

# Synthesis and reactivity of imido niobium complexes containing the functionalized (dichloromethylsilyl)cyclopentadienyl ligand

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Dedicated to Prof. Michael Lappert for his outstanding contribution to chemistry.

## Abstract

The niobium complex  $[\text{NbCp}^{\text{Cl}}\text{Cl}_4]$  ( $\text{Cp}^{\text{Cl}} = \eta^5\text{-C}_5\text{H}_4(\text{SiCl}_2\text{Me})$ ) (**1**) with a functionalized (dichloromethylsilyl)cyclopentadienyl ligand was isolated by the reaction of  $[\text{NbCl}_5]$  with  $\text{C}_5\text{H}_4(\text{SiCl}_2\text{Me})(\text{SiMe}_3)$ . Complex **1** was a precursor for the imido silylamido derivative  $[\text{NbCp}^{\text{N}}\text{Cl}_2(\text{N}t\text{Bu})]$  ( $\text{Cp}^{\text{N}} = \eta^5\text{-C}_5\text{H}_4[\text{SiClMe}(\text{NH}t\text{Bu})]$ ) (**2**) after addition of  $\text{LiNH}t\text{Bu}$ , which subsequently gave the dichlorosilyl compound  $[\text{NbCp}^{\text{Cl}}\text{Cl}_2(\text{N}t\text{Bu})]$  (**3**) when reacted with  $\text{SiCl}_3\text{Me}$ . Addition of  $\text{LiNH}t\text{Bu}$  to complex **2** gave the niobium amido complex  $[\text{NbCp}^{\text{N}}\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$  (**4**), which slowly evolved with exchange of the niobium-amido and the silicon-chloro groups to give the dichloroniobium complex  $[\text{NbCp}^{\text{NN}}\text{Cl}_2(\text{N}t\text{Bu})]$  ( $\text{Cp}^{\text{NN}} = \eta^5\text{-C}_5\text{H}_4[\text{SiMe}(\text{NH}t\text{Bu})_2]$ ) (**5**). Reaction of **2** with excess  $\text{LiNH}t\text{Bu}$  gave the silyl- $\eta$ -amido constrained geometry complexes  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4[\text{SiMe}(\text{NH}t\text{Bu})(-\eta\text{-N}t\text{Bu})]\}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$  (**6**) and  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4[\text{SiClMe}(-\eta\text{-N}t\text{Bu})]\}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$  (**7**), whereas addition of one equimolecular amount of  $\text{LiNH}t\text{Bu}$  to **5** in  $\text{C}_6\text{D}_6$  afforded complex  $[\text{NbCp}^{\text{NN}}\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$  (**8**). All of the new complexes were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy.

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## 1. Introduction

The presence of different functionalities attached to the cyclopentadienyl ligands determines both the steric and electronic properties of the metal centres and modifies the reactivity of their complexes [1]. A particularly useful functionality is that containing a chlorosilyl group because the reactivity of the Si–Cl bond facilitates the formation of the silyl- $\eta$ -amido bridge between the cyclopentadienyl ligand and the metal centre [2–8]. These types of silyl- $\eta$ -amido monocyclopentadienyl group 3 and 4 metal complexes are active catalysts for olefin polymerization (constrained-geometry catalysts) [9–12] and a rich chemistry has been developed [13–17] since their discovery, showing both sim-

ilarities and differences when compared with related dicyclopentadienyl compounds.

We focused our research interest on studies related to cyclopentadienyl group 4–6 metal complexes supporting modified cyclopentadienyl rings [2–8,18–24], and reported the synthesis of silyl- $\eta$ -amido cyclopentadienyl group 4 and 5 metal complexes using the related (chlorodimethylsilyl)cyclopentadienyl metal derivatives [2–8,24]. Hydrolysis of these compounds also led to the isolation of dinuclear derivatives with Si–O–Si bridges for Nb [8,21,25], Mo and W [24] and Si–O–M bridges for Nb [25] and group 4 metals [2,26,27].

The next step in our research was the introduction of a second Si–Cl bond using the (dichloromethylsilyl)cyclopentadienyl ligand or alternatively a second chlorodimethylsilyl group attached to the same cyclopentadienyl ring. These two types of compounds offered the opportunity to introduce a chelating cyclopentadienyl silyl- $\eta$ -amido ligand

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whilst still leaving a second reactive point at the cyclopentadienyl ligand. The first type of complex can be illustrated by the reported constrained geometry group 4 metal complexes with one additional Si–X bond (X = H, Cl, NH*t*Bu) [28–30], which were suitable to explore further reactivity of these bonds. Furthermore, hydrolysis of the Si–Cl bond of the starting  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4(\text{SiCl}_2\text{Me})\}\text{Cl}_3]$  (R = H, Me) complexes gave dinuclear compounds with Si–O–Ti [28] bridges and one additional Si–O–Si bridge (for R = Me) [31]. The second type of compound comprised the bis(silyl- $\eta$ -amido)cyclopentadienyl group 4 metal complexes, which were synthesized [14] and studied as a new type of olefin polymerization catalysts. The bis(chlorosilyl)cyclopentadienyl ligand also allowed the synthesis of a dinuclear complex with carbonate ligands bridging the silicon and titanium atoms when hydrolysis of  $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)_2\}\text{Cl}_3]$  was carried out in the presence of  $\text{CO}_2$  [32].

Continuing our studies on the chemistry of metal compounds with modified monocyclopentadienyl ligands, we report here the synthesis of the (dichloromethylsilyl)cyclopentadienyl niobium derivative  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4(\text{SiCl}_2\text{Me})\}\text{Cl}_4]$  and its reactions with lithium amides to give imidodichloro- and imidochloroamido-niobium complexes with aminosilylcyclopentadienyl ligands  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4[\text{SiMeX}(\text{NH}t\text{Bu})]\}\text{(N}t\text{Bu)ClX}]$  (X = Cl, NH*t*Bu) and imido(cyclopentadienylsilyl- $\eta$ -amido)niobium compounds  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4[\text{SiMeX}(\eta\text{-N}t\text{Bu})]\}\text{(NH}t\text{Bu)(N}t\text{Bu)}]$  (X = Cl, NH*t*Bu). The comparative reactivity of these compounds is also reported.

## 2. Results and discussion

The use of (trimethylsilyl)silylcyclopentadienyl derivatives  $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{X}$  has been demonstrated to be a successful method to synthesize niobium complexes with functionalized cyclopentadienyl ligands [1]. Following this method, the (dichloromethylsilyl)monocyclopentadienyl niobium compound  $[\text{NbCp}^{\text{Cl}}\text{Cl}_4]$  ( $\text{Cp}^{\text{Cl}} = \eta^5\text{-C}_5\text{H}_4(\text{SiCl}_2\text{Me})$ ) (**1**) was isolated as a dark red solid by the reaction of  $[\text{NbCl}_5]$  with  $\text{C}_5\text{H}_4(\text{SiCl}_2\text{Me})(\text{SiMe}_3)$  in dichloromethane (Scheme 1). The  $^1\text{H}$  NMR spectrum of **1** showed the typical AA'BB' pattern for the  $\text{C}_5\text{H}_4$  group in complexes with  $C_s$  symmetry and one resonance at  $\delta$  1.26 for the  $\text{SiMeCl}_2$  group, shifted to a lower field compared with related compounds supporting  $\text{SiClMe}_2$  ( $\delta$  0.90) [21] and  $\text{SiMe}_3$  ( $\delta$  0.41) [33] groups, consistent with the increasing number of electron withdrawing groups attached to the silicon atom.

The presence of two types of chlorine atoms, bound to niobium and silicon atoms in compound **1**, moved us to study their reactivity toward amido and imido transfer reagents. The (silylamido)cyclopentadienyl imido compound  $[\text{NbCp}^{\text{N}}\text{Cl}_2(\text{N}t\text{Bu})]$  ( $\text{Cp}^{\text{N}} = \eta^5\text{-C}_5\text{H}_4[\text{SiClMe}(\text{NH}t\text{Bu})]$ ) (**2**) was obtained by the reaction of **1** with *t*BuNH<sub>2</sub>, LiNH*t*Bu and *t*Bu(SiMe<sub>3</sub>)NH as a yellowish solid. Whatever the conditions, the formation of the puta-

tive derivative  $[\text{NbCp}^{\text{Cl}}\text{Cl}_2(\text{N}t\text{Bu})]$  was never observed. This result is clearly influenced by the presence of two chloro ligands at the silicon atom, since the related dimethylmonochlorosilyl derivative  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4(\text{SiClMe}_2)\}\text{Cl}_4]$  initially gave the imido complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4(\text{SiClMe}_2)\}\text{Cl}_2(\text{N}t\text{Bu})]$  [21], containing the unaltered silyl substituent. However, **2** could be transformed into  $[\text{NbCp}^{\text{Cl}}\text{Cl}_2(\text{N}t\text{Bu})]$  (**3**) by the addition of  $\text{SiCl}_3\text{Me}$ , through the chloro-amido exchange reaction. The  $^1\text{H}$  NMR spectrum of compound **2** showed the ABCD pattern for the  $\text{C}_5\text{H}_4$  group expected for the presence of a chiral silicon atom, whereas for compound **3** the AA'BB' pattern observed for **1** was recovered. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** showed signals corresponding to the presence of two different *t*Bu groups, whereas the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** only showed signals for one *t*Bu group. The  $^{29}\text{Si}$  NMR spectra were the most useful spectroscopic means to distinguish a silicon–amido bond from a niobium–amido bond in complex **2**, the resonance observed at  $\delta$  –9.8 was clearly shifted highfield compared to the values found for compounds **1** and **3**,  $\delta$  12.0 and  $\delta$  13.4, respectively, supporting the presence of two chloro ligands at the silicon atom.

Compound **2** reacted with one additional equivalent of LiNH*t*Bu to give the chloro amido niobium complex  $[\text{NbCp}^{\text{N}}\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$  (**4**) isolated as a mixture of diastereoisomers, due to the presence of two stereogenic centres, at silicon and niobium atoms, demonstrating the substitution of one chloro ligand at the metal centre. The diastereoisomers were in a 1:0.5 molar ratio and were identified by the two ABCD sets of signals observed in the  $^1\text{H}$  NMR spectrum for each  $\text{C}_5\text{H}_4$  group and one resonance for each isomer in the  $^{29}\text{Si}$  NMR spectrum at around  $\delta$  –8, very close to that observed for the starting complex **2**. The presence of a niobium–amido group was also confirmed by the lowfield shifted resonance above  $\delta$  8 for the Nb–NH*t*Bu proton compared with the signal shifted highfield ( $\delta$  1–3) observed for the related aminosilyl Si–NH*t*Bu group.

Complex **4** is the kinetic product of the reaction, since heating a  $\text{C}_6\text{D}_6$  solution of **4** or leaving the oily mixture of diastereoisomers of **4** at room temperature for several days gave the bisamidossilyl complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4[\text{SiMe}(\text{NH}t\text{Bu})_2]\}\text{Cl}_2(\text{N}t\text{Bu})]$  (**5**), isolated as a brownish oil. A similar behaviour was observed in the reaction of the related imido niobium complex  $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4(\text{SiClMe}_2)\}\text{Cl}_2(\text{N}t\text{Bu})]$  with LiNH*t*Bu [7], which proved to be an intermolecular process. In this case, the  $^1\text{H}$  NMR spectrum of **5** again showed an AA'BB' pattern, after recovering the  $C_s$  symmetry; meanwhile, the  $^{29}\text{Si}$  NMR spectrum showed a resonance shifted highfield ( $\delta$  –29.0), due to the presence of two  $\pi$  donor amido ligands bound to the silicon atom [29,30]. Furthermore, the resonances at low field of the H–N niobium–amido groups disappeared, although the new resonances for the silicon–amido ligands could not be observed.

Following the same method based on using the imido chlorosilyl- and (amidossilyl)-monocyclopentadienyl

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