The Reactivity of Niobium and Tantalum Pentahalides with Imines

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Abstract

The reactivity of NbCl$_5$, NbF$_5$ and TaCl$_5$ with a selection of commercial imines was investigated for the first time by using dichloromethane as reaction medium. NbCl$_5$ reacted with Ph$_2$C=NH, in 1:2 molar ratio, affording [Ph$_2$C=NH$_2$][NbCl$_5$(N=CPh$_2$)], 1, in 55% yield, as result of imine self-protonation. The iminium salt [PhCH=NH$^t$Bu][NbCl$_6$], 2, was isolated in 52% yield from NbCl$_5$ and PhCH=N$^t$Bu (1:1 molar ratio), while a low yield of [Bu$_2$C=NH$_2$][NbCl$_6$], 3, was identified from NbCl$_5$/Bu$_2$C=NH. The 1:1 reactions of NbF$_5$ with Ph$_2$C=NH and PhCH=N$^t$Bu were accompanied by electron interchange and led to the isolation of the salts [Ph$_2$C=NH$_2$][NbF$_6$], 4, and [PhCH=NH$^t$Bu][NbF$_6$], 5, respectively, in ca. 50% yields. Few crystals of [Ph$_2$C=NH$_2$]$_2$[Ta$_2$Cl$_{10}$O], 6, were recovered from TaCl$_5$/Ph$_2$C=NH, the anion being probably generated by the action of adventitious water. Compounds 1-6 were characterized by elemental analysis, IR and NMR spectroscopy. The structures of 1, 4 and 6 were ascertained by X-ray diffraction studies.

Keywords: Niobium Pentahalides, Tantalum Pentahalides, Imines, Benzophenone Imine, Azavinylidene

1. Introduction

The chemistry of niobium and tantalum pentahalides, MX$_5$ [1], has experienced a significant progress in the last decade, encouraged by cost effectiveness, low toxicity of the metal elements and unusual reactivity patterns [2]. As a matter of fact, MX$_5$ have found increasing application as catalytic precursors in metal mediated organic synthesis [3], and also many aspects of the coordination chemistry with oxygen [4], nitrogen [5] and soft donors [6] have been elucidated in the recent years. In general, the polynuclear structure of MX$_5$ undergoes cleavage by the addition of one equivalent of a neutral Lewis base (L) in a non coordinating solvent; this cleavage usually takes
place selectively in either symmetric or asymmetric mode, depending on the nature of both X and L [4c, 5c]. In the case of symmetric cleavage, neutral complexes of formula MX₅L can be generated, whereas the ionic complexes [MX₄L₂][MX₆] are the result of the asymmetric rupture [7]. The [MX₅]⁻ anions are quite stable, the stability decreasing on moving down the halogen group [4c], and are suitable for the stabilization of organic cations, including otherwise reactive cations [2b, 4b-c, 8]. In those cases in which the reactions of MX₅ with organic compounds are non selective, the formation of [MX₆]⁻ salts of protonated species is sometimes observed [9]. Usually, both adventitious water and the activation of the organic substrate are possible sources of protonation.

To the best of our knowledge, the direct interaction of MX₅ with imines has not been investigated heretofore. Herein, we describe the results of our study on the reactions of MX₅ with limited amounts (1-2 molar equivalents) of three commercial imines, i.e. benzophenone imine, N-benzylidene-tert-butylamine and 2,2,4,4-tetramethyl-3-pentanone imine. The reactions were carried out in dichloromethane, i.e. a non coordinating, privileged solvent for studying the coordination chemistry of high valent transition metal halides [4c-d, 10]. The isolated metal products were characterized by analytical and spectroscopic techniques, and by X-ray diffraction in a number of cases.

2. Results and Discussion

The reaction of NbCl₅ with a two-fold excess of benzophenone imine, in dichloromethane at room temperature, led to the isolation in 55% yield of the salt [Ph₂C=NH₂][NbCl₅(N=CPh₂)], 1, that was characterized by analytical and spectroscopic methods, and X-ray diffraction (Scheme 1). Compound 1 was obtained, although with minor yield, also by using an imine/Nb 1:1 molar ratio.

\[
\text{NbCl}_5 + \text{Ph}_2\text{C}=\text{NH} \rightarrow [\text{Ph}_2\text{C}=\text{NH}_2][\text{NbCl}_5(\text{N=CPh}_2)]
\]

Scheme 1. The reaction of NbCl₅ with benzophenone imine.
Crystals suitable for X-ray analysis were collected from a CH₂Cl₂/hexane mixture maintained at −30 °C. The molecular structure of 1 (Figure 1 and Table 1) consists of ionic packings of [Ph₂C=N=NH₂]⁺ cations and [NbCl₅(N=CPh₂)]⁻ anions, the iminium N-protons being involved in H-bonds with the halide ligands of the anion (Table 4). The benzophenone iminium cation was previously X-ray characterized [11], while the [NbCl₅(N=CPh₂)]⁻ anion is unprecedented. It consists of an octahedral Nb(V) centre bonded to five chlorides and one diphenylmethyleneamido ligand, and represents the first structurally characterized Nb(V) complex containing an azavinylidene (methyleneamido) ligand [12]. The C(1)–N(1) distance [1.290(4) Å] is typical for a double bond [13] and, accordingly, C(1) displays a perfect sp² hybridization [sum angles at C(1) 360.0(5)°]. The Nb(1)–N(1) distance [1.862(2) Å] is intermediate between a single and a double bond [5a, 14]. The (N=CPh₂)⁻ ligand shows a linear coordination [C(1)-N(1)-Nb(1) 176.3(2)°]. Both linear and bent coordination modes have been observed for a terminal azavinylidene ligand with miscellaneous transition metals [15].

Figure 1. View of the molecular structure of [Ph₂C=N=NH₂][NbCl₅(N=CPh₂)], 1, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

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

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(1)–Cl(1)</td>
<td>2.5258(8)</td>
<td>Nb(1)–Cl(2)</td>
<td>2.3552(9)</td>
</tr>
<tr>
<td>Nb(1)–Cl(3)</td>
<td>2.3893(9)</td>
<td>Nb(1)–Cl(4)</td>
<td>2.4143(8)</td>
</tr>
<tr>
<td>Nb(1)–Cl(5)</td>
<td>2.4005(9)</td>
<td>Nb(1)–N(1)</td>
<td>1.862(2)</td>
</tr>
<tr>
<td>C(1)–N(1)</td>
<td>1.290(4)</td>
<td>C(20)–N(2)</td>
<td>1.293(4)</td>
</tr>
</tbody>
</table>
The IR spectrum of 1 (solid state) displays a broad band envelope around 1660 cm$^{-1}$, probably accounting for both [C=N] moieties. In the $^1$H NMR spectrum (CD$_2$Cl$_2$ solution), the N-bound protons resonate at 11.4 ppm. Major $^{13}$C NMR features are represented by the resonances of the iminium and azavinylidene carbons, occurring at 182.1 and 156.9 ppm, respectively. In the $^{93}$Nb NMR spectrum, the presence of the [NbCl$_6$]$^-$ anion is indicated by a sharp resonance at 10.4 ppm [4c,5a,7,8], while the niobium nucleus belonging to the cation was not observed.

The formation of 1 appears the result of self-ionization of benzophenone imine, via intermolecular H$^+$ migration induced by the Lewis acidic Nb(V) centre. Azavinylidene ligands have been obtained from a variety of building blocks, especially ketimino derivatives LiNCRR$'$ [12a, 16]. On the other hand, the in situ imine deprotonation has been more rarely observed. For instance, the [M=C=CPh$_2$] unit was previously in situ generated from benzophenone imine with a Ti(IV) complex [17], a Ru(IV) porphyrin complex [18] and a Pd(II) acetato complex in the presence of [NBu$_4$]OH [19].

We moved to extend our study to the reactivity of NbCl$_5$ with other imines. The iminium salt [PhCH=NH$^t$Bu][NbCl$_6$], 2, was isolated from NbCl$_5$ and one equivalent of N-benzylidene-tert-butylamine in 52% yield, and no other products could be identified (Scheme 2). The IR spectrum of 2 clearly shows the band related to the iminium function at 1650 cm$^{-1}$. Salient NMR features (CD$_3$CN solution) are the resonances due to the NH (10.85 ppm) and iminium groups ($^1$H: 8.78 ppm; $^{13}$C: 168.1 ppm). The $^{93}$Nb NMR resonance of the [NbCl$_6$]$^-$ anion has been found at −0.7
ppm. The observed variability of the chemical shift due to [NbCl₆]⁻ in a restricted ppm range may be an effect of the solvent and/or the nature of the cation.

Also the 1:1 molar reaction of NbCl₅ with 2,2,4,4-tetramethyl-3-pentanone imine led to the low yield isolation of a solid containing the relevant iminium cation, in admixture with non identified secondary products (Scheme 2). The iminium moiety, [¹Bu₂C=NH₂][20], manifests itself by IR absorptions at 3380 (N-H), 3277 (N-H) and 1639 (C=N) cm⁻¹. The ¹H NMR resonance due to the two N-bound protons has been found at 9.95 ppm (CD₃CN solution).

\[
\begin{align*}
\text{NbCl}_5 \xrightarrow{\text{PhCH=N}^4\text{Bu}} & \quad [\text{PhCH=N}^4\text{Bu}][\text{NbCl}_6] \\
\text{²Bu}₂\text{C}=\text{NH} \xrightarrow{\text{²Bu}_2\text{C}=\text{NH}_2} & \quad [\text{²Bu}_2\text{C}=\text{NH}_2][\text{NbCl}_6]
\end{align*}
\]

Scheme 2. Formation of iminium salts from the reactions of NbCl₅ with N-benzylidene-tert-butylamine and 2,2,4,4-tetramethyl-3-pentanone imine.

The formation of 2 and 3 from NbCl₅ and imines is the consequence of a protonation reaction. In principle, three possible sources may contribute to the protonation, i.e. trace water, the solvent (CH₂Cl₂) and the imine itself. In particular, it is possible that the NH containing imine ²Bu₂C=NH undergoes self protonation in the presence of NbCl₅, analogously to what demonstrated for Ph₂C=NH. We performed several experiments aimed to the identification of the possible coproducts of the proton transfer, but these did not provide conclusive results.

The 1:1 molar reactions of NbF₅ with benzophenone imine and N-benzylidene-tert-butylamine afforded the hexafluoroniobate iminium salts [Ph₂C=NH₂][NbF₆], 4, and [PhCH=N¹Bu][NbF₆], 5, respectively, in ca. 50% yields (Scheme 3).

\[
\begin{align*}
\text{NbF}_5 \xrightarrow{\text{Ph}_2\text{C}=\text{NH}} & \quad [\text{Ph}_2\text{C}=\text{NH}_2][\text{NbF}_6] \\
\text{PhCH}=\text{N}^4\text{Bu} \xrightarrow{\text{PhCH}=\text{N}^4\text{Bu}} & \quad [\text{PhCH}=\text{N}^4\text{Bu}][\text{NbF}_6]
\end{align*}
\]

6
**Scheme 3.** Formation of iminium salts from the reactions of NbF₅ with benzophenone imine and N-benzylidene-tert-butylamine.

The X-ray structure of 4 (Figure 2, Table 2) consists of ionic packings of [Ph₂C=NH₂]⁺ cations and [NbF₆]⁻ anions, with H-bonds involving N-bound hydrogens and fluoride ligands (Table 4). The [NbF₆]⁻ anion displays bonding parameters resembling those previously reported in the literature [6b, 7b, 21].

![Image of molecular structure]

**Figure 2.** View of the molecular structure of [Ph₂C=NH₂][NbF₆], 4, with key atoms labeled. Symmetry transformation used to generate equivalent atoms: (1) –x+3/2, –y+1/2, –z; (2) –x+1, y, –z+3/2. Displacement ellipsoids are at the 50% probability level.

**Table 2.** Selected bond lengths (Å) and angles (°) for 4

<table>
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<th>Bond/Angle</th>
<th>Value</th>
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<td>Nb(1)–F(2)</td>
<td>1.9048(11)</td>
</tr>
<tr>
<td>Nb(1)–F(3)</td>
<td>1.8786(10)</td>
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<td>C(1)–N(1)</td>
<td>1.293(3)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>1.468(2)</td>
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<td>F(1)–Nb(1)</td>
<td>180.00(6)</td>
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<tr>
<td>F(2)–Nb(1)</td>
<td>180.00(5)</td>
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<tr>
<td>F(3)–Nb(1)</td>
<td>180.00(5)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>119.08(10)</td>
</tr>
<tr>
<td>C(2)–C(1)</td>
<td>119.08(10)</td>
</tr>
</tbody>
</table>

Symmetry transformation used to generate equivalent atoms: (1) –x+3/2, –y+1/2, –z; (2) –x+1, y, –z+3/2.

The IR and NMR features related to the iminium cations within 4 and 5 resemble those already discussed for the analogous [NbC₆]⁻ salts, 1 and 2. The [NbF₆]⁻ anion has been characterized by means of NMR spectroscopy. Indeed this species gives raise to typical ¹⁹F and ⁹³Nb resonances, falling at ca. 104 ppm and –1550 ppm, respectively [4c, 5a,c, 6a-c, 7].

Consideration analogous to those discussed for 2 and 3 are still valid here in order to explain the
formation of the iminium cations contained in 4 and 5. In addition, two points should be considered. First, the high stability of the [NbF₆]⁻ anion is an important factor which often forces the formation of ionic species from the interaction of NbF₅ with organic compounds [4c, 5c, 6a-c]. Second, 4 and 5 were isolated by precipitation from a CH₂Cl₂/hexane mixture, and magnetic analysis of the solid residue recovered from the liquid phase evidenced the presence of paramagnetic species (the solid residues recovered from NbCl₅/imines, see above, revealed to be diamagnetic). Moreover, hydrolysis [22] of the paramagnetic substrate obtained from NbF₅/PhCH=N[Me]Bu gave a solution whose NMR analysis indicated the presence of moderate amounts of benzonitrile. The formation of PhC≡N from PhCH=N[Me]Bu indicates the occurrence of C–H bond activation to some extent, possibly contributing to the main protonation reaction leading to 5.

Finally, we included a tantalum pentahalide, i.e. TaCl₅, in the present study. The reaction of TaCl₅ with benzophenone imine was less selective than the analogous one involving NbCl₅, and afforded a complicated mixture of products. After many attempts, few crystals of the salt [Ph₂C=NH₄]₂[Ta₂Cl₁₀O], 6, were collected. The presence of oxygen in the anion is unambiguous evidence of the action of fortuitous water. The X-ray structure of 6 (Figure 3, Tables 3 and 4) is an ionic packing of [Ph₂C=NH₄]⁺ and [Ta₂Cl₁₀O]²⁻ ions. The [Ta₂Cl₁₀O]²⁻ anion was crystallographically characterized in the past, the anion displaying bonding parameters very close to those found in the present case [23].

![Figure 3. View of the molecular structure of [Ph₂C=NH₄]₂[Ta₂Cl₁₀O], 6, with key atoms labeled. Symmetry transformation used to generate equivalent atoms: (1) –x+2, –y+a, –z+1. Displacement ellipsoids are at the 50% probability level.](image)

Table 3. Selected bond lengths (Å) and angles (°) for 6

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
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Table 4. H-bond parameters for 1, 4 and 6.

<table>
<thead>
<tr>
<th></th>
<th>d(D-H)</th>
<th>d(H···A)</th>
<th>d(D···A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.941(10)</td>
<td>2.375(16)</td>
<td>3.268(3)</td>
<td>158(3)</td>
</tr>
<tr>
<td>2</td>
<td>0.938(10)</td>
<td>2.70(2)</td>
<td>3.453(3)</td>
<td>138(3)</td>
</tr>
<tr>
<td>3</td>
<td>0.868(15)</td>
<td>2.004(15)</td>
<td>2.860(16)</td>
<td>169(2)</td>
</tr>
<tr>
<td>4</td>
<td>0.878(10)</td>
<td>2.55(3)</td>
<td>3.311(4)</td>
<td>145(4)</td>
</tr>
<tr>
<td></td>
<td>0.876(10)</td>
<td>2.88(3)</td>
<td>3.676(4)</td>
<td>152(4)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 –x+1,–y+1,–z+1; #2 x,y–1,z; #3 x–1/2,–y+1/2,z+1/2; #4 x–1,y,z; #5 –x+1,–y+1,–z+1.

3. Conclusions

In the framework of our interest in the coordination chemistry of high valent metal halides, we have reported on the reactivity of niobium (tantalum) pentahalides with imines, which has not been explored up to now. In general, the reactions are scarcely selective and lead to the isolation of iminium salts, favored by the basicity of the imine moiety and the stability of [MX₆]⁻ anions. Possible sources of protonation are represented by the solvent (dichloromethane), trace water and the activation of the imine reactant. In particular, the occurrence of benzophenone imine self protonation has been unambiguously observed in the reaction with NbCl₅, resulting in the first crystallographic characterization of a Nb(V) azavinylidene species. Redox processes appear to be operative in the reactions involving NbF₅, presumably triggered by the strong oxidative power of niobium pentafluoride [4b].

4. Experimental
4.1. General considerations. Air/moisture sensitive compounds were manipulated under atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 140°C prior to use, evacuated (10^{-2} \text{mmHg}) and then filled with argon. NbCl$_5$ (99+%), NbF$_5$ (99.5+%), and TaCl$_5$ (99.9%) were purchased from Strem, then sublimed and stored in sealed tubes under argon. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma-Aldrich) were distilled from P$_4$O$_{10}$ before use. Imines (TCI Europe), CD$_2$Cl$_2$ and CD$_3$CN (Cortecnet) were commercial chemicals stored under argon atmosphere as received. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Magnetic susceptibilities were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.) [24]. $^1$H, $^{13}$C NMR and $^{93}$Nb NMR spectra were recorded on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. $^1$H and $^{13}$C NMR assignments were assisted by DEPT, HSQC and HMBC experiments [25]. $^{19}$F NMR spectra were recorded on a Varian Gemini 200BB instrument. All NMR experiments were performed at 298 K. The chemical shifts for $^1$H and $^{13}$C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for $^{19}$F were referenced to external CFCl$_3$; the chemical shifts for $^{93}$Nb were referenced to external [NEt$_4$][NbCl$_6$]. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method [26] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO$_3$ up to neutralization. The metal was analyzed as M$_2$O$_5$ obtained by high temperature treatment of the solid sample with HNO$_3$ solution, followed by calcination in a platinum crucible.

4.2. Reactions of NbCl$_5$ with imines.
4.2.1. Synthesis of [Ph₂C=NH₂][NbCl₅(N=CPH₂)], 1. A suspension of NbCl₅ (0.250 g, 0.925 mmol) in CH₂Cl₂ (15 mL) was treated with benzophenone imine (0.320 mL, 1.91 mmol). The mixture was stirred at room temperature for 18 h, and the resulting dark-brown mixture was filtered in order to remove some insoluble material. Then the filtered solution was concentrated up to ca. 5 mL, layered with pentane and stored at −30 °C. Compound 1 was isolated as a greenish-brown solid after 72 h. Yield 0.322 g, 55%. Crystals suitable for X-ray analysis were collected from a CH₂Cl₂ solution layered with hexane and stored at −30 °C for one week. Anal. Calcd. for C₂₆H₂₂Cl₅N₂Nb: C, 49.36; H, 3.51; N, 4.43; Cl, 28.02; Nb, 14.69. Found: C, 49.45; H, 3.37; N, 4.36; Cl, 27.87; Nb, 14.39. IR (solid state): 3334w, 3267w, 3206w, 3066w, 1675m-sh (νC=N), 1652s (νC=N), 1591s-sh, 1583s, 1571m-sh, 1488m, 1462vs, 1453vs-sh, 1406vs, 1472vs, 1328s, 1292s, 1179m, 1164m-s, 1102w-m, 1026w, 995m, 938w, 822vs, 795s, 777m, 737s, 690s, 665s cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 11.4 (br, 2 H, NH), 8.15, 7.92, 7.74, 7.67 (m, 20 H, Ph) ppm. ¹³C NMR (CD₂Cl₂): δ = 182.1 (CNH₂), 156.9 (CNNb), 138.1, 136.4, 134.9, 134.4, 132.4, 131.6, 130.5, 129.6, 129.0, 127.1 (Ph) ppm. ⁹³Nb (CD₂Cl₂): δ = 10.4 (s, ∆ν½ = 1.3×10 Hz) ppm.

4.2.2. Synthesis of [PhCH=NH₄Bu][NbCl₆], 2 and [²Bu₂C=NH₂][NbCl₆], 3. Only the preparation of 2 is described in detail, 3 being obtained in a similar way. N-benzylidene-tert-butylamine (0.135 mL, 0.759 mmol) was added to a suspension of NbCl₅ (0.200 g, 0.740 mmol) in CH₂Cl₂ (15 mL). The mixture was allowed to react at room temperature for 18 h. The final mixture was treated with hexane (30 mL), and the abundant brown precipitate was separated and then dried in vacuo. Yield 0.185 g, 52% (with reference to the organic reactant). Anal. Calcd. for C₁₁H₁₆Cl₆NNb: C, 28.24; H, 3.45; N, 2.99; Cl, 45.46; Nb, 19.86. Found: C, 28.07; H, 3.38; N, 3.06; Cl, 45.22; Nb, 19.97. IR (solid state): 3306w, 3256w, 3058w, 2978w, 1650s (νC=N), 1594s, 1455w, 1413w, 1382w, 1328w, 1310w, 1262w, 1237m, 1185s, 1023s, 896w, 821m, 744vs, 694m, 673vs cm⁻¹. ¹H NMR (CD₃CN): δ = 10.85 (s, 1 H, NH), 8.78 (s, 1 H, CH), 8.10, 7.88, 7.73 (m, 5
H, Ph), 1.61 (s, 9 H, CMe₅) ppm. ¹³C NMR (CD₃CN): δ = 168.1 (C=N), 137.7, 132.5, 130.2 (Ph),
127.0 (ipso-Ph), 62.4 (CMe₅), 27.5 (CMe₅) ppm. ¹³¹Nb (CD₃CN): δ = −0.7 (s, Δν½ = 1×10² Hz) ppm.

¹⁹³Bu₂C=NH₂[NbCl₆], 3. light-yellow solid, 47% yield from NbCl₅ (0.320 g, 1.18 mmol) and
¹⁹³Bu₂C=NH (1.20 mmol). Anal. Calcd. for C₁₁H₁₆Cl₆NNb: C, 24.13; H, 4.50; N, 3.13; Cl, 47.49;
Nb, 20.74. Found: C, 24.09; H, 4.38; N, 3.03; Cl, 47.72; Nb, 20.01. IR (solid state): 3380w (νN₅H),
3277w (νN₅H), 1639m (νC=N) cm⁻¹. ¹H NMR (CD₃CN): δ = 9.95 (s, NH₂); 1.65 (s, 18 H, tBu) ppm.

4.3. Reactions of NbF₅ with imines.

4.3.1. Synthesis of [Ph₂C=NH₂][NbF₆], 4. A mixture of NbF₅ (0.150 g, 0.798 mmol), CH₂Cl₂ (20 mL) and benzophenone imine (0.135 mL, 0.806 mmol) was allowed to react for 18 h at room temperature. The resulting solution was treated with hexane (30 mL), and the resulting red solid was isolated and dried in vacuo. Yield 0.151 g, 48% (respect to the organic reactant). Crystals suitable for X-ray analysis were collected from a CH₂Cl₂/hexane mixture stored at −30 C for one week. Anal. Calcd. for C₁₃H₁₂F₆NNb: C, 40.12; H, 3.11; N, 3.60; F, 29.29; Nb, 23.87. Found: C, 40.22; H, 3.02; N, 3.65; F, 29.58; Nb, 23.76. IR (solid state): 3260w, 3195w (νN₅H), 3059w-m, 1970vw, 1669m (νC=N), 1596s (νC=C, Ph), 1567m-s, 1489w, 1447s, 1372s, 1299w, 1274w-m, 1192w-m, 1162m, 1074w-m, 1028w-m, 999w-m, 932m, 884s, 790s, 763m-s, 726m, 693vs cm⁻¹. ¹H NMR (CDCl₃): δ = 10.54 (s, 2 H, NH₂); 7.71-7.41 (m, 10 H, Ph) ppm. ¹³C NMR (CDCl₃): δ = 180.3 (C=N); 136.4 (ipso-Ph), 132.2, 129.5, 128.7 (Ph) ppm. ¹⁹F (CDCl₃): δ = 103.5 (m, [NbF₆]⁻) ppm. ¹³¹Nb NMR (CDCl₃): δ = −1549 (m, [NbF₆]⁻) ppm.

4.3.2. Synthesis of [PhCH=NH₅Bu][NbF₆], 5. The reaction of N-benzylidene-tert-butylamine (0.160 mL, 0.900 mmol) with NbF₅ (0.160 g, 0.852 mmol) was carried out by a procedure similar to that described for NbF₅/Ph₂C=NH. Yield 0.170 g, 54%. Anal. Calcd. for C₁₁H₁₆F₆NNb: C,
35.79; H, 4.37; N, 3.79; F, 30.88; Nb, 25.17. Found: C, 35.22; H, 4.60; N, 3.65; F, 30.41; Nb, 25.00. IR (solid state): 3277vw (NH), 2988vw, 1657m (C=N), 1598m, 1458w, 1424vw, 1386w, 1330vw, 1310vw, 1237w, 1184m, 1036w, 906m, 749m cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): δ = 10.90 (m, 1 H, NH); 8.80 (d, 1 H, CH=N); 8.08, 7.90, 7.72 (m, 5 H, Ph); 1.60 (s, 9 H, \(^t\)Bu) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 167.9 (C=N); 137.6, 131.0, 126.8 (arom CH); 126.8 (ipso-5Ph); 62.4 (CMe\(_3\)); 26.9 (CMe\(_3\)) ppm. \(^{19}\)F (CDCl\(_3\)): δ = 103.6 (m, [NbF\(_6\)]\(^-\)) ppm. \(^{93}\)Nb NMR (CDCl\(_3\)): δ = −1550 (m, [NbF\(_6\)]\(^-\)) ppm.

The CH\(_2\)Cl\(_2\)/hexane liquors obtained from the reactions of NbF\(_5\) with imines were separated and then eliminated of the volatile materials in vacuo. Magnetic analyses on the resulting solid residues were as follows. From NbF\(_5\)/Ph\(_2\)C=NH: χ\(_M\)\(^{corr}\) = 1.02×10\(^{-3}\) cgsu. From NbF\(_5\)/PhCH=N\(^t\)Bu: χ\(_M\)\(^{corr}\) = 5.63×10\(^{-4}\) cgsu. The solid obtained from NbF\(_5\)/PhCH=N\(^t\)Bu was treated with CDCl\(_3\) (1.5 mL) and H\(_2\)O (0.2 mL). The mixture was stirred in contact with air for 48 h. Subsequent NMR analysis on the organic phase allowed to detect some PhC≡N.

4.4. Synthesis of [Ph\(_2\)C=NH\(_2\)]\(_2\)[Ta\(_2\)Cl\(_{10}\)O], 6. The reaction of TaCl\(_5\) (0.340 g, 0.949 mmol) with benzophenone imine (0.160 mL, 0.955 mmol) was carried out by using a procedure similar to that described for NbCl\(_5\)/Ph\(_2\)C=NH. Crystals of 6·2CH\(_2\)Cl\(_2\) were collected after several attempts by settling aside an orange reaction mixture, layered with hexane, at −30 °C for one week. Yield 0.031 g, 5% (with reference to the organic reactant). Anal. Calcd. for C\(_{28}\)H\(_{28}\)Cl\(_{14}\)N\(_2\)O\(_2\)Ta\(_2\): C, 26.55; H, 2.23; N, 2.21; Cl, 39.18; Ta, 28.57. Found: C, 26.33; H, 2.15; N, 2.31; Cl, 39.02; Ta, 28.38. IR (solid state): 3381w, 3333w, 3252w, 1659s (νC=N), 1592s, 1515m, 1488m, 1453s, 1375s, 1324w, 1299w, 1186w, 1164w, 1128w, 1087w, 998w, 938w, 777m, 739vs, 694vs, 665s cm\(^{-1}\). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): δ = 9.57 (br, 2 H, NH), 8.11, 8.01, 7.87, 7.78 (m, 10 H, Ph) ppm. \(^{13}\)C NMR (CD\(_2\)Cl\(_2\)): δ = 184.6 (C=N), 137.9, 132.5, 130.3 (Ph), 129.4 (ipso-Ph) ppm.
4.6. X-ray crystallographic studies. Crystal data and collection details for 1·0.5CH₂Cl₂, 4 and 6·2CH₂Cl₂ are listed in Table 5. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [27]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F² [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters. C-bonded hydrogen atoms were fixed at calculated positions and refined by a riding model, whereas N bonded hydrogens have been located in the Fourier map and refined isotropically using the 1.2 fold Uiso value of the parent N-atom with restrained N–H distances. The CH₂Cl₂ molecule of 1·0.5CH₂Cl₂ is disordered over four positions, two by two correlated by an inversion centre. The two independent images have been refined isotropically using similar U restraints [SIMU command in SHELXL; s.u. 0.005] and restrained C–Cl distances [DFIX 1.75 command in SHELXL; s.u. 0.01].

Table 5. Crystal data and details of the structure refinement for [Ph₂C=NH₂][NbCl₅(N=CPh₂)·0.5CH₂Cl₂, 1·0.5CH₂Cl₂, [Ph₂C=NH₂][NbF₆], 4, and [Ph₂C=NH₂][Ta₂Cl₁₀O]·2CH₂Cl₂, 6·2CH₂Cl₂.

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<td>10.166(2)</td>
<td>10.8191(11)</td>
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Independent reflections 5470 \([R_{int} = 0.0430]\) 1679 \([R_{int} = 0.0306]\) 4525 \([R_{int} = 0.0371]\)
Data / restraints /parameters 5470 \(18 / 385\) 1839 \(1 / 78\) 4525 \(2 / 220\)
Goodness of fit on \(F^2\) 1.032 1.043 1.042
\(R_I (I > 2\sigma(I))\) 0.0375 0.0212 0.0301
\(wR_2\) (all data) 0.0789 0.0548 0.0701
Largest diff. peak and hole, e Å\(^{-3}\) 0.891 / –0.859 0.416 / –0.574 1.765 / –1.069

**Supporting Information.** CCDC contain the supplementary crystallographic data for the X-ray studies reported in this paper. CCDC 1471160 \((1\cdot0.5\text{CH}_2\text{Cl}_2)\), 1471161 \((4)\) and 1471162 \((6\cdot2\text{CH}_2\text{Cl}_2)\). For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXX.

**Acknowledgements.** The University of Pisa is gratefully acknowledged for financial support.

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Crystallographically characterized Nb-vinylidene complexes are:


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(b) F. Xu, K. Matsumoto, R. Hagiwara, Dalton Trans. 41 (2012) 3494.
22 The hydrolysis of the reaction mixtures facilitates the release of the organic material from the
highly oxophilic metal species, and allows the spectroscopic identification of the former. This
strategy has been successfully adopted by ourselves in previous works, having proved that
H$_2$O is generally inert towards ligand activation reactions [see ref. 4c].


27 G. M. Sheldrick, SHELX97-Program for the refinement of Crystal Structures, University of Göttingen, Germany (1997).