niobium(V) chloride was purchased from Koch-Light. Trimethylsilylcyclopentadiene was made by the method of Abel and Dunster [23] and the cyclopentadienyl-lithium reagents were prepared by the action of $LiBu^n$ on C_5H_5X (X = H, Me, or $SiMe_3$) in thf as solvent. The alkyl-lithium reagents $Li[CH_2SiMe_3]$ and $Li[CH_2CMe_3]$ were prepared in hexane from Li powder and the corresponding alkyl chloride; $[NbCl_4(thf)_2]$ was prepared by the method of Manzer.[10a]

Physical and Analytical Measurements.—Elemental analyses were performed by the microanalytical laboratory at the University of Sussex and by Alfred Bernhardt Mikroanalytiches Laboratorium, Elbach, Germany. Infrared spectra were obtained from Nujol mulls between KBr plates using a Perkin-Elmer 457 spectrometer. Electron spin resonance spectra were recorded on a Varian E 104A spectrometer.

General Procedures.—Owing to the air-sensitivity of the complexes, all preparations and other operations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from K (toluene), Na (diethyl ether, hexane), or CaH_2 (pentane) under a dinitrogen atmosphere prior to use.

Preparation of Dichlorobis(η-trimethylsilylcyclopentadienyl)niobium(IV), (1c).—To a suspension of $[NbCl_4(thf)_2]$ (20.0 g, 52.7 mmol) in thf (200 cm^3) was added a thf solution (150 cm^3) of trimethylsilylcyclopentadienyl-lithium (15.4 g, 105 mmol). The resulting brown solution was stirred for 1 h and then evaporated to dryness on a rotary evaporator to give a dark brown solid. Sublimation of this solid [220—240 °C (10^{-2} mmHg)]* gave green-brown crystals of the *title compound* (78%).

Preparation of Bis(η-cyclopentadienyl)bis(trimethylsilylmethyl)niobium(IV), (2a).—To a suspension of $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ (1.0 g, 3.4 mmol) in diethyl ether at 0 °C was added dropwise an ether solution of trimethylsilylmethyl-lithium (12.4 cm^3 of a 0.55 mol dm^{-3} solution). The resulting red-brown solution was held at 0 °C for 1 h and then allowed to warm to room temperature. After 1 h, volatiles were removed under vacuum. Extraction of the residue with hexane (40 cm^3) and concentration of the filtrate to *ca.* 10

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

cm^3, followed by cooling to -78 °C, gave the *product* as brown crystals (65%).

Preparation of Bis(η-trimethylsilylcyclopentadienyl)bis(trimethylsilylmethyl)niobium(IV), (2c).—To a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (2.0 g, 4.56 mmol) in hexane (30 cm^3) was added a hexane solution of trimethylsilylmethyllithium (15.2 cm^3 of a 0.60 mol dm^{-3} solution). After stirring for 24 h the solution was concentrated to *ca.* 5 cm^3, filtered, and cooled to -78 °C. After 48 h at -78 °C, brown crystals of the *title compound* had formed which were filtered off from the mother-liquor. Concentration of the mother-liquor to *ca.* 2 cm^3 and cooling to -78 °C afforded a second crop of crystals. The combined yield was 62%.

Preparation of Di(neopentyl)bis(η-trimethylsilylcyclopentadienyl)niobium(IV), (2d).—To a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (2.0 g, 4.56 mmol) in hexane (30 cm^3) was added a hexane solution of neopentyl-lithium (20.3 cm^3 of a 0.45 mol dm^{-3} solution). After 24 h the dark red solution was filtered and the filtrate concentrated to *ca.* 5 cm^3 and cooled to -40 °C to give dark red crystals of the *title compound* (72%).

Preparation of Dibenzylbis(η-cyclopentadienyl)niobium(IV), (2g).—Benzylmagnesium chloride (8.3 cm^3 of a 0.82 mol dm^{-3} solution) was added to a suspension of [Nb(η-$C_5H_5)_2Cl_2$] (1.0 g, 3.4 mmol) in diethyl ether. The resulting red suspension was stirred for 2 h and then taken to dryness *in vacuo*. Extraction of the residual solid with warm toluene (20 cm^3), followed by concentration of the filtrate to *ca.* 5 cm^3, and cooling to -40 °C gave black-red crystals of the *title compound.*

Preparation of Dibenzylbis(η-trimethylsilylcyclopentadienyl)niobium(IV), (2h).—To a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (2.0 g, 4.56 mmol) in diethyl ether (40 cm^3) was added benzylmagnesium chloride (11.1 cm^3 of a 0.82 mol dm^{-3} solution). The red solution was stirred for 24 h and then the volatiles were removed under vacuum. Extraction with warm hexane (30 cm^3), concentration of the filtrate to *ca.* 10 cm^3, followed by cooling to -40 °C, gave black rectangular crystals of the *title compound* (63%).

Preparation of Dimethylbis(η-trimethylsilylcyclopentadienyl)niobium(IV), (2f).—Methylmagnesium iodide (10.1 cm^3 of a 1.1 mol dm^{-3} solution) in diethyl ether was added to a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (2.0 g, 4.56 mmol) in ether (30 cm^3). The solution was stirred for 3 h, whereafter the solvent was removed *in vacuo*. The residue was extracted with hexane (20 cm^3) and filtered to give a dark red solution. Concentration of this solution to 5 cm^3 and cooling to -78 °C gave red crystals of the *title compound* (68%).

Preparation of Chlorobis(η-trimethylsilylcyclopentadienyl)(trimethylsilylmethyl)niobium(IV), (3c).—To a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (5.0 g, 11.4 mmol) in diethyl ether (100 cm^3) was added trimethylsilylmethylmagnesium chloride (21.9 cm^3 of a 0.52 mol dm^{-3} ethereal solution). After 48 h the solvent was removed under vacuum to give a solid green-brown mass. This residue was extracted with warm hexane (100 cm^3), the filtrate concentrated to *ca.* 40 cm^3, and cooled to 0 °C to give brown needles of the *product.* Successive cooling of the mother-liquor to -40 °C and then -78 °C gave substantial second and third crops of material. The total yield was 71%.

Preparation of Chloroneopentylbis(η-trimethylsilylcyclopentadienyl)niobium(IV), (3e).—Neopentylmagnesium chloride (6.9 cm^3 of a 0.33 mol cm^{-3} ethereal solution) was added to a suspension of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (1.0 g, 2.28 mmol) in diethyl ether (30 cm^3). After 24 h the volatiles were removed *in vacuo* and the residue extracted with hexane (30 cm^3). The filtrate was cooled to -40 °C to give copper coloured crystals of the *title compound* (60%).

Preparation of Bis(η-methylcyclopentadienyl)bis(trimethylsilylmethyl)niobium(IV), (2b).—Trimethylsilylmethyllithium (11.3 cm^3 of a 0.55 mol dm^{-3} hexane solution) was added to a suspension of [Nb(η-$C_5H_4Me)_2Cl_2$] (1.0 g, 3.1 mmol) in hexane (30 cm^3). After stirring for 12 h the solution was filtered to give a dark brown solution. Concentration to *ca.* 10 cm^3 and cooling to -40 °C gave brown needles of the *product* (82%).

Preparation of Chlorobis(η-methylcyclopentadienyl)(trimethylsilylmethyl)niobium(IV), (3b).—To a suspension of [Nb(η-$C_5H_4Me)_2Cl_2$] (1.0 g, 3.1 mmol) in diethyl ether (30 cm^3) was added trimethylsilylmethylmagnesium chloride (6.0 cm^3 of a 0.52 mol dm^{-3} ethereal solution). After 48 h the solvent was removed under vacuum to give a green solid. Extraction with warm hexane (20 cm^3), filtration, and cooling to -40 °C of the filtrate give dark green crystals of the *title compound* (72%).

Preparation of Chlorobis(η-methylcyclopentadienyl)neopentylniobium(IV), (3d).—To a suspension of [Nb(η-$C_5H_4Me)_2Cl_2$] (1.0 g, 3.1 mmol) in diethyl ether (30 cm^3) was added neopentylmagnesium chloride (6.0 cm^3 of a 0.52 mol dm^{-3} ethereal solution). After 24 h the solvent was removed under vacuum and the residue extracted with warm hexane (40 cm^3). Filtration and cooling of the filtrate to -40 °C gave pale brown-red crystals of the *title compound* (63%).

Preparation of Chlorobis(η-cyclopentadienyl)(trimethylsilylmethyl)niobium(IV), (3a), *by the Grignard Reaction.*—Trimethylsilylmethylmagnesium chloride (5.9 cm^3 of a 0.52 mol dm^{-3} solution) was added to a diethyl ether suspension of [Nb(η-$C_5H_5)_2Cl_2$] (1.0 g). The mixture was stirred for 48 h whereafter most of the starting material had dissolved to give a green-brown solution. Removal of the volatiles, extraction of the residue with toluene (10 cm^3), and filtration gave a clear brown solution. Concentration to *ca.* 5 cm^3 and cooling to -40 °C gave the *title compound* (58%) as green crystals.

Crystal Data for Complex (2g).—$C_{24}H_{24}Nb$, $M = 405.4$, Orthorhombic, $a = 8.844(1)$, $b = 21.532(2)$, $c = 19.331(2)$ Å, $U = 3\,681.2$ Å^3, $Z = 8$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1\,672$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 6.4$ cm^{-1}, space group $P2_12_12_1$ from systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd.

Data were collected using a crystal of size 0.5 × 0.2 × 0.2 mm on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were derived from the setting angles of 12 reflections. Intensities for hkl with $2 < \theta < 25°$ were measured by an ω—2θ step scan using Mo-K_α radiation with a graphite-crystal monochromator. Three standard reflections remeasured after every 100 reflections showed a slow reduction in intensity up to a maximum of 25% by the end of data collection, but since the three standards showed marked differences no attempt was made to apply a correction to the data. The data were corrected for Lorentz and polarisation effects, but not for absorption. After averaging of equivalent data the 3 158 reflections with $I > 3\sigma(I)$ were used in the structure analysis.

The positions of the non-hydrogen atoms were derived by routine heavy-atom methods. The two independent molecules were refined in alternate cycles of full-matrix least squares with anisotropic temperature factors for the C atoms of the cyclopentadienyl groups and the Nb atoms. A difference map revealed approximate positions for all the hydrogen atoms which were included in subsequent refinement at idealised positions (C–H 1.08 Å) with fixed $U_{\text{iso.}}$ values equal to that of the C atom to which they are attached and constrained to ride on these atoms. Refinement then converged at $R = 0.045$, $R' = 0.064$ with a maximum positional shift-to-error ratio of 0.1. The weighting scheme was $w = 0.85/[\sigma^2(F) + 0.003\,1F^2]$. A refinement of the equivalent enantiomeric solution gave $R = 0.046$, $R' = 0.065$ and was rejected. A final difference map had peaks of up to 0.6 e Å^{-3} near the Nb atoms, but was elsewhere < 0.4 e Å^{-3}.

Scattering factors for neutral atoms and dispersion corrections were taken from refs. 24—26. The structure analysis was done with the SHELX program system of G. M. Sheldrick. Final atom positions are listed in Table 3; deviations of atoms from mean planes, hydrogen-atom parameters, temperature factors, and structure factors have been deposited as Supplementary Publication No. SUP 22924 (19 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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