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

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Supporting Information

ABSTRACT: The 1:1 molar reactions of NbOX₃ with SnBu₃H, in toluene at 0 °C in the presence of oxygen/ nitrogen donors, resulted in the formation of NbOX₂L₂ (X = Cl, L₂ = dme, **2a**; X = Br, L₂ = 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 $NbOCl_2(Imes)_{2J}$, 3, and $NbOBr_2(Ixyl)_{2J}$, 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 examples 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.¹ 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.² In particular, niobium represents a surprising exception in the crowded scenario of NHC chemistry:³ indeed very few Nb-NHC systems have appeared in the literature so far,^{3,4} and we have recently contributed with the unique structurally characterized niobium complex containing a monodentate NHC ligand.³

Nobium pentahalides are among the most easily available and cost-effective niobium species: their chemistry has undergone significant progress in the past decade, encouraged by the low toxicity associated with the metal element and the outstanding reactivity patterns observed in some NbX₅-directed organic transformations.⁵ Niobium(V) pentahalides have been employed as convenient starting reagents to access both Nb(IV) and Nb(III) halides,⁶ which in turn have found

applications in synthetic organic chemistry.^{5b,7} Also niobium-(V) oxide trichlorides and tribromides are rather easily accessible compounds,⁸ whose coordination chemistry has been investigated to some extent.⁹ On the other hand, the synthesis of reduced niobium oxide halides, which are materials of potential interest also in view of their solid-state properties,¹⁰ is a more difficult task. More in detail, the reported synthetic procedures to afford NbOX₂ (X = Cl, Br) require prohibitive experimental conditions,¹¹ 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 NbOX₂ (X = Cl, Br) has been almost unexplored heretofore. The only coordination adducts were claimed to be prepared by hydrolysis of niobium tetrachloride compounds¹² or reduction of NbOCl₃/phosphine systems with Na/Hg; however the products were not unambiguously characterized.^{12a}

Herein we present a convenient room-temperature procedure to afford complexes of $NbOCl_2$ and $NbOBr_2$ with simple oxygen and nitrogen donor ligands, starting from the corresponding niobium pentahalides. These Nb(IV) products undergo substitution reactions with phenoxide and methoxide

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anions and with bulky, monodentate NHC ligands (Chart 1), affording fairly air-stable $NbOX_2(NHC)_2$ complexes. The

Chart 1. NHC Ligands Used in the Present Work



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.

RESULTS AND DISCUSSION

We prepared NbOX₃ (X = Cl, Br) in ca. 80% yields by allowing the respective precursors NbX₅ to react with one equivalent of hexamethyldisiloxane, in dichloromethane at room temperature, eq 1. This method was previously reported for NbOCl₃^{8c} and has been employed here also to obtain NbOBr₃.¹³

$$NbX_{5} + O(SiMe_{3})_{2} \rightarrow NbOX_{3} + 2SiMe_{3}X$$
$$X = Cl, Br$$
(1)

The complexes NbOX₃(dme) (X = Cl,¹⁴ Br; dme = 1,2dimethoxyethane), **1a,b**, were afforded in good yields upon addition of dme to NbOX₃ in toluene, eq 2.

NbOX₃ + dme
$$\rightarrow$$
 NbOX₃(dme)
X = Cl, 1a
X = Br, 1b (2)

According to NMR evidence, the unprecedented **1b** exists in dichloromethane solution as a single isomeric form (⁹³Nb resonance at -205 ppm), presumably ascribable to a (distorted) octahedral geometry with *mer* configuration (¹³C NMR resonances due to the nonequivalent methyl groups occur at 70.3 and 63.6 ppm). This result is consistent with DFT EDF2 calculations, the *mer* isomer being more stable than the *fac* one by about 8.9 kcal mol⁻¹ (Gibbs free energy). Figure S1 and Table S1 within the Supporting Information 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 NbX₅ with the appropriate amount of SnⁿBu₃H.⁶ For instance, NbX₃(dme) can be generated in high yields from NbX₅ and two equivalents of SnⁿBu₃H 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 NbOX₂(dme) (X = Cl, **2a**; 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 workup in 60–65% yields as dark blue-violet solids. Following



NbX₅
$$\xrightarrow{O(SiMe_3)_2}$$
 NbOX₃ $\xrightarrow{L_2}$
CH₂Cl₂, RT NbOX₃ $\xrightarrow{L_2}$
NbOX₃L₂ $\xrightarrow{Sn^nBu_3H}$ NbOX₂L₂
L₂ = dme, X = Cl, 2a; Br, 2b
L₂ = 2 thf, X = Cl, 2c
L₂ = 2 cH₃CN, X = Cl, 2d, not isolated

analogous procedures, also the complexes $NbOCl_2(thf)_2$, 2c, and $NbOCl_2(NCMe)_2$, 2d, were obtained (Scheme 1).

Complexes 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 NbOBr₂ failed.

Compounds **2a**–**c** represent rare examples of well-defined coordination complexes of NbOX₂. They were characterized by elemental and magnetic analysis and IR and UV–vis spectroscopy. The magnetic susceptivity values of **2a**,**b** are lower than the spin-only value (1.73 $\mu_{\rm B}$) for a d¹-species and fall within the interval 1.40–1.65 $\mu_{\rm B}$, resembling previous findings on monoand dinuclear Nb(IV) complexes.¹⁵ The IR spectra of **2a**,**b** display a strong band at ca. 1020 cm⁻¹, attributed to a terminal Nb=O moiety. In the UV–vis spectra, absorptions in the region 450–750 nm feature low molar extinction coefficients and are probably due to d–d transitions within the metal ion.

According to the experimental evidence, we suggest that 2a,b have a dinuclear structure similar to that adopted by NbX₅¹⁶ and MoCl₅¹⁷ in the solid state, with the hexacoordinated metal centers sharing two bridging halide ligands. It should be noted that the d¹ metal based dimeric MoCl₅ displays a magnetic susceptivity corresponding to a magnetic moment of 1.6 $\mu_{\rm B}$.¹⁸ Furthermore, the only two examples of crystallographically characterized vanadium(IV) complexes based on the core VOCl₂L₂ and containing terminal oxide ligands, i.e., VOCl₂(NCMe)₂ and [VOCl₃(OH₂)]⁻, possess a dinuclear structure.¹⁹

On theoretical grounds, among the possible dinuclear structures of **2a** (Figure S2, Table S2), that 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.²⁰ Similar conclusions were achieved by DFT analysis (EDF2 level) on **2b** (Figure S3, Table S3).²⁰ The geometry of the most stable form of **2b**, i.e., **2bA** (Figure S3), was optimized also by using the ω B97X DFT functional in combination with a polarized split-valence basis set and the C-PCM solvation model for dichloromethane: the result is drawn in Figure 1, with the caption reporting selected bonding parameters.

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/ ω B97X DFT level, is provided as Figure 2.

In contrast with the computational findings related to 2a,b,d, major stability of μ -O-containing structures is predictable for the tetrahydrofuran adduct **2c**. The calculated dinuclear



Figure 1. DFT-optimized structure of 2bA (C-PCM/ ω B97X, 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 (deg): 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.



Figure 2. DFT-optimized structure of 2dC (C-PCM/ ω 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 (deg): 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.

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 of 2c is consistent with the experimental data. Indeed, no intense IR absorption was detected in the 1010–1030 cm⁻¹ region (terminal Nb=O, see above); otherwise a band at 672 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 $\mu_{\rm B}$) than what was expected for isolated Nb(IV) centers, in agreement with the presence of bridging oxide groups allowing some communication between the niobium centers.

2a–d are highly air sensitive compounds (see above), their decomposition being completed within a few seconds if allowed contact with air. On account of the fact that simple mononuclear coordination adducts of NbCl₅ with bulky NHC ligands have exhibited superior resistance to hydrolysis, with respect to the precursor NbCl₅,³ we supposed that the introduction of a bulky NHC ligand could significantly improve



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* μ -O) 2.450, 2.452; Nb–O(thf, *trans* Cl) 2.239, 2.248; Nb–O(thf, *trans* μ -O) 2.331, 2.329; Nb–O(μ) 1.894, 2.030, 1.892, 2.021. Selected angles (deg): Cl–Nb–Cl 91.2, 90.8; O(thf)–Nb–O(thf) 88.7, 89.1; O(μ)–Nb–O(μ) 79.5, 79.8.

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 for 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 eqs 3 and 4).

$$\frac{1}{2} [NbOCl_2(NCMe)_2]_2 + 2Imes \rightarrow NbOCl_2(Imes)_2$$

$$+ 2NCMe$$

$$\Delta G(C - PCM/\omega B97X) = -33.2 \text{ kcal mol}^{-1} \qquad (3)$$

$$\frac{1}{2} [NbOBr_2(dme)]_2 + 2Ixyl \rightarrow NbOBr_2(Ixyl)_2 + dme$$

$$4$$

$$\Delta G(\text{C}-\text{PCM}/\omega\text{B97X}) = -26.9 \text{ kcal mol}^{-1}$$
(4)

The NHC complex 4 could actually be afforded from 2b/ Ixyl, while freshly prepared 2d was 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; 3 and 4 were isolated as brown solids in 50–60% yields (Scheme 2).

Compounds 3 and 4 are fairly air stable (decomposition completed within 5–15 min). The IR spectra (in the solid state) contain the absorption related to the Nb=O moiety at 1035 cm⁻¹. Magnetic susceptibilities were as expected for mononuclear Nb(IV) complexes¹⁵ and comparable to the value reported for VOCl₂(Imes)₂.^{2d} 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. Compounds 3 and 4 represent the first examples of structurally characterized Nb(IV) complexes of the type NbOX₂L₂ (X = anionic ligand; L = neutral ligand). From the

Scheme 2. Preparation of Niobium(IV) NHC Complexes



Figure 4. Molecular structure of NbOCl₂(Imes), **3**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.



Figure 5. Molecular structure of $NbOBr_2(Ixyl)$, 4, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

other side, they are isostructural with $VOCl_2(IMes)_2)^{2d}$ 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 structures of **2d** and **2b** (see above), upon addition of two NHCs, seems to be a consequence of the encumbrance of the latter.

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.^{9,14,21} Only two Nb-NHC systems were previously

	3	4
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)

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3 and 4

crystallographically characterized. In $[(C-N-C')NbCl_3(thf)]$, 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.^{4a} On the other hand, in the complex NbCl₅(Ipr), Ipr = 1,3bis(2,6-diisopropylphenyl)imidazol-2-ylidene, in which the NHC binding is affected by steric factors, the Nb(V)-Cdistance is 2.396(12) Å³ 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 moieties²² and even classical Nb(IV)-alkyl σ -bonds.²³ The carbene atoms of 3 and 4 display C…X [3.185– 3.362 Å for 3; 3.323–3.409 Å for 4] and C…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····Cl, 3.55 Å for C··· Br, and 3.22 Å for C···O].²⁴ Similar interactions have been observed in a variety of high-valent metal halide NHC complexes^{2b-d,f-h} and have been associated with a form of π back-donation from the halide ligands to the carbenic carbons (see below for the DFT discussion).

The X(1)–Nb(1)–X(2) angle is considerably larger in 4 $[154.45(5)^{\circ}]$ compared to 3 $[144.99(6)^{\circ}]$, in view of the larger size of Br vs Cl. In fact, VOCl₂(IMes)₂ displays a Cl–V–Cl angle $[146.55^{\circ}]$ very close to that in 3,^{2d} 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 for DFT discussion). It is noteworthy that the corresponding dihedral angle in VOCl₂(IMes)₂ [28.15°] is very close to that found in 4, although the V(IV) complex contains the same IMes and Cl ligands as 3.



Figure 6. DFT-optimized structure of NbOCl₂(IMes)₂ and NbOBr₂(Ixyl)₂ (C-PCM/ ω B97X, dichloromethane as implicit solvent). Hydrogen atoms have been omitted for clarity. Selected bond lengths for NbOCl₂(IMes)₂ (Å): Nb=O 1.682; Nb–Cl 2.519, 2.519; Nb–C 2.366, 2.366. Selected angles for NbOCl₂(IMes)₂ (deg): 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 NbOBr₂(Ixyl)₂ (Å): Nb=O 1.678; Nb–Br 2.697, 2.698; Nb–C 2.371, 2.372. Selected angles for NbOBr₂(Ixyl)₂ (deg): O=Nb–Br 99.8, 99.8; Br–Nb–Br 160.3; O=Nb–C 99.9, 99.9; C–Nb–C 160.2.

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 moduli 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 for Xray discussion).

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

The metal-ligand σ -type interactions found for **4** are qualitatively comparable to those in **3**. The π -bonds of niobium with the two carbenes are mainly accounted for by the α -HOMO-15/ β -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 π -contribution, as ascertained by computer outcomes, is in alignment with the experimental detection of



Figure 7. Selected occupied α -MOs computed for NbOCl₂(IMes)₂, 3. C-PCM/ ω B97X calculations, surface isovalue = 0.025 au. Hydrogen atoms have been omitted for clarity.

C(carbene)–X interactions in the X-ray structures of **3** and **4**. The comparison of the α -HOMO–17/ β -HOMO–13 orbitals of **3** and the α -HOMO–15/ β -HOMO–13 orbitals of **4** (Figure 8) evidences a greater Nb–C π -overlap in the case of the bromo derivative 4. It is, however, to be highlighted that the



Figure 8. Comparison of selected occupied MOs computed for NbOCl₂(IMes)₂ and NbOBr₂(Ixyl)₂. C-PCM/ ω B97X calculations, surface isovalue = 0.025 au. Hydrogen atoms have been omitted for clarity.

calculated dissociation of one carbene moiety, according to the general reaction $NbOX_2(NHC)_2 \rightarrow NbOX_2(NHC) + NHC$, has comparable Gibbs energy variations for 3 (11.8 kcal mol⁻¹) and 4 (12.6 kcal mol⁻¹), respectively.

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 (aryloxide) group. Thus, the novel compounds NbOCl(OR) (R = Ph, **5**; Me, **6**) were obtained from **2b** and NaOR (1:1 molar ratio) in tetrahydrofuran and isolated after workup in 53–65% yields (Scheme 3). The reaction of **2b** with even an excess of NaOPh cleanly led to **5**, while the reaction of **2b** with two equivalents of NaOMe presumably afforded a mixture of **6** and NbO(OMe)₂.

Scheme 3. Preparation of Methoxide and Phenoxide Derivatives of Nb(IV)

NbOCl₂(dme)
$$\xrightarrow{\text{NaOR}}$$
 NbOCl(OR)
- NaCl
- dme R = Ph, 5; Me, 6

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 Section for details).²⁵ We propose that the structures of 5 and 6 resemble that of NbOCl₂, with one chloride ligand per metal center replaced by one OR group. The structure of NbOCl₂ consists of chains of NbOCl₄ pyramids sharing their opposite edges, the distinct chains being linked by Nb=O---Nb contacts.^{10c,11a} Analogously to the case of NbCl₄, each chain shows an alternation of two different Nb-Nb distances, resulting in properties such as semiconduction and diamagnetisms.²⁶ Following the hypothesis of a NbOCl₂-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.



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



Figure 10. DFT-optimized structure (ω B97X functional) of [NbOCl-(OPh)(μ -Cl)(μ -OPh)NbO(μ -Cl)(μ -OPh)NbO((Cl)(μ -OPh)NbO((Cl)(OPh)]^{2-} and spin density surface (isovalue = 0.01 au). Selected bond lengths for the central subunits (Å): Nb=O 1.678, 1.678; Nb-(μ -Cl) 2.566, 2.569; Nb-(μ -O) 2.170, 2.170; Nb--Nb 3.675.

As expected, the unpaired electrons were 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.^{10c}

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.¹⁵ The IR absorption due to the Nb=O moiety has been detected around 800 cm⁻¹, in analogy with what was previously found for NbOCl₂.²⁷

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 dihalide 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 σ NHC to metal donation, reinforced by a π metal to NHC contribution, involving the halide ligands.

EXPERIMENTAL SECTION

General Procedures. 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. NbCl₅ (99+ % purity) was purchased from Strem and stored under an argon atmosphere as received. NbBr5,28 NbOCl3,8c Imes, and Ixyl29 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 an argon atmosphere before use. Infrared spectra were recorded at 298 K on a FT IR-PerkinElmer spectrometer, equipped with a UATR sampling accessory. Conductivity measurements were carried out using a Eutech Con 700 instrument (cell constant = 1.0 cm^{-1}).³⁰ 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 an IPC 610/P566C industrial grade Advantech computer, using an acquisition board³¹ and software package especially designed for EPR experiments.³ Experimental EPR spectra were simulated by the WINSIM 32 program.³³ 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.³⁴ NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ¹H and ¹³C were referenced to the nondeuterated aliquot of the solvent, while the chemical shifts for ⁹³Nb were referenced to external [NEt₄][NbCl₆]. The ¹H and ¹³C NMR spectra were assigned with the assistance of ¹H, ¹³C correlations measured through gs-HSQC and gs-HMBC experiments.³⁵ Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba model 1106 instrument. The halide content was determined by the Mohr method³⁶ on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO₃ up to neutralization. Niobium was analyzed as Nb₂O₅, obtained by hydrolysis of the samples followed by calcination in a platinum crucible.

Synthesis and Isolation of NbOBr₃. A suspension of NbBr₅ (6.40 g, 0.0130 mol) in CH₂Cl₂ (50 mL) was treated with O(SiMe₃)₂ (2.76 mL, 0.0130 mmol). The mixture was stirred at room temperature for 48 h, during which progressive color changing 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 × 30 mL). The product was isolated as a yellow powder. Yield: 3.67 g, 81%. Anal. Calcd for Br₃NbO: Nb, 26.65; Br, 68.76. Found: Nb, 26.30; Br, 69.06. IR (solid state): ν = 740vs (Nb=O) cm⁻¹.

Synthesis and Isolation of NbOBr₃(dme), 1b. NbOBr₃ (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 an additional 30 min. 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 C₄H₁₀Br₃NbO₃: 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): ν = 2943w, 1464w, 1456w, 1446w-m, 1276w, 1240w, 1185w, 1075m, 1020vs (Nb=O), 989m, 959s, 859s, 824w, 759vs cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 4.15 (s, 2H, CH₂), 4.14 ppm (s, 3H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ = 75.6, 70.5 (CH₂); 70.3, 63.6 ppm (CH₃). ⁹³Nb NMR (CD₂Cl₂): δ = -205 ppm ($\Delta \nu_{1/2}$ = 1.5 × 10³ Hz). UV-vis (CH₂Cl₂): λ_{max}/nm (ε/M^{-1} cm⁻¹) = 335(10), 387(7), 444(8).

Synthesis and Isolation of NbOX₂(dme) (X = Cl, 2a; X = Br, 2b). A suspension of NbOCl₃ (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 min. This solution was cooled with an ice bath; then SnBu₃H (0.48 mL, 1.8 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for an 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 C₄H₁₀Cl₂NbO₃: 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): ν = 2949w, 2847vw, 1454m, 1242w, 1191w, 1076m, 1025s (Nb=O), 957m, 866m-sh, 838s, 804vs, 771s, 701m cm⁻¹. Magnetic measurement: $\chi_M^{\text{corr}} = 7.94 \times 10^{-4} \text{ cgsu}, \mu_{\text{eff}} = 1.40 \,\mu_{\text{B}}. \text{UV-vis} (\text{THF}): <math>\lambda_{\text{max}}/\text{nm} (\varepsilon/ M^{-1} \text{ cm}^{-1}) = 278(6 \times 10^2), 632(9), 741(10).$

Compound **2b** was obtained by a procedure similar to that described for **2a**, from NbOBr₃ (514 mg, 1.47 mmol), dme (0.60 mL, 5.8 mmol), and SnBu₃H (0.40 mL, 1.5 mmol). Pentane (30 mL) was added to the final dark blue solution in toluene in order to obtain **2b** as a dark precipitate. Yield: 343 mg, 65%. Anal. Calcd for C₄H₁₀Br₂NbO₃: 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): $\nu = 2943w$, 2845w, 1447m, 1258w, 1187w, 1076m, 1018s (Nb=O), 953m-s, 849s, 799s, 755vs, 695s cm⁻¹. Magnetic measurement: $\chi_{\rm M}^{\rm corr} = 1.13 \times 10^{-3}$ cgsu, $\mu_{\rm eff} = 1.65 \,\mu_{\rm B}$. UV–vis (THF): $\lambda_{\rm max}/{\rm nm}$ ($\varepsilon/{\rm M}^{-1}$ cm⁻¹) = 351(5 × 10²), 461(20), 609(12), 722(10), 805(3 × 10²).

Synthesis and Isolation of NbOCl₂(thf)₂, 2c. This product was obtained by the same procedure described for **2b**, from NbOCl₃ (249 mg, 1.16 mmol), thf (0.21 mL, 2.6 mmol), and SnBu₃H (0.31 mL, 1.2 mmol). Dark blue solid, yield: 195 mg (52%). Anal. Calcd for C₈H₁₆Cl₂NbO₃: 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): ν = 2955w, 2926w, 2872s, 1455w-m, 1251w, 1005m, 892s, 812vs, 672vs (Nb–O–Nb) cm⁻¹. Magnetic measurement: $\chi_{\rm M}^{\rm corr}$ = 5.88 × 10⁻⁴ cgsu, $\mu_{\rm eff}$ = 1.19 μ_B. UV–vis (CH₂Cl₂): $\lambda_{\rm max}/{\rm nm}$ ($\varepsilon/{\rm M}^{-1}$ cm⁻¹) = 270(5 × 10²), 716(5), 746(7).

Synthesis and Isolation of NbOCl₂(Imes)₂, 3. A suspension of NbOCl₃ (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 SnBu₃H (0.29 mL, 1.1 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for an additional 30 min. 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 set aside at -30 °C; a microcrystalline brown material was obtained after 24 h. Yield: 515 mg, 61%. Crystals suitable for X-ray analysis were collected from a toluene/hexane mixture at $-30\,$ °C. Anal. Calcd for $C_{42}H_{48}Cl_2N_4NbO\colon$ 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⁻¹. EPR (solid state): $g_{\parallel} = 2.214$, $A_{\parallel} = 163.7$ G; $g_{\perp} = 2.412, A_{\perp} = 60.9$ G. Magnetic measurement: $\chi_{M}^{corr} = 1.21 \times 10^{-3}$ cgsu, $\mu_{\text{eff}} = 1.70 \ \mu_{\text{B}}$. UV-vis (toluene): $\lambda_{\text{max}}/\text{nm} \ (\epsilon/\text{M}^{-1} \ \text{cm}^{-1}) = 373$ (80), 716 (20).

Synthesis and Isolation of NbOBr₂(Ixyl)₂, 4. A suspension of NbOBr₃ (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 SnBu₃H (0.15 mL, 0.57 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for an 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. Volatiles were eliminated from the filtrated solution, and crystallization of the residue from toluene/pentane afforded a dark brown solid, which was washed with pentane (2×20) mL) and dried under vacuum. Yield: 233 mg, 50%. Crystals suitable for X-ray analysis were collected from a toluene/hexane mixture set aside at -30 °C. Anal. Calcd for C₃₈H₄₀Br₂N₄NbO: 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): $\nu = 3163$ w, 3132w, 3026w, 2917w-m, 1687w, 1603w, 1532w-m, 1472s, 1446m-sh, 1392w-m, 1380m, 1276m, 1215m, 1167w-m, 1100m, 1035m (Nb=O), 960m, 948s, 923m, 866m, 770vs, 730vs, 695vs cm⁻¹. Magnetic measurement: $\chi_{\rm M}^{\rm corr} = 9.42$ × 10⁻⁴ cgsu, μ_{eff} = 1.50 μ_{B} . EPR (solid state): g_{\parallel} = 2.219, A_{\parallel} = 176.5 G; $g_{\perp} = 2.331, A_{\perp} = 73.8 \text{ G. UV-vis (toluene): } \lambda_{\text{max}}^{"}/\text{nm} (\varepsilon/\text{M}^{-1} \text{ cm}^{-1}) =$ $320 (2.0 \times 10^3), 384 (1.0 \times 10^3), 480 (2.5 \times 10^2).$

Synthesis of NbOCI(OR) (R = Ph, 5; Me, 6). A solution of freshly prepared 2a (from 1.10 mmol of NbOCl₃) 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 an 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 $(2 \times 20 \text{ mL})$; thus compound 5 was obtained as a light brown powder. Yield: 170 mg (65%). An aliquot (ca. 20 mg) was dissolved into CDCl₃ (0.7 mL), treated with a large excess of H2O, and allowed to contact air overnight; a subsequent ¹H NMR spectrum of the solution pointed out the presence of PhOH and traces of thf. Anal. Calcd for C₆H₅ClNbO₂: 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): $\nu = 3061$ w, 2958w, 1586m, 1477s, 1451w-sh, 1238s, 1160m, 1098w, 1067w, 1020w, 1000w, 884m, 795s (Nb=O), 749vs, 685vs cm⁻¹. Magnetic measurement: $\chi_{\rm M}^{\rm corr} = 9.69 \times 10^{-4}$ cgsu, $\mu_{\rm eff} = 1.53 \ \mu_{\rm B}$. UV-vis (toluene): $\lambda_{\text{max}}/\text{nm} (\epsilon/\text{M}^{-1} \text{ cm}^{-1}) = 361 (40)$. Λ_{M} (toluene) = 0.1 S $cm^2 mol^{-1}$. Compound 6 was obtained by a procedure analogous to that described above, by allowing 2a (freshly prepared from 1.00 mmol of NbOCl₃) 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 CDCl₃ (0.7 mL) and then treated with a large excess of H₂O pointed out the presence of MeOH. Anal. Calcd for CH₃ClNbO₂: 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): $\nu = 2920$ w, 2821w, 1579w, 1450w, 1373w, 1152m, 1083m, 1014vs, 854m-sh, 816s-sh (Nb=O), 793vs, 682s cm⁻¹. Magnetic measurement: $\chi_{\rm M}^{\rm corr}$ = 8.67×10^{-4} cgsu, $\mu_{\text{eff}} = 1.44 \ \mu_{\text{B}}$. UV-vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon/\text{M}^{-1}$ cm^{-1}) = 362 (6 × 10²), 438 (70). $\Lambda_{\rm M}$ (toluene) = 0.1 S cm² mol⁻¹.

X-ray Crystallography. Crystal data and collection details for 3-($^{1}/_{2}$ 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 α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).³⁷ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using $F^{2,38}$ 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-($^{1}/_{2}$ hexane) is disordered over two equally populated symmetryrelated (by 2) positions. Its independent image has been refined isotropically applying restraints to the thermal parameters (SIMU line

Table 2. Crystal Data and	Experimental	Details	for	3.
$(^{1}/_{2}$ hexane) and 4.toluene	•			

	$3 \cdot (1/_2 hexane)$	4·toluene
formula	C45H55Cl2N4NbO	C45H48Br2N4NbO
fw	831.74	913.60
Т, К	100(2)	100((2)
λ, Å	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	C2/c	Pbca
<i>a,</i> Å	30.131(6)	21.228(3)
<i>b,</i> Å	12.795(2)	15.011(2)
<i>c,</i> Å	24.138(5)	26.045(4)
β , deg	100.206(3)	90
cell volume, Å ³	9159(3)	8299(2)
Ζ	8	8
$D_{c'} \mathrm{g} \mathrm{cm}^{-3}$	1.206	1.462
μ , mm ⁻¹	0.415	2.254
F(000)	3488	3720
cryst size, mm	$0.16\times0.13\times0.10$	$0.18\times0.16\times0.14$
heta limits, deg	1.37-26.00	1.56-25.03
reflns collected	43 118	56 936
indep reflns	8988 $[R_{int} = 0.0821]$	7308 $[R_{int} = 0.0765]$
data/restraints/params	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 ${\rm \AA}^{-3}$	1.981/-0.963	2.824/-2.819

in SHELXL; s.u. 0.005) and to the C–C distances (DFIX 1.53 line in SHELXL; s.u. 0.01).

Computational Studies. The computational geometry optimizations were carried out without symmetry constraints, using the hybrid-GGA EDF2 functional³⁹ in combination with the 6-31G** basis set (ECP-based LANL2DZ basis set for elements beyond Kr).⁴⁰ 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 K) were obtained.⁴¹ Further optimization of selected geometries was carried out using the rangeseparated DFT functional ω B97X,⁴² 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.⁴³ The C-PCM implicit solvation model ($\varepsilon = 9.08$) was added to ω B97X calculations.⁴⁴ The software used for C-PCM/ ω B97X calculations was Gaussian'09,⁴⁵ while EDF2 calculations were performed with Spartan'08.46

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02888. 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 (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).

Figures S1–S5 showing the DFT-calculated structures of 1b and 2a-d; Tables S1–S5 containing the relevant bonding parameters (PDF)

Crystallographic data for 3 and 4 (CIF)

Cartesian coordinates of all DFT-optimized compounds (XYZ)

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Notes

The authors declare no competing financial interest.

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