

# Coordination Compounds of Niobium(IV) Oxide Dihalides Including the Synthesis and the Crystallographic Characterization of NHC Complexes

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## Abstract

The 1:1 molar reactions of NbOX<sub>3</sub> with SnBu<sub>3</sub>H, in toluene at 0 °C in the presence of oxygen/nitrogen donors, resulted in the formation of NbOX<sub>2</sub>L<sub>2</sub> (X = Cl, L<sub>2</sub> = dme, **2a**; X = Br, L<sub>2</sub> = dme, **2b**; X = Cl, L = thf, **2c**; X = Cl, L = NCMe, **2d**; dme = 1,2-dimethoxyethane, thf = tetrahydrofuran), in good yields. The 1:2 reactions of freshly prepared **2d** and **2b** with the bulky NHC ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, Imes, and 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene, Ixyl, respectively, afforded the complexes NbOCl<sub>2</sub>(Imes)<sub>2</sub>, **3**, and NbOBr<sub>2</sub>(Ixyl)<sub>2</sub>, **4**, in 50-60% yields. The reactions of **2b** with NaOR, in tetrahydrofuran, gave NbOCl(OR) (R = Ph, **5**; R = Me, **6**) in about 60% yields. All the products were characterized by analytical and spectroscopic techniques, moreover DFT calculations were carried out in order to shed light on synthetic and structural features. Compounds **3** and **4**, whose molecular structures have been ascertained by X-ray diffraction, represent very rare example of crystallographically characterized niobium-NHC systems.

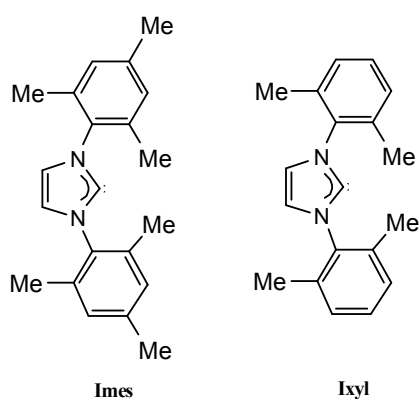
## Introduction

Since Arduengo's isolation of the first crystalline N-heterocyclic carbene (NHC) in 1991, the use of NHC ligands in organometallic chemistry has seen a tremendous advance, with applications ranging from medicinal chemistry to homogeneous catalysis and material science.<sup>1</sup> The chemistry of NHC ligands has been developed especially with reference to low and medium valent metals, belonging to middle to late transition groups. Otherwise NHC systems based on oxophilic, early transition metals have been much less investigated, and one of the reasons may be attributed to the possible moisture sensitivity affecting the reaction systems.<sup>2</sup> In particular, niobium represents a surprising exception in the crowded scenario of the NHC chemistry:<sup>3</sup> indeed very few Nb-NHC systems have appeared in the

literature so far,<sup>3,4</sup> and we have recently contributed with the unique structurally characterized niobium complex containing a monodentate NHC ligand.<sup>3</sup>

Niobium pentahalides are among the most easily available and cost effective niobium species: their chemistry has undergone a significant progress in the last decade, encouraged by the low toxicity associated with the metal element and the outstanding reactivity patterns observed in some NbX<sub>5</sub>-directed organic transformations.<sup>5</sup> Niobium(V) pentahalides have been employed as convenient starting reagents to access both Nb(IV) and Nb(III) halides,<sup>6</sup> which in turn have found applications in synthetic organic chemistry.<sup>5b,7</sup> Also niobium (V) oxide trichlorides and tribromides are rather easily accessible compounds,<sup>8</sup> whose coordination chemistry has been investigated to some extent.<sup>9</sup> On the other hand, the synthesis of reduced niobium oxide halides, that are materials of potential interest also in view of their solid state properties,<sup>10</sup> is a more difficult task. More in detail, the reported synthetic procedures to afford NbOX<sub>2</sub> (X = Cl, Br) require prohibitive experimental conditions,<sup>11</sup> thus determining an important drawback to the acquisition of the knowledge of the reactivity of these compounds. As a matter of fact, the coordination chemistry of NbOX<sub>2</sub> (X = Cl, Br) has been almost unexplored heretofore: the only coordination adducts were claimed to be prepared by hydrolysis of niobium tetrachloride compounds<sup>12</sup> or reduction of NbOCl<sub>3</sub>/phosphine systems with Na/Hg, however the products were not unambiguously characterized.<sup>12a</sup>

Herein we present a convenient room temperature procedure to afford complexes of NbOCl<sub>2</sub> and NbOBr<sub>2</sub> with simple oxygen and nitrogen donor ligands, starting from the corresponding niobium pentahalides. These Nb(IV) products undergo substitution reactions with phenoxide and methoxide anions and with bulky, monodentate NHC ligands (Chart 1), affording fairly air stable NbOX<sub>2</sub>(NHC)<sub>2</sub> complexes. The synthetic aspects and the structural characterization of the new complexes (including X-ray characterization of the NHC complexes) will be discussed, with the assistance of DFT results.



**Chart 1.** NHC ligands used in the present work.

## Results and discussion

We prepared  $\text{NbOX}_3$  ( $X = \text{Cl}, \text{Br}$ ) in *ca.* 80% yields by allowing the respective precursors  $\text{NbX}_5$  to react with one equivalent of hexamethyldisiloxane, in dichloromethane at room temperature, Eqn. 1. This method was previously reported for  $\text{NbOCl}_3$ ,<sup>8c</sup> and has been employed here also to obtain  $\text{NbOBr}_3$ .<sup>13</sup>



The complexes  $\text{NbOX}_3(\text{dme})$  ( $X = \text{Cl}$ ,<sup>14</sup>  $\text{Br}$ ;  $\text{dme} = 1,2\text{-dimethoxyethane}$ ), **1a-b**, were afforded in good yields upon addition of  $\text{dme}$  to  $\text{NbOX}_3$  in toluene, Eqn. 2.

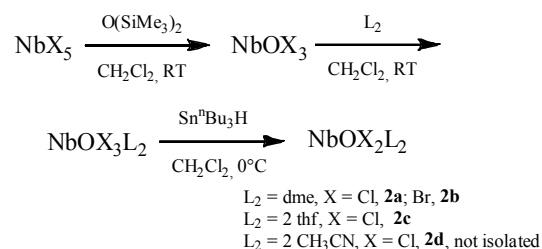


According to NMR evidences, the unprecedented **1b** exists in dichloromethane solution as a single isomeric form (<sup>93</sup>Nb resonance at  $-205$  ppm), presumably ascribable to a (distorted) octahedral geometry with *mer* configuration (<sup>13</sup>C NMR resonances due to the non equivalent methyl groups occur at 70.3 and 63.6 ppm). This result is consistent with DFT EDF2 calculations, the *mer* isomer resulting more stable than the *fac* one by about  $8.9 \text{ kcal mol}^{-1}$  (Gibbs free energy). Figure S1 and Table S1 within the SI show

the calculated structures of the possible isomers of **1b**, and the bonding parameters related to the most stable isomer.

It should be remarked that niobium chlorides and bromides bearing niobium in a reduced oxidation state can be afforded by the straightforward reactions of  $\text{NbX}_5$  with the appropriate amount of  $\text{Sn}^n\text{Bu}_3\text{H}$ .<sup>6</sup> For instance,  $\text{NbX}_3(\text{dme})$  can be generated in high yields from  $\text{NbX}_5$  and two equivalents of  $\text{Sn}^n\text{Bu}_3\text{H}$  in *dme*. Therefore, with the aim of obtaining niobium(IV) oxide dihalides, we studied the possible reduction process of **1a,b** with tributyltin hydride. These reactions successfully led to the formation of  $\text{NbOX}_2(\text{dme})$  ( $\text{X} = \text{Cl}$ , **2a**;  $\text{Br}$ , **2b**). Optimal reaction conditions imply the addition of tributyltin hydride to toluene solutions of *in situ* generated **1a-b** (Scheme 1). By using this method, **2a,b** were isolated after work up in 60-65% yields as dark blue/violet solids. Following analogous procedures, also the complexes  $\text{NbOCl}_2(\text{thf})_2$ , **2c**, and  $\text{NbOCl}_2(\text{NCMe})_2$ , **2d**, were obtained (Scheme 1).

**2c-d** are exceedingly air sensitive products, and especially **2d** is so intractable that a satisfying characterization has not been possible. Attempts to prepare acetonitrile and tetrahydrofuran adducts of  $\text{NbOBr}_2$  did fail.



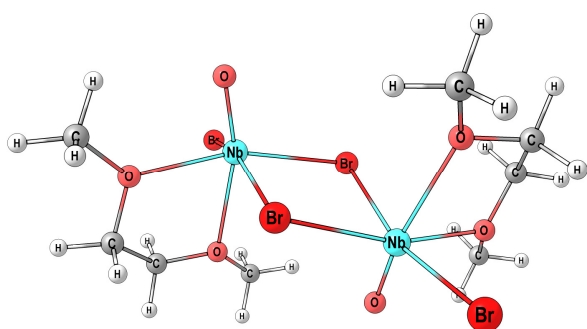
**Scheme 1.** Synthesis of  $\text{NbOX}_2\text{L}_2$  complexes

Compounds **2a-c** represent rare examples of well defined coordination complexes of  $\text{NbOX}_2$ . They were characterized by elemental and magnetic analysis, IR and UV-Vis spectroscopy. The magnetic susceptibility values of **2a-b** are lower than the spin only value (1.73 BM) for a  $d^1$ -species, and fall in within the interval 1.40-1.65 BM, resembling previous findings on mono and dinuclear Nb(IV)

complexes.<sup>15</sup> The IR spectra of **2a-b** display a strong band at *ca.* 1020 cm<sup>-1</sup>, attributed to terminal Nb=O moiety. In the UV-Vis spectra, absorptions in the region 450 - 750 nm are featured by low molar extinction coefficients and are probably due to d-d transitions within the metal ion.

According to the experimental evidences, we suggest that **2a-b** hold a dinuclear structure similar to that adopted by NbX<sub>5</sub><sup>16</sup> and MoCl<sub>5</sub><sup>17</sup> in the solid state, with the hexacoordinated metal centers sharing two bridging halide ligands. It should be noted that the d<sup>1</sup> metal based dimeric MoCl<sub>5</sub> displays a magnetic susceptibility corresponding to a magnetic moment of 1.6 BM.<sup>18</sup> Furthermore, the only two examples of crystallographically characterized vanadium(IV) complexes based on the core VOCl<sub>2</sub>L<sub>2</sub> and containing terminal oxide ligands, *i.e.* VOCl<sub>2</sub>(NCMe)<sub>2</sub> and [VOCl<sub>3</sub>(OH<sub>2</sub>)]<sup>-</sup>, possess a dinuclear structure.<sup>19</sup>

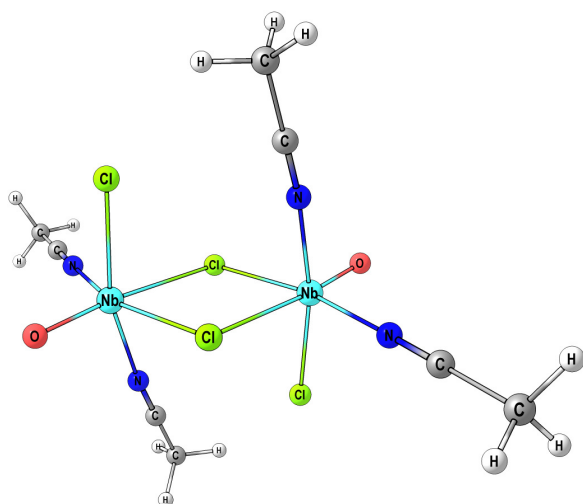
On theoretical grounds, among the possible dinuclear structures of **2a** (Figure S2, Table S2), that one containing two bridging chlorines and the oxide ligands in axial positions (**2aA**) resulted to be the slightly most stable one (EDF2 calculations). Instead **2aA** is largely more stable compared to the corresponding monomeric form.<sup>20</sup> Similar conclusions were achieved by DFT analysis (EDF2 level) on **2b** (Figure S3, Table S3).<sup>20</sup> The geometry of the most stable form of **2b**, *i.e.* **2bA** (Figure S3), was optimized also by using the ωB97X DFT functional in combination with a polarized split-valence basis set and the C-PCM salvation model for dichloromethane: the result is drawn in Figure 1, with the caption reporting selected bonding parameters.



**Figure 1.** DFT-optimized structure of **2bA** (C-PCM/ωB97X, dichloromethane as implicit solvent). Selected bond lengths (Å): Nb=O 1.681, 1.682; Nb–O 2.275, 2.436, 2.277, 2.431;

Nb–Br(terminal) 2.633, 2.631; Nb–Br(bridging) 2.726, 2.793, 2.718, 2.783; Nb---Nb 4.045. Selected angles (°): O=Nb–O 91.4, 160.4, 92.3, 161.0; O–Nb–O 69.5, 69.3; O=Nb–Br(terminal) 102.3, 103.1; O=Nb–Br(bridging) 95.9, 106.3, 95.1, 103.1; Br(bridging)–Nb–Br(bridging) 84.6, 84.9.

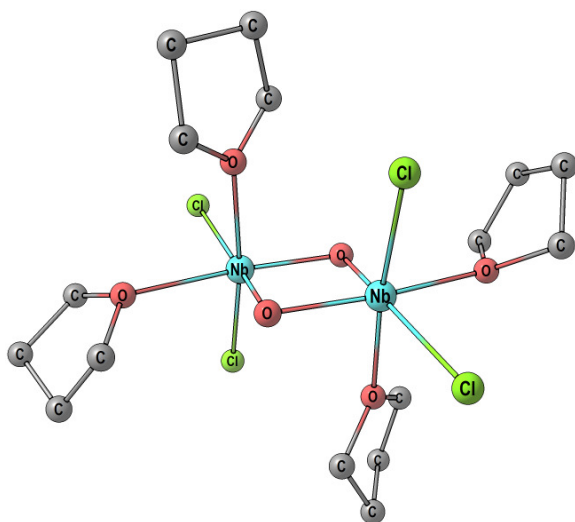
Even though it was not possible to isolate and characterize the acetonitrile adduct **2d**, we studied by DFT the possible dinuclear structures for this compound. The computer outcomes matched the results achieved for **2a-b**. Thus EDF2 calculations indicated **2dC**, containing bridging Cl-ligands, as the most stable dinuclear structure for **2d** (Figure S5, Table S5). A view of **2dC**, optimized at the C-PCM/ $\omega$ B97X DFT level, is provided as Figure 2.



**Figure 2.** DFT-optimized structure of **2dC** (C-PCM/ $\omega$ B97X, dichloromethane as implicit solvent). Selected bond lengths (Å): Nb=O 1.681, 1.681; Nb–N 2.235, 2.249, 2.235, 2.249; Nb–Cl(terminal) 2.476, 2.477; Nb–Cl(bridging) 2.535, 2.945, 2.535, 2.956; Nb---Nb 4.202. Selected angles (°): O=Nb–N 95.1, 97.6, 95.1, 97.6; O–Nb–Cl(terminal) 103.1, 103.1; O=Nb–Cl(bridging) 103.5, 169.7, 103.5, 169.7; Cl(bridging)–Nb–Cl(bridging) 80.2, 80.2.

In contrast with the computational findings related to **2a,b,d**, major stability of  $\mu$ -O containing structures is predictable for the tetrahydrofuran adduct **2c**. The calculated dinuclear structures of **2c** are shown in Figure S4, and a view of the lowest energy structure (**2cE**) is given also as Figure 3. The computer outcome on **2c** is consistent with the experimental data. Indeed, no intense IR absorption was detected in

the 1010-1030  $\text{cm}^{-1}$  region (terminal Nb=O, see above); otherwise a band at 672  $\text{cm}^{-1}$  was attributed to vibration of the Nb–O–Nb moieties. In addition, the magnetic measurement on **2c** furnished a lower value (1.19 BM) than what expected for isolated Nb(IV) centers, in agreement with the presence of bridging oxide groups allowing some communication between the niobium centers.

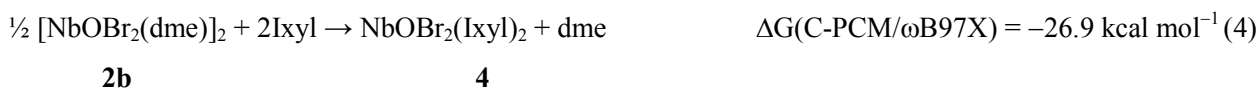
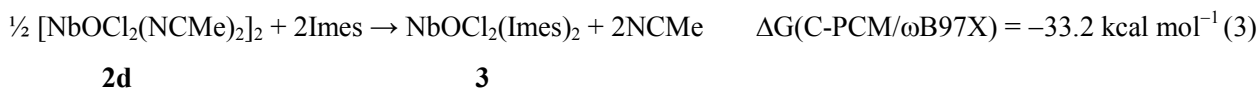


**Figure 3.** Lowest energy DFT EDF2 calculated structure of **2c** (**2cE**, see Figure S4). Selected bond lengths (Å) Nb–Cl (*trans* thf) 2.434; Nb–Cl (*trans*  $\mu$ -O) 2.450, 2.452; Nb–O (thf, *trans* Cl) 2.239, 2.248; Nb–O (thf, *trans*  $\mu$ -O) 2.331, 2.329; Nb–O ( $\mu$ ) 1.894, 2.030, 1.892, 2.021 Selected angles ( $^{\circ}$ ): Cl–Nb–Cl 91.2, 90.8; O(thf)–Nb–O(thf) 88.7, 89.1; O( $\mu$ )–Nb–O( $\mu$ ) 79.5, 79.8.

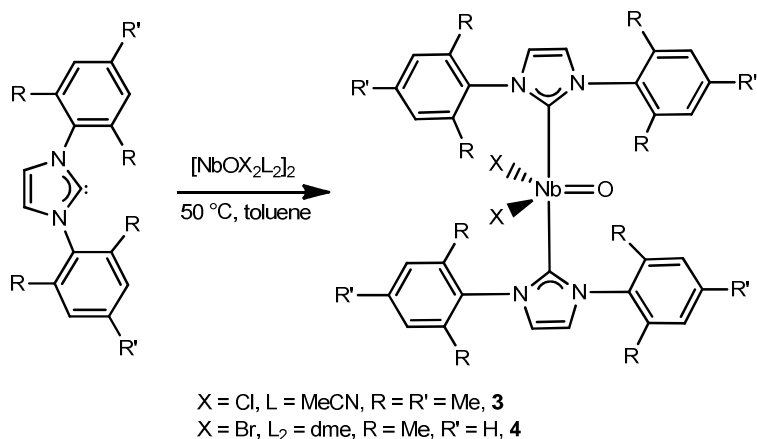
**2a-d** are highly air sensitive compounds (see above), their decomposition being completed within a few seconds if allowed to contact with air. On account of the fact that simple mononuclear coordination adducts of NbCl<sub>5</sub> with bulky NHC ligands have exhibited superior resistance to hydrolysis, respect to the precursor NbCl<sub>5</sub>,<sup>3</sup> we reckoned that the introduction of a bulky NHC ligand could significantly improve the air inertness of the Nb(IV) compounds. The NHC molecules 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, Imes, and 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene, Ixyl, were selected to the present study (Chart 1).



According to DFT, the substitution reactions of the organic ligands in **2a-d** with NHC units appear energetically favorable (see for instance Eqns. 3 and 4).



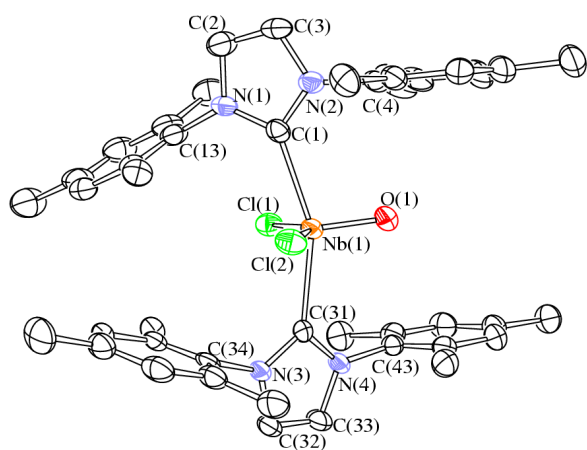
The NHC complex **4** could be actually afforded from **2b**/Ixyl, while freshly prepared **2d** revealed to be the preferential starting material (rather than **2a** and **2c**) for the synthesis of **3**. These reactions were performed in toluene at ca. 50 °C, then **3** and **4** were isolated as brown solids in 50-60% yields (Scheme 2).



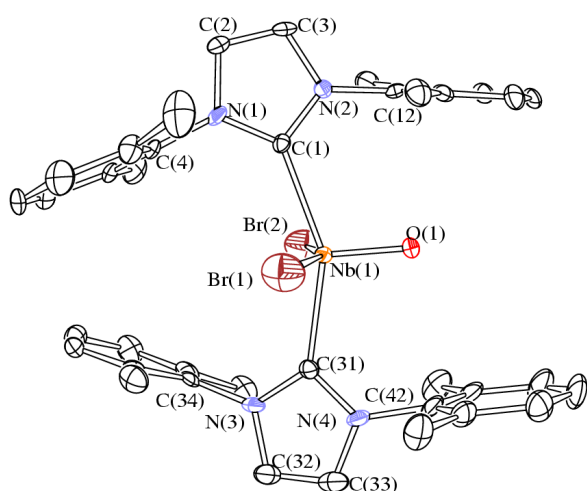
**Scheme 2.** Preparation of niobium(IV) NHC complexes.

Compounds **3** and **4** are fairly air stable (decomposition completed within 5-15 minutes). The IR spectra (in the solid state) contain the absorption related to the Nb=O moiety at 1035 cm<sup>-1</sup>. Magnetic susceptibilities were as expected for mononuclear Nb(IV) complexes,<sup>15</sup> and comparable to the value reported for VOCl<sub>2</sub>(Imes)<sub>2</sub>.<sup>2d</sup> In the UV-Vis spectra, the absorptions in the region 300 - 400 nm are

ascribable to the NHC ligands. Crystals of both **3** and **4** suitable for X-ray diffraction could be collected after several attempts. The molecular structures of **3** and **4** are shown, respectively, in Figures 4 and 5, with relevant bonding parameters reported in Table 1. **3** and **4** represent the first examples of structurally characterized Nb(IV) complexes of the type NbOX<sub>2</sub>L<sub>2</sub> (X = anionic ligand; L = neutral ligand). From the other side, they are isostructural with VOCl<sub>2</sub>(IMes)<sub>2</sub>,<sup>2d</sup> thus displaying a distorted trigonal bipyramidal structure with the oxido and the halide ligands in equatorial positions, whereas the two NHC ligands occupy the two axial positions. The probable cleavage of the dinuclear structure of **2d** and **2b** (see above), upon addition of two NHCs, seems to be consequence of the encumbrance of the latter.



**Figure 4.** Molecular structure of NbOCl<sub>2</sub>(Imes)<sub>2</sub>, **3**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.



**Figure 5.** Molecular structure of NbOBr<sub>2</sub>(lxy), **4**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

**Table 1.** Selected bond distances (Å) and angles (°) for **3** and **4**.

	<b>3</b>	<b>4</b>
Nb(1)–O(1)	1.699(4)	1.688(5)
Nb(1)–X(1)	2.4425(15)	2.5604(13)
Nb(1)–X(2)	2.4348(16)	2.5334(13)
Nb(1)–C(1)	2.322(6)	2.337(7)
Nb(1)–C(31)	2.332(5)	2.305(8)
C(1)–N(1)	1.343(7)	1.353(10)
C(1)–N(2)	1.375(7)	1.367(10)
N(1)–C(2)	1.397(7)	1.399(11)
N(2)–C(3)	1.395(7)	1.393(10)
C(2)–C(3)	1.334(9)	1.331(12)
C(31)–N(3)	1.349(7)	1.354(10)
C(31)–N(4)	1.369(7)	1.371(10)
N(3)–C(32)	1.384(7)	1.410(10)
N(4)–C(33)	1.391(7)	1.374(11)
C(32)–C(33)	1.351(9)	1.343(13)
C(1)–Nb(1)–C(31)	156.22(19)	152.7(3)
X(1)–Nb(1)–X(2)	144.99(6)	154.45(5)
C(1)–Nb(1)–O(1)	102.1(2)	105.2(3)
C(31)–Nb(1)–O(1)	101.66(19)	102.1(3)
O(1)–Nb(1)–X(1)	106.85(16)	102.5(2)
O(1)–Nb(1)–X(2)	108.15(16)	103.0(2)

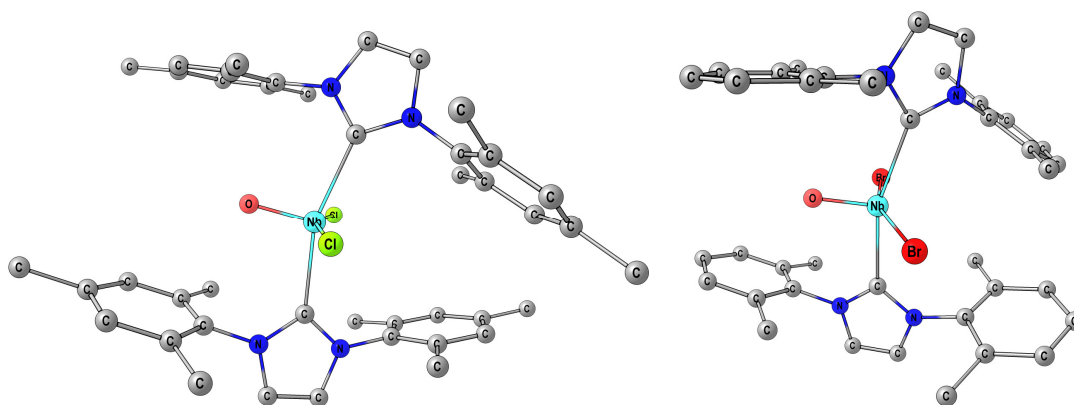
The Nb(1)–O(1) distances [1.699(4) Å for **3**; 1.688(5) for **4**] resemble other reported Nb=O double bond distances.<sup>9,14,21</sup> Only two Nb-NHC systems were previously crystallographically characterized. In [(C-N-C')NbCl<sub>3</sub>(thf)], C-N-C' = 2,6-bis(imidazolylidene)pyridine, in which the binding of the NHC ligand is reinforced by multidentate coordination, the Nb(III)-C distance values are around 2.20 Å.<sup>4a</sup> On the other hand, in the complex NbCl<sub>5</sub>(Ipr), Ipr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, in which the NHC binding is affected by steric factors, the Nb(V)-C distance is 2.396(12) Å.<sup>3</sup> In **3** and **4**, an intermediate situation is observed [Nb(1)–C(1): 2.322(6) Å for **3**, 2.337(7) for **4**; Nb(1)–C(31): 2.332(5) Å for **3**, 2.305(8) for **4**]. However, the Nb-C bonds in **3** and **4** are significantly longer than both Nb(IV)-alkylidene moieties<sup>22</sup> and even classical Nb(IV)-alkyl  $\sigma$ -bonds.<sup>23</sup> The carbene atoms of **3** and **4** display

C $\cdots$ X [3.185-3.362 Å for **3**; 3.323-3.409 Å for **4**] and C $\cdots$ O [3.150-3.151 Å for **3**; 3.128-3.220 Å for **4**] contacts with the terminal X and O ligands, respectively, within the sum of the van der Waals radii of the respective atoms [sum = 3.45 Å for C $\cdots$ Cl, 3.55 Å for C $\cdots$ Br and 3.22 Å for C $\cdots$ O].<sup>24</sup> Similar interactions have been observed in a variety of high valent metal-halide NHC complexes,<sup>2b,c,d,f,g,h</sup> and have been associated with a form of  $\pi$  back-donation from the halide ligands to the carbenic carbons (see below the DFT discussion).

The X(1)–Nb(1)–X(2) angle is considerably larger in **4** [154.45(5)°] compared to **3** [144.99(6)°], in view of the larger size of Br vs. Cl. In fact, VOCl<sub>2</sub>(IMes)<sub>2</sub> displays a Cl–V–Cl angle [146.55°] very close to that one in **3**,<sup>2d</sup> irrespective of the different nature of the central metal atom.

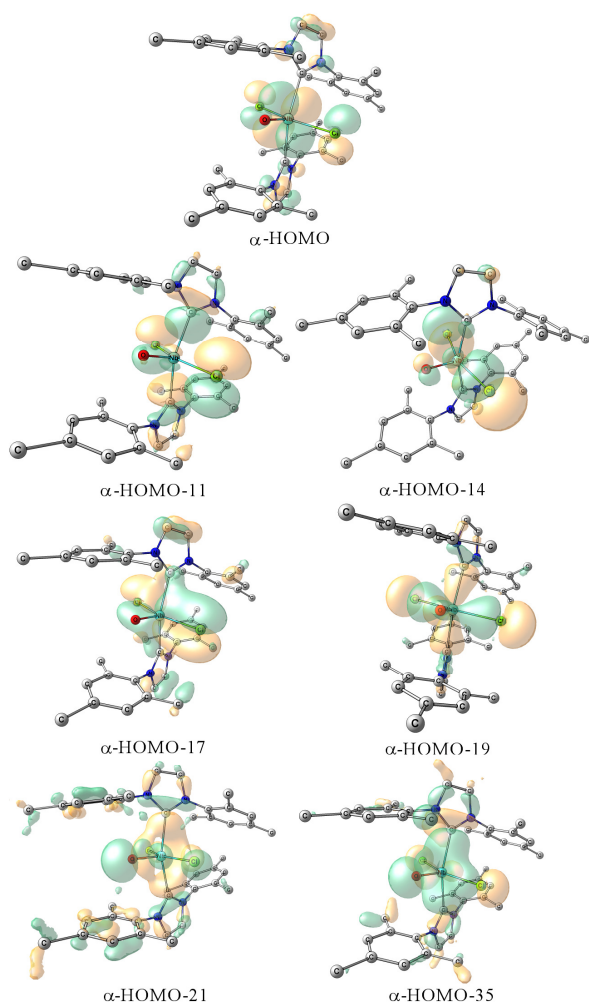
The dihedral angles between the two least squares planes comprising the two NHC rings are different in **3** [49.41°] and **4** [27.60°], leading to different spatial arrangements of the NHC ligands. It is plausible that this feature is the result of different packing effects in the two structures (see below DFT discussion). It is noteworthy that the corresponding dihedral angle in VOCl<sub>2</sub>(IMes)<sub>2</sub> [28.15°] is very close to the one found in **4**, although the V(IV) complex contains the same IMes and Cl ligands as **3**.

In order to shed light on the structural and bonding features of **3** and **4**, we performed DFT calculations. The calculated structures of **3** and **4** are shown in Figure 6, the caption reporting the calculated values of the main bonding parameters. The most important difference with respect to the X-Ray data concerns the dihedral angles between the two least squares planes comprising the two NHC rings. These angles have similar modulus on comparing the computed ground-state geometries of **3** and **4** [X = Cl (**3**): experimental 49.41, calculated 31.2°; X = Br (**4**): experimental 27.60, calculated 38.3°]. This result corroborates the hypothesis that the discrepancy between **3** and **4**, experimentally observed, is due to packing forces operative in the solid state (see above X-ray discussion).



**Figure 6.** DFT-optimized structure of  $\text{NbOCl}_2(\text{IMes})_2$  and  $\text{NbOBr}_2(\text{Ixyl})_2$  (C-PCM/ $\omega$ B97X, dichloromethane as implicit solvent). Hydrogen atoms have been omitted for clarity. Selected bond lengths for  $\text{NbOCl}_2(\text{IMes})_2$  (Å): Nb=O 1.682; Nb–Cl 2.519, 2.519; Nb–C 2.366, 2.366. Selected angles for  $\text{NbOCl}_2(\text{IMes})_2$  (°): O=Nb–Cl 100.5, 100.5; Cl–Nb–Cl 158.9; O=Nb–C 99.5, 99.5; C–Nb–C 161.0. Selected bond lengths for  $\text{NbOBr}_2(\text{Ixyl})_2$  (Å): Nb=O 1.678; Nb–Br 2.697, 2.698; Nb–C 2.371, 2.372. Selected angles for  $\text{NbOBr}_2(\text{Ixyl})_2$  (°): O=Nb–Br 99.8, 99.8; Br–Nb–Br 160.3; O=Nb–C 99.9, 99.9; C–Nb–C 160.2.

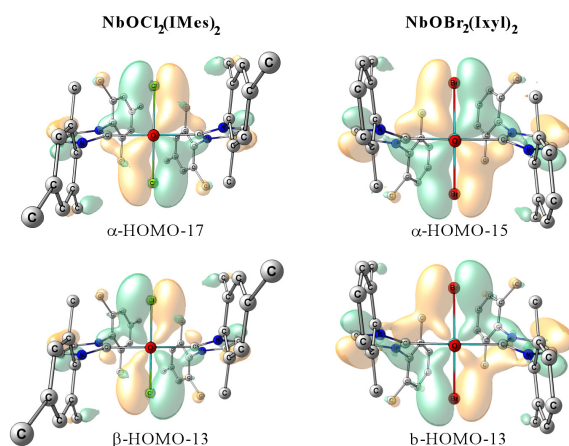
The metal-ligand  $\sigma$ -interactions in **3** are as expected for a distorted trigonal bipyramid. Niobium mainly overlaps with chloro- and carbene ligands with two perpendicular p-type orbitals ( $\alpha$ -HOMO-11/ $\beta$ -HOMO-10,  $\alpha$ -HOMO-14/ $\beta$ -HOMO-14) and one d-type orbital ( $\alpha$ -HOMO-19/ $\beta$ -HOMO-18). Other MOs, where the metal centre participates with s-, p- and d-type functions, account at the same time of Nb–O, Nb–C and Nb–Cl  $\sigma$ -bonding ( $\alpha$ -HOMO-21/ $\beta$ -HOMO-19,  $\alpha$ -HOMO-35/ $\beta$ -HOMO-34). The Nb–O bond is strongly strengthened by  $\pi$ -type interactions. For what concerns the Nb–C bonds, a scarce  $\pi$ -overlap can be detected in  $\alpha$ -HOMO-17/ $\beta$ -HOMO-13, which are orbitals mainly describing  $\pi$ -donation from the chloro-ligands to a d-type orbital of niobium. On considering the  $\pi$ -combinations of the carbene ligands involved, we can conclude that the  $\sigma$ -Nb–C bonds are supported by a weak NHC to Nb  $\pi$ -donation (see the X-ray discussion).  $\alpha$ -HOMO is the antibonding counterpart of  $\alpha$ -HOMO-17 and holds  $\pi^*$  Nb–Cl character. The contribution of the donor carbon atoms to this last MO is negligible. Figure 7 shows the  $\alpha$ -MOs discussed in this section.



**Figure 7.** Selected occupied  $\alpha$ -MOs computed for  $\text{NbOCl}_2(\text{IMes})_2$ , **3**. C-PCM/ $\omega$ B97X calculations, surface isovalue = 0.025 a.u. Hydrogen atoms have been omitted for clarity.

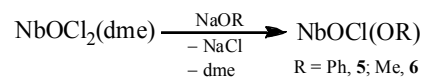
The metal-ligands  $\sigma$ -type interactions found for **4** are qualitatively comparable to the ones in **3**. The  $\pi$ -bonds of niobium with the two carbenes are mainly accounted by the  $\alpha$ -HOMO-15/ $\beta$ -HOMO-13 orbitals. In these MOs, a strong contribution from the two halogens can be observed, as described for **3**. The additional strength of the Nb–C bonds supplied by  $\pi$  contribution, as ascertained by computer outcomes, is in alignment with the experimental detection of C(carbene)–X interactions in the X-ray structures of **3-4**. The comparison of the  $\alpha$ -HOMO-17/ $\beta$ -HOMO-13 orbitals of **3** and the  $\alpha$ -HOMO-15/ $\beta$ -HOMO-13 orbitals of **4** (Figure 8) evidences a greater Nb–C  $\pi$ -overlap in the case of the bromo-

derivative **4**. It is however to be highlighted that the calculated dissociation of one carbene moiety, according to the general reaction  $\text{NbOX}_2(\text{NHC})_2 \rightarrow \text{NbOX}_2(\text{NHC}) + \text{NHC}$ , is featured by comparable Gibbs energy variations for **3** ( $11.8 \text{ kcal mol}^{-1}$ ) and **4** ( $12.6 \text{ kcal mol}^{-1}$ ), respectively.



**Figure 8.** Comparison of selected occupied MOs computed for  $\text{NbOCl}_2(\text{IMes})_2$  and  $\text{NbOBr}_2(\text{IxyI})_2$ . C-PCM/ $\omega$ B97X calculations, surface isovalue = 0.025 a.u. Hydrogen atoms have been omitted for clarity.

We attempted a series of nucleophilic substitution reactions on the Nb(IV) dichloride complex **2b**. We found that one chloride ligand could be displaced by an alkoxide (aryloxy) group. Thus the novel compounds  $\text{NbOCl}(\text{OR})$  ( $\text{R} = \text{Ph}$ , **5**;  $\text{Me}$ , **6**) were obtained from **2b** and  $\text{NaOR}$  (1:1 molar ratio) in tetrahydrofuran, and isolated after work up in 53-65% yields (Scheme 3). The reaction of **2b** with even an excess of  $\text{NaOPh}$  cleanly led to **5**, while the reaction of **2b** with two equivalents of  $\text{NaOMe}$  presumably afforded a mixture of **6** and  $\text{NbO}(\text{OMe})_2$ .

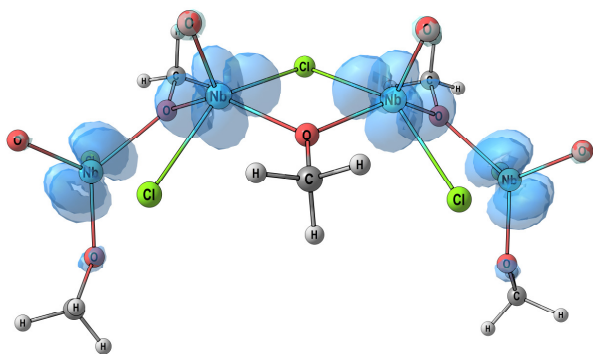


**Scheme 3.** Preparation of methoxide and phenoxide derivatives of Nb(IV)

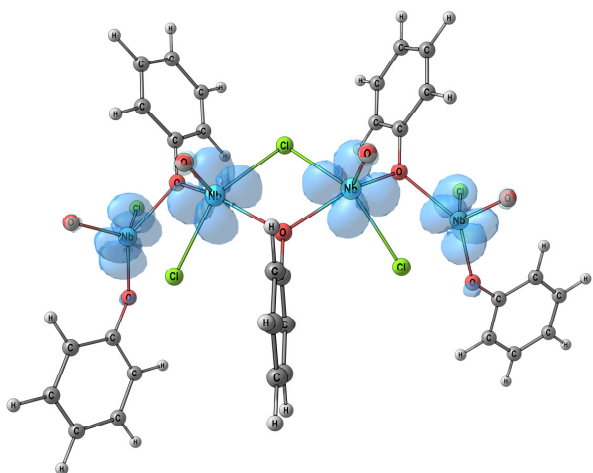
**5** and **6** are neutral compounds that, according to the elemental analyses and the NMR spectra recorded on the respective samples treated with water do not contain dme or thf units (see Experimental for details).<sup>25</sup> We propose that the structure of **5-6** resembles that of NbOCl<sub>2</sub>, with one chloride ligand per metal centre replaced by one OR group. The structure of NbOCl<sub>2</sub> consists of chains of NbOCl<sub>4</sub> pyramids sharing their opposite edges, the distinct chains being linked by Nb=O---Nb contacts.<sup>10c,11a</sup> Analogously to the case of NbCl<sub>4</sub>, each chain shows an alternation of two different Nb–Nb distances, resulting in properties such as semiconduction and diamagnetisms.<sup>26</sup> Following the hypothesis of a NbOCl<sub>2</sub> type structure, we optimized by DFT the geometry of a four chain unit for both **5** and **6**. Views of these structures, obtained considering four unpaired electrons, are reported in Figures 9 and 10, together with the respective spin density surfaces. Attempts to optimize these compounds with lower multiplicity afforded only distorted and high-energy geometries. As expected, the unpaired electrons resulted localized on d-type orbitals of the metal centers. The computed Nb···Nb distances between the two central units are 3.666 and 3.675 Å for R = Me and R = Ph, respectively. The corresponding average Nb···Nb distances in the two models are 3.678 and 3.687 Å. These values are comparable to those reported for similar niobium(IV) coordination polymers in the absence of direct metal-metal interaction.<sup>10c</sup>

In agreement with the DFT calculations, **5** and **6** are paramagnetic compounds, the magnetic susceptibility values being consistent with the presence of isolated Nb(IV) centers.<sup>15</sup> The IR absorption due to the Nb=O moiety has been detected around 800 cm<sup>-1</sup>, in analogy with what previously found for NbOCl<sub>2</sub> (cm<sup>-1</sup>).<sup>27</sup>





**Figure 9.** DFT-optimized structure ( $\omega$ B97X functional) of  $[\text{NbOCl}(\text{OMe})(\mu\text{-Cl})(\mu\text{-OMe})\text{NbO}(\mu\text{-Cl})(\mu\text{-OMe})\text{NbO}(\mu\text{-Cl})(\mu\text{-OMe})\text{NbO}(\text{Cl})(\text{OMe})]^{2-}$  and spin density surface (isovalue = 0.01 a.u.). Selected bond lengths for the central subunits ( $\text{\AA}$ ): Nb=O 1.683,1.684; Nb-( $\mu\text{-Cl}$ ) 2.584, 2.584; Nb-( $\mu\text{-O}$ ) 2.153, 2.155; Nb---Nb 3.666.



**Figure 10.** DFT-optimized structure ( $\omega$ B97X functional) of  $[\text{NbOCl}(\text{OPh})(\mu\text{-Cl})(\mu\text{-OPh})\text{NbO}(\mu\text{-Cl})(\mu\text{-OPh})\text{NbO}(\mu\text{-Cl})(\mu\text{-OPh})\text{NbO}(\text{Cl})(\text{OPh})]^{2-}$  and spin density surface (isovalue = 0.01 a.u.). Selected bond lengths for the central subunits ( $\text{\AA}$ ): Nb=O 1.678,1.678; Nb-( $\mu\text{-Cl}$ ) 2.566, 2.569; Nb-( $\mu\text{-O}$ ) 2.170, 2.170; Nb---Nb 3.675.

## Conclusions

The coordination chemistry of NHC ligands to oxophilic, early transition metal complexes has received less attention than the corresponding chemistry with late transition metals. In particular, very few niobium-NHC complexes have been structurally characterized up to now. In the present paper, we have described a route to the synthesis of niobium(IV) oxide dihalides complexes, which have been

almost unknown so far. These products may represent starting materials for the preparation of a variety of Nb(IV) compounds containing an oxide ligand. In particular, fairly air stable Nb(IV)-NHC coordination adducts have been obtained and crystallographically characterized. According to X-ray and DFT outcomes, the Nb-C(carbene) bonds consist of a  $\sigma$  *NHC to metal* donation, reinforced by a  $\pi$  *metal to NHC* contribution, involving the halide ligands.

### **Experimental Section.**

**General:** *Warning:* the metal compounds reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction, crystallization and separation procedures. The reaction vessels were oven dried at 150 °C prior to use, evacuated ( $10^{-2}$  mmHg) and then filled with argon. NbCl<sub>5</sub> (99+% purity) was purchased from Strem and stored under argon atmosphere as received. NbBr<sub>5</sub>,<sup>28</sup> NbOCl<sub>3</sub>,<sup>8c</sup> Imes and Ixyl<sup>29</sup> were prepared according to the respective literature procedures. All the organic reactants were commercial products (Sigma Aldrich or Apollo Sci.) of the highest purity available. Solvents (Sigma Aldrich) were distilled over appropriate drying agents under argon atmosphere before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Conductivity measurements were carried out using an Eutech Con 700 instrument (cell constant = 1.0 cm<sup>-1</sup>).<sup>30</sup> UV-vis spectra were recorded with an Ultrospec 2100 Pro spectrophotometer. 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>31</sup> and software package especially designed for EPR experiments.<sup>32</sup> Experimental EPR spectra were simulated by the WINSIM 32 program.<sup>33</sup> Magnetic susceptibilities (reported per metal atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.<sup>34</sup>

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, while the chemical shifts for  $^{93}\text{Nb}$  were referenced to external  $[\text{NEt}_4][\text{NbCl}_6]$ . 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.<sup>35</sup> Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The halide content was determined by the Mohr method<sup>36</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. Niobium was analyzed as  $\text{Nb}_2\text{O}_5$ , obtained by hydrolysis of the samples followed by calcination in a platinum crucible.

**Synthesis and isolation of  $\text{NbOBr}_3$ .** A suspension of  $\text{NbBr}_5$  (6.40 g, 0.0130 mol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was treated with  $\text{O}(\text{SiMe}_3)_2$  (2.76 mL, 0.0130 mmol). The mixture was stirred at room temperature for 48 h, during which progressive color turning of the mixture from brick-red to yellow was noticed. Then the volatile materials were removed under vacuum, and the residue was washed with pentane (2 x 30 mL). The product was isolated as a yellow powder. Yield 3.67 g, 81%. Anal. Calcd. for  $\text{Br}_3\text{NbO}$ : Nb, 26.65; Br, 68.76. Found: Nb, 26.30; Br, 69.06. IR (solid state):  $\nu = 740\text{vs}(\text{Nb}=\text{O})\text{ cm}^{-1}$ .

**Synthesis and isolation of  $\text{NbOBr}_3(\text{dme})$ , **1b**.**  $\text{NbOBr}_3$  (225 mg, 0.645 mmol) was suspended in toluene (10 mL), then dme (0.093 mL, 0.90 mmol) was added. A red solution formed in a few minutes, and this solution was stirred for additional 30 minutes. Addition of pentane (30 mL) determined the precipitation of a yellow solid. The solid was isolated and dried under vacuum. Yield 198 mg, 70%. Anal. Calcd. for  $\text{C}_4\text{H}_{10}\text{Br}_3\text{NbO}_3$ : C, 10.95; H, 2.30; Nb, 21.18; Br, 54.64. Found: C, 11.07; H, 2.21; Nb, 21.03; Br, 54.45. IR (solid state):  $\nu = 2943\text{w}, 1464\text{w}, 1456\text{w}, 1446\text{w-m}, 1276\text{w}, 1240\text{w}, 1185\text{w}, 1075\text{m}$ ,

1020vs (Nb=O), 989m, 959s, 859s, 824w, 759vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 4.15$  (s, 2H,  $\text{CH}_2$ ), 4.14 ppm (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 75.6, 70.5$  ( $\text{CH}_2$ ); 70.3, 63.6 ppm ( $\text{CH}_3$ ).  $^{93}\text{Nb}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = -205$  ppm ( $\Delta\nu^{1/2} = 1.5 \cdot 10^3$  Hz). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 335(10), 387(7), 444(8).

### Synthesis and isolation of $\text{NbOX}_2(\text{dme})$ ( $\text{X} = \text{Cl}$ , **2a**; $\text{X} = \text{Br}$ , **2b**).

A suspension of  $\text{NbOCl}_3$  (380 mg, 1.77 mmol) in toluene (20 mL) was treated with dme (0.21 mL, 2.0 mmol). A light-yellow solution was obtained in 5 minutes. This solution was cooled with an ice bath, then  $\text{SnBu}_3\text{H}$  (0.48 mL, 1.8 mmol) was added dropwise. The mixture was allowed to warm to room temperature, and stirred for additional 18 h. A dark-blue precipitate was formed below a green-blue solution. The solid (**2a**) was isolated, washed with pentane (15 mL) and then dried under vacuum. Yield 291 mg, 61%. Anal. Calcd. for  $\text{C}_4\text{H}_{10}\text{Cl}_2\text{NbO}_3$ : C, 17.80; H, 3.73; Nb, 34.42; Cl, 26.27. Found: C, 17.69; H, 3.75; Nb, 34.20; Cl, 26.12. IR (solid state):  $\nu = 2949\text{w}, 2847\text{vw}, 1454\text{m}, 1242\text{w}, 1191\text{w}, 1076\text{m}, 1025\text{s}$  (Nb=O), 957m, 866m-sh, 838s, 804vs, 771s, 701m  $\text{cm}^{-1}$ . Magnetic measurement:  $\chi_{\text{M}}^{\text{corr}} = 7.94 \times 10^{-4}$  cgsu,  $\mu_{\text{eff}} = 1.40$  BM. UV-Vis (THF):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 278( $6 \cdot 10^2$ ), 632(9), 741(10).

Compound **2b** was obtained by a procedure similar to that described for **2a**, from  $\text{NbOBr}_3$  (514 mg, 1.47 mmol), dme (0.60 mL, 5.8 mmol) and  $\text{SnBu}_3\text{H}$  (0.40 mL, 1.5 mmol). The final dark-blue solution in toluene was added of pentane (30 mL) in order to obtain **2b** as a dark precipitate. Yield 343 mg, 65%. Anal. Calcd. for  $\text{C}_4\text{H}_{10}\text{Br}_2\text{NbO}_3$ : C, 13.39; H, 2.81; Nb, 25.89; Br, 44.54. Found: C, 13.27; H, 2.72; Nb, 25.60; Br, 42.88. IR (solid state):  $\nu = 2943\text{w}, 2845\text{w}, 1447\text{m}, 1258\text{w}, 1187\text{w}, 1076\text{m}, 1018\text{s}$  (Nb=O), 953m-s, 849s, 799s, 755vs, 695s  $\text{cm}^{-1}$ . Magnetic measurement:  $\chi_{\text{M}}^{\text{corr}} = 1.13 \times 10^{-3}$  cgsu,  $\mu_{\text{eff}} = 1.65$  BM. UV-Vis (THF):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 351( $5 \cdot 10^2$ ), 461(20), 609(12), 722(10), 805( $3 \cdot 10^2$ ).

### Synthesis and isolation of NbOCl<sub>2</sub>(thf)<sub>2</sub>, **2c**.

This product was obtained by the same procedure described for **2b**, from NbOCl<sub>3</sub> (249 mg, 1.16 mmol), thf (0.21 mL, 2.6 mmol) and SnBu<sub>3</sub>H (0.31 mL, 1.2 mmol). Dark-blue solid, yield 195 mg (52%). Anal. Calcd. for C<sub>8</sub>H<sub>16</sub>Cl<sub>2</sub>NbO<sub>3</sub>: C, 29.65; H, 4.98; Nb, 28.67; Cl, 21.88. Found: C, 29.31; H, 4.75; Nb, 28.89; Cl, 21.60. IR (solid state):  $\nu = 2955w, 2926w, 2872s, 1455w-m, 1251w, 1005m, 892s, 812vs, 672vs$  (Nb-O-Nb) cm<sup>-1</sup>. Magnetic measurement:  $\chi_M^{corr} = 5.88 \times 10^{-4}$  cgsu,  $\mu_{eff} = 1.19$  BM. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}/nm$  ( $\epsilon/M^{-1}cm^{-1}$ ) = 270(5·10<sup>2</sup>), 716(5), 746(7).

### Synthesis and isolation of NbOCl<sub>2</sub>(Imes)<sub>2</sub>, **3**.

A suspension of NbOCl<sub>3</sub> (230 mg, 1.07 mmol) in toluene (15 mL) was treated with MeCN (0.13 mL, 2.5 mmol). The resulting light yellow solution was cooled with an ice bath, then SnBu<sub>3</sub>H (0.29 mL, 1.1 mmol) was added dropwise. The mixture was allowed to warm to room temperature, and stirred for additional 30 minutes. The resulting dark-blue precipitate was formed in a green-blue solution, which was eliminated with a syringe. The solid was washed with toluene (20 mL). Thus, toluene (15 mL) and Imes (660 mg, 2.17 mmol) were added in the order given. The mixture was stirred for 2 h at 50 °C, then it was allowed to cool to room temperature. The final solution was concentrated, layered with pentane and settled aside at -30 °C; a microcrystalline brown material was obtained after 24 hours. Yield 515 mg, 61%. Crystals suitable for X-ray analysis were collected from a toluene/hexane mixture at -30 °C. Anal. Calcd. for C<sub>42</sub>H<sub>48</sub>Cl<sub>2</sub>N<sub>4</sub>NbO: C, 63.96; H, 6.13; N, 7.10; Nb, 11.78; Cl, 8.99. Found: C, 63.60; H, 6.22; N, 7.03; Nb, 12.01; Cl, 8.58. IR (solid state):  $\nu = 2920m, 2855w-m, 2760w-br, 1675w, 1605m, 1587w, 1540m, 1483m-s, 1457m, 1380w, 1319w, 1262w, 1230s, 1163w, 1100w, 1035m$  (Nb=O), 930m, 851s, 756w, 732m, 695w, 677m cm<sup>-1</sup>. EPR (solid state):  $g_{//} = 2.214$ ,  $A_{//} = 163.7$  G;  $g_{\perp} = 2.412$ ,

$A_{\perp} = 60.9$  G. Magnetic measurement:  $\chi_M^{\text{corr}} = 1.21 \times 10^{-3}$  cgsu,  $\mu_{\text{eff}} = 1.70$  BM. UV-Vis (toluene):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 373 (80), 716 (20).

#### **Synthesis and isolation of NbOBr<sub>2</sub>(IxyI)<sub>2</sub>, 4.**

A suspension of NbOBr<sub>3</sub> (198 mg, 0.568 mmol) in toluene (10 mL) was treated with dme (0.062 mL, 0.60 mmol). A light-yellow solution was obtained in a few minutes. This solution was cooled with an ice bath, then SnBu<sub>3</sub>H (0.15 mL, 0.57 mmol) was added dropwise. The mixture was allowed to warm to room temperature, and stirred for additional 18 h. Pentane (25 mL) was added in order to allow the precipitation of a dark-blue solid from a green-blue solution, which was eliminated with a syringe. Thus, toluene (15 mL) and Ixyl (330 mg, 1.19 mmol) were added in the order given. The mixture was stirred for 4 h at 50 °C, then it was allowed to cool to room temperature and filtrated in order to remove some solid. The filtrated solution was eliminated of the volatiles, hence crystallization of the residue from toluene/pentane afforded a dark brown solid which was washed with pentane (2 x 20 mL) and dried in vacuum. Yield 233 mg, 50%. Crystals suitable for X-ray analysis were collected from a toluene/hexane mixture settled aside at -30 °C. Anal. Calcd. for C<sub>38</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>4</sub>NbO: C, 55.56; H, 4.91; N, 6.82; Nb, 11.31; Br, 19.45. Found: C, 55.63; H, 5.02; N, 6.66; Nb, 11.12; Br, 19.28. IR (solid state):  $\nu = 3163\text{w}$ ,  $3132\text{w}$ ,  $3026\text{w}$ ,  $2917\text{w-m}$ ,  $1687\text{w}$ ,  $1603\text{w}$ ,  $1532\text{w-m}$ ,  $1472\text{s}$ ,  $1446\text{m-sh}$ ,  $1392\text{w-m}$ ,  $1380\text{m}$ ,  $1276\text{m}$ ,  $1215\text{m}$ ,  $1167\text{w-m}$ ,  $1100\text{m}$ ,  $1035\text{m}$  (Nb=O),  $960\text{m}$ ,  $948\text{s}$ ,  $923\text{m}$ ,  $866\text{m}$ ,  $770\text{vs}$ ,  $730\text{vs}$ ,  $695\text{vs}$   $\text{cm}^{-1}$ . Magnetic measurement:  $\chi_M^{\text{corr}} = 9.42 \times 10^{-4}$  cgsu,  $\mu_{\text{eff}} = 1.50$  BM. EPR (solid state):  $g_{\parallel} = 2.219$ ,  $A_{\parallel} = 176.5$  G;  $g_{\perp} = 2.331$ ,  $A_{\perp} = 73.8$  G. UV-Vis (toluene):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 320 ( $2.0 \cdot 10^3$ ), 384 ( $1.0 \cdot 10^3$ ), 480 ( $2.5 \cdot 10^2$ ).

**Synthesis of NbOCl(OR) (R = Ph, **5**; Me, **6**).** A solution of freshly prepared **2a** (from 1.10 mmol of NbOCl<sub>3</sub>) in tetrahydrofuran (20 mL) was treated with NaOPh (128 mg, 1.10 mmol). An immediate color change from deep blue to brown was observed, and the mixture was left stirring at room temperature for additional 18 h. Thus the volatiles were removed under vacuum, and the resulting residue was dissolved in toluene (30 mL). The solution was filtered in order to remove some insoluble material, then the solvent was removed under vacuum. The residue was washed with pentane (2 x 20 mL), thus compound **5** was obtained as a light brown powder. Yield 170 mg (65%). An aliquot (ca. 20 mg) was dissolved into CDCl<sub>3</sub> (0.7 mL), treated with a large excess of H<sub>2</sub>O and allowed to contact with air overnight; subsequent <sup>1</sup>H NMR spectrum of the solution pointed out the presence of PhOH and traces of thf. Anal. Calcd. for C<sub>6</sub>H<sub>5</sub>ClNbO<sub>2</sub>: C, 30.35; H, 2.12; Nb, 39.12; Cl, 14.93. Found: C, 30.16; H, 2.18; Nb, 39.02; Cl, 14.76. IR (solid state):  $\nu = 3061\text{w}, 2958\text{w}, 1586\text{m}, 1477\text{s}, 1451\text{w-sh}, 1238\text{s}, 1160\text{m}, 1098\text{w}, 1067\text{w}, 1020\text{w}, 1000\text{w}, 884\text{m}, 795\text{s} (\text{Nb}=\text{O}), 749\text{vs}, 685\text{vs} \text{ cm}^{-1}$ . Magnetic measurement:  $\chi_{\text{M}}^{\text{corr}} = 9.69 \times 10^{-4}$  cgsu,  $\mu_{\text{eff}} = 1.53$  BM. UV-Vis (toluene):  $\lambda_{\text{max}}/\text{nm} (\epsilon/\text{M}^{-1}\text{cm}^{-1}) = 361 (40)$ .  $\Lambda_{\text{M}}$  (toluene) = 0.1 S·cm<sup>2</sup>·mol<sup>-1</sup>. Compound **6** was obtained by a procedure analogous to that described above, by allowing **2a** (freshly prepared from 1.00 mmol of NbOCl<sub>3</sub>) to react with NaOMe (54 mg, 1.00 mmol). Complex **6** could be isolated as a sticky, strongly air sensitive light brown solid. Yield 93 mg, 53%. NMR analysis on an aliquot of **6** (ca. 20 mg) dissolved into CDCl<sub>3</sub> (0.7 mL) and then treated with a large excess of H<sub>2</sub>O pointed out the presence of MeOH. Anal. Calcd. for CH<sub>3</sub>ClNbO<sub>2</sub>: C, 6.85; H, 1.72; Nb, 52.97; Cl, 20.21. Found: C, 6.76; H, 1.75; Nb, 52.65; Cl, 19.98. IR (solid state):  $\nu = 2920\text{w}, 2821\text{w}, 1579\text{w}, 1450\text{w}, 1373\text{w}, 1152\text{m}, 1083\text{m}, 1014\text{vs}, 854\text{m-sh}, 816\text{s-sh} (\text{Nb}=\text{O}), 793\text{vs}, 682\text{s} \text{ cm}^{-1}$ . Magnetic measurement:  $\chi_{\text{M}}^{\text{corr}} = 8.67 \times 10^{-4}$  cgsu,  $\mu_{\text{eff}} = 1.44$  BM. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm} (\epsilon/\text{M}^{-1}\text{cm}^{-1}) = 362 (6 \cdot 10^2), 438 (70)$ .  $\Lambda_{\text{M}}$  (toluene) = 0.1 S·cm<sup>2</sup>·mol<sup>-1</sup>.

## X-ray crystallography.

Crystal data and collection details for **3**·( $\frac{1}{2}$ hexane) and **4**·toluene are reported in Table 2. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–K $\alpha$  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).<sup>37</sup> Structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ .<sup>38</sup> Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise stated. The hexane molecule in **3**·( $\frac{1}{2}$ hexane) is disordered over two equally populated symmetry related (by 2) positions. Its independent image has been refined isotropically applying restraints to the thermal parameters (SIMU line in SHELXL; s.u. 0.005) and to the C-C distances (DFIX 1.53 line in SHELXL; s.u. 0.01).

**Table 2.** Crystal data and experimental details for **3**·( $\frac{1}{2}$ hexane) and **4**·toluene.

	<b>3</b> ·( $\frac{1}{2}$ hexane)	<b>4</b> ·toluene
Formula	C <sub>45</sub> H <sub>55</sub> Cl <sub>2</sub> N <sub>4</sub> NbO	C <sub>45</sub> H <sub>48</sub> Br <sub>2</sub> N <sub>4</sub> NbO
$F_w$	831.74	913.60
T, K	100(2)	100((2)
$\lambda$ , Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pbca$
$a$ , Å	30.131(6)	21.228(3)
$b$ , Å	12.795(2)	15.011(2)
$c$ , Å	24.138(5)	26.045(4)
$\beta$ , °	100.206(3)	90
Cell Volume, Å <sup>3</sup>	9159(3)	8299(2)
Z	8	8
$D_c$ , g cm <sup>-3</sup>	1.206	1.462
$\mu$ , mm <sup>-1</sup>	0.415	2.254



F(000)	3488	3720
Crystal size, mm	0.16×0.13×0.10	0.18×0.16×0.14
$\theta$ limits, °	1.37–26.00	1.56–25.03
Reflections collected	43118	56936
Independent reflections	8988 [ $R_{\text{int}}=0.0821$ ]	7308 [ $R_{\text{int}}=0.0765$ ]
Data / restraints / parameters	8988 / 246 / 475	7308 / 6 / 478
Goodness of fit on $F^2$	1.033	1.044
$R_1$ ( $I > 2\sigma(I)$ )	0.0742	0.0806
$wR_2$ (all data)	0.2383	0.2651
Largest diff. peak and hole, $e \text{ \AA}^{-3}$	1.981 / –0.963	2.824 / –2.819

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### Computational studies.

The computational geometry optimizations were carried out without symmetry constraints, using the hybrid-GGA EDF2 functional<sup>39</sup> in combination with the 6-31G\*\* basis set (ECP-based LANL2DZ basis set for elements beyond Kr).<sup>40</sup> The “unrestricted” formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed  $\langle S^2 \rangle$  values with the theoretical ones. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections ( $T = 298.15 \text{ K}$ ) were obtained.<sup>41</sup> Further optimization of selected geometries was carried out using the range-separated DFT functional  $\omega$ B97X,<sup>42</sup> in combination with a polarized basis set composed by the 6-31G(d,p) set on the light atoms and the ECP-based LANL2TZ(f) and LANL2DZ(d) sets on niobium and bromine, respectively.<sup>43</sup> The C-PCM implicit solvation model ( $\epsilon = 9.08$ ) was added to  $\omega$ B97X calculations.<sup>44</sup> The software used for C-PCM/ $\omega$ B97X calculations was Gaussian ‘09,<sup>45</sup> while EDF2 calculations were performed with Spartan ‘08.<sup>46</sup>

**Supporting Information.** Figures S1-S5 show the DFT-calculated structures of **1b** and **2a-d**; tables S1-S5 contain the relevant bonding parameters. Cartesian coordinates of all DFT-optimized compounds are collected in a separated .xyz file. CCDC reference numbers 1438214 (**3**) and 1438215 (**4**) 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)).

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## Table of Contents Synopsis and graphic

Coordination compounds of Nb(IV) oxide dihalides were synthesized and characterized, including the crystallographic characterization of rare Nb-NHC complexes.

