Bis(η-cyclopentadienyl)imido Compounds of Niobium *

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The compound $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ has been synthesised and its crystal structure determined. It is the precursor for the new compounds $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Me]$, $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Br]$, $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(C_6H_5CH_2)]$ and $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(\sigma\text{-}C_3H_5)]$, and the hydrido derivative $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)H]$.

We have been interested in studying compounds containing both the η-cyclopentadienyl ligand and organoimido ligands :NR since we anticipate that this ligand combination will give rise to interesting reactivities. We and others have reported compounds with this ligand combination for compounds of the early transition metals, including molybdenum, tungsten,[1,2] niobium[3] and tantalum.[4] Recently we described the first example of a bis(η-cyclopentadienyl)imido derivative of niobium.[5] Here we describe further chemistry of bis(η-cyclopentadienyl)imido derivatives of niobium.

Results and Discussion

Treatment of $[Nb(\eta\text{-}C_5H_5)(NBu^t)Cl_2]$, which was prepared according to Gibson and co-workers,[3] with 1 equivalent of $Na(C_5H_5)$ in tetrahydrofuran (thf) at room temperature gave yellow crystals of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1** in *ca.* 85% yield. The characterising data for **1** and for all other new compounds described below are given in Table 1. The crystal structure of **1** has been determined by X-ray diffraction. Compound **1** is a monomer in the solid state and it shows two independent molecules in the unit cell. The structural parameters of each individual $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ molecule were substantially the same and the molecular structure of one of them is depicted in Fig. 1. Selected bond lengths and angles of both molecules are given in Table 2 and the atomic coordinates for all non-hydrogen atoms appear in Table 3. The Nb–N–C linkage is almost linear [Nb(1)–N(1)–C(1) 173.6(4), 179.4(5)°] which implies that the nitrogen is sp hybridised. The metal–nitrogen bond length [Nb(1)–N(1) 1.789(4), 1.737(6) Å] is comparable to the values found for other Nb=NR groups where the NR acts as a four-electron donor ligand.[6,7] The Nb–Cl bond distance [Nb(1)–Cl(1) 2.462(2), 2.453(2) Å] is noticeably longer than the range 2.338–2.358(2) Å observed for $[Nb(\eta\text{-}C_5H_5)(NR)Cl_2]$[3] but comparable to the value of 2.470(4) Å in $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$.[8] The bending angles [φ = 128.6, 130.3°] lie at the lowest end of the range of values previously recorded for other niobium metallocene derivatives.[9,10] Also the perpendicular niobium–ring distances [Nb(1)–$Cp_{(1)}$ 2.202, 2.201 and Nb(1)–$Cp_{(2)}$ 2.201, 2.198 Å] are slightly longer than those normally found in bis(η-cyclopentadienyl)niobium compounds (2.03–2.10 Å).[9] All these features are similar to the ones encountered for the previously reported $[Nb(\eta\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)(NBu^t)]$.[5]

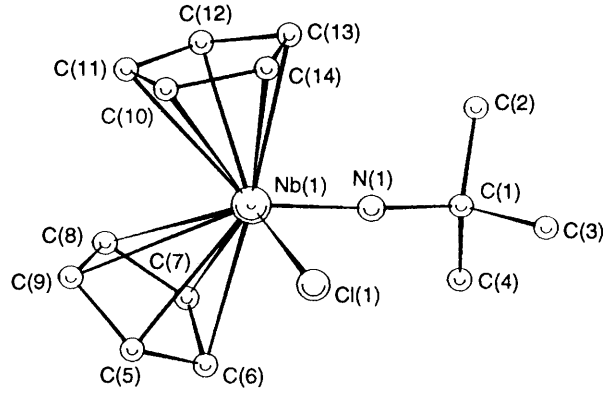

Fig. 1 Molecular structure of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1**. Hydrogen atoms are omitted for clarity

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of compound **1** shows there to be a large chemical shift difference (Δδ = 39.9 ppm, see Table 1) between the quaternary and the methyl carbons of the *tert*-butylimido group. Such a large chemical-shift difference lies at the high end of the range previously recorded for *tert*-butylimido species[7] and indicates a low electron density on the imido nitrogen due to the high degree of N→M π donation[7,11] and is associated with a terminal imido ligand acting as a four-electron ligand. On the basis of these structural and spectroscopic data we conclude that compound **1** apparently has formally a 20-electron configuration and that the lone pair on the imido ligand produces a degree of destabilisation in the bonding in the bis(η-cyclopentadienyl)niobium system. This effect was proposed to explain the same structural spectroscopic features of the bis(η-cyclopentadienyl)molybdenum compounds $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)]$ and $[Mo(\eta\text{-}C_5H_5)_2(NBu^t)Me]^+$.[1]

Treatment of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1** with 1 equivalent of methylmagnesium bromide gave a mixture of the compounds $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Me]$ **2** and $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Br]$ **3**. Pure **3** was obtained by recrystallisation of the mixture from pentane. When the reaction was carried out in the presence of 3 equivalents of the Grignard reagent, compound **2** was the only product. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2** in C_6D_6 shows resonances at δ 30.66 and 66.76, which are assigned to the methyl and quaternary carbon respectively of the *tert*-butylimido ligand. Only one other resonance is observed, the two η-cyclopentadienyl groups at δ 107.81, as is also seen in the ^1H NMR spectrum (δ 5.54). However, the signal expected for the ^{13}C resonance from the methyl ligand attached to the metal is not observed. This is attributed to the quadrupolar moment of the ^{93}Nb nucleus (spin $I = \frac{9}{2}$, natural abundance 100%) which causes broadening of the signal such that it is undetectable at room temperature. This phenomenon has been encountered in other niobium derivatives.[12,13]

The addition of a benzylmagnesium chloride solution to $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1** in diethyl ether gave yellow platelets of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(C_6H_5CH_2)]$ **4**. The $^{13}C\text{-}\{^1H\}$ NMR

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and spectroscopic data

		Analysis[a] (%)			
Compound	Colour	C	H	N	Spectroscopic data[b]
1	Yellow	51.15 (51.00)	6.00 (5.80)	4.25 (4.25)	^{1}H NMR: 5.85 (s, 5 H, C_5H_5), 0.96 (s, 9 H, CMe_3) ^{13}C-{^{1}H} NMR: 111.63 (C_5H_5), 69.81 ($\mathit{C}Me_3$), 29.93 ($C\mathit{Me}_3$) Mass spectrum (EI): *m/z* 330 M^+, 259 $[M - NBu^t]^+$, 194 $[M - NBu^t - C_5H_5]^+$, 129 $[M - NBu^t - (C_5H_5)_2]^+$
2	Yellow	58.35 (58.25)	7.35 (7.15)	4.85 (4.55)	^{1}H NMR: 5.54 (s, 10 H, C_5H_5), 0.98 (s, 9 H, CMe_3), 0.95 (s, 3 H, Me) ^{13}C-{^{1}H} NMR: 107.81 (C_5H_5), 66.76 ($\mathit{C}Me_3$), 30.66 ($C\mathit{Me}_3$) Mass spectrum (EI): *m/z* 310 M^+, 295 $[M - Me]^+$, 224 $[M - Me - NBu^t]^+$, 158 $[M - Me - NBu^t - C_5H_5]^+$
3	Deep yellow	44.80 (44.95)	5.25 (5.10)	3.45 (3.75)	^{1}H NMR: 5.82 (s, 10 H, C_5H_5), 0.96 (s, 9 H, CMe_3) ^{13}C-{^{1}H} NMR: 111.47 (C_5H_5), 70.30 ($\mathit{C}Me_3$), 29.71 ($C\mathit{Me}_3$) Mass spectrum (EI): *m/z* 375, 373 M^+, 303, 301 $[M - NBu^t]^+$, 238, 236 $[M - NBu^t - C_5H_5]$
4	Lemon yellow	65.85 (65.45)	6.75 (6.80)	3.60 (3.65)	^{1}H NMR: 7.39 (d, 2 H, *J* 7, C_6H_5, H_{ortho}), 7.31 (t, 2 H, *J* 8, C_6H_5, H_{meta}), 6.99 (t, 1 H, *J* 7, C_6H_5, H_{para}), 5.45 (s, 5 H, C_5H_5), 3.21 (s, 2 H, CH_2), 1.00 (s, 9 H, CMe_3) ^{13}C-{^{1}H} NMR (CD_2Cl_2): 155.56 (C_6H_5, C_{ipso}), 128.61 (C_6H_5, C_{ortho}), 127.90 (C_6H_5, C_{meta}), 121.62 (C_6H_5, C_{para}), 108.59 (C_5H_5), 67.41 ($\mathit{C}Me_3$), 32.25 (CH_2), 31.30 ($C\mathit{Me}_3$) Mass spectrum (EI): *m/z* 387 M^+, 295 $[M - C_7H_7]^+$, 224 $[M - C_7H_7 - NBu^t]^+$, 159 $[M - C_7H_7 - NBu^t - C_5H_5]^+$
5	Pale yellow	57.55[c] (60.90)	6.80 (7.20)	4.00 (4.20)	^{1}H NMR: 6.55 (m, 1 H, $CH_2{=}\mathit{C}\mathit{H}{-}CH_2$), 5.51 (s, 5 H, C_5H_5), 5.01 (ddt, 1 H, $^3J_{trans}$ 17, ^2J 2.5, ^4J 1.5, $\mathit{CH}_2{=}CH{-}CH_2$), 4.64 (dd, 1 H, ^3J 10, ^2J 2.5, $C\mathit{H}_2{=}CH{-}CH_2$), 2.70 (d, 2 H, *J* 8.5, $CH_2{=}CH{-}C\mathit{H}_2$), 0.95 (s, 9 H, CMe_3) ^{13}C-{^{1}H} NMR: 153.13 ($CH_2{=}\mathit{C}H{-}CH_2$), 108.58 ($C_5H_5$), 103.70 ($\mathit{C}H_2{=}CH{-}CH_2$), 67.37 ($\mathit{C}Me_3$), 32.27 (br, $CH_2{=}CH{-}\mathit{C}H_2$), 30.94 ($\mathit{C}Me_3$) Mass spectrum (EI): *m/z* 336 M^+, 294 $[M - C_3H_5]^+$, 223 $[M - C_3H_5 - NBu^t]^+$, 158 $[M - C_3H_5 - NBu^t - C_5H_5]^+$
6	Bright white	56.65 (56.95)	7.00 (6.85)	4.70 (4.75)	^{1}H NMR ([$^2H_8$]toluene, 230 K): 5.51 (s, 5 H, C_5H_5), 3.17 (br, $\Delta\nu_{\frac{1}{2}}$ 37 Hz, Nb–H), 0.95 (s, 9 H, CMe_3) ^{13}C-{^{1}H} NMR: 102.92 (C_5H_5), 64.23 ($\mathit{C}Me_3$), 31.68 ($C\mathit{Me}_3$) Mass spectrum (EI): *m/z* 296 M^+, 224 $[M - NBu^t]^+$, 159 $[M - NBu^t - C_5H_5]^+$ IR: ν(Nb–H) 1733 cm^{-1}

[a] Calculated values in parentheses. [b] The NMR spectra were obtained at 25 °C in C_6D_6 unless stated otherwise; data given as chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative intensity, ^{1}H–^{1}H coupling constant *J* (Hz) and assignment. [c] Not air stable.

Table 2 Selected bond lengths (Å) and angles (°) for the two independent molecules A and B of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1**

	Molecule A	Molecule B
Nb(1)–N(1)	1.789(4)	1.737(6)
Nb(1)–Cl(1)	2.462(2)	2.453(2)
Nb(1)–C(5)	2.558(8)	2.446(8)
Nb(1)–C(6)	2.439(7)	2.477(9)
Nb(1)–C(7)	2.426(7)	2.57(1)
Nb(1)–C(8)	2.490(7)	2.51(1)
Nb(1)–C(9)	2.612(7)	2.438(8)
Nb(1)–C(10)	2.545(8)	2.54(1)
Nb(1)–C(11)	2.558(8)	2.596(9)
Nb(1)–C(12)	2.399(9)	2.46(1)
Nb(1)–C(13)	2.447(8)	2.438(9)
Nb(1)–C(14)	2.489(8)	2.460(9)
Nb(1)–$Cp_{cent(1)}$	2.214	2.205
Nb(1)–$Cp_{cent(2)}$	2.205	2.211
Nb(1)–N(1)–C(1)	173.6(4)	179.4(5)
N(1)–Nb(1)–Cl(1)	93.6(1)	95.1(2)
$Cp_{cent(1)}$–Nb(1)–$Cp_{cent(2)}$	122.7	124.0
N(1)–Nb(1)–$Cp_{cent(1)}$	114.1	111.8
N(1)–Nb(1)–$Cp_{cent(2)}$	112.6	112.5
Cl(1)–Nb(1)–$Cp_{cent(1)}$	104.8	103.8
Cl(1)–Nb(1)–$Cp_{cent(2)}$	103.6	104.6

$Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the computed $\eta\text{-}C_5H_5$ centroids for atoms C(5)–C(10) and C(11)–C(14) respectively.

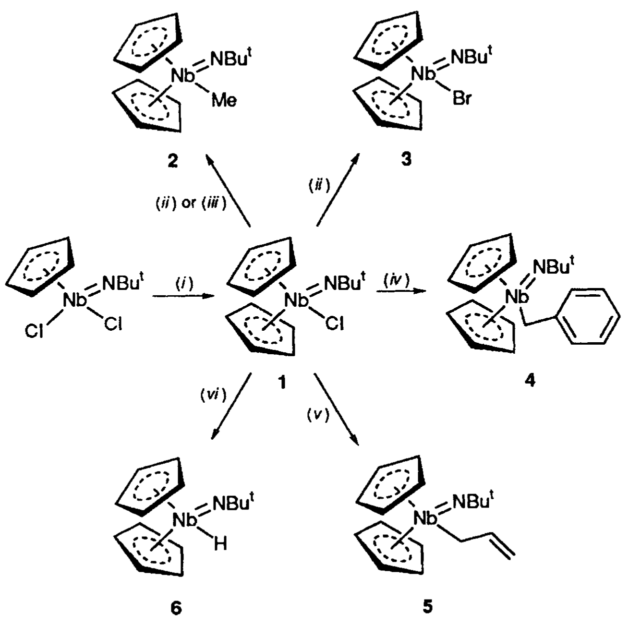
spectrum of **4** shows a small broad signal at δ 32.25 in CD_2Cl_2, corresponding to the α-carbon of the benzyl ligand. This band is the same region as for other benzylniobium derivatives.[14]

Treatment of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1** with allylmagnesium chloride gave pale yellow crystals of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(\sigma\text{-}C_3H_5)]$ **5**. The ^{1}H NMR spectrum of **5** shows bands corresponding to a σ-allyl ligand and there was no evidence for the presence of formation of a η^3-allyl group. For example, there was no evidence for dynamic behaviour associated with η^3-allyl ligands.[15] Besides, the occurrence of an η^3-allyl group would be expected to require one of the cyclopentadienyl rings to become η^3-co-ordinated. The ^{13}C NMR signal for the α-carbon of the allyl moiety of **5** is weak and broad, due to the quadrupolar moment of the niobium nucleus. Although all the spectroscopic studies performed on this compound showed high purity, we could not obtain a satisfactory elemental analysis due to its sensitivity.

Treatment of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ **1** with 1 equivalent of $Na[AlH_2(OCH_2CH_2OMe)_2]$ (Red-Al) in toluene gave the very air-sensitive hydride derivative $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)H]$ **6**. The hydride signal in the ^{1}H NMR spectra was barely observable at room temperature but a broad band was observed at δ 3.17 ($\Delta\nu_{\frac{1}{2}}$ = 37 Hz) in [$^2H_8$]toluene at 230 K. This chemical shift is unusual for a niobium hydride which are normally detected at higher fields.[10,16] We considered the possibility that this signal was due to a N–H resonance in the isomeric amido compound $[Nb(\eta\text{-}C_5H_5)_2(NHBu^t)]$ compound. However the assignment of the band at δ 3.17 to a

Table 3 Fractional atomic coordinates for [Nb(η-C_5H_5)$_2$(NBu^t)Cl] **1**

Atom	*X/a*	*Y/b*	*Z/c*
Nb(1)	0.379 74(6)	0.275 4(1)	0.519 24(4)
Nb(2)	0.147 16(6)	−0.033 9(1)	0.925 99(4)
Cl(1)	0.409 3(2)	0.400 4(2)	0.382 7(2)
Cl(2)	0.347 2(3)	0.036 6(2)	1.089 5(2)
N(1)	0.275 2(6)	0.356 1	0.581 2(4)
N(2)	0.256 8(7)	−0.131 5(5)	0.905 8(5)
C(1)	0.191 0(8)	0.411 1(5)	0.638 1(6)
C(2)	0.258(1)	0.398 0(8)	0.768 0(7)
C(3)	0.206(1)	0.518 1(6)	0.606 0(8)
C(4)	0.026 7(9)	0.380 2(9)	0.599 6(9)
C(5)	0.266(1)	0.186 0(7)	0.327 6(7)
C(6)	0.152(1)	0.220 4(7)	0.368 9(9)
C(7)	0.162(1)	0.166 4(7)	0.468 4(9)
C(8)	0.284(1)	0.103 1(6)	0.487 5(8)
C(9)	0.342(1)	0.113 4(6)	0.398 7(8)
C(10)	0.661 3(9)	0.242 4(8)	0.559 4(8)
C(11)	0.615(1)	0.168 7(6)	0.608 9(9)
C(12)	0.558 (1)	0.206(1)	0.688 8(9)
C(13)	0.588(1)	0.307(1)	0.696 7(9)
C(14)	0.647(1)	0.328 7(7)	0.612(1)
C(15)	0.349 4(8)	−0.212 7(7)	0.888 3(6)
C(16)	0.312(1)	−0.231(1)	0.760 0(9)
C(17)	0.314(2)	−0.304 4(9)	0.941(2)
C(18)	0.511(1)	−0.183 7(9)	0.932(1)
C(19)	−0.020(1)	−0.159 9(8)	0.962 8(8)
C(20)	−0.113(1)	−0.088(1)	0.910 7(9)
C(21)	−0.094(2)	−0.009(1)	0.982(2)
C(22)	0.029(2)	−0.033(2)	1.083(1)
C(23)	0.065(1)	−0.124(1)	1.067 3(8)
C(24)	0.137(2)	0.142 4(8)	0.854(1)
C(25)	−0.001(2)	0.110(1)	0.800(1)
C(26)	0.004(2)	0.031(1)	0.734 5(9)
C(27)	0.154(2)	0.020 0(9)	0.738(1)
C(28)	0.241(1)	0.090(1)	0.818(1)



Scheme 1 Preparation and reactions of [Nb(η-C_5H_5)$_2$(NBu^t)Cl] **1**. Reagents: (*i*) Na(C_5H_5) (1 equivalent) in thf, 12 h, room temperature; (*ii*) MgBrMe (1 equivalent) in diethyl ether at −40 °C for 12 h; (*iii*) MgBrMe (3 equivalents) in diethyl ether at −40 °C for 12 h; (*iv*) MgCl($C_6H_5CH_2$) (1 equivalent) in diethyl ether at −40 °C for 12 h; (*v*) MgCl(C_3H_5) (2 equivalents) in diethyl ether at −40 °C for 24 h; (*vi*) Red-Al (1 equivalent) in toluene for 3 h at 0 °C

niobium-bound hydrogen is supported by the observation of a band at 1733 cm^{-1} in the IR spectrum of **6** which is assignable to ν(Nb-H).[16a,b] Further, the difference in the chemical shift between the quaternary and the methyl carbons of the *tert*-butylimido group in the ^{13}C-{^{1}H} NMR spectrum of **6** is 32.6 ppm, which indicates a low electron density on the nitrogen expected for a linear Nb–N–Bu^t moiety. Finally, Bercaw and co-workers[4] have recently reported a tantalum analogue [Ta(η-C_5Me_5)$_2$(NC_6H_5)H] the Ta–H resonance of which appears in the ^{1}H NMR spectrum at δ 6.38.

In conclusion, the reactions and structures proposed for the new compounds **1**–**6** are given in Scheme 1.

Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen (< 10 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a dry-box.

Solvents were pre-dried over activated 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), sodium–potassium alloy [light petroleum (b.p. 40–60 °C) and diethyl ether] or phosphorus pentaoxide (dichloromethane), under dinitrogen. Deuteriated solvents for NMR samples were stored in ampoules over activated molecular sieves (C_6D_6) or dried using calcium hydride (CD_2Cl_2) and transferred by vacuum distillation. Light petroleum refers to that fraction of b.p. 40–60 °C.

The NMR spectra were recorded on a Brüker AM-300 (^{1}H, 300; ^{13}C, 75.43 MHz) NMR spectrometer and referenced internally using residual protio solvent resonances (^{1}H) and solvent resonances (^{13}C) relative to tetramethylsilane (δ = 0). Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services Ltd. Elemental analyses were performed by the Analytical Laboratory in this Department. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer 1710 FT-IR interferometer.

The Red-Al {Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] in toluene (3.4 mol dm^{-3})} and Grignard reagents were obtained from Aldrich and used as received.

Preparations.—[Nb(η-C_5H_5)$_2$(NBu^t)Cl] **1**. A solution of [Nb(η-C_5H_5)(NBu^t)Cl$_2$][3] (3.5 g, 11.67 mmol) in thf (150 cm^3) was treated with sodium cyclopentadienide (1.13 g, 12.84 mmol) in thf (10 cm^3) dropwise (10 min) at room temperature and the mixture was stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted with toluene (3 × 50 cm^3). After filtration the solvent was removed from the filtrate under reduced pressure. The dark yellow solid residue was extracted with light petroleum and the extract was concentrated and cooled to −25 °C. After 24 h bright yellow crystals separated and were collected and dried *in vacuo*. Yield 3.28 g, 85%.

[Nb(η-C_5H_5)$_2$(NBu^t)Me] **2**. A solution of [Nb(η-C_5H_5)$_2$(NBu^t)Cl] (0.40 g, 1.21 mmol) in diethyl ether (70 cm^3) at −40 °C was treated with methylmagnesium bromide (1.26 cm^3 of 1.92 mol dm^{-3} solution in diethyl ether, 2 equivalents) with stirring and allowed to warm to room temperature. The initially yellow solution became green-yellow after 12 h and a white precipitate formed. The volatiles were removed under reduced pressure and the residue was extracted with light petroleum (3 × 40 cm^3) and filtered. The solvent was evaporated and the solid re-extracted with light petroleum to eliminate any residual magnesium salts. Removal of the solvent gave the compound **2** which was obtained analytically pure by sublimation. Yield 200 mg, 53%.

[Nb(η-C_5H_5)$_2$(NBu^t)Br] **3**. A solution of [Nb(η-C_5H_5)$_2$(NBu^t)Cl] (0.40 g, 1.21 mmol) in diethyl ether (70 cm^3) at −40 °C was treated with methylmagnesium bromide (0.63 cm^3 of 1.92 mol dm^{-3} solution in diethyl ether, 1 equivalent) with stirring and was allowed to warm to room temperature. The initially yellow solution became bright yellow after 12 h and a white precipitate formed. The volatiles were removed under reduced pressure and the solid was extracted with light petroleum (3 × 40 cm^3) and filtered. The solvent was evaporated from the filtrate and the solid was extracted again with light petroleum to remove the residual magnesium salt. After filtration the solvent was removed giving a yellow solid. The ^1H NMR spectrum showed the product to be a mixture of compounds **2** and **3**. The bromide derivative **3** was present in a large excess (> 80%) over the methyl compound **2**. The solid product was dissolved in light petroleum, concentrated and cooled at −80 °C giving deep yellow crystals of **3**. Yield 150 mg, 33%.

$[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(C_6H_5CH_2)]$ **4**. A solution of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ (0.40 g, 1.21 mmol) in diethyl ether (70 cm^3) at −40 °C was treated with benzylmagnesium chloride (1.01 cm^3 of 1.2 mol dm^{-3} solution in diethyl ether, 1 equivalent) with stirring and it was allowed to warm to room temperature. The initially yellow solution became yellow-green after 12 h and a white precipitate formed. The volatiles were removed under reduced pressure and the solid was extracted with light petroleum (3 × 40 cm^3) and filtered. The solvent was evaporated from the filtrate and the solid was re-extracted with light petroleum as previously described in order to eliminate any magnesium salts. After filtration the solvent was removed giving a yellow solid. Recrystallisation from pentane gave lemon-yellow platelets at −80 °C of **4**. Yield 240 mg, 51%.

$[Nb(\eta\text{-}C_5H_5)_2(NBu^t)(\sigma\text{-}C_3H_5)]$ **5**. A solution of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ (0.40 g, 1.21 mmol) in diethyl ether (70 cm^3) at −40 °C was treated with allylmagnesium chloride (3.64 cm^3 of 1.0 mol dm^{-3} solution in diethyl ether, 2 equivalents) with stirring and it was allowed to warm to room temperature. The yellow solution gave a white precipitate after 24 h. The volatiles were removed under reduced pressure and the solid was extracted with light petroleum (3 × 40 cm^3) and filtered. The solvent was evaporated from the filtrate and the solid was extracted again with light petroleum. After filtration the solvent was removed giving a yellow solid. This was extracted with light petroleum and the solution was concentrated and cooled to −80 °C. After 24 h pale yellow crystals separated from the solvent and these were collected and dried *in vacuo*. Yield 340 mg, 84%.

$[Nb(\eta\text{-}C_5H_5)_2(NBu^t)H]$ **6**. A solution of $[Nb(\eta\text{-}C_5H_5)_2(NBu^t)Cl]$ 0.40 g, 1.21 mmol) in toluene (50 cm^3) at −40 °C was treated with Red-Al (0.13 cm^3, 1 equivalent) in toluene (3.7 cm^3) dropwise (5 min) with stirring and it was allowed to warm to room temperature. The yellow solution became brown almost immediately. After 3 h the solution was filtered leaving a black residue. The filtrate was concentrated under reduced pressure and cooled to −80 °C. After 24 h a very air-sensitive solid was isolated and then re-extracted with light petroleum. The extract was concentrated and cooled to −80 °C, giving white crystals of **6**. Yield 110 mg, 40%.

Crystal Data for Compound **1**.—$C_{14}H_{19}ClNNb$, $M = 329.67$, monoclinic, space group $P2_1$, $a = 9.303(1)$, $b = 13.572(2)$, $c = 12.286(1)$ Å, $\beta = 108.70(1)°$, $U = 1469.2$ Å^3, $Z = 4$ (two independent molecules in the asymmetric unit), $F(000) = 672$, $D_c = 1.49$ g cm^{-3}, $\mu = 9.48$ cm^{-1}, crystal size *ca.* 0.14 × 0.28 × 0.62 mm.

Intensities of 3868 total, 3108 independent reflections were measured at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 69$ Å, ω–2θ scanning mode, the ratio of the scanning rates $\omega/\theta = 1.2$, $\theta_{max} = 26.5°$). The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation (2215 reflections with $I > 3\sigma(I)$, 306 variables, observation/variables 7.2, Chebyshev weighting scheme with parameters 5.02, −3.96, 3.51). All hydrogen atoms (70% of them were located in the Fourier-difference maps, positions of others were calculated geometrically) were included in the final refinement with fixed positional and thermal parameters. Correction for Lorentz and polarization effects as well as an empirical correction for absorption[17] were applied. Anomalous-dispersion contributions were included in the calculated structure factors. Convergence was obtained at $R = 0.028$ and $R' = 0.030$, maximum peak in the final Fourier-difference synthesis 0.62 e Å^{-3}. The orientation with respect to the polar axis was assigned using an enantiopole parameter.[18] Crystallographic calculations were carried out using the CRYSTALS[19] program package on a Micro VAX 3800 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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References

1 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.

2 M. L. H. Green, J. D. Hubert and J. T. James, unpublished work.

3 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739.

4 G. Parkin, A. van Asselt, D. J. Leahy, L.-R. Whinnery, N. G. Hua, R. W. Quan, L. M. Henling, W. P. Schaefer, B. D. Santarsiero and J. E. Bercaw, *Inorg. Chem.*, 1992, **31**, 82.

5 M. L. H. Green, D. M. Michaelidou, P. Mountford, A. G. Suárez and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1593.

6 F. A. Cotton, S. A. Duraj and W. J. Roth, *J. Am. Chem. Soc.*, 1984, **106**, 4749; P. A. Finn, M. S. King, P. A. Kitty and R. E. McCarley, *J. Am. Chem. Soc.*, 1975, **97**, 220; L. S. Tan, G. V. Goeden and B. L. Haymore, *Inorg. Chem.*, 1983, **22**, 1744.

7 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Interscience, New York, 1988 and refs. therein.

8 J. C. Green, M. L. H. Green and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 1972, 421.

9 P. H. M. Budzelaar, K. H. den Haan, J. Boersma, B. J. M. Van der Kerkand and A. L. Spek, *Organometallics*, 1984, **3**, 156 and refs. therein; K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290; R. D. Wilson, F. F. Koetzle, D. W. Hart, Åke Kvick, D. L. Tipton and R. Bau, *J. Am. Chem. Soc.*, 1977, **99**, 1775.

10 J. A. Labinger, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, New York, 1982, vol. 3.

11 W. A. Nugent, R. J. McKinney, R. V. Kasowski and F. A. Van-Cartedge, *Inorg. Chim. Acta*, 1982, **65**, L91.

12 M. L. H. Green, A. K. Hughes, P. C. McGowan, P. Mountford, P. Scott and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1992, 1591.

13 M. L. H. Green, D. O'Hare and J. G. Watkin, *J. Chem. Soc., Chem. Commun.*, 1989, 698.

14 G. Watkin, Ph.D. Thesis, Oxford, 1989.

15 B. E. Mann, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, New York, 1982, vol. 3.

16 (*a*) N. M. Doherty and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 2670; (*b*) D. M. Curtis, L. G. Bell and W. M. Butler, *Organometallics*, 1985, 701; (*c*) M. L. H. Green and A. K. Hughes, *J. Chem. Soc., Dalton Trans.*, 1992, 527.

17 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

18 H. D. Fluck, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

19 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS user guide, Chemical Crystallography Laboratory, University of Oxford, 1985.

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