DALTON
FULL PAPER

Synthesis and reactions of (*tert*-butylimido)bis(η-cyclopentadienyl)niobium cations: NMR evidence for d^0 olefin cations $[Nb\{(\eta\text{-}C_5H_5)_2\}(N^tBu)(\eta\text{-}C_2H_4)][B(C_6F_5)_4]$ and $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(N^tBu)(\eta\text{-}C_2H_3Me)][B(C_6F_5)_4]$

Martin J. Humphries, Richard E. Douthwaite and Malcolm L. H. Green *

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

Received 22nd May 2000, Accepted 5th July 2000
Published on the Web 9th August 2000

The new (*tert*-butylimido)η-cyclopentadienylniobium compounds $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ **1***, $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(PMe_3)][O_3SCF_3]$ **2***, $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)][MeB(C_6F_5)_3]$ **3**, $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)][B(C_6F_5)_4]$ **4**, $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(\eta\text{-}C_2H_4)][B(C_6F_5)_4]$ **5**, $[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(O_3SCF_3)]$ **6**, $[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)][B(C_6F_5)_4]$ **7**, $[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(\eta\text{-}C_2H_4)][B(C_6F_5)_4]$ **8** and $[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(\eta\text{-}C_3H_6)][B(C_6F_5)_4]$ **9** have been prepared and characterised; * indicates the crystal structure has been determined.

Introduction

The imido ligand has found widespread use in the chemistry of the early transition metals both due to its isoelectronic relationship with the cyclopentadiene ligand and the ease with which derivatives of differing bulk and electronic properties can be synthesized by variation of the group attached to the nitrogen atom. As such, the literature concerning these complexes is extensive, however it has been reviewed within the past few years.[1] Of particular interest to us were those complexes in which co-ordinatively unsaturated imido complexes of vanadium,[2,3] tantalum[4] and zirconium[5–7] have displayed reactivities including C–H activation.

The molecular fragments $[Zr(\eta\text{-}C_5H_5)_2(N^tBu)]$ and the cation $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)]^+$ are isoelectronic. The neutral transient $[Zr(\eta\text{-}C_5H_5)_2(N^tBu)]$ has been associated with the activation of the C–H bond in benzene and cycloaddition reactions with alkenes and alkynes.[6,7] The presence of a co-ordinatively unsaturated, highly electrophilic niobium atom in the cation $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)]^+$ could lead to high reactivities in comparable reactions and the greater electrophilicity of the metal centre could lead to the cationic niobium compounds being more reactive than their neutral zirconium analogues.

During the course of the work described below two *ansa*-bridged compounds $[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(HNMe_2)(N^tBu)][BPh_4]$[8] and $[Nb\{(\eta\text{-}C_5H_4)CMe_2(\eta^3\text{-}C_9H_7)\}(HNMe_2)(N^tBu)][BPh_4]$[9] have been reported, as well as the tantalum compound $[Ta(\eta\text{-}C_5Me_5)_2(N^tBu)(THF)][B(C_6F_5)_4]$.[10] Here we describe further studies on derivatives of the $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)]^+$ cation.

Results and discussion

Treatment of $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)Cl]$[11,12] with AgO_3SCF_3 yielded $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ **1** as slightly air- and moisture-sensitive orange crystals that were soluble in all common non-protic organic solvents. The analytical and spectroscopic data which characterise the compound **1**, and all the other new compounds described in this work, are given in Table 1. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are consistent with both of the possible formulations, $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ and $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)][O_3SCF_3]$, with the resonances of the nuclei in the cyclopentadienyl and t-butyl groups being observed as singlets. The $^{13}C\text{-}\{^1H\}$ NMR spectrum also shows the resonance of the carbon of the triflate group as a quartet as it is coupled to three equivalent fluorine atoms. There is a large chemical shift difference ($\Delta\delta = 41.6$ ppm) between the quaternary (C_α) and methyl (C_β) carbons of the t-butyl group on the imido ligand. This chemical shift difference is thought to give a qualitative indication of the degree of electron density donated by the nitrogen atom to the metal.[13] A $\Delta\delta$ value of 41.6 ppm lies at the high end of the range previously reported for t-butylimido species, and is higher than any so far reported for a niobium compound.[11,13–18] This indicates a low electron density on the nitrogen atom due to a high degree of nitrogen pπ to metal dπ donation. The electron impact mass spectrum contained an envelope assignable to the molecular ion at $m/z = 443$.

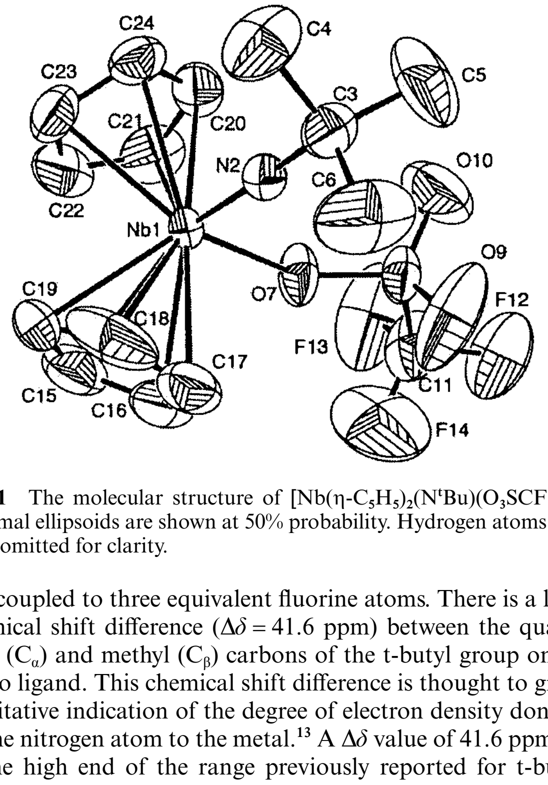


Fig. 1 The molecular structure of $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ **1**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

The crystal structure of $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ **1** has been determined; the molecular structure is given in Fig. 1 and selected interatomic distances and angles are listed in Table 2. The triflate group is bound to the metal centre, as suggested by the solubility of **1**. The imido ligand is almost linear (Nb(1)–N(2)–C(3) 176.4(2)°), implying that the nitrogen is sp hybridised and acting as a four-electron donor. The Nb(1)–N(2) bond length of 1.758(2) Å lies in the range of those in other niobium imido compounds in which the imido ligand formally donates four electrons to the metal centre.[1,8,19–21] The distances from the niobium atom to the carbons of the cyclopentadienyl ring vary

DOI: 10.1039/b004062m

Table 1 Analytical and spectroscopic data

Compound and analytical data[a]	NMR data[b]
$[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(O_3SCF_3)]$ **1** Orange needles C 40.6 (40.6), H 4.3 (4.3), N 3.1 (3.2) EI MS: *m*/*z* = 443, M$^+$, 12%; 428, [M − Me]$^+$, 100%	^{1}H^c in C_6D_6: 5.79 (s, 10 H, C_5H_5), 0.96 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}^{d} in C_6D_6: 120.09 (q, CF_3), 112.49 (C_5H_5), 71.10 (N*C*$(CH_3)_3$), 29.47 (NC(*C*$H_3)_3$) ^{19}F^e in C_6D_6: −77.40 (O_3SCF_3)
$[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(PMe_3)][O_3SCF_3]$ **2** Yellow crystals C 41.7 (41.6), H 5.4 (5.4), N 2.7 (2.7) ES MS: *m*/*z* = 370, M$^+$, 100%	^{1}H in C_4D_8O: 6.29 (d, 10 H, $^3J_{P\text{-}H} = 2$, C_5H_5), 1.99 (d, 9 H, $^2J_{P\text{-}H} = 10$, $P(CH_3)_3$), 1.09 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H} in C_4D_8O: 110.31 (C_5H_5), 68.11 (N*C*$(CH_3)_3$), 31.61 (NC(*C*$H_3)_3$), 19.20 (d, $^1J_{P\text{-}C} = 30.1$, P(*C*$H_3)_3$) ^{19}F in C_4D_8O: −80.56 (O_3SCF_3)
$[Nb(\eta\text{-}C_5H_5)_2(N^tBu)][MeB(C_6F_5)_3]$ **3** Red-brown	^{1}H: 5.65 (s, 10 H, C_5H_5), 1.11 (br s, 3 H, $CH_3B(C_6F_5)_3$), 0.71 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.16 (br d, $^1J_{C\text{-}F} \approx 242$, C_6F_5), 139.14 (br d, $^1J_{C\text{-}F} \approx 240$, C_6F_5), 138.17 (br d, $^1J_{C\text{-}F} \approx 240$, C_6F_5), not found (*ipso* C_6F_5), 114.43 (C_5H_5), 75.38 (N*C*$(CH_3)_3$), 31.17 (NC(*C*$H_3)_3$), 12.61 (br, *C*$H_3B(C_6F_5)_3$) ^{19}F: −136.41 (m, *o*-F of C_6F_5), −168.34 (m, *p*-F of C_6F_5), −170.93 (m, *m*-F of C_6F_5) ^{11}B:^{f} −14.12 ($CH_3B(C_6F_5)_3$)
$[Nb(\eta\text{-}C_5H_5)_2(N^tBu)][B(C_6F_5)_4]$ **4** Red-brown	^{1}H: 5.68 (s, 10 H, C_5H_5), 0.71 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.44 (br d, $^1J_{C\text{-}F} \approx 241$, C_6F_5), 140.20 (br d, $^1J_{C\text{-}F} \approx 248$, C_6F_5), 138.22 (br d, $^1J_{C\text{-}F} \approx 235$, C_6F_5), 126.20 (br s, *ipso*-C of C_6F_5), 114.30 (C_5H_5), 75.01 (N*C*$(CH_3)_3$), 29.90 (NC(*C*$H_3)_3$) ^{19}F: −134.84 (m, *o*-F of C_6F_5), −164.56 (m, *p*-F of C_6F_5), −168.54 (m, *m*-F of C_6F_5) ^{11}B: −15.88 ($B(C_6F_5)_4$)
$[Nb(\eta\text{-}C_5H_5)_2(N^tBu)(\eta\text{-}C_2H_4)][B(C_6F_5)_4]$ **5** Red-brown	^{1}H: 5.40 (s, 10 H, C_5H_5), 4.10 (s, 4 H, C_2H_4), 0.71 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.26 (br d, $^1J_{C\text{-}F} \approx 238$, C_6F_5), 140.09 (br d, $^1J_{C\text{-}F} \approx 231$, C_6F_5), 138.27 (br d, $^1J_{C\text{-}F} \approx 243$, C_6F_5), 126.20 (br s, *ipso*-C of C_6F_5), 112.45 (C_5H_5), 82.97 (C_2H_4), not found (N*C*$(CH_3)_3$), 31.50 (NC(*C*$H_3)_3$) ^{19}F: −134.81 (m, *o*-F of C_6F_5), −164.60 (m, *p*-F of C_6F_5), −168.59 (m, *m*-F of C_6F_5) ^{11}B: −15.91 ($B(C_6F_5)_4$)
$[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(O_3SCF_3)]$ **6** Orange needles C 44.8 (44.7), H 5.0 (4.8), N 2.8 (2.9) EI MS: *m*/*z* = 483, M$^+$, 15%; 468, [M − Me]$^+$, 100%; 412 [M − N^{t}Bu]$^+$, 32%	^{1}H in C_6D_6: δ 6.47 (m, 2 H, C_5H_4), 5.83 (m, 2 H, C_5H_4), 5.63 (m, 2 H, C_5H_4), 5.39 (m, 2 H, C_5H_4), 1.60 (s, 3 H, $C(CH_3)_2$), 0.99 (s, 3 H, $C(CH_3)_2$), 0.93 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H} in C_6D_6: 144.62 (*ipso*-C of C_5H_4), 117.72 (C_5H_4), 112.80 (C_5H_4), 103.58 (C_5H_4), 95.68 (C_5H_4), 70.57 (N*C*$(CH_3)_3$), 29.10 (NC(*C*$H_3)_3$), 25.70 (*C*$(CH_3)_2$), 22.04 (C(*C*$H_3)_2$), 21.02 (C(*C*$H_3)_2$) ^{19}F in C_6D_6: −77.38 (O_3SCF_3)
$[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)][B(C_6F_5)_4]$ **7** Red-brown	^{1}H: 6.04 (m, 2 H, C_5H_4), 5.79 (m, 4 H, C_5H_4), 4.90 (m, 2 H, C_5H_4), 1.27 (s, 3 H, $C(CH_3)_2$), 0.96 (s, 3 H, $C(CH_3)_2$), 0.71 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.01 (br d, $^1J_{C\text{-}F} \approx 236$, C_6F_5), 147.23 (*ipso*-C of C_5H_4), 139.91 (br d, $^1J_{C\text{-}F} \approx 243$, C_6F_5), 138.00 (br d, $^1J_{C\text{-}F} \approx 234$, C_6F_5), 126.20 (br s, *ipso*-C of C_6F_5), 116.46 (C_5H_4), 115.96 (C_5H_4), 104.52 (C_5H_4), 100.38 (C_5H_4), 74.42 (N*C*$(CH_3)_3$), 38.26 (*C*$(CH_3)_2$), 31.31 (NC(*C*$H_3)_3$), 24.22 (C(*C*$H_3)_2$), 22.95 (C(*C*$H_3)_2$) ^{19}F: −134.86 (m, *o*-F of C_6F_5), −164.55 (m, *p*-F of C_6F_5), −168.59 (m, *m*-F of C_6F_5) ^{11}B: −15.90 ($B(C_6F_5)_4$)
$[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(\eta\text{-}C_2H_4)][B(C_6F_5)_4]$ **8** Red-brown	^{1}H: 6.11 (m, 2 H, C_5H_4), 5.21 (m, 2 H, C_5H_4), 5.19 (m, 2 H, C_5H_4), 4.98 (m, 2 H, C_5H_4), 4.87 (s, 4 H, C_2H_4), 1.28 (s, 3 H, $C(CH_3)_2$), 0.99 (s, 3 H, $C(CH_3)_2$), 0.74 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.08 (br d, $^1J_{C\text{-}F} \approx 240$, C_6F_5), 140.59 (*ipso*-C of C_5H_4), 140.73 (br d, $^1J_{C\text{-}F} \approx 243$, C_6F_5), 137.99 (br d, $^1J_{C\text{-}F} \approx 236$, C_6F_5), 126.20 (br s, *ipso*-C of C_6F_5), 115.96 (C_5H_4), 115.21 (C_5H_4), 114.82 (C_5H_4), 100.89 (C_5H_4), 94.02 (C_2H_4), not found (N*C*$(CH_3)_3$), 37.74 (*C*$(CH_3)_2$), 31.38 (NC(*C*$H_3)_3$), 24.22 (C(*C*$H_3)_2$), 22.85 (C(*C*$H_3)_2$) ^{19}F: −134.79 (m, *o*-F of C_6F_5), −164.57 (m, *p*-F of C_6F_5), −168.55 (m, *m*-F of C_6F_5) ^{11}B: −15.90 ($B(C_6F_5)_4$)
$[Nb\{(\eta\text{-}C_5H_4)_2CMe_2\}(N^tBu)(\eta\text{-}C_3H_6)][B(C_6F_5)_4]$ **9** Red-brown	^{1}H: 6.67 (m, 1 H, H_2CC*H*(CH_3)), 6.03 (m, 1 H, C_5H_4 A), 5.94 (m, 1 H, C_5H_4 B), 5.53 (m, 1 H, C_5H_4 A), 5.41 (m, 1 H, C_5H_4 B), 5.39 (m, 1 H, C_5H_4 B), 5.18 (m, 1 H, C_5H_4 A), 5.00 (m, 1 H, C_5H_4 A), 4.84 (m, 1 H, C_5H_4 B), 4.77 (dd, $^2J_{C\text{-}H} = 3$, $^3J_{C\text{-}H} = 17.5$, 1 H, *trans* *H*$_2$CCH(CH_3)), 4.60 (dd, $^2J_{C\text{-}H} = 3$, $^3J_{C\text{-}H} = 9$, 1 H, *cis* *H*$_2$CCH(CH_3)), 1.60 (d, 3 H, H_2CCH(C*H*$_3$)), 1.29 (s, 3 H, $C(CH_3)_2$), 1.02 (s, 3 H, $C(CH_3)_2$), 0.75 (s, 9 H, $NC(CH_3)_3$) ^{13}C-{^{1}H}: 150.26 (br d, $^1J_{C\text{-}F} \approx 242$, C_6F_5), 141.08 (*ipso*-C of C_5H_4 A, B), 140.17 (H_2C*C*HCH_3), 140.16 (br d, $^1J_{C\text{-}F} \approx 243$, C_6F_5), 136.56 (br d, $^1J_{C\text{-}F} \approx 238$, C_6F_5), 126.20 (br s, *ipso*-C of C_6F_5), 116.86 (C_5H_4 A), 116.36 (C_5H_4 B), 115.63 (C_5H_4 B), 114.79 (C_5H_4 A), 102.26 (C_5H_4 B), 101.47 (C_5H_4 A), 98.79 (C_5H_4 A, B), 82.78 (H_2*C*$CHCH_3$), not found (N*C*$(CH_3)_3$), 37.74 (*C*$(CH_3)_2$), 31.46 (NC(*C*$H_3)_3$), 24.69 (H_2CCH*C*H_3), 24.31 (C(*C*$H_3)_2$), 24.10 (C(*C*$H_3)_2$) ^{19}F: −134.84 (m, *o*-F of C_6F_5), −164.58 (m, *p*-F of C_6F_5), −168.54 (m, *m*-F of C_6F_5) ^{11}B: −15.87 ($B(C_6F_5)_4$) A, B signify the two inequivalent cyclopentadienyl rings

[a] Given as % found (calc.). [b] Given as: chemical shift (δ) (multiplicity, rel. intensity, *J*/Hz, assignment), *etc*. In C_6D_5Br unless otherwise stated. [c] At 500 MHz. [d] At 125 MHz. [e] At 470.4 MHz. [f] At 160.4 MHz.

considerably, from 2.402 to 2.565 Å, with the longest bond lengths being those *trans* to the imido ligand (Nb(1)–C(15) 2.565(4), Nb(1)–C(16) 2.516(4) Å). This leads to the niobium–ring centroid distances being relatively long, at 2.188 and 2.201 Å. The intra-ring C–C distances are also irregular, although with no obvious pattern.

These features of the bonding of the cyclopentadienyl ring are similar to those noted in the previously reported compounds $[Mo(\eta\text{-}C_5H_4Me)_2(N^tBu)]$ and $[Mo(\eta\text{-}C_5H_4Me)_2(N^tBu)Me][BF_4]$,[22] $[Nb(\eta\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(N^tBu)]$[15] and $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)Cl]$.[11] These bis(η-cyclopentadienyl)imido compounds formally have a 20 electron configuration, however the structural data suggest that the lone pair on the imido ligand causes some destabilisation of the bonding in the ring

Table 2 Selected interatomic distances (Å) and angles (°) for [Nb-(η-C_5H_5)$_2$(N^tBu)(O_3SCF_3)]

Nb(1)–N(2)	1.758(2)	N(2)–C(3)	1.450(3)
Nb(1)–O(7)	2.142(2)	Nb(1)–C(15)	2.565(4)
Nb(1)–C(16)	2.516(4)	Nb(1)–C(17)	2.435(4)
Nb(1)–C(18)	2.402(4)	Nb(1)–C(19)	2.462(4)
Nb(1)–C(20)	2.462(3)	Nb(1)–C(21)	2.533(3)
Nb(1)–C(22)	2.564(3)	Nb(1)–C(23)	2.455(3)
Nb(1)–C(24)	2.472(3)		
N(2)–Nb(1)–O(7)	97.95(9)	Nb(1)–N(2)–C(3)	176.4(2)
Cp_{cent}–Nb(1)–Cp_{cent}	126.0		

Table 3 Selected interatomic distances (Å) and angles (°) for [Nb-(η-C_5H_5)$_2$(N^tBu)(PMe_3)][O_3SCF_3] **2**

Nb(1)–N(2)	1.779(2)	N(2)–C(3)	1.436(3)
Nb(1)–P(15)	2.5974(7)	Nb(1)–C(19)	2.479(3)
Nb(1)–C(20)	2.486(3)	Nb(1)–C(21)	2.562(3)
Nb(1)–C(22)	2.517(3)	Nb(1)–C(23)	2.485(3)
Nb(1)–C(24)	2.517(3)	Nb(1)–C(25)	2.570(3)
Nb(1)–C(26)	2.530(3)	Nb(1)–C(27)	2.431(3)
Nb(1)–C(28)	2.488(3)		
P(15)–Nb(1)–N(2)	90.71(7)	Nb(1)–N(2)–C(3)	171.90(19)
Cp_{cent}–Nb(1)–Cp_{cent}	126.8		

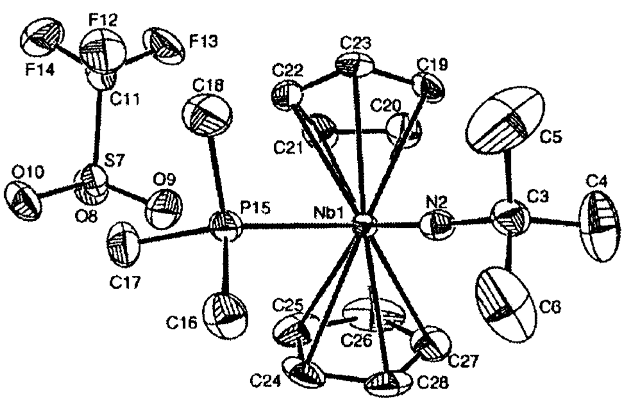


Fig. 2 Molecular structure of [Nb(η-C_5H_5)$_2$(N^tBu)(PMe_3)][O_3SCF_3] **2**. Details as in Fig. 1.

system. They are thus best considered to be 18 + 2 electron compounds, with eighteen bonding electrons, plus two in a ligand-based non-bonding orbital.

The compound [Nb(η-C_5H_5)$_2$(N^tBu)(O_3SCF_3)] **1** in benzene was treated with a solution of trimethylphosphine in benzene to give yellow crystals of [Nb(η-C_5H_5)$_2$(N^tBu)(PMe_3)][O_3SCF_3] **2**, which is soluble in THF but decomposed slowly in dichloromethane. The ^1H NMR spectrum of **2** in d_8-THF is consistent with displacement of the triflate group from the niobium centre to form an ion pair. A singlet was observed for the protons of the t-butyl group, a doublet for the CH_3 groups in PMe_3 and a doublet for the protons of the cyclopentadienyl due to coupling to the phosphorus atom of the phosphine. The difference in chemical shift between the α and β carbons of the t-butyl group, $\Delta\delta$, is 36.5 ppm, reflecting the increased electron density on the niobium centre arising from the replacement of the triflate group by the more electron-donating phosphine group, despite the formal positive charge on the metal centre. The electrospray mass spectrum (positive ion) contained the molecular ion at *m*/*z* 370 as the 100% peak.

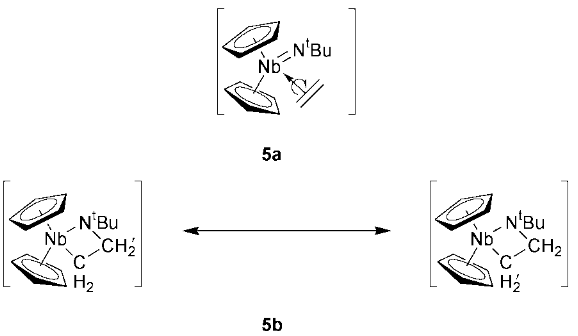
The crystal structure of [Nb(η-C_5H_5)$_2$(N^tBu)(PMe_3)]-[O_3SCF_3] **2** has been determined. The molecular structure is shown in Fig. 2 and selected interatomic distances and angles are given in Table 3. The compound **2** forms an ion pair. The Nb(1)–N(2)–C(3) linkage is slightly more bent than in **1**, however the angle of 171.90(19)° is still in the range that is considered linear,[1] hence the nitrogen is still sp hybridised. The Nb(1)–N(2) distance of 1.779(2) Å is greater than that of the neutral parent compound, however it is still in the region expected for a Nb–N distance where the nitrogen is considered to act as a four electron donor. The Nb–P bond length (2.5974(7) Å) is at the low end of the range of values found for previously reported niobium(V) compounds (2.577–2.649 Å).[14,23–27] The bis(η-cyclopentadienyl)niobium ring system is destabilised in a manner similar to that observed in **1**; however the cyclopentadienyl rings are even further from the metal centre in **2** than in **1**. Thus the Nb–C distances are in the range 2.479–2.570 Å, as opposed to 2.402–2.565 Å, leading to the niobium–ring centroid distances also being longer than in **1**, at 2.192 and 2.211 Å.

The addition of a solution of $B(C_6F_5)_3$ in d_5-bromobenzene to a solution of [Nb(η-C_5H_5)$_2$(N^tBu)Me] in d_5-bromobenzene caused an immediate change from yellow to red-brown. The ^1H NMR spectrum of [Nb(η-C_5H_5)$_2$(N^tBu)Me] in d_5-bromobenzene shows singlets at δ 5.55, 0.90 and 0.77 for the protons on the cyclopentadienyl ring, t-butyl and methyl group in a 10 : 9 : 3 ratio respectively. Addition of $B(C_6F_5)_3$ in d_5-bromobenzene gives a new spectrum with the chemical shifts assignable to the protons of the cyclopentadienyl ring and t-butyl group being δ 5.65 and 0.71 respectively. The methyl protons of the $[MeB(C_6F_5)_3]^-$ anion are observed as a broad singlet at δ 1.11. In addition a small amount of decomposition products is observed. The ^{11}B NMR spectrum of **3** shows a singlet at δ −14.12, in the region expected for a four-co-ordinate boron species, consistent with the formation of the $[MeB(C_6F_5)_3]^-$ anion. The ^{19}F NMR spectrum contained three multiplets at δ −136.41, −168.34 and −170.93. A study of compounds containing the $[MeB(C_6F_5)_3]^-$ anion found that a good indication of its degree of interaction with a metal centre is given by the difference in chemical shifts between the *meta*- and *para*-fluorines. A value greater than 3 ppm indicates a significant interaction between the two ions whilst a value of less than 3 ppm implies that this is not the case.[28] These data suggest the product to be the compound [Nb(η-C_5H_5)$_2$(N^tBu)][MeB-(C_6F_5)$_3$] **3**. The separation of the resonances of the α and β carbons of the t-butyl group, $\Delta\delta$, is 44.2 ppm. This is even greater than that observed for compound **1**, reflecting the greater degree of nitrogen pπ to metal dπ donation required to stabilise the cationic metal centre in **3**. It is likely that the cationic fragment is heavily solvated rather than existing as the naked cation.

The reaction between [Nb(η-C_5H_5)$_2$(N^tBu)Me] and [Ph_3C]-[$B(C_6F_5)_4$] in d_5-bromobenzene affords a compound which NMR data suggest to be the salt [Nb(η-C_5H_5)$_2$(N^tBu)]-[$B(C_6F_5)_4$] **4**, in around 80% yield, along with 1,1,1-triphenylethane. The NMR peaks assignable to the protons of the cyclopentadienyl ring and t-butyl group of **4** are observed as singlets at δ 5.68 and 0.71 respectively, in much the same positions as those of **3**, as would be expected if the two both contain the base-free cation $[Nb(\eta\text{-}C_5H_5)_2(N^tBu)]^+$. The remaining 20% of the product consists of a side-product that could not be identified, but which did not participate in any of the reactions discussed below. The ^{13}C-{^1H} NMR spectrum is also consistent with the formation of the ion pair **4**, along with the minor side-product and Ph_3CMe. The value of $\Delta\delta$ for the t-butyl group of the imido ligand (45.1 ppm) of **4** is even greater than that of **3** (44.2 ppm). The ^{11}B NMR spectrum shows a single peak at δ −15.88, typical of a four-co-ordinate boron species, with the ^{19}F NMR spectrum showing three multiplets at δ −134.84, −164.56 and −168.54.

All further reactions were performed using complex **4** as opposed to **3** as it was found that the $[B(C_6F_5)_4]^-$ anion was less co-ordinating than the $[MeB(C_6F_5)_3]^-$ anion.

A sample of the salt [Nb(η-C_5H_5)$_2$(N^tBu)][$B(C_6F_5)_4$] **4** in d_5-bromobenzene in a NMR tube fitted with a Teflon valve was freeze–pump–thaw degassed and placed under an atmosphere



5a

5b

Fig. 3 Possible equilibrium between complexes **5a** and **5b**.

of ethene at room temperature, and the NMR spectrum recorded. The ^{1}H spectrum showed the original cation still to be present, along with new resonances at δ 5.40, 4.10 and 0.71, with integrals in the ratio 10:4:9, although the overlap of the third peak with the t-butyl peak of the original cation meant that an accurate integral was difficult to obtain. These peaks are attributed to the d^0 η-ethene compound [Nb(η-C_5H_5)$_2$(N^{t}Bu)(C_2H_4)][B(C_6F_5)$_4$] **5**. Removal of the ethene by placing the sample under reduced pressure removes the new peaks associated with **5** leaving only those of the compound **4**. A room temperature ^{13}C-{^{1}H} NMR spectrum of the ethene saturated sample was recorded, along with a ^{13}C–^{1}H correlation. This showed the peak at δ 4.10 in the ^{1}H NMR spectrum to correlate with a carbon resonance at δ 82.97. The ^{11}B and ^{19}F NMR spectra of the solution of **4** in the presence of ethene were closely similar to those of the sample prior to addition, showing that the anion is unaffected by the addition of ethene.

These NMR data are consistent with two compounds, the d^0, η^2-ethene compound [Nb(η-C_5H_5)$_2$(N^{t}Bu)(C_2H_4)][B(C_6F_5)$_4$] **5a**, or the azametallacyclobutane compound [Nb(η-C_5H_5)$_2$(CH_2-CH_2N^{t}Bu)][B(C_6F_5)$_4$] **5b**, formed by cycloaddition of the ethene molecule to the Nb=N bond. For example, the moieties [Zr(η-C_5H_5)$_2$(N^{t}Bu)],[7] [Ti(η-C_5Me_5)$_2$(NPh)][29] and [Ti(NSi-^{t}Bu$_3$)(OSi^{t}Bu)$_2$][30] react with ethene to give rise to azametallacyclobutanes. Also, the displacement of diethyl ether from [V(NSi^{t}Bu$_3$)$_2$(NHSi^{t}Bu$_3$)(Et$_2$O)] by ethene yields an intermediate azametallacyclobutane derivative, which undergoes C–H activation to yield the alkenyl compound [V(NSi^{t}Bu$_3$)(NHSi-^{t}Bu$_3$)$_2$(CHCH$_2$)].[3]

For both compounds **5a** and **5b** the observation of a sharp *singlet* for the CH_2CH_2 hydrogens would require a fluxional equilibrium, as shown in Fig. 3. The reaction of [Nb(η-C_5H_5)$_2$-(N^{t}Bu)][MeB(C_6F_5)$_3$] **3** with ethene in d$_5$-bromobenzene was found to give the same cationic fragment as the reaction of **4**.

Variable temperature studies of complex **5** to −30 °C, the freezing point of bromobenzene, at 500 MHz showed the peak assigned to the four CH_2CH_2 protons to remain as a singlet. The compound **5** was prepared in d$_5$-chlorobenzene, which has a freezing point of −45 °C, and on cooling to −43 °C the singlet assigned to the CH_2CH_2 protons first broadened and then resolved into a doublet with peak separation of 2 Hz but no fine structure could be discerned. The corresponding resonance in the ^{13}C-{^{1}H} NMR spectrum at −43 °C still showed only a broadened singlet full width at half-height, (f.w.h.h. = 12 Hz); the lack of resolution may reflect a broadening effect of the spin $\frac{9}{2}$ niobium nucleus, or simply be due to the increased viscosity of the solvent.

These variable temperature NMR data do not distinguish between the two possible structures **a** or **b** for complex **5**. However, circumstantial evidence supports the structure **a** with the η-ethene ligand. Thus, the peak assigned to the CH_2CH_2 protons occurs at δ 4.10, and this value is relatively close to that for free ethene (δ 5.23). Further, the $^1J_{\text{C-H}}$ coupling constant of the protons of CH_2CH_2 is 167 Hz, as determined from a carbon coupled proton–carbon correlation of the gHSQC type (gradient selected heteronuclear quantum correlations), and the $^1J_{\text{C-H}}$ coupling constant of the sp^2 C–H bonds of free ethene was 160 Hz in the same sample. The azametallacyclobutane species **5b** would be expected to have a lower $^1J_{\text{C-H}}$ coupling constant due to the decreased s character in the bonding between the carbon and protons of the ethene ligand.

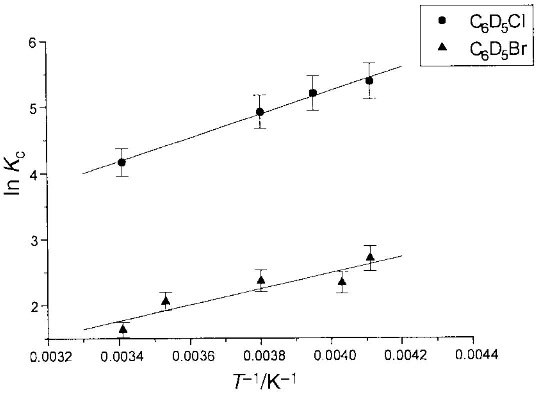


Fig. 4 A Van't Hoff plot of ln(K_c) *vs.* 1/T for the equilibria between complexes **5** and **4** in the presence of free ethene, in both d$_5$-bromobenzene and d$_5$-chlorobenzene.

Finally, we note that the chemical shifts of the η-ethene hydrogens in the d^0 cationic [V{η-C_5H_4(CH_2)$_2$N^{i}Pr}(N^{t}Bu)-(η-C_2H_4)][MeB(C_6F_5)$_3$][31] and [W(=CC_4H_8){OCH$_2$C(CH$_3$)$_3$}$_2$-Br(η-C_7H_{12})][GaBr$_4$][32] lie within 1 ppm of the resonance of the free olefin, and the $^1J_{\text{C-H}}$ coupling constants are slightly higher than those of the unco-ordinated olefin. In comparison the proton chemical shifts arising from the co-ordinated olefin in the four azametallacyclobutane species described above are shifted between 2 and 3.5 ppm downfield of the free olefin and the $^1J_{\text{C-H}}$ coupling constants are measured to be somewhat lower than for the free olefin (145–150 *vs.* 160 Hz). Compound **5** is present in equilibrium with the unco-ordinated or solvated cation and free ethene. The equilibrium constant was determined by measuring the integrals of the appropriate peaks in the ^{1}H NMR spectrum using the integral of the methyl group of Ph$_3$CMe as an internal standard. If the concentration of the solvent was taken to be constant, the equilibrium constant, K_c = [Nb(C_5H_5)$_2$(N^{t}Bu)-(C_2H_4)]/[Nb(C_5H_5)$_2$(N^{t}Bu)][C_2H_4], can be calculated to be 5.0 ± 0.3 dm^3 mol^{-1} at 20 °C.

The equilibrium is temperature dependent, and shifts in favour of the formation of the ethene compound **5a** as the temperature decreases, giving an equilibrium constant of 14.9 ± 0.8 dm^3 mol^{-1} at −30 °C. Variable temperature NMR studies gave the equilibrium constants at various temperatures and a Van't Hoff plot of ln K *vs.* 1/T is shown in Fig. 4. The data show the difference between the binding enthalpy of the ethene ligand and the solvent to [Nb(C_5H_5)$_2$(N^{t}Bu)]$^+$ is $\Delta H°$ = −10.1 ± 3.3 kJ mol^{-1}. This value is notably lower than the experimental, or calculated, values for other d^0 ethene complexes. For comparison, the position of the equilibrium of the compound [W(=CC_4H_8){(OCH$_2$C(CH$_3$)$_3$)$_2$}Br(η^2-C_7H_{12})]$^+$ with the solvated cation at various temperatures in d$_2$-dichloromethane gave $\Delta H°$ = −13.6 ± 0.5 kcal mol^{-1} (−56.8 kJ mol^{-1}).[32] Also the equilibrium for the reaction of [Ti(NSi^{t}Bu$_3$)-(OSi^{t}Bu)$_2$] with ethene in toluene gave $\Delta H°$ for the formation of a d^0 ethene complex to be *ca.* −11 kcal mol^{-1} (−46 kJ mol^{-1}).[30] Density functional calculations performed upon the fragment [V{η-C_5H_4(CH_2)$_2$η-NH}(NH)(η^2-C_2H_4)]$^+$, used as a model for [V{η-C_5H_4(CH_2)$_3$N^{i}Pr}(N^{t}Bu)(η^2-C_2H_4)]$^+$, gave a theoretical ethene binding enthalpy of −31 kcal mol^{-1} (129.6 kJ mol^{-1}).[31]

The equilibrium data in Fig. 4 show a greater degree of ethene association in d$_5$-chlorobenzene as compared to d$_5$-bromobenzene, giving K_c = 64.9 ± 3.3 dm^3 mol^{-1} at 20 °C, increasing to 216 ± 11 dm^3 mol^{-1} at −30 °C. A Van't Hoff plot using these data allowed the binding enthalpy of the ethene

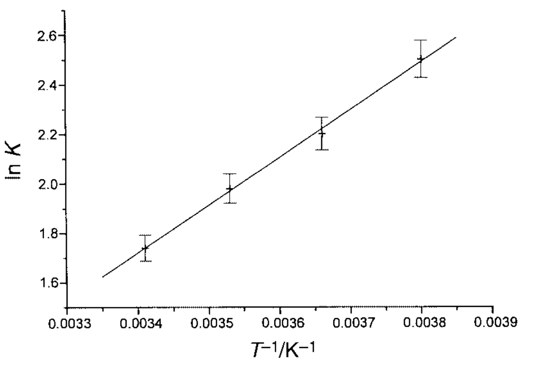


Fig. 5 A Van't Hoff plot of ln(*K*) *vs.* 1/*T* (K^{-1}) for the temperature dependence of the equilibrium between complexes **8** and **7** in the presence of ethene in d_5-bromobenzene.

ligand to be calculated to be $\Delta H° = -14.7 \pm 1.4$ kJ mol^{-1}. This value is not significantly different from that obtained when d_5-bromobenzene was used as the solvent, being within the bounds of experimental error.

The introduction of an atmosphere of propene to a NMR sample of complex **4** in the same manner as that used for ethene did not show any peaks arising from co-ordination of the propene. This is not surprising since it is well known that in olefin–metallocene compounds ethene bonds more readily than the bulkier propene.

The presence of an *ansa* bridge can alter the chemistry of the *ansa*-metallocenes as compared to that of non-bridged analogues.[33–36] The introduction of a single carbon bridge between the two cyclopentadienyl rings causes the angle between the two ring centroid–metal bonds to decrease by approximately 10°. It was decided to compare the reactivity of [Nb(η-$C_5H_5)_2$(N^{t}Bu)Cl] with that of the *ansa* analogue [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)Cl].

The reaction between [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)Cl][9] and AgO_3SCF_3 in benzene gave the compound [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)(O_3SCF_3)] **6** as slightly air- and moisture-sensitive orange needle crystals. These were soluble in non-polar organic solvents. The value of Δδ for the t-butyl group was measured to be 41.5 ppm, virtually identical to that of the non-bridged species. The electron impact mass spectrum of **6** showed the molecular ion at *m*/*z* 483, along with fragments resulting from loss of a methyl group and also from loss of the imido group.

Addition of a solution of [Ph_3C][B($C_6F_5)_4$] in d_5-bromobenzene to a solution of [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)Me][9] in d_5-bromobenzene gave a red-brown solution which the NMR data suggest to be the compound [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)][B($C_6F_5)_4$] **7**. The ^{1}H NMR spectrum shows the chemical shift of the peak due to the protons of the t-butyl to be close to that of the non-bridged compound **4**. The backbone methyl groups occur as two singlets, consistent with the pseudo tetrahedral symmetry expected for **7**. The protons of the cyclopentadienyl ring give rise to three multiplets, integrating as 2, 4 and 2 protons respectively. The ^{13}C-{^{1}H} NMR spectrum was also consistent with the proposed formulation of the product, with all of the peaks expected for **7** being observed. The value of Δδ between the α and β carbons of the t-butyl group was measured to be 43.1 ppm.

The introduction of an atmosphere of ethene into an NMR sample of complex **7** leads to spectral changes consistent with the formation of the ion pair [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)(η-C_2H_4)][B($C_6F_5)_4$] **8**. The ^{1}H NMR spectrum showed a resonance at δ 4.87 assignable to the methylene protons of the co-ordinated ethene. There are seven other new resonances that can be assigned to the protons of the cyclopentadienyl ring, backbone methyl groups and t-butyl group on the imido ligand. The ^{13}C-{^{1}H} NMR spectrum is also consistent with the formation of the ethene adduct, with the carbon resonance of the co-ordinated olefin being observed as a singlet at δ 94.02.

The position of the equilibrium between complexes **7** and **8** was measured at different temperatures by means of variable temperature NMR studies. The values of K_c are of the same order as those of the non-bridged analogue, varying from 5.7 ± 0.3 to 12.1 ± 0.6 dm^3 mol^{-1} over the temperature range 20 to −10 °C. A Van't Hoff plot of ln(K_c) *vs.* 1/*T* (Fig. 5) gave the value of Δ*H*° for the binding of the ethene ligand as -16.0 ± 1.2 kJ mol^{-1}. This value is similar to that of the non-bridged analogue.

The introduction of propene to a sample of complex **7** leads to the production of extremely complex NMR spectra. In the ^{1}H NMR spectrum, in addition to the peaks that have previously been assigned to **7**, a number of new proton resonances were observed, which could be attributed to the η-propene compound [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)(C_3H_7)][B($C_6F_5)_4$] **9**, however a number of resonances proved to be coincident, complicating the assignment. The ^{13}C-{^{1}H} NMR spectrum is better resolved, however there are still many very closely spaced peaks.

The ^{1}H NMR spectrum in d_5-bromobenzene of the solution of compound **9** shows resonances characteristic of the protons of propene species. Of these, four were consistent with the presence of free propene in d_5-bromobenzene, at δ 5.62, 4.86, 4.82 and 1.49, whilst others could be assigned to the three vinylic hydrogens of a co-ordinated propene. The internal vinylic proton was shifted 1 ppm downfield from that of free propene, whilst the resonance of the methyl group was also shifted downfield by approximately 0.1 ppm. The peaks due to the two methylene protons were separated by 0.18 ppm as opposed to 0.05 ppm for free propene, and occurred upfield of the resonances of the free olefin.

In the region containing the resonances of the cyclopentadienyl ring protons, six new singlets were observed which were assigned to the protons of the now inequivalent cyclopentadienyl rings. The coupling to other hydrogens on the ring was unresolved. In addition to these, two other resonances that were coupled to these singlets were found *via* a ^{1}H–^{1}H correlation spectrum. One of these was coincident with the resonance of a cyclopentadienyl proton of complex **7**, whilst the other was coincident with a resonance of the methylene protons of free propene. The unresolved coupling of these new cyclopentadienyl peaks may be due to a dynamic process involving rotation of the co-ordinated propene molecule.

Peaks that could be assigned to the proton resonances of the methyl groups on the backbone of an *ansa*-cyclopentadienyl ligand and to the t-butyl group of an imido ligand of a new species were also observed.

The ^{13}C-{^{1}H} NMR spectrum was assigned with the aid of both one-bond (HSQC) and two-bond (heteronuclear multiple bond correlation, HMBC) ^{13}C–^{1}H correlation spectra. This also showed the presence of a new species in addition to free propene and the solvated cation. Peaks at δ 140.17, 82.78 and 24.69 were found to correlate with the peaks of the second propene molecule observed in the ^{1}H NMR spectrum. These are shifted from the resonances of free propene (δ 135.13, 117.56 and 20.91 in d_5-bromobenzene). The terminal vinyl carbon shows a substantial (−34.78 ppm) shift upfield, whilst the internal vinyl carbon shows a small shift (+5.04 ppm) downfield. These features are similar to those observed for the olefinic groups in the compounds [V{η-$C_5H_4(CH_2)_3$N^{i}Pr}(N^{t}Bu)(η^2-C_3H_7)][B($C_6F_5)_3$Me] (δ −24.2 and +2.2, averaged over the two isomers)[31] and [Zr(η-$C_5H_5)_2${O(CMe_2)($CH_2)_3$-CH=CH_2}][B($C_6F_5)_3$Me] (δ −19.6 and +18.4),[37] in which a substantial amount of olefin polarisation was suggested.

The NMR data are all consistent with an equilibrium between complex **7** and propene giving the adduct [Nb{(η-$C_5H_4)_2CMe_2$}(N^{t}Bu)(η-CH_2CHMe)][B($C_6F_5)_4$] **9**.

The formation of the η-propene compound **9** whilst the analogous compound could not be seen with the non-*ansa* analogue may be attributed to introduction of the single carbon

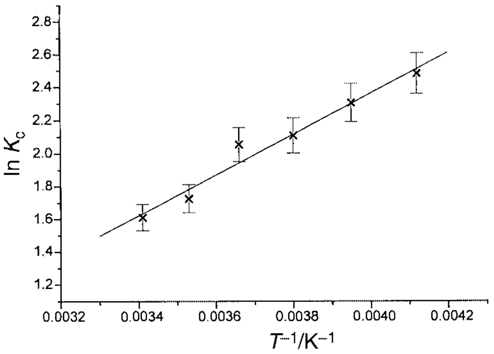


Fig. 6 A Van't Hoff plot of ln(K_c) *vs.* 1/T (K^{-1}) for the temperature dependence of the equilibrium between complexes **9** and **7** in the presence of propene in d_5-bromobenzene.

bridge in **9** which would cause an increase in the bending angle between the cyclopentadienyl rings, and thereby reduce the steric repulsion of the η-propene ligand by the cyclopentadienyl rings. This increase of bending angle is clearly suggested by consideration of the molecular structures of [Nb(η-C_5H_5)$_2$(N^{t}Bu)Cl] (123.4°)[11] and [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Cl] (113.3°).[17]

The position of the equilibrium between complex **7** and C_3H_6 and **9** was measured at different temperatures by means of variable temperature NMR studies, and K_c found to vary from 5.0 ± 0.3 to 12.0 dm^3 mol^{-1} over the temperature range 20 to −30 °C. A Van't Hoff plot of ln(K_c) *vs.* 1/T (Fig. 6) gave a value of $\Delta H°$ of −10.3 ± 1.4 kJ mol^{-1}.

The new compounds, their reactions and proposed structures are shown in Scheme 1.

Experimental

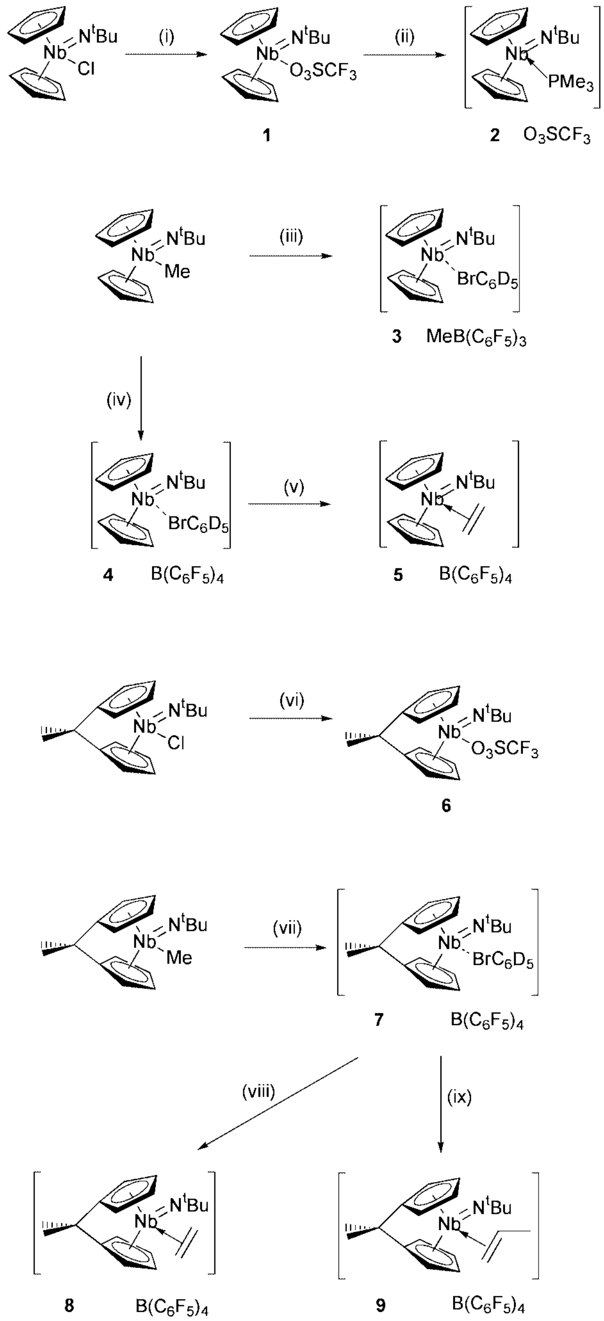
All preparations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere of dinitrogen using standard Schlenk line techniques, or in an inert atmosphere dry box containing dinitrogen. Dinitrogen was purified by passage through columns filled with molecular sieves (4 Å) and either manganese(II) oxide suspended on vermiculite for the vacuum line or BASF catalyst for the dry box. Solvents and solutions were transferred through stainless steel or Teflon cannulæ, using a positive pressure of inert gas. All glassware and cannulæ were thoroughly dried at 150 °C before use. Celite (Fluka) was similarly dried.

All solvents were deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were predried over activated molecular sieves (4 Å) and then distilled over potassium (THF, benzene, toluene, light petroleum bp 100–120 °C), sodium/potassium alloy (n-pentane, light petroleum bp 40–60 °C). Deuteriated solvents were dried over potassium (d_6-benzene, d_8-THF, d_5-bromobenzene, d_5-chlorobenzene) and vacuum distilled prior to use.

NMR spectra were recorded on either a Varian UnityPlus 500 (^{1}H, ^{11}B, ^{13}C and ^{19}F at 499.988, 160.415, 125.718, and 470.374 MHz respectively) or a Varian Hg300 spectrometer (^{1}H, ^{13}C and ^{19}F at 300.178, 75.477 and 282.398 MHz respectively), referenced internally using the residual protio solvent (^{1}H) and solvent (^{13}C) resonances and measured relative to tetramethylsilane (^{1}H and ^{13}C; δ 0) or referenced externally to BF$_3$·Et$_2$O (^{11}B; δ 0) or CFCl$_3$ (^{19}F; δ 0). Electron impact mass spectra were recorded by the mass spectrometry service of the Dyson Perrins Laboratory, electrospray mass spectra by Dr Greg Mullen on a Micromass LC TOF ESI mass spectrometer. We also thank Dr J. A. Ballantine and the Mass Spectroscopy Service at Swansea.

Elemental analyses were obtained by the elemental analysis department of the Inorganic Chemistry Laboratory.

The compounds [Nb(η-C_5H_5)$_2$(N^{t}Bu)Cl],[11] [Nb(η-C_5H_5)(N^{t}Bu)MeCl],[16] [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Cl][17] and [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Me][17] were prepared according to literature procedures. The previously reported compound [Nb{(η-C_5H_5)$_2$(N^{t}Bu)Me][13] was prepared *via* a variation on the literature procedure, as described below. AgO$_3$SCF$_3$ was purchased from the Avocado chemical company.



Scheme 1 (i) AgO$_3$SCF$_3$, THF; (ii) PMe$_3$, C_6H_6; (iii) B(C$_6$F$_5$)$_3$, C_6D_5Br; (iv) [Ph$_3$C][B(C$_6$F$_5$)$_4$], C_6D_5Br; (v) C_2H_4; (vi) AgO$_3$SCF$_3$, C_6H_6; (vii) [Ph$_3$C][B(C$_6$F$_5$)$_4$], C_6D_5Br; (viii) C_2H_4; (ix) C_3H_6.

Syntheses

[Nb(η-C_5H_5)$_2$(N^{t}Bu)Me]. A colourless solution of Mg(C_5H_5)$_2$ (0.77 g, 5 mmol) in toluene (20 ml) was added to a yellow solution of [Nb(η-C_5H_5)(N^{t}Bu)MeCl] (3.00 g, 10 mmol) in toluene (30 ml) at room temperature. A precipitate formed over the course of 5 min, with the solution becoming a darker yellow. The reaction mixture was stirred for 15 min and then filtered to remove MgCl$_2$. Removal of the volatiles gave the crude product as a dark yellow oil in good purity. The product could further be purified by sublimation as described previously.[11] Yield 2.40 g, 73% based on [Nb(η-C_5H_5)(N^{t}Bu)MeCl].

[Nb(η-C_5H_5)$_2$(N^{t}Bu)(O_3SCF_3)] 1. A colourless solution of AgO_3SCF_3 (0.156 g, 0.6 mmol) in THF (15 ml) was added to a yellow solution of [Nb(η-C_5H_5)$_2$(N^{t}Bu)Cl] (0.200 g, 0.6 mmol) in THF (15 ml) at room temperature. A grey-white solid precipitated immediately, and the solution became orange. The reaction mixture was stirred for 20 min, after which time the precipitate of AgCl was allowed to settle and removed by filtration. The volatiles were removed under reduced pressure and the resulting orange solid was extracted with light petroleum (bp 100–120 °C) (3 × 20 ml) to give an orange solution. The solution was concentrated to 10 ml under reduced pressure, and then cooled to −80 °C to yield the product as orange crystals which were isolated by filtration, washed with cold pentane and dried *in vacuo*. Yield 0.159 g, 59% based on [Nb(η-C_5H_5)$_2$(N^{t}Bu)Cl].

[Nb(η-C_5H_5)$_2$(N^{t}Bu)(PMe_3)][O_3SCF_3] 2. An orange solution of [Nb(η-C_5H_5)$_2$(N^{t}Bu)(O_3SCF_3)] (0.300 g, 0.68 mmol) in benzene (5 ml) was placed in one side of an H bridge, and a solution of trimethylphosphine (0.2 ml, 1.93 mmol) in benzene (5 ml) placed in the other half. The apparatus was then sealed and left to stand. Over the course of 2 days a yellow crystalline solid formed from the benzene solution, which gradually became colourless. The supernatant was decanted, and the solid washed with pentane (2 × 5 ml) and dried *in vacuo*. Yield 0.340 g, 96% based on [Nb(η-C_5H_5)$_2$(N^{t}Bu)(O_3SCF_3)].

[Nb(η-C_5H_5)$_2$(N^{t}Bu)][MeB(C_6F_5)$_3$] 3. A colourless solution of B(C_6F_5)$_3$ (26.4 mg, 5.2 × 10^{-2} mmol) in d_5-bromobenzene (0.5 ml) was added to a yellow solution of [Nb(η-C_5H_5)$_2$(N^{t}Bu)Me] (16 mg, 5.2 × 10^{-2} mmol) in the same solvent (0.2 ml). The resulting red-brown solution was then transferred to a NMR tube. Yield 95% (calculated from the ^{1}H NMR spectrum).

[Nb(η-C_5H_5)$_2$(N^{t}Bu)][B(C_6F_5)$_4$] 4. An orange solution of [Ph_3C][B(C_6F_5)$_4$] (48 mg, 5.2 × 10^{-2} mmol) in d_5-bromobenzene or d_5-chlorobenzene (0.5 ml) was added to a yellow solution of [Nb(η-C_5H_5)$_2$(N^{t}Bu)Me] (16 mg, 5.2 × 10^{-2} mmol) in the same solvent. The resulting red-brown solution was then transferred to a NMR tube. Yield 80% (calculated from the ^{1}H NMR spectrum).

[Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)(O_3SCF_3)] 6. A colourless solution of AgO_3SCF_3 (0.31 g, 1.22 mmol) in benzene (20 ml) was added to a yellow solution of [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Cl] (0.45 g, 1.22 mmol) in benzene (15 ml) at room temperature. A white precipitate formed immediately, and the solution became orange. The reaction was then worked up as above. Concentration of the solvent provided orange crystals which were isolated by filtration, washed with cold pentane (2 × 5 ml) and dried *in vacuo*. The filtrate was cooled to −20 °C to yield a further crop of orange crystals. Yield 0.24 g, 53% based on [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Cl].

[Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)][B(C_6F_5)$_4$] 7. An orange solution of [Ph_3C][B(C_6F_5)$_4$] (48 mg, 5.2 × 10^{-2} mmol) in d_5-bromobenzene (0.5 ml) was added to a yellow solution of [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)Me] (18 mg, 5.2 × 10^{-2} mmol) in the same solvent (0.2 ml). The resulting red-brown solution was transferred to an NMR tube. Yield 80% (calculated from the ^{1}H NMR spectrum).

Reactions between [Nb(η-C_5H_5)$_2$(N^{t}Bu)][B(C_6F_5)$_4$] 4 and ethene, and between [Nb{(η-C_5H_4)$_2$CMe$_2$}(N^{t}Bu)][B(C_6F_5)$_4$] 7 and ethene and propene. A solution of the salt prepared as described above was transferred to an NMR tube fitted with a Teflon valve. The sample was freeze–pump–thaw degassed twice, and the appropriate gas admitted to the NMR tube. The NMR spectra were then recorded.

Table 4 Crystal structure data

	1	2
Molecular formula	$C_{15}H_{19}F_3NNbO_3S$	$C_{18}H_{28}F_3NNbO_3PS$
Formula weight	443.28	519.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	8.648(1)	8.868(1)
b/Å	24.018(3)	18.934(2)
c/Å	9.588(2)	13.641(2)
β/°	112.71(2)	92.12(2)
V/Å^3	1837.1(4)	2288.9(4)
Z	4	4
T/K	180	180
μ/mm^{-1}	0.78	0.70
Total data collected	9039	11019
Unique data	3859	4777
Merging R (%)	0.02	0.032
R	0.0410	0.0327
R_w	0.0488	0.0396

Crystallography

Data were collected as previously described,[38] the images being processed with the DENZO and SCALEPACK programs.[39] All solution, refinement and graphical calculations were performed using the CRYSTALS[40] and CAMERON[41,42] software packages. A Chebychev weighting scheme[43] with the parameters 4.37, 2.57 and 2.99 was applied to the crystal structure of compound **1** giving a final R factor of 0.041 and $R_w = 0.0488$ with a maximum residual electron density of 0.52 e Å^{-3}. A similar weighting scheme was applied to the structure of **2** using the parameters 2.54, 0.640 and 2.06. This yielded a final R factor of 0.0327, $R_w = 0.0396$ with a maximum residual electron density of 0.83 e Å^{-3}. The crystallographic data are given in Table 4.

CCDC reference number 186/2082.

See http://www.rsc.org/suppdata/dt/b0/b004062m/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC for a grant (to M. J. H.) and St Johns College, Oxford for partial support.

References

1 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
2 J. de With and A. D. Horton, *Organometallics*, 1990, **9**, 2207.
3 J. de With and A. D. Horton, *Organometallics*, 1993, **12**, 1493.
4 C. P. Schaller and P. T. Wolczanski, *Inorg. Chem.*, 1993, **32**, 132.
5 C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731.
6 P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729.
7 P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705.
8 W. A. Herrmann, W. Baratto and E. Herdtweck, *J. Organomet. Chem.*, 1997, **541**, 445.
9 L. Djakovitch and W. A. Herrmann, *J. Organomet. Chem.*, 1998, **562**, 71.
10 R. E. Blake, D. M. Antonelli, L. M. Henling, W. P. Schaefer, K. I. Hardcastle and J. E. Bercaw, *Organometallics*, 1998, **17**, 718.
11 A. N. Chernega, M. L. H. Green and A. G. Suárez, *J. Chem. Soc., Dalton Trans.*, 1993, 3031.
12 J. Sundermeyer, J. Putterlik, M. Foth, J. S. Field and N. Ramesar, *Chem. Ber.*, 1994, **127**, 1201.
13 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, John Wiley & Sons, New York, 1988.
14 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neill and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739.
15 M. L. H. Green, D. M. Michaelidou, P. Mountford, A. G. Suárez and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1593.
16 V. C. Gibson, A. D. Poole, U. Siemeling and D. N. Williams, *J. Organomet. Chem.*, 1993, **462**, C12.

17 N. J. Bailey, J. A. Cooper, H. Gailus, M. L. H. Green, J. T. James and M. A. Leech, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3579.

18 S. Schmidt and J. Sundermeyer, *J. Organomet. Chem.*, 1994, **472**, 127.

19 M. C. W. Chan, J. M. Cole, V. C. Gibson, J. A. K. Howard, C. Lehmann, A. D. Poole and U. Siemeling, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 103.

20 K. C. Jayaratne, G. P. Yap, B. S. Haggerty, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1996, **35**, 4910.

21 A. A. Danopoulos, R. S. Hay-Motherwell, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *Polyhedron*, 1997, **16**, 1081.

22 J. C. Green, M. L. H. Green, J. T. James, P. C. Konidaris, G. H. Maunder and P. Mountford, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1361.

23 V. C. Gibson, T. P. Ree, R. M. Sorrell, A. P. Bashall and M. McPartlin, *Polyhedron*, 1988, **7**, 2221.

24 A. Bashall, V. C. Gibson, T. P. Kee, M. McPartlin, O. B. Robinson and A. Shaw, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 980.

25 J. K. Cockcroft, V. C. Gibson, J. A. K. Howard, A. D. Poole, U. Siemeling and C. Wilson, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1668.

26 D. M. Antonelli, M. L. H. Green and P. Mountford, *J. Organomet. Chem.*, 1992, **438**, C4.

27 S. G. Bott, D. M. Hoffman and S. P. Rangarajan, *Inorg. Chem.*, 1995, **34**, 4305.

28 A. D. Horton, *Organometallics*, 1996, **15**, 2675.

29 J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 13405.

30 J. L. Bennett and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1994, **116**, 2179.

31 P. T. Witte, A. Meetsma and B. Hessen, *J. Am. Chem. Soc.*, 1997, **119**, 10561.

32 J. Kress and J. A. Osborn, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1585.

33 D. Churchill, J. H. Shin, T. Hascall, J. M. Hahn, B. M. Bridgewater and G. Parkin, *Organometallics*, 1999, **18**, 2403.

34 P. Grebenik, A. J. Downs, M. L. H. Green and R. Mahtab, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 742.

35 A. Chernega, A. J. Cook, M. L. H. Green, L. Labella, S. J. Simpson, J. Souter and A. H. H. Stephens, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3225.

36 H. Lee, P. J. Desrosiers, J. Guzei, A. L. Rheingold and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 3255.

37 Z. Wu and R. F. Jordan, *J. Am. Chem. Soc.*, 1995, **115**, 5867.

38 L. H. Doerrer, M. L. H. Green, D. Häußinger and J. Saßmannhausen, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2111.

39 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.

40 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, *Issue 10*, Chemical Crystallography Laboratory, University of Oxford, 1996.

41 D. J. Watkin, C. K. Prout and L. J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, 1996.

42 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, SIR 92, Program for automatic solution of crystal structures by direct methods, *J. Appl. Crystallogr.*, 1994, **27**, 435J.

43 R. Carruthers and D. J. Watkin, *Acta Crystallogr.*, *Sect. A*, 1979, **35**, 698.