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Metallocene Derivatives of Early Transition Elements. Part 1. Niobium-(IV) Chlorides, Chloroalkyls, and Dialkyls [Nb(η -C₅H₄X)₂RR'], and the Crystal and Molecular Structure of [Nb(η -C₅H₅)₂(CH₂Ph)₂][†],[‡]

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Reaction of $[NbCl_4(thf)_2]$ with $Li[C_5H_4X]$ (X = H, Me, or SiMe₃) in tetrahydrofuran (thf) gives a high yield of the volatile $[Nb(\eta-C_5H_4X)_2Cl_2]$, (1). Treatment of (1) with $2Li[CH_2SiMe_3]$ provides $[Nb(\eta-C_5H_4X)_2(CH_2SiMe_3)_2]$, (2a)—(2c), whereas 2Mg(R)Cl (R = CH_2SiMe_3 or CH_2CMe_3) affords the chloroalkyls $[Nb(\eta-C_5H_4X)_2(CH_2SiMe_3)_2]$, (3a)—(3e); using the less bulky Grignard reagent Mg(Me)I or Mg(CH_2Ph)Cl yields the dialkyls $[Nb(\eta-C_5H_4X)_2R'_2]$, (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 ${}^{s3}Nb$ but not α hydrogens. The g_{av} values are in the range 1.97—2.00 [(1) < (3) < (2)] and $a({}^{s3}Nb)$ (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 $[Nb(\eta-C_5H_5)_2(CH_2Ph)_2]$ shows it to posses 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 $a({}^{s3}Nb)$ 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 $[M(\eta-C_5H_5)_9(CH_2SiMe_3)_2][SbF_6] \quad (M = Nb \quad or \quad Ta).^2$ 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 CH₂SiMe₃ and CH(SiMe₃)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 $[Zr(\eta-C_5H_5)_2 \{CH(SiMe_3)_2\}(\eta^2-N_2)].^3$

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 trimethylsilvl group as in η -C₅H₄SiMe₃⁻, η -C₅H₃(SiMe₃)₂⁻, and η -C₅H₂(SiMe₃)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 $[M(\eta - C_5H_5)_2RR']$ (M = Ti, Zr, Hf, or Nb; $R = R' = CH_2SiMe_3$,⁵ [Ti(η -C₅H₅)₂- $(CH_2GeMe_3)_2]$,⁵⁴ $[Zr(\eta - C_5H_5)_2(CH_2SiMe_3)Cl],^{5a}$ [M(η- $C_5H_5_R[M = Ti \text{ and } R = CHPh_2 \text{ or } CH(SiMe_3)_2; \text{ or }$ M = V and $R = CH(SiMe_3)_2$],⁶ $[M(\eta - C_5H_5)_2\{CH(Si-1)_3\}$ $Me_{3}_{2}Cl] (M = Zr \text{ or } Hg),^{6} [M(\eta - C_{5}H_{5})_{2}(CHPh_{2})_{2}] (M = 1)^{6} [M(\eta - C_{5}H_{5})_{2}(CHPh_{2})_{2}]$ ZrorHf), ${}^{6}[Zr(\eta - C_{5}H_{5})_{2}Bu^{n}\{CH(SiMe_{3})_{2}\}], {}^{6}[Zr(\eta - C_{5}H_{4}X)_{2}-$

[‡] No reprints available.

 $\{ CH(SiMe_3)_2 \} (\eta^2 \cdot N_2) \} (X = H \text{ or } Me),^3 [Zr(\eta \cdot C_5H_4X)_2 \cdot \{ CH(SiMe_3)_2 \}] (X = Et, Pr^i, Bu^t, \text{ or } SiMe_3),^3 [\{ Zr(\eta \cdot C_5H_4X)_2 [CH(SiMe_3)_2] \}_2 N_2] (X = H \text{ or } Me),^3 [M(\eta \cdot C_5H_5)_2 \cdot (\mu \cdot R)_2 (AIR_2)] (M = Sc, Y, Gd, Dy, Ho, Er, Tm, Yb, \text{ or } Ti, R = Me; \text{ or } M = Sc, Y, \text{ or } Ho, R = Et; \text{ or } M = Ti, R = H),^7 [\{ M(\eta \cdot C_5H_5)_2 Me\}_2] (M = Y, Dy, Ho, Er, Tm, or Yb),^8 \text{ and } [Sc(\eta \cdot C_5H_5)_2 MeL] (L = NC_5H_5 \text{ or } thf, tetrahydrofuran).^8$

Prior to this work few compounds of the type $[M(\eta-C_5H_4X)_2R_2]$ (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_2-SiMe_3;⁹ (ii) M = Nb, X = H, R = Me,¹⁰ Ph¹¹ (not isolated),¹⁰⁶ or CH_2SiMe_3;⁵⁶ (iii) M = Nb, X = Me,¹⁰ or (not isolated) ¹² Prⁱ, Bu^t, CH_2Ph, or CMe_2Ph, and R = Me; and (iv) (not isolated) M = Ta, X = Me, R = Me or Ph.¹⁰⁶ 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(η -C₅H₅)₂(CH₂Ph)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 $(\eta$ -cyclopentadienyl)niobium(IV) Dialkyls and Chloroalkyls.—Although a good route for the preparation of $[Nb(\eta-C_5H_5)_2Cl_2]$ 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). Thus $[NbCl_4 [NbCl_4(thf)_2] + 2Li[C_5H_4X] \longrightarrow$

$$[Nb(\eta-C_5H_4X)_2Cl_2] + 2LiCl (1)$$

$$(la) X = H$$

$$(lb) X = Me$$

$$(lc) X = SiMe_3$$

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

[†] Dibenzylbis(cyclopentadienyl)niobium(IV).

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Me, or SiMe₃) 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(η -C₅H₄SiMe₃)₂Cl₂].

Alkylation of $[Nb(\eta-C_5H_4X)_2Cl_2]$ 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

$$[Nb(\eta-C_5H_4X)_2Cl_2] + 2Li[CH_2SiMe_3] \longrightarrow$$

$$[Nb(\eta-C_5H_4X)_2(CH_2SiMe_3)_2] + 2LiCl \quad (2)$$

$$(2a) X = H$$

$$(2b) X = Me$$

$$(2c) X = SiMe_3$$

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

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 $[Nb(\eta-C_5H_4SiMe_3)_2-(CH_2CMe_3)Cl]$,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

TABLE 1

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

				Mn		Analys	is (%) *
Compound	x	R	R′	$(\theta_{c}/^{\circ}C)$	Colour	C	н
(lc)	SiMe ₃	Cl	C1	233 - 240	Green-brown	44.0 (44.1)	5.90 (5.95)
(2c)	SiMe ₃	CH ₂ SiMe ₃	CH ₂ SiMe ₃	4648	Brown	51.9 (53.3)	8.35 (8.85)
(2d)	SiMe ₃	CH ₂ CMe ₃	CH ₂ CMe ₃	7881	Red	59.7 (61.3)	8.65 (9.50)
(2f)	SiMe ₃	Me	Me	50 - 51	Red	(54.4)	(8.05)
(2h)	SiMe ₃	$CH_{2}Ph$	CH,Ph	122 - 124	Deep red	65.4 (65.5)	6.30 (7.35)
(3c)	SiMe ₃	CH ₂ SiMe ₃	Cl	100 - 102	Brown	49.1 (49.0)	7.55 (7.60)
(3e)	SiMe ₃	CH ₂ CMe ₃	Cl		Copper	See text	
(2a)	н	CH ₂ SiMe ₃	CH ₂ SiMe ₃	128 - 130	Brown	54.8 (54.4)	8.50 (8.05)
(2g)	н	CH_2Ph	$CH_{2}Ph$	140 - 142	Deep red	69.1 (69.1)	5.50 (5.95)
(3a)	н	CH ₂ SiMe ₃	Cl		Green	48.3 (48.6)	6.10 (6.10)
(2b)	Me	CH ₂ SiMe ₃	CH ₂ SiMe ₃	100-101	Brown	56.1 (56.4)	9.30 (8.55)
(3b)	Me	CH ₂ SiMe ₃	Cl	111-114	Green	(51.4)	(6.75)
(3d)	Me	CH ₂ CMe ₃	Cl		Russet	(57.1)	(7.05)

* Calculated values are given in parentheses.

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 $[Zr(\eta-C_5H_5)_2(CH_2-SiMe_3)_2]$, but excellent for $[Zr(\eta-C_5H_5)_2(CH_2SiMe_3)Cl].^5$ $[Nb(\eta-C_5H_4X)_2Cl_2] + 2Mg(R)Cl \longrightarrow$

$[ND(\eta-C_5H_4X)_2RCI] (3)$
(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(CH₂Ph)Cl induced dialkylation, equation (4). $Nb(r_{2}CH, X) = 2Mg(R)X \longrightarrow$

$$[Nb(\eta-c_{5}H_{4}X)_{2}Cl_{2}] + 2Mg(R) T - [Nb(\eta-c_{5}H_{4}X)_{2}R_{2}] + 2MgY_{2} \quad (4)$$

$$[Nb(\eta-c_{5}H_{4}X)_{2}R_{2}] + 2MgY_{2} \quad (4)$$

$$(2e) X = H, R = Me$$

$$(2f) X = SiMe_{3}, R = Me$$

$$(2g) X = H, R = CH_{2}Ph$$

$$(2h) X = SiMe_{3}, R = CH_{2}Ph$$

due to hyperfine coupling to ⁹³Nb $(I = \frac{9}{2})$. 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 ⁹³Nb varied monotonically with the degree of alkyl substitution from *ca*. 11.5 mT for [Nb(C₅H₄X)₂Cl₂], through *ca*. 10.0 mT for [Nb(C₅H₄X)₂-RCl], to *ca*. 9.0 mT for [Nb(C₅H₄X)₂R₂]. The magnitude of $a(^{93}$ Nb) decreased in the order X = H > X = Me > X = SiMe₃ 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 $[Nb(\eta-C_5H_5)_2-(CH_2Ph)_2]$, (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

angles

significantly different from the values of 2.316(8) Å for

the Nb-C(ethyl) bond in $[Nb(\eta-C_5H_5)_2(C_2H_5)(C_2H_4)]^{14}$

and 2.309(31) Å for the Nb-C(σ -allyl) bond in [Nb(η -

Nb-C-C(phenyl)

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

TABLE 2 Electron spin resonance parameters a for bis(cyclopentadienyl)niobium dichlorides, dialkyls, and chloroalkyls of the type

NTL /

 $C_5H_5_2(C_3H_4)(CS_2)].^{15}$ The

$\lfloor ND(\eta - C_5 \Pi_4 A)_2 KK \rfloor$							
Compound	x	R	R'	a(93Nb)/mT	gav.	a(1H)/mT	Ref.
	н	Cl	Cl	11.65	1.977 0		10b
	Me	Cl	Cl				12
(lc)	SiMe ₂	Cl	Cl	11.51	1.977 6		b
、	CH, Ph	C1	Cl	11.31	1.977 9		12
	CHMe,	Cl	Cl	11.23	1.978 0		12
	CMe ₂ Ph	C1	Cl	10.96	1.978 4		12
	CMe ₃	Cl	Cl	10.94	1.977 4		12
(3a)	н	CH ₂ SiMe ₃	Cl	10.66	1.983 9		b
(3b)	Me	CH ₂ SiMe ₃	Cl	10 52	1.985 1		b
(3c)	SiMe ₃	CH ₂ SiMe ₃	Cl	9.80	1.991 2		b
(3d)	Me	CH ₂ CMe ₃	Cl	9.97	1.996 6		b
(3e)	SiMe ₃	CH ₂ CMe ₃	Cl	9.82	2.006 7		b
(2a)	H	CH ₂ SiMe ₃	CH ₂ SiMe ₃	9.50	1.996 1		b
(2b)	Me	CH ₂ SiMe ₃	CH ₂ SiMe ₃	9.42	1.994 8		b
(2c)	SiMe ₃	CH ₂ SiMe ₃	CH ₂ SiMe ₃	9.05	1.991 3		b
(2d)	SiMe ₃	CH ₂ CMe ₃	CH ₂ CMe ₃	8.71	$2.000 \ 1$		b
(2g)	н	CH ₂ Ph	CH ₂ Ph	8.76	1.995 6		b
(2h)	SiMe ₃	$CH_{2}Ph$	$CH_{2}Ph$	8.61	1.991 2		b
	н	Me	Me	8.88	1.998 4	0.65	10b
	Me	Me	Me	8.58	1.998 1	0.65	12
(2f)	SiMe ₃	Me	Me				b
	CH ₂ Ph	Me	Me	8.56	$1.999\ 2$	0.64	12
	CHMe ₂	Me	Me	8.54	1.998 1	0.62	12
	CMe ₂ Ph	Me	Me	8.08	2.0006	0.56	12
	CMe ₃	Me	Me	8.04	1.999 6	0.59	12

⁶ Hyperfine coupling constants and isotropic g factors are all corrected to second order using the Breit-Rabi equation. ⁶ This work.

rotations of the phenyl groups about the CH_2 -Ph bonds. The two molecules are related approximately by the transformation $(x, \frac{1}{2} - y, \frac{3}{4} + z)$.



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

average 120.0(5)° again close to the value of 118.6(7)° for the ethyl group in $[Nb(\eta-C_5H_5)_2(C_2H_5)(C_2H_4)]$. 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 $[Nb(\eta - C_5H_5)_2(C_2H_5)(C_2H_4)]$ (132.3°), $[Nb(\eta - C_5H_5)_2(C_3H_4) (CS_2)$] (132.4° and 131.6°), $[Nb(\eta-C_5H_5)_2Cl_2]$, (130.9° and 129.6° , ¹⁶ and $[\{Nb(\eta - C_5H_5)_2Cl\}_2O]^{2+}$ (129.7°).¹⁶ The average Nb-C(η -C₅H₅) 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 $[Nb(\eta-C_5H_5)_2 (C_{2}H_{5})(C_{2}H_{4})$], 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 $[Nb(\eta-C_5H_5)_2(CH_2Ph)_2]$ 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 $[Zr(\eta C_5H_5)_2R_2$], [R = CH₂SiMe₃, 2.279(4) Å; ¹⁷ R = CHPh₂, 2.379(6) Å].⁶ The major difference between the structure of $[Nb(\eta-C_5H_5)_2(CH_2Ph)_2]$ and its zirconium bis-(alkyl) counterparts is the value of the alkyl-M-alkyl angle. The former has an angle of $79.0(4)^{\circ}$, 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,

TABLE 3

Final atomic co-ordinates (\times 10⁴) with estimated standard deviations in parentheses

		-	
Atom	x	v	z
Nb(1)	9 484 6(7)	1 009 0(2)	28194(3)
ND(1)	2314.0(7)	3 925 2(3)	10 301 8(3)
C(1)	4 925/11)	1 549(4)	2 689(5)
	4 025(11)	1 960(4)	2 2 2 2 7 (5)
C(2)	4 933(9)	1 200(4) 1 510(4)	2 757(J)
	3 809(10)	1 010(4)	0 101(±) 9 909(5)
C(4)	3 031(11)	1 974(4)	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C(5)	3 007(12)	2 000(4)	2720(0)
	020(12)	1 333(3)	1 900(0)
C(7)	102(10)	180(0)	2 223(4)
C(8)	1 158(10)	320(4) 608(4)	2 034(4)
C(9)	2 350(11)	1 000(4)	1 0 7 0 (4)
C(10)	2 035(12)	1 238(4)	1042(4) 2195(4)
$U(\Pi)$	3 350(9)	40(3)	3 130(4)
C(12)	4 207(8)	- 338(3)	2 039(4)
C(13)	5 762(9)	-192(4)	2400(4)
C(14)	6 578(10)	004(4)	2014(4)
C(15)	5 956(10)		1 /30(3)
C(16)	4 524(10)	-1234(4)	1 880(4)
C(17)	3 665(9)	-881(4)	2 343(4)
C(18)	937(8)	801(3)	3 7 5 2 (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 U38(4)
C(22)	-1525(9)	2 293(4)	4 699(4)
C(23)	-1960(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)	6014(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)	11240(4)
U(43)	-74(9)	3 611(3)	11 074(4)
C(44)	316(9)	3 390(4)	12 228(4)
U(45)		2 929(4)	12 047(4)
U(46)		2 057(4)	12 231(4)
U(47)	-2226(10)	2 901(4)	11 094(4)
C(48)		3 357(4)	11 209(4)

 $[M(\eta-C_5H_5)_2Cl_2]$; 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 $[M(\eta - C_5H_5)_2L_2]$ is an a_1 orbital (primarily metalcentred) 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 nonbonding electron of a d^1 system).

It is interesting that the L-M-L angle is less for $[Nb(\eta-$

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)	ND(2) = C(27)	2.460(10)
ND(1) = C(4) Nb(1) = C(5)	2.404(9)	ND(2) = C(20) ND(2) = C(20)	2.432(9)
ND(1) = C(3) Nb(1) = C(6)	2.394(9)	$ND(2) \rightarrow C(20)$	2.400(9)
Nb(1) - C(7)	2.420(11) 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)	1402(12)	C(26) = C(27) C(27) = C(29)	1.393(14)
C(3) = C(4) C(4) = C(5)	1.387(12)	C(27) = C(28) C(28) = C(20)	1.362(13)
C(4) = C(3) C(6) = C(7)	1.393(15)	C(30) - C(31)	1.404(17)
C(6) - C(10)	1.333(15) 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) C(28) = C(20)	1.390(12)
C(14) = C(16) C(15) = C(16)	1.300(12)	C(38) = C(39) C(38) = C(40)	1.378(12)
C(16) = C(17)	1.343(12) 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(3) = C(4) = C(3) C(10) = C(6) = C(7)	107.7(10)	C(29) = C(20) = C(21) C(34) = C(30) = C(31)	108.7(10)
C(10) - C(0) - C(1)	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)	121.0(0)
C(16) = C(17) = C(12) C(15) = C(14) = C(13)	120.4(8)	C(40) - C(41) - C(30) C(39) - C(38) - C(37)	121.0(8) 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) C(22) = C(21) = C(21)	120.3(8)	C(40) = C(40) = C(44) C(47) = C(48) = C(45)	119 5(8)
C(24) - C(23) - C(21)	120.4(9)	C(48) - C(47) - C(46)	119.8(9)

C(24) - C(23) - C(22)

TABLE 4 (continued)

(c) Torsion angles (°)

orsion 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 $[Nb(\eta-C_5H_5)_2Cl_2]$ (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 ⁹³Nb 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 $82-83^{\circ}$. Work is in progress on this aspect.

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



(4)

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

EXPERIMENTAL

Materials.—Niobium(v) chloride was purchased from Koch-Light. Trimethylsilylcyclopentadiene was made by the method of Abel and Dunster²³ and the cyclopentadienyl-lithium reagents were prepared by the action of LiBuⁿ on C_5H_5X (X = H, Me, or SiMe₃) in thf as solvent. The alkyl-lithium reagents Li[CH₂SiMe₃] and Li[CH₂-CMe₃] were prepared in hexane from Li powder and the corresponding alkyl chloride; [NbCl₄(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 $(\eta$ -trimethylsilylcyclopentadienyl)niobium(IV), (1c).—To a suspension of $[NbCl_4(thf)_2]$ (20.0 g, 52.7 mmol) in thf (200 cm³) was added a thf solution (150 cm³) 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 $Bis(\eta$ -cyclopentadienyl)bis(trimethylsilylmethyl)niobium(IV), (2a).—To a suspension of $[Nb(\eta-C_5H_5)_2-Cl_2]$ (1.0 g, 3.4 mmol) in diethyl ether at 0 °C was added dropwise an ether solution of trimethylsilylmethyl-lithium (12.4 cm³ of a 0.55 mol dm⁻³ solution). The resulting redbrown 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 cm³) and concentration of the filtrate to *ca*. 10

* Throughout this paper: 1 mmHg \approx 13.6 \times 9.8 Pa.

cm³, 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 -C₅H₄SiMe₃)₂Cl₂] (2.0 g, 4.56 mmol) in hexane (30 cm³) was added a hexane solution of trimethylsilylmethyllithium (15.2 cm³ of a 0.60 mol dm⁻³ solution). After stirring for 24 h the solution was concentrated to ca. 5 cm³, 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 cm³ 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 $[Nb(\eta-C_5H_4-SiMe_3)_2Cl_2]$ (2.0 g, 4.56 mmol) in hexane (30 cm³) was added a hexane solution of neopentyl-lithium (20.3 cm³ of a 0.45 mol dm⁻³ solution). After 24 h the dark red solution was filtered and the filtrate concentrated to ca. 5 cm³ 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 cm³ of a 0.82 mol dm⁻³ solution) was added to a suspension of $[Nb(\eta-C_5H_5)_2-Cl_2]$ (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 cm³), followed by concentration of the filtrate to ca. 5 cm³, 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 -C₅H₄SiMe₃)₂Cl₂] (2.0 g, 4.56 mmol) in diethyl ether (40 cm³) was added benzylmagnesium chloride (11.1 cm³ 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 cm³), concentration of the filtrate to ca. 10 cm³, 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 cm³ of a 1.1 mol dm⁻³ solution) in diethyl ether was added to a suspension of [Nb(η -C₅H₄SiMe₃)₂Cl₂] (2.0 g, 4.56 mmol) in ether (30 cm³). The solution was stirred for 3 h, whereafter the solvent was removed *in vacuo*. The residue was extracted with hexane (20 cm³) and filtered to give a dark red solution. Concentration of this solution to 5 cm³ 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 -C₅H₄SiMe₃)₂Cl₂] (5.0 g, 11.4 mmol) in diethyl ether (100 cm³) was added trimethylsilylmethylmagnesium chloride (21.9 cm³ 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 cm³), the filtrate concentrated to *ca*. 40 cm³, 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 cm³ of a 0.33 mol cm⁻³ ethereal solution) was added to a suspension of [Nb(η -C₅H₄SiMe₃)₂Cl₂] (1.0 g, 2.28 mmol) in diethyl ether (30 cm³). After 24 h the volatiles were removed in vacuo and the residue extracted with hexane (30 cm³). 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(1V), (2b).—Trimethylsilylmethyllithium (11.3 cm³ of a 0.55 mol dm⁻³ hexane solution) was added to a suspension of $[Nb(\eta-C_5H_4Me)_2Cl_2]$ (1.0 g, 3.1 mmol) in hexane (30 cm³). After stirring for 12 h the solution was filtered to give a dark brown solution. Concentration to *ca*. 10 cm³ 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 -C₅H₄Me)₂Cl₂] (1.0 g, 3.1 mmol) in diethyl ether (30 cm³) was added trimethylsilylmethylmagnesium chloride (6.0 cm³ 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 cm³), 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 $[Nb(\eta-C_5H_4Me)_2-Cl_2]$ (1.0 g, 3.1 mmol) in diethyl ether (30 cm³) was added neopentylmagnesium chloride (6.0 cm³ 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 cm³). 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 cm³ of a 0.52 mol dm⁻³ solution) was added to a diethyl ether suspension of [Nb(η -C₅H₅)₂Cl₂] (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 cm³), and filtration gave a clear brown solution. Concentration to ca. 5 cm³ 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 Å³, 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 $0.5 \times 0.2 \times 0.2$ 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 $2 < \theta < 25^{\circ}$ were measured by an ω —20 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

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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_{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 < 0.4е 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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