



# Aryl-imido niobium complexes with chloro-silyl and aryl- $\eta$ -amidosilyl cyclopentadienyl ligands: X-ray structure of the constrained-geometry compound $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-NAr})(\text{NAr})\text{Cl}]$ ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ )

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## Abstract

Reactions of the magnesium imides  $[\text{Mg}(\text{NAr})(\text{THF})_6]$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , **1a**; Ph, **1b**) with  $[\text{NbCp}^{\text{Cl}}\text{Cl}_4]$  ( $\text{Cp}^{\text{Cl}} = \eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})$ ) afforded the imido complexes  $[\text{NbCp}^{\text{Cl}}\text{Cl}_2(\text{NAr})]$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , **2a**; Ph, **2b**) in good yield. Compound **2a** reacted with excess  $\text{LiNH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$  to give the silyl- $\eta$ -amido complex  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-NAr})\text{Cl}(\text{NAr})]$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , **3a**). Hydrolysis of the Si–Cl bond of compounds **2a** and **2b** yielded the dinuclear complexes  $[\{\text{NbCl}_2(\text{NAr})\}_2\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\}_2(\mu\text{-O})]$  ( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , **4a**; Ph, **4b**), respectively. All of the new compounds reported were characterized by NMR spectroscopy and the molecular structure of **3a** was determined by X-ray diffraction methods.

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**Keywords:** Niobium; Constrained-geometry; Half-sandwich; Imido; Hydrolysis

## 1. Introduction

The presence of different functionalities on cyclopentadienyl ligands allows the reactivity of their metal complexes to be modified, inducing changes in both steric and electronic effects on the metal centres [1]. When this functionality on the ring is the  $[\text{SiMe}_2\text{Cl}]$  group, the reactivity of the Si–Cl bond facilitates access to a versatile range of products, including catalysts anchored on solid supports [2–5] and silylamido bridge formation between the cyclopentadienyl ligand and the metal centre (constrained-geometry complexes) [6–11].

Silyl- $\eta$ -amido monocyclopentadienyl groups 3 and 4 metal complexes are active catalysts for olefin polymer-

ization [12–15] and a rich chemistry has been developed [16–20] since their discovery, showing both similarities and differences compared with related dicyclopentadienyl compounds. Half-sandwich group 5 metal imido compounds [21,22] are isolobal with dicyclopentadienyl group 4 metal complexes, the chemistry of which has been widely studied [23]. However, constrained geometry group 5 metal compounds are still a field to be explored. Herrmann and Baratta [24] reported that reaction of  $\text{C}_5\text{H}_5(\text{SiMe}_2\text{NH}^t\text{Bu})$  with  $[\text{M}(\text{NMe}_2)_5]$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) gave the photolitically and thermally unstable silyl- $\eta$ -amido complexes  $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\text{NMe}_2)_3]$ , which transformed into the imido compounds  $[\text{M}(\text{C}_5\text{H}_4\text{SiMe}_2\text{NMe}_2)(\text{NMe}_2)_2(\text{N}^t\text{Bu})]$ . We have reported the isolation of stable imido silyl- $\eta$ -amido niobium complexes  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})\text{X}(\text{N}^t\text{-Bu})]$  ( $\text{X} = \text{Cl}, \text{CH}_2\text{Ph}$ ) through N–H activation of  $[\text{Nb}(\text{C}_5\text{H}_4\text{SiMe}_2\text{NH}^t\text{Bu})(\text{CH}_2\text{Ph})\text{X}(\text{N}^t\text{Bu})]$  or by reaction

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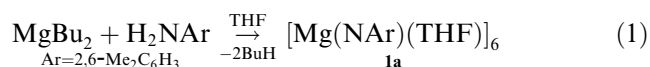
<sup>1</sup> X-ray diffraction studies.

of  $[\text{Nb}(\text{C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2(\text{N}'\text{Bu})]$  with  $\text{LiNH}'\text{Bu}$  [11]. Finally, Chen and co-workers [25] observed that the imido compound  $[\text{Ta}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2(\text{N}'\text{Bu})]$  was obtained on treating  $\text{TaCl}_5$  with the aminosilyl-cyclopentadiene  $\text{C}_5\text{Me}_4\text{H}(\text{SiMe}_2\text{NH}'\text{Bu})$ . From these results, it is clear that the thermodynamic stability of the M-imido bond is much higher than that of the bridging cyclopentadienyl-silyl- $\eta$ -amido-M system (M = group 5 metal).

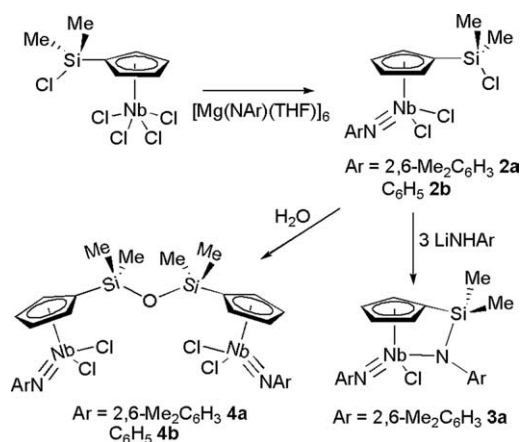
Most of these group 5 metal compounds containing the cyclopentadienyl-silyl- $\eta$ -amido ligand were isolated as oily products. It has been suggested that aryl-imido ligands provide more crystalline solids [26]. Consequently, we decided to extend our research on Si-Cl functionalized monocyclopentadienyl niobium complexes [11,27,28] to isolate new aryl-imido derivatives using the organomagnesium compounds  $[\text{Mg}(\text{NAr})(\text{THF})]_6$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **1a**; Ph, **1b**) as imido transfer reagents. This method was first published by Power and co-workers [29] to obtain titanium and zirconium imido compounds. The main advantage of the organomagnesium compounds is their lower tendency to promote reduction of the metal centre than their lithium amido analogues. The reactivity of the Si-Cl bond of these imido complexes and the first X-ray structure of a group 5 metal silyl- $\eta$ -amido complex is reported.

## 2. Results and discussion

The magnesium imide compound  $[\text{Mg}(\text{NAr})(\text{THF})]_6$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **1a**) was synthesized following the method reported [29] for the analogous phenyl derivative  $[\text{Mg}(\text{NPh})(\text{THF})]_6$  (**1b**). Hence, reaction of  $[\text{Mg}\text{Bu}_2]$  with 1 equivalent of the corresponding aniline  $\text{ArNH}_2$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in THF at -78 °C gave  $[\text{Mg}(\text{NAr})(\text{THF})]_6$  (**1a**) as a scarcely soluble white solid in high yield (Eq. (1)). Compound **1a** was identified by <sup>1</sup>H NMR, but its instability prevented suitable elemental analysis being obtained, and the hexameric structure was proposed by analogy with the phenyl derivative **1b**, for which X-ray structure had been determined [29].



These magnesium imide compounds  $[\text{Mg}(\text{NAr})(\text{THF})]_6$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **1a**; Ph, **1b**) can be used to transfer the imido ligand when reacted with the monocyclopentadienyl niobium complex  $[\text{NbCp}^{\text{Cl}}\text{Cl}_4]$  (Cp<sup>Cl</sup> = C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)) (Scheme 1). Reaction of the niobium complex with 1 equivalent of the magnesium imides gave the new imido compounds  $[\text{NbCp}^{\text{Cl}}\text{Cl}_2(\text{NAr})]$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **2a**; Ph, **2b**) as red oils after 3 h in diethylether at room temperature. Compared with the analogous reaction with the alkaline amide compound LiNHAr, this procedure prevents the formation of the corresponding amine NH<sub>2</sub>Ar as a by-product,



Scheme 1.

which is difficult to eliminate because its solubility is close to that of compounds **2**, although the same compounds can also be obtained using the lithium amide LiNHAr (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Ph). Also, this procedure seems to be a faster way to isolate the imido compounds and demonstrates the remarkable stability of the Nb-imido bond, formation of which is preferred to a bridging silyl- $\eta$ -amido system between the cyclopentadienyl ring and the niobium centre.

The presence of a silicon–chlorine bond in compounds **2** moved us to try the synthesis of the silyl- $\eta$ -amido complexes using the same magnesium imide to transfer the [NAr] moiety, but unfortunately decomposition was observed. However, reaction of **2a** with excess LiNHAr (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in diethylether afforded the desired compound  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-NAr})\text{Cl}(\text{NAr})]$  (**3a**) in moderate yield, whereas the same reaction for Ar = Ph was unsuccessful. We have observed that using more than two equivalents of the lithium amide compound is required although we have never detected the substitution of the remaining chlorine atom by another amido group, probably due to the steric hindrance of the [2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] substituent. However, the related diamido compound  $[\text{NbCp}(\text{NAr})(\text{NHAr})_2]$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was obtained through an analogous procedure [26]. This is the same method reported previously for introducing a bridging amido group between the metal atom and the silylcyclopentadienyl ligand in similar niobium complexes [11].

The dinuclear Si-O-Si bridged compounds  $\{[\text{NbCl}_2(\text{NAr})]_2\{(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2(\mu\text{-O})\}\}$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **4a**; Ph, **4b**) were obtained in low yields upon addition of a stoichiometric amount of H<sub>2</sub>O to toluene solutions of compounds **2a** and **2b**, respectively. The selective hydrolysis of the Si-Cl bond with formation of a Si-O-Si bridge was the expected behaviour for this type of niobium compound [11,27]. In contrast, it was observed [6,30–33] that the hydrolysis reactions of related monocyclopentadienyl group 4 metal complexes with

the chloro-silylcyclopentadienyl ligand afforded Si–O–M bridges. Attempts to produce further hydrolysis of Nb–Cl bonds failed and led to decomposition products with elimination of the corresponding amine.

The molecular structure of compound **3a** was determined by X-ray diffraction studies on a single crystal. Fig. 1 shows a view of the molecular structure of complex **3a** and Table 1 summarizes selected bond distances and angles. The coordination around the niobium centre is typical of half-sandwich imido complexes and could be described as a pseudo-tetrahedral structure with the centroid of the cyclopentadienyl ring, the chloro ligand, the imido nitrogen and the nitrogen of the bridging silyl- $\eta$ -amido system occupying the four coordination sites.

The most remarkable feature of this structure is the distorted geometry due to the presence of this silyl- $\eta$ -amido group bridging the cyclopentadienyl ring and the niobium atom. The Cg–Nb–N(1) (amido-silyl) bond angle (Cg = centroid of the Cp ring) of 100.76° for compound **3a** is the closest angle reported for amido ligands, which showed values in the range 106.60° and 116.67°

Table 1  
Selected bond distances (Å) and bond angles (°) of compound **3a**

Bond lengths (Å)	
N(1)–Nb	2.016(2)
N(2)–Nb	1.786(2)
N(1)–Si	1.754(2)
Nb–Cg	2.1474
Cl–Nb	2.3796(9)
Bond angles (°)	
Cg–Nb–Cl	112.85
Cg–Nb–N(1)	100.76
Cg–Nb–N(2)	130.20
N(2)–Nb–N(1)	102.3(1)
N(2)–Nb–Cl	101.05(8)
N(1)–Nb–Cl	107.83(7)
N(1)–Si–C(1)	91.9(1)
Si–N(1)–Nb	108.9(1)
C(13)–N(1)–Si	126.6(2)
C(13)–N(1)–Nb	124.7(8)
C(21)–N(2)–Nb	172.8(2)

Cg is the centroid of the cyclopentadienyl ring.

for unbridged ligands [11,21,26,34,35], and in addition is smaller than those reported for constrained silyl- $\eta$ -amido group 4 metal complexes (105–108°) [7,36]. Moreover, the Cg–Nb–N(2) (imido ligand) bond angle of 130.20° is the most open observed for half-sandwich imido complexes [11,21,26,34,35], for which the expected value is in the range 119.24–124.15°, whereas the Cg–Nb–Cl bond angle of 112.85° and the angles formed by the three N(1), N(2) and Cl substituents about the niobium atom are in the usual range found for this type of half-sandwich imido compound.

As a consequence of the constrained bridging situation, the silicon atom presents a distorted tetrahedral environment (C(1)–Si–N(1) = 91.9(1)°) and the N(1) a distorted planar environment (Si–N(1)–Nb = 108.2(1)°). Furthermore, the N(1)–Nb and N(1)–Si bond distances of 2.016(2) and 1.754(2) Å are, respectively, slightly longer than the related Nb–N(amide) and Si–N(amide) bonds found in monoamide complexes of the type [NbCp<sup>R</sup>Cl(NHR)(NR)] [26,37] and in the non-bridged aminosilyl compound [NbCp<sup>R</sup>Cl<sub>2</sub>(N<sup>t</sup>Bu)] (Cp<sup>R</sup> = C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>NH<sup>t</sup>Bu), Si–N = 1.719(9) Å) [11]. This is an indication of the lower N–Nb and N–Si  $\pi$ -bonding contribution. These data together with the co-planarity of the Nb, N(1), C(13) and Si atoms are consistent with the behaviour known for group 4 metal constrained geometry cyclopentadienylsilyl- $\eta$ -amido complexes [7,18].

Regarding the cyclopentadienyl ring, the C–C bond distances are in the range 1.401–1.432 Å, indicating a preference for  $\eta^5$ -coordination in contrast to other half-sandwich group 5 metal imido and group 4 metal constrained geometry complexes, for which significant contribution of a  $\eta^3$ -allyl- $\eta^2$ -olefin structure is proposed [7,21]. On the other hand, the Nb–C bond lengths, 2.382–2.519 Å, show two bonds clearly longer,

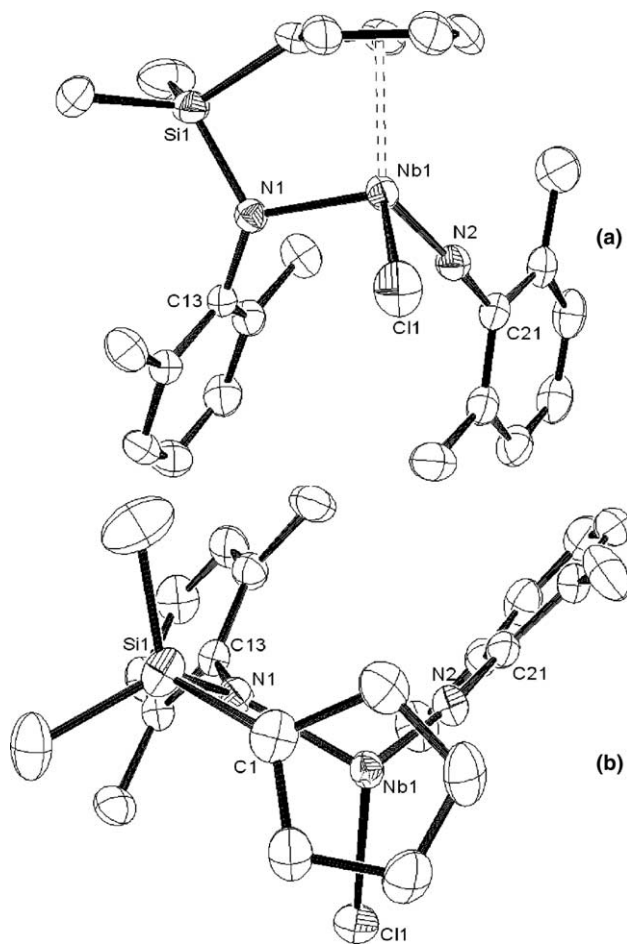


Fig. 1. Molecular structure of compound **3a**. (a) ORTEP ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) View perpendicular to the cyclopentadienyl ring plane.

Nb–C(4) and Nb–C(5), corresponding to the C–C bond opposite to the imido ligand, as typically found for imido complexes [21,35]. Also, the Nb–C(1) bond supporting the bridge is not the shortest one as found in group 4 metal constrained geometry complexes [7,38]. This could be related with the location of the C(1) atom with respect to the imido ligand.

Another notable feature found in the structure of complex **3a** is that the imido-aryl group is almost perpendicular to the Cp ring, whereas in the other 2,6-disubstituted aryl-imido half-sandwich complexes the aromatic ring is almost coplanar with the cyclopentadienyl ligand, regardless of the nature of the other ligands present [21,26,35,37,39]. Moreover, the silyl group does not occupy the *trans* position with respect to the imido ligand as in the silylcyclopentadienyl imido compounds [NbCp<sup>R</sup>Cl<sub>2</sub>(NR)] (Cp<sup>R</sup> = C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>NH<sup>t</sup>-Bu) [11], C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>) [34]). Finally, the Nb–N(2) bond distance of 1.786(2) Å and the almost linear Nb–N(2)–C(21) bond angle of 172.8 (2)° of the imido ligand correspond to a typical triple bond of a 4-electron-donor ligand [23].

### 3. Experimental

All manipulations were performed under argon atmosphere, using standard Schlenk techniques or a glovebox. Solvents used were previously dried and freshly distilled under argon: diethylether and tetrahydrofuran from sodium benzophenone, ketyl and hexane from sodium–potassium amalgam. Deuterated solvents from Scharlau were degassed and stored over molecular sieves. NMR spectra were recorded on a Varian Unity FT-300 and chemical shifts are given in ppm ( $\delta$ ). C, H and N microanalyses were performed on a Perkin–Elmer 240B microanalyzer. Unless otherwise stated, reagents were obtained from commercial sources and used as received. ArNH<sub>2</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Ph) (Aldrich) were distilled before use and stored under argon. LiNHAr was prepared in tetrahydrofuran in almost quantitative yield from ArNH<sub>2</sub> and <sup>n</sup>BuLi (Aldrich, 1.6 M in hexane) and the resulting product was washed with hexane (2 × 10 mL). [Mg(NPh)(THF)]<sub>6</sub> (**1b**) [29] and [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(SiClMe<sub>2</sub>)}Cl<sub>4</sub>] [27] were prepared according to the literature procedures.

#### 3.1. [Mg(NAr)(THF)]<sub>6</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **1a**)

Compound **1a** was isolated as a white solid following the procedure reported for [Mg(NPh)(THF)]<sub>6</sub> (**1b**) [29], from ArNH<sub>2</sub> (5.00 g, 41.25 mmol) and [MgBu<sub>2</sub>] (41.25 mmol) in THF (8.45 g, 95% yield). Data for **1a**: <sup>1</sup>H NMR: 6.71 (d, *J* = 7.6 Hz, 2H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.62 (t, *J* = 7.6 Hz, 1H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 3.55 (m, 4H, OCH<sub>2</sub>), 2.34 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 1.40 (m, 4H, CH<sub>2</sub>).

#### 3.2. [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)}Cl<sub>2</sub>(NAr)] (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **2a**)

Diethylether (50 mL) was added to a solid mixture of [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)}Cl<sub>4</sub>] (1.00 g, 2.54 mmol) and [Mg(NAr)(THF)]<sub>6</sub> (**1a**) (0.54 g, 0.42 mmol) at room temperature and the reaction mixture was stirred for 3 h. Over this time the mixture became dark red and the solvent was removed to half volume under reduced pressure. Hexane (20 mL) was added and the solution was filtered. The volatiles were completely removed to give a dark red oil which was characterized as **2a** (1.11 g, 90%). Data for **2a**: <sup>1</sup>H NMR: 6.78 (d, *J* = 7.1 Hz, 2H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.67 (t, *J* = 7.1 Hz, 1H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.25 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.81 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 2.34 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 0.53 (s, 6H, SiMe<sub>2</sub>). <sup>13</sup>C NMR: 154.1 (C<sub>i</sub>, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 135.1 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 129.8 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 126.1 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 123.1 (C<sub>5</sub>H<sub>4</sub>), 122.0 (C<sub>i</sub>, C<sub>5</sub>H<sub>4</sub>), 113.3 (C<sub>5</sub>H<sub>4</sub>), 19.3 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 2.3 (SiMe<sub>2</sub>). Anal. Calc. for C<sub>15</sub>H<sub>19</sub>Cl<sub>3</sub>NNbSi: C, 40.88; H, 4.35; N, 3.18. Found: C, 41.09; H, 4.45; N, 3.12%.

#### 3.3. [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)}Cl<sub>2</sub>(NAr)] (Ar = C<sub>6</sub>H<sub>5</sub>, **2b**)

Compound **2b** was prepared from [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(SiMe<sub>2</sub>Cl)}Cl<sub>4</sub>] (1.00 g, 2.54 mmol) and [Mg(NAr)(THF)]<sub>6</sub> (**1b**) (0.47 g, 0.42 mmol) following the method given for **2a** and was obtained as a red oil (0.94 g, 90% yield). Data for **2a**: <sup>1</sup>H NMR: 7.02–6.80 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 6.28 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.86 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 0.49 (s, 6H, SiMe<sub>2</sub>). <sup>13</sup>C NMR: 156.0 (C<sub>i</sub>, C<sub>6</sub>H<sub>5</sub>), 129.6 (C<sub>6</sub>H<sub>5</sub>), 128.7 (C<sub>6</sub>H<sub>5</sub>), 126.5 (C<sub>6</sub>H<sub>5</sub>), 124.5 (C<sub>5</sub>H<sub>4</sub>), 122.2 (C<sub>i</sub>, C<sub>5</sub>H<sub>4</sub>), 114.4 (C<sub>5</sub>H<sub>4</sub>), 2.5 (SiMe<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>15</sub>Cl<sub>3</sub>NNbSi: C, 37.84; H, 3.66; N, 3.39. Found: C, 37.12; H, 3.49; N, 3.46%.

#### 3.4. [Nb{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>- $\eta^1$ -NAr}Cl(NAr)] (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **3a**)

A solution of **2a** (1.06 g, 2.40 mmol) in diethylether (30 mL) was treated dropwise with a solution of LiNHAr (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (0.91 g, 7.21 mmol) in diethylether (30 mL) and the mixture was stirred for 16 h at room temperature. After addition of hexane (30 mL), the solution was filtered and the solvents were removed under vacuum to ca. 30 mL. The remaining solution was cooled to –38 °C to give complex **3a** as a yellow crystalline solid (0.70 g, 60% yield). Data for **3a**: <sup>1</sup>H NMR: 6.96–6.69 (m, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.46 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 6.33 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 6.23 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 2.23 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 2.12 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 1.94 (s, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 0.28 (s, 3H, SiMe<sub>2</sub>), 0.07 (s, 3H, SiMe<sub>2</sub>). <sup>13</sup>C NMR: 132.1, 130.1, 124.3, 121.1, 118.2, 112.3, 112.0 and 109.5 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and C<sub>5</sub>H<sub>4</sub>, C<sub>ipso</sub> not observed), 19.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 19.3 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 17.5



( $\text{Me}_2\text{C}_6\text{H}_3$ ), 0.2 ( $\text{SiMe}_2$ ),  $-1.3$  ( $\text{SiMe}_2$ ). *Anal. Calc.* for  $\text{C}_{23}\text{H}_{28}\text{ClN}_2\text{NbSi}$ : C, 56.50; H, 5.77; N, 5.73. Found: C, 55.90; H, 5.43; N, 5.59%.

3.5. [ $\{\text{NbCl}_2(\text{NAr})\}_2\{(\eta^5\text{-C}_5\text{H}_4)_2(\text{Me}_2\text{SiOSiMe}_2)\}$ ]  
( $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , **4a**)

Distilled water (0.02 mL, 1.20 mmol) was added to a mixture of **2a** (1.06 g, 2.40 mmol) and  $\text{NEt}_3$  (0.33 mL, 2.40 mmol) in toluene (60 mL). After stirring for 24 h at room temperature, the solution was filtered and the volatiles removed under vacuum to give **4a** as a brown solid (0.40 g, 40% yield). Data for **4a**:  $^1\text{H NMR}$ : 6.78 (m, 4H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 6.73 (m, 2H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 6.35 (m, 4H,  $\text{C}_5\text{H}_4$ ), 5.91 (m, 4H,  $\text{C}_5\text{H}_4$ ), 2.39 (s, 12H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 0.37 (s, 12H,  $\text{SiMe}_2$ ). *Anal. Calc.* for  $\text{C}_{30}\text{H}_{38}\text{Cl}_4\text{N}_2\text{Nb}_2\text{O-Si}_2$ : C, 43.60; H, 4.63; N, 3.39. Found: C, 42.91; H, 4.29; N, 3.05%.

3.6. [ $\{\text{NbCl}_2(\text{NAr})\}_2\{(\eta^5\text{-C}_5\text{H}_4)_2(\text{Me}_2\text{SiOSiMe}_2)\}$ ]  
( $\text{Ar} = \text{C}_6\text{H}_5$ , **4b**)

This compound was prepared as above from **2b** (1.00 g, 2.42 mmol),  $\text{NEt}_3$  (0.34 mL, 2.42 mmol) and distilled water (0.02 mL, 1.21 mmol) to yield **4b** (0.37 g, 40%). Data for **4b**:  $^1\text{H NMR}$ : 6.92–6.70 (m, 10H,  $\text{C}_6\text{H}_5$ ), 6.40 (m, 4H,  $\text{C}_5\text{H}_4$ ), 5.96 (m, 4H,  $\text{C}_5\text{H}_4$ ), 0.33 (s, 12H,  $\text{SiMe}_2$ ). *Anal. Calc.* for  $\text{C}_{26}\text{H}_{30}\text{Cl}_4\text{N}_2\text{Nb}_2\text{OSi}_2$ : C, 40.54; H, 3.93; N, 3.64. Found: C, 39.88; H, 3.81; N, 3.47%.

3.7. X-ray crystallographic study of **3a**

Suitable single crystals for the X-ray diffraction study were grown by standard techniques from a saturated solution of **3a** ( $\text{C}_{23}\text{H}_{28}\text{ClN}_2\text{NbSi}$ ) in diethylether. A light yellow crystal,  $0.31 \times 0.30 \times 0.16$  mm, monoclinic, space group  $P2_1/n$  was used. Data collection were performed at 200 K on a Kappa-CCD area detecting diffraction system using a Mo  $\text{K}\alpha$  radiation. The unit cell dimensions were determined from 110 reflections between  $\theta = 3.102^\circ$  and  $21.448^\circ$ . Unit cell parameters were  $a = 8.3381(5)$  Å,  $b = 21.597(2)$  Å,  $c = 12.751(1)$  Å,  $\beta = 92.549(7)^\circ$ ,  $V = 2294.0(3)$  Å<sup>3</sup>,  $Z = 4$ . X-ray data were collected within the  $\theta$ -range of  $3.01^\circ < \theta < 27.51^\circ$  to a completeness of 0.998. An empirical absorption correction was applied, and symmetry equivalent and multiple measured reflections were averaged with the program SORTAV [40]. A total of 19118 reflections were collected and merged ( $R_{\text{int}} = 0.0688$ ) to give 5271 unique reflections of which 3884 were observed with  $I > 2\sigma(I)$ . The crystal structure was solved by direct methods and refined using full-matrix least squares on  $F^2$  [41]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. The final cycle of full-matrix

least-squares refinement based on 5271 reflections and 253 parameters converged to final values of  $R_1(F^2 > 2\sigma(F^2)) = 0.0388$ ,  $wR_2(F^2 > 2\sigma(F^2)) = 0.0927$ ,  $R_1(F^2) = 0.0668$ ,  $wR_2(F^2) = 0.1014$  and goodness-of-fit = 1.011. Final difference Fourier maps showed no peaks higher than 0.513 nor deeper than  $-0.453$  e Å<sup>-3</sup>. Geometrical calculations were made with PLATON [42]. The crystallographic plots were made with ORTEP-3. All calculations were made at the University of Alcalá.

#### 4. Supplementary material

Crystallographic data for the structural analysis for **3a** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 259073. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 366 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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