

Accepted Manuscript

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PII: S0277-5387(16)30117-6
DOI: <http://dx.doi.org/10.1016/j.poly.2016.04.034>
Reference: POLY 11961

To appear in: *Polyhedron*

Received Date: 31 March 2016
Accepted Date: 21 April 2016

Please cite this article as: F. Marchetti, G. Pampaloni, S. Zacchini, The Reactivity of Niobium and Tantalum Pentahalides with Imines, *Polyhedron* (2016), doi: <http://dx.doi.org/10.1016/j.poly.2016.04.034>

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The Reactivity of Niobium and Tantalum Pentahalides with Imines

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Received.....; accepted

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Abstract

The reactivity of NbCl₅, NbF₅ and TaCl₅ with a selection of commercial imines was investigated for the first time by using dichloromethane as reaction medium. NbCl₅ reacted with Ph₂C=NH, in 1:2 molar ratio, affording [Ph₂C=NH₂][NbCl₅(N=CPh₂)], **1**, in 55% yield, as result of imine self-protonation. The iminium salt [PhCH=NH^tBu][NbCl₆], **2**, was isolated in 52% yield from NbCl₅ and PhCH=N^tBu (1:1 molar ratio), while a low yield of [^tBu₂C=NH₂][NbCl₆], **3**, was identified from NbCl₅/^tBu₂C=NH. The 1:1 reactions of NbF₅ with Ph₂C=NH and PhCH=N^tBu were accompanied by electron interchange and led to the isolation of the salts [Ph₂C=NH₂][NbF₆], **4**, and [PhCH=NH^tBu][NbF₆], **5**, respectively, in ca. 50% yields. Few crystals of [Ph₂C=NH₂]₂[Ta₂Cl₁₀O], **6**, were recovered from TaCl₅/Ph₂C=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

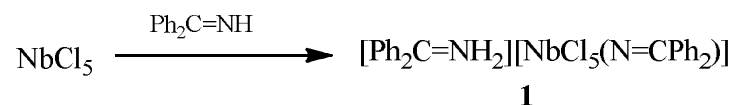
1. Introduction

The chemistry of niobium and tantalum pentahalides, MX₅ [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, MX₅ 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 MX₅ 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 MX_5L can be generated, whereas the ionic complexes $[\text{MX}_4\text{L}_2][\text{MX}_6]$ are the result of the asymmetric rupture [7]. The $[\text{MX}_6]^-$ anions are quite stable, the stability decreasing on moving down the halogen group [4c], and are suitable to the stabilization of organic cations, including otherwise reactive cations [2b, 4b-c, 8]. In those cases in which the reactions of MX_5 with organic compounds are non selective, the formation of $[\text{MX}_6]^-$ 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 MX_5 with imines has not been investigated heretofore. Herein, we describe the results of our study on the reactions of MX_5 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 NbCl_5 with a two-fold excess of benzophenone imine, in dichloromethane at room temperature, led to the isolation in 55% yield of the salt $[\text{Ph}_2\text{C}=\text{NH}_2][\text{NbCl}_5(\text{N}=\text{CPh}_2)]$, **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.



Scheme 1. The reaction of NbCl_5 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=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 diphenylmethylenamido ligand, and represents the first structurally characterized Nb(V) complex containing an azavinylidene (methylenamido) 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].

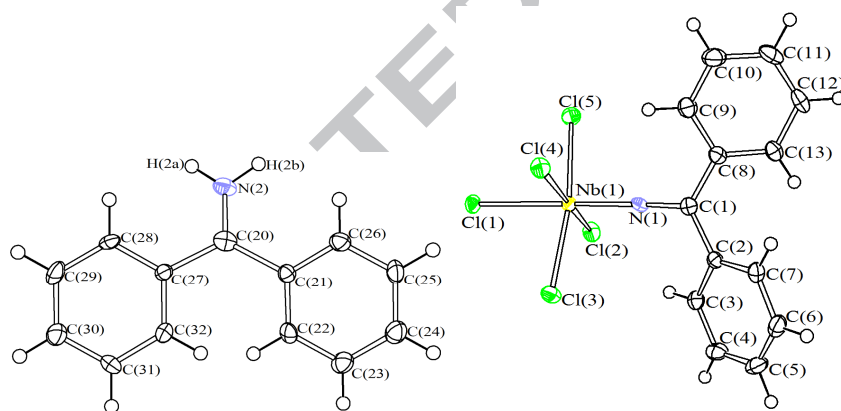


Figure 1. View of the molecular structure of [Ph₂C=NH₂][NbCl₅(N=CPh₂)], **1**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

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

Nb(1)–Cl(1)	2.5258(8)	Nb(1)–Cl(2)	2.3552(9)
Nb(1)–Cl(3)	2.3893(9)	Nb(1)–Cl(4)	2.4143(8)
Nb(1)–Cl(5)	2.4005(9)	Nb(1)–N(1)	1.862(2)
C(1)–N(1)	1.290(4)	C(20)–N(2)	1.293(4)

C(1)–C(2)	1.474(4)	C(20)–C(21)	1.581(4)
C(1)–C(8)	1.472(4)	C(20)–C(27)	1.563(4)
N(1)–Nb(1)–Cl(1)	175.43(8)	Cl(2)–Nb(1)–Cl(4)	176.83(3)
Cl(3)–Nb(1)–Cl(5)	170.12(3)	Nb(1)–N(1)–C(1)	176.3(2)
N(1)–C(1)–C(2)	118.1(3)	N(2)–C(20)–C(21)	118.9(3)
N(1)–C(1)–C(8)	119.5(3)	N(2)–C(20)–C(27)	117.2(3)
C(2)–C(1)–C(8)	122.4(3)	C(21)–C(20)–C(27)	123.9(3)

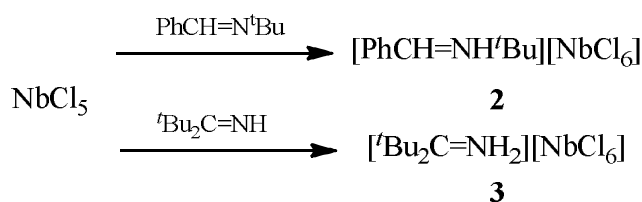
The IR spectrum of **1** (solid state) displays a broad band envelope around 1660 cm^{-1} , probably accounting for both $[\text{C}=\text{N}]$ moieties. In the ^1H NMR spectrum (CD_2Cl_2 solution), the N-bound protons resonate at 11.4 ppm. Major ^{13}C NMR features are represented by the resonances of the iminium and azavinylidene carbons, occurring at 182.1 and 156.9 ppm, respectively. In the ^{93}Nb NMR spectrum, the presence of the $[\text{NbCl}_6]^-$ 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 $[\text{M}=\text{C}=\text{CPh}_2]$ 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 $[\text{NBu}_4]\text{OH}$ [19].

We moved to extend our study to the reactivity of NbCl_5 with other imines. The iminium salt $[\text{PhCH}=\text{NH}^+\text{Bu}][\text{NbCl}_6]$, **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_3CN solution) are the resonances due to the NH (10.85 ppm) and iminium groups (^1H : 8.78 ppm; ^{13}C : 168.1 ppm). The ^{93}Nb NMR resonance of the $[\text{NbCl}_6]^-$ anion has been found at -0.7

ppm. The observed variability of the chemical shift due to $[\text{NbCl}_6]^-$ in a restricted ppm range may be an effect of the solvent and/or the nature of the cation.

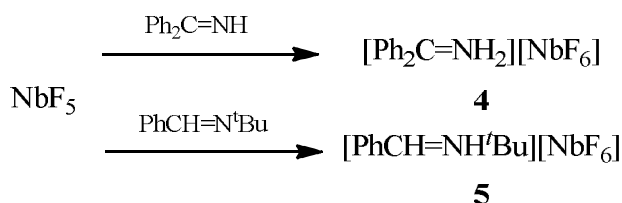
Also the 1:1 molar reaction of NbCl_5 with 2,2,4,4-tetramethyl-3-pentanone imine led to the low yield isolation of a solid containing the relevant iminium cation, in admixture with non identified secondary products (Scheme 2). The iminium moiety, $[\text{tBu}_2\text{C}=\text{NH}_2]^+$ [20], manifests itself by IR absorptions at 3380 (N-H), 3277 (N-H) and 1639 ($\text{C}=\text{N}$) cm^{-1} . The ^1H NMR resonance due to the two N-bound protons has been found at 9.95 ppm (CD_3CN solution).



Scheme 2. Formation of iminium salts from the reactions of NbCl_5 with N-benzylidene-tert-butylamine and 2,2,4,4-tetramethyl-3-pentanone imine.

The formation of **2** and **3** from NbCl_5 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 (CH_2Cl_2) and the imine itself. In particular, it is possible that the NH containing imine $^t\text{Bu}_2\text{C}=\text{NH}$ undergoes self protonation in the presence of NbCl_5 , analogously to what demonstrated for $\text{Ph}_2\text{C}=\text{NH}$. We performed several experiments aimed to the identification of the possible co-products of the proton transfer, but these did not provide conclusive results.

The 1:1 molar reactions of NbF_5 with benzophenone imine and N-benzylidene-tert-butylamine afforded the hexafluoroniobate iminium salts $[\text{Ph}_2\text{C}=\text{NH}_2][\text{NbF}_6]$, **4**, and $[\text{PhCH}=\text{NH}^t\text{Bu}][\text{NbF}_6]$, **5**, respectively, in ca. 50% yields (Scheme 3).



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].

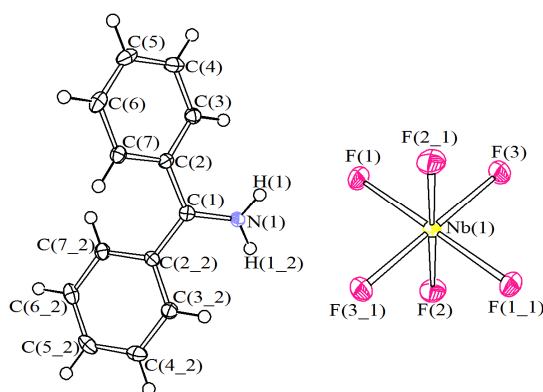


Figure 2. View of the molecular structure of [Ph₂C=NH₂][NbF₆], **4**, with key atoms labeled. Symmetry transformation used to generate equivalent atoms: (1) $-x+3/2, -y+1/2, -z$; (2) $-x+1, y, -z+3/2$. Displacement ellipsoids are at the 50% probability level.

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

Nb(1)–F(1)	1.8838(10)	Nb(1)–F(2)	1.9048(11)
Nb(1)–F(3)	1.8786(10)	C(1)–N(1)	1.293(3)
C(1)–C(2)	1.468(2)		
F(1)–Nb(1)–F(1_1)	180.00(6)	F(2)–Nb(1)–F(2_1)	180.00(7)
F(3)–Nb(1)–F(3_1)	180.00(5)	N(1)–C(1)–C(2)	119.08(10)
C(2)–C(1)–C(2_2)	121.8(2)	N(1)–C(1)–C(2_2)	119.08(10)

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 $[\text{NbC}_6]^-$ salts, **1** and **2**. The $[\text{NbF}_6]^-$ anion has been characterized by means of NMR spectroscopy. Indeed this species gives rise to typical ^{19}F and ^{93}Nb 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 $[\text{NbF}_6]^-$ anion is an important factor which often forces the formation of ionic species from the interaction of NbF_5 with organic compounds [4c, 5c, 6a-c]. Second, **4** and **5** were isolated by precipitation from a CH_2Cl_2 /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 NbCl_5 /imines, see above, revealed to be diamagnetic). Moreover, hydrolysis [22] of the paramagnetic substrate obtained from $\text{NbF}_5/\text{PhCH}=\text{N}^t\text{Bu}$ gave a solution whose NMR analysis indicated the presence of moderate amounts of benzonitrile. The formation of $\text{PhC}\equiv\text{N}$ from $\text{PhCH}=\text{N}^t\text{Bu}$ 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. TaCl_5 , in the present study. The reaction of TaCl_5 with benzophenone imine was less selective than the analogous one involving NbCl_5 , and afforded a complicated mixture of products. After many attempts, few crystals of the salt $[\text{Ph}_2\text{C}=\text{NH}_2]_2[\text{Ta}_2\text{Cl}_{10}\text{O}]$, **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 $[\text{Ph}_2\text{C}=\text{NH}_2]^+$ and $[\text{Ta}_2\text{Cl}_{10}\text{O}]^{2-}$ ions. The $[\text{Ta}_2\text{Cl}_{10}\text{O}]^{2-}$ anion was crystallographically characterized in the past, the anion displaying bonding parameters very close to those found in the present case [23].

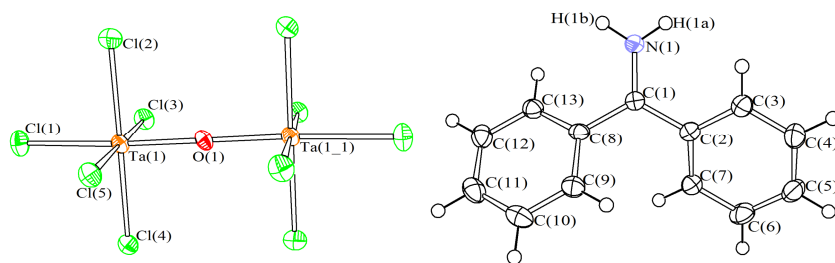


Figure 3. View of the molecular structure of $[\text{Ph}_2\text{C}=\text{NH}_2]_2[\text{Ta}_2\text{Cl}_{10}\text{O}]$, **6**, with key atoms labeled. Symmetry transformation used to generate equivalent atoms: (1) $-x+2, -y+a, -z+1$. Displacement ellipsoids are at the 50% probability level.

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

Ta(1)–Cl(1)	2.3669(11)	Ta(1)–Cl(2)	2.3635(11)
Ta(1)–Cl(3)	2.3665(11)	Ta(1)–Cl(4)	2.3632(11)
Ta(1)–Cl(5)	2.3554(10)	Ta(1)–O(1)	1.8929(2)
C(1)–N(1)	1.304(6)	C(1)–C(2)	1.461(6)
C(1)–C(8)	1.469(6)		

Cl(1)–Ta(1)–O(1)	176.55(3)	Cl(2)–Ta(1)–Cl(4)	179.35(4)
Cl(3)–Ta(1)–Cl(5)	179.67(4)	Ta(1)–O(1)–Ta(1_1)	180.000(5)
N(1)–C(1)–C(2)	119.5(4)	N(1)–C(1)–C(8)	118.6(4)
C(2)–C(1)–C(8)	121.9(4)		

Symmetry transformation used to generate equivalent atoms: (1) $-x+2, -y+a, -z+1$.

Table 4. H-bond parameters for **1**, **4** and **6**.

	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1				
N(2)–H(2A)···Cl(1)#1	0.941(10)	2.375(16)	3.268(3)	158(3)
N(2)–H(2B)···Cl(1)#2	0.938(10)	2.70(2)	3.453(3)	138(3)
N(2)–H(2B)···Cl(4)#1	0.938(10)	2.89(3)	3.405(3)	116(2)
3				
N(1)–H(1)···F(2)#3	0.868(15)	2.004(15)	2.8606(16)	169(2)
4				
N(1)–H(1A)···Cl(4)#4	0.878(10)	2.55(3)	3.311(4)	145(4)
N(1)–H(1B)···Cl(3)#5	0.876(10)	2.88(3)	3.676(4)	152(4)

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 $[\text{MX}_6]^-$ 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 mmHg) and then filled with argon. NbCl₅ (99+%), NbF₅ (99.5+%), and TaCl₅ (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 P₄O₁₀ before use. Imines (TCI Europe), CD₂Cl₂ and CD₃CN (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]. ¹H, ¹³C NMR and ⁹³Nb NMR spectra were recorded on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. ¹H and ¹³C NMR assignments were assisted by DEPT, HSQC and HMBC experiments [25]. ¹⁹F NMR spectra were recorded on a Varian Gemini 200BB instrument. All NMR experiments were performed at 298 K. The chemical shifts for ¹H and ¹³C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for ¹⁹F were referenced to external CFCl₃; the chemical shifts for ⁹³Nb were referenced to external [NEt₄][NbCl₆]. 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 HNO₃ up to neutralization. The metal was analyzed as M₂O₅ obtained by high temperature treatment of the solid sample with HNO₃ solution, followed by calcination in a platinum crucible.

4.2. Reactions of NbCl₅ 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 (ν_{C=N}), 1652s (ν_{C=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, Δν^{1/2} = 1.3×10 Hz) ppm.

4.2.2. *Synthesis of [PhCH=NH^tBu][NbCl₆], 2 and [^tBu₂C=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 $C_{11}H_{16}Cl_6NNb$: 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 ($\nu_{C=N}$), 1594s, 1455w, 1413w, 1382w, 1328w, 1310w, 1262w, 1237m, 1185s, 1023s, 896w, 821m, 744vs, 694m, 673vs cm^{-1} . 1H NMR (CD_3CN): 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, CMe_3) ppm. ^{13}C NMR (CD_3CN): δ = 168.1 (C=N), 137.7, 132.5, 130.2 (Ph), 127.0 (*ipso*-Ph), 62.4 (CMe_3), 27.5 (CMe_3) ppm. ^{93}Nb (CD_3CN): δ = -0.7 (s, $\Delta\nu/2 = 1 \times 10^2$ Hz) ppm.

$[^tBu_2C=NH_2][NbCl_6]$, **3**. light-yellow solid, 47% yield from $NbCl_5$ (0.320 g, 1.18 mmol) and $^tBu_2C=NH$ (1.20 mmol). Anal. Calcd. for $C_{11}H_{16}Cl_6NNb$: 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 (ν_{N-H}), 3277w (ν_{N-H}), 1639m ($\nu_{C=N}$) cm^{-1} . 1H NMR (CD_3CN): δ = 9.95 (s, NH_2); 1.65 (s, 18 H, tBu) ppm.

4.3. Reactions of NbF_5 with imines.

4.3.1. Synthesis of $[Ph_2C=NH_2][NbF_6]$, **4**. A mixture of NbF_5 (0.150 g, 0.798 mmol), CH_2Cl_2 (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 CH_2Cl_2 /hexane mixture stored at -30 °C for one week. Anal. Calcd. for $C_{13}H_{12}F_6NNb$: 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 (ν_{N-H}), 3059w-m, 1970vw, 1669m ($\nu_{C=N}$), 1596s ($\nu_{C=C}$, 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 (CDCl_3): δ = 10.54 (s, 2 H, NH_2); 7.71-7.41 (m, 10 H, Ph) ppm. ^{13}C NMR (CDCl_3): δ = 180.3 ($\text{C}=\text{N}$); 136.4 (*ipso*-Ph), 132.2, 129.5, 128.7 (Ph) ppm. ^{19}F (CDCl_3): δ = 103.5 (m, $[\text{NbF}_6]^-$) ppm. ^{93}Nb NMR (CDCl_3): δ = -1549 (m, $[\text{NbF}_6]^-$) ppm.

4.3.2. *Synthesis of $[\text{PhCH}=\text{NH}^t\text{Bu}][\text{NbF}_6]$, 5.* The reaction of N-benzylidene-tert-butylamine (0.160 mL, 0.900 mmol) with NbF_5 (0.160 g, 0.852 mmol) was carried out by a procedure similar to that described for $\text{NbF}_5/\text{Ph}_2\text{C}=\text{NH}$. Yield 0.170 g, 54%. Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{F}_6\text{NNb}$: 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 ($\text{C}=\text{N}$), 1598m, 1458w, 1424vw, 1386w, 1330vw, 1310vw, 1237w, 1184m, 1036w, 906m, 749m cm^{-1} . ^1H NMR (CDCl_3): δ = 10.90 (m, 1 H, NH); 8.80 (d, 1 H, $\text{CH}=\text{N}$); 8.08, 7.90, 7.72 (m, 5 H, Ph); 1.60 (s, 9 H, ^tBu) ppm. ^{13}C NMR (CDCl_3): δ = 167.9 ($\text{C}=\text{N}$); 137.6, 131.0, 126.8 (arom CH); 126.8 (*ipso*-Ph); 62.4 (CMe_3); 26.9 (CMe_3) ppm. ^{19}F (CDCl_3): δ = 103.6 (m, $[\text{NbF}_6]^-$) ppm. ^{93}Nb NMR (CDCl_3): δ = -1550 (m, $[\text{NbF}_6]^-$) ppm.

The CH_2Cl_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 $\text{NbF}_5/\text{Ph}_2\text{C}=\text{NH}$: $\chi_{\text{M}}^{\text{corr}} = 1.02 \times 10^{-3}$ cgsu. From $\text{NbF}_5/\text{PhCH}=\text{N}^t\text{Bu}$: $\chi_{\text{M}}^{\text{corr}} = 5.63 \times 10^{-4}$ cgsu. The solid obtained from $\text{NbF}_5/\text{PhCH}=\text{N}^t\text{Bu}$ was treated with CDCl_3 (1.5 mL) and H_2O (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 $\text{PhC}\equiv\text{N}$.

4.4. *Synthesis of $[\text{Ph}_2\text{C}=\text{NH}_2]_2[\text{Ta}_2\text{Cl}_{10}\text{O}]$, 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 $\text{NbCl}_5/\text{Ph}_2\text{C}=\text{NH}$. Crystals of $6 \cdot 2\text{CH}_2\text{Cl}_2$ 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 $C_{28}H_{28}Cl_{14}N_2OTa_2$: 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 ($\nu_{C=N}$), 1592s, 1515m, 1488m, 1453s, 1375s, 1324w, 1299w, 1186w, 1164w, 1128w, 1087w, 998w, 938w, 777m, 739vs, 694vs, 665s cm^{-1} . 1H NMR (CD_2Cl_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_2Cl_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 $1 \cdot 0.5CH_2Cl_2$, **4** and $6 \cdot 2CH_2Cl_2$ 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-K α 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 F^2 [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 U_{iso} value of the parent N-atom with restrained N–H distances. The CH_2Cl_2 molecule of $1 \cdot 0.5CH_2Cl_2$ 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 $[Ph_2C=NH_2][NbCl_5(N=CPh_2)] \cdot 0.5CH_2Cl_2$, $1 \cdot 0.5CH_2Cl_2$, $[Ph_2C=NH_2][NbF_6]$, **4**, and $[Ph_2C=NH_2][Ta_2Cl_{10}O] \cdot 2CH_2Cl_2$, $6 \cdot 2CH_2Cl_2$.

Complex	$1 \cdot 0.5CH_2Cl_2$	4	$6 \cdot 2CH_2Cl_2$
Formula	$C_{26.5}H_{23}Cl_6N_2Nb$	$C_{13}H_{12}F_6NNb$	$C_{28}H_{28}Cl_{14}N_2OTa_2$
F_w	675.08	389.15	1266.72
T, K	100(2)	100(2)	100(2)
λ , Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$

a , Å	9.9964(10)	10.050(2)	7.9420(8)
b , Å	11.1707(12)	10.166(2)	10.8191(11)
c , Å	14.6301(15)	13.885(3)	13.3952(13)
α , °	71.4490(10)	90	67.6340(10)
β , °	87.0600(10)	94.885(2)	76.1120(10)
γ , °	65.0340(10)	90	84.4360(10)
Cell Volume, Å ³	1397.5(3)	1413.5(6)	1033.26(18)
Z	2	4	1
D_c , g cm ⁻³	1.604	1.829	2.036
μ , mm ⁻¹	1.024	0.910	6.223
$F(000)$	678	768	602
Crystal size, mm	0.19×0.16×0.12	0.24×0.21×0.15	0.23×0.21×0.18
θ limits, °	1.48–26.00	2.86–27.99	1.69–27.10
Reflections collected	14538	6977	11623
Independent reflections	5470 [$R_{\text{int}} = 0.0430$]	1679 [$R_{\text{int}} = 0.0306$]	4525 [$R_{\text{int}} = 0.0371$]
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_1 ($I > 2\sigma(I)$)	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**·0.5CH₂Cl₂), 1471161 (**4**) and 1471162 (**6**·2CH₂Cl₂). 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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Synopsis

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The reactivity of niobium (tantalum) pentahalides with a selection of simple imines is described, including the first crystallographic characterization of a Nb(V)-azavinylidene complex.

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Pictogram

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