New Dicyclopentadienyl Phosphine, Phosphite, and Acetylene Niobium(III) Complexes. Crystal Structure of [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PhC≡CPh)]†

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The reduction of the niobocene complex [Nb(η-$C_5H_4SiMe_3$)$_2$$Cl_2$] (**1**) with one equivalent of sodium amalgam (10%) in the presence of π-acid ligands yields [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(L)] [L = PMe_3 (**2**), PMe_2Ph (**3**), P(OMe)$_3$ (**4**), P(OEt)$_3$ (**5**), PhC≡CPh (**6**), HC≡CPh (**7**), or HC≡CH (**8**)]. Reactions of (**2**) and (**3**) with LiMe give the new alkyl complexes [Nb(η-$C_5H_4SiMe_3$)$_2$Me(L)] [L = PMe_3 (**9**) or PMe_2Ph (**10**)]. The structural characterization of all these compounds has been carried out by i.r. and n.m.r. spectroscopy and the oxidation potentials of the niobium(III) complexes have been evaluated by cyclic voltammetric measurements. The *X*-ray crystal structure of (**6**) has been determined. It crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 15.388(1), b = 15.148(1), c = 12.397(1) Å, and Z = 4. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods to R = 0.053 for 2 695 observed reflections. The structure obtained was consistent with that expected on the basis of spectroscopic observations. The molecule represents a wedge-like sandwich, with an angle between both closely planar cyclopentadienyl rings of 52.10(42)°, probably due to the repulsions between the $-SiMe_3$ substituents of the cyclopentadienyl rings. The ligand PhC≡CPh behaves as a two-electron donor as indicated by the distance C(1)–C(2) 1.27(1) Å, and angles C(2)–C(1)–C(11) 143.3(8)° and C(1)–C(2)–C(21) 141.1(9)°; these values confirm the π back-donation effect.

Several niobium(III) complexes [Nb(η-C_5H_5)$_2$X(L)], with X = halogen or alkyl and L = π-acid ligand, have been reported previously,[1] but their structural characterization was always limited by their low solubility which prevents their isolation as suitable crystals for *X*-ray diffraction. In fact few *X*-ray crystal structures of this type of compound have been determined. Here we report the isolation and characterization of new niobocene derivatives containing the substituted η-C_5H_4-$SiMe_3$ cyclopentadienyl ring, the electrochemical behaviour of [Nb(η-$C_5H_4SiMe_3$)$_2$$Cl_2$] (**1**), and also the oxidation potentials of the niobium(III) complexes generated *in situ*. We also report the *X*-ray crystal structure of [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PhC≡CPh)].

Results and Discussion

Complex (**1**) was prepared as reported previously.[2] The reduction of (**1**) with one equivalent of Na–Hg (10%) has been studied in the presence of different π-acid ligands, according to equation (1), to give the following products: L = PMe_3 (**2**), PMe_2Ph (**3**), P(OMe)$_3$ (**4**), P(OEt)$_3$ (**5**), PhC≡CPh (**6**), HC≡CPh (**7**), or HC≡CH (**8**).

$$[\mathrm{Nb}(\eta\text{-}C_5H_4SiMe_3)_2Cl_2] + \mathrm{Na{-}Hg} + \mathrm{L} \longrightarrow [\mathrm{Nb}(\eta\text{-}C_5H_4SiMe_3)_2Cl(L)] + \mathrm{NaCl} \quad (1)$$

The addition of tetrahydrofuran (thf) previously saturated with HC≡CH to a mixture of (**1**) and one equivalent of Na–Hg, after stirring under HC≡CH and filtration, gave a solution which on evaporation produced yellow crystals of (**8**).

Table 1. Analyses and physical properties of bis(trimethylsilylcyclopentadienyl)niobium compounds

Complex	Found (Calc.) (%)		Colour	Yield (%)
	C	H		
(**2**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PMe_3)]	46.8 (47.6)	7.8 (7.3)	Green	85
(**3**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PMe_2Ph)]	52.8 (53.2)	7.4 (6.8)	Green	80
(**4**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl{P(OMe)$_3$}]	43.7 (43.3)	6.9 (6.6)	Deep green	75
(**5**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl{P(OEt)$_3$}]			Green	80
(**6**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PhC≡CPh)]	62.1 (62.0)	6.4 (6.2)	Yellow	85
(**7**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(HC≡CPh)]	56.8 (57.1)	6.5 (6.3)	Yellow	80
(**8**) [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(HC≡CH)]	50.2 (50.4)	6.9 (6.5)	Yellow	70
(**9**) [Nb(η-$C_5H_4SiMe_3$)$_2$Me(PMe_3)]			Red	75
(**10**) [Nb(η-$C_5H_4SiMe_3$)$_2$Me(PMe_2Ph)]			Red	75

Complexes (**2**)—(**7**) were similarly obtained by addition of thf solutions containing one mol of the corresponding π-acid ligand. Complexes (**2**)—(**5**) are deep green crystalline solids, much less air sensitive than the previously reported cyclopentadienyl derivatives.[1] Complex (**5**) could not be isolated as a solid but it was characterized spectroscopically in the green oil obtained after evaporation of the solvent. Complexes (**6**)—(**8**) are the most stable compounds, (**6**) being unaltered in air over long periods.

The reported neutral niobium(III) complexes [Nb(η-C_5H_4Si-Me_3)$_2$Cl(L)] were characterized by analysis (see Table 1). They are soluble in chloroform, dichloromethane with decomposition, thf, diethyl ether, and aromatic and aliphatic hydrocarbons.

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† Chloro(diphenylacetylene)bis(η-trimethylsilylcyclopentadienyl)-niobium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

We have also studied the reactions of $[Nb(\eta-C_5H_4SiMe_3)_2Cl(L)]$ with LiMe. The reaction of (**2**) or (**3**) with one equivalent of LiMe gives the corresponding alkyl derivatives $[Nb(\eta-C_5H_4SiMe_3)_2Me(L)]$, according to equation (2), to give

$$[Nb(\eta-C_5H_4SiMe_3)_2Cl(L)] + LiMe \longrightarrow [Nb(\eta-C_5H_4SiMe_3)_2Me(L)] + LiCl \quad (2)$$

the following products: L = PMe_3 (**9**) or PMe_2Ph (**10**). A mixture of (**2**) and unaltered (**4**) was obtained in the reaction with (**4**) when the process was carried out in hexane. The formation of (**2**) is probably due to the nucleophilic attack of LiMe on the $P(OMe)_3$ ligand. No reaction was observed with (**6**) and intractable products were obtained for (**7**) and (**8**). All the reported alkyl derivatives were isolated as very air-sensitive red oils which were identified by spectroscopic data. They are soluble in all the common solvents.

Structural Studies.—The niobium(IV) complex (**1**) is paramagnetic with $\mu_{eff.} = 1.68$ at room temperature. E.s.r. parameters for (**1**) have been described previously.[2] All the niobium(III) derivatives are diamagnetic compounds at room temperature.

Infrared Spectroscopy.—The i.r. spectra of the niobocene derivatives show the absorptions expected for the η-cyclopentadienyl ligand and the $SiMe_3$ group.[3,4] All the i.r. spectra for $[Nb(\eta-C_5H_4SiMe_3)_2Cl(L)]$ contain absorption bands between 240 and 260 cm^{-1} due to the ν(Nb–Cl) stretching vibration (Table 2). Absorptions due to the phosphine and phosphite ligands are observed in the spectra of complexes (**2**)—(**5**) (Table 2). The ν(C≡C) stretching vibration for complexes (**6**)—(**8**) with acetylenes is observed as a medium-weak absorption at 1 734, 1 697, and 1 630 cm^{-1} respectively with a displacement to lower frequencies of 489, 414, and 344 cm^{-1} with respect to the corresponding free acetylene (2 223 and 1 974 cm^{-1} for Raman PhC≡CPh and HC≡CH respectively). This is an indication of the extensive back donation of electronic density from the highest occupied molecular orbital (h.o.m.o.) a' ($1a_1$) of the $Nb(\eta-C_5H_4SiMe_3)_2Cl$ moiety into the acetylene $\pi_{\parallel}^{*}$ orbital.[5,6] These values suggest that the acetylene acts as a two-electron donor primarily by interaction of its filled $\pi_{\parallel}$ molecular orbitals with the lowest unoccupied molecular orbital (l.u.m.o.) a' (b_2) of $Nb(\eta-C_5H_4SiMe_3)_2Cl$.[7]

Table 2. Selected i.r. data for bis(trimethylsilylcyclopentadienyl)niobium complexes (ν/cm^{-1})

Complex	Nb–Cl	C≡C	L
(**2**)	247w		1 285m, 960s, 730s, 675m
(**3**)	247w		1 281w, 939m, 745s, 496m, 402m
(**4**)	248m		1 050vs, 1 020vs, 750vs, 723vs, 523s
(**5**)	250w		1 027vs br, 940vs, 755vs, 565m, 535m
(**6**)	257m	1 734m	1 590m, 1 566w, 770s, 695s
(**7**)	257m	1 697w	1 590w, 1 550w, 1 480m, 1 443m, 735s
(**8**)	258w	1 630m	
(**9**)			1 280m, 945s, 665m
(**10**)			932m, 490w, 408m

N.M.R. Spectroscopy.—As shown in Table 3, all the complexes exhibit ^1H n.m.r. spectra containing the expected singlet for the $SiMe_3$ group and several broad peaks due to the non-equivalent η-C_5H_4 protons.[8] In addition complexes (**2**)—(**5**), (**9**), and (**10**) show the characteristic ^1H signals for the phosphine or phosphite ligands and the expected ^{31}P singlet as a broad signal due to the high ^{93}Nb quadrupolar moment.[9] Complexes (**9**) and (**10**) also show one doublet due to the Me group attached to the Nb atom. The two non-equivalent acetylenic protons in complex (**8**) give two singlets corresponding to internal and external protons whereas only one singlet is observed for complex (**7**) indicating that only the isomer containing the CH as the internal group nearest to Cl is present.

Particularly significant are the observed ^{13}C n.m.r. spectra which show five resonances for the cyclopentadienyl ring carbon atoms in all the niobium(III) complexes reported, indicating that the five carbon atoms are magnetically different, as has also been observed for other cyclopentadienyl complexes containing two different substituents in the reflection plane of the rings,[10] whereas only three resonances are observed if both substituents are the same.[8] This behaviour implies that the ring carbon atoms cannot be made equivalent by rotation when two different substituents are located on the reflection plane. The least intense of these resonances is due to the carbon bearing the $SiMe_3$ substituent probably due to relaxation effects. The chemical shift for this resonance in $[Nb(\eta-C_5H_4SiMe_3)_2Cl(L)]$ (δ 92.7—113.1 p.p.m., Table 4) is dependent on the nature of the substituents, the higher field signals being observed for complexes with phosphines and phosphites but significantly shifted downfield for acetylene complexes. The four more intense resonances can be attributed to the other four ring

Table 3. Hydrogen-1 and ^{31}P n.m.r. spectra for bis(trimethylsilylcyclopentadienyl)niobium complexes[a]

Complex	^1H ($SiMe_3$)	^1H (C_5H_4)	$^1\bar{H}$ (C_5H_4)	^1H (L)	^{31}P
(**2**)	0.15 (s, 18)	5.53 (m, 2), 4.69 (m, 2), 4.52 (m, 4)	4.82	0.83 (d, J_{P-H} = 7.6, 9, Me)	+8.4
(**3**)	0.14 (s, 18)	5.54 (m, 2), 4.84 (m, 2), 4.47 (m, 4)	4.83	7.33—7.00 (m,[b] Ph) 1.24 (d, J_{P-H} = 7.5, 6, Me)	+17.7
(**4**)	0.19 (s, 18)	5.73 (m, 2), 5.01 (m, 4), 4.80 (m, 2)	5.14	3.38 (d, J_{P-H} = 10.1, 9, Me)	+127.8
(**5**)	0.22 (s, 18)	5.88 (m, 2), 5.08 (m, 4), 4.96 (m, 2)	5.25	3.96 (m, 6, CH_2CH_3) 1.06 (t, $J_{H-H'}$ = 6.8, 9, CH_2CH_3)	+138.0
(**6**)	0.17 (s, 18)	6.01 (m, 2), 5.73 (m, 2), 5.41 (m, 2), 5.12 (m, 2)	5.57	7.9—6.96 (m,[b] Ph)	
(**7**)	0.15 (s, 18)	6.06 (m, 2), 5.69 (m, 2), 5.16 (m, 2), 5.05(m, 2)	5.49	7.92 (s, 1, ≡CH) 7.28—7.25 (m, 5, Ph)	
(**8**)	0.18 (s, 18)	5.66 (m, 2), 5.26 (m, 4), 5.00 (m, 2)	5.30	8.43 (s, 1, ≡CH) 7.57 (s, 1, ≡CH′)[c]	
(**9**)[d]	0.16 (s, 18)	4.83 (m, 2), 4.44 (m, 2), 4.22 (m, 4)	4.43	0.79 (d, J_{P-H} = 6.0, 9, Me)	
(**10**)[e]	0.15 (s, 18)	4.86 (m, 2), 4.34 (m, 6)	4.47	7.40—7.00 (m,[b] Ph) 1.15 (d, J_{P-H} = 6.5, 6, Me)	

[a] In C_6D_6; internal standard $SiMe_4$ for ^1H, H_3PO_4 for ^{31}P. Given as δ/p.p.m. (multiplicity, J/Hz, relative intensity, assignment). [b] Partially overlapped with solvent signals. [c] Prime denotes internal ≡CH. [d] −0.79 (d, J_{P-H} 7.5, 3, NbMe). [e] −0.52 (d, J_{P-H} 6.9, 3, NbMe).

Table 4. Carbon-13 n.m.r. spectra for bis(trimethylsilylcyclopentadienyl)niobium complexes[a]

Complex	SiMe$_3$	η-C$_5$H$_4$			L		
		C^1	C^2,C^3,C^4,C^5	$\bar{C}$			
(**2**)	0.6	92.7	109.1, 100.4, 97.2, 93.3	98.5	18.0 (d, J_{P-C} = 23.0, Me)		
(**3**)	0.5	95.9	110.7, 100.8, 97.3, 92.6	99.4	16.6 (d, J_{P-C} = 23.0, Me)	143.0 [d, J_{P-C} = 27.5, C^1 (Ph)] 130.6 [d, J_{P-C} = 8.0, C^{2,6} (Ph)] 129.5 [d, J_{P-C} = 1.5, C^4 (Ph)] 128.8 [d, J_{P-C} = 8.0, C^{3,5} (Ph)]	
(**4**)	0.4	94.7	110.6, 100.3, 97.2, 95.4	99.6	53.2 (d, J_{P-C} = 6.0, Me)		
(**5**)	0.4	93.9	110.9, 100.5, 96.9, 95.7	99.6	61.9 (d, J_{P-C} = 6.5, CH_2CH_3) 16.6 (d, J_{P-C} = 5.5, CH_2CH_3)		
(**6**)[b]	0.2	113.1	121.3, 120.6, 108.9, 103.7	113.5	156.1 (≡CPh) 140.1 (≡CPh′)	140.1 [C^1 (Ph)], 130.8 [C^{2,6} (Ph)], 129.4 [C^{3,5} (Ph)], 128.5 [C^4 (Ph)] 138.9 [C^1 (Ph′)], 129.8 [C^{2,6} (Ph′)], 128.1 [C^{3,5} (Ph′)], 126.4 [C^4 (Ph′)]	
(**7**)	−0.2	112.9	127.2, 115.9, 104.7, 102.9	112.7	160.8 (≡CPh) 134.0 (≡CH)	136.8 [C^1 (Ph)],131.5 [C^{2,6} (Ph)], 129.2 [C^{3,5} (Ph)], 128.7 [C^4 (Ph)]	
(**8**)[c]	0.0	109.8	125.0, 117.2, 106.9, 105.6	112.9	148.3 (d, J_{C-H} = 202.5, ≡CH) 128.8 (d, J_{C-H} = 207.0, ≡CH′)		
(**9**)	0.7	86.0	102.5, 94.8, 92.8, 89.0	93.0	19.5 (d, J_{P-C} = 20.0, Me)		−20.0 (br, NbMe)
(**10**)	0.6	89.0	104.4, 95.1, 94.2, 87.8	94.1	17.7 (d, J_{P-C} = 20.0, Me)	144.3 [d,J_{P-C} = 27.5, C^1 (Ph)] 130.4 [d, J_{P-C} = 8.5, C^{2,6} (Ph)] 128.8 [C^4 (Ph)] 128.6 [d, J_{P-C} = 8.0, C^{3,5} (Ph)]	−19.3 (br, NbMe)

[a] In thf; internal standard SiMe$_4$. Given as δ/p.p.m. (multiplicity, J/Hz, assignment). [b] Prime denotes internal ≡CPh. [c] Prime denotes internal ≡CH.

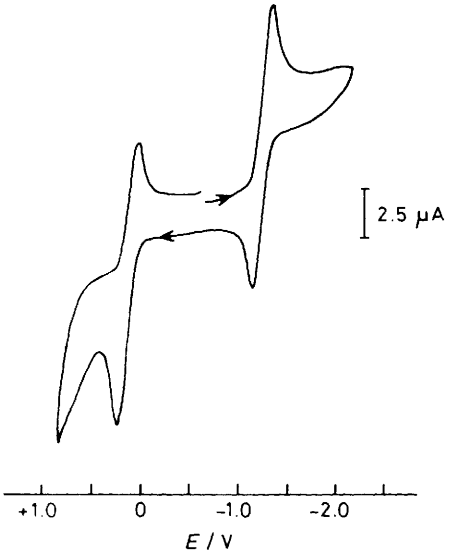

Figure 1. Cyclic voltammogram of [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$] at 20 °C

Table 5. Cyclic voltammetric data for bis(trimethylsilylcyclopentadienyl)niobium complexes in thf

Complex	$E_{\frac{1}{2}}$(Nb$^{III/IV}$)*/V	ΔE/mV
(**1**)	−1.15	90
(**2**)	−0.85	60
(**3**)	−0.60	75
(**4**)	−0.35	60
(**5**)	−0.48	70

* Internal reference ferrocene–ferrocenium, $E_{\frac{1}{2}}$ = 0.535 V in thf.

carbon atoms but we cannot make a definitive assignment. However the average values for acetylenes (δ 112.7—113.5 p.p.m.) are downfield from those of phosphines or phosphites (*ca.* δ 99 p.p.m.). This reflects the different electron-donating and -accepting capacities of the substituents on the reflection plane.

Resonances due to the SiMe$_3$ group and the ligands are also observed. Two resonances are observed for the two non-equivalent acetylenic carbon atoms in complexes (**6**)—(**8**); that for the internal carbon atom is shifted to high field and that for the phenyl-substituted carbon is shifted downfield.

The ^{13}C spectra for (**9**) and (**10**) show a resonance corresponding to the carbon bearing the SiMe$_3$ substituent at δ 86.0 and 89.0 p.p.m. These values are at the highest field for all the niobium(III) complexes described. However, the average values for the other four ring carbons are displaced downfield (δ 93.0 and 94.1 p.p.m.). Compared to the corresponding η-cyclopentadienyl derivatives, all the ring-carbon resonances are shifted downfield, according to the known deshielding attributed to the electron-withdrawing capacity of the SiMe$_3$ group.[8]

Electrochemical Studies.—Not only the formation of new species such as [Nb(η-C$_5$H$_5$)$_2$Cl{P(OMe)$_3$}],[11] but also many significant and useful data on the behaviour, interconversion, and stability of this type of compound can be obtained by studies of cyclic voltammetry.

The electrochemical study of complex (**1**) gives results similar to those known for the corresponding η-C$_5$H$_5$ derivative as shown in Figure 1 (Table 5). One oxidation and one reduction peak are observed due to the practically reversible processes shown in the equilibria (3), with the anionic niobium(III) species

$$[\mathrm{Nb}(\eta\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}]^+ \underset{-\,1e^-}{\overset{+\,1e^-}{\rightleftharpoons}} [\mathrm{Nb}(\eta\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}] \underset{-\,1e^-}{\overset{+\,1e^-}{\rightleftharpoons}} [\mathrm{Nb}(\eta\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}]^- \quad (3)$$

being relative stable. The decreasing reduction potentials for complexes with SiMe$_3$ substituted rings indicate a higher electronic delocalization due to the strong negative mesomeric effect induced by the substituent. The h.o.m.o.[5] is stabilized by the presence of the SiMe$_3$ group so that the reducing capacity of the anionic niobium(III) species decreases. Consequently the

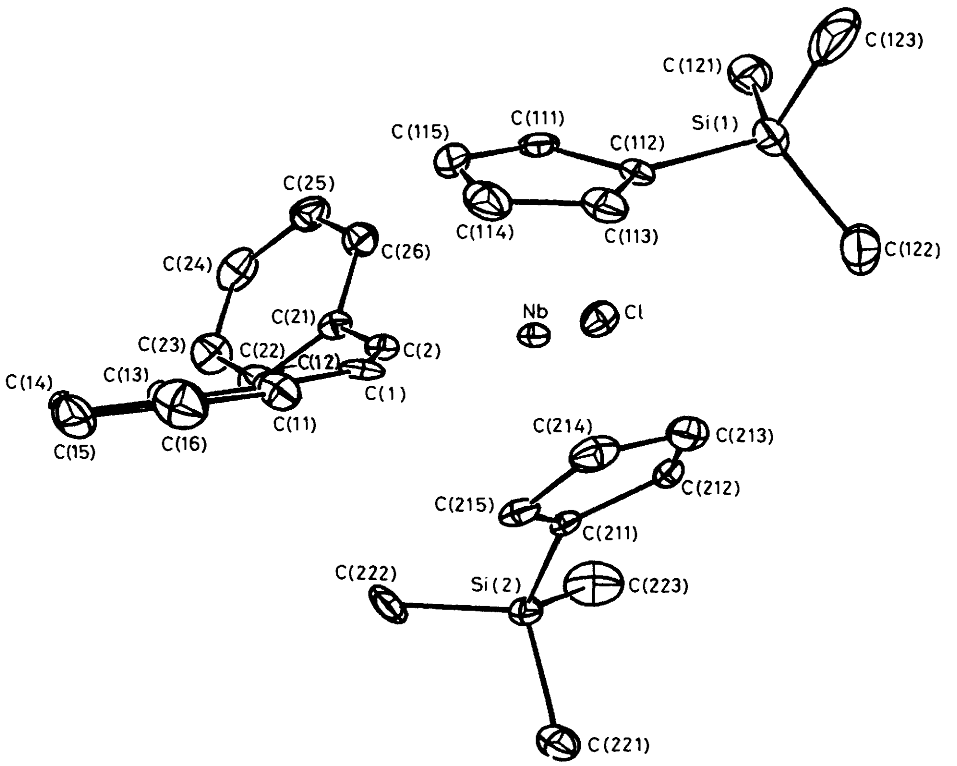

Figure 2. View of the complex [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PhC≡CPh)] with the atomic numbering scheme

generation of cationic niobium(v) species produced by oxidation must be more difficult as these will have higher oxidation potentials.

We have evaluated the oxidation potentials of the niobium(III) complexes generated *in situ* to avoid the presence of decomposition products which are observed during manipulation of samples separately prepared. The values found are presented in Table 5. They show an increasing stability of the niobium(III) complex as the π-acceptor ability of the ligand increases.

Crystal Structure of [Nb(η-$C_5H_4SiMe_3$)$_2$Cl(PhC≡CPh)] (**6**).—An ORTEP drawing of (**6**) based on the *X*-ray structural analysis is shown in Figure 2, with the numbering scheme adopted. Atomic co-ordinates for the non-hydrogen atoms are listed in Table 6. Important bond distances and bond angles are listed in Table 7.

The structure obtained for (**6**) by *X*-ray analysis is consistent with that expected on the basis of the other physical methods (i.r. and n.m.r. spectroscopy). The molecule represents a 'wedge-like' sandwich; the angle between the two cyclopentadienyl ring planes is 52.10(42)°. The cyclopentadienyl rings are closely planar with the greatest deviations from the least-squares plane being 0.040 for cp(1) [C(111)—C(115)] and 0.012 Å for cp(2) [C(211)—C(215)]. The C–C ring bond lengths vary from 1.35(2) to 1.47(1) Å. This variation is probably evidence of their low thermal rigidity, fairly common in cyclopentadienyl complexes.[12,13] The Nb–C(cp) bond lengths vary from 2.43(1) to 2.50 (1) Å, as expected from the above mentioned data; the mean value (2.47 Å) is slightly longer than that found for similar Nb^{III} complexes, such as [Nb(η-C_5H_5)$_2$(O_2CCMe_3)-(PhC≡CPh)] (2.44 Å).[14] Accordingly, the two cyclopentadienyl rings may be considered to be η^5-bonded to Nb. In the same way the distances from Nb to the centroid of the η-C_5H_4 groups are 2.16 Å for cp(1) and 2.15 Å for cp(2), longer than those found previously in some Nb^{IV} [12] and Nb^{III} complexes.[14] The cp(1)–Nb–cp(2) angle is 128.4°, which is slightly smaller than those known for other cyclopentadienyl complexes but consistent with the larger distances observed and probably due to the repulsions between the $-SiMe_3$ substituents. The Nb–Cl distance is 2.538(2) Å, longer than those found for Nb^{IV}–Cl [2.475(4) Å] and Nb^{V}–Cl [2.370(4) Å],[12] as expected for a Nb^{III}–Cl bond.

The atoms NbC(1)C(2)Cl define the molecular plane with deviations from the least-squares plane of 0.093(7) Å for C(1) and −0.106(8) Å for C(2), so that the molecular plane bisecting the dihedral angle formed by the rings must be described by Nb–Cl and the centre of the acetylene. The distances Nb–C(1) [2.171(8) Å] and Nb–C(2) [2.185(9) Å] are similar and they fall in the range of known Nb–C(sp^2) distances.[14] In the PhC≡CPh ligand the following features are of primary importance: C(1)–C(2) 1.27(1) Å, C(2)–C(1)–C(11) 143.3(8), and C(1)–C(2)–C(21) 141.1(9)°. The lengthening of the C≡C bond and the bending of the C≡C–Ph angle reflects the effect of π back-donation. This value is in agreement with others previously reported[13,14] and indicates that the ligand PhC≡CPh behaves as a two-electron donor although these data do not definitely rule out an alternative four-electron co-ordination. The phenyl rings are closely planar and the angles formed by the phenyl planes with the molecular plane are 0.55(28) and 52.68(27)°; the angle between the phenyl planes is 53.18(39)°, different from that known for [Nb(η-C_5H_5)$_2$-(O_2CCMe_3)(PhC≡CPh)] (89.5°). This may be due to the $SiMe_3$ substituent causing the phenyl ring to adopt this angle for steric reasons.

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk-type glassware. Solvents were dried

Table 6. Fractional atomic co-ordinates with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
C(121)	−0.140 37(92)	−0.052 07(108)	0.525 73(107)	C(113)	−0.014 52(87)	0.175 20(81)	0.365 08(91)
C(122)	−0.232 13(80)	0.040 14(95)	0.338 17(115)	C(114)	0.077 27(94)	0.179 01(109)	0.360 64(111)
C(123)	−0.190 47(104)	0.145 24(133)	0.542 98(154)	C(115)	0.109 36(77)	0.104 74(121)	0.405 40(100)
C(221)	−0.002 61(79)	0.016 03(93)	−0.200 78(89)	C(211)	0.002 04(54)	0.051 52(66)	0.036 47(65)
C(222)	0.150 12(78)	−0.049 96(124)	−0.070 40(105)	C(212)	−0.082 15(58)	0.054 92(76)	0.093 44(72)
C(223)	−0.030 08(125)	−0.137 50(90)	−0.046 40(120)	C(213)	−0.091 46(76)	0.136 79(79)	0.142 13(88)
Cl	−0.020 80(16)	−0.090 73(14)	0.253 37(21)	C(214)	−0.015 58(89)	0.186 92(77)	0.118 50(90)
C(1)	0.172 34(57)	0.077 41(61)	0.187 35(63)	C(215)	0.040 07(76)	0.135 74(64)	0.052 39(69)
C(2)	0.160 00(60)	−0.003 36(63)	0.210 77(70)	C(11)	0.240 76(62)	0.143 99(66)	0.164 54(72)
C(21)	0.208 11(58)	−0.085 64(58)	0.231 02(77)	C(12)	0.224 62(70)	0.233 03(71)	0.162 81(83)
C(22)	0.275 58(77)	−0.113 79(72)	0.162 91(88)	C(13)	0.291 49(92)	0.292 40(79)	0.144 87(110)
C(23)	0.326 86(85)	−0.185 55(78)	0.188 71(108)	C(14)	0.375 81(83)	0.263 59(93)	0.125 43(100)
C(24)	0.314 78(79)	−0.229 68(72)	−0.287 74(108)	C(15)	0.392 17(78)	0.174 22(89)	0.123 33(104)
C(25)	0.248 73(78)	−0.203 40(77)	0.354 65(52)	C(16)	0.326 15(71)	0.114 75(77)	0.142 18(95)
C(26)	0.195 38(68)	−0.132 78(71)	0.327 77(85)	Nb	0.036 35(5)	0.065 45(5)	0.231 55(5)
C(111)	0.040 02(73)	0.048 19(71)	0.429 87(64)	Si(1)	−0.151 70(19)	0.054 77(26)	0.449 75(25)
C(112)	−0.042 37(71)	0.090 50(68)	0.404 59(69)	Si(2)	0.031 45(19)	−0.031 84(17)	−0.067 68(19)

Table 7. Relevant bond distances (Å) and angles (°)

Nb–C(1)	2.171(8)	Nb–C(2)	2.185(9)	C(211)–C(212)	1.47(1)	C(211)–C(215)	1.42(1)
Nb–Cl	2.538(2)	Nb–C(111)	2.473(8)	C(212)–C(213)	1.39(2)	C(213)–C(214)	1.42(2)
Nb–C(112)	2.493(9)	Nb–C(113)	2.473(11)	C(214)–C(215)	1.42(1)	C(1)–C(2)	1.27(1)
Nb–C(114)	2.432(15)	Nb–C(115)	2.502(12)	C(1)–C(11)	1.48(1)	C(2)–C(21)	1.47(1)
Nb–C(211)	2.484(8)	Nb–C(212)	2.506(8)	Si(1)–C(112)	1.85(1)	Si(1)–C(121)	1.86(2)
Nb–C(213)	2.503(11)	Nb–C(214)	2.447(11)	Si(1)–C(122)	1.87(1)	Si(1)–C(123)	1.89(2)
Nb–C(215)	2.464(8)	C(111)–C(112)	1.45(1)	Si(2)–C(221)	1.88(1)	Si(2)–C(211)	1.86(1)
C(111)–C(115)	1.40(2)	C(112)–C(113)	1.44(1)	Si(2)–C(222)	1.85(1)	Si(2)–C(223)	1.88(1)
C(113)–C(114)	1.41(2)	C(114)–C(115)	1.35(2)				
C(1)–Nb–C(2)	33.9(3)	C(2)–Nb–Cl	82.5(2)	C(21)–C(2)–Nb	145.3(7)	C(1)–C(2)–C(21)	141.1(9)
C(1)–Nb–Cl	116.0(2)	C(11)–C(1)–Nb	142.0(6)	C(2)–C(21)–C(26)	120.3(8)	C(2)–C(21)–C(22)	121.8(8)
C(2)–C(1)–Nb	73.6(6)	C(1)–C(2)–Nb	72.4(6)	C(1)–C(11)–C(16)	118.9(8)	C(1)–C(11)–C(12)	122.8(8)
						C(2)–C(1)–C(11)	143.3(8)

and distilled under N_2 and degassed before use. $NbCl_5$ (Fluka) was used without further purification. Trimethylphosphine was obtained by thermal decomposition of $AgI{\cdot}PMe_3$, prepared as described in ref. 15. Other commercial products (phosphines, phosphites, acetylenes, and LiMe) were used without further purification. Infrared spectra were recorded as Nujol mulls between CsI plates in the region 4 000—200 cm^{-1} using a Perkin-Elmer 599 spectrophotometer. Magnetic measurements were carried out by the Faraday method at room temperature under nitrogen with a Bruker magnetic system. Carbon and hydrogen analyses were performed with a Perkin-Elmer 240B microanalyser. Hydrogen-1, ^{31}P, and ^{13}C n.m.r. spectra were recorded on a Varian FT80A and Bruker WP-60-CW instruments. Cyclic voltammetry measurements were carried out under dry nitrogen using distilled and dried thf as solvent. Tetrabutylammonium tetrafluoroborate (0.2 mol dm^{-3}), prepared as described in ref. 16, was used as electrolyte support. A three-platinum-electrode cell and ferrocene as internal reference were used. Niobium(III) complexes were formed *in situ* following the method reported previously.[11]

$[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(L)]$, **(2)**—**(8)**.—The procedure was similar in all cases. A solution of the ligand (2.0 mmol) (except with HC≡CH for which the solvent was saturated with gaseous HC≡CH) was added to a mixture of sodium amalgam (10%, 2.0 mmol of Na) and **(1)** (2.0 mmol) in thf (100 cm^3). The mixture was vigorously stirred overnight at room temperature, filtered, and the solution evaporated to dryness under vacuum. Pentane was used to extract the solids for **(2)**—**(5)** and toluene for **(6)**—**(8)**; the resulting solutions were concentrated to give green [**(2)**, **(3)**, **(4)**] and yellow [**(6)**, **(7)**, **(8)**] crystals of the complexes. The crystals were dried under vacuum. Compound **(5)** was obtained as a deep green oil.

$[Nb(\eta\text{-}C_5H_4SiMe_3)_2Me(L)]$, **(9)** *and* **(10)**.—Methyl-lithium (1.5 mmol) in diethyl ether (20 cm^3) was added to a green solution of **(2)** or **(3)** (1.5 mmol) in hexane–diethyl ether (5:1) and the reaction mixture was stirred overnight at room temperature. The resulting red solution was evaporated to dryness under vacuum; the mixture obtained was extracted with pentane to give a red oil containing pure **(9)** or **(10)**.

The reaction of LiMe with **(4)** in hexane as solvent yielded a mixture of **(2)** and unaltered **(4)**. When the same process was carried out using an excess of LiMe (1:3 molar ratio) only **(2)** was isolated. The same reaction with **(7)** and **(8)** yielded red oily residues which were not characterized. No reaction was observed with **(6)**.

Crystal Structure of Complex **(6)**.—*Crystal data.* $C_{30}H_{36}ClNbSi_2$, $M = 581.14$ orthorhombic, space group $P2_12_12_1$, $a = 15.388(1)$, $b = 15.148(1)$, $c = 12.397(1)$ Å, $U = 2\,889.7(1)$ Å^3, $Z = 4$, $D_c = 1.335$ g cm^{-3}, $F(000) = 1\,208$, Cu-K_α radiation ($\lambda = 1.5418$ Å), μ(Cu-K_α) = 52.64 cm^{-1}.

Intensity data collection and refinements. A yellow hexagonal plate crystal of **(6)** was mounted on a Phillips 1100 four-circle diffractometer with graphite-monochromated Cu-K_α radiation. Lattice parameters were determined by least-squares refinement of 25 reflections. Data collections were recorded using the $\omega/2\theta$ scan technique: h = 0—18, k = 0—17, l = 0—14. Two standard reflections (3 0 3, $\bar{3}$ 0 $\bar{3}$) were measured after every 100 reflections, and no significant change in intensities was detected. A total of 2 776 unique reflections were collected in the range $2 < \theta < 65^\circ$, but only 2 695 were considered observed, with $I > 2\sigma(I)$, and used in further calculations.

Intensities were corrected for Lorentz and polarization effects in the usual manner. Neither absorption nor extinction corrections were made. The structure was solved by the heavy-atom method. The Nb atom was found by Patterson synthesis and other non-hydrogen atoms by Fourier synthesis. The structure was refined (on F) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. In the later stages of the refinement, H atoms were included from geometric calculations, with fixed positions and thermal parameters equivalent to those of the atoms to which they are attached. Final values of $R = 0.053$ and $R' = 0.060$ (weighting scheme: empirical fit as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and *vs.* $\langle \sin\theta/\lambda\rangle$) were obtained. The maximum residual electron density in the final difference Fourier synthesis was 0.76 e Å^{-3}. Anomalous dispersion corrections and atomic scattering factors were taken from International Tables.[17] Calculations were performed with the *X*-RAY System,[18] and the programs PARST[19] and PESOS[20] on VAX-11750 and UNIVAC computers.

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