

# Stable Coordination Complexes of $\alpha$ -Diimines with Nb(V) and Ta(V) Halides

Niccolò Bartalucci,<sup>a,b</sup> Marco Bortoluzzi,<sup>b,c</sup> Guido Pampaloni,<sup>a,b</sup> Calogero Pinzino,<sup>d</sup> Stefano Zacchini,\*<sup>b,e</sup> and Fabio Marchetti\*<sup>a,b</sup>

<sup>a</sup> Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa.

<sup>b</sup> CIRCC, via Celso Ulpiani 27, I-70126 Bari, Italy.

<sup>c</sup> Università Ca' Foscari Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Via Torino 155, I-30170 Mestre (VE), Italy.

<sup>d</sup> ICCOM-CNR UOS Pisa, Area di Ricerca, Via Moruzzi 1, I-56124 Pisa, Italy.

<sup>e</sup> Università di Bologna, Dipartimento di Chimica Industriale "Toso Montanari", Viale Risorgimento 4, I-40136 Bologna, Italy.

\* Corresponding authors email addresses: [fabio.marchetti1974@unipi.it](mailto:fabio.marchetti1974@unipi.it); [stefano.zacchini@unibo.it](mailto:stefano.zacchini@unibo.it)

**Abstract.** Uncommon examples of coordination compounds of high valent transition metals with  $\alpha$ -diimines were obtained and characterized by IR and NMR spectroscopy, X-ray diffraction and/or DFT analysis. The 1:1 molar reactions of NbF<sub>5</sub> with a selection of  $\alpha$ -diimines afforded the ionic compounds [NbF<sub>4</sub>(DAD<sup>R</sup>)<sub>2</sub>][NbF<sub>6</sub>] (DAD<sup>R</sup> = **DAD<sup>Dip</sup>**, **1a**; **DAD<sup>Xyl</sup>**, **1b**; **DAD<sup>Mes</sup>**, **1c**), in 80-90% yields. The addition of **DAD<sup>Dip</sup>** to NbOCl<sub>3</sub> gave NbOCl<sub>3</sub>(**DAD<sup>Dip</sup>**), **7** (62% yield). [MBr<sub>4</sub>(**DAD<sup>Dip</sup>**)] [MBr<sub>6</sub>] (M = Nb, **7a**; M = Ta, **7b**) were afforded in moderate yields from MBr<sub>5</sub> and **DAD<sup>Dip</sup>**. The reactions of NbCl<sub>5</sub> with **DAD<sup>Dip</sup>** and **DAD<sup>Xyl</sup>** proceeded with non selective activation of the organic substrate affording complex mixtures of products, including the quinoxalium salt [{2,6-C<sub>6</sub>H<sub>3</sub>(CHMe<sub>2</sub>)<sub>2</sub>}N(CH)<sub>2</sub>NCC(CHMe<sub>2</sub>)(CH)<sub>3</sub>C][NbCl<sub>6</sub>], **2**, the Nb(IV) coordination complex NbCl<sub>4</sub>(**DAD<sup>Dip</sup>**), **3**, the *N*-(monoprotonated)  $\alpha$ -diimine salts [**DAD<sup>Dip</sup>**(H)][MCl<sub>6</sub>], **4a-b**, and the

iminomethyl-imidazolium [(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)NCHCHN(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)CCHN(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)] [NbCl<sub>6</sub>],

5.

## Introduction

$\alpha$ -Diimines, also called 1,4-diaza-1,3-dienes (DAD), are among the most versatile ligands available in synthetic coordination chemistry, whose steric and electronic effects may be finely tuned by varying the substituents on the N=CC=N skeleton.<sup>1</sup> Many robust  $\alpha$ -diimine complexes have been reported, showing a chelating coordination fashion for the DAD unit, and a metal centre ranging from main group elements, transition metals, lanthanides and actinides.<sup>2</sup>

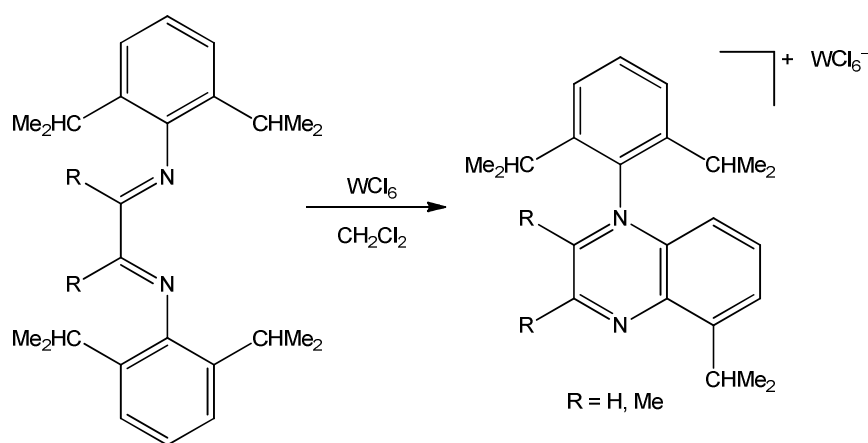
In this setting, studies on the reactivity of  $\alpha$ -diimines with compounds containing a high valent transition metal centre (HVM<sup>3</sup>) are rare in the literature, being limited to MO<sub>2</sub>Cl<sub>2</sub> derivatives<sup>4</sup> and W(V),<sup>5</sup> W(VI)<sup>6</sup> and Ta(V)<sup>7</sup> mixed chlorido(alkyl)-imido complexes.<sup>6,8,9</sup>

A sort of demarcation line can be observed, in the power of activating organic compounds, between the homoleptic halides of transition metal elements in +4 oxidation state and those of higher valent metals (HVM). For instance, TiCl<sub>4</sub> forms stable adducts of formula TiCl<sub>4</sub>L<sub>2</sub> with imines,<sup>10</sup> tetrahydrofuran and acetone,<sup>11</sup> whereas activation pathways are working at room temperature when the same organics are allowed to contact with NbCl<sub>5</sub>,<sup>12</sup> MoCl<sub>5</sub><sup>13</sup> or WCl<sub>6</sub>.<sup>14</sup> Analogous considerations can be traced with the metal fluorides. Thus, TiF<sub>4</sub> dissolves into tetrahydrofuran to give TiF<sub>4</sub>(thf)<sub>2</sub>,<sup>15</sup> while a small amount of MF<sub>5</sub> (M = Nb, Ta) is effective to promote thf polymerization;<sup>16</sup> TiF<sub>4</sub>(dme) (dme = 1,2-dimethoxyethane) is a thermally stable compound,<sup>17</sup> while [MF<sub>4</sub>(dme)<sub>2</sub>][MF<sub>6</sub>] release 1,4-dioxane upon thermal treatment.<sup>18</sup>

In accordance with the trend, if on one hand coordination adducts of TiCl<sub>4</sub> and ZrCl<sub>4</sub> with  $\alpha$ -diimines have been prepared by simple Lewis acid-base combination,<sup>19</sup> on the other hand all the reported reactions of HVM-chlorides, i.e. NbCl<sub>5</sub>,<sup>20</sup> TaCl<sub>5</sub>,<sup>21</sup> MoCl<sub>5</sub><sup>22</sup> and WCl<sub>6</sub>,<sup>23</sup> have been performed in the presence of reductants (e.g. Na/naphthalene,<sup>21b</sup> Na,<sup>22</sup> Zn/Hg<sup>23b</sup>) or a chlorine abstractor agent [1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene<sup>20,21a,23a</sup>], in order to

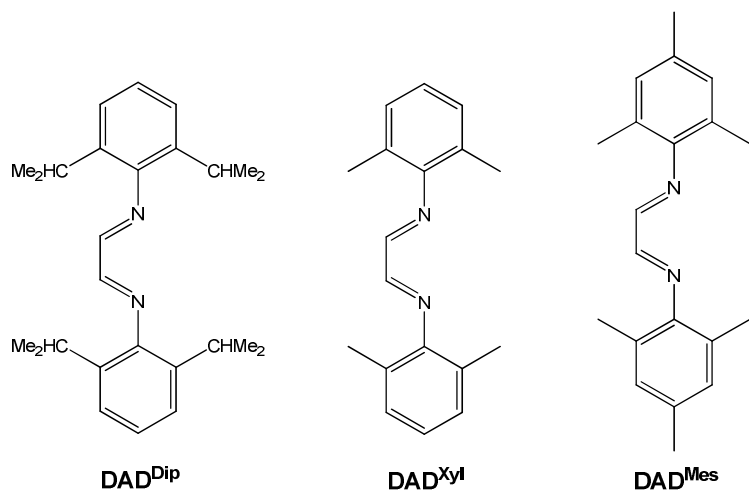
preliminarily reduce the metal centre. This synthetic method permits the clean isolation of coordination compounds containing intact  $\alpha$ -diimine ligands, thus quenching the strong activation potential typical of the high valent metal species.<sup>12,13,14,24</sup>

The first direct interaction (i.e., in the absence of further reactants) of  $\alpha$ -diimines with a HVM halide ( $WCl_6$ ) was recently reported by us, allowing the unusual conversion of the organic substrate into quinoxalium cations (Scheme 1).<sup>25</sup>



**Scheme 1.**  $WCl_6$ -mediated conversion of  $\alpha$ -diimine to quinoxalium.

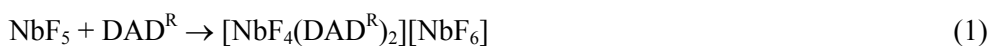
In the light of this preamble, we moved to explore the direct interaction of a selection of N-aryl substituted  $\alpha$ -diimines (Chart 1) with various Nb(V) and Ta(V) halides. Herein, we report the results of this study, and the structural characterization of rare examples of  $\alpha$ -diimine complexes with HVM halides. The factors stabilizing coordination products respect to activation reactions will be discussed.



**Chart 1.**  $\alpha$ -Diimine compounds cited in the present work.

## Results and discussion

The reactions of NbF<sub>5</sub> with a series of  $\alpha$ -diimines, in 1:1 molar ratio, proceeded straightforwardly in CH<sub>2</sub>Cl<sub>2</sub> to afford the ionic derivatives [NbF<sub>4</sub>(DAD<sup>R</sup>)<sub>2</sub>][NbF<sub>6</sub>] (DAD<sup>R</sup> = **DAD<sup>Dip</sup>**, **1a**; **DAD<sup>Xyl</sup>**, **1b**; **DAD<sup>Mes</sup>**, **1c**) in 82-91% yields, Eq. 1. Compounds **1a-c** were generated in lower yields (in admixture with non identified by-products) when the reactions were carried out with different molar ratios (Nb/DAD<sup>R</sup> = 2 or 0.5), thus ruling out the possible formation of products with formula [NbF<sub>4</sub>(DAD<sup>R</sup>)][NbF<sub>6</sub>].



### **1a-c**

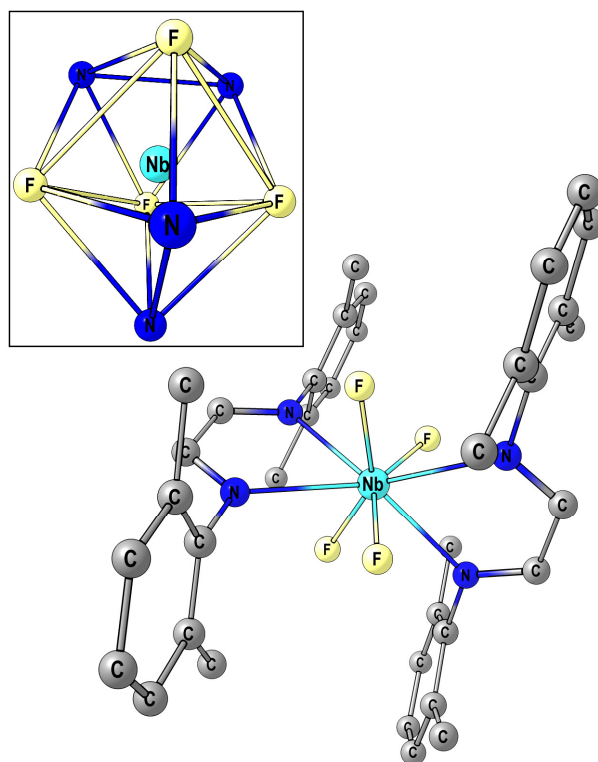
Compounds **1a-c** were characterized by elemental analysis, IR (solid state) and multinuclear NMR (CD<sub>3</sub>CN solution) spectroscopy. The <sup>1</sup>H and <sup>13</sup>C NMR spectra clearly exhibited one set of resonances due to the two equivalent  $\alpha$ -diimine ligands. The <sup>19</sup>F NMR pattern consists of the typical decet related to the [NbF<sub>6</sub>]<sup>-</sup> anion around 102 ppm,<sup>26,27,28</sup> and one additional resonance ascribable to the cation, occurring in the range 144.4-156.1 ppm. The <sup>93</sup>Nb spectra confirmed the presence of [NbF<sub>6</sub>]<sup>-</sup> (heptet centred at 1555 ppm).<sup>26,28</sup>

Due to the scarce solubility in organic solvents, it was not possible to collect crystals of **1a-c** suitable to X-ray analysis. Therefore, a DFT study was carried out to give insight into the structure of **1a-c**. First, the computational analysis suggested the major stability of [NbF<sub>4</sub>(DAD<sup>R</sup>)<sub>2</sub>]<sup>+</sup> respect to the [NbF<sub>4</sub>(DAD<sup>R</sup>)]<sup>+</sup> (Eq. 2), in agreement with the experiments (see above).



**DAD<sup>Dip</sup>**,  $\Delta G = -15.9 \text{ kcal mol}^{-1}$ ; **DAD<sup>Xyl</sup>**,  $\Delta G = -21.0 \text{ kcal mol}^{-1}$ ; **DAD<sup>Mes</sup>**,  $\Delta G = -19.7 \text{ kcal mol}^{-1}$

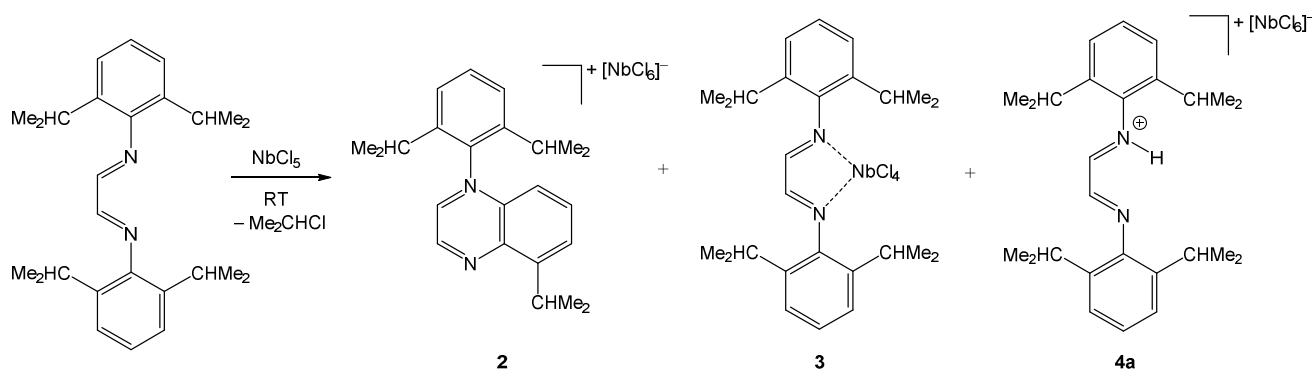
The DFT optimized structures of **1a-c** resemble previously reported  $[\text{NbF}_4(\text{L-L})_2][\text{NbF}_6]$  compounds (L-L = bidentate donor ligand), the cation being based on eight-coordinated metal centre.<sup>26a,c,27a</sup> The first coordination spheres of **1b** and **1c** have approximate  $D_{2d}$  symmetry and the donor atoms describe trigonal dodecahedra. The calculated structure of the cation in **1b** is shown in Figure 1, while that of the cation in **1c** is supplied as Supporting Information (see Figure SI-1). The symmetry lowers to  $D_2$  in the case of **1a**, because the steric bulk of the isopropyl substituents forces the angle between the planes defined by the two DAD moieties to be less than  $90^\circ$  (computed value =  $64.3^\circ$ , Figure SI-2).



**Figure 1.** DFT-optimized geometry of the cation,  $[\text{NbF}_4(\text{DAD}^{\text{Xyl}})_2]^+$ , within **1b** (C-PCM/ $\omega$ B97X, dichloromethane as continuous medium). Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ): Nb-F 1.888, 1.888, 1.888, 1.888; Nb-N 2.400, 2.402, 2.402, 2.402; C=N 1.271, 1.271, 1.271, 1.271. Selected angles ( $^\circ$ ): N-Nb-N (*chelate*) 67.5, 67.6; F-Nb-F (*trans*) 145.2, 145.3. Inset: polyhedron around the metal centre.

To the best of our knowledge, **1a-c** represent the first coordination compounds of  $\alpha$ -diimines with a HVM fluoride, and, more in general, rare examples of  $\alpha$ -diimine complexes bearing a fluoride ligand.

We moved to study the reactivity of  $\alpha$ -diimines with the heavier Nb(V) halides. The direct reaction of **DAD<sup>Dip</sup>** with NbCl<sub>5</sub>, i.e. in the absence of further reactants (see Introduction), was carried out in chlorinated solvent at room temperature. According to NMR spectroscopy, activation of the organic substrate occurred, resulting in the formation of a complicated mixture of products. Different crystallization procedures allowed to obtain variable solid mixtures containing [ $\{2,6\text{-C}_6\text{H}_3(\text{CHMe}_2)_2\}\text{N}(\text{CH})_2\text{NCC}(\text{CHMe}_2)(\text{CH})_3\text{C}\}[\text{NbCl}_6]$ , **2**, NbCl<sub>4</sub>(**DAD<sup>Dip</sup>**), **3**, and [**DAD<sup>Dip</sup>**(H)][NbCl<sub>6</sub>], **4a**, see Scheme 1, which were identified by X-ray diffraction (see Experimental for details). The parallel reaction with TaCl<sub>5</sub> in the place of NbCl<sub>5</sub> proceeded in a similar way, and in this case [**DAD<sup>Dip</sup>**(H)][TaCl<sub>6</sub>], **4b**, was isolated in very low yield. Carrying out the reactions at different temperatures (e.g., at -60 °C and 80 °C) did not substantially modify the composition of the final reaction mixtures.

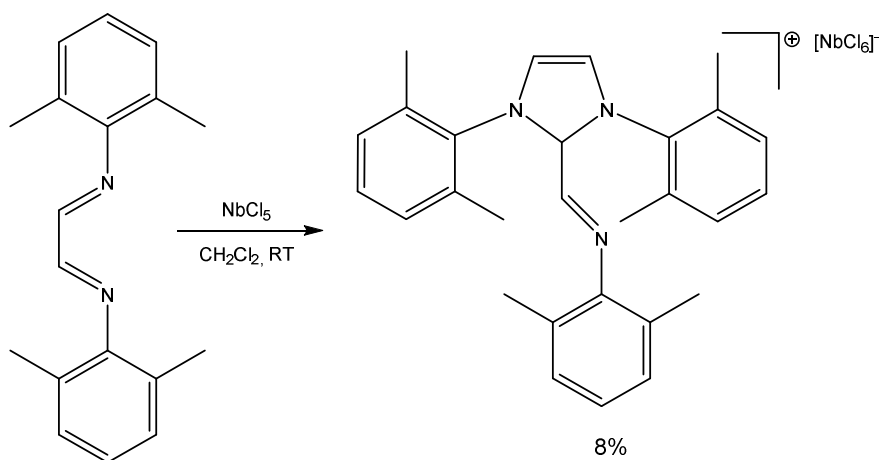


**Scheme 1.** Products identified in the non selective reaction of **DAD<sup>Dip</sup>** with NbCl<sub>5</sub>.

The details of the X-ray structures of **2**, **3**, **4a** and **4b** are provided in the Supporting Information. Compound **3** has been already reported, and its unprecedented X-ray structure strictly resembles that reported for the analogous NbCl<sub>4</sub>(**Me-DAD<sup>Dip</sup>**), differing from **3** in the presence of methyl substituents on the carbon atoms of the diazadiene backbone.<sup>20</sup> The unclear NbCl<sub>5</sub> directed activation of **DAD<sup>Dip</sup>** produces, among the other products, the quinoxalium salt **2** and, in this respect, matches the outcome of the reaction with WCl<sub>6</sub>.<sup>25</sup> The formation of **2** from **DAD<sup>Dip</sup>** presumably takes place via **DAD<sup>Dip</sup>** to Nb electron transfer, and release of one isopropyl group. The latter was detected by GC-MS as isopropyl chloride in the final reaction mixture; on the other hand,

a variable temperature EPR study suggested the presence of minor amounts of the isopropyl radical,  $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2$ , at  $-60\text{ }^\circ\text{C}$  (Figures SI-7 and SI-8). NMR experiments were not helpful to detect possible Nb(V) coordination adducts as intermediates. The activation pathway provided by  $\text{NbCl}_5$  seems strictly associated to two properties of this metal halide: 1) the oxidative power, as indicated by the co-formation of the Nb(IV) complex **3**; 2) the chlorinating capability (release of isopropyl chloride, see above). Accordingly, the different outcome observed in the reaction of  $\text{NbF}_5$  with **DAD<sup>Dip</sup>** could be explained on the basis of the stronger Nb-F bond compared to Nb-Cl.<sup>29</sup> In fact, if on one hand  $\text{NbF}_5$  is a potential strong oxidant,<sup>12b,30</sup> activation routes involving fluoride transfer to the organic substrate are inhibited (compare Scheme 1, formation of isopropyl chloride). This feature probably results in the stabilization of the coordination adduct **1a** (Eq. 1).

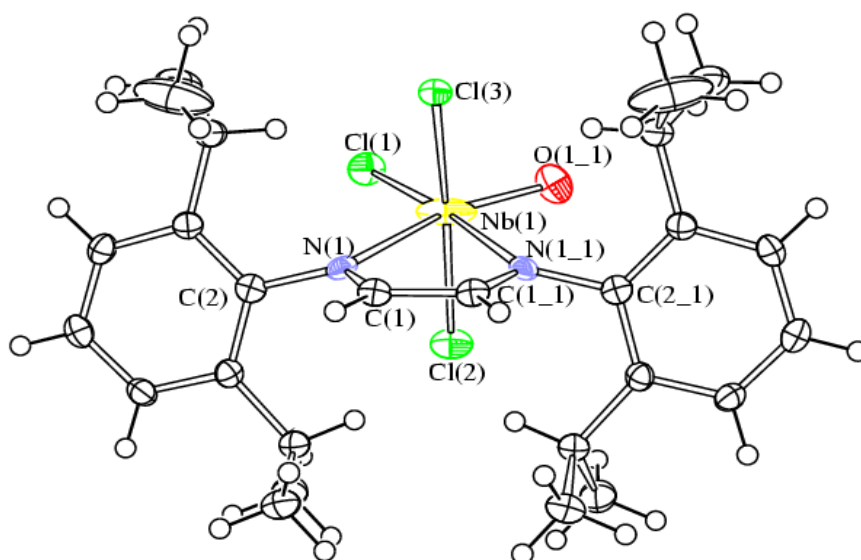
The attitude of  $\text{NbCl}_5$  to activate the  $\alpha$ -diimine frame was observed also in the reaction with **DAD<sup>Xyl</sup>**. Unfortunately, even in this case, the reaction took place with the formation of several products, and only the functionalized imidazolium salt  $[(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{NCHCHN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\text{CCHN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)][\text{NbCl}_6]$ , **5**, could be isolated in low yield and X-ray characterized (Scheme 2, Figure SI-9 and Table SI-5). The transformation of the  $\alpha$ -diimine skeleton into iminomethyl-imidazolium is a rare reaction, albeit not novel in the literature: it was previously reported to be promoted by Lewis acidic species such as HCl and  $\text{AlCl}_3$ .<sup>31</sup>



**Scheme 2.** Non selective  $\text{NbCl}_5$ -directed **DAD<sup>Xyl</sup>** to imidazolium conversion.



It is documented that the substitution of two chlorides with an oxide ligand in NbCl<sub>5</sub> decreases the oxophilicity and, more in general, the activation power of the metal species, possibly also in view of reinforcement of the remaining Nb–Cl bonds.<sup>29</sup> For instance, NbOCl<sub>3</sub>(thf)<sub>2</sub> is stable in tetrahydrofuran solution,<sup>32</sup> while NbCl<sub>5</sub>(thf) triggers thf polymerization in the same conditions.<sup>12a</sup> On account of this consideration, and with the aim of finding the way to stable  $\alpha$ -diimine coordination complexes other than **1a-c**, we decided to investigate the chemistry of NbOCl<sub>3</sub> with **DAD**<sup>Dip</sup>. The 1:1 molar ratio reaction afforded NbOCl<sub>3</sub>(**DAD**<sup>Dip</sup>), **6**, as the prevalent product. Complex **6** was purified by crystallization, and its molecular structure was determined by X-ray diffraction (Figure 2, Table 1).



**Figure 2.** Molecular structure of **6**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

**Table 1.** Selected bond distances (Å) and angles (°) for **6**.

Nb(1)–Cl(1)	2.176(3)	Nb(1)–O(1_1)	1.874(8)
Nb(1)–Cl(2)	2.3415(16)	Nb(1)–Cl(3)	2.3876(15)
Nb(1)–N(1)	2.417(4)	N(1)–C(1)	1.283(5)
N(1)–C(2)	1.449(5)	C(1)–C(1_1)	1.469(8)
Cl(2)–Nb(1)–Cl(3)	161.03(6)	Cl(1)–Nb(1)–N(1_1)	172.32(12)
O(1_1)–Nb(1)–N(1)	154.5(3)	O(1_1)–Nb(1)–Cl(1)	103.5(3)
N(1)–Nb(1)–N(1_1)	70.25(15)	Nb(1)–N(1)–C(1)	113.7(3)

Nb(1)–N(1)–C(2)	130.0(2)	C(1)–N(1)–C(2)	115.8(3)
N(1)–C(1)–C(1_1)	120.8(2)		

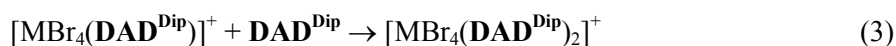
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Nb(1) is located on a mirror plane and, consequently, Cl(1) and O(1) are disordered over two equally populated positions related by *m*. The niobium centre displays a distorted octahedral coordination, with the three chlorides in a *mer* arrangement and the oxido ligand O(1) on the equatorial plane defined by the chelating **DAD<sup>Dip</sup>** ligand. The Nb(1)–O(1) distance [1.874(8) Å] is typical for a  $\pi$ -bond of an oxido ligand.<sup>33</sup> The mutually *trans* Nb(1)–Cl(2) [2.3415(16) Å] and Nb(1)–Cl(3) [2.3876(15) Å] are considerably longer than Nb(1)–Cl(1) [2.176(3) Å], *trans* to N(1). The C(1)–N(1) [1.283(5) Å] and C(1)–C(1\_1) [1.469(8) Å] interactions within the **DAD<sup>Dip</sup>** ligand are very close to the values found in non coordinated **DAD<sup>Dip</sup>** [1.265 and 1.467 Å, respectively],<sup>34</sup> and account for an imino double bond and a single C–C bond, respectively. As a consequence, the Nb(1)–N(1) distance [2.417(4) Å] is indicative of a N(sp<sup>2</sup>)-Nb dative bond.<sup>33b,35</sup> It is noteworthy that in the case of NbCl<sub>3</sub>(DAD<sup>tBu</sup>)(thf), formally containing Nb(V) and a reduced [DAD<sup>tBu</sup>]<sup>2-</sup> ligand, the Nb–N distances are considerably shorter [1.961(3) and 1.973(3) Å] in keeping with the amido nature of the reduced ligand.<sup>23a</sup> The Nb(1) centre of **6** is only slightly out [0.272 Å] of the NCCN backbone, as usually found in five-membered metallacycles containing  $\alpha$ -diimine ligands.<sup>2d,20</sup> Indeed, coplanarity or small deviations (as in this case) are indicative of a neutral  $\alpha$ -diimine ligand forming dative bonds, whereas in the case of reduced [DAD]<sup>2-</sup> the metal is generally found far from the NCCN plane [ $>1$  Å].

The <sup>1</sup>H, <sup>13</sup>C and <sup>93</sup>Nb NMR spectra of **6** evidenced the presence in CD<sub>2</sub>Cl<sub>2</sub> solution of a single isomeric form, reasonably bearing the same *mer* configuration as found in the solid state. Indeed, DFT calculations indicated the *mer* geometry of **6** to be more stable than the alternative *fac* isomer by about 3.3 kcal mol<sup>-1</sup> (Gibbs free energy), see Figure SI-10. Diagnostic IR data for **6** (solid state) are given by absorptions at 1626 (C=N) and 960 (Nb=O) cm<sup>-1</sup>, in accord with the DFT simulated spectrum.

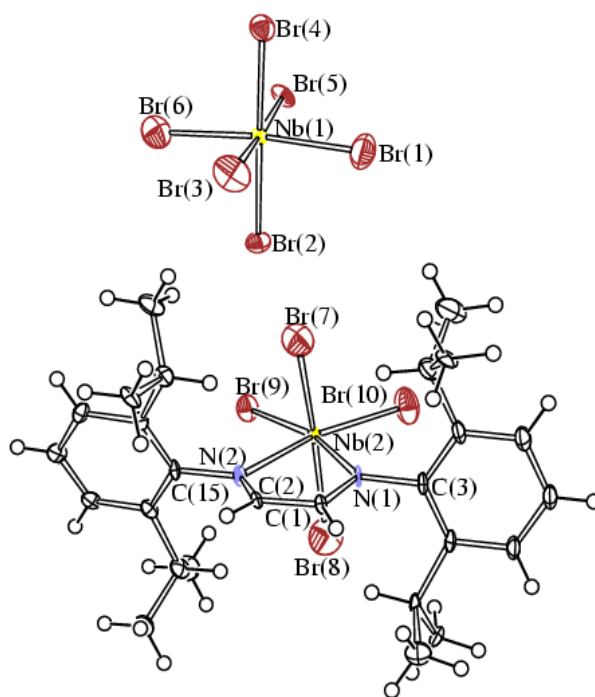
We finally explored the chemistry of niobium and tantalum pentabromides with **DAD<sup>Dip</sup>**. According to NMR analyses, complex activation pathways may be working in these reactions. Notwithstanding, the treatment of MBr<sub>5</sub>, in CH<sub>2</sub>Cl<sub>2</sub>, with 0.5 eq. of **DAD<sup>Dip</sup>** allowed to obtain after work up [MBr<sub>4</sub>(**DAD<sup>Dip</sup>**)]<sup>+</sup>[MBr<sub>6</sub>]<sup>-</sup> (M = Nb, **7a**; M = Ta, **7b**), in 25-30% yields. The viable isolation of coordination compounds from MBr<sub>5</sub>/α-diimine, although in moderate yield, is likely to be the consequence of the decreased oxidative power of the bromides compared to the corresponding pentafluorides or pentachlorides. Errore. Il segnalibro non è definito.a

DFT calculations pointed out the higher stability of the cations [MBr<sub>4</sub>(**DAD<sup>Dip</sup>**)]<sup>+</sup> respect to the addition of a second **DAD<sup>Dip</sup>** ligand (Eq. 3). A reverse situation has been found for the homologous niobium fluoride complexes (see above).



M = Nb, ΔG = 17.1 kcal mol<sup>-1</sup>; M = Ta, ΔG = 20.3 kcal mol<sup>-1</sup>

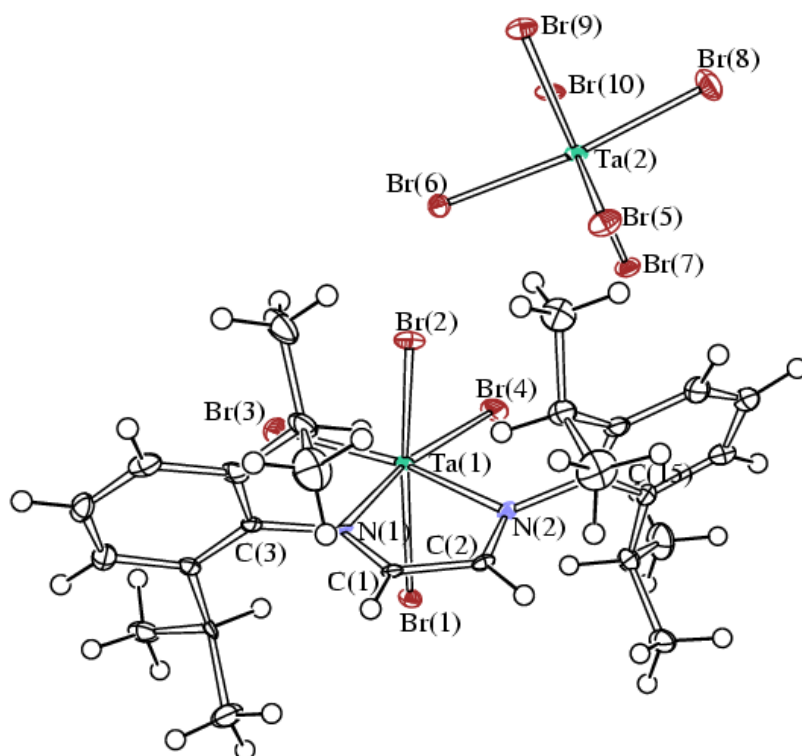
Compounds **7a-b** are isostructural, as ascertained by X-ray crystallography (Figures 3 and 4; Table 2 and 3). Both structures consist of an ionic packing of [MBr<sub>6</sub>]<sup>-</sup> anions and [MBr<sub>4</sub>(**DAD<sup>Dip</sup>**)]<sup>+</sup> cations. Regarding the coordination of **DAD<sup>Dip</sup>** to the M(V) centres in the cationic octahedral complexes, it is possible to do almost the same considerations reported for **6**. Thus, the chelating ligand retains the α-diimine nature of the free form, binding to the metal atom via dative bonds. The Nb(2)–N(1) [2.31(3) Å] and Nb(2)–N(2) [2.31(2) Å] distances of **7a** are rather elongated as in **6**. The Ta(1)–N(1) [2.320(8) Å] and Ta(1)–N(2) [2.302(8) Å] distances of **7b** are very similar to the dative Ta(V)–N(imino) bond [2.395(6) Å] of TaCl<sub>4</sub>(Cl<sub>3</sub>CCH<sub>2</sub>CH(Ph)-amido-imino) rather than its Ta(V)–N(amido) short contact [1.971(6) Å].<sup>21a</sup> The Nb centre in **7a** is almost coplanar respect to the NCCN backbone [0.049 Å out], whereas the tantalum in **7b** lays 0.347 Å outside of the same plane.



**Figure 3.** Molecular structure of **7a**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

**Table 2.** Selected bond distances (Å) and angles (°) for **7a**.

Nb(1)–Br(1)	2.428(6)	Nb(1)–Br(2)	2.542(5)
Nb(1)–Br(3)	2.423(6)	Nb(1)–Br(4)	2.457(5)
Nb(1)–Br(5)	2.551(4)	Nb(1)–Br(6)	2.452(6)
Nb(2)–Br(7)	2.384(6)	Nb(2)–Br(8)	2.384(7)
Nb(2)–Br(9)	2.388(4)	Nb(2)–Br(10)	2.367(5)
Nb(2)–N(1)	2.31(3)	Nb(2)–N(2)	2.31(2)
N(1)–C(1)	1.28(4)	N(2)–C(2)	1.25(4)
C(1)–C(2)	1.43(4)		
Br(1)–Nb(1)–Br(6)	173.4(2)	Br(2)–Nb(1)–Br(4)	177.68(18)
Br(3)–Nb(1)–Br(5)	177.8(2)	Br(7)–Nb(2)–Br(8)	169.6(2)
Br(9)–Nb(2)–N(1)	163.6(6)	Br(10)–Nb(2)–N(2)	161.0(6)
N(1)–Nb(2)–N(2)	70.5(8)	Nb(2)–N(1)–C(1)	114.9(19)
Nb(2)–N(1)–C(3)	126.2(17)	C(1)–N(1)–C(3)	118(3)
Nb(2)–N(2)–C(2)	116(2)	Nb(2)–N(2)–C(15)	126.0(17)
C(2)–N(2)–C(15)	118(2)	N(1)–C(1)–C(2)	119(3)
N(2)–C(2)–C(1)	120(3)		



**Figure 4.** Molecular structure of **7b**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

**Table 3.** Selected bond distances (Å) and angles (°) for **7b**.

Ta(2)–Br(5)	2.5637(11)	Ta(2)–Br(6)	2.5414(11)
Ta(2)–Br(7)	2.5051(11)	Ta(2)–Br(8)	2.4759(11)
Ta(2)–Br(9)	2.4593(12)	Ta(2)–Br(10)	2.4931(11)
Ta(1)–Br(1)	2.4508(11)	Ta(1)–Br(2)	2.4476(11)
Ta(1)–Br(3)	2.4103(10)	Ta(1)–Br(4)	2.3890(11)
Ta(1)–N(1)	2.320(8)	Ta(1)–N(2)	2.302(8)
N(1)–C(1)	1.276(12)	N(2)–C(2)	1.270(12)
C(1)–C(2)	1.446(13)		
Br(5)–Ta(2)–Br(10)	177.50(4)	Br(6)–Ta(2)–Br(8)	172.92(4)
Br(7)–Ta(2)–Br(9)	179.01(4)	Br(1)–Ta(1)–Br(2)	166.52(4)
Br(4)–Ta(1)–N(1)	166.27(19)	Br(3)–Ta(1)–N(2)	161.4(2)
N(1)–Ta(1)–N(2)	71.3(3)	Ta(1)–N(1)–C(1)	115.3(6)
Ta(1)–N(1)–C(3)	124.5(6)	C(1)–N(1)–C(3)	118.9(8)
Ta(1)–N(2)–C(2)	113.1(6)	Ta(1)–N(2)–C(15)	129.9(6)
C(2)–N(2)–C(15)	116.4(9)	N(1)–C(1)–C(2)	120.7(10)
N(2)–C(2)–C(1)	117.9(9)		

The NMR spectra of **7a-b** display one set of resonances. The  $[\text{NbB}_6]^-$  anion in **7a** gives rise to a diagnostic  $^{93}\text{Nb}$  signal at characteristic low field ( $\delta = 735$  ppm).<sup>28,36</sup>

## Conclusions

$\alpha$ -Diimines have been widely employed as feasible ligands for coordination chemistry, nevertheless their interaction with "high valent" metal halides (oxidation state of the metal  $> +4$ ) has been scarcely elucidated up to now. This feature should be related to the strong activation capability that homoleptic halides of metals such as Nb(V), Ta(V), Mo(V) and W(VI) may exhibit towards organic compounds containing hard donor atoms. Herein, we have presented the reactions of a small series of N-aryl  $\alpha$ -diimines with various Nb(V) and Ta(V) halides, in the absence of reducing agents. Non selective activation pathways, probably involving the oxidation of the organic substrate and halide transfer, are operative in the case of  $\text{NbCl}_5$ . However, stable coordination compounds can be designed by either introducing a metal-oxido function ( $\text{NbOCl}_3$ ), or replacing the chloride ligands with fluorides or bromides. All of these strategies inhibit activation routes and provide the first examples of structurally characterized coordination compounds of  $\alpha$ -diimines with halides of metals in an oxidation state higher than +4. In particular, the stabilization of  $\text{NbF}_5$  coordination compounds is presumably due to the presence of strong Nb-F bonds, disfavoring fluorine transfer, while the stabilization of  $\text{MBr}_5$  coordination compounds may be related to the relatively low oxidative power of the M(V) centre.

## Experimental section

*Warning! The metal reactants used in this work are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and isolation procedures.* The reaction vessels were oven dried at 150 °C prior to use, evacuated ( $10^{-2}$  mmHg) and then filled with nitrogen.  $\text{NbF}_5$  (99.5%) was purchased from Apollo Sci., sublimed and stored under argon atmosphere in sealed glass tubes.  $\text{NbCl}_5$  (99+%),  $\text{NbF}_5$  (99.5%) and  $\text{TaCl}_5$  (99.9%) were purchased from Strem and stored under

argon in sealed glass tubes.  $\text{NbOCl}_3$  (from  $\text{NbCl}_5$ ),<sup>37</sup>  $\text{NbBr}_5$  and  $\text{TaBr}_5$  (from  $\text{MBr}_5$ ,  $\text{M} = \text{Nb}$  or  $\text{Ta}$ ),<sup>38</sup> and  $\alpha$ -diimines<sup>39</sup> were prepared according to the literature by using organic reactants (TCI Europe) of the highest purity available. All the metal products were stored under inert atmosphere ( $\text{Ar}$  or  $\text{N}_2$ ) in sealed glass tubes. Solvents (Sigma Aldrich) were distilled from appropriate drying agents before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for  $^{93}\text{Nb}$  were referenced to external  $[\text{NEt}_4][\text{NbCl}_6]$ ; the chemical shifts for  $^{19}\text{F}$  were referenced to external  $\text{CFCl}_3$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were assigned with the assistance of  $^1\text{H}$ ,  $^{13}\text{C}$  correlation measured through *gs*-HSQC and *gs*-HMBC experiments. EPR spectra were recorded at 298 K on a Varian (Palo Alto, CA, USA) E112 spectrometer operating at X band, equipped with a Varian E257 temperature control unit and interfaced to IPC 610/P566C industrial grade Advantech computer, using acquisition board<sup>40</sup> and software package especially designed for EPR experiments.<sup>41</sup> Experimental EPR spectra were simulated by the WINSIM 32 program.<sup>42</sup> Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. Chloride and bromide were determined by the Mohr method<sup>43</sup> on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of  $\text{HNO}_3$  up to neutralization. The metal ( $\text{M} = \text{Nb}$ ,  $\text{Ta}$ ) was analyzed as  $\text{M}_2\text{O}_5$ , obtained by hydrolysis of the samples followed by calcination in a platinum crucible. GC-MS analyses were performed on a HP6890 instrument, interfaced with MSD-HP5973 detector and equipped with a Phenomenex Zebron column.

**Reactions of  $\text{NbF}_5$  with  $\alpha$ -diimines: synthesis of  $[\text{NbF}_4(\text{DAD}^{\text{R}})_2][\text{NbF}_6]$  ( $\text{DAD}^{\text{R}} = \text{DAD}^{\text{Dip}}$ , **1a**;  $\text{DAD}^{\text{Xyl}}$ , **1b**;  $\text{DAD}^{\text{Mes}}$ , **1c**).** *General procedure:*  $\text{NbF}_5$  was added to a solution of the appropriate organic reactant in  $\text{CH}_2\text{Cl}_2$  (5-10 mL). The mixture was stirred at room temperature for 24 h, then

the solvent was removed in vacuo. An air sensitive, yellow-orange microcrystalline solid was obtained.

**[NbF<sub>4</sub>(DAD<sup>Dip</sup>)<sub>2</sub>][NbF<sub>6</sub>], 1a.** Yellow-orange solid, 82% yield from NbF<sub>5</sub> (167 mg, 0.889 mmol) and DAD<sup>Dip</sup> (335 mg, 0.890 mmol). Anal. Calcd. for C<sub>52</sub>H<sub>72</sub>F<sub>10</sub>N<sub>4</sub>Nb<sub>2</sub>: C, 55.32; H, 6.43; N, 4.96; Nb, 16.46. Found: C, 55.20; H, 6.58; N, 4.26; Nb, 16.36. IR (solid state): 3063w, 2974m-s, 2971m-s, 2931m, 2870w-m, 1626w (C=N), 1585w-m, 1460m-s-sh, 1386m-s, 1366m-s, 1353w-m, 1331w-m, 1305w, 1266m, 1174m-s, 1110m, 1097m, 1058m-s, 1044m, 942m, 925w, 905s, 839w-m, 799vs, 755vs, 737vs, 704w-m, 677w-m cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ = 8.34 (s, 2 H, CH=N); 7.31-7.24 (6 H, *arom* CH); 2.97 (m, 4 H, CHMe<sub>2</sub>); 1.23, 1.06 ppm (d, <sup>3</sup>J<sub>HH</sub> = 6.85 Hz, 24 H, CHMe<sub>2</sub>). <sup>13</sup>C NMR {<sup>1</sup>H} (CD<sub>3</sub>CN): δ = 164.7 (CH=N), 144.9, 141.8, 128.9, 124.3 (*arom*); 28.2, 27.9 (CHMe<sub>2</sub>); 24.7, 22.6 ppm (CHMe<sub>2</sub>). <sup>19</sup>F NMR (CD<sub>3</sub>CN): δ = 156.1 (s, Δv<sup>1/2</sup> = 21 Hz, NbF<sub>4</sub>); 102.7 (decet, <sup>1</sup>J<sub>NbF</sub> = 338 Hz, NbF<sub>6</sub>) ppm. <sup>93</sup>Nb NMR (CD<sub>3</sub>CN): δ = 1555 (hept, <sup>1</sup>J<sub>NbF</sub> = 337 Hz, NbF<sub>6</sub>) ppm.

**[NbF<sub>4</sub>(DAD<sup>Xyl</sup>)<sub>2</sub>][NbF<sub>6</sub>], 1b.** Dark-brown solid, 84% yield from NbF<sub>5</sub> (203 mg, 1.08 mmol) and DAD<sup>Xyl</sup> (282 mg, 1.07 mmol). Anal. Calcd. for C<sub>36</sub>H<sub>40</sub>F<sub>10</sub>N<sub>4</sub>Nb<sub>2</sub>: C, 47.80; H, 4.46; N, 6.19; Nb, 20.54. Found: C, 47.55; H, 4.56; N, 6.12; Nb, 20.36. IR (solid state): 3050w, 2965w, 2906vw, 1607m-br (C=N), 1539m, 1473s, 1384w, 1372w, 1322w, 1262m, 1179s, 1097m-s, 1030w, 940w, 894w-m, 838w, 810w-m, 776vs, 736w, 684w cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ = 8.45 (s, 2 H, CH=N); 7.31-7.13 (6 H, *arom* CH); 2.39, 2.06 ppm (s, 12 H, Me). <sup>19</sup>F NMR (CD<sub>3</sub>CN): δ = 145.9 (s, Δv<sup>1/2</sup> = 38 Hz, NbF<sub>4</sub>); 101.7 (decet, <sup>1</sup>J<sub>NbF</sub> = 337 Hz, NbF<sub>6</sub>) ppm. <sup>93</sup>Nb NMR (CD<sub>3</sub>CN): δ = 1555 (hept, <sup>1</sup>J<sub>NbF</sub> = 337 Hz, NbF<sub>6</sub>) ppm.

**[NbF<sub>4</sub>(DAD<sup>Mes</sup>)<sub>2</sub>][NbF<sub>6</sub>], 1c.** Orange solid, 91% yield from NbF<sub>5</sub> (188 mg, 1.00 mmol) and DAD<sup>Mes</sup> (294 mg, 1.01 mmol). Anal. Calcd. for C<sub>40</sub>H<sub>48</sub>F<sub>10</sub>N<sub>4</sub>Nb<sub>2</sub>: C, 50.01; H, 5.04; N, 5.83; Nb, 19.34. Found: C, 49.86; H, 5.12; N, 5.71; Nb, 19.12. IR (solid state): 3037w-br, 2964w-m, 2918w-m, 2867w, 1654w, 1607m (C=N), 1475m-s-sh, 1365m-s-sh, 1319w, 1304w, 1262m, 1202s, 1143s, 1098m, 1038m-s, 1022m-s, 963w, 924m, 907w-m, 855vs, 801s, 721w-m, 678w-m cm<sup>-1</sup>. <sup>1</sup>H NMR

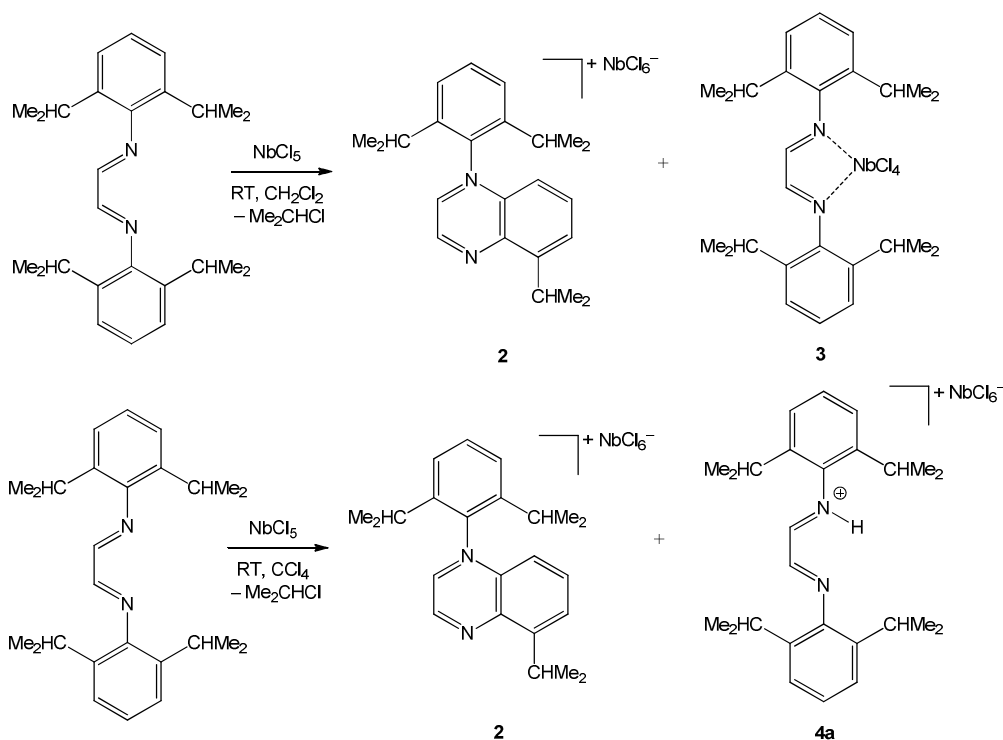


(CD<sub>3</sub>CN):  $\delta$  = 8.43 (s, 2 H, CH=N); 7.01 (4 H, *arom* CH); 2.34, 2.31, 2.02, 1.99 ppm (s, 18 H, Me).

<sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$  = 144.4 (s,  $\Delta\nu^{1/2}$  = 24 Hz, NbF<sub>4</sub>); 102.5 (decet, <sup>1</sup>J<sub>NbF</sub> = 339 Hz, NbF<sub>6</sub>) ppm.

<sup>93</sup>Nb NMR (CD<sub>3</sub>CN):  $\delta$  = 1555 (hept, <sup>1</sup>J<sub>NbF</sub> = 337 Hz, NbF<sub>6</sub>) ppm.

**Reactions of MCl<sub>5</sub> (M = Nb, Ta) with DAD<sup>Dip</sup>. Formation and isolation of [{2,6-C<sub>6</sub>H<sub>3</sub>(CHMe<sub>2</sub>)<sub>2</sub>}N(CH)<sub>2</sub>NCC(CHMe<sub>2</sub>)(CH)<sub>3</sub>C][NbCl<sub>6</sub>], **2**, NbCl<sub>4</sub>(DAD<sup>Dip</sup>), **3**, and [DAD<sup>Dip</sup>(H)][MCl<sub>6</sub>] (M = Nb, **4a**; M = Ta, **4b**).** A solution of DAD<sup>Dip</sup> (358 mg, 0.950 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated with NbCl<sub>5</sub> (255 mg, 0.925 mmol). A dark red solution formed in a few minutes, and this was allowed to stir for additional 24 hours. Isopropyl chloride was detected in the mixture by GC-MS. The volatile materials were removed in vacuo. <sup>93</sup>Nb NMR analysis of the red-brown residue (in CDCl<sub>3</sub>) suggested the presence of [NbCl<sub>6</sub>]<sup>-</sup> as largely prevalent niobium species ( $\delta$  = 7.8 ppm,  $\Delta\nu^{1/2}$  = 2·10<sup>2</sup> Hz). Crystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub>/hexane at -30 °C afforded a mixture of red and yellow crystals, which were mechanically separated under a nitrogen atmosphere. X-ray diffraction analysis allowed to identify **2** and **3** (see SI for details). However, NMR analysis of the crystalline material revealed the presence of several species. When the reaction was performed in CCl<sub>4</sub> (10 mL) using analogous quantities of reactants, a red residue was recovered after elimination of the volatiles in vacuo. Crystallization of this residue from CH<sub>2</sub>Cl<sub>2</sub>/hexane at -30 °C afforded few crystals of **2** and **4a**.



The reaction of TaCl<sub>5</sub> (0.80 mmol) with DAD<sup>Dip</sup> (0.80 mmol) in CCl<sub>4</sub> (10 mL) allowed to isolate few crystals of **4b** after work up.

**Reaction of DAD<sup>Xyl</sup> with NbCl<sub>5</sub>. Isolation of [(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)NCHCHN(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)CCHN(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)] [NbCl<sub>6</sub>], **5**.**

A solution of DAD<sup>Xyl</sup> (148 mg, 0.560 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated with NbCl<sub>5</sub> (149 mg, 0.552 mmol). The mixture was allowed to react at room temperature for 18 h. The resulting solution was concentrated to ca. 3 mL, layered with hexane and stored at -30 °C. Few crystals of **5** suitable for X-ray analysis were recovered after one week. Yield 40 mg, 8%. Anal. Calcd. for C<sub>28</sub>H<sub>30</sub>Cl<sub>6</sub>N<sub>3</sub>Nb: C, 47.09; H, 4.23; N, 5.88; Cl, 29.78; Nb, 13.01. Found: C, 46.85; H, 4.14; N, 5.84; Cl, 29.55; Nb, 13.10. IR (solid state): 1631m (C=N) cm<sup>-1</sup>. The reaction of NbCl<sub>5</sub> with DAD<sup>Xyl</sup> was repeated under analogous conditions but using CD<sub>2</sub>Cl<sub>2</sub> as solvent. Subsequent NMR analysis of the reaction mixture indicated the formation of several products, including MeCl.

**Reaction of NbOCl<sub>3</sub> with DAD<sup>Dip</sup>: synthesis of NbOCl<sub>3</sub>(DAD<sup>Dip</sup>), 6.** A solution of DAD<sup>Dip</sup> (298 mg, 0.791 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was treated with NbOCl<sub>3</sub> (171 mg, 0.794 mmol). The mixture stirred at room temperature for 18 h. Then, the volatile materials were removed in vacuo, and the residue was washed with hexane (2 x 20 mL). Compound **6** was recovered as a light red solid. Yield 290 mg, 62%. Crystals suitable for X-ray analysis were obtained from a dichloromethane solution layered with pentane and stored at -30 °C. Anal. Calcd. for C<sub>26</sub>H<sub>36</sub>Cl<sub>3</sub>N<sub>2</sub>NbO: C, 52.76; H, 6.13; N, 4.73; Cl, 17.97; Nb, 15.70. Found: C, 52.60; H, 6.18; N, 4.66; Nb, 15.36. IR (solid state): 3062w-br, 2965m-s, 2928w-m, 2869w-m, 1626w (C=N), 1586w, 1567w, 1465m-s, 1436w-m, 1384w-m, 1370m-s, 1330w-m, 1300w, 1262w-m, 1184w-m, 1166m, 1097m-s, 1058m-s, 1043m-s, 1014m, 960vs (Nb=O), 930m, 906m-s, 833m, 799s, 752s, 691w-m cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.22 (s, 2 H, CH=N); 7.45-7.35 (6 H, *arom* CH); 2.99 (m, 2 H, CHMe<sub>2</sub>); 1.37, 1.17 ppm (m, 12 H, CHMe<sub>2</sub>). <sup>13</sup>C NMR{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>): δ = 162.5 (C=N); 151.8 (*ipso*-CN); 143.0 (*arom* C-*ortho*); 129.5, 124.9 (*arom* CH); 29.1 (CHMe<sub>2</sub>); 26.0, 23.4 ppm (CHMe<sub>2</sub>). <sup>93</sup>Nb NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 431 ppm (Δν<sup>1/2</sup> = 2.9·10<sup>3</sup> Hz).

**Reactions of MBr<sub>5</sub> with DAD<sup>Dip</sup>: isolation of [MBr<sub>4</sub>(DAD<sup>Dip</sup>)] [MBr<sub>6</sub>] (M = Nb, **7a**; M = Ta, **7b**).** *General procedure:* the metal bromide was added to a solution of DAD<sup>Dip</sup> in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The mixture was allowed to react for 18 h at room temperature. Then the volatile materials were removed, and the NMR analysis of the residue indicated the presence of a mixture of products. X-ray quality crystals of **7a-b** were obtained from dichloromethane solutions layered with hexane and stored at -30 °C for 48 h.

**[NbBr<sub>4</sub>(DAD<sup>Dip</sup>)] [NbBr<sub>6</sub>], **7a**.** Dark red crystals, 31% yield from NbBr<sub>5</sub> (273 mg, 0.555 mmol) and DAD<sup>Dip</sup> (105 mg, 0.279 mmol). Anal. Calcd. for C<sub>26</sub>H<sub>36</sub>Br<sub>10</sub>N<sub>2</sub>Nb<sub>2</sub>: C, 22.94; H, 2.67; N, 2.06; Br, 58.69; Nb, 13.65. Found: C, 23.12; H, 2.50; N, 1.90; Br, 58.40; Nb, 13.52. IR (solid state): 3061w-br, 2965s, 2926m, 2867m, 1646w-br (C=N), 1622w-br (C=N), 1587w-m, 1562w-br, 1533w-br, 1507w-m, 1463s, 1426s, 1386m, 1363s, 1320m-sh, 1300w-m, 1263w-m, 1227w, 1214w, 1182w,

1155w-m-sh, 1095m, 1059m, 1044m, 959s, 936m, 904w-m, 867m, 798vs, 751vs, 690m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 8.50$  (s, 2 H,  $\text{CH}=\text{N}$ ); 7.4-7.2 (6 H, *arom* CH); 2.84 (m, 4 H,  $\text{CHMe}_2$ ); 1.20, 1.08 ppm (d, 24 H,  $\text{CHMe}_2$ ).  $^{93}\text{Nb}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 735$  ( $\Delta\nu^{1/2} = 1 \cdot 10^2$  Hz,  $\text{NbBr}_6^-$ ).

**[TaBr<sub>4</sub>(DAD<sup>Dip</sup>)]<sub>2</sub>[TaBr<sub>6</sub>], 7b.** Red crystals, 24% yield from TaBr<sub>5</sub> (350 mg, 0.603 mmol) and DAD<sup>Dip</sup> (115 mg, 0.306 mmol). Anal. Calcd. for C<sub>26</sub>H<sub>36</sub>Br<sub>10</sub>N<sub>2</sub>Ta<sub>2</sub>: C, 20.31; H, 2.36; N, 1.82; Br, 51.97; Ta, 23.54. Found: C, 20.18; H, 2.46; N, 1.78; Br, 51.66; Ta, 23.36.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 8.45$  (s, 2 H,  $\text{CH}=\text{N}$ ); 7.4-7.2 (6 H, *arom* CH); 2.83 (m, 4 H,  $\text{CHMe}_2$ ); 1.20, 1.08 ppm (d, 24 H,  $\text{CHMe}_2$ ).

**X-ray Crystallographic Studies.** Crystal data and collection details for **2**, **3**, **4a**·CH<sub>2</sub>Cl<sub>2</sub>, **4b**·CH<sub>2</sub>Cl<sub>2</sub>, **5**·0.5CH<sub>2</sub>Cl<sub>2</sub>, **6**, **7a** and **7b** are listed in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).<sup>44</sup> The structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ .<sup>45</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except the N-bonded hydrogen of **4a**·CH<sub>2</sub>Cl<sub>2</sub> which has been located in the Fourier map and refined isotropically. The Nb atom of **6** is located on a mirror plane and, consequently, Cl(1) and O(1) are disordered over two equally populated positions related by *m*. A second solvate of **4b**·CH<sub>2</sub>Cl<sub>2</sub>, *i.e.*, **4b**·CCl<sub>4</sub> has been obtained. Nonetheless, its data are not very good and are not included in the discussion (the cif file has been deposited within the Cambridge Crystallographic Datacentre for sake of completeness). The Nb atom of **5** is located on a mirror plane and, thus, only half of the molecule is present within the asymmetric unit of the unit cell. The CH<sub>2</sub>Cl<sub>2</sub> molecule of **5**·0.5CH<sub>2</sub>Cl<sub>2</sub> is disordered over four positions (two by two related by

an inversion centre). The crystals of **7a** are racemically twinned with refined Flack parameter 0.14(3).<sup>46</sup>

**Insert Table 4 about here.**

**Computational studies.** The computational geometry optimizations were carried out without symmetry constraints, using the range-separated DFT functional  $\omega$ B97X<sup>47</sup> in combination with the split-valence polarized basis set of Ahlrichs and Weigend, with ECP on the metal centre.<sup>48</sup> The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.<sup>49</sup> The C-PCM implicit solvation model ( $\epsilon = 9.08$ ) was added to  $\omega$ B97X calculations.<sup>50</sup> Gaussian '09 was used as software.<sup>51</sup>

**Supplementary Material.** X-ray details for **2**, **3**, **4a-b**, **5**, DFT structures, EPR analysis. Cartesian coordinates of all DFT-optimized compounds are collected in a separated .xyz file. CCDC reference numbers 1551417 (**2**), 1551418 (**3**), 1814760 (**4a**·CH<sub>2</sub>Cl<sub>2</sub>), 1814759 (**4b**·CH<sub>2</sub>Cl<sub>2</sub>), 1814761 (**5**·½CH<sub>2</sub>Cl<sub>2</sub>), 1814762 (**6**), 1814758 (**7a**), 1814763 (**7b**) and 1814764 (**4b**·CCl<sub>4</sub>) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### **Acknowledgements.**

The authors thank the University of Pisa for financial support.

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**Table 4.** Crystal data and experimental details for **2**, **3**, **4a·CH<sub>2</sub>Cl<sub>2</sub>**, **4b·CH<sub>2</sub>Cl<sub>2</sub>**, **5·½CH<sub>2</sub>Cl<sub>2</sub>**, **6**, **7a** and **7b**.

	<b>2</b>	<b>3</b>	<b>4a·CH<sub>2</sub>Cl<sub>2</sub></b>	<b>4b·CH<sub>2</sub>Cl<sub>2</sub></b>	<b>5·½CH<sub>2</sub>Cl<sub>2</sub></b>	<b>6</b>	<b>7a</b>	<b>7b</b>
Formula	C <sub>23</sub> H <sub>29</sub> Cl <sub>6</sub> N <sub>2</sub> Nb	C <sub>26</sub> H <sub>36</sub> Cl <sub>4</sub> N <sub>2</sub> Nb	C <sub>27</sub> H <sub>39</sub> Cl <sub>8</sub> N <sub>2</sub> Nb	C <sub>27</sub> H <sub>39</sub> Cl <sub>8</sub> N <sub>2</sub> Ta	C <sub>28.5</sub> H <sub>31</sub> Cl <sub>7</sub> N <sub>3</sub> Nb	C <sub>26</sub> H <sub>36</sub> Cl <sub>3</sub> N <sub>2</sub> NbO	C <sub>26</sub> H <sub>36</sub> Br <sub>10</sub> N <sub>2</sub> Nb <sub>2</sub>	C <sub>26</sub> H <sub>36</sub> Br <sub>10</sub> N <sub>2</sub> Ta <sub>2</sub>
Fw	639.09	611.28	768.11	856.15	756.62	591.83	1361.49	1537.57
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<b>P1</b>	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>Pnma</i>	<i>P2<sub>1</sub></i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	10.004(2)	12.8295(9)	16.0202(4)	16.105(7)	8.3272(6)	12.5172(8)	10.805(4)	11.6799(4)
<i>b</i> , Å	10.785(3)	21.6973(15)	13.0226(3)	13.078(5)	18.4834(12)	21.3437(14)	13.497(4)	12.2717(5)
<i>c</i> , Å	12.934(3)	10.3071(7)	17.8448(4)	17.933(8)	22.5408(15)	10.4112(6)	13.691(5)	27.3280(10)
α°	85.466(3)	90	90	90	90	90	90	90
β°	88.650(3)	90	113.1630(10)	113.164(5)	97.617(4)	90	109.104(4)	98.414(2)
γ°	83.733(3)	90	90	90	90	90	90	90
Cell volume, Å <sup>3</sup>	1382.7(6)	2869.1(3)	3422.76(14)	3473(3)	3438.8(4)	2781.5(3)	1886.7(11)	3875.2(3)
<i>Z</i>	2	4	4	4	4	4	2	4
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.535	1.415	1.491	1.638	1.461	1.413	2.397	2.635
μ, mm <sup>-1</sup>	1.030	0.809	0.997	3.801	0.917	0.742	11.217	15.975
<i>F</i> (000)	648	1260	1568	1696	1532	1224	1276	2808
θ limits, °	0.22×0.20×0.16	0.21×0.16×0.14	1.45 – 25.03	1.44 – 26.00	1.82–25.02	1.91 – 25.00	1.57–25.03	1.51 – 25.00
Reflections collected	13141	24389	36558	28556	49289	37999	15974	54924
Independent reflections	5167 [ <i>R</i> <sub>int</sub> = 0.0405]	3209 [ <i>R</i> <sub>int</sub> = 0.0351]	6047 [ <i>R</i> <sub>int</sub> = 0.0666]	6772 [ <i>R</i> <sub>int</sub> = 0.0973]	6041 [ <i>R</i> <sub>int</sub> = 0.0872]	2528 [ <i>R</i> <sub>int</sub> = 0.0903]	6558 [ <i>R</i> <sub>int</sub> = 0.1192]	6811 [ <i>R</i> <sub>int</sub> = 0.1469]
Data / restraints / parameters	5167 / 0 / 295	3209 / 0 / 154	6047 / 1 / 346	6772 / 0 / 343	6041 / 9 / 366	2528 / 1 / 164	6558 / 465 / 338	6811 / 228 / 369
Goodness of fit on <i>F</i> <sup>2</sup>	1.014	1.077	1.041	1.045	1.034	1.093	1.040	1.038
<i>R</i> 1 ( <i>I</i> > 2σ( <i>I</i> ))	0.0399	0.0321	0.0370	0.0464	0.0670	0.0475	0.0931	0.0448
<i>wR</i> 2 (all data)	0.0955	0.0842	0.0903	0.1174	0.2200	0.1250	0.2441	0.1092
Largest diff. peak and hole, e.Å <sup>-3</sup>	0.530 / -0.699	0.751 / -0.777	0.717 / -0.492	2.402 / -1.942	2.335 / -1.134	0896 / -1.294	2.690 / -1.928	2.694 / -2.486