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Synthesis of niobocene imido cations: X-ray crystal structure of [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$]

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Abstract

The reduction of [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] by sodium amalgam followed by oxidation by [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] in the presence of CNBu^t gave [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (**1**). In a similar manner, [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (**2**), [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)][BPh$_4$] (**3**) and [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}(CNBu^t)][BPh$_4$] (**4**), were prepared. The reduction of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] gave, depending on the experimental conditions, either the d^1–d^1 dimer [(Nb{Me$_2$Si(η^5-C$_5$H$_4$)$_2$}(μ-NBu^t))$_2$] (**5**) or the hydride derivative [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}H] (**6**). The reaction of **5** with I$_2$ led to the formation of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}I] (**7**). The molecular structure of **1** was determined by single-crystal X-ray diffraction studies.
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1. Introduction

The use of imido groups in the organometallic chemistry of group 5 elements is widespread [1]. The chemistry of half sandwich imido complexes has been extensively studied due principally to its isoelectronic relationship with catalytically active group 4 metallocenes [2]. To a lesser extent the chemistry of group 5 metallocene imido complexes has been developed [3]. Nevertheless, few niobocene imido cations have been reported [4]. As a continuation of our ongoing studies on group 5 imido complexes [5], we present the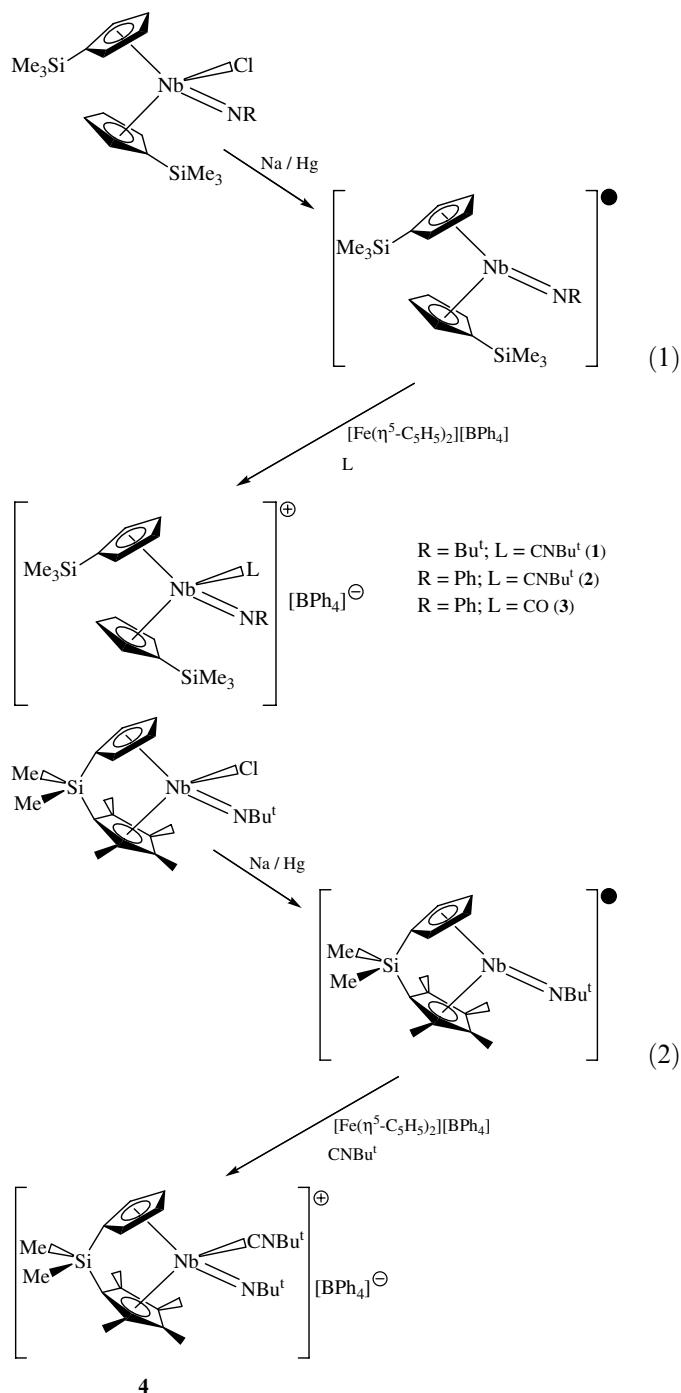 synthesis and structural characterization of several niobocene cationic species. We also report the preparation of only the second d^1–d^1 niobocene imido dimer [6].

2. Results and discussion

The reduction of the niobocene (V) imido complex, [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] by sodium amalgam gave, presumably, at first the niobocene (IV) radical [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$] which was rapidly oxidized, by [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] in the presence of CNBu^t, to give the niobocene (V) cationic species [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (**1**) (Eq. (1)). In a similar manner the complexes [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (**2**), [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)][BPh$_4$] (**3**) and [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}(CNBu^t)][BPh$_4$] (**4**) were prepared in the following equations:

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two singlets, at 0.54 and 0.79 ppm, for the methyl substituents of the silicon *ansa* bridge, four multiplets, between 6.1 and 6.9 ppm, for the C_5 ring protons, four singlets, between 1.9 and 2.7 ppm, for the tetramethylcyclopentadienyl moiety and two singlets, at 1.02 and 1.73 ppm, for the distinct *tert*-butyl groups. The ^{13}C NMR spectrum for **1** gave one signal for the trimethylsilyl moiety, four signals for the two *tert*-butyl groups, five signals for the cyclopentadienyl carbon atoms, one signal for the isocyanide carbon atom, and four signals corresponding to the BPh_4 fragment. Complexes **2–4** gave similar ^{13}C NMR spectral patterns.

The molecular structure of $[Nb(=NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2(CNBu^t)][BPh_4]$ (**1**) was established by X-ray crystal diffraction studies. The molecular structure and atomic numbering scheme are shown in Fig. 1. Selected bond lengths and bond angles for **1** are given in Table 1.

1 presents a bent metallocene structure with two additional ligands. The two cyclopentadienyl rings are η^5 bonded to the metal with a Cent–Nb–Cent angle of 128.0°. The silicon atom of the trimethylsilyl moiety is located approximately 10° out of the plane defined by the cyclopentadienyl unit. The isocyanide ligand is sigma bonded to the metal as indicated by the N(1)–C(1) distance of 1.159(3) Å which is typical for a N–C triple bond and the Nb–C(1)–N(1) angle of 173.5(2)° whose linear nature confirms that the N(1) and C(1) atoms are sp hybridized. The Nb–N(2) bond distance of 1.796(2) Å, is at the upper limit for those observed for niobium imido complexes (1.73–1.80 Å) (see Table 2) with a Nb–N triple bond.

The imide ligand is able to act as either a two or four electron donor. In the first case the nitrogen atom would be sp^2 hybridized and therefore result in the bending back of the imide substituent. In the second case the nitrogen would be sp hybridized and the metal–nitrogen-substituent angle linear. In **1**, this angle (Nb(1)–N(2)–C(6) 177.2(2)°),

The complexes were characterized spectroscopically. The ^1H NMR spectra of **1–3** showed the two cyclopentadienyl ligands to be chemically equivalent and thus one singlet ($SiMe_3$), at ca. 0.2 ppm, and four multiplets, between 5.2 and 6.7 ppm, for the ring protons were observed. The BPh_4 anion gave three multiplets, between 6.8 and 7.3 ppm, in the ^1H NMR spectrum. For **1**, two singlets, assigned to the *tert*-butyl substituents of the imido and isocyanide ligands appeared at 1.05 and 1.70 ppm, respectively. Three signals for the protons of the phenylimido fragment were observed, for **2–3**, as multiplets between 6.4 and 7.4 ppm. The chiral *ansa*-niobocene complex, **4**, gave a similar ^1H spectrum to **1**. Signals were observed and assigned to;

Fig. 1. Molecular structure and atom-labeling scheme for $[Nb(=NBu^t)(\eta^5\text{-}C_5H_4SiMe_3)_2(CNBu^t)]^+$ (**1**), with thermal ellipsoids at 30% probability.

Table 1
Selected bond lengths (Å) and bond angles (°) for [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (1)

Bond lengths (Å)	
Nb(1)–Cent(1)	2.203
Nb(1)–Cent(2)	2.205
av Nb(1)–C(10–14)	2.517(3)
av Nb(1)–C(15–19)	2.516(3)
Nb(1)–C(1)	2.238(2)
Nb(1)–N(2)	1.796(2)
N(1)–C(1)	1.159(3)
N(1)–C(2)	1.490(3)
N(2)–C(6)	1.472(3)
Bond angles (°)	
Cent(1)–Nb(1)–Cent(2)	128.0
Nb(1)–N(2)–C(6)	177.2(2)
Nb(1)–C(1)–N(1)	173.5(2)
C(1)–N(1)–C(2)	178.1(2)
C(1)–Nb(1)–Cent(1)	100.8
C(1)–Nb(1)–Cent(2)	104.2
N(2)–Nb(1)–Cent(1)	113.0
N(2)–Nb(1)–Cent(2)	112.3
C(1)–Nb(1)–N(2)	88.78(9)
Si(1)–C(10)–Cent(1)	170.0
Si(2)–C(15)–Cent(2)	169.5

Cent(1) and Cent(2) are the centroids of C(10)–C(14) and C(15)–C(19), respectively.

is essentially linear thus revealing the latter case to be true. This phenomenon has also been observed in other niobocene imido complexes, although steric effects may cause some degree of bending back (see Table 2).

The formal electron count of **1** is 20 electrons with the excess two electrons probably being located in a non-bonding orbital similar to that proposed by Green et al. for [Mo(=NBu^t)(η^5-C$_5$H$_5$)$_2$] [13]. The two limiting descriptions, Nb$^-$≡N$^+$–R and Nb=N:–R, proposed by Bercaw et al. for [Ta(=NPh)(η^5-C$_5$Me$_5$)$_2$(H)], may also explain the true bonding situation [3c]. Similar '20 electron' niobocene imido complexes [Nb(=NR)(η^5-C$_5$H$_4$Si-Me$_3$)$_2$Cl] have shown a lengthening of the Nb-centroid distances in comparison with their 18- and 17-electron analogues and this too is the case in **1** (see Table 3) [3b,4e,10,11].

Applying the same reactions conditions to [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] we did not isolate the expected cationic species but instead the dimeric derivative [(Nb{Me$_2$Si(η^5-C$_5$H$_4$)$_2$}(μ-NBu^t))$_2$] (**5**) (Scheme 1). This behaviour has previously been reported by Sundermeyer et al. who observed that the reduction of [Nb(=NBu^t)(η^5-C$_5$H$_5$)$_2$Cl] gave the dimer [{Nb(η^5-C$_5$H$_5$)$_2$(μ-NBu^t)}$_2$] [6]. **5** was characterized spectroscopically. The four cyclopentadienyl ligands were shown to be chemically equivalent, at room temperature, by NMR spectroscopy and therefore a symmetrical structure is proposed for **5**. However it should be noted that the X-ray structure of a similar tantalum derivative gave an unsymmetrical dimer where one of the cyclopentadienyl groups is η^1-bonded to the metal [6].

On increasing the temperature and reaction time we isolated, after the appropriate work up, the hydride derivative, [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)}$_2$H] (**6**) (Scheme 1). When the reaction was repeated in deuterated solvent,

Table 2
Selected structural data on niobocene imido complexes

	CpR–Nb–CpR (°)	Nb–N–C (°)	Nb–N (Å)	Ref.
[Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (**1**)	128.0	177.2(2)	1.796(2)	This work
[Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(C≡CPh)]	128.2	167.9(6)	1.804(5)	[4e]
(*S*)-[Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me-3)}Cl][a]	122.7	168.0(4)	1.790(5)	[7]
(*R*)-[Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Me-3)}Cl][a]	122.3	167.5(4)	1.782(5)	[7]
[Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$Pr^i-3)}Cl][b]	122.1	172.34(4)	1.772(2)	[7]
[Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl]	121.21	178.8(2)	1.756(3)	[8]
[Nb(=NSiMe$_3$){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Cl]	114.2	167.71(7)	1.777(1)	[9]
[Nb(=NBu^t){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Cl]	113.3	178.4(3)	1.762(3)	[9]
[Nb(=NBu^t){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Br]	113.4	178.3(2)	1.765(2)	[9]
[Nb(=NBu^t){Me$_2$C(η^5-C$_5$H$_4$)$_2$}I]	114.2	171.8(2)	1.770(2)	[9]
[Nb(=NAr){Me$_2$C(η^5-C$_5$H$_4$)$_2$}Cl][c]	114.4	167.5(1)	1.798(2)	[4b]
[Nb(=NAr){Me$_2$C(η^5-C$_5$H$_4$)$_2$}(NMe$_2$)][B(C$_6$H$_5$)$_4$][c]	114.0	166.8(1)	1.803(2)	[4b]
[Nb(=NBu^t)(η^5-C$_5$H$_5$)$_2$Cl][d]	122.7	173.6(4)	1.789(4)	[3e]
	124.0	179.4(5)	1.737(6)	
[Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl]	124.9	165.1(2)	1.792(2)	[3b]
[Nb(=NC$_6$H$_4$OMe-4)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl]	125.23	163.0(2)	1.787(3)	[10]
[{NbCp$'_2$Cl}$_2$(μ-1, 3-N$_2$C$_6$H$_4$)]	124.5	167.4(14)	1.754(20)	[11]
	125.6	168.4(15)	1.763(18)	
(*R,S,R*)-[Nb(=NBu^t){(η^5-C$_5$H$_4$)CMe$_2$PPh-κ*P*}{(η^5-C$_5$H$_4$)CMe$_2$PHPh}][a]	128.6	171.9(2)	1.779(2)	[12]
(*S,R,S*)-[Nb(=NBu^t){(η^5-C$_5$H$_4$)CMe$_2$PPh-κ*P*}{(η^5-C$_5$H$_4$)CMe$_2$PHPh}][a]	128.9	170.9(2)	1.780(2)	[12]

[a] Both enantiomers observed in the asymmetric unit.
[b] *R* and *S* enantiomers related by symmetry.
[c] Ar = C$_6$H$_3$Pr$^i_2$-2, 6.
[d] Two independent molecules exist in the asymmetric unit.

Table 3
Comparison of Nb–Cent distances in selected Cp′ containing niobocene complexes (Cp′ = η^5-C$_5$H$_4$SiMe$_3$)

Compound	Average Nb–Cent (Å)	Ref.
[Nb(=NBu^t)Cp′$_2$(CNBu^t)][BPh$_4$] (1)	2.204	This work
[Nb(=NC$_6$H$_4$OMe-4)Cp′$_2$Cl]	2.189	[10]
[{NbCp′$_2$Cl}$_2$(μ-1, 3-N$_2$C$_6$H$_4$)]	2.188	[11]
[Nb(=O)Cp′$_2$Me]	2.181	[14]
[Nb(=NPh)Cp′$_2$(C≡CPh)]	2.180	[4e]
[Nb(=NPh)Cp′$_2$Cl]	2.180	[3b]
[NbCp′$_2$Cl(η^2-N, C-OCNPh)]	2.121	[11]
[NbCp′$_2$Cl$_2$]	2.079	[14,15]
[{NbCp′$_2$Cl}$_2$]	2.07	[3b]
[NbCp′$_2$(C$_6$F$_5$)(CO)]	2.04	[14]

Cent = the centroid of the C$_5$ ring.
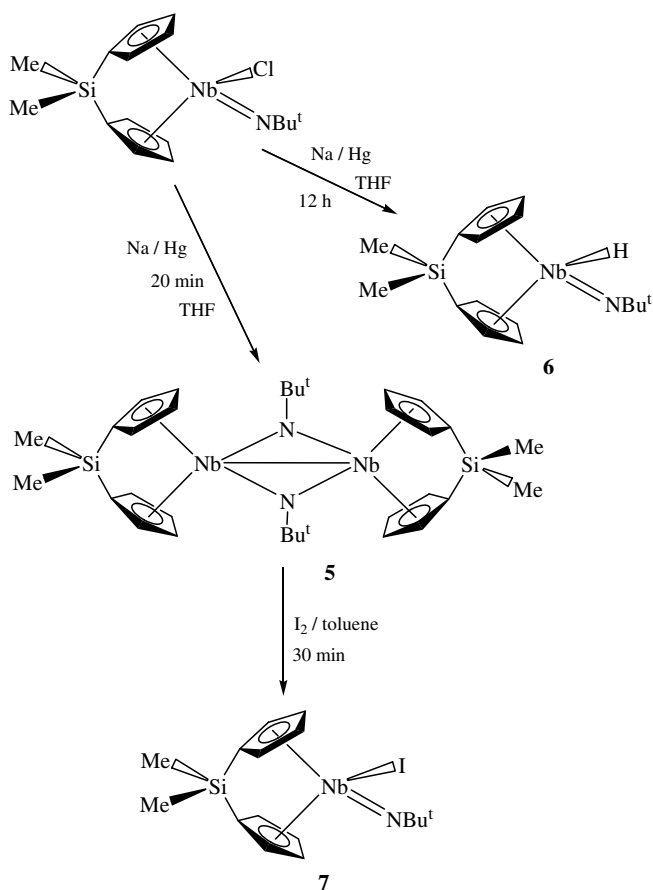
Scheme 1.

the deuterium derivative of **6** was identified by NMR spectroscopy, thus indicating that in the synthesis of **6**, hydrogen abstraction from the reaction solvent occurs.

The ^{1}H NMR spectrum of **6** showed the two cyclopentadienyl rings to be chemically equivalent. However an ABCD spin system was observed for the ring protons indicating the asymmetric nature around the niobium atom. The hydride resonance in the ^{1}H NMR spectrum was observed as a broad signal at 2.70 ppm ($\Delta\nu_{1/2}$ = 30 Hz). This chemical shift could possibly indicate the presence of an N–H bond in the isomeric amido, [Nb(NHBu^t){Me$_2$-Si(η^5-C$_5$H$_4$)}$_2$] compound. Such isomers have previously been postulated by Green et al. [3e] in analogous hydride imido niobocene derivatives. Nonetheless, the presence of an IR band at 1725 cm^{-1} for **6**, which is assignable to ν(Nb–H) [3c,3e,3f], lends support to the presence of a niobium-bound hydrogen. In addition, low temperature NMR spectroscopy of **6** showed no appreciable changes and therefore a dynamic situation in solution between imido-hydride and amido species can be ruled out.

The reaction of **5** with I$_2$ gave the monomeric niobocene (V) iodide derivative, [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)}$_2$I] (**7**), via a formally oxidative addition mechanism (Scheme 1). The ^{1}H NMR spectrum of **7** is similar to that described previously for its chloride analogue [8], namely, an ABCD system of four multiplets, between 6.0 and 6.7 ppm, for the C$_5$ ring protons, two singlets, at − 0.03 and 0.24 ppm, for the methyl substituents of the *ansa*-bridge and a singlet, at 0.99 ppm, assigned to the *tert*-butyl protons.

3. Conclusions

In this paper we report the synthesis and structural characterization of new cationic niobocene derivatives. We have also described the preparation of niobocene imido dimeric, hydride and iodide compounds.

4. Experimental

4.1. Materials and 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. [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] [10], [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] [3b], [Nb(=NBu^t){Me$_2$-Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl] [7], [Nb(=NBu^t){Me$_2$Si-(η^5-C$_5$H$_4$)}$_2$Cl] [8] and [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] [16] were prepared as described earlier. CNBu^t was purchased from Aldrich and used without further purification. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Varian Mercury FT-400 spectrometer and referenced to the residual deuterated solvent. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. Microanalyses were carried out with a Heraeus-CHN-O-Rapid microanalyser.

4.2. Synthesis of [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$-(CNBu^t)][BPh$_4$] (1)

A solution of [Nb(=NBu^t)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] (1.05 g, 2.22 mmol) in THF (50 ml) was added, at 0 °C, to Na amalgam (0.051 g, 2.22 mmol of Na). The mixture was allowed to warm to room temperature and stirred for 30 min. THF was removed under reduced pressure and hexane (50 ml) added. The resulting suspension was filtered and solvent was removed, from the filtrate, in vacuo to yield a red oily solid. A solution of [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$]

(1.12 g, 2.22 mmol) in THF (50 ml) and *tert*-butylisocyanide (0.18 g, 2.22 mmol) were subsequently added to this solid at −30 °C. The reaction mixture was allowed to warm to room temperature and stirred for 40 min. Solvent was then removed by applying reduced pressure and the resulting residue washed with Et_2O (3 × 30 ml) to yield the title complex as an orange crystalline solid (1.50 g, 80%). IR (Nujol mull): ν_{CN} 2215, $\nu_{Nb=N}$ 1232 cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ 0.34 (s, 18H, Si*Me*$_3$), 1.05 (s, 9H, N*Bu^t*), 1.70 (s, 9H, CN*Bu^t*), 6.11 (2H), 6.17 (2H), 6.20 (2H), 6.59 (2H) (m, C$_5$*H*$_4$), 6.83 (4H), 6.98 (8H), 7.26 (8H) (m, *Ph*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 0.1 (Si*Me*$_3$), 29.5 (CNC*Me*$_3$), 30.7 (NC*Me*$_3$), 62.7 (CN*C*Me$_3$), 72.5 (N*C*Me$_3$), 107.1, 114.2, 119.7, 122.4, 123.3 (C$_5$*H*$_4$), 128.0 (*C*NBu^t), 126.2, 134.3, 138.3, 164.3 (*Ph*). Anal. Calc. for C$_{49}$H$_{64}$BN$_2$NbSi$_2$: C, 69.98; H, 7.67; N, 3.33. Found C, 69.67; H, 7.61; N, 3.31%.

4.3. Synthesis of [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CNBu^t)]-[BPh$_4$] (2)

The preparation of **2** was carried out in an identical manner to **1**. [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] (0.21 g, 0.43 mmol), Na (0.010 g, 0.43 mmol), [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] (0.22 g, 0.43 mmol) and *tert*-butylisocyanide (0.035 g, 0.43 mmol). Yield 0.20 g, 54%. IR (Nujol mull): ν_{CN} 2216, $\nu_{Nb=N}$ 1246 cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ 0.15 (s, 18H, Si*Me*$_3$), 1.72 (s, 9H, CN*Bu^t*), 6.29 (2H), 6.35 (2H), 6.50 (2H), 6.69 (2H) (m, C$_5$*H*$_4$), 6.39 (2H), 6.88 (2H), 7.20 (1H) (m, N*Ph*), 6.83 (4H), 6.98 (8H), 7.26 (8H) (m, B*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ −0.1 (Si*Me*$_3$), 29.6 (CNC*Me*$_3$), 63.5 (CN*C*Me$_3$), 113.7, 114.6, 117.8, 119.5, 120.3 (C$_5$*H*$_4$), 128.1 (*C*NBu^t), 122.8, 126.7, 136.8, 162.8 (B*Ph*), 124.4, 126.5, 129.5, 158.0 (N*Ph*). Anal. Calc. for C$_{51}$H$_{60}$BN$_2$NbSi$_2$: C, 71.15; H, 7.02; N, 3.25. Found C, 70.89; H, 7.10; N, 3.16%.

4.4. Synthesis of [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)]-[BPh$_4$] (3)

A solution of [Nb(=NPh)(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl] (0.21 g, 0.42 mmol) in THF (50 ml) was added, at 0 °C, to Na amalgam (0.010 g, 0.43 mmol of Na). The mixture was allowed to warm to room temperature and stirred for 30 min. THF was removed under reduced pressure and hexane (50 ml) added. The resulting suspension was filtered and solvent was removed, from the filtrate, in vacuo to yield a red oily solid. A solution of [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] (0.22 g, 0.43 mmol) in THF (50 ml) was subsequently added to this solid at −30 °C. Nitrogen pressure was reduced by applying vacuum and replaced by CO gas. The reaction mixture was allowed to warm to room temperature and stirred for 40 min. Solvent and excess CO were then removed by applying reduced pressure and the resulting residue washed with Et_2O (3 × 30 ml) to yield the title complex as a pink crystalline solid (0.22 g, 61%). IR (Nujol mull): ν_{CO} 1932, $\nu_{Nb=N}$ 1239 cm^{-1}. ^{1}H NMR

(400 MHz, CD$_3$CN): δ 0.16 (s, 18H, Si*Me*$_3$), 5.18 (4H), 5.79 (2H), 5.87 (2H) (m, C$_5$*H*$_4$), 6.60 (2H), 7.15 (2H), 7.40 (1H) (m, N*Ph*), 6.83 (4H), 6.99 (8H), 7.26 (8H) (m, B*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 0.3 (Si*Me*$_3$), 112.8, 113.9, 118.0, 119.6, 121.1 (C$_5$*H*$_4$), 122.7, 126.7, 136.8, 164.5 (B*Ph*), 124.0, 126.8, 129.6, 156.3 (N*Ph*), 259.8 (*CO*). Anal. Calc. for C$_{47}$H$_{51}$BNNbOSi$_2$: C, 70.05; H, 6.38; N, 1.74. Found C, 69.89; H, 6.34; N, 1.77%.

4.5. Synthesis of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)-(η^5-C$_5$H$_4$)}(CNBu^t)][BPh$_4$] (4)

The preparation of **4** was carried out in an identical manner to **1**. [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl] (0.45 g, 1.02 mmol), Na (0.023 g, 1.02 mmol), [Fe(η^5-C$_5$H$_5$)$_2$][BPh$_4$] (0.51 g, 1.02 mmol) and *tert*-butylisocyanide (0.085 g, 1.02 mmol). Yield 0.52 g, 63%. IR (Nujol mull): ν_{CN} 2215, $\nu_{Nb=N}$ 1260 cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$CN): δ 0.54 (3H), 0.79 (3H) (s, Si*Me*$_2$), 1.02 (s, 9H, N*Bu^t*), 1.73 (s, 9H, CN*Bu^t*), 1.88 (3H), 2.08 (3H), 2.14 (3H), 2.68 (3H) (s, C$_5$*Me*$_4$), 6.12 (4H), 6.60 (2H), 6.87 (2H) (m, C$_5$*H*$_4$), 6.83 (4H), 6.97 (8H), 7.25 (8H) (m, B*Ph*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ −1.8, −0.7 (Si*Me*$_2$), 12.6, 13.9, 14.6, 16.7 (C$_5$*Me*$_4$), 29.9 (CNC*Me*$_3$), 31.2 (NC*Me*$_3$), 68.8 (CN*C*Me$_3$), 71.1 (N*C*Me$_3$), 105.8, 111.1, 111.3, 119.5, 120.3 (C$_5$*H*$_4$), 106.7, 125.4, 125.6, 130.9, 135.6 (C$_5$*Me*$_4$), 128.5 (*C*NBu^t), 122.6, 126.5, 136.6, 164.5 (B*Ph*). Anal. Calc. for C$_{49}$H$_{60}$BN$_2$NbSi: C, 72.76; H, 7.48; N, 3.46. Found C, 72.58; H, 7.46; N, 3.49%.

4.6. Synthesis of [(Nb{Me$_2$Si(η^5-C$_5$H$_4$)$_2$}(μ-NBu^t))$_2$] (5)

A solution of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] (0.40 g, 1.04 mmol) in THF (50 ml) was added, at −30 °C, to Na amalgam (0.024 g, 1.04 mmol of Na). The mixture was initially stirred for 10 min at − 30 °C and then allowed to warm to room temperature whilst stirring for a further 10 min. THF was removed under reduced pressure and hexane (50 ml) added. The resulting suspension was cooled to −40 °C and then filtered. Solvent was removed, from the filtrate, in vacuo, to yield the title complex as a brown crystalline solid (0.29 g, 81%). IR (Nujol mull): ν_{Nb-N} 1095 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.49 (s, 12H, Si*Me*$_2$), 1.44 (s, 18H, N*Bu^t*), 5.04 (8H), 5.79 (8H) (m, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ −3.4 (Si*Me*$_2$), 35.8 (NC*Me*$_3$), 72.9 (N*C*Me$_3$), 100.0, 109.8, 116.2 (C$_5$*H*$_4$). Anal. Calc. for C$_{32}$H$_{46}$N$_2$Nb$_2$Si$_2$: C, 54.85; H, 6.62; N, 4.00. Found C, 54.51; H, 6.57; N, 4.05%.

4.7. Synthesis of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}H] (6)

A solution of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl] (0.47 g, 1.22 mmol) in THF (50 ml) was added, at 25 °C, to Na amalgam (0.028 g, 1.22 mmol of Na). The mixture was stirred for 12 h. THF was removed under reduced pressure and hexane (50 ml) added. The resulting suspension was filtered. The filtrate was cooled to −40 °C to yield

brown crystals of the title complex which were isolated by filtration (0.29 g, 67%). IR (Nujol mull): v_{Nb-H} 1725, $v_{Nb=N}$ 1237 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.07 (3H), 0.32 (3H) (s, SiMe_2), 1.16 (s, 9H, NBu^t), 2.70 (s, 1H, Nb–H), 5.59 (2H), 6.20 (2H), 6.25 (2H), 7.39 (2H) (m, C$_5H_4$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ −6.2, −5.0 (SiMe_2), 33.3 (NCMe_3), 66.0 (NCMe$_3$), 97.0, 100.1, 104.4, 109.3, 119.3 (C_5H_4). Anal. Calc. for C$_{16}$H$_{24}$NNbSi: C, 54.69; H, 6.88; N, 3.99. Found C, 54.48; H, 6.81; N, 3.93%.

4.8. Synthesis of [Nb(=NBu^t){Me$_2$Si(η^5-C$_5H_4$)$_2$}I] (7)

I$_2$ (0.072 g, 0.29 mmol) was added to a solution of **5** (0.20 g, 0.29 mmol) in toluene (30 ml). The mixture was stirred at room temperature for 30 min. Solvent was removed by applying reduced pressure to yield the title complex as a brown crystalline solid (0.27 g, 100%). IR (Nujol mull): $v_{Nb=N}$ 1265 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −0.03 (3H), 0.24 (3H) (s, SiMe_2), 0.99 (s, 9H, NBu^t), 6.06 (2H), 6.10 (2H), 6.27 (2H), 6.68 (2H) (m, C$_5H_4$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ −6.9, −4.7 (SiMe_2), 30.0 (NCMe_3), 66.0 (NCMe$_3$), 100.3, 115.2, 116.8, 117.4, 130.0 (C_5H_4). Anal. Calc. for C$_{16}$H$_{23}$INNbSi: C, 40.27; H, 4.86; N, 2.93. Found C, 40.21; H, 4.82; N, 2.94%.

4.9. X-ray structure determination of [Nb(=NBu^t)-(η^5-C$_5H_4$SiMe$_3$)$_2$(CNBu^t)][BPh$_4$] (1)

Orange crystals of **1** were obtained from THF/hexane at −25 °C. A summary of crystal data, data collection and refinement parameters for the structural analysis is given in Table 4. The crystal was fixed with mineral oil to a glass fibre and mounted on Kappa-CCD Bruker-Nonius diffrac-

tometer with area detector and data were collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 200 K, with an exposure time of 60 s per frame (13 sets; 679 frames). Raw data were corrected for Lorenz and polarization effects. A semi-empirical absorption correction was made. The structure was solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97) [17]. Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. The hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. All calculations were made using the WINGX system [18].

Appendix A. Supplementary material

Crystallographic data for the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 602096. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http//www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.017.

Table 4
Crystal data and structure refinement details for **1**

Empirical formula	C$_{49}$H$_{64}$BN$_2$NbSi$_2$
FW	840.92
T (K)	200(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.699(5)
b (Å)	12.767(5)
c (Å)	19.682(5)
α (°)	92.798(5)
β (°)	103.097(5)
γ (°)	109.819(5)
V (Å^3)	2440.1(16)
Z	2
D_c (g cm^{-3})	1.145
μ (mm^{-1})	0.328
Crystal dimension (mm)	$0.4 \times 0.3 \times 0.2$
Reflections collected/unique [R_{int}]	96 781/11 181 [0.1506]
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0431$
	$wR_2{}^b = 0.0935$
Largest difference in peak and hole (e Å^{-3})	0.399 and −0.995

^{a} $R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$.
^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

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