

The synthesis of alkyl niobocene imido complexes and the X-ray crystal structure of $[\text{Nb}(=\text{O})\text{Cp}_2\text{Me}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)

Antonio Antiñolo, Isabel López-Solera, Antonio Otero *, Sanjiv Prashar

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Campus Universitario, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

Received 17 April 2001; accepted 29 May 2001

Abstract

The following new niobium imido complexes containing alkyl ligands have been prepared and characterised: $[\text{Nb}(=\text{NBu}')\text{Cp}_2\text{Et}]$ (**1**), $[\text{Nb}(=\text{NBu}')\text{Cp}_2(\text{CH}_2\text{SiMe}_3)]$ (**2**), $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Me}]$ (**3**), $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Et}]$ (**4**), $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{Ph})]$ (**5**), $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{SiMe}_3)]$ (**6**), $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ (**7**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Ar} = \text{C}_6\text{H}_4\text{Me-4}$). The synthetic pathway to these complexes is by the reaction of the appropriate magnesium reagent MgRCl with the metallocene complexes $[\text{Nb}(=\text{NBu}')\text{Cp}_2\text{Cl}]$ or $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Cl}]$. The hydrolysis of **3** gave the oxo-alkyl complex $[\text{Nb}(=\text{O})\text{Cp}_2\text{Me}]$ (**8**). The molecular structure of **8** has been determined by X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

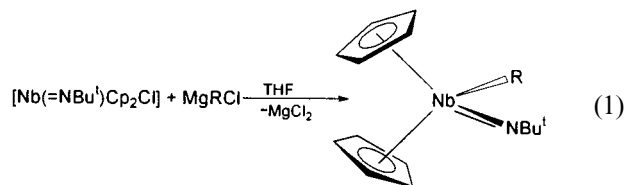
Keywords: Niobium; Imido; Alkyl; Niobocene; Oxo

1. Introduction

Half sandwich complexes are well known in niobium imido chemistry [1] and to a lesser degree so are their metallocene counterparts [2]. Our previous studies in the chemistry of niobium imido complexes have been centred on substituted metallocene [3], *ansa*-metallocene [4] and alkynyl [5] derivatives. However, in spite of the broad scope of this chemistry only a handful of alkyl-containing niobocene imido complexes have previously been reported [2a,b,4a,6]. Following our research in this field, we have explored the preparation of new alkyl-containing niobocene species with the non-substituted cyclopentadienyl ring and this work is focussed on the synthesis of alkyl niobocene imido complexes and the preparation and X-ray crystal structure characterisation of an oxo-alkyl niobocene complex.

2. Results and discussion

The complexes $[\text{Nb}(=\text{NBu}')\text{Cp}_2\text{Et}]$ (**1**), and $[\text{Nb}(=\text{NBu}')\text{Cp}_2(\text{CH}_2\text{SiMe}_3)]$ (**2**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), were prepared by the reaction of $[\text{Nb}(=\text{NBu}')\text{Cp}_2\text{Cl}]$ and MgRCl in THF (Eq. (1)). The methyl and benzyl derivatives have previously been described by Green et al. [2a].



R = Et (**1**), CH_2SiMe_3 (**2**)

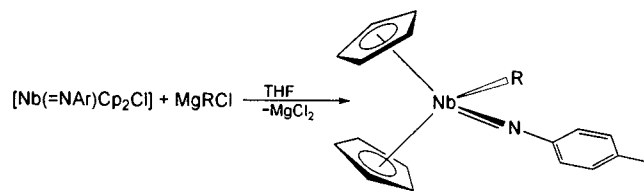
Compounds **1** and **2** were isolated as yellow air-sensitive crystalline solids which were characterised by NMR spectroscopy. The expected singlet signals for the Cp and Bu' groups in the $^1\text{H-NMR}$ spectra of **1** and **2** were observed. In the case of **2** only a singlet was observed for the Nb-CH₂ protons indicating their equivalency. In the $^1\text{H-NMR}$ spectrum of **1** the ethyl group displays an A₃BC pattern ($J_{\text{AB}} = 7.0$ Hz, $J_{\text{AC}} = 7.5$ Hz, $J_{\text{BC}} = 14.0$ Hz), similar to that reported previously in three ethyl complexes of niobium [4a,7]. This

* Corresponding author. Tel.: +34-26-295326; fax: +34-26-295318.

E-mail address: aotero@qino-cr.uclm.es (A. Otero).

observation indicates the inequivalency of the methylene protons due to either H-bonding interactions C–H···N between the alkyl and imido groups, which restrict rotation about the Nb–C bond or the presence of an unusually weak agostic interaction between an α -hydrogen atom of the ethyl group and the metal centre. The latter explanation is favoured because in complexes that do not contain electronegative ligands, e.g. $[\text{NbCp}_2(\text{Et})(\text{RC}\equiv\text{CR})]$, the same phenomenon of possible agostic interactions is observed in the NMR spectra [7b]. However, it must be pointed out that in the ^{13}C -NMR spectrum of **1** we were unable to distinguish the two $^1J(^{13}\text{C}-^1\text{H})$ constants corresponding to the CH_2 group.

The complexes $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Me}]$ (**3**), $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Et}]$ (**4**), $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{Ph})]$ (**5**), $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{SiMe}_3)]$ (**6**), and $[\text{Nb}(=\text{NAr})\text{Cp}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$ (**7**) ($\text{Ar} = \text{C}_6\text{H}_4\text{Me-4}$), were prepared in a similar manner to their Bu' analogues **1** and **2** by the reaction of $[\text{Nb}(=\text{NAr})\text{Cp}_2\text{Cl}]$ and MgRCl in THF (Eq. (2)).



R = Me (**3**), Et (**4**), CH_2Ph (**5**), CH_2SiMe_3 (**6**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**7**)

(2)

Compounds **3–7** were isolated as orange or red air-sensitive crystalline solids. Their ^1H -NMR spectra were similar to those recorded for **1** and **2**. In **4** the ethyl group displays the same A_3BC pattern observed for **1**. In the ^1H -NMR spectra of compounds **5** and **6**, the CH_2 protons of the alkyl group are equivalent

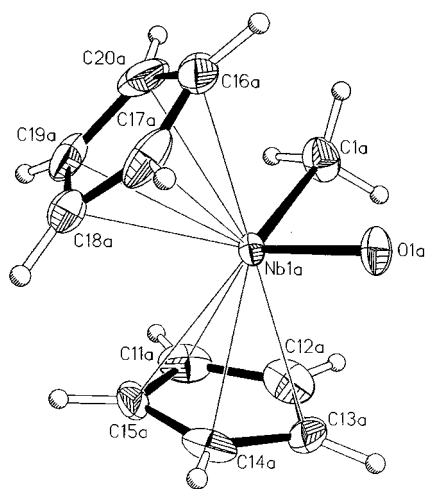
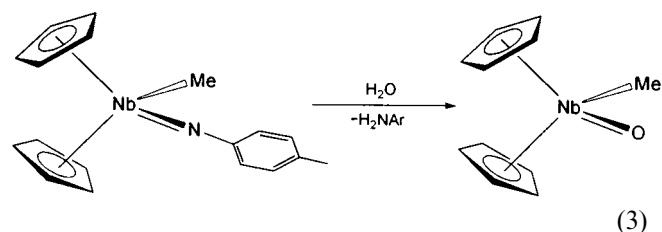


Fig. 1. Molecular structure and atom-labelling scheme for $[\text{Nb}(=\text{O})\text{Cp}_2\text{Me}]$ (**8**), with thermal ellipsoids at 10% probability.

indicating free rotation of the niobium–carbon bond in solution. This is also observed in **7** which, furthermore, shows an AB system for the terminal olefinic protons of the η^1 -allyl group (see Section 3) similar to that previously reported for other η^1 -allyl niobium complexes [3d,8].

IR spectroscopy of **1–7** showed a band between 1245 and 1300 cm^{-1} characteristic of the terminal imido ligand [1a]. Several vibrational spectroscopic studies of Group 5 imido complexes have been reported in the literature [9].

It was found that when **3** reacted with moist O_2 , the subsequent hydrolysis reaction took place at the Nb–N and not the Nb–C bond of the alkyl group. The oxo-alkyl complex, $[\text{Nb}(=\text{O})\text{Cp}_2\text{Me}]$ (**8**), was isolated by recrystallisation from a hexane solution. The amine, $\text{H}_2\text{NC}_6\text{H}_4\text{Me-4}$, was identified by ^1H -NMR spectroscopy to be the by-product of this reaction (Eq. (3)).



(3)

The molecular structure of **8** was established by X-ray crystal studies. The molecular structure and the atom-numbering scheme are shown in Fig. 1. Selected bond lengths and angles are given in Table 1. This complex was previously synthesised via the decomposition of $[\text{NbCp}_2(\text{Me})(\text{ONCH}_3)]$ [10]. Several oxoniobocene complexes have also been reported [11].

Suitable X-ray quality crystals of **8** were obtained by the slow evaporation of a hexane solution. The compound crystallises in, $P2_1$ space group, monoclinic and with four distinct molecules in the asymmetric unit. The niobium atom shows a geometry that is typical for pseudo-tetrahedral niobocene derivatives. The structure consists of a typical bent metallocene with distances between the metal atom and the centroids of the Cp rings of between 2.175 and 2.189 Å and the angle $\text{Cent}(1)\text{--Nb}(1)\text{--Cent}(2)$ between 127.0 and 128.3°. The environment of the niobium atom is completed by an oxygen atom and the carbon atom of the methyl group. The structure of **8** is similar to that reported for $[\text{Nb}(=\text{O})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Me}]$ [11h] and $[\text{Nb}(=\text{O})(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CH}_2\text{SiMe}_3)]$ [11f,g]. The Nb–O (1.744–1.746 Å) and Nb–CH₃ (2.230–2.247 Å) bond distances in **8** are longer and comparable, respectively, to the corresponding bonds found in $[\text{Nb}(=\text{O})\text{Cp}_2\{\text{C}_7\text{H}_5(\text{CF}_3)_2\}]$ [11d] (1.63(3) and 2.27(4) Å), containing a σ -bonded substituted nornorbornadienyl ligand. The lesser d-electron density on the metal determining the reduced double-bond character of the Nb–O distance in **8** can be

Table 1
Selected bond lengths (Å) and bond angles (deg) for [Nb(=O)Cp₂Me] (**8**)

	a	b	c	d
<i>Bond lengths</i>				
Nb(1)–Cent(1)	2.186	2.182	2.179	2.185
Nb(1)–Cent(2)	2.178	2.189	2.186	2.175
Av. Nb(1)–C(11–15)	2.479	2.473	2.469	2.475
Av. Nb(1)–C(16–20)	2.469	2.476	2.474	2.463
Nb(1)–C(1)	2.247(8)	2.230(8)	2.237(8)	2.239(8)
Nb(1)–O(1)	1.744(5)	1.746(5)	1.746(5)	1.746(5)
<i>Bond angles</i>				
Cent(1)–Nb(1)–Cent(2)	127.0	128.3	128.0	127.2
C(1)–Nb(1)–Cent(1)	102.6	102.1	102.2	102.5
C(1)–Nb(1)–Cent(2)	103.8	102.9	103.3	104.0
O(1)–Nb(1)–Cent(1)	110.7	110.8	110.6	110.4
O(1)–Nb(1)–Cent(2)	111.4	110.8	111.0	111.4
C(1)–Nb(1)–O(1)	95.5(3)	95.7(3)	95.6(3)	95.5(3)

The letters a, b, c and d refer to the four distinct molecules in the asymmetric unit. Cent(1) and Cent(2) are the centroids of C(11)–C(15) and C(16)–C(20), respectively.

attributable to the smaller σ -donating character of the methyl group with respect to that of the norbornadienyl ligand. The greater steric demand of this latter ligand seems to explain the larger O–Nb–C angle (99(5)°) compared with that observed in **8** (95.5–95.7°). A comparison of **8** with related oxo-niobocene complexes is given in Table 2.

Hydrogen bond interactions between oxygen and C–H groups have been reported [12]. We have found that this kind of interaction also exists in niobocene complexes that have previously been described by our research group [11h]. The crystal is stabilised by an extensive hydrogen-bonding network (see Table 3 and Fig. 2). Each oxygen is involved in two hydrogen bonds with the cyclopentadienyl ring protons of other molecule. The C–H \cdots O hydrogen bond distances are between 2.42 and 2.52 Å, slightly shorter than the sum of the van der Waals radii of H and O which is equal

Table 2
Comparison of structural data of oxo-niobocene complexes

Complex	Nb=O (Å)	Cp–Nb–Cp (°)	O–Nb–X (°)	Ref.
[Nb(=O)Cp ₂ Cl]	1.737(6)	128.2(1)	98.4	[11c]
[Nb(=O)Cp ₂ {C ₇ H ₅ (CF ₃) ₂ }]	1.63(3)	127.2	99(5)	[11d]
[Nb(=O)(η^5 -C ₅ H ₄ Me) ₂ Cl]	1.732(1)	129.1(1)	99.6	[11e]
[Nb(=O)(η^5 -C ₅ H ₄ Me) ₂ (CH ₂ SiMe ₃)]	1.741(3)	131.0(1)	97.3(1)	[11f,g]
[Nb(=O)(η^5 -C ₅ H ₄ SiMe ₃) ₂ Me]	1.720(7)	126.5(5)	95.0(6)	[11h]
[Nb(=O)(η^5 -C ₅ Me ₃) ₂ (OC(O)H)]	1.738(3)	136.3	97.9(1)	[11i]
[Nb(=O)Cp ₂ Me] ^a	1.745(5)	127.6	95.6(3)	This work
[Nb(=O)(η^5 -C ₅ H ₄ SiMe ₃) ₂ (OC(O)CF ₃)]	1.718(4)	127.35(3)	99.7(2)	[11j]
[Nb(=O)(η^5 -C ₅ H ₄ Pr ⁱ) ₂ Cl]	1.7366(17)	129.22(6)	98.95(7)	[11k]
[Nb(=O)(η^5 -C ₅ H ₄ Bu ^t)(η^5 -C ₅ H ₄ Me)Cl]	1.7413(11)	129.28(7)	98.41(4)	[11k]

^a Average value.

to 2.72 Å [13]. The C–H \cdots O angles (153.0–170.7°) show a linear disposition.

In conclusion we report the synthesis of new alkyl niobocene imido complexes by the reaction of the appropriate halide niobocene imido complexes with the corresponding Grignard reagents, the reactivity of one of these complexes with O₂ to give an oxo-containing niobocene species as well as the X-ray crystal structure of the isolated oxo-niobocene complex [Nb(=O)Cp₂Me].

3. Experimental

3.1. General procedures

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyser. Tetrahydrofuran or Et₂O solutions of MgRCl (R = Me, Et, CH₂Ph, CH₂SiMe₃ and CH₂CH=CH₂) were purchased from Aldrich and used directly. [NbCp₂(=NBu')Cl] [2a] was prepared as described earlier. [Nb(=NAr)Cp₂Cl] was prepared by the reaction of two equivalents of NaCp with [Nb(=NAr)Cl₃(DME)] in THF (key data: ¹H-NMR (200 MHz, C₆D₆): δ 2.16 (s, 3H, NC₆H₄CH₃), 5.80 (s, 10H, C₅H₅), 6.49 (2H), 6.94 (2H) (d, NC₆H₄CH₃) (J = 8.1 Hz)).

3.2. Synthesis of [Nb(=NBu')Cp₂Et] (**1**)

A 2 M solution of MgEtCl in Et₂O (0.64 ml, 1.28 mmol) was added to a stirring solution of [Nb(=NBu')Cp₂Cl] (0.35 g, 1.07 mmol) in THF (25 ml) at –78 °C. The yellow solution was allowed to warm

Table 3
Hydrogen bond distances (Å) and bond angles (°) for **8**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)	Symmetry ^a
C(14A)–H(14A)···O(1C)	0.93	2.51	3.37(1)	153.5	– <i>x</i> , <i>y</i> +1/2, 1– <i>z</i>
C(15A)–H(15A)···O(1A)	0.93	2.43	3.34(1)	167.0	<i>x</i> –1, <i>y</i> , <i>z</i>
C(14B)–H(14B)···O(1D)	0.93	2.51	3.37(1)	153.1	1– <i>x</i> , <i>y</i> +1/2, – <i>z</i>
C(15B)–H(15B)···O(1B)	0.93	2.43	3.35(1)	170.7	<i>x</i> –1, <i>y</i> , <i>z</i>
C(14C)–H(14C)···O(1A)	0.93	2.51	3.37(1)	153.3	1– <i>x</i> , <i>y</i> –1/2, 1– <i>z</i>
C(15C)–H(15C)···O(1C)	0.93	2.43	3.35(1)	171.0	<i>x</i> +1, <i>y</i> , <i>z</i>
C(14D)–H(14D)···O(1B)	0.93	2.52	3.37(1)	153.0	2– <i>x</i> , <i>y</i> –1/2, – <i>z</i>
C(15D)–H(15D)···O(1D)	0.93	2.42	3.34(1)	167.8	<i>x</i> +1, <i>y</i> , <i>z</i>

^a Symmetry operation for A.

to room temperature (r.t.) and stirred for 15 h. Solvent was removed in vacuo and the remaining yellow oil extracted in hexane (50 ml). A yellow crystalline solid was obtained by concentrating (5 ml) and cooling (–30 °C) the solution (0.25 g, 74%). IR (Nujol mull, cm^{–1}): $\nu_{\text{Nb=N}}$ 1280. ¹H-NMR (200 MHz, C₆D₆): δ 0.94 (s, 9H, C(CH₃)₃), 1.80 (q, 2H, CH₂CH₃), 1.88 (t, 3H, CH₂CH₃), 5.49 (s, 10H, C₅H₅). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 19.80 (CH₂CH₃), 22.39 (CH₂CH₃), 31.05 (C(CH₃)₃), 69.42 (C(CH₃)₃), 107.59 (C₅H₅). Anal. Found: C, 59.28; H, 7.41; N, 4.33. Calc. for C₁₆H₂₄NNb: C, 59.45; H, 7.48; N, 4.33%.

3.3. Synthesis of [Nb(=NBu')Cp₂(CH₂SiMe₃)] (**2**)

The synthesis of **2** was carried out in an identical manner to that of **1** with a 1 M solution of Mg(CH₂SiMe₃)Cl in Et₂O (1.20 ml, 1.20 mmol) and [Nb(=NBu')Cp₂Cl] (0.33 g, 1.00 mmol). Yield 0.23 g, 61%. IR (Nujol mull, cm^{–1}): $\nu_{\text{Nb=N}}$ 1290. ¹H-NMR (200 MHz, C₆D₆): δ 0.32 (s, 9H, CH₂SiMe₃), 0.60 (s, 2H, CH₂SiMe₃), 0.91 (s, 9H, C(CH₃)₃), 5.58 (s, 10H, C₅H₅). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 3.85 (SiMe₃), 30.77 (C(CH₃)₃), 30.9 (CH₂), 69.34 (C(CH₃)₃), 107.80 (C₅H₅). Anal. Found: C, 56.37; H, 7.84; N, 3.63. Calc. for C₁₈H₃₀NNbSi: C, 56.68; H, 7.93; N, 3.67%.

3.4. Synthesis of [Nb(=NAr)Cp₂Me] (**3**)

The synthesis of **3** was carried out in an identical manner to that of **1** with a 3 M solution of MgMeCl in THF (0.36 ml, 1.08 mmol) and [Nb(=NAr)Cp₂Cl] (0.33 g, 0.90 mmol). Yield 0.24 g, 77%. IR (Nujol mull, cm^{–1}): $\nu_{\text{Nb=N}}$ 1300. ¹H-NMR (200 MHz, C₆D₆): δ 0.95 (s, 3H, Me), 2.16 (s, 3H, NC₆H₄CH₃), 5.43 (s, 10H, C₅H₅), 6.47 (2H), 6.93 (2H) (d, NC₆H₄CH₃) (*J* = 8.26 Hz). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 3.95 (Me), 20.75 (NC₆H₄CH₃), 108.69 (C₅H₅), 118.55, 129.00 (CMe), 129.25, 131.52 (CN) (NC₆H₄CH₃). Anal. Found: C, 62.79; H, 5.76; N, 4.01. Calc. for C₁₈H₂₀NNb: C, 62.98; H, 5.87; N, 4.08%.

3.5. Synthesis of [Nb(=NAr)Cp₂Et] (**4**)

The synthesis of **4** was carried out in an identical manner to that of **1** with a 2 M solution of MgEtCl in Et₂O (0.54 ml, 1.08 mmol) and [Nb(=NAr)Cp₂Cl] (0.33 g, 0.90 mmol). Yield 0.24 g, 75%. IR (Nujol mull, cm^{–1}): $\nu_{\text{Nb=N}}$ 1290. ¹H-NMR (200 MHz, C₆D₆): δ 1.80 (q, 2H, CH₂CH₃), 1.93 (t, 3H, CH₂CH₃), 2.17 (s, 3H, NC₆H₄CH₃), 5.43 (s, 10H, C₅H₅), 6.48 (2H), 6.94 (2H) (d, NC₆H₄CH₃) (*J* = 8.20 Hz). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 20.94 (CH₂CH₃), 26.76 (CH₂CH₃), 22.45 (NC₆H₄CH₃), 107.63 (C₅H₅), 118.71, 129.07, 129.72 (CMe), 132.45 (CN) (NC₆H₄CH₃). Anal. Found: C, 63.61; H, 6.12; N, 4.00. Calc. for C₁₉H₂₂NNb: C, 63.87; H, 6.21; N, 3.92%.

3.6. Synthesis of [Nb(=NAr)Cp₂(CH₂Ph)] (**5**)

The synthesis of **5** was carried out in an identical manner to that of **1** with a 1 M solution of

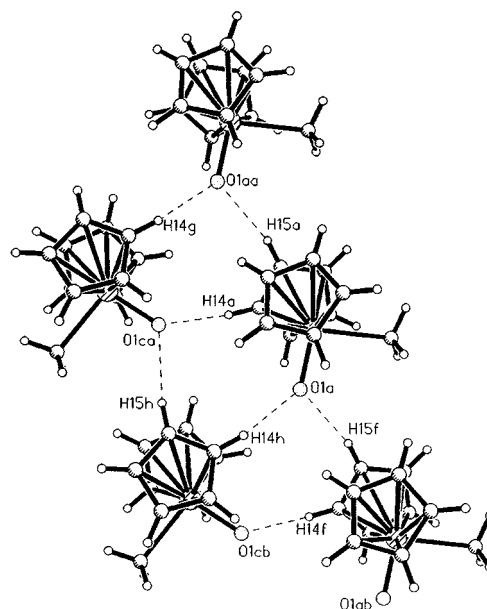


Fig. 2. Hydrogen bonding in [Nb(=O)Cp₂Me] (**8**).

Mg(CH₂Ph)Cl in Et₂O (1.10 ml, 1.10 mmol) and [Nb(=NAr)Cp₂Cl] (0.34 g, 0.92 mmol). Yield 0.32 g, 82%. IR (Nujol mull, cm⁻¹): $\nu_{\text{Nb=N}}$ 1260. ¹H-NMR (200 MHz, C₆D₆): δ 2.18 (s, 3H, NC₆H₄CH₃), 3.15 (s, 2H, CH₂Ph), 5.35 (s, 10H, C₅H₅), 6.54 (2H), 6.96 (2H) (d, NC₆H₄CH₃) ($J = 8.3$ Hz), 6.86–6.99, 7.19–7.37 (m, 5H, CH₂Ph). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 22.75 (NC₆H₄CH₃), 34.87 (CH₂Ph), 109.33 (C₅H₅), 121.67 (C¹), 128.00, 129.18, 130.31 (CH₂Ph), 118.95, 129.00, 129.97 (CMe), 132.75 (CN) (NC₆H₄CH₃). Anal. Found: C, 68.51; H, 5.70; N, 3.33. Calc. for C₂₄H₂₄NNb: C, 68.74; H, 5.77; N, 3.34%.

3.7. Synthesis of [Nb(=NAr)Cp₂(CH₂SiMe₃)] (6)

The synthesis of **6** was carried out in an identical manner to that of **1** with a 1 M solution of Mg(CH₂SiMe₃)Cl in Et₂O (1.10 ml, 1.10 mmol) and [Nb(=NAr)Cp₂Cl] (0.34 g, 0.92 mmol). Yield 0.26 g, 67%. IR (Nujol mull, cm⁻¹): $\nu_{\text{Nb=N}}$ 1270. ¹H-NMR (200 MHz, C₆D₆): δ 0.29 (SiMe₃), 0.66 (s, 2H, CH₂SiMe₃), 2.12 (s, 3H, NC₆H₄CH₃), 5.51 (s, 10H, C₅H₅), 6.50 (2H), 6.94 (2H) (d, NC₆H₄CH₃) ($J = 8.3$ Hz). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 3.39 (SiMe₃), 31.9 (CH₂SiMe₃), 20.93 (NC₆H₄CH₃), 108.24 (C₅H₅), 119.47, 129.15, 130.12 (CMe), 131.53 (CN) (NC₆H₄CH₃). Anal. Found: C, 60.46; H, 6.70; N, 3.31. Calc. for C₂₁H₂₈NNbSi: C, 60.71; H, 6.79; N, 3.37%.

3.8. Synthesis of [Nb(=NAr)Cp₂(CH₂CH=CH₂)] (7)

The synthesis of **7** was carried out in an identical manner to that of **1** with a 2 M solution of Mg(CH₂CHCH₂)Cl in THF (0.56 ml, 1.12 mmol) and [Nb(=NAr)Cp₂Cl] (0.34 g, 0.93 mmol). Yield 0.27 g, 77%. IR (Nujol mull, cm⁻¹): $\nu_{\text{Nb=N}}$ 1245. ¹H-NMR (200 MHz, C₆D₆): δ 2.17 (s, 3H, NC₆H₄CH₃), 2.68 (d, 2H, CH₂–CH=CH₂) ³J(¹H–¹H) = 8.3 Hz, 4.78 (*cis*), 4.91 (*trans*) (dd, 2H, CH₂–CH=CH₂) ²J_{gem}(¹H–¹H) = 2.5 Hz, ³J_{*cis*}(¹H–¹H) = 9.9 Hz, ³J_{*trans*}(¹H–¹H) = 16.8 Hz, 5.45 (s, 10H, C₅H₅), 6.40 (m, 1H, CH₂–CH=CH₂), 6.44 (2H), 6.95 (2H) (d, NC₆H₄CH₃) ($J = 8.2$ Hz). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 21.50 (NC₆H₄CH₃), 36.93 (CH₂–CH=CH₂), 107.79 (C₅H₅), 102.96 (CH₂–CH=CH₂), 155.31 (CH₂–CH=CH₂), 120.03, 129.15, 130.03 (CMe), 131.53 (CN) (NC₆H₄CH₃). Anal. Found: C, 64.79; H, 5.93; N, 3.77. Calc. for C₂₀H₂₂NNb: C, 65.05; H, 6.00; N, 3.79%.

3.9. Synthesis of [Nb(=O)Cp₂Me] (8)

A solution of **3** (0.24 g, 0.70 mmol) in hexane (25 ml) was stirred for 30 min at r.t., under 1 atm of O₂. A colour change was observed from red to yellow. Crystals were obtained by concentrating (5 ml) and cooling

(–30 °C) the solution (0.12 g, 75%). IR (Nujol mull, cm⁻¹): $\nu_{\text{Nb=O}}$ 910. ¹H-NMR (200 MHz, C₆D₆): δ 1.06 (s, 3H, Me), 5.47 (s, 10H, C₅H₅). ¹³C{¹H}-NMR (300 MHz, C₆D₆): δ 3.16 (Me), 107.50 (C₅H₅). Anal. Found: C, 51.73; H, 5.07. Calc. for C₁₁H₁₃NbO: C, 51.99; H, 5.16%.

3.10. X-ray crystal structure determination for [Nb(=O)Cp₂Me] (8)

Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator Mo–K_α radiation ($\lambda = 0.71073$ Å) using the ω – 2θ scan technique. The final unit cell parameters were determined from 25 well-centred peaks and refined by least-squares method. The structures were solved by direct methods using the SHELXS computer program [14] and refined on F^2 by full-matrix least-squares (SHELXL-97) [15]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimised in the final cycles. Crystallographic data are given in Table 4.

Table 4

Crystal data and structure refinement parameters for [Nb(=O)Cp₂Me] (**8**)

Empirical formula	C ₁₁ H ₁₃ NbO
Formula weight	254.12
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	6.366(1)
b (Å)	15.803(1)
c (Å)	20.506(1)
V (Å ³)	2062.9(4)
Z	2
D_{calc} (g cm ⁻³)	1.636
Absorption coefficient (mm ⁻¹)	1.123
$F(000)$	1024
Crystal size (mm)	0.2 × 0.1 × 0.1
Theta range for data collection (°)	2.37–27.98
Index ranges	$-8 \leq h \leq 8, 0 \leq k \leq 20, 0 \leq l \leq 27$
Reflections measured	5271
Reflections observed	4142
Independent reflections	5147
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0301^a$, $wR_2 = 0.0592^b$
Flack parameter	–0.1(6)
Goodness-of-fit on F^2	1.037
Largest difference peak and hole (e Å ⁻³)	0.678 and –0.809

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 161085 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica, Spain (Grant. No. PB 98-0159-C02-01-02), and a fellowship to S.P. under the Programa Nacional de Formación de Personal Investigador.

References

- [1] See, for example: (a) D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neil, V.C. Gibson, *J. Chem. Soc. Dalton Trans.* (1992) 739; (b) V.C. Gibson, D.N. Williams, W. Clegg, D.C.R. Hockless, *Polyhedron* 8 (1989) 1819; (c) U. Siemeling, V.C. Gibson, *J. Organomet. Chem.* 426 (1992) C25; (d) V.C. Gibson, A.D. Poole, U. Siemeling, D.N. Williams, W. Clegg, D.C.R. Hockless, *J. Organomet. Chem.* 462 (1993) C12; (e) T.C. Baldwin, S.R. Huber, M.A. Bruck, D.E. Wigley, *Inorg. Chem.* 32 (1993) 5682; (f) A.D. Poole, V.C. Gibson, W. Clegg, *J. Chem. Soc. Chem. Commun.* (1992) 237; (g) J.K. Cockcroft, V.C. Gibson, J.A.K. Howard, A.D. Poole, U. Siemeling, C. Wilson, *J. Chem. Soc. Chem. Commun.* (1992) 1668; (h) M.C.W. Chan, J.M. Cole, V.C. Gibson, J.A.K. Howard, C. Lehmann, A.D. Poole, U. Siemeling, *J. Chem. Soc. Dalton Trans.* (1998) 103; (i) M.L.H. Green, J.T. James, J.F. Saunders, J. Souter, *J. Chem. Soc. Dalton Trans.* (1997) 1281.
- [2] See, for example: (a) A.N. Chernega, M.L.H. Green, A.G. Suarez, *J. Chem. Soc. Dalton Trans.* (1993) 3031; (b) S. Schmidt, J. Sundermeyer, *J. Organomet. Chem.* 472 (1994) 127; (c) M.L.H. Green, J.T. James, A.N. Chernega, *J. Chem. Soc. Dalton Trans.* (1997) 1719; (d) W.A. Hermann, W. Baratta, E. Herdtweck, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1951; (e) A.N. Chernega, M.L.H. Green, A.G. Suarez, *Can. J. Chem.* 73 (1995) 1157.
- [3] (a) A. Antiñolo, S. García-Lledó, J. Martínez de Ilarduya, A. Otero, *J. Organomet. Chem.* 335 (1987) 85; (b) A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín-Alonso, A. Otero, *J. Chem. Soc. Dalton Trans.* (1995) 1007; (c) Z. Modarres, D. Lucas, Y. Mugnier, A. Antiñolo, A. Otero, M. Fajardo, A. Garces, C. López-Mardomingo, *J. Organomet. Chem.* 548 (1997) 309; (d) A. Antiñolo, M. Fajardo, C. Huertas, A. Otero, S. Prashar, A.M. Rodríguez, *J. Organomet. Chem.* 585 (1999) 154.
- [4] (a) A. Antiñolo, A. Otero, S. Prashar, A.M. Rodríguez, *Organometallics* 17 (1998) 5454; (b) A. Antiñolo, I. López-Solera, I. Orive, A. Otero, S. Prashar, A.M. Rodríguez, E. Villaseñor, *Organometallics* 20 (2001) 71.
- [5] A. Antiñolo, M. Fajardo, C. López-Mardomingo, I. López-Solera, A. Otero, Y. Pérez, S. Prashar, *Organometallics* (2001), in press.
- [6] (a) A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, M. Fajardo, A. Garcés, P. Gómez-Sal, C. López-Mardomingo, A. Martín, C. Miranda, *J. Chem. Soc. Dalton Trans.* (1998) 59; (b) M.J. Humphries, M.L.H. Green, R.E. Douthwaite, L.H. Rees, *J. Chem. Soc. Dalton Trans.* (2000) 4555.
- [7] (a) A. Antiñolo, F. Carrillo-Hermosilla, I. del Hierro, A. Otero, M. Fajardo, Y. Mugnier, *Organometallics* 16 (1997) 4161; (b) H. Yasuda, H. Yamamoto, T. Arai, A. Nakamura, J. Chen, Y. Kai, N. Kasai, *Organometallics* 10 (1991) 4058.
- [8] A. Antiñolo, C. Huertas, I. del Hierro, M.F. Lappert, A. Otero, S. Prashar, A.M. Rodríguez, E. Villaseñor, *Organometallics* 17 (1998) 5874.
- [9] (a) A.V. Korolev, A.L. Rheingold, D.S. Williams, *Inorg. Chem.* 36 (1997) 2647; (b) K.S. Heinselman, V.M. Miskowski, S.J. Geib, L.C. Wang, M.D. Hopkins, *Inorg. Chem.* 36 (1997) 5530.
- [10] A.R. Middleton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1980) 1888.
- [11] (a) R. Broussier, J.D. Olivier, B. Gautheron, *J. Organomet. Chem.* 251 (1983) 307; (b) M. Gómez, J. Martínez de Ilarduya, P. Royo, *J. Organomet. Chem.* 369 (1989) 197; (c) A.L. Rheingold, J.B. Strong, *Acta Crystallogr. Sect. C* 47 (1991) 1963; (d) R. Mercier, J. Douglade, J. Amaudrut, J. Sala-Pala, J.E. Guerschais, *J. Organomet. Chem.* 244 (1983) 145; (e) P.-F. Fu, M.A. Khan, K.M. Nicholas, *Organometallics* 11 (1992) 2607; (f) P.-F. Fu, M.A. Khan, K.M. Nicholas, *J. Organomet. Chem.* 506 (1996) 49; (g) P.-F. Fu, M.A. Khan, K.M. Nicholas, *Organometallics* 10 (1991) 382; (h) A. Antiñolo, J. Martínez de Ilarduya, A. Otero, P. Royo, A.M.M. Lanfredi, A. Tiripicchio, *J. Chem. Soc. Dalton Trans.* (1988) 2685; (i) H. Brunner, J.-C. Leblanc, D. Lucas, W. Meier, C. Moise, Y. Mugnier, B. Nuber, S. Rigny, A. Sadorge, J. Wachter, *J. Organomet. Chem.* 566 (1998) 203; (j) A. Antiñolo, I. del Hierro, I. López-Solera, S. García-Yuste, A. Otero, M. Fajardo, A. Rodríguez, *J. Organomet. Chem.* 598 (2000) 167; (k) E. Kolehmainen, K. Laihia, M. Nissinen, J. Linnanto, A. Perjéssy, B. Gautheron, R. Broussier, *J. Organomet. Chem.* 613 (2000) 7.
- [12] M.G. Davidson, C. Lambert, I. López-Solera, P.R. Raithby, R. Snaith, *Inorg. Chem.* 34 (1995) 3765.
- [13] A.J. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [14] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [15] G.M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Göttingen, Germany, 1997.