Niobium η-cyclopentadienyl compounds with imido and amido ligands derived from *tert*-butylamine

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The niobium η-cyclopentadienyl compounds with imido and amido ligands $[Nb(\eta-C_5H_5)(N^tBu)(NH^tBu)Cl]$
1,* $[Nb(\eta-C_5H_5)(N^tBu)(NH^tBu)^nBu]$ **2**, $[Nb(\eta-C_5H_5)(N^tBu)(NH^tBu)_2]$ **3**, $[Nb(\eta-C_5H_5)(N^tBu)(NH^tBu)Me]$ **4**,
$[Nb(\eta-C_5H_5)(\eta^1-C_5H_5)(N^tBu)(NH^tBu)]$ **5**, $[Nb\{(\eta-C_5H_4)CMe_2(\eta^1-C_5H_4)\}(N^tBu)(NH^tBu)]$ **6**, $[Nb(\eta-C_5H_5)$-
$\{N(C_6H_3{}^iPr_2-2,6)\}(NH^tBu)Cl]$ **7**,* $[Nb(\eta-C_5H_5)\{N(C_6H_3{}^iPr_2-2,6)\}(NH^tBu)Me]$ **8**, $[Nb(\eta-C_5H_5)(N^tBu)(NEt_2)Cl]$
9 and $[Nb(\eta-C_5H_5)(N^tBu)(NH^tBu)(NEt_2)]$ **10** have been prepared (* indicates the crystal structure has been
determined). A correlation between the chemical shift of the NH proton and the value of $\Delta\delta$ measured between
the α and β carbons of the *tert*-butyl groups of the amido ligands is discussed in relation to the degree of electron
donation from the amido ligand to the niobium centre.

Introduction

Complexes containing metal–nitrogen multiple bonds are
widespread within transition metal chemistry.[1,2] High reactivity
of these complexes can be achieved by synthesizing co-
ordinatively unsaturated complexes containing multiple
π-bonded ligands. Such "π loading" destabilises the strong
metal–nitrogen π interactions and can lead to reactive imido
moieties. The reactions of the transient imido complex [Zr-
$(\eta-C_5H_5)_2(N^tBu)]$ with isobutylene oxide (Me_2COCH_2) and iso-
cyanides, its applications in the metathesis of ketones, imines
and isocyanates, and its cycloaddition reactions with olefins,
alkynes and azides have extensively been reported.[3] Other
salient examples include imido complexes of titanium,[4] zirco-
nium,[5] vanadium[6] and tantalum[7] which have been shown to
activate the C–H bonds of hydrocarbons. However, to date no
such reactivity has been reported for niobium complexes.

With this in mind it was decided to investigate the synthesis
and reactivity of (η-cyclopentadienyl)niobium compounds
containing both imido and amido ligands of the general
formula $[Nb(\eta-C_5H_5)(NR)(NHR)X]$ where R is an organic
group and X a group capable of being eliminated as HX, either
through an inter- or intra-molecular process, to yield a bisimido
compound. Previously, the niobium bisimido compounds
$[Nb(NC_6H_3{}^iPr_2-2,6)_2Cl(PMe_3)_2]$[8] and $[Nb(NC_6H_3{}^iPr_2-2,6)_2-$
$X(py)_2]$[9] (X = Cl or $\eta-C_5H_5$) have been described: they are
stable molecules, and are sterically and electronically saturated.
However, no reactivity studies were reported.

During the course of this work the compounds [Nb-
$(\eta-C_5H_4SiMe_2NH^tBu)Cl(NH^tBu)(N^tBu)]$ and its derivatives
were described.[10]

Results and discussion

The reaction between the compound $[Nb(\eta-C_5H_5)(N^tBu)-$
$Cl_2]$[11,12] and $LiNH^tBu$ in benzene at room temperature yielded
the pale yellow microcrystalline compound $[Nb(\eta-C_5H_5)(N^tBu)-$
$(NH^tBu)Cl]$ **1** as an air- and moisture-sensitive solid that was
soluble in non-protic organic solvents. The NMR data for **1**,
and for all the other new compounds **2–10** described in this
paper, are given in the Table 1. The ${}^1H$ NMR spectrum shows a
peak assignable to the amido proton resonance at δ 7.56 which
is in the region expected for an alkylamido co-ordinated to a
metal atom. The assignment of the two *tert*-butyl groups
between the imido and amido ligands was made from a one-
dimensional NOE difference spectrum in which the amido
proton was irradiated. This showed an NOE to only one of the
tert-butyl peaks, and this was assigned to be that of the amido
NH^tBu ligand.

The ${}^{13}C$-$\{{}^1H\}$ NMR spectrum of **1** was also consistent with
the proposed structure of compound **1**. It has been proposed
that the chemical shift difference $(\Delta\delta)$ between the quaternary
and methyl carbons of the *tert*-butyl group of the imido ligand
can provide some insight into the nature of the metal–nitrogen
bonding.[2] It is likely that the shift between C_α and C_β for the
amido moiety also gives an indication of the electron density on
the nitrogen of this group in the same manner as for the imido
ligand. The values of $\Delta\delta$ found for this compound were 35.6
and 23.5 ppm for the imido and amido groups respectively. The
value of $\Delta\delta$ for the imido group lies in the middle of the range
previously reported for imido compounds whilst the $\Delta\delta$ value
of 23.5 ppm for the NH^tBu ligand lies toward the high end of
the range found in this work (see below). The values of $\Delta\delta$
measured for this and other compounds in this work are given
in Table 5.

The crystal structure of compound **1** has been determined,
the molecular structure is shown in Fig. 1 and selected inter-
atomic distances and angles are given Table 2. The asymmetric
unit contains the two enantiomers of **1**. There were no signifi-
cant differences in the interatomic distances and angles between
the two enantiomers. The molecular structure shows **1** to be a
monomer, with structurally distinct Nb–N–C linkages. The
$Nb–N_{imido}$ distances of 1.7676(12) Å and 1.7686(13) Å are in
the range expected for the imido group acting as a four electron
donor to niobium, with the ligand adopting a quasi-linear
geometry. The imido *tert*-butyl group is angled slightly towards

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Table 1 Analytical and spectroscopic data

Compound and analytical data[a]	NMR data[b,c]
1 [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)Cl] Pale yellow crystals C 46.0 (46.4), H 7.4 (7.2), N 8.1 (8.3) MS, EI: m/z = 336, M⁺, 4%; 321, (M − Me)⁺, 82%	¹H: 7.56 (br s, 1 H, NHC(CH₃)₃), 5.88 (s, 5 H, C₅H₅), 1.25 (s, 9 H, NHC(CH₃)₃), 1.19 (s, 9 H, NC(CH₃)₃) ¹³C-{¹H}: 108.46 (C₅H₅), 67.46 (NC(CH₃)₃), 57.00 (NHC(CH₃)₃), 33.49 (NHC(CH₃)₃), 31.72 (NC(CH₃)₃)
2 [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)ⁿBu] Yellow oil	¹H: 6.54 (br s, 1 H, NHC(CH₃)₃), 5.70 (s, 5 H, C₅H₅), 1.92 (m, 2 H, CH₂CH₂CH₂CH₃), 1.55 (m, 2 H, CH₂CH₂CH₂CH₃), 1.50 (m, 1 H, CH₂CH₂CH₂CH₃), 1.41 (m, 1H, CH₂CH₂CH₂CH₃), 1.29 (s, 9 H, NHC(CH₃)₃), 1.26 (s, 9 H, NC(CH₃)₃), 1.11 (t, 3 H, ³J_HH = 7, CH₂CH₂CH₂CH₃) ¹³C-{¹H}: 105.44 (C₅H₅), 64.59 (NC(CH₃)₃), 54.98 (NHC(CH₃)₃), 37.50 (CH₂CH₂CH₂CH₃), 32.96 (NHC(CH₃)₃), 31.46 (NC(CH₃)₃), 28.22 (CH₂CH₂CH₂CH₃), 12.83 (CH₂CH₂CH₂CH₃)
3 [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)₂] Yellow oil C 54.1 (54.7), H 9.0 (9.2), N 11.0 (11.25) MS, EI: m/z = 373, M⁺, 17%; 358, (M − Me)⁺, 100%	¹H: 5.88 (s, 5 H, C₅H₅), 4.81 (br s, 2 H, NHC(CH₃)₃), 1.30 (s, 18 H, NHC(CH₃)₃), 1.26 (s, 9 H, NC(CH₃)₃) ¹³C-{¹H}: 106.83 (C₅H₅), 65.82 (NC(CH₃)₃), 53.87 (NHC(CH₃)₃), 34.33 (NHC(CH₃)₃), 32.55 (NHC(CH₃)₃)
4 [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)Me] Yellow solid C 53.1 (53.2), H 9.0 (8.6), N 7.9 (8.9) Ms, EI: m/z = 316, M⁺, 50%; 301 (M − Me)⁺, 32%; 285, (M − 2Me)⁺, 100%	¹H: 6.72 (br s, 1 H, NHC(CH₃)₃), 5.71 (s, 5 H, C₅H₅), 1.28 (s, 9 H, NHC(CH₃)₃), 1.25 (s, 9 H, NC(CH₃)₃), 0.55 (s, 3 H, NbCH₃) ¹³C-{¹H} (C₆D₆, 125 MHz): 105.92 (C₅H₅), 64.89 (NC(CH₃)₃), 55.12 (NHC(CH₃)₃), 34.19 (NHC(CH₃)₃), 32.51 (NC(CH₃)₃), 10.00 (br, NbCH₃)
5 [Nb(η-C₅H₅)(η¹-C₅H₅)(NᵗBu)(NHᵗBu)] Yellow waxy solid	¹H: 7.06 (br s, 1 H, NHC(CH₃)₃), 5.87 (s, 5 H, C₅H₅), 1.23 (s, 9 H, NHC(CH₃)₃), 1.19 (s, 9 H, NC(CH₃)₃) ¹³C-{¹H}: 111.93 (C₅H₅), 66.58 (NC(CH₃)₃), 56.35 (NHC(CH₃)₃), 33.71 (NHC(CH₃)₃), 32.29 (NC(CH₃)₃)
6 [Nb{(η-C₅H₄)CMe₂(η¹-C₅H₄)}(NᵗBu)(NHᵗBu)] Yellow solid MS, EI: m/z = 406, M⁺, 22%; 301, (M − Me)⁺, 100%	¹H: 6.88 (br s, 1 H, NHC(CH₃)₃), 6.20 (m, 2 H, C₅H₄), 6.17 (m, 2 H, C₅H₄), 5.63 (m, 2 H, C₅H₄), 5.18 (m, 2 H, C₅H₄), 1.63 (s, 3 H, C(CH₃)₂), 1.60 (s, 3 H, C(CH₃)₂), 1.28 (s, 9 H, NHC(CH₃)₃), 1.11 (s, 9 H, NC(CH₃)₃) ¹³C-{¹H}: 142.50 (ipso-C of C₅H₄), 119.29 (C₅H₄), 111.86 (C₅H₄), 97.26 (C₅H₄), 96.40 (C₅H₄), 66.25 (NC(CH₃)₃, 56.13 (NHC(CH₃)₃, 36.03 (C(CH₃)₂), 33.99 (NHC(CH₃)₃), 31.89 (NC(CH₃)₃), 28.03 (C(CH₃)₂), 27.13 (C(CH₃)₂)
7 [Nb(η-C₅H₅){N(C₆H₃ⁱPr₂-2,6)}(NHᵗBu)Cl] Yellow crystals C 54.7 (54.5), H 6.9 (7.3), N 6.0 (6.35) MS, EI: m/z = 440, M⁺; 425, (M − Me)⁺	¹H:[d] 8.0 (br s, 1 H, NHC(CH₃)₃), 7.06 (d, 2 H, ³J_HH = 7.3, m-H of C₆H₃ⁱPr₂), 6.97 (t, 1 H, ³J_HH = 7.3, p-H of C₆H₃ⁱPr₂), 5.89 (s, 5 H, C₅H₅), 4.03 (sept, 2 H, ³J_HH = 6.7, CH(CH₃)₂), 1.32 (d, 12 H, ³J_HH = 6.7, CH(CH₃)₂), 1.15 (s, 9 H, NC(CH₃)₃) ¹³C-{¹H}:[e] 152.14 (C₆H₃ⁱPr₂), 144.78 (C₆H₃ⁱPr₂), 124.29 (C₆H₃ⁱPr₂), 122.97 (C₆H₃ⁱPr₂), 110.00 (C₅H₅), 59.54 (NHC(CH₃)₃), 32.64 (NHC(CH₃)₃), 28.08 (CH(CH₃)₂), 24.57 (CH(CH₃)₂)
8 [Nb(η-C₅H₅){N(C₆H₃ⁱPr₂-2,6)}(NHᵗBu)Me] Yellow crystals C 62.4 (62.85), H 8.3 (8.4), N, 6.3 (6.7) MS, CI: m/z = 420, M⁺	¹H:[d] NHC(CH₃)₃ not found, 7.10 (d, 2 H ³J_HH = 7.7, m-H of C₆H₃ⁱPr₂), 6.96 (t, 1 H, ³J_HH = 7.7, p-H of C₆H₃ⁱPr₂), 5.71 (s, 5 H, C₅H₅), 4.10 (sept, 2 H, ³J_HH = 7.0, CH(CH₃)₂), 1.33 (d, 12 H, ³J_HH = 7.0, (CH(CH₃)₂), 1.16 (s, 9 H, NC(CH₃)₃), 0.75 (s, 3 H, NbCH₃) ¹³C-{¹H}:[e] 152.04 (C₆H₃ⁱPr₂), 144.01 (C₆H₃ⁱPr₂), 123.28 (C₆H₃ⁱPr₂), 122.71 (C₆H₃ⁱPr₂), 107.45 (C₅H₅), 65.34 (br s, NbCH₃), 57.58 (NHC(CH₃)₃), 33.38 (NHC(CH₃)₃), 28.02 (CH(CH₃)₂), 24.32 (CH(CH₃)₂)
9 [Nb(η-C₅H₅)(NᵗBu)(NEt₂)Cl] Dark red oil C 45.95 (46.4), H 6.9 (7.2), N 8.1 (8.3) MS, EI: m/z = 336, M⁺; 321, (M − Me)⁺	¹H:[d] 5.94 (s, 5 H, C₅H₅), 4.15 (m, 1 H, NC¹HHCH₃), 3.70 (m, 1 H, NC¹HHCH₃), 3.26 (m, 1 H, NC²HHCH₃), 3.01 (m, 1 H, NC²HHCH₃), 1.13 (s, 9 H, NC(CH₃)₃), 1.04 (m, 1 H NC¹HHCH₃), 0.91 (m, 1 H, NC²HHCH₃) ¹³C-{¹H}:[e] 107.77 (C₅H₅), 67.80 (NC(CH₃)₃), 59.95 (NC¹H₂CH₃), 51.62 (NC¹H₂CH₃), 31.54 (NC(CH₃)₃), 17.67 (NC¹H₂CH₃), 13.34 (NC²H₂CH₃)
10 [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)(NEt₂)] Orange-brown oil C 54.05 (54.7), H 8.9 (9.2), N 11.0 (11.25) MS, EI: m/z = 373, M⁺; 358, (M − Me)⁺	¹H:[d] 5.94 (s, 5 H, C₅H₅), 4.55 (br s, 1 H, NHC(CH₃)₃), 3.50 (m, 2 H, NCHHCH₃), 3.27 (m, 2 H, NCHHCH₃), 1.37 (br s, 1 H, NHC(CH₃)₃), 1.26 (s, 9 H, NC(CH₃)₃), 1.08 (m, 1 H, NCH₂CH₃) ¹³C-{¹H}:[e] 106.18 (C₅H₅), 65.66 (NC(CH₃)₃), 54.00 (NCH₂CH₃), 53.99 (NHC(CH₃)₃), 34.68 (NHC(CH₃)₃), 32.78 (NC(CH₃)₃), 15.33 (NCH₂CH₃)

[a] Calculated values given in parentheses. [b] NMR data are given as chemical shift (δ) (multiplicity, relative intensity, J/Hz, assignment). [c] 500 MHz (¹H) and 125 MHz (¹³C-{¹H}) unless otherwise stated. [d] 400 MHz. [e] 100 MHz.
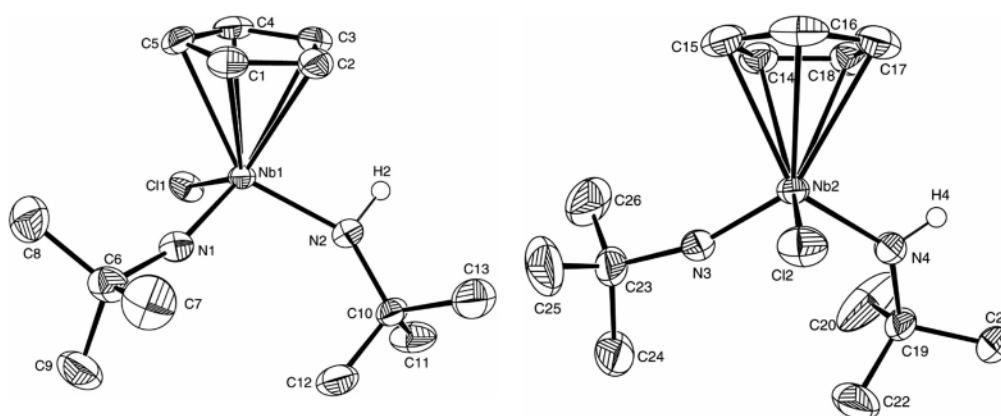

Fig. 1 The molecular structure of the two enantiomers of [Nb(η-C₅H₅)(NᵗBu)(NHᵗBu)Cl] **1**. Hydrogen atoms attached to carbon have been omitted for clarity.

Table 2 Selected interatomic distances (Å) and angles (°) for [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl] **1**

Nb(1)–N(1)	1.7676(12)	Nb(2)–N(3)	1.7686(13)
Nb(1)–N(2)	1.9674(12)	Nb(2)–N(4)	1.9677(14)
N(1)–C(6)	1.4574(19)	N(3)–C(23)	1.455(2)
N(2)–C(10)	1.467(2)	N(4)–C(19)	1.480(2)
Nb(1)–Cl(1)	2.4204(3)	Nb(2)–Cl(2)	2.4085(4)
Nb(1)–C(1)	2.4209(15)	Nb(2)–C(14)	2.4055(14)
Nb(1)–C(2)	2.4401(15)	Nb(2)–C(15)	2.4411(17)
Nb(1)–C(3)	1.5098(15)	Nb(2)–C(16)	2.4964(16)
Nb(1)–C(4)	2.5014(16)	Nb(2)–C(17)	2.5218(15)
Nb(1)–C(5)	2.4528(16)	Nb(2)–C(18)	2.4627(14)
C(1)–C(2)	1.406(2)	C(14)–C(15)	1.415(2)
C(2)–C(3)	1.408(2)	C(15)–C(16)	1.407(3)
C(3)–C(4)	1.403(2)	C(16)–C(17)	1.395(3)
C(4)–C(5)	1.399(3)	C(17)–C(18)	1.407(2)
C(1)–C(5)	1.409(2)	C(14)–C(18)	1.410(2)
Nb(1)–N(1)–C(6)	162.97(12)	Nb(2)–N(3)–C(23)	164.05(12)
Nb(1)–N(2)–C(10)	143.2(1)	Nb(2)–N(4)–C(19)	137.0(1)
Nb(1)–N(2)–H(2)	111.8(17)	Nb(2)–N(4)–H(4)	114.6(16)
C(10)–N(2)–H(2)	104.9(17)	C(19)–N(4)–H(4)	107.5(16)
Σ N(2)	359.9	Σ N(4)	359.1
N(1)–Nb(1)–N(2)	105.88(6)	N(3)–Nb(2)–N(4)	105.54(6)
N(2)–Nb(1)–Cl(1)	103.40(4)	N(4)–Nb(2)–Cl(2)	104.13(4)

the cyclopentadienyl ligand, as has been observed in other half-sandwich imido compounds.[11-13] This has been postulated to be due to the primary interaction of the nitrogen lone pair being with a metal orbital *trans* to the cyclopentadienyl ring.[11] The Nb–N–C angles in the imido ligands of the two molecules in the unit cell, 162.97(12) and 164.05(12)°, deviate further from linear than the parent dichloride, for which the two molecules in the unit cell have angles of 172.5(3) and 170.0(3)°. This is most likely due to the presence of the *tert*-butylamido ligand increasing the steric bulk around the niobium atom.

The Nb–N$_{amido}$ bond lengths (1.9674(13) and 1.9677(14) Å) lie at the lower end of the reported range (1.935–2.102 Å).[14] The sum of the angles around the nitrogen atom is 359.9 and 359.1° for the two molecules in the asymmetric unit. This indicates that the nitrogen atom is planar, and hence sp^2 hybridised, however the angles around the nitrogen deviate from the ideal 120°. The short bond length and hybridisation imply that significant pπ ⟶ dπ bonding is occurring between the nitrogen and the metal centre, as has been determined for the dimethylamido group in homoleptic transition metal dimethylamido compounds.[15] If the π orbital of the amido ligand is taken to lie perpendicular to the plane of the three atoms around the amido nitrogen atom it will lie approximately in the plane containing the Nb, Cl and N$_{amido}$ atoms. The *tert*-butyl group of the amido ligand is oriented toward the imido group in both of the molecules in the asymmetric unit. This minimises the steric interactions of the *tert*-butylamido ligand with the other parts of the molecule. The orientation of the amido ligand in **1** is consistent with that predicted theoretically for the [Nb(η-C$_5$H$_5$)(NR)] fragment.[11,16]

The Nb–Cl distances of 2.4204(3) and 2.4085(4) Å are considerably longer than those of the parent dichloride [Nb-(η-C$_5$H$_5$)(NMe)Cl$_2$], which lie in the range 2.348–2.358 Å.[11] The amido group is a much stronger π donor than the chloride, thus the π interactions of the chloride with the niobium centre are much reduced, leading to a lengthening of the Nb–Cl bond. The packing diagram for **1** shows the *tert*-butyl groups of the molecules locking together, with the methyl group of one locking between two methyl groups on an adjacent molecule. This helps to explain the absence of disorder that is often evident in compounds containing *tert*-butyl groups.

The cyclopentadienyl ligand is oriented such that one of the apices is very close to eclipsing the bond between the niobium and the imido group, with the niobium atom displaced towards this side of the cyclopentadienyl ring. This results in a variation of the Nb–C distances around the ring, with the two bonds

trans to the imido ligand being the longest. This effect is less pronounced than in most other early transition metal half-sandwich imido compounds, in addition the C–C distances around the ring show no significant differences, thus the ring shows no real tendency toward an η^3 allyl-ene co-ordination.

The reaction between Li^{n}Bu and [Nb(η-C$_5$H$_5$)(N^{t}Bu)-(NH^{t}Bu)Cl] **1** in pentane at −78 °C yielded, after distillation, the yellow oil [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)^{n}Bu] **2** as the only tractable product (Scheme 1). Compound **2** was partially
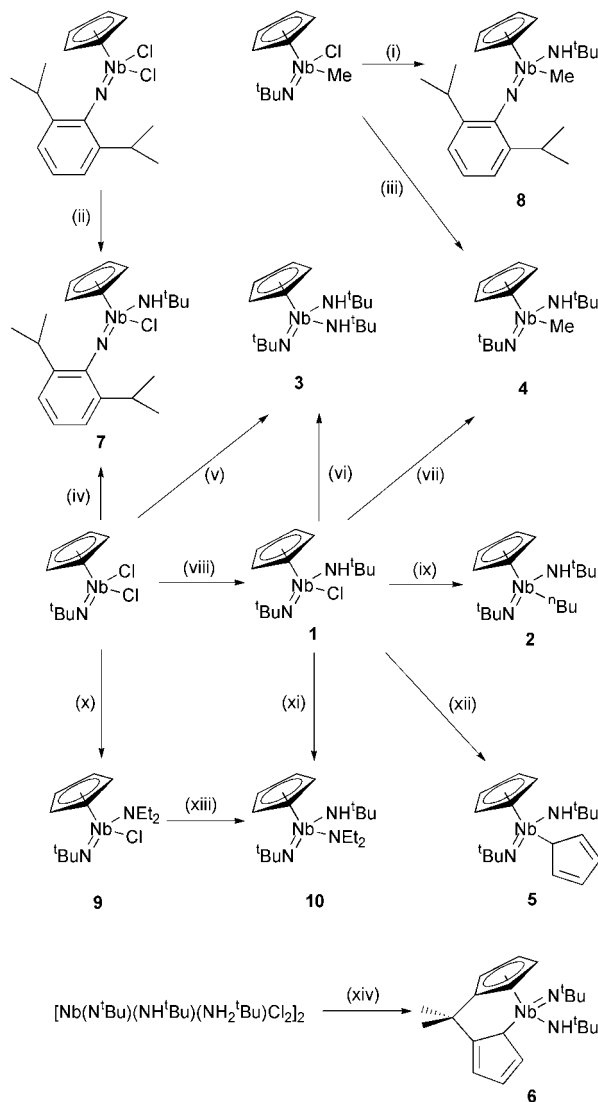
Scheme 1 *Reagents and conditions*: (i) LiNH(2,6-C$_6$H$_3$^{i}Pr$_2$), Et$_2$O, −78 °C. (ii) LiNH^{t}Bu, C$_6$H$_6$. (iii) LiNH^{t}Bu, C$_6$H$_6$. (iv) LiNH(2,6-C$_6$H$_3$^{i}Pr$_2$), Et$_2$O, −78 °C. (v) 2 LiNH^{t}Bu, C$_6$H$_6$. (vi) LiNH^{t}Bu, C$_6$H$_6$. (vii) LiMe, Et$_2$O, −78 °C. (viii) LiNH^{t}Bu, C$_6$H$_6$. (ix) ^{n}BuLi, C$_5$H$_{12}$, −78 °C. (x) LiNEt$_2$, Et$_2$O, −78 °C. (xi) LiNEt$_2$, Et$_2$O, −78 °C. (xii) Mg(C$_5$H$_5$)$_2$, C$_6$H$_6$. (xiii) LiNH^{t}Bu, C$_6$H$_6$. (xiv) Li$_2${(C$_5$H$_4$)$_2$CMe$_2$}, THF, −78 °C.

characterised by NMR spectroscopy. It sensitivity precluded an accurate elemental analysis, with decomposition occurring in a matter of seconds. The same difficulties were encountered for all of the compounds **2–6**. The resonances arising from the *n*-butyl group were assigned with the aid of a proton–proton correlation spectrum; the methylene protons adjacent to the chiral niobium centre are diastereotopic, due to the chiral niobium centre, and give rise to two multiplets. The ^{13}C-{^{1}H} NMR spectrum was assigned with the help of a ^{13}C–^{1}H correlation of the gHSQC type. The resonance due to the α-carbon of the *n*-butyl ligand was not observed.

The reaction between compound **1** and one equivalent of LiNH^{t}Bu gave [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)$_2$] **3**. However a

more convenient route to **3** was the reaction between two equivalents of LiNH^{t}Bu and [Nb(η-C$_5$H$_5$)(N^{t}Bu)Cl$_2$] in benzene. The initial yellow-brown oil was purified by distillation to give **3** as a bright yellow oil which was highly air- and moisture-sensitive and decomposed in air in seconds to a yellow material. Compound **3** could also be synthesized from the reaction of four equivalents of the lithium amide with [Nb(η-C$_5$H$_5$)Cl$_4$] in benzene.

Compound **3** was partially characterised by NMR and mass spectrometry, but proved too moisture-sensitive for an accurate elemental analysis to be obtained. The ^{1}H NMR spectrum in d$_6$-benzene contained three sharp singlets with integrals in the ratio 5:18:9 and a broad singlet at δ 4.81, integrating as two protons. The NH resonance at δ 4.81 is at a considerably lower chemical shift than that of other niobium alkylamido groups which normally occur in the region δ 6.5–7.6. A one-dimensional NOE difference spectrum of **3**, with the amido NH being irradiated, showed an NOE only to the peak integrating as 18 protons. These data clearly assign the structure of **3** in solution as [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)$_2$] rather than the isomer [Nb(η-C$_5$H$_5$)(N^{t}Bu)$_2$(NH$_2$^{t}Bu)].

The amido ligands can only donate two π electrons to the metal centre between them, *i.e.* four electrons in total, as there is only one orbital with π symmetry with respect to these ligands remaining on the metal centre.[16] This is borne out by the low Δδ values found for the amido ligands (see below). Thus **3** is not a 20-electron compound, as it would be if both of the amido lone pairs were donated to the metal centre, but can be considered as an 18 + 2 electron compound, with a pair of electrons residing on the amido ligands.

Reaction between compound **3** and a solution of HCl in diethyl ether yielded a yellow waxy solid which the ^{1}H NMR spectrum showed to be [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl] **1**. Reaction between **3** and Brookhart's acid [H(OEt$_2$)$_2$][B(C$_6$H$_3$-(CF$_3$)$_2$-3,5)$_4$][17] yielded [H$_3$N^{t}Bu][B(C$_6$H$_3$(CF$_3$)$_2$-3,5)$_4$] as the only tractable product.

The reaction between compound **1** and either LiMe or MgBrMe gave [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Me] **4**. However, the products of these reactions could not easily be purified. A better route involved the reaction between [Nb(η-C$_5$H$_5$)(N^{t}Bu)-Me(Cl)] and LiNH^{t}Bu in benzene. This yielded a red oil from which pure **4** could be isolated by sublimation as a pale yellow low-melting solid, highly air- and moisture-sensitive, and soluble in non-protic organic solvents. Compound **4** was partially characterised by NMR and mass spectrometry, its sensitivity precluded an accurate elemental analysis.

The thermal elimination of *tert*-butylamine or methane from compound **3** or **4** respectively was investigated. Heating solutions of either **3** or **4** in benzene to 140 °C for prolonged periods did not yield any tractable products. The same reactions were studied in a sealed NMR tube, with d$_6$-benzene as the solvent, in the presence of trimethylphosphine to trap out any unsaturated species formed. Prolonged heating to 140 °C did not afford a clean elimination. The formation of *tert*-butylamine and methane was observed in the cases of **3** and **4** respectively, however a mixture of products resulted, none of which contained co-ordinated trimethylphosphine.†

The reaction between compound **1** and Mg(C$_5$H$_5$)$_2$ in benzene affords [Nb(η-C$_5$H$_5$)$_2$(N^{t}Bu)(NH^{t}Bu)] **5** as an extremely air- and moisture-sensitive waxy yellow solid. The product could not be further purified as it could not be induced to crystallise, and decomposition occurred when sublimation was attempted. It was partially characterised by NMR spectroscopy; repeated attempts to obtain a mass spectrum were

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† We note that the complex [Ta(η-C$_5$H$_5$)(NPh)(NHPh)$_2$] was reported to be 'inactive under thermolysis conditions'.[9] In addition, during the production of this manuscript, Royo and Sánchez–Nieves reported the elimination of methane from [Ta(η-C$_5$Me$_5$)(N^{t}Bu)(NH^{t}Bu)Me] and subsequent aryl C–H activation of benzene and toluene.[19]

unsuccessful. It would seem reasonable to describe the structure as [Nb(η-C$_5$H$_5$)(η^1-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)], by which the compound achieves an eighteen electron configuration at the metal. However, all of the cyclopentadienyl resonances are observed to be equivalent in both the ^{1}H and ^{13}C-{^{1}H} NMR spectra, and variable temperature NMR studies showed no changes in either of these spectra on cooling to −90 °C in d$_8$-toluene. The two inequivalent rings must therefore be involved in a rapid exchange process, as has been observed previously for the compound [Nb{(η-C$_5$H$_4$)CMe$_2$(η^1-C$_5$H$_4$)}(NMe$_2$){N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}].[20] In this instance broadening of the ^{13}C resonances of the cyclopentadienyl ring was observed at low temperatures. The authors concluded that this broadening was due to an η^1–η^5 exchange rather than two fluxional η^3 rings, which would also satisfy the 18 electron rule.

It was postulated that the introduction of an *ansa* bridge between the two cyclopentadienyl ligands might aid in the isolation of a η^5, η^1 biscyclopentadienyl compound by increasing its crystallinity. This is observed for the corresponding methyl compounds, [Nb(η-C$_5$H$_5$)$_2$(N^{t}Bu)Me] is isolated as an oil,[21] whereas [Nb{(η-C$_5$H$_4$)$_2$CMe$_2$}(N^{t}Bu)Me] is a solid at room temperature.[22]

The reaction between Li$_2$(C$_5$H$_4$)$_2$CMe$_2$ and [Nb(N^{t}Bu)-(NH^{t}Bu)(NH$_2$^{t}Bu)Cl$_2$]$_2$[23] in THF at −78 °C afforded an approximately 7:1 mixture of the desired amido compound [Nb{(η-C$_5$H$_4$)CMe$_2$(η^1-C$_5$H$_4$)}(N^{t}Bu)(NH^{t}Bu)] **6** and the chloride [Nb{(η-C$_5$H$_4$)$_2$CMe$_2$}(N^{t}Bu)Cl]. Attempts to purify **6** by fractional crystallisation were unsuccessful. The ^{1}H NMR spectrum of **6** contained a broad singlet at δ 6.88 that was assigned to the amido proton. In addition to this the resonances of the protons of the cyclopentadienyl rings were observed as four multiplets integrating as two protons each, showing the two cyclopentadienyl rings to be equivalent at room temperature. The protons of the *tert*-butyl groups in the amido and imido groups were observed as sharp singlets.

On cooling a sample of compound **6** in d$_8$-toluene to −93 °C no changes were observed in the ^{1}H NMR spectrum, however the ^{13}C-{^{1}H} spectrum showed a significant broadening of the peaks due to the carbon atoms of the cyclopentadienyl rings. The peak widths (Δν) at −93 °C were in the range 9.5–23.5 Hz, as compared to the spectrum at 20 °C where the peak widths are 2.1–6.7 Hz. The analogous peaks due to the chloride impurity remain sharp, allowing this broadening to be attributed to a dynamic process rather than the increased viscosity of the solvent. This broadening is similar to that observed for the compound [Nb{(η-C$_5$H$_4$)CMe$_2$(η^1-C$_5$H$_4$)}(NMe$_2$){N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}], described previously.[20] It is reasonable to assume that the broadening observed for **6** results from the same dynamic process.

In an attempt to synthesize more crystalline analogues of these compounds, [Nb(η-C$_5$H$_5$)(N^{t}Bu)Cl$_2$] was treated with LiNH(C$_6$H$_3$^{i}Pr$_2$-2,6) to afford [Nb(η-C$_5$H$_5$){N(C$_6$H$_3$^{i}Pr$_2$-2,6)}-(NH^{t}Bu)Cl] **7**. The same product is obtained from the reaction between [Nb(η-C$_5$H$_5$){N(C$_6$H$_3$^{i}Pr$_2$-2,6)}Cl$_2$][11] and LiNH^{t}Bu; α proton transfer is occurring in the first instance so that the proton resides on the more basic nitrogen atom. That this is the case in solution is implied by the ^{13}C NMR chemical shifts for the ^{t}Bu group. The chemical shift of the α carbon is δ 59.54, in the range more normally associated with amido rather than imido ligands. In addition the value of Δδ for this group is 25 ppm. Although this is the highest value found in this work, it is still more typical of an amido rather than an imido group.

In order to confirm this the crystal structure of compound **7** was determined. The molecular structure is shown in Fig. 2 and selected interatomic distances and angles are given in Table 3. The data set was unfortunately not of sufficient quality to be able to find the amide proton in the difference map. However, the assignment between amido and imido moieties can easily be made from the two respective Nb–N–C angles (Nb–N(1)–C(6) 168.5(3), Nb–N(2)–C(18) 137.7(3)°). The crystal structure is

Table 3 Selected interatomic distances (Å) and angles (°) for [Nb(η-C_5H_5){N($C_6H_3{}^iPr_2$-2,6)}(NH${}^tBu$)Cl] **7**

Nb–N(1)	1.794(3)	N(1)–C(6)	1.393(5)
Nb–N(2)	1.958(3)	N(2)–C(10)	1.478(5)
Nb–Cl(1)	2.4004(11)	Nb–C(1)	2.475(5)
Nb–C(2)	2.436(4)	Nb–C(3)	2.400(5)
Nb–C(4)	2.471(5)	Nb–C(5)	2.512(5)
C(1)–C(2)	1.372(8)	C(2)–C(3)	1.401(7)
C(3)–C(4)	1.401(7)	C(4)–C(5)	1.386(8)
C(1)–C(5)	1.409(7)		
Nb–N(1)–C(6)	168.5(3)	Nb–N(2)–C(18)	137.7(3)
N(1)–Nb–N(2)	103.62(14)	N(1)–Nb–Cl(1)	102.36(10)
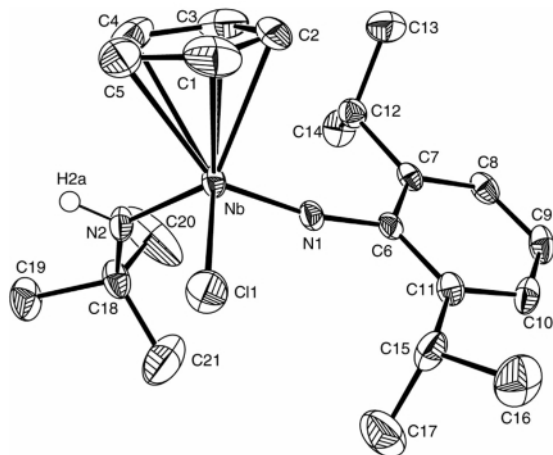
Fig. 2 The molecular structure of [Nb(η-C_5H_5){N($C_6H_3{}^iPr_2$-2,6)}-(NH${}^tBu$)Cl] **7**. Hydrogen atoms attached to carbon have been omitted for clarity.

found to bear out the structure inferred from the solution NMR data, in that the amide group contains the *tert*-butyl moiety.

The basic geometry is the same as that observed for compound **1**, with the *tert*-butyl group of the amido ligand oriented away from the cyclopentadienyl ring, whilst the aryl ring of the imido ligand is twisted so as to minimise steric interaction with the *tert*-butyl group. The Nb–N$_{imido}$ and Nb–N$_{amido}$ bond lengths in **1** and **7** are also comparable. The Nb–Cl bond is again longer than in the parent imido compound (2.4004(11) *vs.* 2.338(2) Å).[11]

The reaction between [Nb(η-C_5H_5)(N${}^tBu$)Me(Cl)] and LiNH($C_6H_3{}^iPr_2$-2,6) afforded [Nb(η-C_5H_5){N($C_6H_3{}^iPr_2$-2,6)}-(NH${}^tBu$)Me] **8** as yellow crystals. The $\Delta\delta$ value observed for the *tert*-butyl group in this compound, which is more typical of an amido rather than an imido group (see below), implies the transfer of the α-proton as occurred in the synthesis of **7**. The resonance of the amido proton in this compound could not be found; it may be too broad to be observed.

As α-proton transfer between amido and imido groups appears to be facile in these complexes, more basic amido groups were introduced to aid the formation of a complex of the form [Nb(η-C_5H_5)(N${}^tBu$)$_2$(NHR$_2$)]. The reaction between [Nb(η-C_5H_5)(N${}^tBu$)Cl$_2$] and LiNEt$_2$ afforded [Nb(η-C_5H_5)-(N${}^tBu$)(NEt$_2$)Cl] **9** as a dark red oil. The ${}^1H$ NMR spectrum revealed four multiplets at δ 4.15, 3.70, 3.26 and 3.01, each integrating to one proton. These signals were assigned as the four methylene protons on the diethylamido ligand. As a consequence of the chiral niobium centre these protons are diastereotopic; furthermore, slow rotation about the niobium–nitrogen bond renders them inequivalent on the NMR timescale. The coupling of the methylene protons to the two inequivalent methyl groups produces two pseudo triplets at δ 1.04 and 0.91. The assignment of these protons was aided by homonuclear decoupling experiments.

Table 4 Experimentally determined rates of rotation about the Nb–N$_{amide}$ bond in compound **9**

T/K	k/s^{-1}
263	0.11
268	0.47
273	1.29
278	4.53
283	14.93

The rate of rotation of the amido group was determined by ${}^1H$ NMR saturation transfer experiments at a series of different temperatures. At 263 K the rate of rotation was found to be 0.11 s^{-1}; as the sample was warmed to 283 K this rate increased to 14.93 s^{-1}. The rates obtained over the range of temperatures are listed in Table 4. An Arrhenius plot of these data afforded the activation energy barrier $E_a = 151(5.0)$ kJ mol^{-1}. There are two possible factors that may account for this high energy barrier. First nitrogen lone pair donation to the niobium centre will make rotation about the Nb–N$_{amido}$ bond disfavourable, secondly steric interactions of the bulky diethylamido group within the half-sandwich niobium imido environment may hinder its rotation.

The reaction between compound **9** and LiNH${}^tBu$ afforded [Nb(η-C_5H_5)(N${}^tBu$)(NH${}^tBu$)(NEt$_2$)] **10**. The same compound is also formed in the reaction between **1** and LiNEt$_2$. The ${}^1H$ NMR spectrum of this molecule displayed two inequivalent resonances for the protons of the *tert*-butyl groups at δ 1.37 and 1.26. Two sets of *tert*-butyl C$_\beta$ resonances were observed in the ${}^{13}C$ NMR spectrum, however only one C$_\alpha$ resonance was observed, at δ 65.7. The second C$_\alpha$ resonance is coincident with the methylene carbon signal of the diethylamido group at δ 54.0. These data are consistent with the formation of the bisamido as opposed to the isomeric bisimide [Nb(η-C_5H_5)-(N${}^tBu$)$_2$(NHEt$_2$)]. The resonances of the α-protons of the diethylamido ligand were observed as two multiplets in this instance; the barrier to rotation of the diethylamido group is thus significantly lower than that for **9**. As a *tert*-butylamido group is significantly bulkier than a chloride, this implies that the main barrier to rotation in **9** is electronic in nature. As described for **3** the two amido ligands compete for a single remaining orbital of π* symmetry with respect to the amido ligands; the others are involved in bonding to the much more strongly π donating cyclopentadienyl and imido ligands. This decreased π donation from the amido ligand to the niobium atom lowers the barrier to rotation about the Nb–N$_{amido}$ bonds.

The presence of a basic amido group in compound **10** does not facilitate the formation of a bisimido complex *via* the transfer of an α-proton; **10** still contains one imido and two amido groups.

Study of the $\Delta\delta$ values of *tert*-butyl containing ligands in complexes 1–10

The values of $\Delta\delta$ for the *tert*-butyl groups of the imido and amido ligands of compounds **1**–**10** are listed in Table 5. The trends observed for the values of $\Delta\delta_{imido}$ measured in this work follow those that have been noted previously, in that the presence of more electronegative substituents on the metal centre leads to a greater degree of π donation from the imido nitrogen, and hence a greater value of $\Delta\delta_{imido}$.[2,24] Thus the greatest value (36.3 ppm) is observed for [Nb(η-C_5H_5)(N${}^tBu$)(NEt$_2$)Cl] **9**, and the least for [Nb(η-C_5H_5)(N${}^tBu$)(NH${}^tBu$)${}^nBu$] **2** (32.0 ppm). The values of $\Delta\delta_{amido}$ show a similar trend, with the greatest value in a monoamido compound being observed for [Nb(η-C_5H_5){N($C_6H_3{}^iPr_2$-2,6)}(NH${}^tBu$)Cl] **7** (26.9 ppm), and the smallest for [Nb(η-C_5H_5)(N${}^tBu$)(NH${}^tBu$)Me] **4** (20.9 ppm). The two bisamido compounds **3** and **10** both show values lower than this (19.7 and 19.3 ppm respectively) due to the competition between the amido groups for the single π orbital that is

Table 5 The values of $\Delta\delta$ and δ_{NH} measured for compounds **1–10**

Compound	$\Delta\delta_{imido}$ (ppm)	$\Delta\delta_{amido}$ (ppm)	δ_{NH}
1 [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl]	35.6	23.5	7.56
2 Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)^{n}Bu]	32.0	21.0	6.54
3 [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)$_2$]	33.5	19.7	4.80
4 [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Me]	32.4	20.9	6.72
5 [Nb(η-C$_5$H$_5$)(η^1-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)]	34.3	22.6	7.06
6 [Nb{(η-C$_5$H$_4$)CMe$_2$(η^1-C$_5$H$_4$)}(N^{t}Bu)(NH^{t}Bu)]	34.4	22.1	6.88
7 [Nb(η-C$_5$H$_5$){N(C$_6$H$_3^i$Pr$_2$-2,6)}(NH^{t}Bu)Cl]	—	26.9	8.00
8 [Nb(η-C$_5$H$_5$){N(C$_6$H$_3^i$Pr$_2$-2,6)}(NH^{t}Bu)Me]	—	24.2	^{a}
9 [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NEt$_2$)Cl]	36.3	—	—
10 [Nb(η-C$_5$H$_5$(N^{t}Bu)(NH^{t}Bu)(NEt$_2$)]	32.9	19.3	4.55

^{a} Not found.
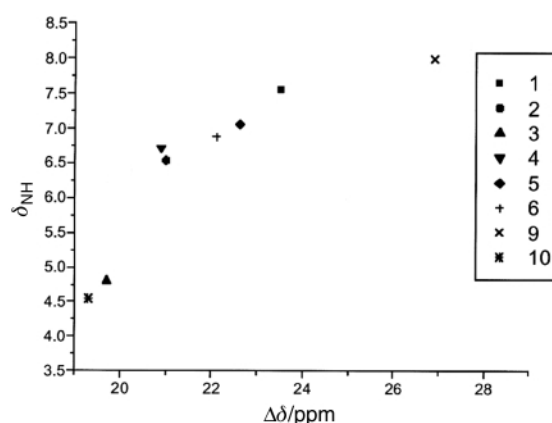
Fig. 3 A scatter plot of δ_{NH} against $\Delta\delta$ for the *tert*-butylamido groups of compounds **1–6**.

not involved in bonding to the cyclopentadienyl or imido ligands.

As the electron density on the nitrogen atom is decreased the amido proton will become more acidic, and hence deshielded. It may therefore be expected that, in addition to the $\Delta\delta$ values decribed above, δ_{NH} should also give a qualitative indication of the electron density on the amido nitrogen. Thus the chemical shift of the NH proton in **4** ($\Delta\delta = 20.9$ ppm) is 6.72 whereas that of **7** ($\Delta\delta = 26.9$ ppm) is 8.00. Those of the other monoamido complexes occur between these two extreme values, whilst the chemical shifts of the two bisamido complexes **3** and **10** are again found to be much lower than those of the monoamido complexes at δ 4.80 and 4.55 respectively.

A scatter plot of $\Delta\delta_{amido}$ against δ_{NH} is shown in Fig. 3. It can be seen that compounds with greater values of $\Delta\delta_{amido}$ do indeed have greater values of δ_{NH}, with an approximately linear trend for the monoamido compounds. However, even a cursory examination of the literature shows that compounds of other metals containing the *tert*-butylamido group do not give data points that lie near those in Fig. 3. For example, [Ta(η-C$_5$Me$_5$){N(C$_6$H$_3$Me$_2$-2,6)}(NH^{t}Bu)Me] (δ_{NH} 5.04, $\Delta\delta = 22.5$),[25] [Zr(η-C$_5$H$_5$)$_2$(NH^{t}Bu)Me] (δ_{NH} 5.28, $\Delta\delta = 22.0$)[3] and [Zr(η-C$_5$H$_5$)$_2$(NH^{t}Bu)$_2$] (δ_{NH} 3.77, $\Delta\delta = 20.8$),[3] thus any such trend can only be considered within a closely related family of compounds.

Experimental

General

All manipulations of air- and/or moisture-sensitive materials were performed under an inert atmosphere of dinitrogen using standard Schlenk line techniques, or in an inert atmosphere dry box containing dinitrogen. Solvents were dried over the appropriate drying agent and distilled under nitrogen. Deuteri-

ated solvents were dried over potassium and vacuum distilled prior to use.

The compounds [Nb(η-C$_5$H$_5$)Cl$_4$],[26] [Nb(η-C$_5$H$_5$)(N^{t}Bu)-Cl$_2$],[11] [Nb(η-C$_5$H$_5$)(N^{t}Bu)Me(Cl)],[18] [Nb(N^{t}Bu)(NH^{t}Bu)(NH$_2$-^{t}Bu)Cl$_2$]$_2$,[23] [Mg(C$_5$H$_5$)$_2$][27] and [H(OEt$_2$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$-3,5)$_4$][17] were prepared according to literature procedures. The compound (C$_5$H$_5$)$_2$CMe$_2$ was prepared according to the literature procedure[28] and its dilithium salt *via* reaction with Li^{n}Bu in pentane. The lithium salts of *tert*-butylamine and 2,6-diisopropylaniline were prepared in a similar manner.

The compounds NbCl$_5$, LiNEt$_2$, *tert*-butylamine, 2,6-diisopropylaniline and solutions of LiMe in diethyl ether, Li^{n}Bu in hexanes, MgClMe in ether, and hydrogen chloride in ether were purchased from the Aldrich chemical company. The amines were dried over calcium hydride and distilled prior to use; NbCl$_5$ was purified by sublimation at 80 °C, 10^{-3} mbar. All other compounds were used as received.

NMR spectra were recorded on a Varian UnityPlus 500 (^{1}H and ^{13}C at 499.988 and 125.718 MHz respectively) or a Varian VXR 400 spectrometer (^{1}H and ^{13}C at 399.95 and 100.58 MHz respectively) at room temperature in d$_6$-benzene unless otherwise stated. They were 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). Electron impact mass spectra were recorded by the mass spectrometry service of the Dyson Perrins Laboratory in Oxford or on a VG7070E Organic Mass Spectrometer. Elemental analyses were provided by the microanalytical departments of the Inorganic Chemistry Laboratory, Oxford or the Chemistry Laboratory, Durham.

Crystallography

Crystallographic data and details of the data collection procedures and structure refinement for structures **1** and **7** are presented in Table 6. Data for **1** were collected as previously described,[29] the images being processed with the DENZO and SCALEPACK programs.[30] All solution, refinement and graphical calculations were performed using the CRYSTALS[31] and CAMERON[32] software packages. The program SHELXTL[33] was used for crystal structure solution and refinement of compound **7**. A peak of 3.3 e Å^{-3}, 1.76 Å from Nb and close to N(2), was modelled as a part chlorine atom with occupancy of *ca.* 9% with an isotropic displacement parameter. All attempts at modelling this peak as part O or N failed. We tentatively suggest that either the crystal contained a small quantity of Nb(η-C$_5$H$_5$)Cl$_2${N(C$_6$H$_3^i$Pr$_2$-2,6)} or that the peak arises from a crystallographic artefact such as unresolved twinning.

CCDC reference number 186/2204.

See http://www.rsc.org/suppdata/dt/b0/b006333i/ for crystallographic files in .cif format.

Preparations

[Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl] 1. A colourless solution of LiNH^{t}Bu (0.534 g, 6.67 mmol) in benzene (30 ml) was added

Table 6 Crystal data and structure refinement for compounds **1** and **7**

	1	**7**
Empirical formula	$C_{13}H_{24}ClN_2Nb$	$C_{21}H_{32}ClN_2Nb$
Formula weight	336.71	440.85
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	9.2540(2)	9.165(2)
b/Å	12.8240(4)	14.166(4)
c/Å	15.2510(5)	16.807(3)
α/°	84.936(2)	
β/°	75.035(2)	96.78(3)
γ/°	69.865(2)	
U/Å³	1641.6	2166.8(9)
Z	2	4
T/K	150	160
μ/mm^{-1}	0.88	0.69
Reflections collected	6297	4433
Independent reflections	6037	3824
R	0.0286	0.0396
Rw	0.0328	0.1021

dropwise at room temperature to a stirred yellow solution of [Nb(η-C_5H_5)(N^{t}Bu)Cl$_2$] (2.00 g, 6.67 mmol) in benzene (50 ml) over the course of 10 minutes. The solution rapidly became a paler yellow, and a precipitate formed. The reaction mixture was stirred for 20 minutes at which time the volatiles were removed under reduced pressure and the resulting yellow solid was extracted in pentane (3 × 20 ml). The pale yellow extracts were filtered to remove LiCl, and the volume reduced to 30 ml under reduced pressure. Slow cooling of this solution to −20 °C gave the desired product as a very pale yellow microcrystalline solid which was isolated by filtration, washed with cold pentane (10 ml) and dried *in vacuo*. A further reduction in volume of the filtrate to 15 ml, followed by cooling to −20 °C, yielded a second crop of crystals. Yield 2.0 g, 90% based upon [Nb(η-C_5H_5)-(N^{t}Bu)Cl$_2$].

[Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)^{n}Bu] 2. A solution of Li^{n}Bu in hexanes (0.36 ml of a 2.5 M solution, 0.9 mmol) was added to a pale yellow solution of [Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)Cl] (0.305 g, 0.91 mmol) in pentane at −78 °C. The addition caused the solution to become a darker yellow. The solution was stirred at low temperature for 30 minutes, then allowed to warm slowly to room temperature, during which time a white precipitate was produced, with a concomitant change from pale yellow to red-brown. The reaction mixture was filtered to remove LiCl and the volatiles were removed under reduced pressure to yield the crude product as a brown oil. This oil was then purified by sublimation at 80 °C, 10^{-3} mbar to afford the product as a bright yellow oil. Yield 0.06 g, 19.4% based on [Nb(η-C_5H_5)-(N^{t}Bu)(NH^{t}Bu)Cl].

[Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)$_2$] 3. A colourless solution of LiNH^{t}Bu (0.790 g, 10.0 mmol) in benzene (15 ml) was added dropwise at room temperature to a yellow solution of [Nb(η-C_5H_5)(N^{t}Bu)Cl$_2$] (1.500 g, 5.0 mmol) in benzene (20 ml) over 10 minutes. On addition of LiNH^{t}Bu the reaction mixture became very pale yellow, and a white precipitate formed. The mixture was stirred for 20 minutes at which time the volatiles were removed under reduced pressure and the resulting yellow-brown oil was extracted with pentane (2 × 20 ml). The volatiles were removed from the combined extracts under reduced pressure to yield the crude product as a yellow-brown oil. Sublimation at 100 °C, 2 × 10^{-4} mbar afforded the product as a bright yellow oil. Yield 1.11 g, 59.5% based on [Nb(η-C_5H_5)-(N^{t}Bu)Cl$_2$].

[Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)Me] 4. A colourless solution of LiNH^{t}Bu (0.155 g, 1.97 mmol) in benzene (15 ml) was added dropwise over 10 minutes to a yellow solution of [Nb(η-

C_5H_5)(N^{t}Bu)Me(Cl)] (0.550 g, 1.97 mmol) in benzene (10 ml). The reaction mixture was stirred for further 4 hours, after which time a white precipitate was observed, whilst the solution had become pale yellow. The volatiles were removed under reduced pressure and the resulting red-brown oil was extracted with pentane (2 × 10 ml) to give a yellow-brown solution. The volatiles were removed from the combined extracts under reduced pressure to give the crude product as a red oil. Sublimation at 80 °C, 8 × 10^{-4} mbar afforded the product as a yellow low-melting solid. Yield 0.48 g, 77.5% based upon [Nb(η-C_5H_5)-(N^{t}Bu)Me(Cl)].

[Nb(η-C_5H_5)(η^1-C_5H_5)(N^{t}Bu)(NH^{t}Bu)] 5. A colourless solution of Mg(η-C_5H_5)$_2$ (0.344 g, 2.23 mmol) in toluene (15 ml) was added to a pale yellow, stirred solution of [Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)Cl] (1.5 g, 4.45 mmol) in toluene (15 ml) at room temperature. The reaction mixture became a darker yellow, and a white precipitate occurred. The solution was stirred for 20 minutes. The volatiles were removed under reduced pressure and the resulting yellow solid was extracted with pentane (2 × 20 ml). The volatiles were removed from the combined extracts under reduced pressure to leave the crude product as a waxy yellow solid. Yield 1.3 g, 77.3% based upon [Nb(η-C_5H_5)(N^{t}Bu)(NH^{t}Bu)Cl].

[Nb{(η-C_5H_5)CMe$_2$(η^1-C_5H_5)}(N^{t}Bu)(NH^{t}Bu)] 6. A solution of Li$_2${(η-C_5H_4)$_2$CMe$_2$} (0.145 g, 0.78 mmol) in THF (15 ml) was cooled to −78 °C and added dropwise to a pre-cooled, yellow solution of [Nb(N^{t}Bu)(NH^{t}Bu)(NH$_2$^{t}Bu)Cl$_2$]$_2$ (0.300 g, 0.39 mmol) in THF (10 ml). The reaction mixture was stirred at low temperature for 30 minutes, allowed to warm to room temperature over the course of 3 hours, then stirred for 30 minutes. The volatiles were removed under reduced pressure and the resulting yellow oily solid was extracted into pentane (2 × 20 ml). This yellow solution was filtered to remove LiCl, concentrated to 5 ml and cooled to −80 °C to yield a yellow solid, which was isolated by filtration, washed with cold pentane (5 ml) and dried *in vacuo*. Yield 0.22 g (88% product), 61.6% based upon [Nb(N^{t}Bu)(NH^{t}Bu)(NH$_2$^{t}Bu)Cl$_2$]$_2$.

[Nb(η-C_5H_5){N(C_6H_3^{i}Pr$_2$-2,6)}(NH^{t}Bu)Cl] 7. *Method A.* Cold Et$_2$O (100 ml, −78 °C) was added to a solid mixture of [Nb(η-C_5H_5)(N^{t}Bu)Cl$_2$] (0.99 g, 3.30 mmol) and LiNH-(C_6H_3^{i}Pr$_2$-2,6) (0.61 g, 3.33 mmol), and allowed to reach room temperature. On stirring for 12 hours a pale flocculent precipitate and an orange-red solution were formed. Subsequent filtration and removal of the volatiles under reduced pressure afforded an orange-red oil. This oil was washed with cold light petroleum (bp 40–60 °C, −30 °C), and the yellow powder residue recrystallised from toluene at −78 °C to afford the product as yellow crystals which were isolated by filtration and dried *in vacuo*. Yield 0.45 g, 31% based on [Nb(η-C_5H_5)(N^{t}Bu)Cl$_2$].

Method B. Cold Et$_2$O (100 ml, −78 °C) was added to a solid mixture of [Nb(η-C_5H_5)(NC_6H_3^{i}Pr$_2$-2,6)Cl$_2$] (0.99 g, 3.30 mmol) and LiNH^{t}Bu (0.61 g, 3.33 mmol), and the mixture allowed to reach room temperature. After stirring for 16 hours an orange solution and a pale precipitate were formed. The supernatant was filtered and reduced to half volume under reduced pressure. Cooling to −20 °C afforded the product as yellow cubic crystals which were collected by filtration, washed with cold pentane (10 ml) and dried *in vacuo*. Yield 0.21 g, 34% based on [Nb(η-C_5H_5)(NC_6H_3^{i}Pr$_2$-2,6)Cl$_2$].

[Nb(η-C_5H_5){N(C_6H_3^{i}Pr$_2$-2,6)}(NH^{t}Bu)Me] 8. A solution of [Nb(η-C_5H_5)(N^{t}Bu)Me(Cl)] (0.5 g, 1.79 mmol) in diethyl ether (15 ml) at −78 °C was added to a stirred suspension of LiNH(C_6H_3^{i}Pr$_2$-2,6) in diethyl ether (15 ml). On warming to room temperature an immediate reaction occurred, leading to a yellow solution and a pale precipitate. The reaction mixture was

stirred for 12 hours. The supernatant was filtered and concentrated to half volume under reduced pressure. Cooling to −78 °C afforded the product as yellow crystals, which were isolated by filtration and dried *in vacuo*. Yield 0.58 g, 78% based on [Nb(η-C$_5$H$_5$)(N^{t}Bu)Me(Cl)].

[Nb(η-C$_5$H$_5$)(N^{t}Bu)(NEt$_2$)Cl] 9. Cold Et$_2$O (100 ml, −78 °C) was added to a solid mixture of [Nb(η-C$_5$H$_5$)(N^{t}Bu)Cl$_2$] (1.5 g, 5.17 mmol) and LiNEt$_2$ (0.41 g, 5.18 mmol) and allowed to reach room temperature. After stirring for 12 hours a pale precipitate and a red solution were formed. The supernatant was filtered, and the volatiles were removed under reduced pressure to afford the product as a dark red oil. Yield 1.57 g, 90% based on [Nb(η-C$_5$H$_5$)(N^{t}Bu)Cl$_2$].

[Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)(NEt$_2$)] 10. *Method A.* A solution of [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NEt$_2$)Cl] (1.16 g, 3.44 mmol) in Et$_2$O (30 ml) at −78 °C was added to a stirred suspension of LiNH^{t}Bu (0.27 g, 3.44 mmol) in Et$_2$O (50 ml) at room temperature. The mixture was allowed to reach room temperature, and stirred for 16 hours to a yield a pale precipitate and an orange-red solution. Filtration of the supernatant, followed by removal of the volatiles under reduced pressure, afforded the product as an orange-brown oil. Yield 1.11 g, 86% based on [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NEt$_2$)Cl].

Method B. Cold Et$_2$O (100 ml, −78 °C) was added to a solid mixture of [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl] (0.5 g, 1.48 mmol) and LiNEt$_2$ (0.12 g, 1.50 mmol) and allowed to reach room temperature. After stirring for 24 hours a pale precipitate and orange-brown solution were formed. The supernatant was filtered, and the volatiles were removed under reduced pressure to afford the product as an orange-brown oil. Yield 0.41 g, 74% based on [Nb(η-C$_5$H$_5$)(N^{t}Bu)(NH^{t}Bu)Cl].

Acknowledgements

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