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The selective reactions of niobium pentachloride with two bulky NHC carbenes afforded NbCl₅(NHC) complexes, bearing the highest oxidation state ever found for a metal centre in a transition metal halide–NHC adduct. The X-ray structure of 2a is the first one reported for a monodentate NHC-niobium species, and exhibits abnormally long Nb–C bond.

Since the discovery of the first stable N-heterocyclic carbene (NHC),¹ the preparation of a huge variety of NHC complexes has followed with reference to almost all the metal elements of the periodic table,² stimulated by the outstanding features that such ligands may confer to the resulting species.³ In this context, niobium still remains an exception, despite its attractive properties (cheapness, low toxicity, peculiar catalytic behaviours).⁴ Indeed very few Nb-NHC derivatives have been prepared up to now,⁵ and the only crystallographic characterization regards a Nb(III) complex with a pincer 2,6-bis(imidazolylidene)pyridine.⁶

It should be remarked also that the chemistry of NHCs has primarily focused on low and medium valent metals,⁶ while the isolation of derivatives of high valent metals may be a hard task. This is particularly true for the homoleptic halides of high oxidation state metals, due to the extreme moisture sensitivity generally exhibited by the reaction systems. Indeed the progressive replacement of halide ligands with oxo groups reduces the “water hunger”; for instance, the addition of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene to W⁶⁰Cl₄ afforded an intractable product whose controlled hydrolysis allowed the isolation and the full characterization of the more stable W⁵O₄Cl₂–NHC adduct.⁶ As a matter of fact, NHC adducts of homoleptic metal halides with the metal in oxidation state above +4 have not been reported hitherto.

In the framework of our interest in the coordination chemistry of group 5 pentahalides,⁷ we present herein the synthesis and the characterization of two NbCl₅ coordination compounds with bulky monodentate NHC ligands. The reactions of NbCl₅, 1,⁸ with equimolar amounts of NHC compounds⁹ were conducted in toluene at room temperature and afforded, after work up, the products NbCl₅(NHC), 2a-b, in good yields (Scheme 1).

Compounds 2a,b are more tolerant to air with than the precursor NbCl₅ (see SI for details), and have been characterized by elemental analysis and IR and NMR spectroscopy. The ¹H and ¹³C NMR spectra of 2a,b in CD₃Cl solution (Figures S1-S4) show the presence of single NHC species; the carbenic carbon of 2a has been recognized at 187.0 ppm by means of ¹H–¹³C HMBC experiment.

Crystals of 2a suitable for X-ray analysis (see SI for details) could be collected from a toluene/pentane mixture: the molecular structure is shown in Figure 1.
The Nb(1) centre displays approximate octahedral coordination, and is slightly displaced [0.145 Å towards the apical Cl(1)] from the plane individuated by the four equatorial chlorides. This configuration is common with other NbCl₃L complexes (L = monodentate organic ligand). The steric effect of the chloride ligands on the NHC unit is evident in that especially one C₆-ring is forced away from the C₁-equatorial plane [C₁–N(1)–C(4) angle is 139.6(15)°]. The Nb(1)–C(1) [2.396(12) Å] distance is significantly longer than both Nb(V)–alkylidene moieties and even classical Nb(V)–alkyl σ-bonds; for instance, the Nb–C₃ distances in NbCl₃Me₃ measure 2.133(5) Å. Interestingly, the Nb(III)–C lengths in the chelating NHC adduct [(C–N)–C]NbCl₃(thf)], C–N–C = 2,6-bis(imidazolylidene)pyridine, were found to be around 2.20 Å.

On the other hand, the carbene atom in 2a displays C–Cl contacts with the four equatorial Cl-ligands [3.14–3.36 Å] which are within the sum of the van der Waals radii of the respective atoms [sum = 3.45 Å]. Analogous situation was previously observed in a range of d⁰ transition metal-chloride NHC complexes, including VOCl₃(IMes) and TiCl₄(IPr)₂, and was attributed to some π interaction between the Cl-lone pairs and the p-orbital of the carbonic carbon. Such an interaction has been envisaged as an essential back-bonding donation, made possible by the electron density on the Cl-ligands, in spite of the formal absence of electrons at the metal centre.

In order to shed light into structural aspects, we carried out a DFT study. Thus the structure of 2a was optimised without symmetry constrains by restricted DFT calculations (EDF2 and PBE functionals). The calculated structure of 2a is provided as Supporting Information (Figure S5), together with relevant bonding parameters (Table S1). The latter are in good agreement with the corresponding data obtained by the X-ray diffraction study. The computational analysis suggests that the C–Nb bond essentially consists of a σ-donation from carbon to a niobium d-type orbital; the relevant molecular orbital includes the axial Cl–Nb bond (see Figure 2).

The computational analysis on the hypothetical NbCl₃ adduct of 1,3-diphenylimidazol-2-ylidene, 3 (Figure 3), was helpful in the understanding of the niobium-NHC π bonding system of 2a.

Figure 2. Isosurface of C–Nb–Cl σ-bonding orbital in 2a (isovalue 0.05 e⁻/bohr⁻³). H-atoms have been omitted for clarity.

Figure 3. DFT-calculated structure of NbCl₃[CN(Ph)CCHN(Ph)]. 3 (hydrogen atoms omitted for clarity).

The formal replacement of the isopropyl groups in 2a with hydrogen atoms, giving 3, determines a twisting of the NbCl₃ frame respect to the imidazole ring, by about 24° (see Figure 3 and compare Tables S1 and S2). A molecular orbital possible candidate for the π interaction in 2a receives small contribution from the NHC ligand and is extended over both the equatorial chlorines with the Cl–Nb axis perpendicular to the imidazole ring, and the chlorine in trans position respect to the carbene (Figure S7A). The contribution of the NHC moiety appears nearly absent in the corresponding orbital calculated for 3; this seems reasonable because the rotation of the NbCl₃ frame around the Nb–C axis inhibits overlapping of the Cl and NHC orbitals, respectively (Figure S7B). On considering that the Nb–C distance does not vary substantially due to the absence of π interaction in 3 respect to 2a (Tables S1–S2), the Nb–NHC bond in 2a should be envisaged as an essential σ one. Accordingly, the Nb–C dissociation energy values calculated for 2a (31 kcal mol⁻¹, EDF2 functional) and 3 (29 kcal mol⁻¹, EDF2 functional) are very close (Table S4). With reference to the Nb–C bond, it is noteworthy that computer simulation on the hypothetical complex NbCl₃(1,3-methylimidazol-2-ylidene), 4 (Figure S8), has pointed out that the Nb–C distance is negligibly shortened on replacing the hindered aromatic N-substituents (compounds 2a, 3) with methyl groups (Table S3).

The computational analysis of the charge distribution of 2a has revealed some deficiency of electron density on the carbene carbon (the Mulliken charge resulted about 0.3 a.u. more positive than on the other C atoms of the NHC ring). This feature suggests that 2a,b are Fischer-type carbene complexes and, thus, provides an example of extension of the latter to high-oxidation-state metal centers.

In conclusion, we have obtained monodentate NHC derivatives of niobium pentachloride by straightforward synthesis. Three main points of novelty may be traced: 1) we have proved that stableNbCl₃ adducts of homoleptic metal halides can be isolated with the metal centre in the +5 oxidation state; 2) the X-ray structure ascertained for 2a is the first one comprising the Nb-NHC (monodentate) moiety; 3) the Nb–C bond in 2a is abnormally elongated and lacks of π contribution, in contrast with what previously reported for a series of d⁰ transition metal-NHC...
complexes. The structural features highlighted for 2a contribute to the knowledge of the yet poorly investigated high-valent metal-NHC bonding systems.

Notes and references

8. Niobium pentachloride has dinuclear structure in the solid state [see ref. 4], however it will be mentioned by the empirical formula NbCl₅ throughout this paper.
16. Polarized double-ζ quality basis sets and pseudopotentials on heavy atoms were used in combination with both functionals. The Grimme’s dispersion correction and the COSMO solvation model for dichloromethane were added to PBE calculations. References are reported in the Supplementary file.