

The Versatile Chemistry of Niobium Pentachloride with Aliphatic Amines: Aminolysis, Metal Reduction and C–H Activation

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Received.....; accepted

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Abstract

The reactions of NbCl₅ with limited amounts (1-2 molar equivalents) of a series of primary, secondary and tertiary amines were investigated in dichloromethane as solvent. The 1:1 reaction of NbCl₅ with NHEt₂ cleanly afforded an equimolar mixture of [NbCl₄(NEt₂)₂], **1**, and [NH₂Et₂][NbCl₆], **2a**; the former product constitutes the first example of structurally characterized Nb(V) chlorido-amido complex. The ammonium salts [NH₃ⁿPr][NbCl₆], **2b**, and [NH₂ⁱPr₂][NbCl₆], **2c**, were isolated in 20-30% yields from the 1:1 reactions of NbCl₅ with NH₂ⁿPr and NHⁱPr₂, respectively. C_α-H bond activation and Nb(V) to Nb(IV) reduction took place in the reactions of NbCl₅ with NR₃ (R = Bz, Et; Bz = CH₂Ph). The iminium salt [(PhCH₂)₂N=CHPh][NbCl₆], **3**, and the ammonium ion [NH(CH₂Ph)₃]⁺ were identified as the prevalent species generated from the 1:1 NbCl₅/NBz₃ interaction. [NHEt₃][NbCl₆], **4**, and [NHEt₃]₂[NbCl₆], **5**, were isolated in moderate yields from, respectively, the 1:1 and 1:2 molar reactions of NbCl₅ with NEt₃. The solid state structures of **1**, **2a**, **3**, **4** and **5** were ascertained by single crystal X-ray studies.

Keywords: Niobium pentachloride; Aliphatic Amines; C-H Bond Activation; Ammonium Salts; X-ray structure.

1. Introduction

Easily available niobium pentachloride [1] has been typically employed as starting material for the preparation of a variety of inorganic and organometallic derivatives [2]. In view of the low cost and the relatively low toxicity of the metal element, in the last decade NbCl₅ has found increasing application as an effective Lewis acidic catalytic precursor for several organic reactions [3]. Examples include polymerization of alkenes [4], esterification of alcohols [5], dealkylation of alkyl-aryl ethers [6], epoxidation of allylic alcohols [7], and transformations involving CO₂

activation [8]. The coordination chemistry of NbCl₅ (and other niobium and tantalum pentahalides) with both oxygen [3a] and soft donors [9] has been intensively investigated in the recent times, showing in certain cases unusual activation pathways for the organic ligand [10]. Respect to this preamble, the direct interaction of NbCl₅ with amines, in the absence of further reactants, has been limitedly explored up to now. The formation of simple coordination adducts was hypothesized for the combinations of NbCl₅ with 2,2'-bipyridyl [11] and different ratios of NPh₃, respectively [12]. It was reported that the addition of pyridine to NbCl₅ promoted Nb(V) to Nb(IV) reduction, being 4-pyridyl-pyridinium the major oxidation product of the reaction [13]. Nevertheless, the presence of opportune substituents on the pyridine ring may inhibit the redox process and thus determine different outcomes [14].

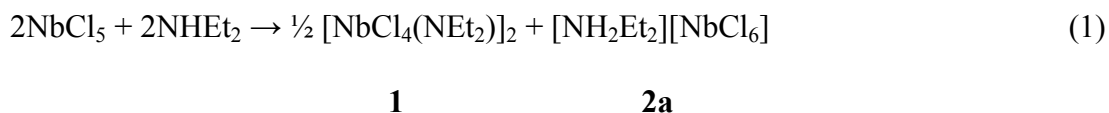
To the best of our knowledge, the chemistry of NbCl₅ with tertiary aliphatic amines and with limited amounts (1-3 molar equivalents) of primary and secondary aliphatic amines has never been described hitherto [15]. The addition to NbCl₅ of an excess of mono alkylamines, NH₂R (R = CMe₃, CHMe₂, Et), was reported to proceed with exhaustive aminolysis, to give dinuclear [NbCl₂(NR)(NHR)(NH₂R)]₂ and mononuclear NbCl₂(NR)(NHR)(NH₂R)₂ complexes containing amido, imido and amino ligands [16].

It should be noted that a series of high valent transition metal chlorides (*e.g.* TiCl₄ [17], MoCl₅ [18], WCl₆ [19]) have been supposed to activate C_α-H bonds belonging to trialkylamines in mild conditions. Although the mechanism is not clear, the TiCl₄/NEt₃ system efficiently works as a catalyst for a variety of organic transformations [20]. Recently, we have elucidated the straightforward 1:1 reaction of WCl₆ with tribenzylamine (NBz₃) [21]; this is initiated by amine to metal monoelectron transfer and affords a 1:1 mixture of the relevant iminium and ammonium ions. Herein, we present the results of our investigation on the 1:1 molar reactions of NbCl₅ with a selection of aliphatic amines (*i.e.*, NH₂ⁿPr, NHEt₂, NHⁱPr₂, NEt₃, NBz₃). The reactions were carried out at room temperature in dichloromethane, *i.e.* a commonly considered poorly

coordinating solvent [22], under strictly anhydrous conditions. The isolated metal products were characterized by analytical and spectroscopic techniques, and by X-ray diffractometry in a number of cases.

2. Results and Discussion

The 1:1 molar reaction of NbCl₅ with *N,N*-diethylamine resulted in the clean formation of equimolar amounts of [NbCl₄(NEt₂)₂], **1**, and [NH₂Et₂][NbCl₆], **2a**, Eqn. 1. The formation of **1** appears to be the result of aminolysis reaction proceeding with release of HCl, which is entrapped by still unreacted NbCl₅/NHEt₂ to give **2a**.



Homoleptic Nb-amido complexes have been usually prepared by metathesis between NbCl₅ and lithium amides [23], although this procedure may be complicated by metal reduction and C–H activation processes [23,24]. To the best of our knowledge, **1** represents the first example of simple chlorido-amido Nb(V) species ever reported.

A crystallization procedure allowed to obtain X-ray quality crystals of both **1** and **2a**, which were mechanically separated. The ORTEP molecular structures of **1** and **2a** are shown in Figures 1 and 2, respectively, while relevant bonding parameters are listed in Tables 1-2.

Compound **1** is a dinuclear one, which occupies an inversion centre in the crystal structure. It is composed by two distorted octahedral Nb(V) units sharing one edge. This originates a “Nb₂Cl₈N₂” framework which was previously found only in the phosphine-imino derivative [NbCl₄(NPPH₃)]₂ [25]. The NEt₂ amido groups occupy equatorial positions in a relative pseudo-*trans* orientation. The Nb(1)–N(1) distance [1.902(2) Å] is in keeping with what recognized in other Nb(V)-NEt₂

frames [24b,26], and intermediate between a Nb–N single bond and a Nb=N double bond [16a,25]. The Nb₂Cl₂ ring is asymmetric [Nb(1)–Cl(4) 2.4695(9) Å; Nb(1)–Cl(4_1) 2.7880(9) Å], due to the *trans* influence of the amido ligands. As expected, the terminal niobium-chlorine bond lengths [Nb(1)–Cl(1) 2.3289(9) Å; Nb(1)–Cl(2) 2.3292(8) Å; Nb(1)–Cl(3) 2.3262(8) Å] are substantially shorter than those associated with the bridging chlorines.

Insert Figure 1

Insert Table 1

The molecular structure of **2a** is composed by an ionic packing of [NH₂Et₂]⁺ cations²⁷ and [NbCl₆][−] anions,²⁸ which have been already described in the literature. The asymmetric unit of the unit cell of **2a** contains one [NH₂Et₂]⁺ cation (on a general position) and two halves of two [NbCl₆][−] anions (located on *m*). Only one of the two independent anions is considered in Figure 2 and Table 2. Hydrogen bonds are present within the crystal involving the N–H groups of the cations and the chlorines of the anions.

Insert Figure 2

Insert Table 2

In accordance with a NMR experiment, the synthesis of **1/2a** is a selective reaction (see Experimental), and **1** exists in solution as a single isomeric form. The two equivalent niobium centers in **1** resonate as a single broad peak in the ⁹³Nb spectrum (CD₂Cl₂ solution), at 214.1 ppm. Instead the ⁹³Nb NMR spectrum of **2a** exhibits the typical sharp resonance due to [NbCl₆][−] close

to 0 ppm.^{3a} The ¹H-NMR spectrum of **2a** contains the resonance due to the N-bound protons at 6.43 ppm; further evidence for the [NH₂] group has been provided by two medium intensity absorptions in the IR spectrum (solid state), at 3162 and 3103 cm⁻¹.

In the attempt of extending the result represented in Eqn. 1, a series of primary (NH₂ⁿPr, NH₂Cy) and secondary amines (NHⁱPr₂, pyrrolidine) were considered. However the 1:1 reactions of NbCl₅ with such amines were not selective, and mixtures of products of difficult identification were obtained. Notwithstanding, [NH₃ⁿPr][NbCl₆], **2b**, and [NH₂ⁱPr₂][NbCl₆], **2c**, were isolated by crystallization procedures in 20-30% yields from NbCl₅/NH₂ⁿPr and NbCl₅/NHⁱPr₂, respectively (Scheme 1). Salient IR and NMR features of **2b-c** resemble those discussed above for **2a**. As well as **2a** (Eqn. 1), the formation of **2b-c** is presumably the consequence of HCl addition to NbCl₅/amine, being HCl produced with aminolysis (see above).

Insert Scheme 1

We moved our attention to trialkylamines. The 1:1 reaction of NbCl₅ with tribenzylamine afforded a mixture of products; the cations [(PhCH₂)₂N=CHPh]⁺ and [NH(CH₂Ph)₃]⁺ were clearly identified in significant, comparable amounts by NMR spectroscopy [21]. Repeated crystallization procedures allowed to isolate X-ray quality crystals of the iminium salt [(PhCH₂)₂N=CHPh][NbCl₆], **3**, in 29% yield (Scheme 2).

Insert Scheme 2

The molecular structure of **3** is shown in Figure 3, with relevant bonding parameters reported in Table 3. Crystals of **3** are isomorphs of the previously reported [(PhCH₂)₂N=CHPh][WCl₆] [21]. They consist of an ionic packing of octahedral [NbCl₆]⁻ anions and [(PhCH₂)₂N=CHPh]⁺ cations.

All bonding parameters are comparable to those previously reported in the literature.^{21,27} The double N(1)–C(15) interaction [1.289(7) Å] is considerably shorter than N(1)–C(1) [1.494(7) Å] and N(1)–C(8) [1.488(7) Å], which are single bonds [29]. Both N(1) [sum angles 360.0(8)°] and C(15) [sum angles 360.1(5)°] regularly display sp² hybridizations.

Insert Figure 3

Insert Table 3

Crystals of **3** showed the typical IR absorption at 1635 cm⁻¹, due to the iminium moiety [21]. Evidence for the presence of the [NbCl₆]⁻ anion was provided in CD₃CN solution by the ⁹³Nb NMR spectrum, showing a resonance at 6.8 ppm.

The unambiguous identification of the [(PhCH₂)₂N=CHPh]⁺ cation points out that amine C_α-H bond activation occurs during the interaction of NbCl₅ with NBz₃. Such activation may act as source of the proton found in [NH(CH₂Ph)₃]⁺. A mixture of the same two cations, *i.e.* [(PhCH₂)₂N=CHPh]⁺ and [NH(CH₂Ph)₃]⁺, was previously generated upon treatment of NBz₃ with WCl₆ [21] or Br₂ [29], respectively. The reaction of WCl₆ with NBz₃ was proposed to take place *via* a multi-step pathway directed by the oxidative power of the metal chloride [W(VI) to W(V) conversion], see Scheme 3.

Insert Scheme 3

The NbCl₅-mediated conversion of NBz₃ into [(PhCH₂)₂N=CHPh]⁺/[NH(CH₂Ph)₃]⁺ may proceed with a mechanism resembling that traced in Scheme 3.

In agreement with such hypothesis and with the detection of a considerable amount of [NbCl₆]⁻

(see above), formation of Nb(IV) tetrachloride should be expected to some extent [10a]. In order to investigate this point, the solid residue obtained from the reaction mixture NbCl₅/NBz₃ by removal of the volatile materials underwent magnetic analysis (see Experimental for details). Interestingly, the analysis revealed some paramagnetism, in accordance with the possible formation of Nb(IV) species. These could not be better identified.

The reactivity of NbCl₅ with NEt₃ was studied by using different stoichiometries. Hence the crystalline compounds [NHEt₃][NbCl₆], **4**, and [NHEt₃]₂[NbCl₆], **5**, were isolated in moderate yields from the 1:1 and 1:2 molar reactions, respectively. Both compounds were characterized by analytical and spectroscopic methods, and by X-ray diffractometry (Scheme 4).

Insert Scheme 4

The structure of **4** (Figure 4, Table 4) is closely related to that of **2a**, being composed of [NHEt₃]⁺ cations and [NbCl₆]⁻ anions, which display intermolecular H-bonds.

Insert Figure 4

Insert Table 4

The structure of **5** (Figure 4, Table 4) is composed of [NHEt₃]⁺ cations and [NbCl₆]²⁻ anions, displaying inter-molecular H-bond [N(1)-H(1) 0.894(17) Å; H(1)⋯Cl(1_3) 2.66(2) Å; N(1)⋯Cl(1_3) 3.397(3) Å; <N(1)H(1)Cl(1_3) 141(2)°; symmetry transformation used: -x, -y+1, -z+1]. The [NbCl₆]²⁻ anion has been, previously to this work, crystallographically characterized only as its [NEt₄]₂[NbCl₆] salt [30]. It displays an octahedral geometry with the Nb-Cl distances [2.3750(10)-2.4402(9) Å] sensibly elongated compared to the related mono-anion [NbCl₆]⁻

[2.3189(6)-2.4006(6) Å in **4**], in view of the different oxidation state of Nb.

Insert Figure 5

Insert Table 5

The main spectroscopic features of **4** resemble those of the related ammonium salts **2a-c**. The magnetic susceptibility observed for **5** was consistent with previous findings on Nb(IV) tetrachloride derivatives [31]. The ^{93}Nb NMR spectrum of **4** showed a large resonance around -500 ppm, attributed to the NbCl_6^{2-} anion.

Probably, the $\text{NEt}_3/\text{NbCl}_5$ system behaves as a source for self-protonation, according to a redox mechanism [17] analogous to that discussed for $\text{NbCl}_5/\text{NBz}_3$ (Scheme 3). The isolation of the Nb(IV) containing salt **5** strongly supports this hypothesis. In addition, magnetic analysis on the solid residue obtained from a 1:1 reaction mixture showed paramagnetism.

We tried to identify the organic counterpart of the possible $\text{C}_\alpha\text{-H}$ activation process leading to NHEt_3^+ (Scheme 4), but spectroscopic analyses were not conclusive. Notwithstanding, the IR spectrum of a 1:1 $\text{NbCl}_5/\text{NEt}_3$ reaction mixture eliminated of the volatiles displayed broad, weak-medium intensity absorptions at 1661 and 1608 cm^{-1} . These absorptions might be ascribable to derivatives comprising the $[\text{C}=\text{N}]$ function, possibly being produced by amine H-elimination (Scheme 5) [21].

Insert Scheme 5

3. Conclusions

This manuscript provides insights into the chemistry of niobium pentachloride with aliphatic amines, which was scarcely explored in the past. The 1:1 molar reactions of NbCl₅ with mono- and dialkylamines generally proceed with facile aminolysis to give mixtures of metal products. Among the latter, ammonium salts have been isolated in a number of cases as a result of the *in situ* production of HCl. The first structurally-characterized Nb(V) chlorido amido complex has been accessed by the straightforward 1:1 molar reaction of NbCl₅ with NHEt₂. Evidence has been collected for the occurrence of electron interchange in the reactions of NbCl₅ with trialkylamines, resulting in reduction of the metal centre and amine C–H bond activation.

4. Experimental

4.1. General procedures

Warning: all of the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at 140°C prior to use, evacuated (10⁻² mmHg) and then filled with argon. NbCl₅ was purchased from Strem (99+% purity), sublimed before use and stored in sealed tubes under argon atmosphere. Once isolated, the metal products were conserved in sealed glass tubes under argon. Amines were commercial products (Sigma-Aldrich) which were distilled over BaO and then stored under argon atmosphere. Solvents (Sigma-Aldrich) were distilled from appropriate drying agents. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. Magnetic susceptibilities (reported per Nb atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König [32]. NMR spectra were recorded at 293 K on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ¹H and ¹³C were referenced to the non-deuterated aliquot of the solvent, while the chemical shifts for ⁹³Nb were

referenced to $[\text{NEt}_4][\text{NbCl}_6]$ as external reference. Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method [33] on solutions prepared by dissolution of the solids in aqueous KOH and heated at boiling temperature for 72 hours, followed by cooling to room temperature and addition of HNO_3 up to neutralization.

4.2. Reactivity of NbCl_5 with NH_2Et_2 : synthesis and isolation of $[\text{NbCl}_4(\text{NEt}_2)]_2$, **1**, $[\text{NH}_2\text{Et}_2][\text{NbCl}_6]$, **2a**.

A suspension of NbCl_5 (383 mg, 1.42 mmol) in CH_2Cl_2 (ca. 20 mL) was treated with NH_2Et_2 (0.147 mL, 1.42 mmol). The mixture was allowed to stir at room temperature for 40 h. The final dark-red solution was concentrated to ca. 5 mL, layered with hexane and settled down at -30°C . A large crop of mixed dark-red (**1**) and yellow (**2a**) crystals was collected after one week, then the crystals were mechanically separated.

$[\text{NbCl}_4(\text{NEt}_2)]_2$, 1. Yellow solid, yield 179 mg (41%). Anal. Calcd for $\text{C}_4\text{H}_{10}\text{Cl}_4\text{NNb}$: C, 15.66; H, 3.28; N, 4.56; Cl, 46.22. Found: C, 15.56; H, 3.34; N, 4.51; Cl, 46.01. ^1H NMR (CD_2Cl_2): $\delta = 3.38$ (q, 2 H, $^3J_{\text{HH}} = 6.85$ Hz, CH_2); 1.44 (m, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 44.4$ (CH_2); 11.2 (CH_3) ppm. ^{93}Nb NMR (CD_2Cl_2): $\delta = 214.1$ ($\Delta\nu^{1/2} = 3 \cdot 10^3$ Hz) ppm.

$[\text{NH}_2\text{Et}_2][\text{NbCl}_6]$, 2a. Dark-red solid, yield 237 mg (44%). Anal. Calcd for $\text{C}_4\text{H}_{12}\text{Cl}_6\text{NNb}$: C, 12.65; H, 3.18; N, 3.69; Cl, 56.01. Found: C, 12.55; H, 3.07; N, 3.77; Cl, 55.87. IR (solid state): $\nu = 3162\text{m-br}, 3103\text{m}$ ($\nu_{\text{N-H}}$) cm^{-1} . ^1H NMR (CD_2Cl_2): $\delta = 6.43$ (br, 2 H, NH_2); 4.90 (q, 2 H, $^3J_{\text{HH}} = 6.85$ Hz, CH_2); 1.52 (m, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 55.6$ (CH_2); 11.6 (CH_3) ppm. ^{93}Nb NMR (CD_2Cl_2): $\delta = 8.0$ ($\Delta\nu^{1/2} = 2 \cdot 10^2$ Hz) ppm.

In a different experiment, NbCl_5 (0.35 mmol), NH_2Et_2 (0.35 mmol), CD_2Cl_2 (0.6 mL) and CHCl_3 (0.35 mmol) were introduced into a NMR tube. The tube was sealed, briefly shaken in order to

homogenize the content, and then stored at room temperature for one week. Subsequent NMR analysis revealed the clean presence of **1**, **2a** and CHCl_3 (approximate ratio 0.4:0.5:1).

4.3. Synthesis and isolation of $[\text{NH}_3^n\text{Pr}][\text{NbCl}_6]$, **2b**, and $[\text{NH}_2^i\text{Pr}_2][\text{NbCl}_6]$, **2c**.

General procedure: NbCl_5 , suspended in CH_2Cl_2 (ca. 15 mL), was allowed to react with the appropriate amine for 48 h. The mixture was filtered off in order to remove some solid, then it was layered with hexane and settled aside at $-30\text{ }^\circ\text{C}$ for one week. Thus **2b,c** were recovered as microcrystalline materials. The crystallization liquors were isolated and dried in vacuo: the resulting residues were analyzed by IR (solid state) and NMR (CDCl_3 solution), showing the presence of mixtures of products which were not identified.

$[\text{NH}_3^n\text{Pr}][\text{NbCl}_6]$, 2b. Pale-yellow solid, from NbCl_5 (250 mg, 0.925 mmol) and NH_2^nPr (0.076 mL, 0.924 mmol). Yield 74 mg (22%). Anal. Calcd for $\text{C}_3\text{H}_{10}\text{Cl}_6\text{NNb}$: C, 9.85; H, 2.76; N, 3.83; Cl, 58.16. Found: C, 9.66; H, 2.88; N, 3.77; Cl, 58.03. IR (solid state): $\nu = 3223\text{m-br}, 3160\text{m}, 3127\text{m}$ ($\nu_{\text{N-H}}$) cm^{-1} . ^1H NMR (CDCl_3): $\delta = 6.04$ (br, 3 H, NH); 2.89 (br, 2 H, CH_2); 1.63 (br, 2 H, CH_2); 0.95 (br, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 41.9$ (CH_2); 20.1 (CH_2); 10.1 (CH_3) ppm. ^{93}Nb NMR (CDCl_3): $\delta = -0.1$ ($\Delta\nu^{1/2} = 1 \cdot 10^2$ Hz) ppm.

$[\text{NH}_2^i\text{Pr}_2][\text{NbCl}_6]$, 2c. Grey solid, from NbCl_5 (290 mg, 1.07 mmol) and NH^iPr_2 (0.150 mL, 1.07 mmol). Yield 127 mg (29%). Anal. Calcd for $\text{C}_6\text{H}_{16}\text{Cl}_6\text{NNb}$: C, 17.67; H, 3.95; N, 3.43; Cl, 52.16. Found: C, 17.55; H, 4.04; N, 3.38; Cl, 52.27. IR (solid state): $\nu = 3131\text{s}, 3095\text{s}$ ($\nu_{\text{N-H}}$) cm^{-1} . ^1H NMR (CDCl_3): $\delta = 5.70$ (br, 2 H, NH); 3.75 (m, 2 H, CH); 1.58 (m, 12 H, CH_3) ppm. ^{93}Nb NMR (CDCl_3): $\delta = 7.0$ ($\Delta\nu^{1/2} = 2 \cdot 10^3$ Hz) ppm.

4.4. Reactivity of NbCl_5 with $\text{N}(\text{CH}_2\text{Ph})_3$: synthesis and isolation of $[(\text{PhCH}_2)_2\text{N}=\text{CHPh}][\text{NbCl}_6]$, **3**, and identification of $[\text{NH}(\text{CH}_2\text{Ph})_3]^+$.

The reaction of NbCl₅ (320 mg, 1.18 mmol) with N(CH₂Ph)₃ (341 mg, 1.19 mmol) was carried out with a procedure analogous to that described for the synthesis of **1/2a**. Crystallization from CH₂Cl₂/hexane at -30 °C afforded **3** as yellow crystals. Yield 205 mg (29%). Anal. Calcd for C₂₁H₂₀Cl₆NNb: C, 42.60; H, 3.41; N, 2.37; Cl, 35.93. Found: C, 42.47; H, 3.48; N, 2.29; Cl, 35.80. IR (solid state): $\nu = 1635\text{w-m (}\nu_{\text{C=N}}\text{) cm}^{-1}$. ¹H NMR (CD₃CN): $\delta = 9.22$ (s, 1 H, HC=N); 7.94, 7.73, 7.46 (15 H, Ph); 5.40, 5.23 (s, 4 H, CH₂) ppm. ¹³C NMR{¹H} (CD₃CN): $\delta = 174.4$ (HC=N); 136.9, 132.8-128.3 (Ph); 64.9, 56.7 (CH₂) ppm. ⁹³Nb NMR (CD₃CN): $\delta = 6.8$ ($\Delta\nu^{1/2} = 2 \cdot 10^2$ Hz) ppm.

In a different experiment, NbCl₅ (0.35 mmol), N(CH₂Ph)₃ (0.35 mmol), CD₂Cl₂ (0.6 mL) and CHCl₃ (0.35 mmol) were introduced into a NMR tube. The tube was sealed, briefly shaken in order to homogenize the content, and then stored at room temperature for one week. Subsequent NMR analysis revealed the presence of **3**, [NH(CH₂Ph)₃]⁺ [δ (¹H, CD₃CN) = 7.56, 7.33 (15 H, Ph); 6.53 (br, 1 H, NH); 4.42 (s, 6 H, CH₂) ppm; δ (¹³C, CD₃CN) = 131.4-127.8 (Ph); 57.4 (CH₂) ppm] and CHCl₃ (approximate ratio 0.3:0.3:1). ⁹³Nb spectrum (in CD₃CN) exhibited resonances at 6.8 ($\Delta\nu^{1/2} = 2 \cdot 10^2$ Hz) and -350 ($\Delta\nu^{1/2} = 2 \cdot 10^3$ Hz) ppm.

Then the tube was opened and the content was transferred into a Schlenk tube. The volatile materials were removed in vacuo. The yellow-orange residue underwent magnetic analysis: $\chi_M = 4.81 \times 10^{-5}$ cgsu.

4.5. Synthesis and isolation of [NHEt₃][NbCl₆], **4**, and [NHEt₃]₂[NbCl₆], **5**.

NEt₃ (0.115 mL, 0.825 mmol) was added dropwise to a suspension of NbCl₅ (230 mg, 0.851 mmol) in CH₂Cl₂ (15 mL). Immediate colour change to dark-brown was observed, and the mixture was allowed to stir at room temperature for additional 24 h. The final mixture was filtered in order to remove a minor amount of solid. The dark-brown solution was concentrated to ca. 5 mL, layered with hexane and settled aside at -30 °C. An ochre yellow microcrystalline material was

recovered after 48 h. Yield 87 mg (26%). Anal. Calcd for C₆H₁₆Cl₆NNb: C, 17.67; H, 3.95; N, 3.43; Cl, 52.16. Found: C, 17.78; H, 3.84; N, 3.52; Cl, 52.03. IR (solid state): $\nu = 3132\text{m}$ ($\nu_{\text{N-H}}$), 3007w, 2988w, 2942w, 1599w, 1469s, 1455s, 1448s-sh, 1395m, 1354w, 1285w, 1171w, 1155w, 1056w, 1029m, 1009m, 832s, 807vs, 790s, 733s cm⁻¹. ¹H NMR (CD₂Cl₂): $\delta = 6.11$ (br, 1 H, NH); 3.29 (m, 6 H, CH₂); 1.45 (m, 9 H, CH₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 48.6$ (CH₂); 9.8 (CH₃) ppm. ⁹³Nb NMR (CD₂Cl₂): $\delta = 6.1$ ($\Delta\nu^{1/2} = 4 \cdot 10^2$ Hz) ppm.

The reaction of NbCl₅ (290 mg, 1.07 mmol) with NEt₃ (0.300 mL, 2.15 mmol) was carried out with a procedure analogous to that described for the synthesis of **4**. Crystallization from CH₂Cl₂/hexane at -30 °C afforded red crystals of **5** suitable for X-ray analysis. Yield 203 mg, 37%. Anal. Calcd for C₁₂H₃₂Cl₆N₂Nb: C, 28.26; H, 6.32; N, 5.49; Cl, 41.71. Found: C, 28.12; H, 6.27; N, 5.53; Cl, 41.48. IR (solid state): $\nu = 3088\text{s}$, 2981m, 1468vs, 1456s, 1415m, 1390s, 1360w, 1287w, 1157m, 1062w, 1012s, 939s, 839vs, 804vs, 729m cm⁻¹. ¹H NMR (CD₃CN): $\delta = 9.0$ (br, 1 H, NH); 3.13 (m, 6 H, CH₂); 1.29 (t, ³J_{HH} = 7.15 Hz, 9 H, CH₃) ppm. ¹³C{¹H} NMR (CD₃CN): $\delta = 46.6$ (CH₂); 8.3 (CH₃) ppm. ⁹³Nb NMR (CD₃CN): $\delta = -495$ ($\Delta\nu^{1/2} = 1.1 \cdot 10^3$ Hz) ppm. Magnetic measurement: $\chi_{\text{M}}^{\text{corr}} = 6.68 \times 10^{-4}$ cgsu, $\mu_{\text{eff}} = 1.27$ BM.

In a different experiment, NbCl₅ (0.35 mmol) and NEt₃ (0.35 mmol) were allowed to react in CH₂Cl₂ (10 mL). The final dark-red/brown mixture was dried under vacuo. Subsequent IR spectrum recorded on the dark-brown residue displayed bands at 1661 (w) and 1608 (w-m) cm⁻¹.

Magnetic analysis was as follows: $\chi_{\text{M}} = 3.06 \times 10^{-4}$ cgsu.

4.6. X-ray crystallographic studies.

Crystal data and collection details for [NbCl₄(NEt₂)₂], **1**, [NH₂Et₂][NbCl₆], **2a**, [(PhCH₂)₂N=CHPh][NbCl₆], **3**, [NHET₃][NbCl₆], **4**, and [NHET₃]₂[NbCl₆], **5**, are reported in Table 6. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with

a CCD detector and using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).³⁴ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .³⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The H-atoms bonded to N-atoms in **4** and **5** have been located in the Fourier map and refined with the N-H distances restrained to 0.91 \AA (s.u. 0.02). The H-atoms bonded to N(1) in **2a** were initially located in the Fourier map but, then, they were refined with a riding model. The asymmetric unit of the unit cell of **1** contains half of a molecule located on an inversion centre. The asymmetric unit of the unit cell of **2a** contains one $[\text{NH}_2\text{Et}_2]^+$ cation (on a general position) and two halves of two $[\text{NbCl}_6]^-$ anions (located on m). The asymmetric unit of the unit cell of **4** contains two independent anions and cations (located on general positions). The crystals of **3** are isomorphs of the previously reported $[(\text{PhCH}_2)_2\text{N}=\text{CHPh}][\text{WCl}_6]$.²¹ The asymmetric unit of the unit cell of **5** contains one $[\text{NHEt}_3]^+$ cation (on a general position) and half of a $[\text{NbCl}_6]^{2-}$ anions (located on an inversion centre).

Insert Table 6 about here

Supporting Information. CCDC contain the supplementary crystallographic data for the X-ray studies reported in this paper. CCDC 1052819 (**1**), 1052820 (**2a**), 1052821 (**3**), 1052822 (**4**) and 1052823 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: xxxxxxxxxxxxxxxxxxxx.

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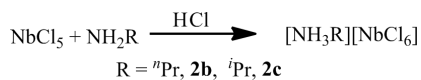
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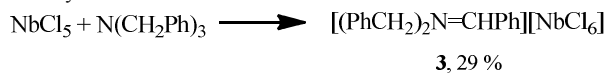
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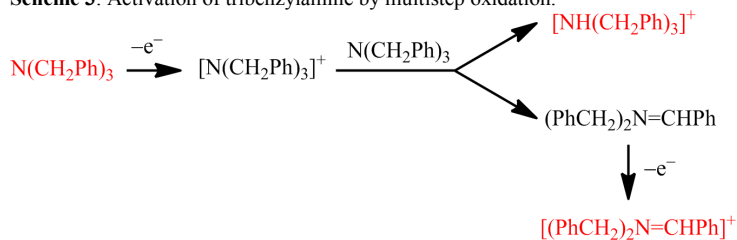
Scheme 1. Formation of $[\text{NbCl}_6]^-$ ammonium salts from NbCl_5 /amines.



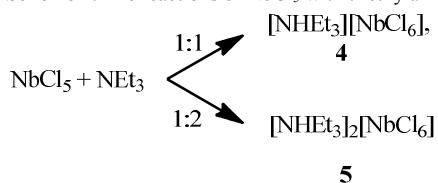
Scheme 2. C–H bond activation in the reaction of NbCl_5 with tribenzylamine.



Scheme 3. Activation of tribenzylamine by multistep oxidation.



Scheme 4. The reactions of NbCl_5 with triethylamine.



Scheme 5. Possible activation of triethylamine (C–H bond activation and H intermolecular migration) during the reaction with NbCl_5 .

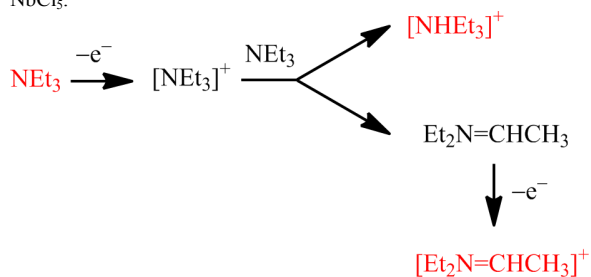


Figure 1. Molecular structure of $[\text{NbCl}_4(\text{NEt}_2)_2]$, **1**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level. Symmetry operations used to generate equivalent atoms: $-x, -y+1, -z+2$.

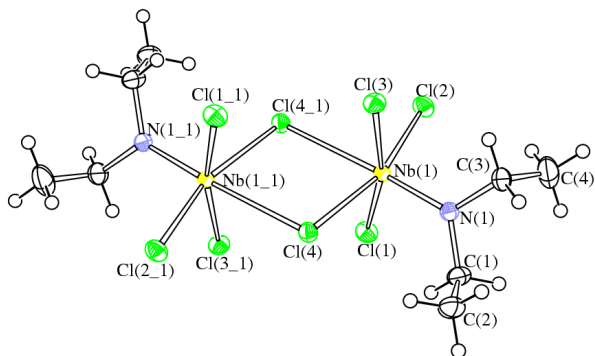


Figure 2. Molecular structure of $[\text{NH}_2\text{Et}_2][\text{NbCl}_6]$, **2a**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. Symmetry operations used to generate equivalent atoms: $-x+1, y, z$.

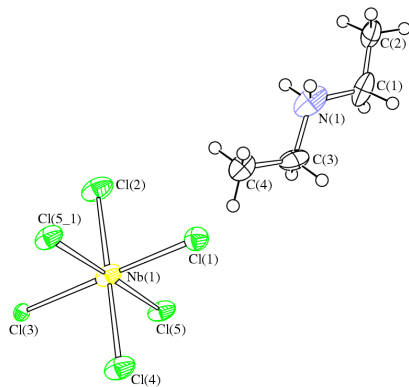


Figure 3. Molecular structure of $[(\text{PhCH}_2)_2\text{N}=\text{CHPh}][\text{NbCl}_6]$, **3**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level.

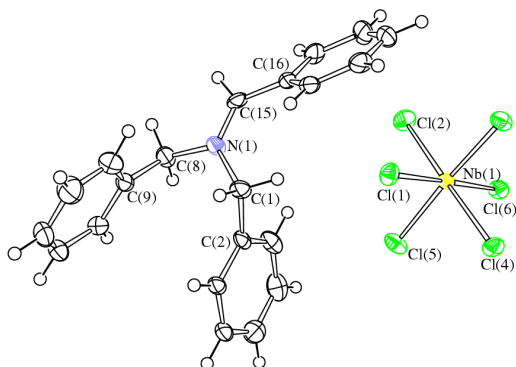


Figure 4. Molecular structure of $[\text{NHEt}_3][\text{NbCl}_6]$, **4**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level.

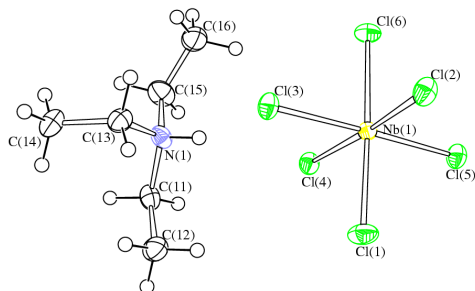


Figure 5. Molecular structure of $[\text{NHEt}_3]_2[\text{NbCl}_6]$, **5**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. Symmetry operations used to generate equivalent atoms: $-x, -y+1, -z$.

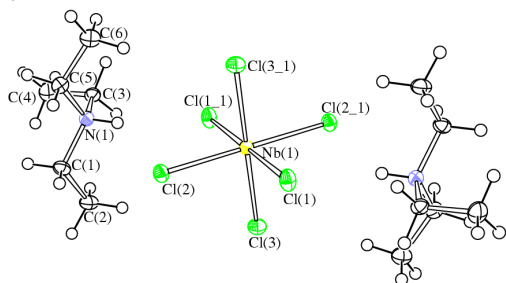


Table 1. Selected bond distances (Å) and angles (°) for **1**.

Nb(1)-N(1)	1.902(2)	Nb(1)-Cl(1)	2.3289(9)
Nb(1)-Cl(2)	2.3292(8)	Nb(1)-Cl(3)	2.3262(8)
Nb(1)-Cl(4)	2.4695(9)	Nb(1)-Cl(4_1)	2.7880(9)
N(1)-C(1)	1.494(3)	N(1)-C(3)	1.495(3)
C(1)-C(2)	1.511(4)	C(3)-C(4)	1.525(4)
Cl(1)-Nb(1)-Cl(3)	166.25(2)	Cl(2)-Nb(1)-Cl(4)	162.72(2)
N(1)-Nb(1)-Cl(4_1)	174.63(6)	Cl(4)-Nb(1)-Cl(4_1)	78.32(3)
Nb(1)-Cl(4)-Nb(1_1)	101.68(3)	Nb(1)-N(1)-C(1)	124.93(16)
Nb(1)-N(1)-C(3)	122.82(17)	C(1)-N(1)-C(3)	112.2(2)

Table 2. Selected bond distances (Å) and angles (°) for **2a**.

Nb(1)-Cl(1)	2.358(6)	Nb(1)-Cl(2)	2.350(5)
Nb(1)-Cl(3)	2.442(5)	Nb(1)-Cl(4)	2.351(5)
Nb(1)-Cl(5)	2.416(4)	Nb(1)-Cl(5_1)	2.416(4)
N(1)-C(1)	1.51(2)	N(1)-C(3)	1.53(2)
C(1)-C(2)	1.44(2)	C(3)-C(4)	1.46(2)
Cl(1)-Nb(1)-Cl(3)	179.54(18)	Cl(2)-Nb(1)-Cl(4)	179.5(3)
Cl(5)-Nb(1)-Cl(5_1)	179.02(19)	C(2)-C(1)-N(1)	112.1(14)
C(1)-N(1)-C(3)	118.2(14)	N(1)-C(3)-C(4)	112.7(13)

Table 3. Selected bond distances (Å) and angles (°) for **3**.

Nb(1)-Cl(1)	2.3298(16)	Nb(1)-Cl(2)	2.3360(16)
Nb(1)-Cl(3)	2.3397(16)	Nb(1)-Cl(4)	2.3636(15)
Nb(1)-Cl(5)	2.3680(16)	Nb(1)-Cl(6)	2.3694(15)
N(1)-C(1)	1.494(7)	C(1)-C(2)	1.503(8)
N(1)-C(8)	1.488(7)	C(8)-C(9)	1.505(8)
N(1)-C(15)	1.289(7)	C(15)-C(16)	1.447(7)
Cl(1)-Nb(1)-Cl(6)	178.55(6)	Cl(2)-Nb(1)-Cl(4)	176.83(6)
Cl(5)-Nb(1)-Cl(3)	176.10(6)	C(1)-N(1)-C(15)	123.5(5)
C(1)-N(1)-C(8)	117.3(4)	C(8)-N(1)-C(15)	119.2(5)
N(1)-C(15)-C(16)	129.7(5)	N(1)-C(1)-C(2)	112.5(4)
N(1)-C(8)-C(9)	113.4(5)		

Table 4. Selected bond distances (Å) and angles (°) for **4**.

Nb(1)-Cl(1)	2.3294(6)	Nb(1)-Cl(2)	2.3289(6)
Nb(1)-Cl(3)	2.3833(6)	Nb(1)-Cl(4)	2.4006(6)
Nb(1)-Cl(5)	2.3189(6)	Nb(1)-Cl(6)	2.3445(6)
N(1)-C(11)	1.499(3)	N(1)-C(13)	1.509(3)
N(1)-C(15)	1.481(3)	C(11)-C(12)	1.504(3)
C(13)-C(14)	1.513(3)	C(15)-C(16)	1.511(3)
Cl(1)-Nb(1)-Cl(6)	177.88(2)	Cl(2)-Nb(1)-Cl(4)	176.30(2)
Cl(3)-Nb(1)-Cl(5)	178.12(2)	C(11)-N(1)-C(13)	113.60(18)
C(11)-N(1)-C(15)	109.31(18)	C(13)-N(1)-C(15)	114.80(19)

Table 5. Selected bond distances (Å) and angles (°) for **5**.

Nb(1)-Cl(1)	2.4276(9)	Nb(1)-Cl(2)	
	2.4402(9)		
Nb(1)-Cl(3)	2.3750(10)		
N(1)-C(1)	1.502(4)	N(1)-C(3)	1.511(4)
N(1)-C(5)	1.511(4)	C(1)-C(2)	1.517(4)
C(3)-C(4)	1.507(4)	C(5)-C(6)	1.509(4)
Cl(1)-Nb(1)-Cl(1_1)	180.0	Cl(2)-Nb(1)-Cl(2_2)	180.0
Cl(3)-Nb(1)-Cl(3_3)	180.0	C(1)-N(1)-C(3)	113.8(2)
C(1)-N(1)-C(5)	109.8(2)	C(3)-N(1)-C(5)	113.5(2)

Table 6. Crystal data and details of the structure refinement for [NbCl₄(NEt₂)₂], **1**, [NH₂Et₂][NbCl₆], **2a**, [(PhCH₂)₂N=CHPh][NbCl₆], **3**, [NHEt₃][NbCl₆], **4**, and [NHEt₃]₂[NbCl₆], **5**.

Complex	1	2a	3	4	5
Formula	C ₈ H ₂₀ Cl ₈ N ₂ Nb ₂	C ₄ H ₁₂ Cl ₆ NNb	C ₂₁ H ₂₀ Cl ₆ NNb	C ₆ H ₁₆ Cl ₆ NNb	C ₁₂ H ₃₂ Cl ₆ N ₂ Nb
<i>F</i> _w	613.68	379.76	591.99	407.81	510.01
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)	100(2)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Cmc</i> 2 ₁	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	7.764(2)	14.479(10)	10.319(3)	14.2189(14)	9.792(3)
<i>b</i> , Å	12.200(3)	14.570(10)	10.964(3)	15.8578(16)	10.514(3)
<i>c</i> , Å	11.346(3)	12.427(9)	11.321(3)	14.4037(14)	10.634(3)
α , °	90	90	68.825(3)	90	90
β , °	106.360(3)	90	85.270(3)	112.6850(10)	100.167(4)
γ , °	90	90	85.626(3)	90	90
Cell Volume, Å ³	1031.1(5)	2622(3)	1188.8(5)	2996.5(5)	1077.6(6)
<i>Z</i>	2	8	2	8	2
<i>D</i> _c , g cm ⁻³	1.977	1.924	1.654	1.808	1.572
μ , mm ⁻¹	2.139	2.097	1.190	1.841	1.298
<i>F</i> (000)	600	1488	592	1616	522
Crystal size, mm	0.25×0.20×0.15	0.16×0.12×0.10	0.15×0.13×0.11	0.21×0.16×0.12	0.22×0.16×0.12
θ limits, °	2.51–27.00	1.98–25.02	1.93–26.00	1.55–28.00	2.61–27.00
Reflections collected	10978	7631	11759	33766	11352
Independent reflections	2247 [<i>R</i> _{int} = 0.0477]	2406 [<i>R</i> _{int} = 0.0985]	4620 [<i>R</i> _{int} = 0.0404]	7122 [<i>R</i> _{int} = 0.0395]	2355 [<i>R</i> _{int} = 0.0631]
Data / restraints / parameters	2247 / 0 / 91	2406 / 1 / 121	4620 / 0 / 262	7122 / 2 / 261	2355 / 1 / 101
Goodness on fit on <i>F</i> ²	1.101	1.021	1.120	1.020	1.020
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0244	0.0700	0.0558	0.0246	0.0363
<i>wR</i> ₂ (all data)	0.0582	0.2018	0.1066	0.0582	0.0835
Largest diff. peak and hole, e Å ⁻³	0.420 / -0.516	2.741 / -1.145	0.710 / -0.673	0.831 / -0.367	1.010 / -0.606