# Preparation of Carbonyl, Halogeno, and Alkyl Niobocene Complexes and their Reactions with Oxygen. Crystal Structures of $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$, $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)Me]$, and $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(C_6F_5)(CO)]$†

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The complexes $[Nb(cp)_2Cl_2]$ [cp = $\eta$-$C_5H_5$, $\eta$-$C_5H_4SiMe_3$, or $\eta$-$C_5H_3(SiMe_3)_2$-1,3] are reduced with Na–Hg in the presence of CO to give the carbonylniobium(III) complexes $[Nb(cp)_2Cl(CO)]$. The alkylation of these compounds using LiR, MgRX, or $MgR_2$ leads to the alkyl derivatives $[Nb(cp)_2R(CO)]$ (cp = $\eta$-$C_5H_5$ or $\eta$-$C_5H_4SiMe_3$; R = Me, $CH_2CMe_3$, $CH_2SiMe_3$, $CH_2Ph$, or $C_6F_5$). These alkyl carbonyl niobium(III) complexes react with oxygen to produce an unresolved mixture of compounds when cp = $\eta$-$C_5H_5$ whereas the complex $[Nb(cp)_2(O_2)Me]$ is obtained in the reaction of $[Nb(cp)_2Me(PMe_3)]$ (cp = $\eta$-$C_5H_4SiMe_3$) with oxygen. Similar reactions of $[Nb(cp)_2Cl(CO)]$ with $O_2$ lead to the oxo-halogenoniobium(V) derivatives $[Nb(cp)_2(O)Cl]$ [cp = $\eta$-$C_5H_5$, $\eta$-$C_5H_4SiMe_3$, or $\eta$-$C_5H_3(SiMe_3)_2$-1,3]. However, the corresponding peroxo-chloro complex $[Nb(cp)_2(O_2)Cl]$ (cp = $\eta$-$C_5H_4SiMe_3$) results from the reaction with oxygen of the chloro(alkyl isocyanide) niobium(III) complex and can be preparated alternatively by reaction of the dichloride with $H_2O_2$. The oxo-chloro niobium(V) complex $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)Cl]$ can be easily alkylated in reactions with LiR (R = Me, $Bu^n$, $CH_2CMe_3$, or $CH_2SiMe_3$). All these complexes were characterised by i.r., $^1H$ and $^{13}C$ n.m.r. spectroscopy and the chloro-carbonyl niobium(III) and oxo niobium(V) complexes were studied by cyclic voltammetry. The crystal structures of $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ (**2**), $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(C_6F_5)(CO)]$ (**2f**), and $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)Me]$ (**2h**) have been determined by *X*-ray diffraction methods. Compound (**2**) crystallizes in the triclinic space group $P1$, with $a$ = 12.680(5), $b$ = 12.923(5), $c$ = 6.806(3) Å, $\alpha$ = 97.82(2), $\beta$ = 104.18(3), $\gamma$ = 67.79(2)°, and $Z$ = 2; (**2h**) crystallizes in the monoclinic space group $P2_1/n$, with $a$ = 8.842(4), $b$ = 37.108(10), $c$ = 6.331(3) Å, $\beta$ = 108.03(4)°, and $Z$ = 4; (**2f**) crystallizes in the triclinic space group $P\bar{1}$, with $a$ = 9.781(4), $b$ = 14.440(6), $c$ = 8.765(4) Å, $\alpha$ = 90.84(2), $\beta$ = 85.86(2), $\gamma$ = 93.90(2)°, and $Z$ = 2. All the structures were solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares methods to $R$ = 0.0377 for 2 889 observed reflections [(**2**)], $R$ = 0.0441 for 2 269 observed reflections [(**2f**)], and $R$ = 0.0385 for 1 466 observed reflections [(**2h**)]. All structures contain a niobium atom bonded to two cyclopentadienyl rings in a $\eta^5$ fashion; the co-ordination of the metal is completed by two Cl atoms in (**2**), by a terminal carbonyl group and a carbon atom from the $C_6F_5$ ligand in (**2f**), and by an oxygen atom and a carbon atom from a methyl group in (**2h**).

We have been studying reductions with Na–Hg of niobocene complexes of the type $[Nb(cp)_2Cl_2]$ [1,2] as part of our program to isolate niobium(III) derivatives containing different ligands and different halogeno and alkyl substituents. The reaction of these complexes with oxygen can lead to oxoacyl and halogeno-oxo or -peroxo niobium(V) complexes or alternatively to carbon dioxide niobium(III) derivatives [3] of potential interest in relation to various catalytic processes.[4] The results of our synthetic studies and the first observations on the different behaviour in reactions with oxygen are described in this paper.

## Experimental

*Materials and Methods.*—All reactions were performed by using standard Schlenk techniques in an atmosphere of dry, oxygen-free argon. Solvents were distilled from appropriate drying agents and degassed before use. The complexes $[Nb(cp)_2Cl_2]$ [cp = $\eta$-$C_5H_5$ (**1**), $\eta$-$C_5H_4SiMe_3$ (**2**), or $\eta$-$C_5H_3(SiMe_3)_2$ (1,3 isomer throughout) (**3**)] were prepared as previously reported.[5]

Niobium pentachloride was purchased and used without further purification. Elemental analyses were performed with a Perkin-Elmer 240B microanalyser. Proton and $^{13}C$ n.m.r. spectra were recorded in sealed tubes on a Varian FT80A instrument. Chemical shifts ($^1H$ and $^{13}C$) are reported relative to $SiMe_4$ with all chemical shifts positive to high frequency. Cyclic voltammetry (c.v.) measurements were carried out under dry nitrogen using distilled and dried tetrahydrofuran (thf) as solvent. Tetrabutylammonium tetrafluoroborate (0.2 mol dm$^{-3}$), prepared as previously described,[6] was used as electrolyte support. A three platinum electrode cell, with ferrocene as internal reference were used, with an Amel 473 polarographic analyser.

*Preparation of* $[Nb(cp)_2Cl(CO)]$, (**2a**) *and* (**3a**).—Tetrahydrofuran (150 cm$^3$) previously saturated with CO was added

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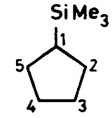
† Dichlorobis[$\eta$-(trimethylsilyl)cyclopentadienyl]niobium(IV), methyl(oxo)bis[$\eta$-(trimethylsilyl)cyclopentadienyl]niobium(V), and carbonyl(pentafluorophenyl)bis[$\eta$-(trimethylsilyl)cyclopentadienyl]niobium(III) respectively.

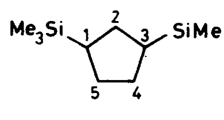
*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

to a mixture of [Nb(cp)$_2$Cl$_2$] (**2**) and (**3**) (2.28 mmol) and Na–Hg (10%) (2.30 mmol). The mixture was stirred for 4 h with continuous slow bubbling of CO for the first 2 h. The brown solution was evaporated to dryness to give a solid which was extracted with warm hexane. Grey-violet crystals of [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$Cl(CO)] (**2a**) (60% yield) or brown crystals of [Nb{η-C$_5$H$_3$(SiMe$_3$)$_2$}Cl(CO)] (**3a**) (80%) were collected by cooling and dried under vacuum; (**2a**) is stable for long periods in the solid and in solution under argon but is moderately air sensitive in the solid and highly air sensitive in solution. Complex (**3a**), with increasing substitution in the ring, shows higher solubility and stability.

(**2a**) (Found: C, 47.3; H, 6.55. Calc. for $C_{17}H_{26}ClNbOSi_2$: C, 47.4; H, 6.1%). I.r. ($CH_2Cl_2$): ν(CO) 1 929vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 930vs cm$^{-1}$, ν(Nb–Cl) 245w cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 5.16 (2 H), 4.91 (6 H) (each a complex signal, $C_5H_4$), 0.18 (s, 18 H, SiMe$_3$); $^1$H n.m.r. ($CDCl_3$): δ 5.62 (t, 4 H), 5.19 (t, 4 H) ($J_{H\text{-}H'}$ = 2.3 Hz, $C_5H_4$), 0.21 (s, 18 H, SiMe$_3$); $^{13}$C-{$^1$H} n.m.r. (thf): δ 213.6 (br, CO), 107.4, 104.5, 103.8, 95.2, (C$^2$,C$^3$,C$^4$,C$^5$; exact assignment not possible), 98.6 (C$^1$), 0.1 (SiMe$_3$).



(**3a**) (Found: 48.0; H, 7.9. Calc. for $C_{23}H_{42}ClNbOSi_4$: C, 48.0; H, 7.35%). I.r. ($C_6H_{14}$): ν(CO) 1 921vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 920vs, ν(Nb–Cl) 247w cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 5.76 (2 H), 4.97 (4 H) (each a complex signal, $C_5H_3$), 0.31 (s, 18 H), 0.19 (s, 18 H), SiMe$_3$; $^1$H n.m.r. ($CDCl_3$): δ 5.59 (t, 2 H), 5.03 (q, 4 H, $C_5H_4$), 0.24 (s, 18 H), 0.19 (s, 18 H) (SiMe$_3$); $^{13}$C-{$^1$H} n.m.r. (thf): δ 255.7 (br, CO), 122.1, 97.2, 95.3 (C$^2$,C$^4$,C$^5$; exact assignment not possible), 121.1, 99.6 (C$^1$,C$^3$; exact assignment not possible), 0.1, −0.1 (SiMe$_3$).



*Preparation of* [Nb(η-C$_5$H$_5$)$_2$R(CO)] [R = Me (**1b**), CH$_2$CMe$_3$ (**1c**), CH$_2$SiMe$_3$ (**1d**), CH$_2$Ph (**1e**), *or* C$_6$F$_5$ (**1f**).—A thf solution containing a small excess of the alkylating agent, LiMe, Mg(CH$_2$CMe$_3$)$_2$, Mg(CH$_2$SiMe$_3$)$_2$, Mg(CH$_2$Ph)$_2$, or Li(C$_6$F$_5$) was added to a thf (50 cm$^3$) solution of complex [Nb(η-C$_5$H$_5$)$_2$Cl(CO)] (**1a**) (1 mmol). After stirring at room temperature for 12 h the solvent was pumped off and the residue extracted with pentane. Complexes (**1b**)—(**1f**) were obtained by evaporation as microcrystalline solids (yields 20—30%). The spectroscopic properties of (**1b**) and (**1e**) have been reported previously.[7,8]

(**1c**) (Found: C, 59.45; H, 6.8. Calc. for $C_{16}H_{21}NbO$: C, 59.05; H, 6.45%). I.r. (Nujol): ν(CO), 1 900vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.50 (s, 10 H, $C_5H_5$), 1.16 (s, 9 H, CH$_2$C*Me*$_3$), 0.53 (s, 2 H, C*H*$_2$CMe$_3$).

(**1d**) (Found: C, 53.65; H, 6.65. Calc. for $C_{15}H_{21}NbOSi$: C, 53.25; H, 6.2%). I.r. (Nujol): ν(CO) 1 902s cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.48 (s, 10 H, $C_5H_5$), 0.22 (s, 9 H, CH$_2$Si*Me*$_3$), −1.31 (s, 2 H, C*H*$_2$SiMe$_3$).

(**1f**) (Found: C, 48.0; H, 2.80. Calc. for $C_{17}H_{10}F_5NbO$: C, 48.85; H, 2.40%). I.r. (Nujol): ν(CO) 1 903s cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.75 (s, $C_5H_5$).

*Preparation of* [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$Me(CO)] (**2b**).—A suspension of (**2a**) (1.0 g, 2.32 mmol) in hexane (40 cm$^3$) at −78 °C was treated with an equimolar amount of a 1.6 mol dm$^{-3}$ diethyl ether solution of LiMe (1.45 cm$^3$, 2.32 mmol). The solution was slowly allowed to warm to room temperature and after stirring for 12 h it was filtered and evaporated to 3 cm$^3$. Crystals of (**2b**) were obtained by cooling, yield 60% (Found: C, 52.7; H, 7.25. Calc. for $C_{18}H_{29}NbOSi_2$: C, 52.65; H, 7.1%). I.r. ($C_6H_{14}$): ν(CO) 1 910vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 908vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.93 (2 H), 4.73 (2 H), 4.49 (2 H), 4.35 (2 H) (each a complex signal, $C_5H_4$), 0.12 (s, 18 H, SiMe$_3$), −0.61 (s, 3 H, Me).

*Preparation of* [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$R(CO)] [R = CH$_2$CMe$_3$ (**2c**), CH$_2$SiMe$_3$ (**2d**), CH$_2$Ph (**2e**) *or* C$_6$F$_5$ (**2f**)].—*Method A*. A freshly prepared ether solution containing an excess (1:4) of MgRX (R = CH$_2$SiMe$_3$, X = Cl; R = CH$_2$CMe$_3$, CH$_2$Ph, or C$_6$F$_5$, X = Br) was added to an ether (70 cm$^3$) solution of (**2a**) (0.5 g, 1.16 mmol). The mixture was stirred for 5 d at room temperature. The solution became increasingly green-brown and a white insoluble solid appeared, which was filtered off. Dioxane (2 cm$^3$) was added to the filtrate and during stirring for 1 d a white precipitate was formed.

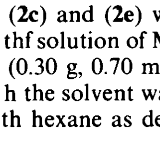
The solution was filtered, the solvent was pumped off and the residue extracted with pentane or hexane four or five times until no insoluble solid was observed. The solution was then evaporated to give (**2f**) as a crystalline solid and the rest of the complexes as oily residues characterized as spectroscopically pure complexes or as solids after drying under vacuum; yields *ca.* 50%.

(**2c**). I.r. ($C_6H_{14}$): ν(CO) 1 906vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 905 vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.95 (4 H), 4.67 (2 H), 4.51 (2 H) (each a complex signal, $C_5H_4$), 1.16 (s, 9 H, CH$_2$C*Me*$_3$), 0.49 (s, 2 H, C*H*$_2$CMe$_3$), 0.07 (s, 18 H, SiMe$_3$).

(**2d**). I.r. ($C_6H_{14}$): ν(CO) 1 906vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 902vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.94 (2 H), 4.85 (2 H), 4.58 (4 H) (each a complex signal, $C_5H_4$), 0.27 (s, 9 H, CH$_2$Si*Me*$_3$), 0.09 (s, 18 H, SiMe$_3$), −1.46 (s, 2 H, C*H*$_2$SiMe$_3$).

(**2e**) (Found: C, 59.2; H, 7.3. Calc. for $C_{24}H_{33}NbOSi_2$: C, 59.25; H, 6.85%). I.r. ($C_6H_{14}$): ν(CO) 1 983vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 903vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 7.24—7.11 (m, 5 H, CH$_2$C$_6$*H*$_5$), 4.94 (2 H), 4.68 (2 H), 4.45 (2 H), 4.22 (2 H) (each a complex signal, $C_5H_4$), 1.80 (s, 2 H, C*H*$_2$C$_6$H$_5$), 0.08 (s, 18 H, SiMe$_3$).

(**2f**) (Found: C, 48.6; H, 4.85. Calc. for $C_{23}H_{26}F_5NbOSi_2$: C, 49.1; H, 4.65%). I.r. ($C_6H_{14}$): ν(CO) 1 935vs cm$^{-1}$; i.r. (Nujol): ν(CO) 1 932vs cm$^{-1}$. $^1$H N.m.r. ($C_6D_6$): δ 4.90 (2 H), 4.70 (2 H), 4.63 (2 H), 4.55 (2 H) (each a complex signal, $C_5H_4$), 0.02 (s, 18 H, SiMe$_3$). $^{19}$F N.m.r. ($C_7D_8$, ref. CFCl$_3$): δ −92.0, −100.3 (each a dd; F$^1$,F$^5$; $^3J_{1-2}$, $^3J_{4-5}$ = 33.9, 33.5 Hz; $^5J_{1-4}$, $^5J_{2-5}$ = 2.6, 1.9 Hz; exact assignment not possible), −159.4 (t, F$^3$, $^3J_{2-3}$ = $^3J_{3-4}$ = 18.9 Hz), −161.8, −164.0 (c; F$^3$,F$^5$, exact assignment not possible).[9]



*Method B*. Complexes (**2c**) and (**2e**) were also prepared by addition of an excess of a thf solution of MgR$_2$ to a thf (20 cm$^3$) solution of complex (**2a**) (0.30 g, 0.70 mmol). After stirring at room temperature for 48 h the solvent was pumped off and the residue was extracted with hexane as described in method A; yield *ca.* 70%.

*Preparation of* [Nb(cp)$_2$(O)Cl], (**2g**) *and* (**3g**).—Dry oxygen was bubbled through a solution of (**2a**) or (**3a**) (1.74 mmol) in ether (100 cm$^3$) until saturation and then stirred for 4 h [(**2a**)] or 48 h [(**3a**)] at room temperature, becoming yellow in colour. Following filtration, the solvent was removed *in vacuo*. The resulting yellow solid was recrystallized from warm hexane to give yellow crystals of [Nb(η-$C_5H_4SiMe_3)_2$(O)Cl] (**2g**) (50% yield) or [Nb{η-$C_5H_3(SiMe_3)_2\}_2$(O)Cl] (**3g**) (60%).

(**2g**) (Found: C, 46.05; H, 6.75. Calc. for $C_{16}H_{26}ClOSi_2$: C, 45.9; H, 6.25%). I.r. (Nujol): ν(Nb=O) 865s, ν(Nb–Cl) 270w $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.40 (2 H), 6.20 (2 H), 5.75 (2 H), 5.61 (2 H) (each a complex signal, $C_5H_4$), 0.30 (s, 18 H, $SiMe_3$); $^1H$ n.m.r. ($CDCl_3$): δ 6.58 (4 H), 6.42 (2 H), 6.17 (2 H) (each a complex signal, $C_5H_4$), 0.28 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 127.1, 117.6, 116.5, 115.3 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 126.2 ($C^1$), −0.5 ($SiMe_3$).

(**3g**) (Found: C, 47.1; H, 7.80. Calc. for $C_{22}H_{42}ClNbOSi_4$: C, 46.9; H, 7.5%). I.r. (Nujol): ν(Nb=O) 875s, ν(Nb–Cl) 240w $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.92 (t, 2 H), 6.34 (t, 2 H), 6.04 (t, 2 H) ($C_5H_3$), 0.33 (s, 36 H, $SiMe_3$); $^1H$ n.m.r. ($CDCl_3$): δ 6.82 (t, 2 H), 6.39 (t 2, H), 6.18 (t 2, H) ($C_5H_3$), 0.32 (s, 18 H), 0.25 (s, 18 H) ($SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 139.7, 125.2, 113.5 ($C^2,C^4,C^5$; exact assignment not possible), 127.5, 126.8 ($C^1,C^3$; exact assignment not possible), 0.1—0.4 ($SiMe_3$).

*Preparation of* [Nb(η-$C_5H_4SiMe_3)_2$(O)R] [R = Me (**2h**), $Bu^n$ (**2i**), $CH_2CMe_3$ (**2j**), *or* $CH_2SiMe_3$ (**2k**)].—A hexane solution of LiR (1.79 mmol) or an ether solution of LiMe (1.6 mol $dm^{-3}$) was added to a suspension of (**2g**) (0.75 g, 1.79 mmol) in hexane (70 $cm^3$) at −78 °C. This mixture was allowed to warm at room temperature and stirred for 24 h. The white precipitate was separated by filtration and the solvent was evaporated *in vacuo* to give white crystals of (**2h**)—(**2k**) (50—60% yield). Occasionally an intermediate violet colour was observed which disappeared on standing.

(**2h**) (Found: C, 51.5; H, 7.85. Calc. for $C_{17}H_{29}NbOSi_2$: C, 51.25; H, 7.35%). I.r. (Nujol): ν(Nb=O) 865s $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 5.65 (2 H), 5.59 (2 H), 5.17 (2 H), 5.03 (2 H) (each a complex signal, $C_5H_4$), 1.07 (s, 3 H, Me), 0.28 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 122.3 ($C^1$), 121.1, 114.5, 113.2, 109.5 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 9.6 (br, Me), −0.5 ($SiMe_3$).

(**2i**) (Found: C, 54.8; H, 8.2. Calc. for $C_{20}H_{35}NbOSi_2$: C, 54.5; H, 8.0%). I.r. (Nujol): ν(Nb=O) 864s $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.08 (4 H), 5.54 (2 H), 5.10 (2 H) (each a complex signal, $C_5H_4$), 2.05—1.11 (complex, 9 H, $Bu^n$), 0.30 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 121.9 ($C^1$), 120.4, 114.3, 112.9, 109.9 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 39.3, 29.6, 14.3 ($Bu^n$, except $C^1$), 32.5 (br, $C^1$, $Bu^n$), −0.3 ($SiMe_3$).

(**2j**) (Found: C, 55.6; H, 8.4. Calc. for $C_{21}H_{37}NbOSi_2$: C, 55.5; H, 8.2%). I.r. (Nujol): ν(Nb=O) 857s $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.16 (2 H), 5.89 (4 H), 5.04 (2 H) ($C_5H_4$), 2.13 (s, 2 H, $C\mathit{H}_2CMe_3$), 1.36 (s, 9 H, $CH_2C\mathit{Me}_3$), 0.26 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 122.3 ($C^1$), 118.8, 115.6, 114.9, 111.0 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 38.9 (br, $\mathit{C}H_2CMe_3$), 36.0 ($CH_2\mathit{C}Me_3$), 34.4 ($CH_2C\mathit{Me}_3$), −0.2 ($SiMe_3$).

(**2k**) (Found: C, 51.8; H, 8.2. Calc. for $C_{20}H_{37}NbOSi_3$: C, 51.05; H, 7.9%). I.r. (Nujol): ν(Nb=O) 865s $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.15 (2 H), 5.95 (2 H), 5.85 (2 H), 5.16 (2 H) (each a complex signal, $C_5H_4$), 0.91 (s, 2 H, $C\mathit{H}_2SiMe_3$), 0.35 (s, 9 H, $CH_2Si\mathit{Me}_3$), 0.28 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 122.3 ($C^1$), 119.6, 114.2, 114.2, 114.2, 111.8 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 12.8 (br, $\mathit{C}H_2SiMe_3$), 2.9 ($CH_2Si\mathit{Me}_3$), −0.3 ($SiMe_3$).

*Preparation of* [Nb(η-$C_5H_4SiMe_3)_2(O_2)$Cl] (**2l**).—*Method A*. An excess of an aqueous 30% $H_2O_2$ solution (15 $cm^3$) was added to a dichloromethane (150 $cm^3$) solution of (**2**) (1.0 g, 2.28 mmol). The mixture was stirred at room temperature to give a yellow solution after 36 h. The organic layer was decanted and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* and the resulting crystalline solid washed with hexane and dried *in vacuo* (50% yield).

*Method B*. Dry oxygen was bubbled through a solution of [Nb(η-$C_5H_4SiMe_3)_2Cl(CNC_6H_{11})$][9] (0.50 g, 0.98 mmol) in hexane (30 $cm^3$) for 5 min at room temperature. The starting red colour became yellow with simultaneous precipitation of a yellow solid, which was filtered off, washed with hexane and dried *in vacuo* (70% yield) (Found: C, 43.65; H, 5.7. Calc. for $C_{16}H_{26}ClNbO_2Si_2$: C, 44.2; H, 6.05%). I.r. (Nujol): ν(O–O) 872s, $\nu_{sym}(NbO_2)$ 516m, $\nu_{asym}(NbO_2)$ 538s, ν(Nb–Cl) 280w $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 6.20 (2 H), 5.75 (2 H), 5.59 (2 H), 5.33 (2 H) (each a complex signal, $C_5H_4$), 0.29 (s, 18 H, $SiMe_3$); $^1H$ n.m.r. ($CDCl_3$): δ 6.37—6.17 (complex signals, 8 H, $C_5H_4$), 0.27 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 129.4, 120.3, 113.3, 110.5 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 128.2 ($C^1$), −10 ($SiMe_3$).

**Table 1.** Experimental data for the *X*-ray diffraction studies on (**2**), (**2h**), and (**2f**)*

| | (**2**) | (**2h**) | (**2f**) |
|---|---|---|---|
| Molecular formula | $C_{16}H_{26}Cl_2NbSi_2$ | $C_{17}H_{29}NbOSi_2$ | $C_{23}H_{26}F_5NbOSi_2$ |
| *M* | 438.37 | 398.49 | 562.53 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | *P*1 | $P2_1/n$ | $P\bar{1}$ |
| *a*/Å | 12.680(5) | 8.842(4) | 9.781(4) |
| *b*/Å | 12.923(5) | 37.108(10) | 14.440(6) |
| *c*/Å | 6.806(3) | 6.331(3) | 8.765(4) |
| α/° | 97.82(2) | | 90.84(2) |
| β/° | 104.18(3) | 108.03(4) | 85.86(2) |
| γ/° | 67.79(2) | | 93.90(2) |
| $U/Å^3$ | 999.9(7) | 1 975(1) | 1 231.8(9) |
| *Z* | 2 | 4 | 2 |
| $D_c/g\ cm^{-3}$ | 1.456 | 1.340 | 1.517 |
| *F*(000) | 450 | 832 | 572 |
| Crystal dimensions (mm) | 0.15 × 0.20 × 0.25 | 0.13 × 0.40 × 0.55 | 0.10 × 0.28 × 0.50 |
| Linear absorption coefficient, $\mu/cm^{-1}$ | 9.57 | 7.00 | 6.12 |
| 2θ Range (°) | 6—54 | 6—48 | 6—48 |
| Reflections measured | $\pm h, \pm k, l$ | $\pm h, k, l$ | $\pm h, \pm k, l$ |
| Unique total data | 4 335 | 3 414 | 3 895 |
| Unique observed data [$I > 2\sigma(I)$] | 2 889 | 1 466 | 2 269 |
| *R* | 0.0377 | 0.0385 | 0.0441 |
| *R'* | 0.0530 | 0.0502 | 0.0603 |

* Data common to all three determinations: Nb-filtered Mo-$K_\alpha$ radiation (λ = 0.710 69 Å); Siemens AED diffractometer; θ/2θ scan, scan speed 3—12° $min^{-1}$, scan width (θ − 0.60) − (θ + 0.60 + 0.346tanθ)°; one standard reflection measured every 50.

*Preparation of* [Nb(η-$C_5H_4SiMe_3)_2(O_2)$Me] (**2m**).—Dry oxygen was bubbled through a solution of [Nb(η-$C_5H_4SiMe_3)_2Me(PMe_3)$][2] (0.40 g, 0.87 mmol) in hexane (20 $cm^3$). The starting red solution became instantaneously colourless and bubbling was ceased. After filtration, the solution was evaporated to give white crystals of (**2m**) on cooling (61% yield) (Found: C, 49.1; H, 7.30. Calc. for $C_{17}H_{29}NbO_2Si_2$: C, 49.25; H, 7.05%). I.r. (Nujol): ν(O–O) 875s, $\nu_{sym}(NbO_2)$ 527 (sh), $\nu_{asym}(NbO_2)$ 537 s $cm^{-1}$. $^1H$ N.m.r. ($C_6D_6$): δ 5.77 (2 H), 5.64 (2 H), 5.26 (4 H) (each a complex signal, $C_5H_4$), 1.09 (s, 3 H, Me), 0.28 (s, 18 H, $SiMe_3$); $^{13}C-\{^1H\}$ n.m.r. (thf): δ 125.2 ($C^1$), 122.0, 110.9, 109.9, 107.3 ($C^2,C^3,C^4,C^5$; exact assignment not possible), 20.2 (Me), −0.9 ($SiMe_3$).

**Table 2.** Fractional atomic co-ordinates ( × $10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (**2**)

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| Nb(1) | 4 415 | 352 | 1 299 | C(121) | 7 988(21) | −823(14) | 3 420(45) |
| Nb(2) | −879(1) | 5 352(1) | −1 526(2) | C(131) | 7 901(21) | 1 623(26) | 5 065(45) |
| Cl(11) | 5 639(7) | −408(7) | −1 265(12) | C(141) | 893(29) | −305(40) | −896(30) |
| Cl(21) | 2 844(3) | 1 079(8) | −1 659(14) | C(151) | 1 081(26) | 1 567(13) | 2 373(44) |
| Cl(12) | 722(7) | 4 611(7) | 1 406(12) | C(161) | 1 446(30) | −962(27) | 3 425(53) |
| Cl(22) | −2 150(8) | 6 014(8) | 926(12) | C(12) | −515(16) | 6 256(20) | −4 033(36) |
| Si(11) | 7 385(8) | 709(9) | 2 892(16) | C(22) | −1 630(12) | 6 832(13) | −3 642(30) |
| Si(21) | 1 603(7) | 17(7) | 1 779(14) | C(32) | −1 528(16) | 7 373(19) | −1 661(32) |
| Si(12) | 1 951(7) | 5 654(7) | −1 951(13) | C(42) | −322(13) | 6 936(22) | −639(39) |
| Si(22) | −3 845(8) | 5 001(8) | −3 130(17) | C(52) | 327(10) | 6 255(17) | −2 190(28) |
| C(11) | 5 248(21) | 1 179(24) | 4 328(38) | C(62) | −1 240(15) | 3 723(18) | −1 629(33) |
| C(21) | 4 026(17) | 1 358(18) | 3 856(26) | C(72) | −240(20) | 3 432(20) | −2 484(45) |
| C(31) | 3 846(20) | 2 368(18) | 2 041(36) | C(82) | −497(23) | 3 915(25) | −4 329(48) |
| C(41) | 4 933(19) | 2 018(20) | 1 360(38) | C(92) | −1 724(20) | 4 562(24) | −4 629(36) |
| C(51) | 5 779(11) | 1 268(18) | 2 818(34) | C(102) | −2 223(11) | 4 437(20) | −3 041(26) |
| C(61) | 3 834(19) | −1 249(17) | 522(32) | C(112) | 2 632(28) | 5 323(33) | 748(27) |
| C(71) | 5 027(23) | −1 670(23) | 1 520(41) | C(122) | 2 263(31) | 6 423(23) | −3 792(49) |
| C(81) | 5 205(20) | −1 173(21) | 3 504(39) | C(132) | 2 428(23) | 4 191(13) | −3 083(39) |
| C(91) | 4 040(14) | −496(21) | 3 739(30) | C(142) | −4 235(27) | 4 687(34) | −872(37) |
| C(101) | 3 213(12) | −560(23) | 1 955(36) | C(152) | −4 693(20) | 4 333(22) | −5 520(31) |
| C(111) | 7 542(29) | 956(40) | 329(33) | C(162) | −4 552(24) | 6 515(13) | −3 812(48) |

**Table 3.** Fractional atomic co-ordinates ( × $10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (**2f**)

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| Nb | 4 085(1) | 2 049(1) | 2 371(1) | C(8) | 1 434(12) | 3 492(12) | −1 939(13) |
| Si(1) | 1 745(2) | 3 564(1) | 114(2) | C(9) | 2 084(14) | 4 789(7) | 669(19) |
| Si(2) | 6 461(2) | 3 236(2) | 5 255(3) | C(10) | 4 379(9) | 1 675(7) | 4 949(11) |
| F(1) | 3 221(7) | 79(3) | 514(7) | C(11) | 4 261(11) | 838(7) | 4 235(13) |
| F(2) | 1 107(9) | −1 124(4) | 496(8) | C(12) | 5 345(12) | 797(7) | 3 120(13) |
| F(3) | −1 212(7) | −859(5) | 2 350(9) | C(13) | 6 162(9) | 1 630(6) | 3 216(10) |
| F(4) | −1 278(6) | 653(4) | 4 231(8) | C(14) | 5 566(7) | 2 209(5) | 4 372(8) |
| F(5) | 856(5) | 1 836(4) | 4 302(6) | C(15) | 7 728(15) | 2 805(14) | 6 459(20) |
| O(1) | 2 624(6) | 3 622(4) | 4 092(6) | C(16) | 7 264(16) | 4 021(10) | 3 744(16) |
| C(1) | 3 075(8) | 3 067(5) | 3 550(8) | C(17) | 5 241(10) | 3 652(8) | 6 534(12) |
| C(2) | 4 632(7) | 3 325(6) | 780(8) | C(18) | 2 150(8) | 1 060(5) | 2 339(9) |
| C(3) | 5 611(9) | 2 697(7) | 425(9) | C(19) | 2 118(11) | 283(6) | 1 444(11) |
| C(4) | 4 986(10) | 1 915(7) | −247(9) | C(20) | 1 035(16) | −370(7) | 1 420(14) |
| C(5) | 3 608(10) | 2 083(7) | −287(10) | C(21) | −112(15) | −253(10) | 2 338(19) |
| C(6) | 3 321(7) | 2 949(5) | 346(8) | C(22) | −150(10) | 490(9) | 3 257(14) |
| C(7) | 213(10) | 3 024(9) | 1 178(14) | C(23) | 957(9) | 1 135(6) | 3 290(10) |

**Table 4.** Fractional atomic co-ordinates ( × $10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (**2h**)

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| Nb | −880(1) | 1 214(1) | 277(2) | C(71) | 3 939(19) | 270(4) | 1 974(31) |
| Si(1) | 2 601(4) | 543(1) | 3 051(6) | C(81) | 3 685(22) | 936(5) | 4 623(34) |
| Si(2) | 1 594(5) | 2 067(1) | 949(6) | C(12) | −336(15) | 1 841(3) | −458(20) |
| O(1) | 206(9) | 1 283(2) | 3 012(12) | C(22) | −800(17) | 1 672(4) | −2 544(21) |
| C(1) | −3 056(20) | 1 028(6) | 1 001(34) | C(32) | −2 380(16) | 1 566(3) | −3 130(24) |
| C(11) | 892(13) | 675(3) | 639(20) | C(42) | −2 940(17) | 1 672(3) | −1 435(27) |
| C(21) | −654(16) | 547(3) | 43(27) | C(52) | −1 716(17) | 1 842(4) | 159(25) |
| C(31) | −1 514(22) | 652(4) | −2 053(28) | C(62) | 3 210(18) | 1 796(4) | 517(37) |
| C(41) | −527(21) | 858(5) | −2 849(25) | C(72) | 1 823(32) | 2 115(7) | 3 875(30) |
| C(51) | 911(19) | 885(4) | −1 1199(21) | C(82) | 1 617(26) | 2 499(4) | −327(34) |
| C(61) | 1 852(20) | 262(5) | 4 861(28) | | | | |

*Crystal Structure Determination of Compounds* (**2**), (**2f**), *and* (**2h**).—Crystals of compounds (**2**), (**2f**), and (**2h**) were sealed in Lindemann glass capillaries under nitrogen and used for data collection. The crystallographic data are summarized in Table 1. Unit-cell parameters were determined from the setting angles of 30 carefully centred reflections, with θ in the range 10—16°. Data were collected at room temperature, the individual profiles having been analysed following Lehmann and Larsen.[10] The structure amplitudes were obtained after usual Lorentz and polarization reduction. Corrections for absorption were not applied in view of the very low absorbance of the samples.

All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods using the SHELX system of computer programs[11] first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms of (**2f**) and (**2h**) were clearly located from the final difference Fourier maps and refined isotropically; some of the hydrogen atoms of (**2**) were clearly localized in the final *F* map, some were placed at their geometrically calculated positions; all were introduced in the final structure factor calculations with fixed isotropic thermal parameters.

The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.0725$ [(**2**)], 0.922 [(**2f**)], or 0.619 [(**2h**)] and $g = 0.007$ [(**2**)], 0.002 [(**2f**)], or 0.008 [(**2h**)]. Atomic scattering factors, corrected for anomalous dispersion of Nb, Cl, and F, were taken from ref. 12. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 2—4.

Calculations were carried out on the CRAY X-MP/12 computer of the Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-orientale (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), with financial support from the University of Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

## Results and Discussion

*Synthesis of Chloro and Alkyl Carbonylniobium*(III) *Complexes.*—Addition of CO-saturated thf to a mixture of dichloroniobium(IV) compounds and Na–Hg (10%) in 1:1 molar ratio with stirring under CO at room temperature results in the formation of the appropriate chloro carbonylniobium(III) complex, equation (1). The yield previously reported[7,13] for

$$[Nb(cp)_2Cl_2] + CO \xrightarrow[-NaCl]{+Na\text{-}Hg} [Nb(cp)_2Cl(CO)] \qquad (1)$$

$$\begin{array}{l} (\mathbf{1a}),\ cp = \eta\text{-}C_5H_5 \\ (\mathbf{2a}),\ cp = \eta\text{-}C_5H_4SiMe_3 \\ (\mathbf{3a}),\ cp = \eta\text{-}C_5H_3(SiMe_3)_2 \end{array}$$

(**1a**) can be substantially increased by extracting the residue obtained after evaporation with HCl-saturated thf at 0 °C, or alternatively by reducing with Zn in the presence of $PPh_4Cl$, equation (2). Compound (**3a**) is obtained in a particularly high yield whereas (**2a**) results in lower yields as successive recrystallizations are required. Compounds (**2a**) and (**3a**) are much more soluble than (**1a**) in all common organic solvents; in addition, (**3a**) is soluble in alkanes in which (**2a**) is only scarcely soluble. They are indefinitely stable under $N_2$ and can be manipulated in air for short periods without apparent decomposition. Solutions are rather unstable and cannot be stored for long periods.

$$[Nb(\eta\text{-}C_5H_5)_2Cl_2] + CO + PPh_4Cl \xrightarrow[-ZnCl_3^-]{Zn} [Nb(\eta\text{-}C_5H_5)_2Cl(CO)] \qquad (2)$$
$$(\mathbf{1a})$$

The alkylation of (**1a**) and (**2a**) has been carried out by using different alkylating reagents, equation (3). Compound (**1a**) is resistant to substitution and a low yield was initially reported for (**1b**) in the reaction with LiMe, although a higher yield was obtained when MgMeBr was used instead of LiMe.[8] We obtained (**1b**) in a reasonably higher yield (60%) by reaction with LiMe using thf as solvent. Compound (**2a**) reacts easily under moderate conditions giving higher yields due to its higher solubility and also the higher stability of its alkylated products (**2b**)—(**2f**), whereas (**1b**)—(**1f**) are always obtained in lower yields.

$$[Nb(cp)_2Cl(CO)] + \text{`MR'} \longrightarrow [Nb(cp)_2R(CO)] + \text{`MCl'} \qquad (3)$$

$$cp = \eta\text{-}C_5H_5 \text{ or } \eta\text{-}C_5H_4SiMe_3$$

$$\begin{array}{lll} R = Me & (\mathbf{1b}) & (\mathbf{2b}) \\ R = CH_2CMe_3 & (\mathbf{1c}) & (\mathbf{2c}) \\ R = CH_2SiMe_3 & (\mathbf{1d}) & (\mathbf{2d}) \\ R = CH_2Ph & (\mathbf{1e}) & (\mathbf{2e}) \\ R = C_6F_5 & (\mathbf{1f}) & (\mathbf{2f}) \end{array}$$

The lithium reagents can be used only in the case of complexes (**1b**), (**2b**), and (**1f**). Reactions with other alkyls go further or decomposition takes place to give oily residues which could not be resolved and were not further studied. Grignard reagents MgRBr were used to isolate complexes (**2c**)—(**2e**), and (**2f**); a better yield was obtained for (**2c**) by using $MgR_2$, which were also the best reagents to prepare (**1c**)—(**1e**) and (**2e**).

All the alkyls are much more sensitive compounds than the corresponding halides. They are soluble in all common organic solvents and even in the alkanes from which they were recrystallized. The high solubility of (**2c**) and (**2d**) prevented their isolation as solids, but oily residues containing only the pure products were obtained and characterized by n.m.r. spectroscopy. Analytical data were not obtained for the most air-sensitive complexes but all those which were analysed gave compositions according to their formulae.

*Reactions with Oxygen.*—It has been reported[14] that complex (**1b**) cannot be acylated. This behaviour is probably due to the high energy of the niobium lowest unoccupied molecular orbital (l.u.m.o.) which prevents the formation of the $\eta^2$-acyl complex and also to the strong back donation to the CO groups which stabilizes the M–CO bond. In order to facilitate the reaction we attempted carbonylation in the presence of oxygen to produce simultaneous oxidation of the metal. Under these conditions, a mixture of compounds probably containing the oxo-acyl derivative along with other non-identified products was obtained.

An easier acylation is expected for complexes (**2**) as the negative mesomeric effect of the $SiMe_3$ group[15] reduces the electron density on the ring and therefore the back donation to the CO group. Complexes (**2**) have higher oxidation potentials, as shown by electrochemical studies described below, and have a lower-energy highest occupied molecule orbital (h.o.m.o.). However, only oxidation but no acylation was observed in reactions with mixtures of CO and $O_2$. This means that the negative mesomeric effect of the $SiMe_3$ group mainly affects the alkyl ligand, producing a stabilization of the M–C bond. The nature of the products obtained by oxidation depends on the substituent, equation (4). The oxo complexes (**1g**),[16] (**2g**), and (**3g**) are obtained when the reaction is done with the chloro derivatives (X = Cl) but the peroxo complex (**2m**) results when starting from the methyl derivative (**2b**) (X = Me). The same complex (**2m**) is also obtained from $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Me(PMe_3)]$.[2]

$$[Nb(cp)_2X(CO)] + O_2 \begin{array}{l} \nearrow [Nb(cp)_2(O)Cl] \\ \quad (\mathbf{1g}), (\mathbf{2g}), (\mathbf{3g}) \\ \searrow [Nb(cp)_2(O_2)Me] \\ \quad (\mathbf{2m}) \end{array} \qquad (4)$$

It appears that the less electron-donating substituent favours conversion into an oxo instead of a peroxo group. This tendency is also dependent on the nature of the ligand which is lost in the reaction. We have observed that $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(CNR)]$[9] (R = cyclo-$C_6H_{11}$ or $Bu^t$) when treated with oxygen give the peroxo complex (**2l**) instead of the oxo derivative, indicating that less electron-accepting ligands favour the

**Table 5.** Cyclic voltammetric data for niobocene complexes[a]

| Complex | $Nb^{II/III}$ | $Nb^{III/IV}$ | | $Nb^{IV/V}$ | | |
|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$/V | $E_{\frac{1}{2}}$/V | $\Delta E$/mV | $E_{\frac{1}{2}}$/V | $\Delta E$/mV | Ref. |
| (**1**) $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ | | −1.22 | 200 | 0.35 | 80 | 21*a*, 22 |
| (**2**) $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ | | −1.15 | 80 | 0.30 | 80 | 2 |
| (**3**) $[Nb\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$ | | −1.00 | 80 | 0.60 | 80 | |
| $[Nb(\eta\text{-}C_5H_4Me)_2Cl(CO)]$ | −1.30[b] | 0.00 | | | | 21*b* |
| (**2a**) $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(CO)]$ | −1.16[b] | 0.34 | 60 | | | |
| (**3a**) $[Nb\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2Cl(CO)]$ | −1.35[b] | 0.46 | 70 | | | |
| (**2g**) $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)Cl]$ | | | | −1.80[b] | | |
| (**3g**) $[Nb\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(O)Cl]$ | | | | −1.82[b] | | |

[a] Solutions (*ca.* $10^{-3}$ mol $dm^{-3}$) of the complexes in thf (0.2 mol $dm^{-3}$) in $NBu_4BF_4$. Scan rate 200 mV $s^{-1}$. Internal reference ferrocene–ferrocenium ($E_{\frac{1}{2}}$ = 0.535 V in thf *vs.* normal hydrogen electrode). [b] Cathodic peaks only.

**Table 6.** Relevant bond distances (Å) and angles (°) in (**2**)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (*i*) In the Nb co-ordination sphere | | | | | | | |
| Nb(1)–Cl(11) | 2.475(9) | Nb(2)–Cl(12) | 2.467(7) | Nb(1)–$c_{g1}$ | 2.10(2) | Nb(2)–$c_{g3}$ | 2.07(3) |
| Nb(1)–Cl(21) | 2.475(8) | Nb(2)–Cl(22) | 2.450(10) | Nb(1)–$c_{g2}$ | 2.07(3) | Nb(2)–$c_{g4}$ | 2.05(3) |
| Cl(11)–Nb(1)–Cl(21) | 83.8(3) | Cl(12)–Nb–Cl(22) | 86.0(3) | Cl(21)–Nb(1)–$c_{g1}$ | 106.5(7) | Cl(22)–Nb–$c_{g3}$ | 107.1(6) |
| Cl(11)–Nb(1)–$c_{g1}$ | 109.2(7) | Cl(12)–Nb–$c_{g3}$ | 108.6(6) | Cl(21)–Nb–$c_{g2}$ | 109.2(7) | C(22)–Nb(2)–$c_{g4}$ | 108.8(8) |
| Cl(11)–Nb(1)–$c_{g2}$ | 104.8(7) | Cl(12)–Nb(2)–$c_{g4}$ | 107.7(7) | $c_{g1}$–Nb(1)–$c_{g2}$ | 132.5(9) | $c_{g3}$–Nb(2)–$c_{g4}$ | 129.9(9) |
| (*ii*) In the (trimethylsilyl)cyclopentadienyl groups | | | | | | | |
| C(11)–C(21) | 1.44(2) | C(12)–C(22) | 1.42(2) | C(61)–C(71) | 1.42(3) | C(62)–C(72) | 1.42(4) |
| C(21)–C(31) | 1.41(3) | C(22)–C(32) | 1.39(3) | C(71)–C(81) | 1.42(4) | C(72)–C(82) | 1.39(5) |
| C(31)–C(41) | 1.45(4) | C(32)–C(42) | 1.43(3) | C(81)–C(91) | 1.44(3) | C(82)–C(92) | 1.44(3) |
| C(41)–C(51) | 1.42(3) | C(42)–C(52) | 1.45(3) | C(91)–C(101) | 1.41(3) | C(92)–C(102) | 1.43(4) |
| C(11)–C(51) | 1.40(4) | C(12)–C(52) | 1.43(3) | C(61)–C(101) | 1.40(3) | C(62)–C(102) | 1.45(2) |
| C(51)–Si(11) | 1.88(2) | C(52)–Si(12) | 1.88(1) | C(101)–Si(21) | 1.87(2) | C(102)–Si(22) | 1.89(2) |
| Si(11)–C(111) | 1.88(3) | Si(12)–C(112) | 1.87(2) | Si(21)–C(141) | 1.89(3) | Si(22)–C(142) | 1.90(4) |
| Si(11)–C(121) | 1.89(2) | Si(12)–C(122) | 1.90(4) | Si(21)–C(151) | 1.88(2) | Si(22)–C(152) | 1.90(3) |
| Si(11)–C(131) | 1.91(3) | Si(12)–C(132) | 1.87(2) | Si(21)–C(161) | 1.89(4) | Si(22)–C(162) | 1.89(2) |
| C(21)–C(11)–C(51) | 109(2) | C(22)–C(12)–C(52) | 107(2) | C(71)–C(61)–C(101) | 107(2) | C(72)–C(62)–C(102) | 107(2) |
| C(11)–C(21)–C(31) | 106(2) | C(12)–C(22)–C(32) | 110(2) | C(61)–C(71)–C(81) | 111(2) | C(62)–C(72)–C(82) | 112(2) |
| C(21)–C(31)–C(41) | 110(2) | C(22)–C(32)–C(42) | 107(2) | C(71)–C(81)–C(91) | 103(2) | C(72)–C(82)–C(92) | 104(2) |
| C(31)–C(41)–C(51) | 106(2) | C(32)–C(42)–C(52) | 108(2) | C(81)–C(91)–C(101) | 111(2) | C(82)–C(92)–C(102) | 112(2) |
| C(41)–C(51)–C(11) | 109(2) | C(42)–C(52)–C(12) | 106(2) | C(91)–C(101)–C(61) | 107(2) | C(92)–C(102)–C(62) | 104(2) |
| C(11)–C(51)–Si(11) | 126(2) | C(12)–C(52)–Si(12) | 125(1) | C(61)–C(101)–Si(21) | 128(2) | C(62)–C(102)–Si(22) | 132(1) |
| C(41)–C(51)–Si(11) | 124(2) | C(42)–C(52)–Si(12) | 128(1) | C(91)–C(101)–Si(21) | 124(2) | C(92)–C(102)–Si(22) | 123(5) |

* $c_{g1}$ = Centroid of the C(11)—C(51) ring; $c_{g2}$ = centroid of the C(61)—C(101) ring; $c_{g3}$ = centroid of the C(12)—C(52) ring; $c_{g4}$ = centroid of the C(62)—C(102) ring.

formation of the peroxo compound. We are carrying out further studies to explain these observations. As far as we know, these are the first examples of direct conversion of molecular oxygen into a peroxo group by niobium(III) complexes. The chloro peroxo complex (**2l**) which can be made by this direct reaction can also be isolated by the method reported for $[Nb(\eta\text{-}C_5H_5)_2(O_2)Cl]$[17] using $H_2O_2$, equation (5).

$$[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2] + H_2O_2 \longrightarrow [Nb(\eta\text{-}C_5H_4SiMe_3)_2(O_2)Cl] \quad (5)$$

(**2l**)

The oxo complexes (**2g**) and (**3g**) are crystalline compounds stable in the solid and in solution. They are soluble in all usual organic solvents; in addition, (**3g**) is soluble in alkanes in which (**2g**) is scarcely soluble. The peroxo complex (**2l**) is a very stable compound which remains unaltered in air for long periods; it is soluble in $CH_2Cl_2$ and thf. Complex (**2m**) is stable under $N_2$ and decomposes very slowly in air, being practically soluble in all organic solvents. Finally, the oxo complex (**2g**) can be alkylated by reaction with lithium alkyls, equation (6). Complexes

$$[Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)Cl] + LiR \longrightarrow LiCl + [Nb(\eta\text{-}C_5H_4SiMe_3)_2(O)R] \quad (6)$$

(**2h**)—(**2k**)

(**2h**)—(**2k**) are crystalline compounds stable under nitrogen and soluble in most organic solvents.

*Spectroscopic Characterization.*—All the niobium-(III) and -(V) complexes reported are diamagnetic. The i.r. spectra show the characteristic absorptions for the cyclopentadienyl[18] and trimethylsilyl[19] groups as well as other internal vibrations of the different substituents. The ν(CO) absorption for the carbonyl niobium(III) complexes appears between 1 890 and 1 940 $cm^{-1}$. A displacement to higher wavenumbers is observed for complex (**2a**) with $SiMe_3$-substituted rings according to their higher π-acceptor capacity. However, a second $SiMe_3$ group in the ring as in complex (**3a**) produces a positive inductive effect partially compensating the negative mesomeric effect due to the first one and ν(CO) for this complex appears at a slightly lower wavenumber.

The ν(Nb=O) absorption is observed at 800—900 $cm^{-1}$ in

**Table 7.** Relevant bond distances (Å) and angles (°) in (**2f**)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (*i*) In the Nb co-ordination sphere | | | | | | | |
| Nb–C(1) | 2.052(7) | Nb–$c_{g1}$ | 2.018(9) | C(1)–Nb–C(18) | 93.4(3) | C(18)–Nb–$c_{g1}$ | 107.0(3) |
| Nb–C(18) | 2.294(7) | Nb–$c_{g2}$ | 2.052(9) | C(1)–Nb–$c_{g1}$ | 102.6(4) | C(18)–Nb–$c_{g2}$ | 100.7(3) |
| | | | | C(1)–Nb–$c_{g2}$ | 104.8(3) | $c_{g1}$–Nb–$c_{g2}$ | 139.3(3) |
| (*ii*) In the (trimethylsilyl)cyclopentadienyl groups | | | | | | | |
| C(2)–C(3) | 1.380(12) | C(10)–C(11) | 1.355(14) | C(6)–Si(1) | 1.855(7) | C(14)–Si(2) | 1.858(7) |
| C(3)–C(4) | 1.391(13) | C(11)–C(12) | 1.393(15) | Si(1)–C(7) | 1.839(11) | Si(2)–C(15) | 1.830(18) |
| C(4)–C(5) | 1.389(14) | C(12)–C(13) | 1.403(13) | Si(1)–C(8) | 1.847(12) | Si(2)–C(16) | 1.852(14) |
| C(5)–C(6) | 1.398(12) | C(13)–C(14) | 1.422(11) | Si(1)–C(9) | 1.842(11) | Si(2)–C(17) | 1.842(11) |
| C(6)–C(2) | 1.433(10) | C(14)–C(10) | 1.415(11) | | | | |
| C(6)–C(2)–C(3) | 109.7(7) | C(14)–C(10)–C(11) | 111.4(9) | C(5)–C(6)–C(2) | 103.4(7) | C(13)–C(14)–C(10) | 103.8(7) |
| C(2)–C(3)–C(4) | 108.8(8) | C(10)–C(11)–C(12) | 108.2(9) | C(5)–C(6)–Si(1) | 125.8(6) | C(13)–C(14)–Si(2) | 125.2(6) |
| C(3)–C(4)–C(5) | 106.2(8) | C(11)–C(12)–C(13) | 107.2(9) | C(2)–C(6)–Si(1) | 128.5(6) | C(10)–C(14)–Si(2) | 128.6(6) |
| C(4)–C(5)–C(6) | 112.0(8) | C(12)–C(13)–C(14) | 109.4(8) | | | | |
| (*iii*) In the pentafluorophenyl group | | | | | | | |
| C(18)–C(19) | 1.359(12) | C(21)–C(22) | 1.333(20) | C(19)–F(1) | 1.351(12) | C(22)–F(4) | 1.377(12) |
| C(19)–C(20) | 1.370(16) | C(22)–C(23) | 1.381(14) | C(20)–F(2) | 1.350(12) | C(23)–F(5) | 1.340(10) |
| C(20)–C(21) | 1.351(21) | C(23)–C(18) | 1.394(11) | C(21)–F(3) | 1.339(16) | | |
| C(19)–C(18)–C(23) | 113.3(8) | C(20)–C(21)–C(22) | 118.9(12) | C(19)–C(20)–C(21) | 119.2(11) | C(22)–C(23)–C(18) | 122.1(9) |
| C(18)–C(19)–C(20) | 125.2(10) | C(21)–C(22)–C(23) | 121.3(11) | C(19)–C(18)–Nb | 121.4(6) | C(23)–C(18)–Nb | 125.1(6) |
| (*iv*) In the carbonyl group | | | | | | | |
| C(1)–O(1) | 1.034(9) | Nb–C(1)–O(1) | 175.0(7) | | | | |

* $c_{g1}$ = Centroid of the C(2)—C(6) ring; $c_{g2}$ = centroid of the C(10)—C(14) ring.

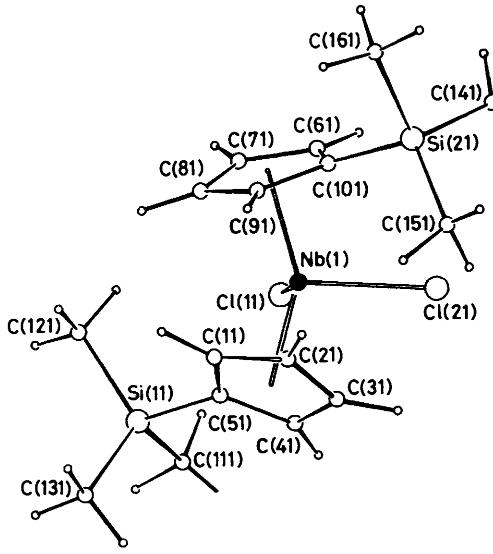


**Figure 1.** View of one of the two independent molecules of [Nb($\eta$-$C_5H_4SiMe_3$)$_2$$Cl_2$] (**2**) with the atomic numbering scheme

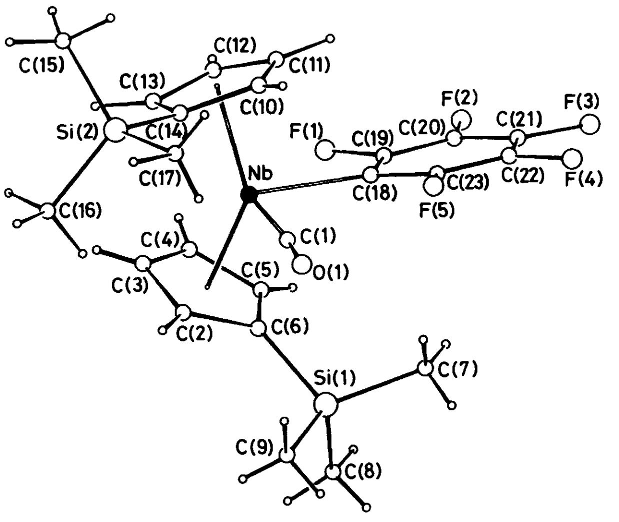


**Figure 2.** View of the complex [Nb($\eta$-$C_5H_4SiMe_3$)$_2$($C_6F_5$)(CO)] (**2f**) with the atomic numbering scheme

agreement with data reported[13] for other oxo niobium derivatives. The absorption at *ca.* 870 cm$^{-1}$ for complexes (**2l**) and (**2m**) must be assigned[17] to the $\nu$(O–O) vibration of a peroxo group, and two additional absorptions at 525 and 545 cm$^{-1}$ are observed which are probably due to the $\nu_{sym}$($NbO_2$) and $\nu_{asym}$($NbO_2$) vibrations respectively.

The $^1H$ n.m.r. spectra for all the unsubstituted cyclopentadienyl niobium(III) complexes show one singlet at $\delta$ 4.39—4.75 p.p.m. The $^{13}C$ spectra of complexes containing mono- and di-substituted rings with different ligands on the reflection plane of the ring show the expected[2] five resonances due to the non-equivalent ring carbon atoms. The chemical shift observed for the $C^1$ atom in the monosubstituted ring reveals the negative mesomeric effect of the $SiMe_3$ group[15] which is partially compensated by the substituent on $C^3$ acting as a more electron-donating group in the disubstituted ring, so that both $SiMe_3$ groups are non-equivalent. The broad signals observed at $\delta$ 213.6 and 255.7 p.p.m. for complexes (**2a**) and (**3a**) are assigned to the CO carbon atom presumably broadened by the nuclear quadrupole moment of the niobium atom.[20]

The $^{19}F$ n.m.r. spectrum of complex (**2f**) shows five resonances due to five non-equivalent F atoms, probably due to rotation being sterically restricted and the $C_6F_5$ ring being not exactly perpendicular to the reflection plane of the cyclopentadienyl rings.

**Table 8.** Relevant bond distances (Å) and angles (°) in (**2h**)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (*i*) In the Nb co-ordination sphere | | | | | | | |
| Nb–O(1) | 1.720(7) | Nb–$c_{g1}$ | 2.186(16) | O(1)–Nb–C(1) | 95.0(6) | C(1)–N(b)–$c_{g1}$ | 101.1(7) |
| Nb–C(1) | 2.221(21) | Nb–$c_{g2}$ | 2.176(12) | O(1)–Nb–$c_{g1}$ | 112.5(5) | C(1)–Nb–$c_{g2}$ | 103.0(7) |
| | | | | O(1)–Nb–$c_{g2}$ | 112.0(4) | $c_{g1}$–Nb–$c_{g2}$ | 126.5(5) |
| (*ii*) In the (trimethylsilyl)cyclopentadienyl groups | | | | | | | |
| C(11)–C(21) | 1.38(2) | C(12)–C(22) | 1.40(2) | C(11)–Si(1) | 1.85(1) | C(12)–Si(2) | 1.86(1) |
| C(21)–C(31) | 1.37(2) | C(22)–C(32) | 1.39(2) | Si(1)–C(61) | 1.82(2) | Si(2)–C(62) | 1.84(2) |
| C(31)–C(41) | 1.37(3) | C(32)–C(42) | 1.37(2) | Si(1)–C(71) | 1.84(2) | Si(2)–C(72) | 1.81(2) |
| C(41)–C(51) | 1.38(2) | C(42)–C(52) | 1.38(2) | Si(1)–C(81) | 1.86(2) | Si(2)–C(82) | 1.80(2) |
| C(11)–C(51) | 1.40(2) | C(12)–C(52) | 1.39(2) | | | | |
| C(21)–C(11)–C(51) | 103(1) | C(22)–C(12)–C(52) | 104(1) | C(11)–Si(1)–C(61) | 107.9(7) | C(12)–Si(2)–C(62) | 108.8(7) |
| C(11)–C(21)–C(31) | 112(1) | C(11)–C(22)–C(32) | 111(1) | C(11)–Si(1)–C(71) | 107.1(7) | C(12)–Si(2)–C(72) | 109.3(9) |
| C(21)–C(31)–C(41) | 107(2) | C(22)–C(32)–C(42) | 107(1) | C(11)–Si(1)–C(81) | 112.9(7) | C(12)–Si(2)–C(82) | 108.8(8) |
| C(31)–C(41)–C(51) | 108(1) | C(32)–C(42)–C(52) | 108(1) | C(61)–Si(1)–C(71) | 108.6(8) | C(62)–Si(2)–C(72) | 111.2(9) |
| C(41)–C(51)–C(11) | 110(1) | C(42)–C(52)–C(12) | 111(1) | C(61)–Si(1)–C(81) | 109.9(9) | C(62)–Si(2)–C(82) | 107.7(9) |
| C(21)–C(11)–Si(1) | 128.2(9) | C(22)–C(12)–Si(2) | 127.5(9) | C(71)–Si(1)–C(81) | 110.3(8) | C(72)–Si(2)–C(82) | 111.0(9) |
| C(51)–C(11)–Si(1) | 127.9(9) | C(52)–C(12)–Si(2) | 128.2(9) | | | | |

* $c_{g1}$ = Centroid of the C(11)—C(51) ring; $c_{g2}$ = centroid of the C(12)—C(52) ring.

*Electrochemical Studies.*—The disubstituted complexes (**3a**) and (**3b**) were synthesized in order to compare their electrochemical behaviour with compounds containing mono- or un-substituted rings. The behaviour of the dichloro niobium(IV) complexes is similar to that described for those containing unsubstituted rings, equation (7).[2,21,22] Both

$$[\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl_2] \underset{-1\,e^-}{\overset{+1\,e^-}{\rightleftharpoons}} [\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl_2]^- \qquad (7)$$

$$R^1 = H,\ R^2 = SiMe_3,\ (\mathbf{2});\ R^1 = R^2 = SiMe_3,\ (\mathbf{3})$$

anionic species are stable as shown by the quasi-reversibility of the cyclic voltammetric data. The increasing substitution in the rings produces increasing potentials (see Table 5), indicating an increasing negative mesomeric effect of the $SiMe_3$ groups[15] stabilizing the l.u.m.o. orbital and decreasing the reducing capacity of the anionic species. This behaviour means that the corresponding cationic niobium(V) species, $[\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl_2]^+$, which would be generated by oxidation should have a higher oxidizing capacity.

The carbonyl niobium(III) complexes (**2a**) and (**3a**) show oxidation potentials of +0.34 and +0.46 V respectively, equation (8). These values are respectively 1.49 and 1.46 V

$$[\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl(CO)]^- \underset{-1\,e^-}{\overset{+1\,e^-}{\rightleftharpoons}} [\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl(CO)] \underset{+1\,e^-}{\overset{-1\,e^-}{\rightleftharpoons}} [\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2Cl(CO)]^+ \qquad (8)$$

higher than those in equation (7) corresponding to the same $\mathrm{Nb^{III/IV}}$ transformation, as a consequence of the stabilizing effect of the π-acceptor carbonyl ligand, which decreases the energy of the h.o.m.o. Moreover the reduction potentials of (**2a**) and (**3a**) are −1.16 and −1.35 V respectively, indicating that the CO group makes lower oxidation states more accessible. Another anodic peak is observed at +1.2 V in the oxidation of (**2a**) probably corresponding to the $\mathrm{Nb^{IV/V}}$ step. This value justifies the lack of stability of niobium(V) in this type of compound which show an oxidation potential +0.9 V higher.

The oxo-niobium(V) complexes (**2g**) and (**3g**) show similar behaviour with irreversible cathodic peaks at −1.8 and −1.82 V, equation (9). These values suggest the stability of $\mathrm{Nb^V}$ in the

$$[\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2(O)Cl] \xrightarrow{+1\,e^-} [\mathrm{Nb}(\eta\text{-}C_5H_3R^1R^2)_2(O)Cl]^- \qquad (9)$$

presence of the σ- and π-donor oxo ligand which increases the energy of the l.u.m.o. The consequent decrease of the energy of the h.o.m.o. leads to the oxidation process not being observed. Increasing $SiMe_3$ ring substitution therefore favours the

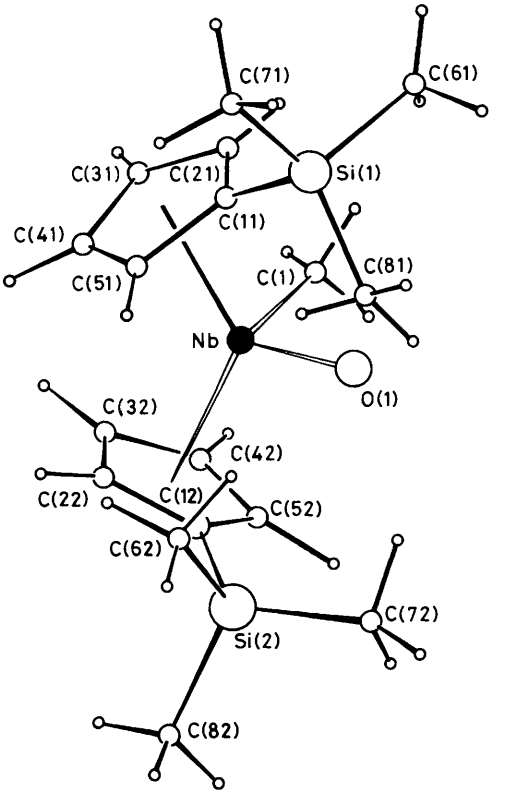


**Figure 3.** View of the complex $[\mathrm{Nb}(\eta\text{-}C_5H_4SiMe_3)_2(O)Me]$ (**2h**) with the atomic numbering scheme

stability of the lower oxidation states and decreases the stability of the higher oxidation states.

*Crystal Structures of* [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] (**2**), [Nb(η-$C_5H_4SiMe_3)_2(C_6F_5)$(CO)] (**2f**), *and* [Nb(η-$C_5H_4SiMe_3)_2$(O)-Me] (**2h**).—Crystals of (**2**) contain two crystallographically independent, but almost identical molecules. Views of one of them and of (**2f**) and (**2h**) are shown in Figures 1—3 respectively, together with the atomic numbering schemes; important bond distances and angles are given in Tables 6—8.

All complexes have a wedge-like sandwich configuration, the angles between the two cyclopentadienyl rings being 45.5(9) and 51.3(8)° in (**2**), 43.9(4)° in (**2f**), and 53.1(5)° in (**2h**). The environment of the Nb atom is completed by two Cl atoms in (**2**), by a terminal carbonyl group and a carbon atom from the $C_6F_5$ ligand in (**2f**), and by a terminal oxygen atom and a carbon atom from a methyl group in (**2h**). The Nb–C(cp) distances are 2.31(2)—2.48(3) Å in (**2**), 2.33(1)—2.43(1) in (**2f**), and 2.41(2)—2.52(2) Å in (**2h**), so that the $C_5H_4SiMe_3$ rings can be considered to be $\eta^5$-bonded to the metal.

If the structure of (**2**) is compared with that of [Nb(η-$C_5H_5)_2Cl_2$],[23] only insignificant differences can be noted in the Nb–$c_g$ ($c_g$ is the centroid of the cyclopentadienyl ring) distances [2.08(1) (av.) *vs.* 2.09 Å (av.)], in the $c_g$–Nb–$c_g$ angles [131.2(6) (av.) *vs.* 130.2° (av.)], and the Cl–Nb–Cl angles [84.5(7) (av.) *vs.* 85.6(1)° (av.)]. The introduction of the trimethylsilyl substituent into the cyclopentadienyl ring does not cause substantial modifications in the bonding to the metal, as already observed by Hitchcock *et al.*,[5] probably because the contribution of the cyclopentadienyl rings to the h.o.m.o.s for a $d^1$ [M(η-$C_5H_5)_2L_2$] type complex is small.

The structure of (**2f**), compared with [Nb(η-$C_5H_5)_2$(CO)-($SnCl_3$)] and [Nb(η-$C_5H_5)_2$(CO)($SnPh_3$)],[24] shows an enlargement of the $C_6F_5$–Nb–CO angle [93.4(3)°] with respect to the Sn–Nb–CO angles [85.2(5)—88.8(2)°], which could be attributable to the steric demand of the closer [Nb–C 2.294(7) *vs.* Nb–Sn 2.825(2) and 2.764(1) Å] and bulkier $C_6F_5$ ligand. In (**2h**) the Nb–O and Nb–$CH_3$ bonds [1.720(2) and 2.22(2) Å] are longer and comparable, respectively, to the corresponding bonds found in [Nb(η-$C_5H_5)_2O\{C_7H_5(CF_3)_2\}$][25] [1.63(3) and 2.27(4) Å], containing a σ-bonded substituted norbornadienyl ligand. The lesser *d*-electron density on the metal determining the reduced double-bond character of the Nb–O distance in (**2h**) can be attributable to the smaller σ-donating character of the methyl group with respect to that of the norbornadienyl ligand. The greater steric demand of this latter ligand seems to explain the larger O–Nb–C angle [99(5)°] compared with that observed in (**2h**) [95.0(6)°].

The complexes (**2h**) ($d^0$), (**2**) ($d^1$), and (**2f**) ($d^2$) offer the opportunity to observe the structural perturbations arising from the sequential addition of a single electron to a $d^0$ configuration. The average distances of the niobium atom to the ring centroid are 2.18(1), 2.08(1), and 2.04(1) Å respectively and the corresponding $c_g$–Nb–$c_g$ angles are 126.5(5), 131.2(6), and 139.3(3)°. The enlargement of these angles together with the shortening of the Nb–$c_g$ distances can be related to the increase in the number of *d* electrons. As already observed,[23,26] the distance of the metal atom to the centroid of the cyclopentadienyl ring decreases, in a series of $d^0$—$d^2$ metallocene [M($\eta^5$-$C_5H_5)_2L_2$] compounds, for a given ligand L, leading to stronger ring–ring and ligand–ring repulsions and consequently to larger ring–normal angles and narrower L–M–L angles: the reported (theoretical) L–M–L angles for $d^0$ complexes are in the range 94—97°, for $d^1$ 85—88°, and for $d^2$ 76—82°.[27]

In the present complexes, even with different auxiliary ligands, the metal–ring centroid distances and the $c_g$–Nb–$c_g$ angles follow the expected trend. The L–Nb–L angles decrease from $d^0$ [95.0(6)°] to $d^1$ [83.8(3)°], however, for the $d^2$ complex this angle is larger [93.4(3)°] than that expected, probably because the electronic and steric properties of the different ligands play an important role.

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*Received 4th August* 1987; *Paper* 7/1434