

Synthesis and reactivity of new mono- and dinuclear niobium and tantalum imido complexes: X-ray crystal structure of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$

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Abstract

The reaction of $[1,4\text{-}\{\text{SiMe}_3(\text{H})\text{N}\}_2\text{C}_6\text{Me}_4]$ (**1**) with 2 equivalents of LiBu^n followed by the addition of SiMe_3Cl gave the diamine compound $[1,4\text{-}\{\text{SiMe}_3\text{N}\}_2\text{C}_6\text{Me}_4]$ (**2**). $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ reacts with **2**, in a 2:1 stoichiometric ratio, to initially yield a mixture of the dinuclear, $[\{\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{Me}_4\text{N})]$ (**3**), and mononuclear, $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ (**4**), imido complexes. **3** can be obtained exclusively by submitting the reaction mixture to repeated cycles of evacuation, to remove volatiles, followed by addition of solvent and subsequent heating. The mononuclear imido complex **4** was isolated from the reaction of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ with **2** in a 1:1 stoichiometric ratio. The molecular structure of **4** was determined by X-ray diffraction studies. $[\text{TaCl}_3(\text{CH}_3\text{CN})_2\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ (**5**) has been prepared by the reaction of one molar equivalent of TaCl_5 with **2** in a $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ solvent mixture. The synthesis of the niobium complexes, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{Me}_4\text{N})]$ (**6**) and $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ (**7**), was achieved in a similar manner to their tantalum analogues. The reactivity of **7** towards nucleophilic reagents, namely lithium benzamidinate, lithium (trimethylsilyl)cyclopentadienyl or lithium dimethylamide, has been studied and the following compounds prepared: $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{RCl}\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ ($\text{R} = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ (**8**), $\text{PhC}(\text{NSiMe}_3)_2$ (**9**), NMe_2 (**10**)). In an attempt to form the hetero bimetallic complex, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{Me}_4\text{N})\{\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}]$ (**11**), the reaction of **7** with $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ has been studied. Analysis of the reaction products showed that **11** may exist in equilibrium with the homo bimetallic complexes **3** and **6**.

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Keywords: Imido; Niobium; Tantalum

1. Introduction

In recent years, there has been a great interest in the synthesis of homo- and hetero-dinuclear complexes in which two transition metals are united by a π -conjugated organic ligand [1] due to the potential applications in the design of

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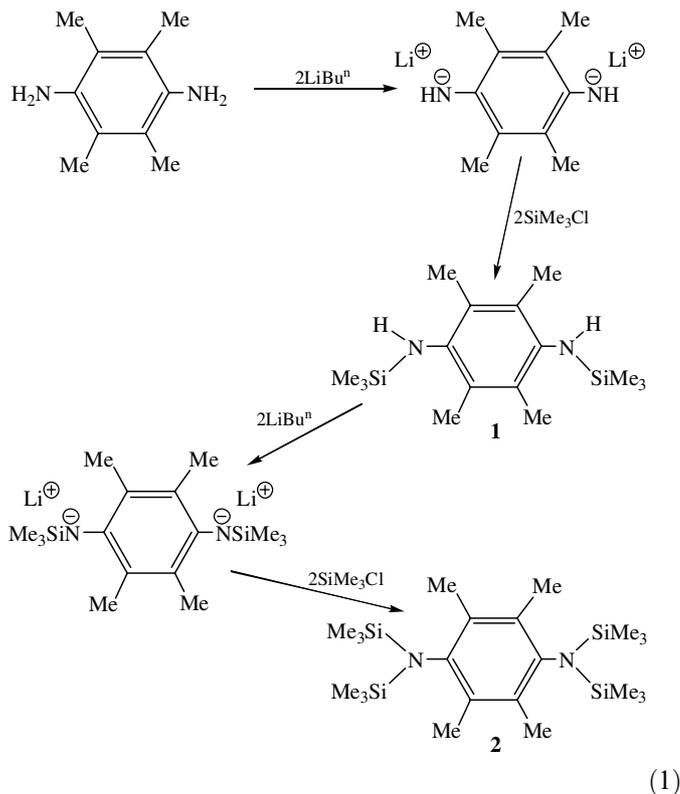
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low-dimensional, polymeric materials with novel electrical and/or magnetic properties [2].

The presence of imido groups in the organometallic chemistry of niobium and tantalum is well documented [3] and our contribution to this field has recently been published [4]. Part of our research work has been dedicated to the use of metal centre bridging di-imido ligands [5] and as a continuation of this, we now report the synthesis, structural characterization and reactivity of mono- and dinuclear niobium and tantalum imido complexes.

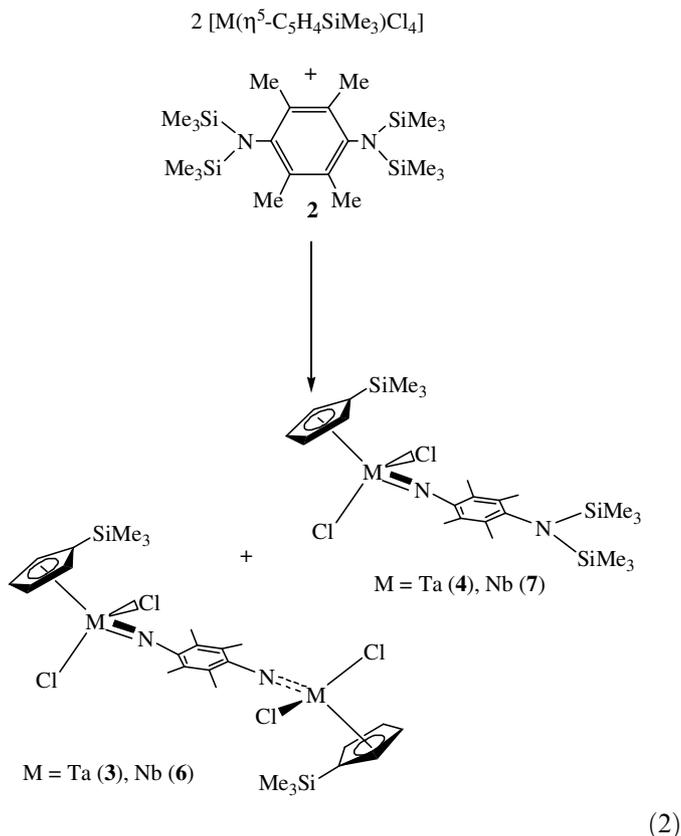
2. Results and discussion

The preparation of *N,N,N',N'*-tetrakis(trimethylsilyl)-2,3,5,6,-tetramethyl-1,4-phenylenediamine (**2**) was achieved adapting the method previously described for similar ligands [6]. The reaction of 2,3,5,6,-tetramethyl-1,4-phenylenediamine with 2 molar equivalents of LiBu^n in THF and the subsequent addition of SiMe_3Cl gave *N,N'*-bis(trimethylsilyl)-2,3,5,6,-tetramethyl-1,4-phenylenediamine (**1**). Repeating this procedure with **1** yielded the desired compound **2** (Eq. (1)).



The reaction, in CH_2Cl_2 , of **2** with 2 molar equivalents of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ (Eq. (2)) initially afforded a mixture of the dinuclear, $[\{\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{Me}_4\text{N})]$ (**3**), and mononuclear, $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-}4\text{-(N(SiMe}_3)_2)\}]$ (**4**), imido complexes along with **2**. In order to favour the production of **3**, the volatile SiMe_3Cl was removed from the medium by placing the reaction mixture under reduced pressure. Solvent was then

readded and the reaction mixture heated. On repeating this process two more times, **3** could be obtained in yields of ca. 60%.



3 was characterized by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **3** exhibit the characteristic signals for both the cyclopentadienyl and phenylene groups. The symmetry of the molecule leads to the equivalency of the four methyl groups of the phenylene moiety (one signal in the ^1H and ^{13}C NMR spectra). Two multiplets were observed in the ^1H NMR spectra corresponding to the cyclopentadienyl protons.

The synthesis of the mononuclear complex **4** was achieved in a 54% yield by the reaction of a 1:1 molar ratio of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ with **2**. The ^1H NMR spectra of **4** gave two singlets for the methyl protons of the phenylene moiety. Two multiplets were observed for the cyclopentadienyl ring protons. Suitable crystals for X-ray diffraction studies were obtained on cooling ($-20\text{ }^\circ\text{C}$) a concentrated solution of **4** in hexane. The molecular structure of **4** and atomic numbering scheme are shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

In the molecular structure of **4** the tantalum atom is bound to the cyclopentadienyl ring in a formally η^5 mode, to two chlorine atoms and to the nitrogen of the imido group in a three-legged piano-stool conformation about the metal centre. The tantalum atom is out of the plane defined by N(1), C(10), C(11) and C(6) by 0.274(8) Å.

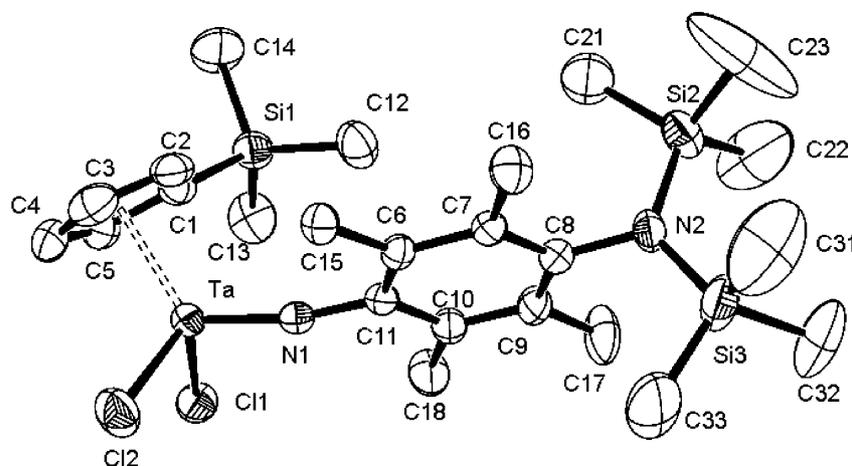


Fig. 1. Molecular structure and atom-labelling scheme for $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ (**4**), with thermal ellipsoids at 30% probability.

Table 1
Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths (Å)	
Ta(1)–N(1)	1.777(4)
Ta(1)–Cl(1)	2.329(2)
Ta(1)–Cl(2)	2.334(2)
Ta(1)–Ct(1)	2.114
Ta(1)–C(1)	2.386(5)
Ta(1)–C(2)	2.367(5)
Ta(1)–C(3)	2.415(7)
Ta(1)–C(4)	2.504(6)
Ta(1)–C(5)	2.472(1)
N(1)–C(11)	1.396(6)
N(2)–C(8)	1.452(6)
N(2)–Si(2)	1.743(5)
N(2)–Si(3)	1.741(5)
Bond angles (°)	
N(1)–Ta(1)–Cl(1)	102.9(1)
N(1)–Ta(1)–Cl(2)	101.9(1)
Cl(1)–Ta(1)–Cl(2)	103.16(7)
Ct(1)–Ta(1)–Cl(1)	113.5
Ct(1)–Ta(1)–Cl(2)	112.0
Ct(1)–Ta(1)–N(1)	121.3
Ta(1)–N(1)–C(11)	169.3(3)
C(8)–N(2)–Si(3)	117.5(3)
C(8)–N(2)–Si(2)	116.5(3)
Si(2)–N(2)–Si(3)	125.9(3)

Ct(1) is the centroid of C(1)–C(5).

The tantalum–nitrogen distance, 1.777(4) Å, lies within the range expected for a triple bond [7] although, the N(1)–C(11) bond distance of 1.397 Å (compare with N(2)–C(8) 1.452 Å) indicates a degree of conjugation with the phenyl π -system. The Ta(1)–N(1)–C(11) angle of 169.3(3)° deviates slightly from linear. Such deviations from linear are normally in the range 10–15° (see Table 2). In the case of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{=NPh})]$ extended-Hückel molecular-orbital calculations established that the imido bond angles for “linear imide” in this class of com-

Table 2
Selected structural data of some group 5 metal imido complexes

	M–N (Å)	M–N–C (°)	Ref.
$[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})_2\}_2\text{-}(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$	1.79(1), 1.75(1)	159(1), 168(1)	[5e]
$[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2\text{-}(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$	1.776(8)	160.9(7)	[5d]
$[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$	1.783(5)	166.4(5)	[5d]
$[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)_2\}_2\text{-}(\mu\text{-1,4-NC}_6\text{H}_4\text{N})]$	1.794(5)	167.4(5)	[5d]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{NHBu}^t)\text{Cl}(\text{=NAr})]^a$	1.793	168.5	[7c]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{=NAr})]^a$	1.761	165.6	[7a]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{=NAr})]^b$	1.763	166.6	[7d]
$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-NHBu}^t)\text{-}(\text{CH}_2\text{Bu}^t)\text{H}(\text{=NAr})]^a$	1.787	174.6	[7e]
$[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2(\text{=NAr})]^a$	1.780	171.3	[7a]
$[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2(\text{=NAr})]^b$	1.774	169.9	[7b]
$[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\{\text{Si}(\text{SiMe}_3)_3\}\text{-}(\text{H}(\text{=NAr}))]^a$	1.812	171.4	[7f]
$[\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)\text{-}(\text{SiMe}_2\text{Cl})\text{H}(\text{=NAr})]^a$	1.821	171.8	[7g]
$[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\text{-}\{\text{=NC}_6\text{Me}_4\text{-4-(N(SiMe}_3)_2)\}]$ (4)	1.777(4)	169.3(3)	This work

^a Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$.

^b Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$.

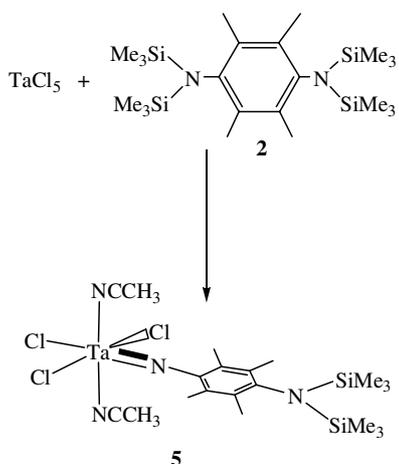
plex can vary up to 140° with little effect on the metal–nitrogen bonding [8]. Therefore, we propose that in **4** that the nitrogen atom is sp hybridized.

The cyclohexadienyl group is in a typical [7a] eclipsed fashion with respect to the imido group. There is slight lengthening of the distances Ta(1)–C(4), 2.504(6) Å, and Ta(1)–C(5), 2.472(1) Å, with respect to other Ta–C ring distances. The $\eta^5\text{-}\eta^3$ slippage of the cyclohexadienyl ring is most probably due to the electron repulsions between the Ta–N triple bond and the C(2)–H bond. The N(1), Ta(1), and C(2) atoms and the C₅ centroid are roughly co-planar.

The reaction of the **2** with 2 molar equivalents of TaCl_5 in a solvent mixture of $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ has been studied.

A mixture of products was obtained, consisting of $[\text{TaCl}_5(\text{CH}_3\text{CN})]$, the mononuclear imido complex $[\text{TaCl}_3(\text{CH}_3\text{CN})_2\{\text{=NC}_6\text{Me}_4\text{-4-(N}(\text{SiMe}_3)_2)\}]$ (**5**) as the major product and another compound tentatively assigned to the corresponding diimido derivative. Unfortunately, we were unable to isolate or characterize this possible dinuclear complex.

Complex **5** can, however, be directly prepared by the reaction of two molar equivalents of **2** with one molar equivalent of TaCl_5 (Eq. (3)). After successive recrystallizations from CH_2Cl_2 , **5** was obtained in a yield of 30%.

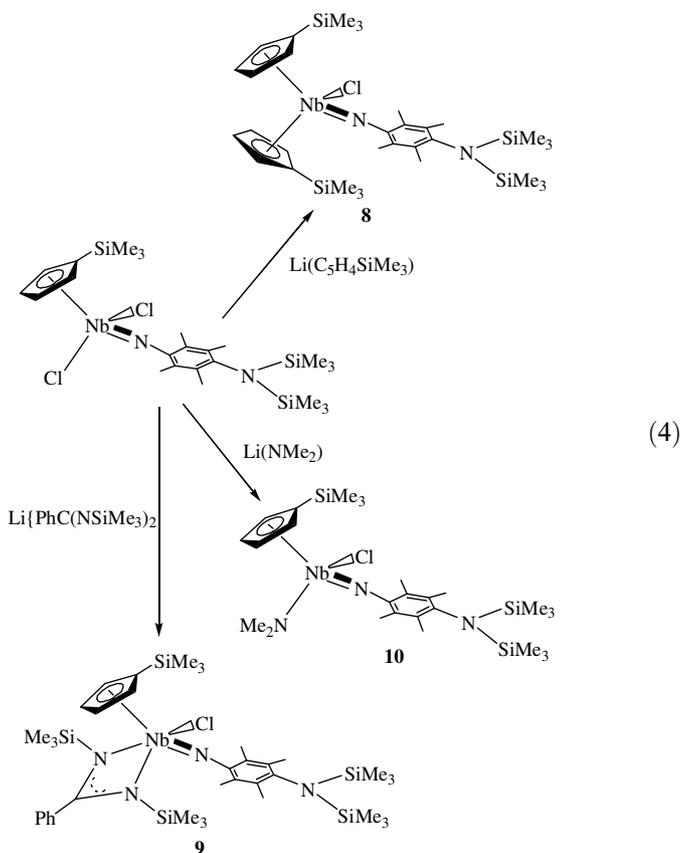


The ^1H NMR spectrum of **5** showed a singlet for the trimethylsilyl moieties, two singlets for the methyl groups of the phenylene fragment and a broad signal corresponding to the protons of the acetonitrile ligand.

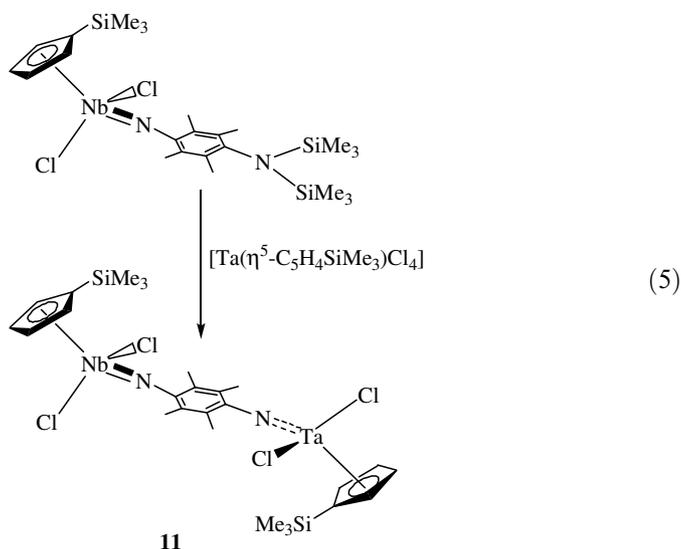
The preparation of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\{\text{=NC}_6\text{Me}_4\text{-4-(N}(\text{SiMe}_3)_2)\}]$ (**7**) was achieved by the reaction of **2** with $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ in a 1:1 stoichiometric ratio. However, in order to obtain a reasonable yield the reaction mixture was submitted to three repeated cycles of volatile removal by reduced pressure followed by addition of solvent and subsequent heating. Finally, **7** was isolated by recrystallization from hexane although in lower yields (45%) than those obtained, employing a simpler reaction work up, for its tantalum analogue **4** (54%).

The preparation of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-1,4-NC}_6\text{Me}_4\text{N})]$ (**6**) (Eq. (2)) required 17 repeated cycles of volatile removal, solvent addition and heating in order to obtain a reasonable yield. The final product was washed with hexane and recrystallized from CH_2Cl_2 .

The reactivity of **7** towards nucleophilic reagents has been studied. The metathesis reaction of **7** with lithium benzamidinate, lithium (trimethylsilyl)cyclopentadienyl or lithium dimethylamide gave the following compounds: $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{RCl}\{\text{=NC}_6\text{Me}_4\text{-4-(N}(\text{SiMe}_3)_2)\}]$ ($\text{R} = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ (**8**), $\text{PhC}(\text{NSiMe}_3)_2$ (**9**), NMe_2 (**10**)), respectively (Eq. (4)). **8–10** were isolated in good yields and high purity. The ^1H NMR spectra of **8–10** provide evidence of an ABCD system for the cyclopentadienyl rings, and two signals for the methyl groups of the phenylene ring.



With the aim of forming the hetero bimetallic complex, $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}(\mu\text{-1,4-NC}_6\text{Me}_4\text{N})\{\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}]$ (**11**), the reaction of **7** with $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ has been studied (Eq. (5)).



Analysis of the reaction products, by ^1H NMR spectroscopy, showed the presence of the homo bimetallic complexes **3** and **6** along with a third compound, in minor quantities, that logically can be assumed to be **11**. The formation of **3** and **6** can be explained by the initial synthesis of **11** which undergoes an imido exchange reaction to give a

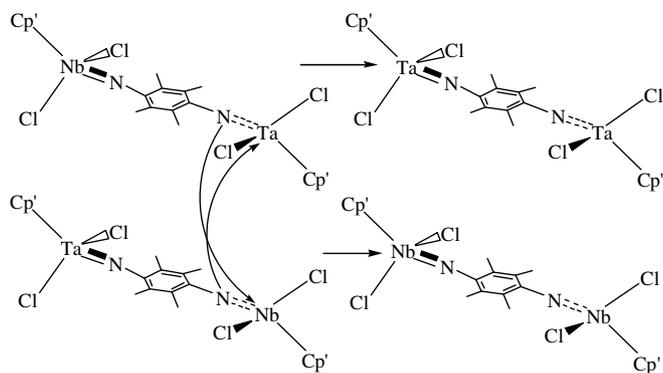


Fig. 2. Possible imido exchange mechanism.

mixture the homo bimetallic complexes of niobium and tantalum (Fig. 2). This type of imido exchange reaction has previously been reported by Gibson and coworkers [9]. Similar results were obtained when the reaction of **4** with $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ was carried out.

3. Conclusions

In this paper, we report the synthesis and characterization of new mono- and dinuclear imido complexes of niobium and tantalum. We have also studied their reactivity towards nucleophilic reagents. In our attempt to form hetero bimetallic niobium/tantalum complexes, we observed an imido exchange reaction which yielded the homo bimetallic derivatives.

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. $\text{Li}\{\text{PhC}(\text{NSiMe}_3)_2\}$ [10], $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ [11], $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ [12] and $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ [13] were prepared as described earlier. LiNMe_2 and 2,3,5,6-tetramethyl-1,4-phenylenediamine were purchased from Aldrich and used without further purification. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were recorded on Gemini-200, Varian UNITY-300 and Varian Mercury FT-400 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Heraeus-CHN-O-Rapid microanalyser.

4.2. Synthesis of $[1,4\text{-}(\text{SiMe}_3\text{HN})_2\text{C}_6\text{Me}_4]$ (**1**)

To a solution of 2,3,5,6-tetramethyl-1,4-phenylenediamine (5.00 g, 30.44 mmol) in THF (75 ml) was added dropwise, at -78°C , LiBu^n (1.6 M in hexane) (39.0 ml, 62.40 mmol). The mixture was stirred for 16 h at room temperature to give a white suspension. SiMe_3Cl (8.0 ml, 63.11 mmol) was added at 0°C the reaction mixture stirred for 12 h at room temperature. Solvent was removed in

vacuo and the residue extracted with hexane (3×50 ml). Evaporation of hexane gave the title compound as a white solid (8.52 g, 91%). ^1H NMR (300 MHz, CDCl_3): δ 0.09 (s, 18H, SiMe_3), 2.20 (s, 12H, C_6Me_4), 3.35 (br, 2H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 0.9 (SiMe_3), 16.6 (C_6Me_4), 129.7, 137.4 (CN) (C_6Me_4). Anal. Calc. for $\text{C}_{16}\text{H}_{32}\text{N}_2\text{Si}_2$: C, 62.27; H, 10.45; N, 9.08. Found: C, 62.26; H, 10.76; N, 9.05%.

4.3. Synthesis of $[1,4\text{-}\{(\text{SiMe}_3)_2\text{N}\}_2\text{C}_6\text{Me}_4]$ (**2**)

To a solution of **1** (8.50 g, 27.54 mmol) in THF (75 ml) was added dropwise, at -78°C , LiBu^n (1.6 M in hexane) (34.4 mL, 55.04 mmol). The mixture was stirred for 6 h at room temperature giving a yellow suspension. SiMe_3Cl (7.0 ml, 55.22 mmol) was added at 0°C and subsequently stirred 18 h at room temperature. The solvent was removed in vacuo and the residue extracted with hexane (3×50 ml). The resulting yellow solution was concentrated to the half its initial volume and cooled to -40°C to yield the title compound as a white crystalline solid (9.50 g, 76%). ^1H NMR (300 MHz, CDCl_3): δ 0.08 (s, 36H, SiMe_3), 2.18 (s, 12H, C_6Me_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 2.0 (SiMe_3), 17.9 (C_6Me_4), 132.7, 140.6 (CN) (C_6Me_4). Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_2\text{Si}_4$: C, 58.33; H, 10.68; N, 6.18. Found: C, 58.07; H, 10.67; N, 6.41%.

4.4. Synthesis of $[\{ \text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2 \}_2(\mu\text{-}1,4\text{-NC}_6\text{Me}_4\text{N})]$ (**3**)

CH_2Cl_2 (40 ml) was added to a mixture of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ (0.50 g, 1.09 mmol) and **2** (0.25 g, 0.55 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 90°C during 48 h. The resulting deep red solution was allowed to cool down to room temperature and volatiles were removed by applying reduced pressure. CH_2Cl_2 (20 ml) was then added to the ampoule and the reaction mixture at 90°C during 16 h. This process (removal of volatiles, solvent addition and heating) was repeated two more times. Finally, solvent was removed in vacuo to give a red solid which was washed with hexane (3×15 ml). Recrystallization from CH_2Cl_2 gave the title complex (0.48 g, 94%). ^1H NMR (300 MHz, CDCl_3): δ 0.27 (s, 18H, SiMe_3), 2.28 (s, 12H, C_6Me_4), 6.51 (4H), 6.63 (4H) (m, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ -0.6 (SiMe_3), 15.4 (C_6Me_4), 113.1, 121.2, 124.7 (C_5H_4), 130.3, 149.9 (CN) (C_6Me_4). Anal. Calc. for $\text{C}_{26}\text{H}_{38}\text{Cl}_4\text{N}_2\text{Si}_2\text{Ta}_2$: C, 33.28; H, 4.08; N, 2.97. Found: C, 33.49; H, 4.08; N, 3.36%.

4.5. Synthesis of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2 \{ \text{=NC}_6\text{Me}_4\text{-}4\text{-N}(\text{SiMe}_3)_2 \}]$ (**4**)

CH_2Cl_2 (40 ml) was added to a mixture of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4]$ (0.27 g, 0.59 mmol) and **2** (0.40 g, 0.88 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 90°C during 60 h. The resulting deep red solution was allowed to cool down

to room temperature and volatiles were removed by applying reduced pressure. The resulting red solid was extracted with hexane (3 × 15 ml). Recrystallization from hexane gave the title complex (0.22 g, 54%). ¹H NMR (300 MHz, CDCl₃): δ 0.01 (s, 18H, NSiMe₃), 0.21 (s, 9H, C₅H₄SiMe₃), 2.04 (6H), 2.35 (6H) (s, C₆Me₄) 6.58 (2H), 6.64 (2H) (m, C₅H₄). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ -0.7 (C₅H₄SiMe₃), 2.17 (NSiMe₃), 15.8, 17.5 (C₆Me₄), 114.4, 120.8, 123.1 (C₅H₄), 131.4, 131.9, 142.9 (CN), 148.4 (CN) (C₆Me₄). Anal. Calc. for C₂₄H₄₃Cl₂N₂Si₃Ta: C, 41.43; H, 6.23; N, 4.03. Found: C, 41.72; H, 6.35; N, 4.24%.

4.6. Synthesis of [TaCl₃(CH₃CN)₂{=NC₆Me₄-4-(N(SiMe₃)₂)}] (5)

To a solution of **2** (1.00 g, 2.20 mmol) in CH₂Cl₂ (25 ml) was added, at -40 °C, to a solution of TaCl₅ (0.40 g, 1.12 mmol) in CH₃CN (30 ml). The mixture was stirred, at room temperature, for 18 h. Solvent was removed by applying reduced pressure to give a yellow solid, which was washed with hexane (3 × 15 ml) and recrystallized from CH₂Cl₂ (40 ml) (0.23 g, 30%) ¹H NMR (300 MHz, CDCl₃): δ 0.03 (s, 18H, NSiMe₃), 2.23 (6H), 2.35 (6H) (s, C₆Me₄) 2.52 (br, 6H, CH₃CN). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 2.15 (NSiMe₃), 3.79 (CH₃CN), 15.5, 17.6 (C₆Me₄), 126.9, 136.2, 140.0 (CN), 148.5 (CN) (C₆Me₄), 130.7 (CH₃CN). Anal. Calc. for C₂₀H₃₆Cl₃N₄Si₂Ta: C, 35.53; H, 5.37; N, 8.29. Found: C, 35.72; H, 5.51; N, 8.41%.

4.7. Synthesis of [Nb(η⁵-C₅H₄SiMe₃)Cl₂]₂(μ-1,4-NC₆Me₄N)] (6)

CH₂Cl₂ (40 ml) was added to a mixture of [Nb(η⁵-C₅H₄SiMe₃)Cl₄] (1.02 g, 2.75 mmol) and **2** (0.62 g, 1.37 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 90 °C during 48 h. The resulting deep brown solution was allowed to cool down to room temperature and volatiles were removed by applying reduced pressure. CH₂Cl₂ (20 ml) was then added to the ampoule and the reaction mixture at 90 °C during 16 h. This process (removal of volatiles, solvent addition and heating) was repeated 17 more times. Finally, solvent was removed in vacuo to give a green solid which was washed with hexane (3 × 15 ml). Recrystallization from CH₂Cl₂ gave the title complex (0.58 g, 56%). ¹H NMR (400 MHz, CDCl₃): δ 0.30 (s, 18H, SiMe₃), 2.28 (s, 12H, C₆Me₄) 6.49 (4H), 6.68 (4H) (m, C₅H₄). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ -0.5 (SiMe₃), 15.7 (C₆Me₄), 113.4, 122.7, 126.8 (C₅H₄), 130.5, 151.8 (CN) (C₆Me₄). Anal. Calc. for C₂₆H₃₈Cl₄N₂Nb₂Si₂: C, 40.96; H, 5.02; N, 3.67. Found: C, 41.12; H, 5.09; N, 3.78%.

4.8. Synthesis of [Nb(η⁵-C₅H₄SiMe₃)Cl₂]{=NC₆Me₄-4-(N(SiMe₃)₂)}] (7)

CH₂Cl₂ (40 ml) was added to a mixture of [Nb(η⁵-C₅H₄SiMe₃)Cl₄] (2.02 g, 5.43 mmol) and **2** (2.46 g,

5.43 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at 90 °C during 48 h. CH₂Cl₂ (20 ml) was then added to the ampoule and the reaction mixture at 90 °C during 16 h. This process (removal of volatiles, solvent addition and heating) was repeated two more times. Finally, solvent was removed in vacuo and the residue was extracted with hexane (3 × 15 ml). Recrystallization from hexane gave the title complex as a purple solid (1.50 g, 45%). ¹H NMR (400 MHz, CDCl₃): δ 0.04 (s, 18H, NSiMe₃), 0.25 (s, 9H, C₅H₄SiMe₃), 2.09 (6H), 2.34 (6H) (s, C₆Me₄), 6.55 (2H), 6.69 (2H) (m, C₅H₄). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ -0.5 (C₅H₄SiMe₃), 2.3 (NSiMe₃), 16.4, 17.5 (C₆Me₄), 114.6, 122.1, 125.2 (C₅H₄), 130.9, 132.6, 143.7 (CN), 150.3 (CN) (C₆Me₄). Anal. Calc. for C₂₄H₄₃Cl₂N₂NbSi₃: C, 47.44; H, 7.13; N, 4.61. Found: C, 47.55; H, 7.25; N, 4.72%.

4.9. Synthesis of [Nb(η⁵-C₅H₄SiMe₃)₂Cl]{=NC₆Me₄-4-(N(SiMe₃)₂)}] (8)

A suspension of Li(C₅H₄SiMe₃) (0.09 g, 0.63 mmol) in hexane (30 ml) was added, at -78 °C, to a solution of **6** (0.35 g, 0.57 mmol) in hexane (30 ml). The mixture was allowed to warm to room temperature and stirred for 12 h. The suspension was filtered and solvent removed in vacuo to yield the title compound as a red solid (0.39 g, 96%). ¹H NMR (400 MHz, C₆D₆): δ 0.16 (s, 18H, NSiMe₃), 0.28 (s, 18H, C₅H₄SiMe₃), 2.19 (6H), 2.34 (6H) (s, C₆Me₄) 5.48 (2H), 6.14 (2H), 6.22 (2H), 6.31 (2H) (m, C₅H₄). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 0.2 (C₅H₄-SiMe₃), 2.6 (NSiMe₃), 17.0, 18.0 (C₆Me₄), 108.6, 113.3, 120.6, 121.4, 129.0 (C₅H₄), 130.6, 132.4, 139.9 (CN), 154.1 (CN) (C₆Me₄). Anal. Calc. for C₃₂H₅₆ClN₂NbSi₄: C, 54.17; H, 7.96; N, 3.95. Found: C, 54.48; H, 8.21; N, 4.15%.

4.10. Synthesis of [Nb(η⁵-C₅H₄SiMe₃){PhC(NSiMe₃)₂}-Cl]{=NC₆Me₄-4-(N(SiMe₃)₂)}] (9)

A suspension of Li{PhC(NSiMe₃)₂} (0.193 g, 0.71 mmol) in hexane (30 ml) was added, at -78 °C, to a solution of **6** (0.43 g, 0.71 mmol) in hexane (30 ml). The mixture was allowed to warm to room temperature and stirred for 12 h. The suspension was filtered and solvent removed in vacuo to yield the title compound as a yellow solid (0.52 g, 88%). ¹H NMR (400 MHz, C₆D₆): δ -0.16 (9H), 0.48 (9H) (s, PhC(NSiMe₃)₂), 0.11 (s, 18H, SiN-SiMe₃), 0.26 (s, 9H, C₅H₄SiMe₃), 2.16 (6H), 2.70 (6H) (s, C₆Me₄) 6.42 (1H), 6.52 (1H), 6.66 (1H), 6.78 (1H) (m, C₅H₄), 6.99 (m, 5H, Ph). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 0.9 (C₅H₄SiMe₃), 2.6 (NSiMe₃), 2.7, 3.9 (PhC(NSiMe₃)₂) 17.5, 18.0 (C₆Me₄), 112.8, 114.4, 117.5, 117.7, 128.0 (C₅H₄), 131.6, 132.5, 140.8 (CN), 152.0 (CN) (C₆Me₄), 128.8, 129.4, 131.9, 142.4 (Ph), 179.8 (PhC(NSiMe₃)₂). Anal. Calc. for C₃₇H₆₆ClN₄NbSi₅: C, 53.17; H, 7.96; N, 6.70. Found: C, 53.40; H, 8.18; N, 6.85%.

4.11. Synthesis of $[Nb(\eta^5-C_5H_4SiMe_3)(NMe_2)Cl-\{=NC_6Me_4-4-(N(SiMe_3)_2)\}]$ (**10**)

A suspension of $Li(NMe_2)$ (0.036 g, 0.71 mmol) in Et_2O (30 ml) was added, at $-78^\circ C$, to a solution of **6** (0.43 g, 0.71 mmol) in Et_2O (30 ml). The mixture was allowed to warm to room temperature and stirred for 12 h. The suspension was filtered and solvent removed in vacuo to yield the title compound as a brown solid (0.39 g, 89%). 1H NMR (400 MHz, C_6D_6): δ 0.14 (s, 18H, $NSiMe_3$), 0.18 (s, 9H, $C_5H_4SiMe_3$), 2.17 (6H), 2.54 (6H) (s, C_6Me_4), 2.88 (3H), 3.60 (3H) (br, NMe_2), 5.93 (1H), 5.96 (1H), 6.13 (1H), 6.53 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ -0.1 ($C_5H_4SiMe_3$), 2.6 ($NSiMe_3$), 2.7, 3.9 ($PhC(NSiMe_3)_2$), 17.0, 18.0 (C_6Me_4), 50.1, 59.5 (NMe_2), 111.4, 112.1, 112.3, 120.0, 124.0 (C_5H_4), 130.9, 132.8, 141.9 (CN), 153.0 (CN) (C_6Me_4). Anal. Calc. for $C_{26}H_{49}ClN_3NbSi_3$: C, 50.67; H, 8.01; N, 6.82. Found: C, 50.82; H, 8.14; N, 6.91%.

4.12. Attempted synthesis of $[Nb(\eta^5-C_5H_4SiMe_3)Cl_2]-(\mu-1,4-NC_6Me_4N)\{Ta(\eta^5-C_5H_4SiMe_3)Cl_2\}$ (**11**)

CH_2Cl_2 (40 ml) was added to a mixture of $[Ta(\eta^5-C_5H_4SiMe_3)Cl_4]$ (1.13 g, 2.47 mmol) and **7** (1.50 g, 2.47 mmol) in a Teflon valve ampoule. The ampoule was placed in an oil bath and heated at $90^\circ C$ during 60 h. The resulting deep red solution was allowed to cool down to room temperature and volatiles were removed by applying reduced pressure. The solid was washed with hexane (3×15 ml) and identified by 1H NMR spectroscopy as a mixture of **3** and **6** along with a third complex.

4.13. X-ray structure determination of $[Ta(\eta^5-C_5H_4SiMe_3)Cl_2-\{=NC_6Me_4-4-(N(SiMe_3)_2)\}]$ (**4**)

A red irregularly shaped ($0.4 \times 0.2 \times 0.1$ mm) crystal of **4** has been mounted on Nonius KappaCCD diffractometer. Unit cell and intensity measurements have been carried out with Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at 115(2) K. No absorption correction was applied. Intensity data were reduced with DENZO and SCALEPACK programs [14]. The structure was solved using the SHELXTL structure determination package [15] by direct methods and refined by full-matrix least-squares based on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in a riding model. Crystallographic data are given in Table 3.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 288820. 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.jorgchem.2005.12.016.

Table 3
Crystal data and structure refinement details for **4**

Formula	$C_{24}H_{43}Cl_2N_2Si_3Ta$
Formula weight	695.72
T (K)	115
Crystal system	Monoclinic
Space group	$P2_1/a$ (No. 14)
a (Å)	14.3882(3)
b (Å)	14.5795(4)
c (Å)	16.4813(4)
β ($^\circ$)	109.7049(11)
V (Å ³)	3254.87(14)
Z	4
D_{calc} (g cm ⁻³)	1.420
μ (mm ⁻¹)	3.666
$F(000)$	1400
θ Range ($^\circ$)	2.05–27.50
hkl Ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$
Data/parameters	7426/289
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.041$, $wR_2 = 0.089$
R indices (all data)	$R_1 = 0.071$, $wR_2 = 0.104$
Largest difference peak and hole (e Å ⁻³)	+0.93; -1.17 at 1.28 and 0.83 Å from Ta

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$$

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