

New Bis(silyl)cyclopentadienidoniobium and -tantalum Complexes: X-ray Crystal Structures of $[\text{NbCp}^{\wedge}\text{Cl}_4]$ and $[\text{NbCp}^{\wedge}\text{Cl}_4(\text{CNAr})]$ [$\text{Cp}^{\wedge} = \eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$; $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$]

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The [bis(silyl)cyclopentadienido]tetrachloroniobium and -tantalum complexes $[\text{MCp}^{\wedge}\text{Cl}_4]$ [$\text{Cp}^{\wedge} = \eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$; $\text{M} = \text{Nb}$ **3**, Ta **4**] were synthesized by reaction of the pentachlorides MCl_5 with $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)_2$ (**1**). Although the Lewis acidity of tetrachloro complexes **3** and **4** is lower than that of the pentahalides, two adducts $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_4(\text{CNAr})]$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\text{M} = \text{Nb}$ **5**, Ta **6**) have been isolated by reaction with ArNC . Complexes **3** and **4** react with *tert*-butylamine or lithium amides to afford the dichloroimido and amidochloroimido complexes $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_2(\text{NR})]$ ($\text{R} = t\text{Bu}$, $\text{M} = \text{Nb}$ **7**, Ta **8**; $\text{R} = \text{Me}$, $\text{M} = \text{Nb}$ **9**) and $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$ (**10**), respectively. In addition, **7** and **8** can be prepared by treatment of the pentachlorides with

$[\text{C}_5\text{H}_3(\text{SiMe}_2\text{NH}t\text{Bu})(\text{SiMe}_3)_2]$ (**2**) by elimination of **1**. The tetrachloro compound **3** reacts with four equivalents of *t*BuNH₂ to give the constrained-geometry derivative $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}t\text{Bu}-\kappa\text{N})(\text{SiMe}_3)\}\text{Cl}(\text{N}t\text{Bu})]$ (**11**), whereas the treatment of toluene solutions of **3** and **4** with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ in the presence of triethylamine leads to the trichloro complexes $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NH}_2-\kappa^2\text{N},\text{N})(\text{SiMe}_3)\}\text{Cl}_3]$ ($\text{M} = \text{Nb}$ **12**, Ta **13**). All the reported complexes were studied by IR and NMR spectroscopy and the molecular structures of complexes **3** and **5** were determined by X-ray diffraction methods.

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Introduction

Mono- and bis(cyclopentadienido) complexes of early transition metals with silyl-substituted cyclopentadienido rings have been extensively used as reagents in organic synthesis and also as precursors to prepare soluble Ziegler–Natta-type olefin polymerization catalysts.^[1] The presence of different substituents in the cyclopentadienido moiety modifies the steric and electronic requirements of the central metal atom, particularly when such substituents contain reactive functional groups. Thus, when chlorine is present in these silyl groups the complex offers a new reactivity center that allows their fixation on silica supports and the cyclopentadienido ring loses its exclusive role as an ancillary ligand. In the last few years various studies have been published regarding the comparative reactivity between the Si–Cl and M–Cl bonds of different chlorosilylcyclopentadienido complexes^[2] that have been used as versatile starting compounds in significant synthetic strategies for constrained-geometry catalysts^[2d,3] with bidentate η^5 -silylcyclopentadienido- η^1 -amido ligands.

The imido group is a strong π -donor ligand that is useful for stabilizing high-valent metal complexes.^[4] It is isolobal

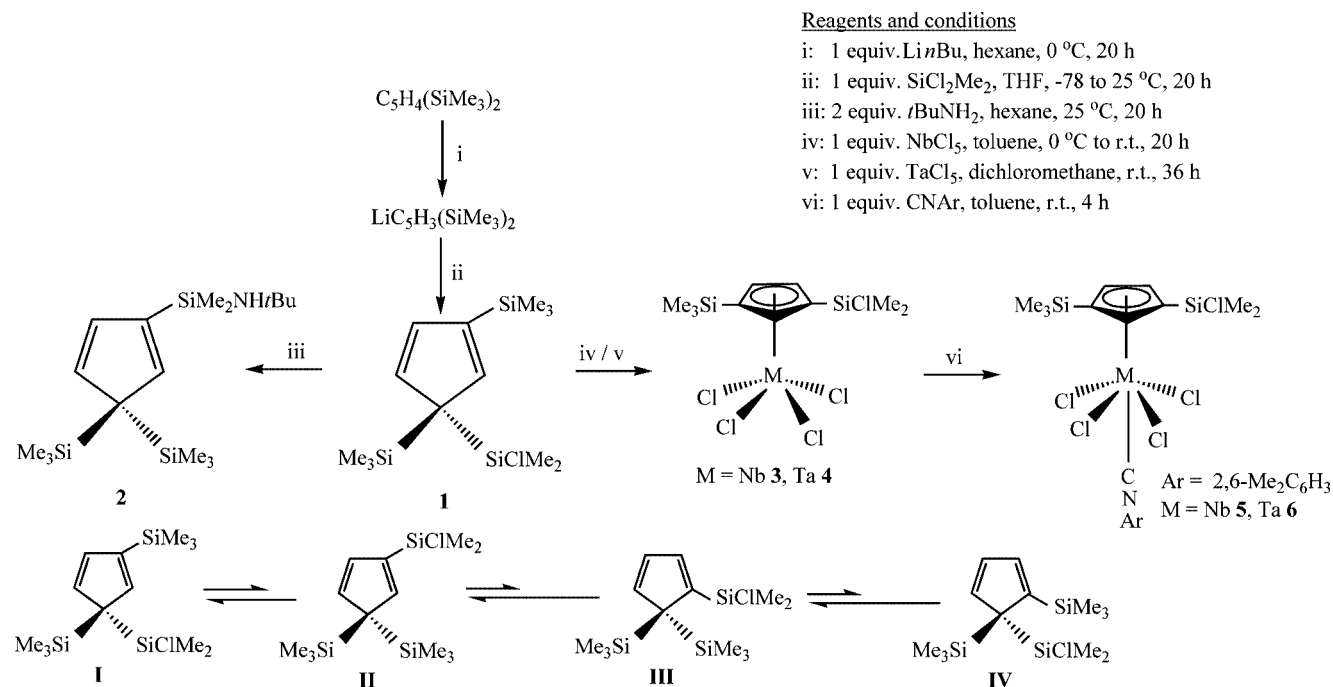
with the cyclopentadienido moiety^[5] and therefore provides group 5 metal complexes that are isoelectronic with the group 4 metallocenes that are extensively used as Ziegler–Natta catalysts. Furthermore, the easy modification of the steric and electronic properties of the imido ligand by varying its alkyl moiety make this type of compound very versatile. For these reasons a rich chemistry of imido group 5 metal complexes has been reported in the last few years.^[6]

As part our interest in the structure–reactivity relationship analysis in group 5 metal monocyclopentadienido compounds, we report here the synthesis of new bis(silyl)-cyclopentadienidoniobium and -tantalum complexes and the results obtained in the study of the simultaneous aminolysis of Si–Cl and M–Cl bonds. In addition, the molecular structures of complexes **3** and **5**, as determined by X-ray diffraction methods, are reported.

Results and Discussion

The synthesis of $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)_2$ (**1**) was effected by treatment of a tetrahydrofuran suspension of the lithium salt $[\text{Li}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}]$ ^[7] with dichlorodimethylsilane at -78°C (Scheme 1). After work-up, **1** was obtained as a yellow oil which can be stored in the dark under an inert atmosphere for several weeks (yield 85%) and was identified by ¹H NMR spectroscopy (see Experimental Section) as an equilibrium mixture of isomers in which 1-(chlorodimethyl-

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Scheme 1.

silyl)-1,3-bis(trimethylsilyl)cyclopentadiene (**I**) and 1,1-bis(trimethylsilyl)-3-(chlorodimethylsilyl)cyclopentadiene (**II**) are the major components in a 3:2 ratio, as usually occurs in all cyclopentadienes of the type $\text{C}_5\text{H}_3\text{X}_2\text{Y}$.^[8]

The precursor $\text{C}_5\text{H}_3(\text{SiMe}_2\text{NH}t\text{Bu})(\text{SiMe}_3)_2$ (**2**) was prepared in good yields (90%) as an orange oil by treatment of **1** with two equivalents of *tert*-butylamine in hexane at room temperature. Compound **2** was characterized by NMR spectroscopy as essentially the only product of the reaction.

Compound **1** reacts with one equivalent of the pentachlorides MCl_5 (M = Nb, Ta) in toluene (M = Nb) or dichloromethane (M = Ta) at 0 °C (M = Nb) or room temperature (M = Ta) to give the corresponding monocyclopentadienido complexes $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{-Cl}_4]$ (M = Nb **3**, Ta, **4**) with elimination of SiClMe_3 . The red (M = Nb) and green (M = Ta) compounds were isolated in 90 and 70% yield, respectively, upon cooling their solutions to -20 °C. Both tetrachloro complexes **3** and **4** show a Lewis acidic character and adducts $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)(\text{SiClMe}_2)\}\text{Cl}_4(\text{CNAr})]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$; M = Nb **5**, Ta, **6**) can be isolated by addition of one equivalent of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ to their toluene solutions.

The molecular structure and atom-labeling scheme of **3** are shown in Figure 1, while the most relevant geometrical parameters are summarized in Table 1. In the solid state, this complex presents a dimeric structure with the two half moieties related by a symmetric center and the niobium atoms bonded through two asymmetrically bridging chlorine atoms. The coordination sphere of the niobium atom

is completed by two terminal chlorine atoms and two bridging chlorine atoms. The coordination sphere of the niobium atom is completed by two terminal chlorine atoms and two bridging chlorine atoms. The coordination sphere of the niobium atom is completed by two terminal chlorine atoms and two bridging chlorine atoms.

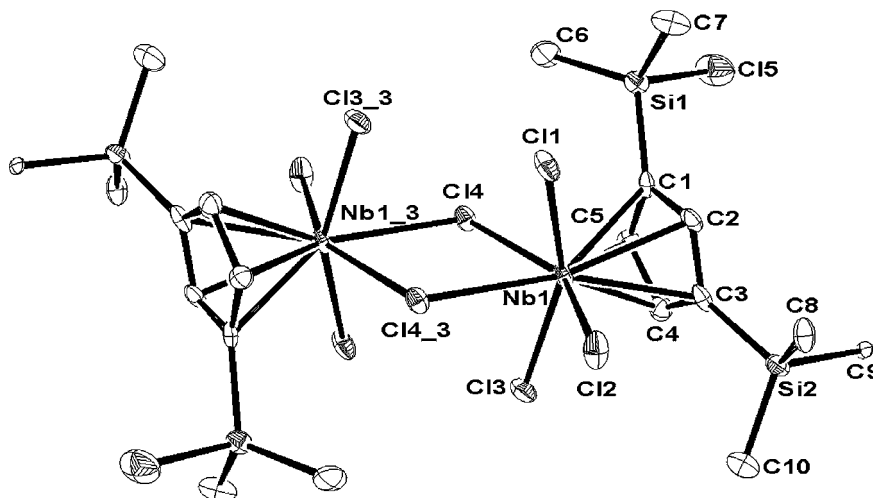
Figure 1. ORTEP drawing of compound **3** with thermal ellipsoids at the 50% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for compound **3**.^[a]

Nb(1)–Cl(1)	2.380(2)	Nb(1)–Cl(2)	2.3765(19)
Nb(1)–Cl(3)	2.401(2)	Nb(1)–Cl(4)	2.4808(18)
Nb(1)–Cl(4)#1	2.764(2)	Cl(4)–Nb(1)#1	2.764(2)
Nb(1)–C(1)	2.443(7)	Nb(1)–C(2)	2.422(8)
Nb(1)–C(3)	2.480(8)	Nb(1)–C(4)	2.457(8)
Nb(1)–C(5)	2.426(8)	Nb(1)–Cp(1)	1.235
Si(2)–C(3)	1.894(8)	Si(1)–C(1)	1.885(8)
Si(2)–C(8)	1.869(8)	Cl(5)–Si(1)	2.072(3)
Si(2)–C(9)	1.922(7)	Si(1)–C(6)	1.832(9)
Si(2)–C(10)	1.848(9)	Si(1)–C(7)	1.847(9)
Cp(1)–Nb(1)–Cl(1)	102.99	Cp(1)–Nb(1)–Cl(2)	108.17
Cp(1)–Nb(1)–Cl(3)	103.39	Cp(1)–Nb(1)–Cl(4)	103.17
Cl(2)–Nb(1)–Cl(1)	87.23(8)	Cl(2)–Nb(1)–Cl(3)	86.43(8)
Cl(1)–Nb(1)–Cl(3)	153.54(7)	Cl(1)–Nb(1)–Cl(4)	86.65(7)
Cl(2)–Nb(1)–Cl(4)	148.61(7)	Cl(3)–Nb(1)–Cl(4)	85.50(7)
Cl(4)–Nb(1)–Cl(4)#1	71.90(6)	Nb(1)–Cl(4)–Nb(1)#1	108.10(6)
C(6)–Si(1)–Cl(5)	108.6(4)	C(1)–Si(1)–Cl(5)	99.7(3)
Cp(1)–Nb(1)–Cl(4)#1	175.03		

[a] Cp(1) is the centroid of C(1)–C(5); symmetry operation #1: $-x + 2, -y + 1, -z$.

can be described as elongated octahedral, with the cyclopentadienido ring and a chlorine atom in the apical positions and with four chlorine atoms in the equatorial plane. The niobium atom is located 0.6 Å above the equatorial plane.^[6d,6f,9,10] The Nb–Cl_{equatorial} bond lengths range from 2.375(2) to 2.482(2) Å, with the largest distance corresponding to the chlorine atom implicated in the bridging system that is also bonded at the apical position of the symmetry-related niobium atom, although in this case with a larger distance of 2.763(2) Å. The Cp–Nb–Cl(4)_{apical} angle and the Nb–Cp distance are 175.03° and 1.235 Å, respectively, both of which are in the normal range. A similar asymmetric bridge has been described for the complexes $[(\text{NbCl}_2)_2(\mu\text{-O})(\mu\text{-Cl})_2]\{(\eta^5\text{-C}_5\text{H}_4)(\text{Me}_2\text{SiOSiMe}_2)\}$ ^[6c] and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2\}_2(\mu\text{-O})(\mu\text{-Cl})_2]$,^[11] although in these cases a bridging oxygen atom is also present.

The two silicon atoms of the substituents in the cyclopentadienido ring [Si(1) and Si(2)] are located above the Cp plane by 0.37 and 0.39 Å, respectively, and the chlorine atom is perpendicular to this plane. This position for the chlorine atom has been described in other complexes containing a C₅H₄(SiClMe₂) ring.^[12] It is relevant to note that no other similar structures with a disubstituted Cp ring have been described.

A view of the molecular structure of complex **5** is shown in Figure 2 together with the atom-numbering scheme. Selected bond lengths and angles are given in Table 2. The Cp[^] ring is bound to the niobium atom in a nearly symmetric η^5 -fashion with the distance between the metal and the centroid of the ring being 2.137 Å and with the two silicon atoms of the substituents Si(6) and Si(7) located 0.31 Å above the ring plane. The isocyanide ligand is linearly bound to the niobium atom, the values of the Nb–C(6) bond length and of the Nb–C(6)–N(1) and C(6)–N(1)–C(7) angles being 2.215(13) Å and 176.3(11)° and 175.2(13)°, respectively; the length of the N(1)–C(6) bond [1.192(15) Å] is in agreement with a triple bond.^[6,13] The coordination around the niobium atom is completed by four chlorine atoms with Nb–Cl bond lengths ranging from 2.412(3) to

2.442(3) Å. Complex **5** is pseudo-octahedral if the centroid of the Cp[^] ring is considered as occupying a coordination site, although the niobium atom is displaced by 0.60 Å from the mean equatorial plane passing through the four chlorine atoms toward the cyclopentadienido ring.

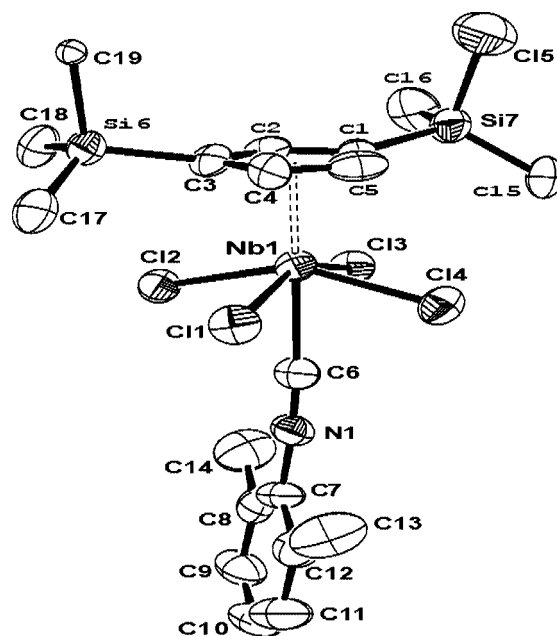


Figure 2. ORTEP drawing of compound **5** with thermal ellipsoids at the 50% probability level.

The comparative reactivity of the two different types of Si–Cl and M–Cl bonds present in the starting tetrachloro complexes **3** and **4** was studied in reactions with amines and amides. Related studies with chlorocyclopentadienidotitanium^[3g,3h,14] and -niobium^[2d] derivatives led to the formation of constrained monomeric cyclic species containing the pendant amido group of the cyclopentadienido ligand coordinated to the metal center. The dichloroimido complexes $[\text{MCp}^{\wedge}\text{Cl}_2(\text{NR})]$ [$\text{Cp}^{\wedge} = \eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)$; R =

Table 2. Selected bond lengths [Å] and angles [°] for compound **5**.^[a]

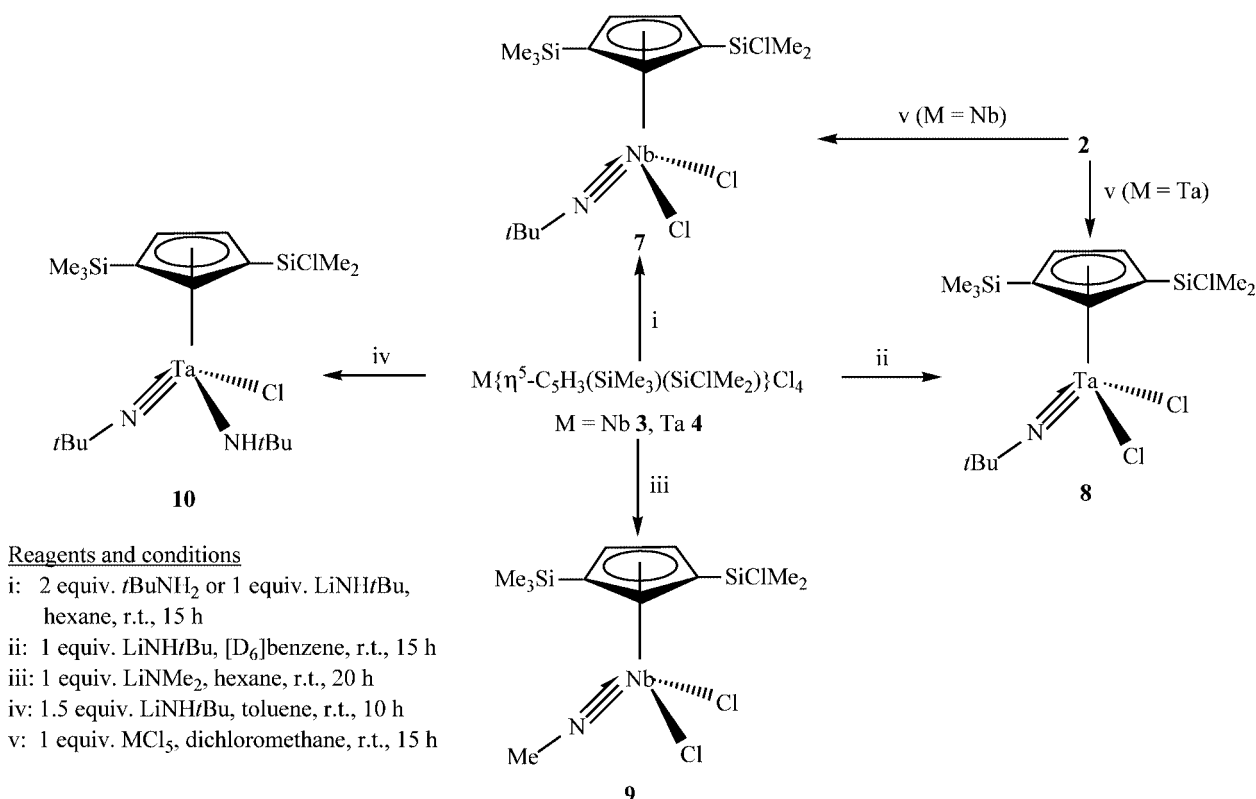
Nb(1)–Cl(1)	2.412(3)	Nb(1)–Cl(2)	2.418(3)
Nb(1)–Cl(3)	2.442(3)	Nb(1)–Cl(4)	2.430(3)
Nb(1)–C(6)	2.215(13)	Nb(1)–C(1)	2.458(10)
Nb(1)–C(2)	2.431(11)	Nb(1)–C(3)	2.485(11)
Nb(1)–C(4)	2.475(11)	Nb(1)–C(5)	2.444(12)
Si(6)–C(3)	1.894(12)	Si(7)–C(1)	1.897(11)
Si(6)–C(17)	1.861(13)	Si(7)–Cl(5)	2.064(6)
Si(6)–C(18)	1.852(13)	Si(7)–C(15)	1.809(13)
Si(6)–C(19)	1.955(10)	Si(7)–C(16)	1.897(11)
Cp(1)–Nb(1)	2.137	C(6)–N(1)	1.192(15)
C(6)–Nb(1)–Cl(1)	76.2(3)	C(6)–Nb(1)–Cl(2)	74.5(4)
C(6)–Nb(1)–Cl(3)	75.2(3)	C(6)–Nb(1)–Cl(4)	76.2(4)
Cl(1)–Nb(1)–Cl(2)	87.31(12)	Cl(1)–Nb(1)–Cl(4)	86.93(12)
Cl(1)–Nb(1)–Cl(3)	151.39(12)	Cl(2)–Nb(1)–Cl(4)	150.68(11)
Cl(2)–Nb(1)–Cl(3)	84.74(11)	Cl(4)–Nb(1)–Cl(3)	86.74(11)
Cp(1)–Nb(1)–N(1)	178.56	Cp(1)–Nb(1)–Cl(1)	104.44
Cp(1)–Nb(1)–Cl(2)	104.33	Cp(1)–Nb(1)–Cl(3)	104.11
Cp(1)–Nb(1)–Cl(14)	105.03	Nb(1)–C(1)–N(1)	176.3(11)
C(6)–N(1)–C(7)	175.2(13)		

[a] Cp is the centroid of C(1)–C(5).

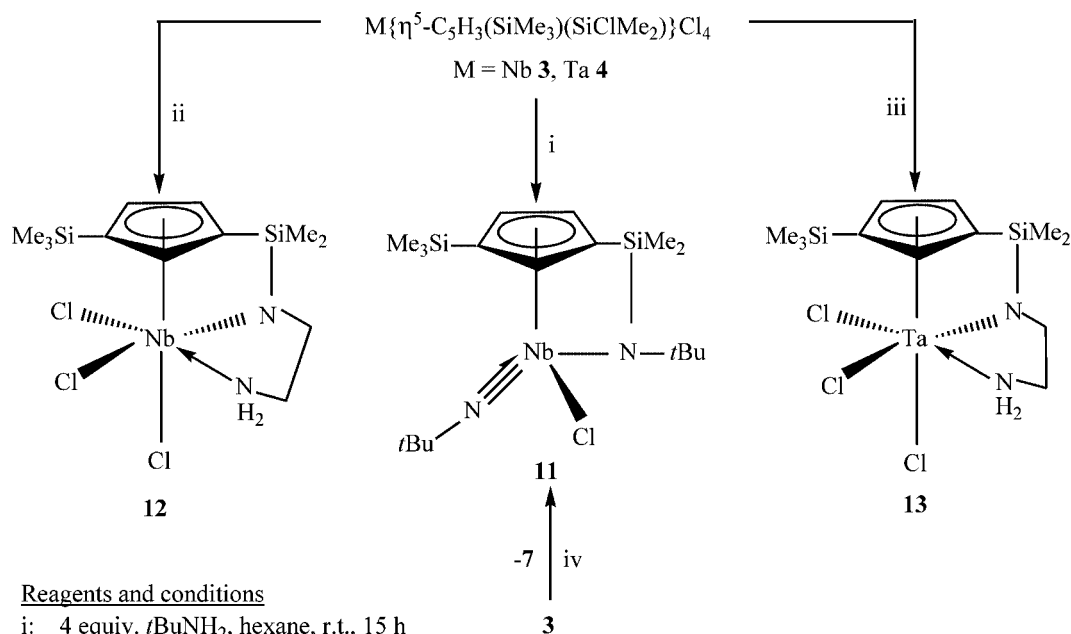
*t*Bu, M = Nb **7**, Ta, **8**; R = Me, M = Nb **9**] were isolated in good yields upon treatment of **3** and **4** with one equivalent of the appropriate lithium amide (see Scheme 2). Complex **7** also can be prepared with two equivalents of *tert*-butylamine, whereas the treatment of **4** with 1.5 equivalents of LiNH*t*Bu leads to the amidochloroimido complex [Ta{ η^5 -C₅H₃(SiMe₃)(SiClMe₂)}Cl(NH*t*Bu)(N*t*Bu)] (**10**). The formation of the imido complexes **7**–**10** takes place with elimination of LiCl and HCl but the Si–Cl bond of the cyclopentadienido ring remaining unaltered.

Alternatively, the reaction of **2** with niobium and tantalum pentachlorides in a 1:1 ratio leads to the dichloroimido compounds **7** and **8**, respectively, by elimination of HCl, cyclopentadiene **1**, and a mixture of other, unidentified products.

Partial substitution of the chloride moieties occurs upon treatment of a hexane solution of **3** with four equivalents of *t*BuNH₂ (Scheme 3) and leads to the constrained-geometry complex [Nb{ η^5 -C₅H₃(SiMe₃)(SiMe₂N*t*Bu- κ N)}Cl(N*t*Bu)] (**11**) with evolution of HCl. Furthermore, the addition of



Scheme 2.



Reagents and conditions

- i: 4 equiv. *t*BuNH₂, hexane, r.t., 15 h
 ii: 1 equiv. en, 2 equiv. NEt₃, toluene, r.t., 48 h
 iii: 1 equiv. en, 2 equiv. NEt₃, toluene, -78 °C to r.t., 16 h
 iv: 2 equiv. LiNH*t*Bu, hexane, r.t., 20 h

Scheme 3.

one equivalent of ethylenediamine and two equivalents of NEt₃ to toluene solutions of the tetrachloro complexes **3** and **4** gives, after separation of the ammonium salt formed, the pseudo-octahedral trichloro species $[M\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)[\text{SiMe}_2\text{N}(\text{CH}_2)_2\text{NH}_2\text{-}\kappa^2\text{N,N}\}]\text{Cl}_3$ ($M = \text{Nb } 12, \text{Ta } 13$). However, a mixture of complexes **7** and **11** was obtained upon treatment of **3** with two equivalents of LiNH*t*Bu.

Complexes **3–13** are soluble in most organic solvents, including saturated hydrocarbons. They are extremely air- and moisture-sensitive, so rigorously dried solvents and handling under dry inert atmosphere were found to be imperative for successful preparations. Their spectroscopic data (see Experimental Section) are in agreement with the proposed structures. The IR spectra show the characteristic absorptions for a cyclopentadienido ring ($\nu_{\text{C-H}} \approx 839 \text{ cm}^{-1}$)^[15] and the trimethylsilyl substituent [$\delta_{\text{s}}(\text{CH}_3) \approx 1254 \text{ cm}^{-1}$].^[6f,15] Complexes **5** and **6** show $\nu_{\text{C=N}}$ ^[6a,13] at around 2221 cm^{-1} , whereas the imido complexes show the $\nu_{\text{M=N}}$ ^[6,15,16] IR absorption at about 1348 cm^{-1} . The M–C, M–N, and N–H stretching vibrations are observed at $\tilde{\nu} \approx 469$,^[6a,17] 594 ,^[6d] and 3248 cm^{-1} ,^[6a,18] respectively.

The ¹H NMR spectra of complexes **3** and **4** show the expected resonances for the methyl groups bonded to silicon. Three broad multiplets corresponding to an ABC spin system are observed for the cyclopentadienido ring protons. These assignments were confirmed by the ¹³C{¹H} NMR spectra. The NMR spectroscopic data of adducts **5** and **6** are in agreement with the expected behavior for pseudo-octahedral compounds^[6a,13] with the cyclopentadienido ring and the isocyanide ligand mutually *trans*. The *o*-methylphenyl isocyanide groups are equivalent and, in addition,

three and five resonances for the C₅H₃(SiClMe₂)(SiMe₃) ring protons and carbons are observed, respectively.

Although the structures of complexes **7–10** in the solid state have not been determined, we assume them to be monomers that are pseudo-tetrahedral and isostructural with other half-sandwich imido group 5 metal derivatives.^[6b,6d,6e] Their formulation as dichloroimido complexes is supported by analytical and spectroscopic data (see Experimental Section) according to the behavior expected for three-legged piano-stool species.

Complex **11** is a disymmetric molecule due to the enantiotopic faces of the cyclopentadienido ring and the niobium atom. Its ¹H NMR spectrum shows a singlet for the equivalent methyl protons of the SiMe₃ substituent, two singlets for the inequivalent methyl groups bonded to the silicon in the SiClMe₂ moiety, and three low-field multiplets for the ring protons due to the presence of the chiral niobium center. In addition, three methylsilyl resonances, two *Nt*Bu signals, and five ring carbon resonances appear in the ¹³C{¹H} NMR spectrum.

The trichloro complexes **12** and **13** show a similar NMR behavior to that discussed above for **11**, and all these *ansa* compounds exhibit a characteristic ¹³C signal due to the ring carbon C¹–SiClMe₂ [$\delta = 110$ (**11**), 106 (**12**), 105.2 ppm (**13**)], which is shifted upfield with respect to the other ring carbon resonances.^[3h,19]

Conclusions

The tetrachlorobis(silyl)cyclopentadienidoniobium and -tantalum complexes $[M\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_4]$

(M = Nb **3**, Ta **4**) have been prepared by a conventional reaction between MCl_5 and $\text{C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)_2$ (**1**). Its Lewis acid character has been established by reaction with isocyanides to give $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_4\text{L}]$ (M = Nb **5**, Ta **6**; L = 2,6-Me₂C₆H₃NC), while in the presence of stoichiometric amounts of amines or lithium amides the dichloroimido and amidochloroimido complexes $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}_2(\text{NR})]$ (R = *t*Bu, M = Nb **7**, Ta **8**; R = Me, M = Nb **9**) and $[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$ (**10**), respectively, are isolated. In addition, the constrained-geometry niobium derivative $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}t\text{Bu-}\kappa\text{N})(\text{SiMe}_3)\}\text{Cl}(\text{N}t\text{Bu})]$ (**11**) can be prepared by treatment of the tetrachloro compound with four equivalents of *t*BuNH₂, whereas with ethylenediamine the pseudo-octahedral trichloro complexes $[\text{M}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NH}_2\text{-}\kappa^2\text{N,N})(\text{SiMe}_3)\}\text{Cl}_3]$ (M = Nb **12**, Ta **13**) were obtained.

Experimental Section

General: All reactions and manipulations were carried out under argon using standard Schlenk-tube and glove-box techniques. Solvents were refluxed in the presence of an appropriate drying agent and distilled and degassed prior use: [D₆]benzene and hexane (Na/K alloy), [D]chloroform (NaH), tetrahydrofuran (Na/benzophenone), dichloromethane (P₂O₅), and toluene (Na). Bis(trimethylsilyl)cyclopentadienide^[7d] was synthesized as described previously, while LiNH*t*Bu was prepared by treatment of *t*BuNH₂ with LinBu. Reagent-grade chemicals were purchased from commercial sources and used without further purification: SiClMe₃, SiCl₂Me₂, *t*BuNH₂, TaCl₅, LinBu (1.6 m in hexanes), LiNMe₂, NEt₃, and H₂N-(CH₂)₂-NH₂ from Aldrich, and NbCl₅ from Fluka. Infrared spectra were recorded with a Perkin–Elmer Spectrum 2000 spectrophotometer (4000–400 cm^{−1}) with samples as KBr pellets. ¹H and ¹³C{¹H} NMR spectra were recorded with a “Unity 300” or a “Mercury VX 300” (Varian NMR Systems) spectrometer; chemical shifts are referenced to the ¹H (δ = 7.15 and 7.24 ppm) and ¹³C (δ = 128 and 77 ppm) residual resonances of [D₆]benzene and [D₁]chloroform, respectively. Microanalyses (C,H,N) were performed with a LECO CHNS 932 microanalyzer.

[C₅H₃(SiClMe₂)(SiMe₃)₂] (1**):** A 1.6 M hexane solution of LinBu (62.5 mL, 100 mmol) was added dropwise at 0 °C to a solution of freshly distilled C₅H₄(SiMe₃)₂ (21.02 g, 100 mmol) in hexane (400 mL). The reaction mixture was slowly warmed to room temperature and stirred for 20 h to afford a white precipitate, which, after filtration, was washed with hexane (2 × 100 mL), dried under vacuum, and identified as LiC₅H₃(SiMe₃)₂ (19.45 g, 90.00 mmol, 90%).

A suspension of LiC₅H₃(SiMe₃)₂ (19.45 g, 90.00 mmol) in tetrahydrofuran (300 mL) was treated with SiCl₂Me₂ (10.92 mL, 90.00 mmol) at −78 °C. The reaction mixture was then warmed to room temperature and stirred for 20 h. After filtration, the solvent was removed by evaporation under vacuum and the residue extracted with hexane (2 × 100 mL). The solvent was again removed to give a yellow oil, which was characterized as compound **1** (23.18 g, 80.00 mmol, 85%). ¹H NMR ([D₆]benzene, 25 °C): **I** (major): δ = 6.85 (m, 1 H, C₅H₃), 6.81 (m, 1 H, C₅H₃), 6.49 (m, 1 H, C₅H₃), 0.24 (s, 9 H, SiMe₃), 0.19 (s, 3 H, SiClMe₂), 0.16 (s, 3 H, SiClMe₂), 0.07 ppm (s, 9 H, SiMe₃); **II** (minor): δ = 6.95 (m, 1 H, C₅H₃), 6.90 (m, 1 H, C₅H₃), 6.46 (m, 1 H, C₅H₃), 0.54 (s, 6 H,

SiClMe₂), −0.04 ppm (s, 18 H, SiMe₃). ¹³C{¹H} NMR ([D₆]benzene, 25 °C): **I** (major): δ = 147.3 (C³), 143.2, 136.7, 135.2, 71.5 (br., C¹ of C⁵ ring), 1.8, 1.4 (SiClMe₂), −0.77 (SiMe₃), −0.83 ppm (SiMe₃); **II** (minor): δ = 147.1 (C³), 137.5, 135.3, 133.6, 71.5 (br., C¹ of C⁵ ring), 2.7 (SiClMe₂), −0.7 ppm (SiMe₃). ²⁹Si NMR ([D₆]benzene, 25 °C): **I** (major): δ = 19.7 (SiClMe₂), −1.0 (SiMe₃), −10.4 ppm (SiMe₃); **II** (minor): δ = 14.4 (SiClMe₂), −1.9 ppm (SiMe₃).

[C₅H₃(SiMe₂NH*t*Bu)(SiMe₃)₂] (2**):** A solution of **1** (10.00 g, 33.00 mmol) in hexane (150 mL) was treated with *tert*-butylamine (4.83 g, 66.00 mmol) at room temperature. The reaction mixture was stirred for 20 h and then the resulting suspension was filtered. The solvent was evaporated to dryness to give an orange oil, which was identified as compound **2**. Yield: 7.95 g (90%). ¹H NMR ([D₆]benzene, 25 °C): δ = 7.00 (m, 1 H, C₅H₃), 6.85 (m, 1 H, C₅H₃), 6.51 (m, 1 H, C₅H₃), 1.17 (s, 9 H, *t*Bu), 0.36 (s, 6 H, SiMe₂NH*t*Bu), −0.02 ppm (s, 18 H, SiMe₃); NH signal not detected. ¹³C{¹H} NMR ([D₆]benzene, 25 °C): δ = 146.7 (C³), 145.3, 136.2, 135.3, 60 (C¹ of C⁵ ring), 49.6 (CMe₃), 33.9 (CMe₃), 2.0 (SiMe₂), −0.5 ppm (SiMe₃).

[Nb{η⁵-C₅H₃(SiClMe₂)(SiMe₃)}\text{Cl}_4] (**3**): Compound **1** (2.24 g, 7.40 mmol) was added to a suspension of NbCl₅ (2.00 g, 7.40 mmol) in toluene (150 mL) at 0 °C. The reaction was slowly warmed at room temperature and stirred for 20 h. After filtration, the resulting solution was concentrated to about 25 mL and cooled to −20 °C to give a dark red microcrystalline solid which was characterized as **3**. Yield: 3.10 g (90%). IR (KBr): $\tilde{\nu}$ = 3091 cm^{−1} w, 1397 m, 1262 vs, 1089 m, 839 vs, 488 vs, 455 s. ¹H NMR ([D₁]chloroform, 25 °C): δ = 7.49 (br., 1 H, C₅H₃), 7.41 (br., 1 H, C₅H₃), 7.20 (br., 1 H, C₅H₃), 0.92 (s, 6 H, SiClMe₂), 0.43 ppm (s, 9 H, SiMe₃). ¹³C{¹H} NMR ([D₁]chloroform, 25 °C): δ = 146.6 (C¹), 139.7 (C³), 134, 133.6, 133.2 (C₅H₃), 1.9 (SiClMe₂), −0.6 ppm (SiMe₃). C₁₀H₁₈Cl₅NbSi₂ (464.60): calcd. C 25.85, H 3.90; found C 25.78, H 3.63.

[Ta{η⁵-C₅H₃(SiClMe₂)(SiMe₃)}\text{Cl}_4] (**4**): A mixture of equimolar amounts of **1** (2.53 g, 8.36 mmol) and freshly sublimed TaCl₅ (3.00 g, 8.36 mmol) in dichloromethane (200 mL) was stirred at room temperature for 36 h in a sealed ampoule. After the ampoule was opened, the suspension was filtered and the resulting green solution was concentrated to about 25 mL and cooled to −20 °C to give **4** as a green microcrystalline solid. Yield: 3.23 g (70%). IR (KBr): $\tilde{\nu}$ = 3093 cm^{−1} w, 1393 m, 1252 vs, 1093 s, 831 vs, 497 vs, 455 s. ¹H NMR ([D₁]chloroform, 25 °C): δ = 7.32 (m, 1 H, C₅H₃), 7.23 (m, 1 H, C₅H₃), 7.00 (m, 1 H, C₅H₃), 0.91 (s, 6 H, SiClMe₂), 0.42 ppm (s, 9 H, SiMe₃). ¹³C{¹H} NMR ([D₁]chloroform, 25 °C): δ = 142.5 (C¹), 131.6 (C³), 131.1, 130.9, 130.8 (C₅H₃), 2.0 (SiClMe₂), −0.5 ppm (SiMe₃). C₁₀H₁₈Cl₅Si₂Ta (552.64): calcd. C 21.73, H 3.28; found C 21.65, H 3.13.

[M{η⁵-C₅H₃(SiClMe₂)(SiMe₃)}\text{Cl}_4(\text{CNAr})] [Ar = 2,6-Me₂C₆H₃; M = Nb (**5**), Ta (**6**): 2,6-Me₂C₆H₃NC (0.17 g, 1.30 mmol) was added to a toluene (70 mL) solution of **3** (0.60 g, 1.30 mmol) or **4** (0.72 g, 1.30 mmol) under rigorously anhydrous conditions. The mixture was stirred for 4 h and then filtered. Concentration and cooling of the filtrate gave **5** and **6** as rose (**5**) and green (**6**) microcrystalline solids.

5: Yield: 0.70 g (90%). IR (KBr): $\tilde{\nu}$ = 3100 cm^{−1} w, 2957 m, 2218 s, 1625 m, 1473 m, 1401 m, 1255 vs, 1089 s, 842 vs, 484 vs, 455 vs. ¹H NMR ([D₁]chloroform, 25 °C): δ = 7.52 (t, ³J_{H,H} = 2.1 Hz, 1 H, C₅H₃), 7.41 (t, ³J_{H,H} = 2.1 Hz, 1 H, C₅H₃), 7.21 (t, ³J_{H,H} = 2.1 Hz, 1 H, C₅H₃), 7.25 (t, ³J_{H,H} = 7.8 Hz, 1 H, *p*-C₆H₃), 7.11 (d, ³J_{H,H} = 7.8 Hz, 2 H, *m*-C₆H₃), 2.54 (s, 6 H, C₆H₃Me₂NC), 0.95 (s, 3 H, SiClMe₂), 0.88 (s, 3 H, SiClMe₂), 0.41 ppm (s, 9 H, SiMe₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_1]\text{chloroform}$, 25 °C): δ = 195 (CN), 142.4, 139.2, 139, 138.4, 136.8 (C_5H_3), 130.5 ($\text{C}^{2,6}$), 129 (C^1), 128.1 ($\text{C}^{3,5}$), 125.3 (C^4 , $\text{C}_6\text{H}_3\text{Me}_2\text{NC}$), 18.4 ($\text{C}_6\text{H}_3\text{Me}_2\text{NC}$), 3.02, 2.97 (SiClMe_2), 0.03 ppm (SiMe_3). $\text{C}_{19}\text{H}_{27}\text{Cl}_5\text{NNbSi}_2$ (595.775): calcd. C 38.30, H 4.57, N 2.35; found C 38.49, H 4.65, N 2.30.

6: Yield: 0.62 g (70%). IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1} w, 2954 m, 2223 s, 1629 s, 1474 m, 1403 m, 1252 vs, 1091 s, 840 vs, 490 vs, 457 s. ^1H NMR ($[\text{D}_1]\text{chloroform}$, 25 °C): δ = 7.23 (t, 1 H), 7.20 (t, 1 H), 6.88 (t, $^3J_{\text{H,H}}$ = 2.1 Hz, 1 H, C_5H_3), 7.10 (m, 3 H, $\text{C}_6\text{H}_3\text{Me}_2\text{NC}$), 2.52 (s, 6 H, $\text{C}_6\text{H}_3\text{Me}_2\text{NC}$), 0.99 (s, 3 H, SiClMe_2), 0.88 (s, 3 H, SiClMe_2), 0.41 ppm (s, 9 H, SiMe_3). $\text{C}_{19}\text{H}_{27}\text{Cl}_5\text{NSi}_2\text{Ta}$ (683.817): calcd. C 33.37, H 3.98, N 2.05; found C 33.17, H 3.83, N 2.00.

$[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}_2\text{Cl}_2(\text{N}t\text{Bu})]$ (7): Complex 7 can be prepared by two synthetic methods.

Method A: $t\text{BuNH}_2$ (0.07 g, 0.96 mmol) was added under rigorously anhydrous conditions to a solution of **3** (0.22 g, 0.48 mmol) in hexane (50 mL) and the reaction mixture was stirred for 15 h. The solution was filtered and the solvent reduced to dryness to give an orange oil which was identified as **7**.

Method B: A solution of $\text{LiNH}t\text{Bu}$ (0.04 g, 0.48 mmol) in hexane (15 mL) was added to a solution of **3** (0.22 g, 0.48 mmol) in hexane (50 mL) at room temperature. The reaction mixture was stirred for 15 h. Filtration of the supernatant solution from the solid, followed by concentration to dryness, produced **7** as an orange oil. Yield: 0.16 g (70%). IR (KBr): $\tilde{\nu}$ = 3190 cm^{-1} w, 2973 m, 1404 m, 1359 m, 1254 vs, 1084 vs, 840 vs, 503 vs, 459 m. ^1H NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 7.04 (m, 1 H, C_5H_3), 6.49 (m, 1 H, C_5H_3), 6.45 (m, 1 H, C_5H_3), 1.13 (s, 9 H, $\text{N}t\text{Bu}$), 0.59 (s, 6 H, SiClMe_2), 0.21 ppm (s, 9 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 130 (C^1), 129.3 (C^3), 124.4, 122.1, 121.6 (C_5H_3), 70.2 [$\text{N}(\text{CMe}_3)$], 30.5 [$\text{N}(\text{CMe}_3)$], 3.6, 3.1 (SiClMe_2), 0.02 ppm (SiMe_3). $\text{C}_{14}\text{H}_{27}\text{Cl}_3\text{NNbSi}_2$ (464.814): calcd. C 36.18, H 5.85, N 3.01; found C 35.93, H 5.96, N 2.90.

$[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}_2\text{Cl}_2(\text{N}t\text{Bu})]$ (8): $\text{LiNH}t\text{Bu}$ (0.003 g, 0.040 mmol) was added to a solution of **4** (0.20 g, 0.40 mmol) in $[\text{D}_6]\text{benzene}$ (0.7 mL) in a valved NMR tube under rigorously anhydrous conditions. The reaction was monitored by ^1H NMR spectroscopy until no further changes were observed. The final spectrum was indicative of complete transformation of the starting material and confirmed the formation of **8** in quantitative yield. Evaporation of the solvent gave **8** as a yellow oil. Yield: 0.17 g (75%). ^1H NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 7.03 (m, 1 H, C_5H_3), 6.42 (m, 2 H, C_5H_3), 1.20 (s, 9 H, $\text{N}t\text{Bu}$), 0.58 (s, 3 H, SiClMe_2), 0.56 (s, 3 H, SiClMe_2), 0.2 ppm (s, 9 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 127 (C^1), 127.3, 122.3, 121.6, 121.2 (C_5H_3), 66.6 [$\text{N}(\text{CMe}_3)$], 32.1 [$\text{N}(\text{CMe}_3)$], 3.4, 3.0 (SiClMe_2), -0.1 ppm (SiMe_3). $\text{C}_{14}\text{H}_{27}\text{Cl}_3\text{NNbSi}_2$ (552.86): calcd. C 30.42, H 4.92, N 2.53; found C 30.44, H 4.71, N 2.37.

Reaction of $\text{C}_5\text{H}_3(\text{SiMe}_2\text{NH}t\text{Bu})(\text{SiMe}_2)$ (2) with MCl_5 (M = Nb, Ta): $\text{C}_5\text{H}_3(\text{SiMe}_2\text{NH}t\text{Bu})(\text{SiMe}_2)$ (0.63 g, 1.85 mmol) was added to a suspension of NbCl_5 (0.50 g, 1.85 mmol) in dichloromethane (80 mL) and the reaction mixture stirred for 15 h. After filtration, the volatiles were removed under vacuum to give a yellow oil, which was identified as a mixture of **1** and **7** by ^1H NMR spectroscopy. With TaCl_5 a mixture of **1** and **8** was identified by ^1H NMR spectroscopy.

$[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}_2\text{Cl}_2(\text{NMe})]$ (9): A mixture of **3** (0.30 g, 0.64 mmol) and LiNMe_2 (0.03 g, 0.64 mmol) was dissolved in hexane (50 mL) under rigorously anhydrous conditions. The reaction mixture was stirred for 20 h at room temperature and then filtered. The filtrate was evaporated to dryness and the residue ex-

tracted with hexane (2×10 mL). Concentration and cooling of the filtrate produced **9** as a brown solid. Yield: 0.10 g (37%). ^1H NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 6.85 (m, 1 H, C_5H_3), 6.34 (m, 1 H, C_5H_3), 6.27 (m, 1 H, C_5H_3), 3.31 (s, 3 H, NMe), 0.55 (s, 3 H, SiClMe_2), 0.53 (s, 3 H, SiClMe_2), 0.17 ppm (s, 9 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 129.5, 122.7, 122.5, 122.1, 121.6 (C_5H_3), 54.3 (NMe), 3.2, 2.7 (SiClMe_2), -0.3 ppm (SiMe_3). $\text{C}_{11}\text{H}_{21}\text{Cl}_3\text{NSi}_2\text{Ta}$ (422.733): calcd. C 31.25, H 5.01, N 3.31; found C 31.12, H 4.94, N 3.25.

$[\text{Ta}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}_2\text{Cl}(\text{NH}t\text{Bu})(\text{N}t\text{Bu})]$ (10): A toluene (15 mL) solution of $\text{LiNH}t\text{Bu}$ (0.06 g, 0.81 mmol) was slowly added to a solution of **4** (0.30 g, 0.54 mmol) in toluene (60 mL) and the reaction mixture was stirred overnight. The resulting suspension was filtered and the solvent evaporated to dryness. The residue was extracted with hexane (2×10 mL) and the solution was concentrated and cooled to -20 °C to give an oily yellow product which was characterized as **10**. Yield: 0.09 g (30%). IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1} w, 1403 m, 1358 s, 1261 vs, 1085 vs, 840 vs, 633 m, 504 s, 548 m. ^1H NMR ($[\text{D}_1]\text{chloroform}$, 25 °C): δ = 8.09 (br., 1 H, $\text{NH}t\text{Bu}$), 7.05 (m, 1 H, C_5H_3), 6.79 (m, 2 H, C_5H_3), 1.24 (s, 18 H, $\text{NH}t\text{Bu} + \text{N}t\text{Bu}$), 0.74 (s, 3 H, SiClMe_2), 0.72 (s, 3 H, SiClMe_2), 0.31 ppm (s, 9 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_1]\text{chloroform}$, 25 °C): δ = 134.8, 127.8, 127.3, 121.6, 121.2 (C_5H_3), 66.6 ($\text{N}(\text{CMe}_3)$), 53.2 ($\text{N}(\text{H}(\text{CMe}_3))$), 32.1 ($\text{N}(\text{H}(\text{CMe}_3)) + \text{N}(\text{CMe}_3)$), 3.4 (SiClMe_2), 2.9 (SiClMe_2), -0.1 ppm (SiMe_3). $\text{C}_{18}\text{H}_{37}\text{Cl}_2\text{N}_2\text{Si}_2\text{Ta}$ (589.53): calcd. C 36.67, H 6.33, N 4.75; found C 36.47, H 6.43, N 4.57.

$[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}t\text{Bu}-\kappa\text{N})(\text{SiMe}_3)\}_2\text{Cl}(\text{N}t\text{Bu})]$ (11): A solution of **3** (0.22 g, 0.48 mmol) in hexane (50 mL) was treated with $t\text{BuNH}_2$ (0.14 g, 1.92 mmol). The mixture was stirred at room temperature for 15 h and then filtered. Solvent was removed from the resulting solution to give **11** as a yellow oil. Yield: 0.14 g (60%). IR (KBr): $\tilde{\nu}$ = 3196 cm^{-1} w, 1448 m, 1359 s, 1250 vs, 1081 vs, 841 vs, 633 m, 499 m. ^1H NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 7.09 (m, 1 H, C_5H_3), 6.64 (m, 1 H, C_5H_3), 6.50 (m, 1 H, C_5H_3), 1.19 (s, 9 H, $t\text{Bu}$), 1.03 (s, 9 H, $t\text{Bu}$), 0.48 (s, 3 H, SiMe_2), 0.42 (s, 3 H, SiMe_2), 0.27 ppm (s, 9 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 137.3 (C^1), 123.1, 122.2, 122.1, 110 (C^3 , C_5H_3), 49.9, 48.5 ($\text{N}(\text{CMe}_3)$), 33.8, 30.6 ($\text{N}(\text{CMe}_3)$), 2.9, 2.7 (SiMe_2), 0.15 ppm (SiMe_3). $\text{C}_{18}\text{H}_{36}\text{ClN}_2\text{NbSi}_2$ (465.03): calcd. C 46.49, H 7.80, N 6.02; found C 46.38, H 7.69, N 5.92.

Reaction of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiClMe}_2)(\text{SiMe}_3)\}_2\text{Cl}_4$ (3) with $\text{LiNH}t\text{Bu}$: $\text{LiNH}t\text{Bu}$ (0.07 g, 0.86 mmol) was added to a solution of **3** (0.20 g, 0.43 mmol) in hexane (30 mL). The reaction mixture was stirred for 20 h and the solvent was then completely removed under vacuum. The resulting oily brown product was characterized as a mixture of complexes **7** and **11** by ^1H NMR spectroscopy.

$[\text{Nb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NH}_2-\kappa^2\text{N}_2\text{N})(\text{SiMe}_3)\}_2\text{Cl}_3]$ (12): A solution of **3** (1.40 g, 3.00 mmol) in toluene (150 mL) was treated at room temperature with a solution of ethylenediamine (0.18 g, 3.00 mmol) and triethylamine (0.61 g, 6.00 mmol) in toluene (20 mL). The reaction mixture was stirred for 48 h and the solvent was evaporated to dryness. The resulting yellow residue was washed with cool hexane (2×5 mL) and the solid was dried in vacuo and identified as **12**. The result was similar when **3** was treated with 2 equiv. of ethylenediamine. Yield: 1.00 g (75%). IR (KBr): $\tilde{\nu}$ = 3249 cm^{-1} m, 3072 w, 1448 w, 1259 vs, 1248 vs, 1089 s, 836 vs, 553 s, 493 m. ^1H NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 6.94 (m, 1 H, C_5H_3), 6.86 (m, 2 H, C_5H_3), 4.60 (br, 2 H, $\text{CH}_2\text{CH}_2\text{NH}_2$), 3.27 (m, 2 H, NCH_2CH_2), 2.68 (m, 2 H, NCH_2CH_2), 0.51 (s, 9 H, SiMe_3), 0.08 (s, 3 H, SiMe_2), 0.05 ppm (s, 3 H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{benzene}$, 25 °C): δ = 140.8 (C^1), 133.4, 130.1, 130, 106 [C^3 , $\text{C}_5\text{H}_3(\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{SiMe}_3)$], 59.7 (NCH_2CH_2), 45.4 (NCH_2CH_2),

Table 3. Crystal data and structure refinement for **3** and **5**.^[a]

	3	5
Formula	C ₁₀ H ₁₈ Cl ₅ NbSi ₂	C ₁₉ H ₂₇ Cl ₅ NNbSi ₂
<i>F</i> _w	464.58	595.76
<i>T</i> [K]	170(2)	200(2)
λ (Mo- <i>K</i> α) [Å]	0.71073	0.71073
Crystal system, space group	monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	monoclinic, <i>P</i> ₂ ₁ / <i>a</i>
<i>a</i> [Å]	7.0559(8)	12.936(2)
<i>b</i> [Å]	12.0123(13)	10.1328(8)
<i>c</i> [Å]	20.8380(15)	20.959(3)
β [°]	92.751(6)	106.01(1)
<i>V</i> [Å ³]	1764.1(3)	2640.8(6)
<i>Z</i>	4	4
ρ_{calcd} [g cm ⁻³]	1.749	1.498
μ [mm ⁻¹]	1.557	1.060
<i>F</i> (000)	928	1208
Crystal size [mm]	0.4 × 0.4 × 0.3	0.43 × 0.23 × 0.2
θ range [deg]	5.05 to 27.50	3.03 to 26.02
Index ranges	−9 ≤ <i>h</i> ≤ 9 −15 ≤ <i>k</i> ≤ 15 25 ≤ <i>l</i> ≤ 27	−15 ≤ <i>h</i> ≤ 15 −11 ≤ <i>k</i> ≤ 12 −25 ≤ <i>l</i> ≤ 25
No. of data collected	21029	14858
No. of unique data [<i>I</i> > 2σ(<i>I</i>)]	3914 [<i>R</i> (int) = 0.2754]	5147 [<i>R</i> (int) = 0.2309]
Absorption correction	none	semiempirical from equivalents
Max. and min. transmission		1.446 and 0.774
Parameters refined	158	248
Goodness-of-fit on <i>F</i> ²	1.133	1.086
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0827 <i>wR</i> ₂ = 0.1986	<i>R</i> ₁ = 0.0924 <i>wR</i> ₂ = 0.1997
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0990 <i>wR</i> ₂ = 0.2072	<i>R</i> ₁ = 0.2300 <i>wR</i> ₂ = 0.2798
Largest diff. peak and hole [e Å ⁻³]	1.602 and −2.254	1.544 and −1.364

[a] $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$.

0.05 (SiMe₃), −3.9 (SiMe₂), −5.4 ppm (SiMe₂). ²⁹Si NMR ([D₆]benzene, 25 °C): δ = −3.9 (SiMe₃), −12.3 ppm (SiMe₂). C₁₂H₂₄Cl₃N₂NbSi₂ (451.78): calcd. C 31.90, H 5.35, N 6.20; found C 32.00, H 5.32, N 5.73.

[Ta{η⁵-C₅H₃(SiMe₂NCH₂CH₂NH₂-κ²N,N)(SiMe₃)Cl₃} (13): A solution of ethylenediamine (0.039 g, 0.65 mmol) and triethylamine (0.13 g, 1.30 mmol) in toluene (10 mL) was slowly added to a solution of **4** (0.36 g, 0.65 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. The volatiles were removed in vacuo and the residue was extracted with hexane (2 × 10 mL). The resulting solution was concentrated and cooled to −20 °C to afford **11** as a pale-yellow crystalline solid. Yield: 0.15 g (40%). IR (KBr): $\tilde{\nu}$ = 3247 cm⁻¹ br. s, 3073 w, 1443 w, 1248 vs, 1089 s, 847 vs, 556 s, 492 m. ¹H NMR ([D₆]benzene, 25 °C): δ = 6.79 (d, ³*J*_{H,H} = 2.1 Hz, 1 H, C₅H₃), 6.67 (d, ³*J*_{H,H} = 2.1 Hz, 2 H, C₅H₃), 4.28 (br, 2 H, CH₂CH₂NH₂), 3.54 (m, 2 H, CH₂CH₂NH₂), 2.63 (m, 2 H, CH₂CH₂NH₂), 0.51 (s, 9 H, SiMe₃), 0.12 (s, 3 H, SiMe₂), 0.09 ppm (s, 3 H, SiMe₂). ¹³C{¹H} NMR ([D₆]benzene, 25 °C): δ = 131.3 (C¹), 129.3, 126.4, 125.6, 105.2 (C³, C₅H₃), 55.4, 45.3 (CH₂CH₂NH₂), 1.4 (SiMe₃), 0.4 (SiMe₂), 0.2 ppm (SiMe₂). ²⁹Si NMR ([D₆]benzene, 25 °C): δ = −4.5 (SiMe₃), −13.2 ppm (SiMe₂). C₁₂H₂₄Cl₃N₂Si₂Ta (539.82): calcd. C 26.70, H 4.48, N 5.19; found C 26.55, H 4.33, N 5.25.

X-ray Structure Determination of 3 and 5: Crystallographic and experimental details of the crystal structure determinations are given in Table 3. Suitable crystals of complexes **3** and **5** were covered with mineral oil and mounted in the N₂ stream of a Bruker-Nonius Kappa CCD diffractometer; data were collected using graphite monochromated Mo-*K* α radiation (λ = 0.71073 Å). Data collections were performed at low temperature (see Table 3), in the case of

compound **3** with an exposure time of 8 s per frame (5 sets; 391 frames) and for compound **5** with an exposure time of 36 s per frame (5 sets; 240 frames). Raw data were corrected for Lorentz and polarization effects.

Both structures were solved by direct methods, completed by the subsequent difference Fourier techniques, and refined by full-matrix least-squares on *F*² with SHELXL-97.^[20] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms. The hydrogen atoms were included from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.^[21]

CCDC-613239 (for **3**) and -613240 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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