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Oxidation of niobocene dichloride to niobium(V) cationic species[1]

Richard J. Harrison [a,*], Malcolm G.H. Wallbridge [a], Eric DeBoer [b], David J. Duncalf [a], Andrew McCamley [a]

[a] *Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, UK*
[b] *Shell International Chemicals B.V., Amsterdam, Badhuisweg 3, 1031 CM Amsterdam, PO Box 38000, 1030 BN Amsterdam, Netherlands*

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Abstract

Oxidations of **1** using copper(II) dichloride and silver tetrafluoroborate produces a niobocene dichloride cation in $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2][CuCl_2]$ **1**, and a mixed halide cation in $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2(Cl)F][BF_4]$ **2**.

Keywords: Niobium; Oxidation

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1. Introduction

In recent years many groups have studied the use of Group 4 metallocene complexes as catalysts for alkene polymerisation [1] and insertion [2] reactions of olefins and particular emphasis has been placed on the involvement of cationic species in such processes [3]. As a result, this area of chemistry is reasonably well understood. Examples of Group 6 catalysts for alkene polymerisation are also known [4]. In contrast, relatively little is known about the properties of Group 5 metallocene compounds in these areas. Although niobocene and tantalocene derivatives of the type $[MCp_2X_2]$ (where X = halogen, alkyl, OR, etc.) are known, there is relatively little knowledge of their chemistry as catalysts apart from an appreciation of their instability towards both oxygen and moisture. Other Group 5 cationic metallocene compounds for example those of the type $[M(\eta^5\text{-}C_5H_4Bu^t)_2(XPh)_2]^+$ (where X = S, O or CH_2) are known [5] but have not been extensively worked on. Previous work in this area was hindered by the lack of a general entry point into niobocene chemistry. However work by Lappert and co-workers has described the convenient synthesis of neutral niobocene complexes of Nb(IV) such as $[Nb(\eta^5\text{-}C_5H_4R)_2Cl_2]$ (where R = H, or $SiMe_3$) [5].

The majority of known niobium(V) complexes exist as neutral moieties [6–8], but there are a small number of niobium species which exist in the ionic form, [9,10] and these complexes have usually been obtained by the oxidation of niobium(IV) compounds. This paper deals with the latter case, where the starting niobium(IV) complex is a neutral niobocene dichloride. Herein we describe the oxidation of such dichlorides using either copper(II) dichloride or silver tetrafluoroborate to produce a niobocene dichloride cation, or a mixed halide cation, respectively. The synthesis of Nb(V) complexes of the type $[Nb(\eta^5\text{-}C_5H_4R)_2X_2]^+$ (where X = halide) is of interest as the oxidised species representing the last stage in the synthetic procedure and the procedure offers a convenient route to these cationic derivatives. It is also known, as described in the work by Lappert,

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* Corresponding author. Present address: Department of Chemistry, University of York, Heslington, York YO10 5DD, UK.

[1] Dedicated to the memory of Andrew McCamley.

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Table 1
Crystal data and structure refinement for complexes **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{18}H_{26}Cl_4CuNb$	$C_{20}H_{30}BClF_5NbO$
Formula weight	540.64	520.61
Colour	Red	Sandy yellow
Temperature (K)	293(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/c$
Unit cell dimensions		
a (Å)	14.450(3)	13.5556(3)
b (Å)	7.980(2)	9.4839(2)
c (Å)	19.624(4)	17.68390(10)
α (°)	90	90
β (°)	111.60(3)	103.4060(10)
γ (°)	90	90
V (Å^3)	2103.8(7)	2211.49(7)
Z	4	4
$D_{calc.}$ (Mg m^{-3})	1.707	1.564
Absorption coefficient (mm^{-1})	2.062	0.715
F(000)	1088	1064
Crystal size (mm)	0.20 × 0.10 × .05	0.50 × 0.05 × .05
Theta range for data collection	2.79 to 28.50°	1.54 to 25.00°
Limiting indices	$-4 \leq h \leq 18$, $-1 \leq k \leq 10$, $-18 \leq l \leq 10$	$-14 \leq h \leq 18$, $-12 \leq k \leq 12$, $-22 \leq l \leq 23$
Reflections collected	1744	10675
Independent reflections	1726 [$R_{int} = 0.0677$]	3870 [$R_{int} = 0.0906$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1726/0/217	3870/0/258
Goodness-of-fit on F^2	1.0350	0.967
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0480$, $wR_2 = 0.1189$ (for 1210 reflections)	$R_1 = 0.0545$, $wR_2 = 0.0914$ (for 2269 reflections)
R indices (all data)	$R_1 = 0.0885$, $wR_2 = 0.1571$	$R_1 = 0.1234$, $wR_2 = 0.1171$
Largest diff. peak and hole (e Å^{-3})	0.351 and −0.388	0.492 and −0.530

[5] Antinolo [11] and McCamley [12] that the dialkyl cations can also be synthesised via oxidation of the neutral dialkyl Nb(IV) complex.

2. Experimental

2.1. General experimental details

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under either an atmosphere of argon, or in a dry-box under an atmosphere of nitrogen. All solvents were purified and dried by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere, light-petroleum ether (40–60°C) and THF over molten potassium. Other materials were purchased from commercial sources and used without further purification. Celite and glassware were flame dried in vacuo prior to use.

Nuclear magnetic resonance spectra were recorded using a Bruker WH-400 spectrometer. Spectra were referenced using the resonances of residual protons in the deuterated solvents. IR spectra were recorded using a Perkin-Elmer 1720X FTIR spectrometer using CsI plates. Microanalyses were obtained using a Leeman Labs CE440 analyser.

2.2. Preparation of $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2][CuCl_2]$ **1**

A sample of $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2]$ (0.30 g, 0.74 mmol) in THF (50 cm^5) was treated with a suspension of copper(II) chloride (0.11 g, 0.82 mmol) at 0°C. The red solution was stirred for 18 h, after which THF was removed under reduced pressure. The resulting red product was extracted with THF, and filtered through celite. After concentrating (15 cm^3), the solution was cooled to −30°C. The supernatant solution was decanted from the resultant red solid, was washed with light-petroleum ether and dried in vacuo. (Yield 0.19 g, 85%); m.p. 156–158°C; (Found: C, 40.48; H, 4.56. $C_{18}H_{26}Cl_4CuNb$ requires C, 39.99; H, 4.85%); ^{1}H-NMR, δ (acetone (d$_6$)) 7.42 (8H, s, C_5H_4) and 1.48 (18H, s, CH_3); ^{13}C, δ (acetone (d$_6$)) 139.26 (C_q, C_5H_4), 101.35 (C_5H_4), 95.51 (C_5H_4), 32.05 (C_q, CMe_3), 31.20 (CH_3); m/z (FAB) 522 (M^+, 20%), 405 ($M^+ - CuCl_2^+$, 61), 387 (100), 370 ($Nb(C_5H_4Bu^t)_2Cl^+$, 31) and 336 ($Nb(C_5H_4Bu^t)_2^+$, 7).

2.3. Preparation of [Nb(η^5-$C_5H_4Bu^t$)$_2$(Cl)F][BF$_4$] **2**

A sample of [Nb(η^5-$C_5H_4Bu^t$)$_2Cl_2$] (0.30 g, 0.7 mmol) in THF (100 cm^3) was treated with a solution of silver tetrafluoroborate (0.16 g, 0.83 mmol) at 0°C. The resulting red solution was stirred for 42 h, after which THF was removed under reduced pressure. The resulting green product was extracted with THF, and filtered through celite. After concentrating (15 cm^3), the solution was cooled to -30°C. The supernatant solution was decanted from the resultant green crystals **2**, which were washed with light-petroleum ether and dried in vacuo. (Yield 0.22 g, 86%); m.p. decomposes 160°C; (Found: C, 45.01; H, 5.92. $C_{18}H_{26}BClF_5Nb$ requires C, 45.37; H, 5.50%); ^{1}H-NMR δ (CD_2CN) 7.71 (1H, quart, $J\{HH\} = 2.96$, C_5H_4), 7.24 (1H, quart, $J\{HH\} = 2.96$, C_5H_4), 6.82 (1H, quart, $J\{HH\} = 2.96$, C_5H_4), 6.42 (1H, quart, $J\{HH\} = 1.96$, C_5H_4) and 1.28 (18H, s, CH_3); ^{13}C δ (CD_2CN) 115.82 (C_q, C_5H_4), 107.59 (C_5H_4), 35.96 (C_q, CMe_3) and 29.51 (CH_3); ^{19}F δ (CD_2CN) -147.33 (Nb–F) and -150.38 (BF_4).

2.4. Crystal structure determination

A suitable single crystal was quickly coated in nujol, glued to a quartz fibre and cooled to in the cold nitrogen gas stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection. Crystal data for all complexes were collected on a Siemens diffractometer, equipped with a SMART CCD area detector, operating with Mo–K$_\alpha$ graphite monochromatised radiation ($\lambda = 0.71073$ Å), fitted with an Oxford Cryosystems Cryostream Cooler.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å $\times 10^3$) for [Nb(η^5-$C_5H_4Bu^t$)$_2Cl_2$][$CuCl_2$] **1**

	x	*y*	*z*	*U*(eq)*
Nb	5368.7(6)	5776.3(10)	7683.8(9)	18(1)
Cu	6965.8(10)	8567.8(17)	3318.5(13)	34(1)
Cl(1)	5958(2)	3205(3)	7414(3)	40(2)
Cl(2)	6825.3(17)	7343(3)	7998(3)	30(2)
Cl(3)	7211(3)	7934(5)	4406(4)	62(2)
Cl(4)	6721(2)	9165(3)	2220(3)	33(2)
C(1)	4651(7)	6582(13)	8554(10)	18(6)
C(2)	4301(8)	4945(15)	8286(11)	31(7)
C(3)	5123(8)	3891(13)	8567(11)	31(7)
C(4)	5965(7)	4816(14)	8976(10)	24(6)
C(5)	5662(8)	6503(14)	8990(11)	21(7)
C(6)	6235(8)	7855(16)	9525(12)	27(7)
C(7)	5873(11)	7700(2)	10172(14)	43(9)
C(8)	7359(8)	7592(15)	9828(11)	42(7)
C(9)	5981(8)	9618(14)	9178(12)	46(8)
C(10)	4517(7)	5563(13)	6340(10)	20(7)
C(11)	38309(7)	5688(13)	6683(11)	28(7)
C(12)	3918(7)	7308(12)	7000(10)	20(6)
C(13)	4691(7)	8142(11)	6853(9)	13(6)
C(14)	5070(7)	7074(13)	6451(10)	20(7)
C(15)	5776(8)	7522(13)	6049(12)	28(7)
C(16)	6254(8)	9266(13)	6309(10)	26(6)
C(17)	6587(8)	6161(14)	6158(11)	33(7)
C(18)	5111(9)	7604(15)	5255(11)	29(7)

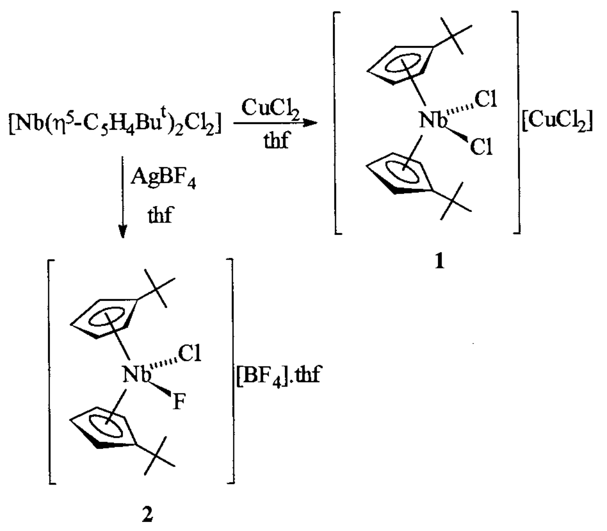
* *U*(eq) is defined as one third of the trace of the orthogoanlized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å $\times 10^3$) for [Nb(η^5-$C_5H_4Bu^t$)$_2$(Cl)F][BF$_4$] **2**

	x	*y*	*z*	*U*(eq)*
Nb(1)	7686.8(4)	7014.5(6)	−4275.7(3)	24(1)
B(1)	8477(6)	8498(8)	−825(5)	36(3)
F(1)	7506(3)	8883(5)	−1155(3)	77(2)
F(2)	8543(3)	8226(5)	−45(2)	70(1)
F(3)	8741(3)	7274(3)	−1193(2)	38(1)
F(4)	9141(4)	9543(4)	−887(3)	87(2)
Cl(2)	7459.7(16)	4843.4(18)	−3706.2(10)	56(1)
F(5)	6305(3)	7527(4)	−4648(2)	44(1)
O(2)	10 000	5501(7)	2500	63(2)
C(1)	7723(5)	7531(6)	−5607(3)	30(2)
C(2)	8713(5)	7629(7)	−5154(4)	35(2)
C(3)	9004(5)	6277(7)	−4859(4)	31(2)
C(4)	8201(5)	5340(6)	−5153(3)	26(2)
C(5)	7396(5)	6102(6)	−5623(3)	25(2)
C(6)	6425(5)	5489(7)	−6112(4)	30(2)
C(7)	6692(5)	4886(7)	−6844(3)	46(2)
C(8)	6007(5)	4297(8)	−5676(4)	52(2)
C(9)	5590(5)	6598(7)	−6361(4)	47(2)
C(10)	7654(4)	7910(6)	−2989(3)	26(1)
C(11)	8646(5)	7397(6)	−2973(3)	30(2)
C(12)	9067(5)	8227(6)	−3463(3)	28(2)
C(13)	8332(5)	9260(6)	−3806(3)	27(2)
C(14)	7478(5)	9106(6)	−3473(3)	25(2)
C(15)	6585(5)	10 118(6)	−3568(4)	34(2)
C(16)	5637(5)	9403(7)	−3411(4)	48(2)
C(17)	6941(6)	11 266(7)	−2951(4)	55(2)
C(18)	6342(5)	10 806(7)	−4377(4)	47(2)
C(1S)	9657(7)	6377(9)	3020(5)	69(3)
C(2S)	9964(8)	7817(9)	2911(5)	93(3)

* *U*(eq) is defined as one third of the trace of the orthogoanlized U_{ij} tensor.

Semi-empirical absorption correction was carried out based upon psi scans. The structure solutions were carried out using SHELXTL PLUS software on a Silicon Graphics Indy workstation [13]. The niobium atom positions were determined by the Patterson method. Subsequent Fourier difference syntheses revealed the positions of the other non-hydrogen atoms. Refinements were carried out with SHELXL 93 [14] software on an Elonex 486DX computer, minimising on the weighted *R* factor wR_2 (where $R = \Sigma|F_o - F_c|/\Sigma F_o$ (for $F_o \geq 4\sigma(F_o)$) and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$). The weighting scheme used was of the form $w = 1/\sigma^2(F_o^2) + aP^2 + bP$ (where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, where $\max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms



Scheme 1. Preparation of complexes **1** and **2**.

were placed in calculated positions and refined, with fixed isotropic thermal parameters ($U = 0.08$ Å^3). Crystal and structure refinement data for complexes **1** and **2** are contained in Table 1, whilst thermal parameters for **1** and **2** are given in Table 2 and Table 3, respectively.

Suitable crystals for an X-ray diffraction analysis of **1** were grown by cooling the supernatant to −30°C, yielding red crystals of the monoclinic space group $P2_1/n$. Crystals of the monofluoride complex **2** were grown from the partially soluble fraction by cooling to −30°C, and a suitable crystal was obtained for single X-ray diffraction analysis. Additional data available from the Cambridge Crystallographic Data Centre comprise H-atom coordinates and thermal parameters.

3. Results and discussion

3.1. Synthesis and characterisation

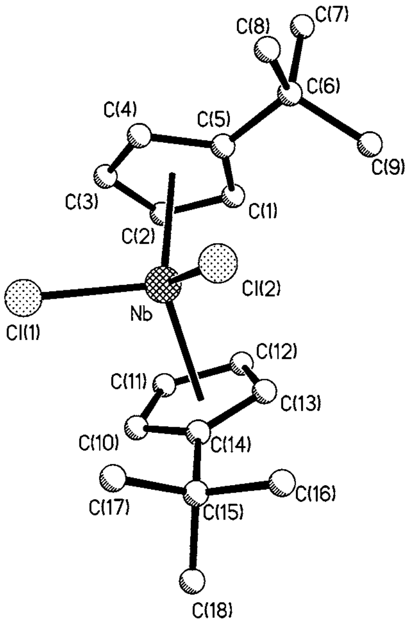


Fig. 1. Molecular structure of the cation in the ionic complex $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2][CuCl_2]$ **1**.

$$[NbCp'_2Cl_2] \xrightarrow[AgBF_4]{\text{Oxidation}} [NbCp'_2Cl_2][BF_4] \xrightarrow[BF_4^-]{F^-\text{abstraction}} [NbCp'_2(Cl)F][BF_4]$$

$$Cp' = \eta^5\text{-}C_5H_4Bu^t$$

Scheme 2. Possible reaction pathway for the preparation of **2**.

In this work we have investigated the use of $CuCl_2$ as a possible oxidising agent. When $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2]$ **(A)** was treated with a suspension of anhydrous copper(II) chloride, the initial brown THF solution immediately turned bright red. Upon work-up the reaction yielded fine red micro-crystals of **1**, containing the copper(I) anion $[CuCl_2]^-$ in high yield. The mass spectroscopy data for **1**, obtained using fast atom bombardment (FAB) and 2-nitrobenzyl alcohol (Noba) as a matrix, gave a peak at $m/z = 405$ consistent with the loss of $CuCl_2$, from the parent ion. Peaks at $m/z = 407$ and 409 were also observed, consistent with a complex containing $^{35}Cl/^{37}Cl$ isotopes, $[\{M+2\}-CuCl_2]$ and $[\{M+4\}-CuCl_2]$, respectively. The peaks were of appropriate intensity for a dichloride complex containing the chlorine isotopes. Peaks at $m/z = 370$ and 336 were assigned as the loss of one and two chloride ligands, respectively the latter with addition of a proton. The ^{1}H-NMR spectrum showed one broad resonance for the cyclopentadienyl protons.

Other examples of similar copper(II) reactions are with either a molybdocene or rhenocene dihydride. Bulychev and co-workers [15] were able to reduce copper(II) chloride by using rhenium biscyclopentadienyl hydride, which liberates the rhenocene cation $[ReCp_2][CuCl_2]$ and hydrogen gas. Unlike the redox reaction involving niobocene (Scheme 1), the oxidation state of rhenium atom remains unaltered (+3), due to the loss of a hydride ligand, whilst the copper(II) chloride is reduced. Whereas the reaction of $[MoCp_2H_2]$

Table 4
bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)			
Nb–cent(1)	2.116	Nb–cent(2)	2.120
Nb–Cl(1)	2.356(3)	Nb–Cl(2)	2.328(2)
Cu–Cl(3)	2.092(7)	Cu–Cl(4)	2.107(5)
Bond angles (°)			
Cent(1)–Nb–cent(2)	130.9	Cl(1)–Nb–Cl(2)	99.24(10)
Cent(1)–Nb–Cl(1)	104.9	Cent(2)–Nb–Cl(1)	106.0
Cent(1)–Nb–Cl(2)	106.0	Cent(2)–Nb–Cl(2)	105.5
Cl(3)–Cu–Cl(4)	179.1(2)		

Table 5
Principal bond lengths (Å) and angles (°) for **2**

Bond length (Å)			
Nb–cent(1)	2.097	Nb–cent(2)	2.096
Nb–Cl(2)	2.344(2)	Nb–F(5)	1.899(3)
Bond angle (°)			
Cent(1)–Nb–cent(2)	131.5	Cl(2)–Nb–F(5)	99.02(12)
Cent(1)–Nb–F(5)	104.7	Cent(2)–Nb–F(5)	104.8
Cent–Nb–Cl(2)	107.0	Cent(2)–Nb–Cl(2)	105.2

with copper(II) chloride yields $[(Cp_2MoH)_2H][CuCl_2]$ and hydrogen gas.

When **A** is reacted with a slight excess of silver tetrafluoroborate in THF, the expected niobocene dichloride cation is not obtained. Instead a partially insoluble yellow–green solid is obtained, and this has been shown to contain an Nb–F bond, formed by abstraction of a fluorine from the tetrafluoroborate anion (Scheme 1).

The mixed complex **2** was identified by NMR and mass spectrometry. The ^{19}F-NMR spectrum showed two resonances at −147.33 (Nb–F) and −150.38 (B–F), whilst mass spectrometry showed three principal ions at $m/z = 506$ $Nb(C_5H_4Bu^t)_2F^+ + Noba$, 354 $Nb(C_5H_4Bu^t)_2F^+$, and a peak at 373 for which an exact assignment was not possible. ^{1}H-NMR established the existence of a solvate THF molecule in the crystal lattice, H_α 1.81ppm and H_β 3.65ppm, and the resonances were shifted downfield compared to free THF. The solvent molecule was also seen in the molecular structure of **1**.

Other oxidation-fluoride abstraction reactions are known to occur, for example Antiñolo et al. have described and structurally characterised the oxidation of $[Nb(C_5H_4SiMe_3)_2(\eta^2\text{-}C,N)\text{-}Ph_2CCNPh)]$ with fluoroboric acid to form $[Nb(C_5H_4SiMe_3)_2F(\eta^2\text{-}\{C,N\}\text{–}Ph_2CCNPh)][BF_4]$ [16].

The formation of the fluorinated cation is thought to proceed through a two step reaction, oxidation then fluoride abstraction. Thus one possible reaction pathway for the synthesis of **2** is shown in Scheme 2.

3.2. Single crystal X-ray studies

The oxidation of niobocene dichloride and the subsequent reduction of copper(II) is very unusual and **1** represents the first structurally characterised example of such a complex. The molecular structure of the oxidised dichloride cation is illustrated in Fig. 1. The ligands adopt a distorted tetrahedral orientation around the central niobium atom, and the *tert*-butylcyclopentadienyl rings are bound in a staggered orientation. The average Nb-centroid distance is 2.118 Å, slightly longer than other niobocene dichlorides of a similar nature, e.g. $[NbCp_2Cl_2][SbF_6]$ 2.087 Å, [17] and $[Nb(C_5H_4Bu^t)_2Cl_2]$ 2.099 Å [18]. The angle defined by the vectors connecting the centroids of the cyclopentadienyl rings is 130.9°, comparable with $[NbCp_2Cl_2][SbF_6]$ 131°, and $[Nb(C_5H_4Bu^t)_2Cl_2]$ 129.2°. Selected bond lengths and angles are presented in Table 4. The Nb–Cl bond distances at 2.356(3) and 2.328(2) Å, are comparable with other niobium–chloride bonds found in other simple Group 5 chloride complexes (Table 6). The Cl–Nb–Cl bond angle of 99.24(10)° is slightly larger that expected for a d^o system, as predicted by the Alcock model [19]. The angles in other oxidised examples of niobocene dichlorides similar in nature to **1** are $[NbCp_2Cl_2][SbF_6]$ 98.10(5) [17], $[NbCp_2Cl_2]$-$[BF_4]\cdot CH_3CN$ 97.6(1) [20] and $[NbCp_2Cl_2]_4^+[WF_6]^{2-}$-$[WCl_6]^{2-}$ 98.8(6)° [21]. The Cl–Cu–Cl angle in **1** is essentially linear 179.1(2)°, and comparable to the angle in the related complex $[ReCp_2][CuCl_2]$ 174.80(15)°. As expected, the Cu–Cl bond lengths are approximately equal at 2.092(7) and 2.107(5) Å, respectively.

The basic pseudo-tetrahedral geometry for the cation in **2** is typical of a $[MCp_2XY]$ type complex with observed bond lengths and angles being unexceptional (Table 5). The structure of **2** shows a niobium atom (oxidation state +5) bonded to two cyclopentadienyl groups, with *tert*-butyl substitutents attached, as illustrated in Fig. 2. The cyclopentadienyl rings are orientated in a partially eclipsed geometry, as indicated by the torsion angle between the two planes, C(5)–cent(1)–cent(2) and cent(1)–cent(2)–C(14), 44.7°. The consequence of the much larger chloride ligand on the increased steric repulsions is seen in the conformation adopted by the *tert*-butyl groups. The angle between the two planes (55.4°) is much smaller than that in the corresponding dichloride cation $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2]^+$. Since the fluoride is more electro-negative than the chloride, it would be expected that the fluoride would increase the centroid-Nb-centroid angle, because of the presence of a better donor in the bisecting plane, resulting in enhanced repulsions between the rings [16,22]. This is partially borne out in structures **1** and **2**. An increase of 0.6° is noted in the centroid-Nb-centroid angle on changing from the dichloride complex **1**, to the monochloride complex **2**. This can be attributed to the fluoride ligand removing electron density from the cyclopentadienyl rings, thus allowing them to adopt a sterically hindered conformation [23]. Crystallographically determined Cp_2Nb–F bond lengths are rare, other examples are also the result of oxidation–fluoride abstraction reactions. Comparison of the Nb–F bond length in **2** {1.899(3) Å} with other such examples shows a very close relationship, e.g. $[Nb(CpMe)_2(CH_2SiMe_3)F][PF_6]$, 1.910(2) [24], $[Nb(C_5H_4SiMe_3)_2F(\eta^2\text{-}(C,N)\text{-}Ph_2CCNPh)][BF_4]$, 2.199(5) [16], $[Nb(C_5Me_4Et)_2F_2]$ $[PF_6]$, average 1.913 [22] and $[Nb(C_5Me_4Et)_2(Cl)F][PF_6]$, 2.269(2) Å [22] (also see

Table 6
Selected data for other related Nb–Halide containing complexes

Complex		X–Nb–X	Nb–X	Ref.
$[Nb(\eta^5\text{-}C_5H_4Bu^t)_2(Cl)F][BF_4]$	*Nb–F, Nb–Cl*	99.02(12)	1.899(3), 2.344(2)	This work
$[Nb(L)O(F)]$ (L = porphyrinate)	*Nb–F*		1.888(3)	[23]
$[Nb(C_5Me_4Et)_2F_2][PF_6]$	*Nb–F*	102.3(4)	1.920(8), 1.906(10)	[26]
$[Nb(C_5Me_4Et)_2F(Cl)][PF_6]$	*Nb–F, Nb–Cl*	96.8(1)	2.269(2), 2.352(2)	[26]
$[Nb(C_5H_4Me)_2F(CH_2SiMe_3)][PF_6]$	*Nb–F*	99.8(1)	1.910(2)	[24]
$[Nb(C_5H_4SiMe_3)_2F(\eta^2\text{-}(C,N)\text{-}Ph_2CCNPh)][BF_4]$	*Nb–F*		2.199(5)	[16]
$[NbF_7][K_2]$	*Nb–F*		1.940–1.978	[27]
$[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2][CuCl_2]$	*Nb–Cl*	99.24(10)	2.356(3), 2.328(2)	This work
$[Nb(C_5H_4SiMe_3)_2Cl(\eta^2\text{-}(C,N)\text{-}Ph_2CCNPh)][BF_4]$	*Nb–Cl*		2.468(2)	[16]
$[Nb(C_5H_4Bu^t)_2Cl_2]$	*Nb–Cl*	84.15(6)	2.483(2)	[18]
$[NbCp_2Cl_2]$	*Nb–Cl*	85.70(0.2)	2.464(5), 2.475(4)	[25]
$[Nb(C_5H_4SiMe_3)_2Cl_2]$	*Nb–Cl*	84.8(2)	2.461(2)	[28]
$[Nb(C_5Me_4Et)_2Cl_2]$	*Nb–Cl*	85.2(1)	2.461(2)	[26]
$[NbCp_2Cl_2][SbF_6]$	*Nb–Cl*	98.10	2.341	[17]
$[NbCp_2Cl_2][BF_4]\cdot CH_3CN$	*Nb–Cl*	97.6(1)	2.43(1)	[20]
$[NbCp_2Cl_2]_4[WF_6]_2^-[WCl_6]^{2-}$	*Nb–Cl*	98.8(6)	2.34(2)	[21]

Table 6). In the last example the structure solution required the occupation of one chloride site by 1/3 of a fluoride, and this example is not a true representation of a Nb–F bond, producing a longer than normal Nb–F bond, but a shorter than average Nb–Cl bond. The complex is the result of co-crystallization of the complexes $[Nb(C_5Me_4Et)_2F_2][PF_6]$ and $[Nb(C_5Me_4Et)_2Cl_2][PF_6]$. In **2** the angle Cl–Nb–F 99.02(12)°, is also unexceptional and similar to that in $[Nb(C_5H_4Me)_2(CH_2SiMe_3)F][PF_6]$ at 99.8(1)°. The bond lengths and angles in the $[BF_4]^-$ anion are unremarkable and consistent with other such examples [20,25]. A THF molecule is also contained within the crystal lattice, but is too far from the Nb centre (11.7 Å (Nb to O distance)) to interact. Formation of **2** requires F/Cl exchange of the BF_4 anion, although no crystallographic evidence was noted for the formation of mixed ligand anions of the type $[BCl_xF_{4-x}]$.

In summary, the use of $CuCl_2$ for the oxidation of the niobocene(IV) dichloride affords a convenient synthesis of the niobium(V) cation, $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2Cl_2]^+$, while the use of $AgBF_4$ results in the formation of the corresponding niobium(V) mixed halide cation. Both reactions occur in high yield.

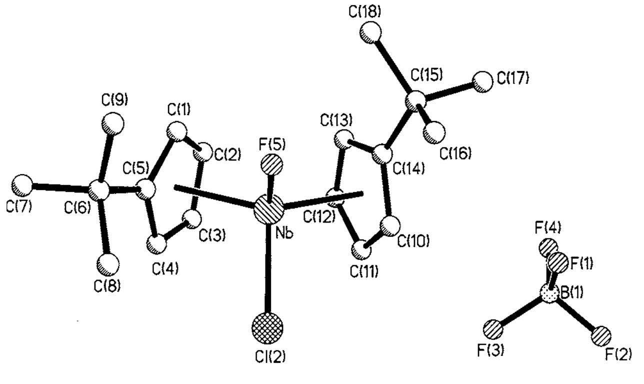


Fig. 2. Molecular structure of the cation in the ionic complex $[Nb(\eta^5\text{-}C_5H_4Bu^t)_2(Cl)F][BF_4]$ **2**.

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References

[1] R.F. Jordan, C.S. Bajgur, R. Willettand, B. Scott, J. Am. Chem. Soc. 108 (1986) 7410.
[2] T. Woo, L. Fan, T. Ziegler, Organometallics 13 (1994) 432.
[3] M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255.
[4] A. Bell, P. Clegg, P.W. Dyer, M.R.J. Elsegood, V.C. Gibson, E.L. Marshall, J. Chem. Soc. Chem. Commun. (1994) 2547.
[5] P.B. Hitchcock, M.F. Lappert, M.C.R.C. Milne, J. Chem. Soc. Dalton Trans. (1981) 180.
[6] D.N. Williams, J.P. Mitchell, A.D. Poole, et al., J. Chem. Soc. Dalton Trans. (1992) 739.
[7] J.D. Fellman, G.A. Rupprecht, C.D. Wood, R.R. Schrock, J. Am. Chem. Soc. 100 (1978) 5964.
[8] J.M. Mayer, C.J. Curtis, J.E. Bercaw, J. Am. Chem. Soc. 106 (1984) 4749.
[9] This work.
[10] G.R. Wiley, M.L. Butcher, T.J. Woodman, M.G.B. Drew, J. Chem. Soc. Chem. Commun. (1994) 2721.
[11] A. Antinolo, M. Farjardo, S. Garcia-Yuste, et al., J. Chem. Soc. Dalton Trans. (1995) 3409.
[12] D.J. Duncalf, R.J. Harrison, A. McCamley, B.W. Royan, J. Chem. Soc. Chem. Commun. (1995) 2421.
[13] G.M. Sheldrick, SHELXTLPLUS, Siemens Analytical Instruments, Madison, WI, 1990 and 1994.
[14] G.M. Sheldrick, SHELXL93, University of Göttingen, 1993.
[15] V.M. Ishchenko, B.M. Bulychev, G.L. Soloveichik, V.K. Bel'sky, O.G. Ellert, Polyhedron 3 (1984) 771.
[16] A. Antinolo, M. Fajardo, R. Gil-Sanz, et al., Organometallics 12 (1993) 381.

[17] P. Gowik, T. Klapotke, J. Pickardt, Organometallics 8 (1989) 2953.

[18] T.J. Miller, A. McCamley, W. Clegg, Acta Crystallogr. Sect. C 50 (1994) 33.

[19] N.W. Alcock, J. Chem. Soc. Sect. A (1967) 2001.

[20] K.H. Thiele, W. Kabuki, J. Sieler, H. Borrmann, A. Simon, Z. Anorg. Allg. Chem. 587 (1990) 80.

[21] A. Schulz, T.M. Klapotke, T.S. Cameron, P.K. Bakshi, J. Organomet. Chem. 480 (1994) 191.

[22] M.M. Kubicki, R. Kergoat, J.E. Guerchais, I. Bkouche-Waskman, C. Bois, P.L. O'Haridon, J. Organomet. Chem. 219 (1981) 329.

[23] C. Lecomte, J. Protas, P. Richard, J.M. Barle, R. Guilard, J. Chem. Soc. Dalton Trans. (1982) 247.

[24] P.F. Fu, M.A. Khan, K.M. Nicholas, Organometallics 11 (1992) 2607.

[25] K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, G.V. Rees, Acta Crytallogr. Sect. B 30 (1974) 2290.

[26] H. Brunner, G. Gehart, W. Meier, et al., Organometallics 13 (1994) 134.

[27] G.M. Brown, L.A. Walker, Acta Crystallogr. Sect. B. 20 (1996) 220.

[28] A.M.M. Lanfreidi, A. Tiripicchio, M. Kapon, G.M. Reisner, J. Chem. Soc. Dalton Trans. (1990) 375.