

Synthesis and structural characterization of isocyanate, amido and imido niobocene derivatives: crystal structures of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N,C-OCNPh})]$ and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2(\mu\text{-1,3-N}_2\text{C}_6\text{H}_4)]^\dagger$

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The niobium complex $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2]$ **1** reacted with phenyl isocyanate, 1,3- and 1,4-phenylenediisocyanate to give the corresponding complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N,C-OCNPh})]$ **2**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N,C-}\mu\text{-1,3-(OCN)}_2\text{C}_6\text{H}_4\}]$ **3** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N,C-}\mu\text{-1,4-(OCN)}_2\text{C}_6\text{H}_4\}]$ **4**, respectively. The spectroscopic data were not sufficient unequivocally to differentiate between the presence of a $\kappa^2\text{C,N}$ or $\kappa^2\text{C,O}$ co-ordination mode. However the crystal structure of **2** showed it to have $\kappa^2\text{C,N}$ co-ordination. Complexes **3** and **4** have an analogous structure in which two metal centres are linked through an aryl ring containing a diisocyanate ligand. The reactivity of these complexes under reduction and thermal decomposition conditions was examined. Complexes **2–4** with Na/Hg underwent a reduction at each metal centre followed by protonation to afford the corresponding $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{OCHNPh})]$ **5**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\mu\text{-1,3-(OCHN)}_2\text{C}_6\text{H}_4\}]$ **6** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\mu\text{-1,4-(OCHN)}_2\text{C}_6\text{H}_4\}]$ **7**. The imido $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NPh})]$ **8** and diimido derivatives $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2(\mu\text{-1,3-N}_2\text{C}_6\text{H}_4)]$ **9** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2(\mu\text{-1,4-N}_2\text{C}_6\text{H}_4)]$ **10** were isolated by heating **2**, **3** or **4** or alternatively by treating **1** with the appropriate amount of the corresponding aniline, 1,3- or 1,4-phenylenediamine, respectively. The molecular crystal structure of **9** was determined by single-crystal diffractometry. It contains two bent niobocene units linked by a 1,3-diimidophenylene ligand, with the niobium atoms slightly deviating from the plane formed by this ligand. Complexes **8–10** reacted with Grignard reagents MgRCl ($\text{R} = \text{Me}$, Et or Pr^i) or MgMe_2 in tetrahydrofuran solution to give the corresponding substitution products $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{R}(\text{NPh})]$ ($\text{R} = \text{Me}$ **11**, Et **12** or Pr^i **13**), $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{R}\}_2(\mu\text{-1,3-N}_2\text{C}_6\text{H}_4)]$ ($\text{R} = \text{Me}$ **14**, Et **15** or Pr^i **16**) and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{R}\}_2(\mu\text{-1,4-N}_2\text{C}_6\text{H}_4)]$ ($\text{R} = \text{Me}$ **17**, Et **18** or Pr^i **19**). The reaction of **8–10** with Na/Hg in appropriate molar ratios afforded the corresponding hydride complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{H}(\text{NPh})]$ **20**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{H}\}_2(\mu\text{-1,3-N}_2\text{C}_6\text{H}_4)]$ **21** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{H}\}_2(\mu\text{-1,4-N}_2\text{C}_6\text{H}_4)]$ **22**. Finally, the monoimido complexes **8** and **11–13** were easily protonated with 1 equivalent of $\text{HBF}_4 \cdot \text{OEt}_2$ to give, in one step, the corresponding amido cationic complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{X}(\text{NHPh})]^+ [\text{BF}_4]^-$ ($\text{X} = \text{Cl}$ **23**, Me **24**, Et **25** or Pr^i **26**). The structures of the different families of complexes isolated were determined by spectroscopic methods.

Although numerous studies on the reactivity of isocyanates toward various metal centres have been described,¹ few examples of complexes containing the metal isocyanate moiety are known² due to the high reactivity exhibited by these ligands. We recently prepared the first examples of isocyanate complexes of early transition metals although differentiation between the existence of a $\kappa^2\text{C,N}$ or a $\kappa^2\text{C,O}$ co-ordination mode based on spectroscopic data could not be unequivocally made.³ It is noteworthy, however, that numerous examples of early transition-metal imido complexes exist, and in particular a great number of d⁰ niobium and tantalum complexes containing imido groups is known.⁴ Nonetheless, despite the fact that the chemistry of monocyclopentadienyl imido complexes of these metals is well documented,⁵ few examples of bent imido metallocenes have been described.^{2h,3,6}

Transition-metal complexes in which the metal centres are linked by a bridging ligand possessing a delocalized π system

are well known and have been the subject of intense research, because of their potential applications in the design of low-dimensional, polymeric materials with novel electrical and/or magnetic properties. With respect to such complexes, the strong metal–imido interaction⁷ in organoimido complexes allows redox-active binuclear complexes containing a delocalized π -bonded bridge with bis(imide) ligands to be prepared which are much less labile than the alternative bifunctional σ -donor/ π -acceptor pyrazine-type ligands in Creutz–Taube systems.⁸ In particular several complexes which incorporate aryldiimido bridges have been described.⁹ We recently reported the preparation of a family of mononuclear imidoniobocene complexes, $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NR})]$, by thermal decomposition of the corresponding isocyanate derivatives or by reaction of the monochloride niobocene, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2]$ **1**, with the appropriate primary amines NRH_2 .³ As a continuation of our research in this field we examined the reactivity of these mononuclear complexes in several types of reactions, the results of which could then be applied to the syntheses of binuclear

[†] Dedicated to Professor P. Royo on the occasion of his 60th birthday.

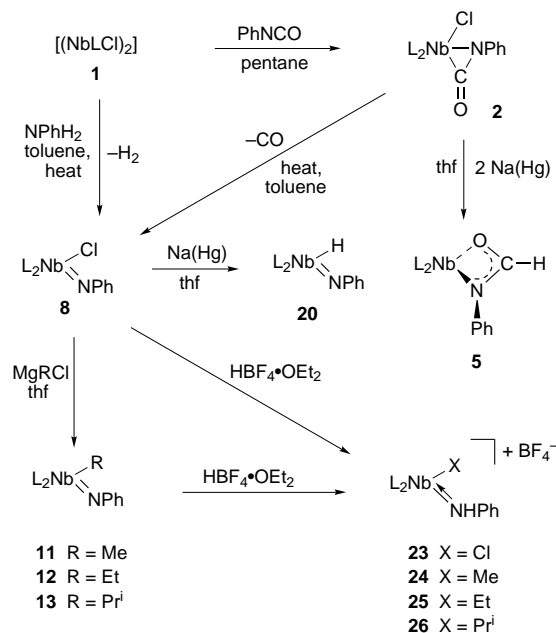
niobocene complexes with niobium centres linked by conjugated π systems.

Results and Discussion

The starting niobium complex $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2]$ **1** reacts with phenyl isocyanate, 1,3- and 1,4-phenylenediisocyanate to give the corresponding complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N,C-OCNPh})]$ **2**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N,C-}\mu\text{-1,3-(OCN)}_2\text{C}_6\text{H}_4\}]$ **3** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N,C-}\mu\text{-1,4-(OCN)}_2\text{C}_6\text{H}_4\}]$ **4**, respectively, Schemes 1 and 2. The complexes were isolated as white or pale yellow air-sensitive precipitates. The preparation of **2** has previously been reported³ although, as stated therein, the spectroscopic data did not allow for an unambiguous assignment of one or other of two possible $\kappa^2\text{C,N}$ or $\kappa^2\text{C,O}$ co-ordination modes for the

isocyanate ligand. We have now successfully grown crystals from a toluene–pentane solution which were used to determine the first crystal structure of an isocyanate metallocene complex. The molecular structure for **2** is depicted in Fig. 1, together with the atomic numbering scheme.

Selected bond lengths and angles appear in Table 1. The compound crystallized in the space group $P2_1/n$ with four molecules per unit cell. There was no intermolecular contact distance which could be considered to imply a bonding interaction. Compound **2** is a monomer in the solid state and shows a typical bent-metallocene structure where the Cl, Nb, N, C(11) and O atoms practically lie in the equatorial plane [maximum deviation 0.01 Å for C(11)]. The isocyanate ligand is $\kappa^2\text{C,N}$ coordinated with bond distances $[\text{Nb-C}(11)]$ 2.164(7) and Nb–N



Scheme 1 L = C₅H₄SiMe₃

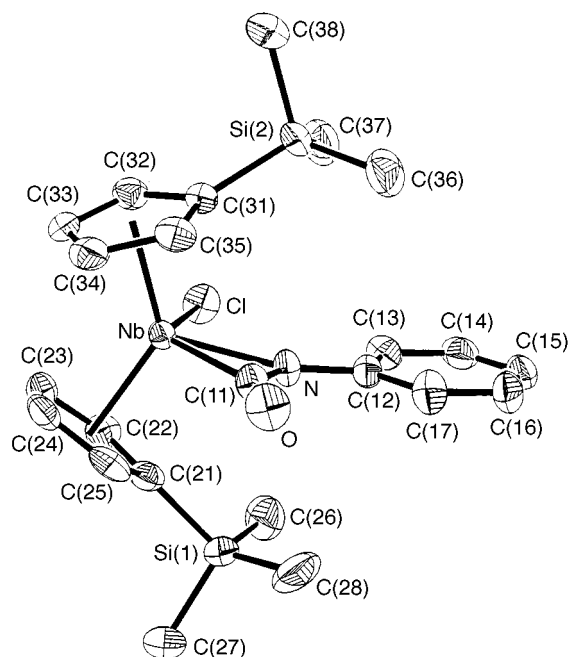
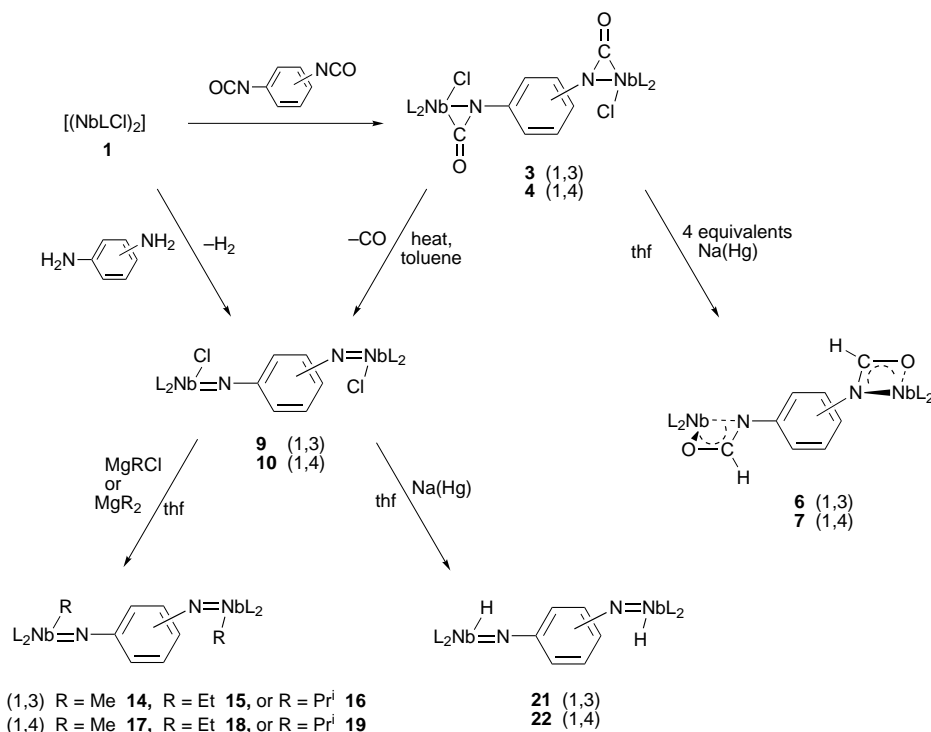


Fig. 1 An ORTEP¹⁰ view of the complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N,C-OCNPh})]$ **2**



Scheme 2 L = C₅H₄SiMe₃

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

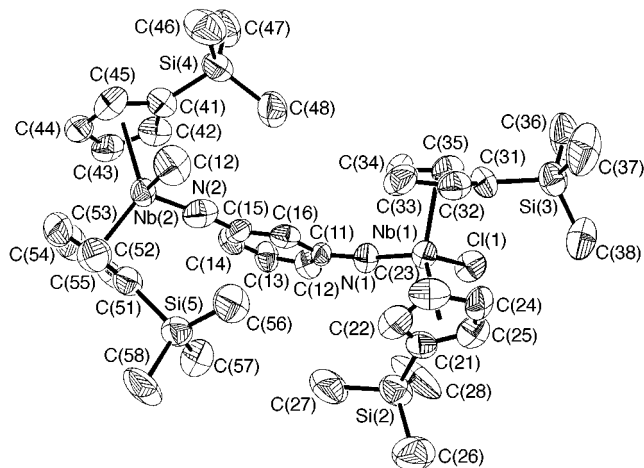
| | | | |
|---------------|-----------|----------------|-----------|
| Nb–Cl | 2.494(2) | Si(2)–C(36) | 1.840(9) |
| Nb–C(11) | 2.164(7) | Si(2)–C(37) | 1.856(10) |
| Nb–N | 2.166(5) | Si(2)–C(38) | 1.869(9) |
| Si(1)–C(21) | 1.881(7) | O–C(11) | 1.197(8) |
| Si(1)–C(26) | 1.864(10) | N–C(11) | 1.301(9) |
| Si(1)–C(27) | 1.874(8) | N–C(12) | 1.415(8) |
| Si(1)–C(28) | 1.867(10) | Nb–Cp(1) | 2.121 |
| Si(2)–C(31) | 1.886(7) | Nb–Cp(2) | 2.120 |
| Cl–Nb–N | 85.0(1) | N–C(11)–Nb | 72.6(4) |
| Cl–Nb–C(11) | 120.0(2) | Cp(1)–Nb–Cl | 102.0 |
| C(11)–Nb–N | 35.0(2) | Cp(1)–Nb–N | 112.0 |
| C(11)–N–C(12) | 130.6(6) | Cp(1)–Nb–C(11) | 101.7 |
| C(11)–N–Nb | 72.4(4) | Cp(1)–Nb–Cp(2) | 129.5 |
| C(12)–N–Nb | 156.2(5) | Cp(2)–Nb–Cl | 104.7 |
| O–C(11)–N | 141.3(7) | Cp(2)–Nb–N | 112.4 |
| O–C(11)–Nb | 146.0(5) | Cp(2)–Nb–C(11) | 100.9 |

Cp(1), Cp(2) = centroids of cyclopentadienyl rings.

2.166(5) Å]. This co-ordination mode for the isocyanate ligand can also be assigned to complexes **3** and **4**, where it is proposed that the two metal centres are linked through a bis(isocyanate) ligand containing an aryl ring, by analogy of some fundamental spectroscopic properties of these complexes and those of **2**. The complexes were also characterized by spectroscopic techniques. The IR spectra for **2–4** display strong bands at *ca.* 1721, 1740 and 1716 cm⁻¹ respectively (see Experimental section) which can be assigned to the ν(C=O) stretching vibration of co-ordinated RNCO. The ¹³C NMR spectra show resonances at *ca.* δ 187.2, 186.0 and 188.1 (see Experimental section) which are due to the carbonyl group of the isocyanate ligand. In addition, five resonances appear for the carbon atoms of the two cyclopentadienyl ligands which indicate the presence of an unsymmetrical environment.

Once prepared and characterized, the reactivity of these complexes in two types of reactions, namely reduction and thermal decomposition processes, was examined. When a solution of complex **2**, **3** or **4** in tetrahydrofuran (thf) is treated with an excess of sodium amalgam a reduction at each metal centre, followed by protonation of the carbon atom of the isocyanate group, takes place to give the corresponding niobocene complexes NCHO **5–7** (see Schemes 1 and 2 respectively). Complex **5** was previously synthesized by heating the carbonyl complex [Nb(η⁵-C₅H₄SiMe₃)₂(CO)(PhNCHO)], which was prepared by an insertion reaction of PhNCO into the Nb–H bond of the hydride derivative [Nb(η⁵-C₅H₄SiMe₃)₂H(CO)].¹¹ Other similar niobium or tantalum derivatives have been described previously.¹² The structural characterization of the present derivatives was carried out by mass spectrometry and spectroscopic techniques (see Experimental section). The IR spectra of **5–7** show a characteristic band at *ca.* 1550 cm⁻¹ which is indicative of a chelating NCHO ligand.¹³ Resonances assignable to the NCHO group have been observed in both ¹H and ¹³C NMR spectra, the hydrogen appearing at *ca.* δ 8.21, 8.31 and 8.25 and the carbon at *ca.* δ 175.5, 175.4 and 175.0 for **5**, **6** and **7** respectively. These shifts are comparable to those found for related derivatives.^{11,12}

Following the synthetic methods previously described,^{2h,3} imido [Nb(η⁵-C₅H₄SiMe₃)₂Cl(NPh)] **8** and diimido derivatives [Nb(η⁵-C₅H₄SiMe₃)₂Cl]₂(μ-1,3-N₂C₆H₄) **9** and [Nb(η⁵-C₅H₄SiMe₃)₂Cl]₂(μ-1,4-N₂C₆H₄) **10** were synthesized by heating the corresponding isocyanate-containing complexes **2**, **3** and **4** or by treating **1** with the appropriate amount of aniline, 1,3- or 1,4-phenylenediamine, respectively (see Schemes 1 and 2). These compounds were cleanly isolated in good yields as air-stable materials. The preparation and molecular structure of complex **8** has previously been described.³ Complexes **9** and **10** constitute a singular example of early transition-metal imido bent

**Fig. 2** An ORTEP view of the complex [Nb(η⁵-C₅H₄SiMe₃)₂Cl]₂(μ-1,3-N₂C₆H₄) **9****Table 2** Selected bond lengths (Å) and angles (°) for complex **9**

| | | | |
|-------------------|----------|-------------------|---------|
| Nb(1)–N(1) | 1.75(2) | Si(3)–C(36) | 1.90(3) |
| Nb(1)–Cl(1) | 2.453(5) | Si(4)–C(46) | 1.79(3) |
| Nb(2)–N(2) | 1.76(2) | Si(4)–C(41) | 1.84(2) |
| Nb(2)–Cl(2) | 2.447(6) | Si(4)–C(47) | 1.85(2) |
| N(1)–C(11) | 1.38(2) | Si(4)–C(48) | 1.90(3) |
| N(2)–C(15) | 1.45(3) | Si(5)–C(57) | 1.81(3) |
| Si(2)–C(28) | 1.79(3) | Si(5)–C(58) | 1.85(2) |
| Si(2)–C(26) | 1.92(3) | Si(5)–C(51) | 1.87(2) |
| Si(2)–C(27) | 1.94(4) | Si(5)–C(56) | 1.88(2) |
| Si(2)–C(21) | 1.96(3) | Nb(1)–Cp(1) | 2.193 |
| Si(3)–C(31) | 1.86(2) | Nb(1)–Cp(2) | 2.169 |
| Si(3)–C(38) | 1.89(3) | Nb(2)–Cp(3) | 2.200 |
| Si(3)–C(37) | 1.89(3) | Nb(2)–Cp(4) | 2.190 |
| N(1)–Nb(1)–Cl(1) | 97.0(5) | Cp(2)–Nb(1)–Cl(1) | 105.0 |
| N(2)–Nb(2)–Cl(2) | 98.9(6) | Cp(2)–Nb(1)–N(1) | 108.0 |
| C(11)–N(1)–Nb(1) | 167(2) | Cp(3)–Nb(2)–Cl(2) | 104.0 |
| C(15)–N(2)–Nb(2) | 168(2) | Cp(3)–Nb(2)–N(2) | 109.4 |
| Cp(1)–Nb(1)–Cl(1) | 106.5 | Cp(3)–Nb(2)–Cp(4) | 125.6 |
| Cp(1)–Nb(1)–N(1) | 111.8 | Cp(4)–Nb(2)–Cl(2) | 104.9 |
| Cp(1)–Nb(1)–Cp(2) | 124.5 | Cp(4)–Nb(2)–N(2) | 110.0 |

metallocenes⁶ and in order unequivocally to confirm the proposed structure for these complexes a crystal and molecular structure determination of **9** was undertaken. An ORTEP drawing is depicted in Fig. 2, together with the atomic numbering scheme. Selected bond lengths and angles appear in Table 2.

The compound crystallized in the *Cc* space group with four molecules per unit cell. There was no intermolecular contact distance which could be considered to imply a bonding interaction. The complex shows two bent niobocene units linked by a diimidophenylene ligand, in which Nb(1) and Nb(2) deviate by –0.30 and 0.11 Å from the plane formed by this ligand. As far as we know this is the first structurally characterized complex in which a diimidophenylene group bridges two metallocene moieties. To date only two non-metallocene species containing a diimidophenylene bridge have been structurally characterized.⁹ As can be seen in Fig. 2, the two niobocene units show different conformations. The unit containing Nb(2) presents two eclipsed cyclopentadienyl rings with a torsion angle Si(4)–C(41)–C(51)–Si(5) of –19.4°, while the other two ligands bonded to Nb(1) are alternated, with a torsion angle Si(2)–C(21)–C(31)–Si(3) –96.1°. The Nb(1)–N(1) and Nb(2)–N(2) bond distances are 1.754(20) and 1.763(18) Å respectively, which are close to the value 1.792(2) Å found in the phenylimido niobocene complex **8**,³ and are intermediate between that expected for a double and triple Nb–N bond. The angles Nb(1)–N(1)–C(11) and Nb(2)–N(2)–C(15) are 167.4(14) and 168.4(15)° respectively, in accordance with the value of

165.1(2)° found for Nb–N–C_{ipso} in **8**. For reasons similar to those described for **8**,³ we propose that both nitrogen atoms are sp hybridized, with the following two limiting descriptions, $\text{Nb}=\text{N}=\text{R}$ and $\text{Nb}=\text{N}-\text{R}$, explaining the true bonding situation. Finally, the Cl(1)–Nb(1)–Nb(2)–Cl(2) torsion angle is –161.3°, the chlorine atoms being in a *trans* position with respect to the Nb–Nb line. The imido complexes which were obtained as air-stable orange-red solids have been characterized by elemental analysis and ¹H and ¹³C NMR spectroscopy (see Experimental section).

In order to obtain information about the chemical behaviour of these imido and diimido complexes, two types of reactions were carried out (see Schemes 1 and 2). Complexes **8**–**10**, like the monoimido complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}(\text{NBu}^t)]$ described by Green and co-workers,^{6c} underwent substitution reactions with Grignard reagents, MgRCl (R = Me, Et or Prⁱ) in thf solution to give the complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{R}(\text{NPh})]$ (R = Me **11**, Et **12** or Prⁱ **13**), $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,3\text{-N}_2\text{C}_6\text{H}_4)]$ (R = Me **14**, Et **15** or Prⁱ **16**) and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4)]$ (R = Me **17**, Et **18** or Prⁱ **19**). They were isolated as air-stable yellow-orange oils and characterized by spectroscopic techniques (see Experimental section).

In addition, solutions of complexes **8** and **9**, **10** in thf react with sodium amalgam in 1:1 and 1:2 ratios respectively to afford the corresponding hydride derivatives $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{H}(\text{NPh})]$ **20**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,3\text{-N}_2\text{C}_6\text{H}_4)]$ **21** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4)]$ **22** (see Schemes 1 and 2 respectively), which were isolated as reddish brown oils unstable in air. They were characterized by spectroscopic techniques (see Experimental section). The hydride resonances in the ¹H NMR spectra were observed as broad signals at δ 2.75, 2.87 and 2.94, respectively (Δν₃ = 30 Hz). These chemical shifts could possibly indicate the presence of an N–H bond in the isomeric amido $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{NHPh})]$ and diamido $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,3\text{-NHC}_6\text{H}_4\text{NH})]$ and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2(\mu\text{-}1,4\text{-NHC}_6\text{H}_4\text{NH})]$ compounds. Such isomers have previously been described by Green and co-workers^{6c} in analogous hydride imido niobocene derivatives. Nonetheless, the presence of IR bands at *ca.* 1721, 1730 and 1735 cm⁻¹ for complexes **20**, **21** and **22** respectively, which are assignable to ν(Nb–H),^{6a,c,d} lend support to the presence of a niobium-bound hydrogen. Finally, monoimido complexes **8**, **11**, **12** and **13** were easily protonated with HBF₄·OEt₂ to give, in one step, the corresponding amido cationic complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{X}(\text{NHPh})]^+[\text{BF}_4]^-$ (X = Cl **23**, Me **24**, Et **25** or Prⁱ **26**). The standard reaction procedure involved the addition of 1 equivalent of HBF₄·OEt₂ to ether solutions of the complexes in question (see Scheme 1). The compounds were isolated, after appropriate work-up, as air-stable dark red solids and characterized by elemental analysis and ¹H NMR spectroscopy (see Experimental section). Complex **23** has previously been described.¹³ The ¹H NMR spectra exhibit a broad high-field resonance for the amide ligand and between δ 8.26 and 12.79.¹⁴ It is noteworthy that the electrophilic proton attack takes place exclusively on the nitrogen atom of the imide ligand and not on the Nb–Cl or Nb–alkyl bonds. Several examples of electrophilic attack on the latter are known.¹⁵ For halogenoketenimine complexes this reaction has been observed to give cationic iminoacylniobocene complexes¹⁶ and recently alkyl or hydride containing ketene or ketenimine niobocene derivatives have been protonated to form the corresponding acyl and iminoacyl compounds.¹⁷

In conclusion we have been able unequivocally to establish that the isocyanate ligand in $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N},\text{C-OCNPh})]$ **2** is co-ordinated in a κ²C,N mode and that this mode could also be assigned to $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\kappa^2\text{N},\text{C-}(\mu\text{-}1,3\text{-}(\text{OCN})_2\text{C}_6\text{H}_4)\}]$ **3** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\kappa^2\text{N},\text{C-}(\mu\text{-}1,4\text{-}(\text{OCN})_2\text{C}_6\text{H}_4)\}]$ **4** by analogy of their spectroscopic data. These compounds can easily be reduced to give the corresponding NCHO niobocene complexes. Diimido deriv-

atives containing ligands with delocalized π systems linking two niobocene moieties can easily be prepared in good yields. Efforts to broaden the scope of this reaction and gain knowledge as to possible non-linear optical properties are currently in progress.

Experimental

General procedures

All operations were performed under an inert atmosphere using standard vacuum-line (Schlenk) techniques or an MBraun glovebox. Solvents were purified by distillation from appropriate drying agents before use. The NMR spectra were obtained on Varian Unity FT-300 and FT-500 PLUS instruments, IR spectra as Nujol mulls between CsI plates (in the region between 4000 and 200 cm⁻¹) on a Perkin-Elmer 883 spectrometer. Elemental microanalyses were performed on a Perkin-Elmer 240B microanalyser. Mass spectral analyses were performed on a Hewlett-Packard 5890 instrument, *m/z* 50–1000, using the chemical ionization technique. The following compounds were prepared as described earlier: $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2]$,^{2b} $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\kappa^2\text{N},\text{C-OCNPh})]$,^{2h,3} $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NPh})]$,^{2h,3} $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NHPh})]^+[\text{BF}_4]^-$.¹⁴ Aniline was purified by distillation and other reagents were used as purchased.

Preparations

$[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N},\text{C-}\mu\text{-}1,3\text{-}(\text{OCN})_2\text{C}_6\text{H}_4\}]$ **3** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2\{\kappa^2\text{N},\text{C-}\mu\text{-}1,4\text{-}(\text{OCN})_2\text{C}_6\text{H}_4\}]$ **4**. To a solution of complex **1** in pentane was added an equimolar quantity of 1,3- or 1,4-phenylenediisocyanate. The mixture was vigorously stirred overnight at room temperature after which a pale yellow microcrystalline precipitate was obtained. This was filtered off, dried under vacuum and identified as **3** or **4**.

Complex **3**: from **1** (0.87 g, 1.1 mmol) and 1,3-phenylenediisocyanate (0.20 g, 1.3 mmol) 0.97 g was obtained (yield >90%); IR (Nujol mull) ν(C=O) 1740 cm⁻¹; ¹H NMR (C₆D₆, 300 MHz) δ 0.24 (s, 36 H, SiMe₃), 5.37 (4 H), 5.51 (4 H), 5.62 (4 H), 6.34 (4 H) (m, C₅H₄SiMe₃), 7.25 (t, 1 H), 7.99 (d, 2 H), 8.67 (m, 1 H) (phenylene ring); ¹³C-¹H} (C₆D₆, 500 MHz) δ 0.4 (SiMe₃), 106.2, 111.3, 114.4 (C_{ipso}), 119.5, 121.0 (C₅H₄SiMe₃), 115.5, 120.0, 127.2 (phenylene ring), 149.5 (C_{ipso} of phenylene ring) and 186.0 (RNCO) [Found (Calc. for C₄₀H₅₆Cl₂N₂Nb₂O₂Si₄): C, 49.50 (49.74); H, 5.88 (5.84); N, 2.95 (2.90)%].

Complex **4**: from **1** (0.87 g, 1.1 mmol) and 1,4-phenylenediisocyanate (0.20 g, 1.3 mmol) 0.96 g was obtained (yield >90%); IR (Nujol mull) ν(C=O) 1716 cm⁻¹; ¹H NMR (C₆D₆, 300 MHz) δ 0.18 (s, 36 H, SiMe₃), 5.22 (4 H), 5.34 (4 H), 5.59 (4 H), 6.10 (4 H) (m, C₅H₄SiMe₃), 8.49 (s, 4 H) (phenylene ring); ¹³C-¹H} (C₆D₆, 500 MHz) δ –0.4 (SiMe₃), 104.7, 109.4, 115.7 (C_{ipso}), 119.9, 121.2 (C₅H₄SiMe₃), 123.8 (phenylene ring), 138.1 (C_{ipso} of phenylene ring) and 188.1 (RNCO) [Found (Calc. for C₄₀H₅₆Cl₂N₂Nb₂O₂Si₄): C, 49.00 (49.74); H, 5.69 (5.84); N, 3.08 (2.90)%].

$[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{OCHNPh})]$ **5**, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\mu\text{-}1,3\text{-}(\text{OCHN})_2\text{C}_6\text{H}_4\}]$ **6** and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\}_2\{\mu\text{-}1,4\text{-}(\text{OCHN})_2\text{C}_6\text{H}_4\}]$ **7**. A solution in thf of complex **2**, **3** or **4** was added over a slight excess (to the corresponding 1:2 or 1:4 molar ratio) of sodium amalgam and the mixture was stirred for 12 h at room temperature whereupon the yellow solution became an increasingly deeper brown. The solvent was removed under vacuum and the residue extracted with hexane. After filtration the solvent was removed under vacuum to give a brown solid or oil which identified as **5**, **6** or **7** respectively.

Complex **5**: from **2** (0.45 g, 0.86 mmol) and Na (0.04 g, 1.74 mmol) in Hg (0.4 cm³) 0.35 g was obtained (yield 83%); ¹H NMR (C₆D₆, 300 MHz) δ 0.06 (s, 18 H, SiMe₃), 4.40 (2 H), 4.61 (2 H), 5.15 (2 H), 6.01 (2 H) (m, C₅H₄SiMe₃), 6.40 (d, 2 H), 6.96

(t, 2 H), 6.99 (m, 1 H) (phenyl ring) and 8.21 (s, 1 H, CHO); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.3 (SiMe₃), 95.3 (C_{ipso}), 99.0, 100.6, 103.5, 109.3 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 120.2, 123.8, 128.8 (phenyl ring), 145.8 (C_{ipso} of phenyl ring) and 175.5 (RNCHO) [Found (Calc. for $\text{C}_{23}\text{H}_{32}\text{NNbOSi}_2$): C, 56.26 (56.66); H, 6.50 (6.61); N, 2.90 (2.87)%]; m/z (relative intensity) 487 [26, base peak, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{OCHNPh})$] and 122 (100%, OCHNHPH).

Complex **6**: from **3** (1.15 g, 1.19 mmol) and Na (0.11 g, 4.76 mmol) in Hg (1.1 cm³) 0.62 g of a brown oil, was obtained (yield 58%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.08 (s, 36 H, SiMe₃), 4.43 (4 H), 4.72 (4 H), 5.10 (4 H), 6.03 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 6.10 (d, 1 H), 6.82 (t, 2 H), 7.08 (m, 1 H) (phenylene ring) and 8.31 (s, 2 H, CHO); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.3 (SiMe₃), 98.7, 100.4, 102.8, 109.7, 111.1 (C_{ipso}) ($\text{C}_5\text{H}_4\text{SiMe}_3$), 115.9, 120.0, 126.9 (phenylene ring), 146.5 (C_{ipso} of phenylene ring) and 175.4 (RNCHO); m/z (relative intensity) 409 [95, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{NCO})$], 367 [44, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2$], 162 [46, (OCHNH)₂C₆H₄] and 122 (65, OCHNHPH).

Complex **7**: from **4** (0.85 g, 0.88 mmol) and Na (0.08 g, 3.52 mmol) in Hg (0.8 cm³) 0.63 g of a brown oil was obtained (yield 80%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.08 (s, 36 H, SiMe₃), 4.31 (4 H), 4.43 (4 H), 4.70 (4 H), 4.97 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 6.18 (s, 4 H) (phenylene ring) and 8.25 (s, 2 H, CHO); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.4 (SiMe₃), 86.1, 89.7, 90.2, 91.2, 93.0 (C_{ipso}) ($\text{C}_5\text{H}_4\text{SiMe}_3$), 120.0 (phenylene ring), 142.7 (C_{ipso} of phenylene ring) and 175.0 (RNCHO); m/z (relative intensity) 409 [95, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{NCO})$], 367 [44, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2$], 162 [46, (OCHNH)₂C₆H₄] and 122 (65, OCHNHPH).

[Nb(η⁵-C₅H₄SiMe₃)₂Cl]₂(μ-1,3-NC₆H₄N) **9. Method A. A solution of complex **3** (0.80 g, 0.833 mmol) in toluene was heated under reflux overnight. The initial pale yellow solution changed to dark red. After concentration to dryness, extraction with diethyl ether, concentration and cooling to -30 °C, red-orange crystals of **9** (0.49 g, 0.532 mmol) were obtained. Yield *ca.* 70%.**

Method B. A solution of complex **1** (0.67 g, 0.832 mmol) in toluene was heated with 1,3-phenylenediamine (0.101 g, 0.994 mmol) overnight. The brown solution changed to dark red. After concentration to dryness, extraction with diethyl ether, concentration and cooling to -30 °C, red-orange crystals of **9** (0.46 g, 0.499 mmol) were obtained (yield 60%). ^1H NMR (C_6D_6 , 300 MHz): δ 0.31 (s, 36 H, SiMe₃); 5.49 (4 H), 6.01 (4 H), 6.31 (4 H), 6.46 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$); 5.75 (t, 1 H), 6.04 (d, 2 H), 6.97 (m, 1 H) (phenylene ring). ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz): δ 0.4 (SiMe₃); 110.5, 111.0, 119.7 (C_{ipso}), 119.8, 127.5 ($\text{C}_5\text{H}_4\text{SiMe}_3$); 106.7, 112.0, 128.2 (phenylene ring); 159.9 (C_{ipso} of phenylene ring) [Found (Calc. for $\text{C}_{38}\text{H}_{56}\text{Cl}_2\text{N}_2\text{Nb}_2\text{Si}_4$): C, 49.90 (50.16); H, 6.21 (6.20); N, 3.15 (3.08)%].

[Nb(η⁵-C₅H₄SiMe₃)₂Cl]₂(μ-1,4-NC₆H₄N) **10. Method A. A solution of complex **4** (0.80 g, 0.833 mmol) in toluene was heated under reflux overnight. The initial pale yellow solution changed to dark red. After concentration to dryness, the red-orange microcrystalline solid was washed several times with diethyl ether and identified as **10** (0.49 g, 0.532 mmol). Yield *ca.* 70%.**

Method B. A solution of complex **1** (1.49 g, 1.202 mmol) in toluene was heated with 1,4-phenylenediamine (0.135 g, 1.242 mmol) overnight. The brown solution changed to dark red. After concentration to dryness, the red-orange microcrystalline solid was washed several times with diethyl ether and identified as **10** (0.86 g, 0.932 mmol). Yield 75%. ^1H NMR (C_6D_6 , 300 MHz): δ 0.29 (s, 36 H, SiMe₃), 5.58 (4 H), 5.99 (4 H), 6.29 (4 H), 6.36 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$) and 6.47 (s, 4 H, phenylene ring). ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz): δ 0.3 (SiMe₃), 111.0, 112.1, 119.0 (C_{ipso}), 119.8, 126.9 ($\text{C}_5\text{H}_4\text{SiMe}_3$); 118.7 (phenylene ring) and 155.7 (C_{ipso} of phenylene ring) [Found (Calc. for $\text{C}_{38}\text{H}_{56}\text{Cl}_2\text{N}_2\text{Nb}_2\text{Si}_4$): C, 50.19 (50.16); H, 6.04 (6.20); N, 3.22 (3.08)%].

[Nb(η⁵-C₅H₄SiMe₃)₂R(NPh)] (R = Me **11**, Et **12** or Prⁱ **13**), **[Nb(η⁵-C₅H₄SiMe₃)₂R]₂(μ-1,3-N₂C₆H₄)** (R = Me **14**, Et **15** or Prⁱ **16**) and **[Nb(η⁵-C₅H₄SiMe₃)₂R]₂(μ-1,4-N₂C₆H₄)** (R = Me **17**, Et **18** or Prⁱ **19**). To a red solution of complex **8**, **9** or **10** in thf (50 cm³) was added a solution of MgRCl or MgMe₂ in thf. The mixture was stirred for 12 h at room temperature whereupon it became an increasingly deeper red. The solvent was removed under vacuum and the residue extracted with hexane to eliminate the inorganic salts and excess of alkylating reagent. The extract was filtered and the filtrate concentrated under vacuum to give a reddish orange oil which was identified as the corresponding compound **11–19**.

Complex **11**: from **8** (0.58 g, 1.17 mmol) and MgMeCl (3.0 M, 0.45 cm³, 1.35 mmol) 0.38 g was obtained (yield 69%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.17 (s, 18 H, SiMe₃), 1.04 (s, 3, CH₃), 5.60 (4 H), 5.87 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 6.55 (d, 2 H), 6.70 (t, 2 H) and 7.13 (m, 1 H) (phenyl ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.2 (SiMe₃), 7.1 (CH₃), 110.3, 111.3, 113.9 (C_{ipso}), 114.2, 119.3 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 118.8, 120.2, 128.3 (phenyl ring) and 160.0 (C_{ipso} of phenyl ring).

Complex **12**: from **8** (0.56 g, 1.14 mmol) and MgEtCl (2.0 M, 0.65 cm³, 1.30 mmol) 0.33 g was obtained (yield 59%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.17 (s, 18 H, SiMe₃), 1.86 (t, 3 H, CH₂CH₃), 2.07 (q, 2 H, CH₂CH₃), 5.53 (2 H), 5.68 (2 H), 5.93 (2 H), 5.97 (2 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 6.59 (d, 2 H), 6.70 (t, 2 H) and 7.12 (m, 1 H) (phenyl ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.2 (SiMe₃), 20.8 (CH₂CH₃), 22.1 (CH₂CH₃), 109.5, 112.1, 113.7 (C_{ipso}), 114.9, 119.2 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 118.5, 120.4, 127.3 (phenyl ring) and 158.8 (C_{ipso} of phenyl ring).

Complex **13**: from **8** (0.52 g, 1.06 mmol) and MgPrⁱCl (2.0 M, 0.60 cm³, 1.20 mmol) 0.42 g was obtained (yield 79%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.15 (s, 18 H, SiMe₃), 1.84 [d, 6 H, CH(CH₃)₂], 3.17 [m, 1 H, CH(CH₃)₂], 5.47 (2 H), 5.77 (2 H), 6.05 (2 H), 6.05 (2 H), 6.09 (2 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 6.59 (d, 2 H), 6.63 (t, 2 H) and 7.10 (m, 1 H) (phenyl ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.4 (SiMe₃), 21.9 [CH(CH₃)₂], 32.1 [CH(CH₃)₂], 108.2, 113.2, 113.4 (C_{ipso}), 116.2, 119.1 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 119.4, 120.1, 128.2 (phenyl ring) and 156.0 (C_{ipso} of phenyl ring).

Complex **14**: from **9** (0.50 g, 0.54 mmol) and MgMe₂ (0.242 M, 9.05 cm³, 2.19 mmol) 0.20 g was obtained (yield 42%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.22 (s, 36 H, SiMe₃), 1.05 (s, 3 H, CH₃), 5.63 (8 H), 5.91 (8 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 5.89 (t, 1 H), 6.03 (d, 2 H) and 6.95 (m, 1 H) (phenylene ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.2 (SiMe₃), 7.1 (CH₃), 110.4, 111.4, 113.8 (C_{ipso}), 114.2, 119.3 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 108.5, 111.9, 127.4 (phenylene ring) and 159.9 (C_{ipso} of phenylene ring).

Complex **15**: from **9** (0.55 g, 0.60 mmol) and MgEtCl (2.0 M, 1.6 cm³, 3.2 mmol) 0.49 g was obtained (yield 89%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.24 (s, 36 H, SiMe₃), 1.91 (t, 3 H, CH₂CH₃), 2.10 (q, 2 H, CH₂CH₃), 5.59 (4 H), 5.76 (4 H), 5.99 (4 H), 6.03 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 5.84 (t, 1 H), 6.09 (d, 2 H) and 6.96 (m, 1 H) (phenylene ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.4 (SiMe₃), 21.8 (CH₂CH₃), 22.2 (CH₂CH₃), 109.7, 112.2, 113.5 (C_{ipso}), 115.0, 118.3 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 109.2, 112.5, 128.3 (phenylene ring) and 159.6 (C_{ipso} of phenylene ring).

Complex **16**: from **9** (0.70 g, 0.76 mmol) and MgPrⁱCl (2.0 M, 0.76 cm³, 1.53 mmol) 0.42 g was obtained (yield 59%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.22 (s, 36 H, SiMe₃), 1.85 [d, 6 H, CH(CH₃)₂], 3.15 [m, 1 H, CH(CH₃)₂], 5.55 (4 H), 5.72 (8 H), 5.98 (4 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$), 5.81 (t, 1 H), 6.06 (d, 2 H) and 6.93 (m, 1 H) (phenylene ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.4 (SiMe₃), 22.1 [CH(CH₃)₂], 31.7 [CH(CH₃)₂], 109.5, 112.1, 113.4 (C_{ipso}), 115.1, 118.2 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 108.1, 112.6, 128.3 (phenylene ring) and 159.6 (C_{ipso} of phenylene ring).

Complex **17**: from **10** (0.55 g, 0.60 mmol) and MgMeCl (3 M, 0.40 cm³, 1.20 mmol) 0.27 g was obtained (yield 51%); ^1H NMR (C_6D_6 , 300 MHz) δ 0.21 (s, 36 H, SiMe₃), 1.06 (s, 3 H, CH₃), 5.61 (8 H), 5.91 (8 H) (m, $\text{C}_5\text{H}_4\text{SiMe}_3$) and 6.46 (s, 4 H) (phenylene ring); ^{13}C - $\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 0.3 (SiMe₃), 7.1

Table 3 Crystal data and structure refinement for complexes **2** and **9***

| | 2 | 9 |
|---|--|---|
| Empirical formula | C ₂₃ H ₃₁ CINNbOSi ₂ | C ₃₈ H ₅₆ Cl ₂ N ₂ Nb ₂ Si ₄ |
| <i>M</i> | 522.03 | 909.93 |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>Cc</i> |
| <i>a</i> , <i>b</i> , <i>c</i> /Å | 10.721(7), 19.039(2), 12.587(8) | 15.252(3), 24.962(5), 14.714(3) |
| β/° | 108.62(3) | 119.72(3) |
| <i>U</i> /Å ³ | 2435(2) | 4865(2) |
| <i>D</i> _c /g cm ⁻³ | 1.424 | 1.242 |
| μ(Mo-Kα)/mm ⁻¹ | 0.717 | 0.704 |
| <i>F</i> (000) | 1080 | 1880 |
| Crystal size/mm | 0.40 × 0.22 × 0.20 | 0.37 × 0.33 × 0.23 |
| Scan mode | ω-2θ | ω-θ |
| θ Range for data collection/° | 3.02–25.07 | 3.08–24.97 |
| Index ranges | -12 < <i>h</i> < 12, 0 < <i>k</i> < 22, 0 < <i>l</i> < 14 | -15 < <i>h</i> < 18, 0 < <i>k</i> < 29, -17 < <i>l</i> < 0 |
| Reflections collected | 4667 | 4554 |
| Independent reflections (<i>R</i> _{int}) | 4269 (0.0001) | 4447 (0.001) |
| Absorption correction | ψ Scan | |
| Maximum, minimum transmission | 1.000, 0.184 | |
| Data, restraints, parameters | 4264, 0, 262 | 4447, 2, 433 |
| Goodness of fit on <i>F</i> ² | 1.029 | 0.962 |
| Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0841, 0.2384 | 0.0666, 0.1791 |
| (all data) | 0.0973, 0.2621 | 0.1742, 0.2285 |
| Weighting scheme, <i>w</i> | 1/[σ ² (<i>F</i> _o ²) + (0.2115 <i>P</i>) ² + 4.5966 <i>P</i>] | 1/[σ ² (<i>F</i> _o ²) + (0.1361 <i>P</i>) ² + 38.1828 <i>P</i>] |
| Largest difference peak, hole/e Å ⁻³ | 3.066, -2.922 | 1.520, -0.500 |

* Details in common: Mo-Kα radiation (λ 0.710 73 Å); monoclinic; *Z* = 4; *P* = (*F*_o² + 2*F*_c²)/3.

(CH₃), 110.2, 112.1, 113.1 (*C*_{ipso}), 114.4, 119.3 (*C*₅H₄SiMe₃), 119.1 (phenylene ring) and 154.5 (*C*_{ipso} of phenylene ring).

Complex **18**: from **10** (0.52 g, 0.57 mmol) and MgEtCl (2 m, 0.57 cm³, 1.14 mmol) 0.17 g was obtained (yield 33%); ¹H NMR (C₆D₆, 300 MHz) δ 0.21 (s, 36 H, SiMe₃), 1.88 (t, 3 H, CH₂-CH₃), 2.09 (q, 2 H, CH₂CH₃), 5.52 (4 H), 5.70 (8 H), 5.99 (4 H) (m, C₅H₄SiMe₃) and 6.47 (s, 4 H) (phenylene ring); ¹³C-{¹H} (C₆D₆, 500 MHz) δ 0.3 (SiMe₃), 21.8 (CH₂CH₃), 22.0 (CH₂-CH₃), 109.4, 112.8, 114.9 (*C*_{ipso}), 115.0, 118.3 (C₅H₄SiMe₃), 119.7 (phenylene ring) and 154.4 (*C*_{ipso} of phenylene ring).

Complex **19**: from **10** (0.39 g, 0.42 mmol) and MgPrCl (2 m, 0.43 cm³, 0.85 mmol) 0.24 g was obtained (yield 59%); ¹H NMR (C₆D₆, 300 MHz) δ 0.21 (s, 36 H, SiMe₃), 1.85 [d, 6 H, CH(CH₃)₂], 3.14 [m, 1 H, CH(CH₃)₂], 5.48 (4 H), 5.76 (4 H), 6.08 (4 H), 6.12 (4 H) (m, C₅H₄SiMe₃) and 6.51 (s, 4 H) (phenylene ring); ¹³C-{¹H} (C₆D₆, 500 MHz) δ 0.4 (SiMe₃), 32.1 [CH(CH₃)₂], 34.5 [CH(CH₃)₂], 107.8, 112.2 (*C*_{ipso}), 113.8, 116.0, 120.4 (C₅H₄SiMe₃), 119.3 (phenylene ring) and 154.54 (*C*_{ipso} of phenylene ring).

[Nb(η⁵-C₅H₄SiMe₃)₂H(NPh)] **20**, [{Nb(η⁵-C₅H₄SiMe₃)₂H}-(μ-1,3-N₂C₆H₄)] **21** and [{Nb(η⁵-C₅H₄SiMe₃)₂H}-(μ-1,4-N₂C₆H₄)] **22**. A solution of complex **8**, **9** or **10** in thf was added to sodium amalgam in an equimolar proportion (for **8**) or in a 1 : 2 molar ratio (for **9** and **10**) and the mixture was stirred for 12 h at room temperature whereupon the solution became an increasingly deeper red-brown. The solvent was removed under vacuum and the residue extracted with hexane. After filtration the solvent was removed under vacuum to give a brown oil which was identified as **20**, **21** or **22** respectively.

Complex **20**: from **8** (0.40 g, 0.81 mmol) and Na (0.020 g) in Hg (0.2 cm³, 0.87 mmol) 0.29 g was obtained (yield 78%); IR (Nujol mull) ν(Nb-H) 1721 cm⁻¹; ¹H NMR (C₆D₆, 300 MHz) δ 0.28 (s, 18 H, SiMe₃), 2.75 (br, 1 H, NbH, Δ*v*₃ = 30 Hz), 5.18 (2 H), 5.54 (2 H), 5.59 (2 H), 6.65 (2 H) (m, C₅H₄SiMe₃), 6.45 (d, 2 H), 6.67 (t, 2 H) and 7.11 (m, 1 H) (phenyl ring); ¹³C-{¹H} (C₆D₆, 500 MHz) δ 0.4 (SiMe₃), 103.6, 106.7, 109.7, 111.3, 111.8 (*C*_{ipso}) (C₅H₄SiMe₃), 118.1, 119.4, 127.9 (phenyl ring) and 159.9 (*C*_{ipso} of phenyl ring) [Found (Calc. for C₂₂H₃₂NNbSi₂): C, 57.35 (57.50); H, 7.00 (7.02); N, 2.98 (3.05)%].

Complex **21**: from **9** (0.50 g, 0.55 mmol) and Na (0.025 g) in Hg (0.2 cm³, 1.10 mmol) 0.33 g was obtained (yield 71%); IR (Nujol mull) ν(Nb-H) 1730 cm⁻¹; ¹H NMR (C₆D₆, 300 MHz)

δ 0.34 (s, 36 H, SiMe₃), 2.87 (br, 2 H, NbH), 5.26 (4 H), 5.63 (8 H), 5.70 (4 H) (m, C₅H₄SiMe₃), 5.20 (t, 1 H), 5.91 (d, 2 H) and 6.92 (m, 1 H) (phenylene ring); ¹³C-{¹H} (C₆D₆, 500 MHz) δ 0.5 (SiMe₃), 103.8, 106.8, 109.8, 110.9 (*C*_{ipso}), 111.2 (C₅H₄SiMe₃), 106.6, 111.6, 128.9 (phenylene ring) and 159.7 (*C*_{ipso} of phenylene ring).

Complex **22**: from **10** (0.52 g, 0.57 mmol) and Na (0.026 g) in Hg (0.2 cm³, 1.14 mmol) 0.11 g was obtained (yield 23%); IR (Nujol mull) ν(Nb-H) 1735 cm⁻¹; ¹H NMR (C₆D₆, 300 MHz) δ 0.29 (s, 36 H, SiMe₃), 2.94 (br, 2 H, NbH), 5.23 (4 H), 5.58 (4 H), 5.62 (4 H), 5.68 (4 H) (m, C₅H₄SiMe₃) and 6.36 (s, 4 H) (phenylene ring); ¹³C-{¹H} (C₆D₆, 500 MHz) δ 0.5 (SiMe₃), 103.8, 107.0, 110.0, 111.1 (*C*_{ipso}) 111.5 (C₅H₄SiMe₃), 118.8 (phenylene ring) and 154.2 (*C*_{ipso} of phenylene ring).

[Nb(η⁵-C₅H₄SiMe₃)₂X(NHPh)]⁺[BF₄]⁻ (X = Me **24**, Et **25** or Prⁱ **26**). To a solution of complex **11**, **12** or **13** in diethyl ether (50 cm³) a diethyl ether solution containing 1 equivalent of HBF₄·OEt₂ was added dropwise at 0 °C until complete precipitation of the corresponding amido cationic complexes **24–26** occurred.

Complex **24**: from **11** (0.50 g, 1.06 mmol) and HBF₄·OEt₂ (6 m, 0.19 cm³, 1.14 mmol) 0.42 g was obtained (yield 70%); ¹H NMR (CD₃CN, 300 MHz) δ 0.26 (s, 18 H, SiMe₃), 1.38 (s, 3, CH₃), 6.55 (2 H), 6.65 (2 H), 6.76 (2 H), 6.88 (2 H) (m, C₅H₄SiMe₃), 7.27 (d, 2 H), 7.42 (m, 1 H), 7.52 (t, 2 H) (phenyl ring) and 8.26 (br, 1 H, NHC₆H₅) [Found (Calc. for C₂₃H₃₅BF₄NNbSi₂): C, 49.25 (49.21); H, 6.30 (6.28); N, 2.45 (2.49)%].

Complex **25**: from **12** (0.50 g, 1.03 mmol) and HBF₄·OEt₂ (6 m, 0.18 cm³, 1.08 mmol) 0.44 g was obtained (yield 74%); ¹H NMR (CD₃CN, 300 MHz) δ 0.22 (s, 18 H, SiMe₃), 1.53 (t, 3, CH₃), 2.00 (q, 2 H, CH₂CH₃), 6.15 (2 H), 6.54 (2 H), 6.65 (2 H), 6.75 (2 H) (m, C₅H₄SiMe₃), 7.00 (d, 2 H), 7.23 (m, 1 H), 7.54 (t, 2 H) (phenyl ring) and 10.69 (br, 1 H, NHC₆H₅) [Found (Calc. for C₂₄H₃₇BF₄NNbSi₂): C, 50.00 (50.09); H, 6.34 (6.48); N, 2.40 (2.43)%].

Complex **26**: from **13** (0.50 g, 1.00 mmol) and HBF₄·OEt₂ (6 m, 0.18 cm³, 1.08 mmol) 0.40 g was obtained (yield 68%); ¹H NMR (CD₃CN, 300 MHz) δ 0.26 (s, 18 H, SiMe₃), 2.10 [d, 6 H, CH(CH₃)₂], 3.37 [m, 1 H, CH(CH₃)₂], 6.71 (2 H), 6.73 (2 H), 6.99 (2 H), 7.08 (2 H) (m, C₅H₄SiMe₃), 7.39 (d, 2 H), 7.46 (m, 1 H), 7.52 (t, 2 H) (phenyl ring) and 9.26 (br, 1 H, NHC₆H₅)

[Found (Calc. for $C_{25}H_{39}BF_4NNbSi_2$): C, 50.50 (50.94); H, 6.60 (6.67); N, 2.43 (2.38)%].

Crystallography

Data collections for complexes **2** and **9** were performed at 20 °C using an Enraf-Nonius CAD4 diffractometer. The structures were solved by direct methods (SHELXS 90)¹⁸ and refined by full-matrix least squares against F^2 (SHELXL 93).¹⁹ All the non-hydrogen atoms were refined anisotropically, hydrogen atoms were positioned geometrically and refined using a riding model. Final values of $R1 = 0.0841$ and $wR2 = 0.2384$ [for 3657 reflections with $I \geq 4\sigma(I)$] for **2** and $R1 = 0.067$ and $wR2 = 0.179$ [for 2743 reflections with $I \geq 4\sigma(I)$] for **9** were obtained. The values of $R1$ and $wR2$ are defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]$. Details are given in Table 3.

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