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A structurally-characterized $NbCl_5$–NHC adduct†

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The selective reactions of niobium pentachloride with two bulky NHC carbenes afforded $NbCl_5$(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 an abnormally long Nb–C bond.

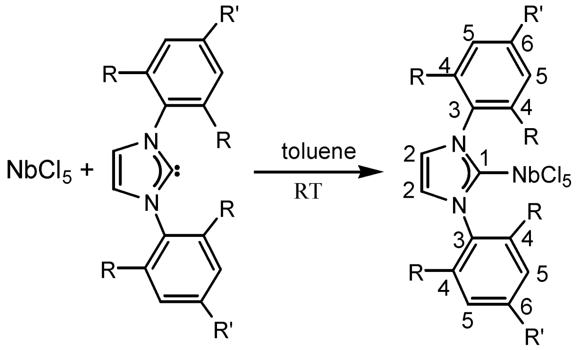
Since the discovery of the first stable N-heterocyclic carbene (NHC),[1] the preparation of a huge variety of NHC complexes has followed with reference to almost all the metal elements of the periodic table,[2] stimulated by the outstanding features that such ligands may confer on the resulting species.[3] 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 is regarding a Nb(III) complex with a pincer 2,6-bis(imidazolylidene)pyridine.[5a]

It should be also remarked that the chemistry of NHCs has been 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 $W^{VI}OCl_4$ afforded an intractable product whose controlled hydrolysis allowed the isolation and the full characterization of the more stable $W^{VI}O_2Cl_2$–NHC adduct.[6] As a matter of fact, NHC adducts of homoleptic metal halides with the metal in an oxidation state of above +4 have not been reported hitherto.

In the framework of our interest in the coordination chemistry of group 5 pentahalides,[4,7] we present herein the synthesis and the characterization of two $NbCl_5$ coordination compounds with bulky monodentate NHC ligands. The reactions of $NbCl_5$, **1**,[8] with equimolar amounts of NHC compounds[9] were conducted in toluene at room temperature and afforded, after work-up, the products $NbCl_5$(NHC), **2a–b**, in good yields (Scheme 1).

Compounds **2a,b** are more tolerant to air than the precursor $NbCl_5$ (see ESI† for details), and have been characterized using elemental analysis and IR and NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **2a,b** in C_6D_6 solution (Fig. S1–S4, ESI†) show the presence of single NHC species; the carbenic carbon of **2a** has been recognized at 187.0 ppm by means of the ^1H-^{13}C HMBC experiment.

Crystals of **2a** suitable for X-ray analysis (see ESI† for details) could be collected from a toluene–pentane mixture: the molecular structure is shown in Fig. 1.



IPr (R = ^{i}Pr, R' = H)
IMes (R = R' = Me)

2a (R = ^{i}Pr, R' = H)
2b (R = R' = Me)

Scheme 1 Synthesis of NHC complexes of $NbCl_5$.

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† Electronic supplementary information (ESI) available: Experimental details, NMR spectra, DFT structures and their relevant data. CCDC 980212. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01575d

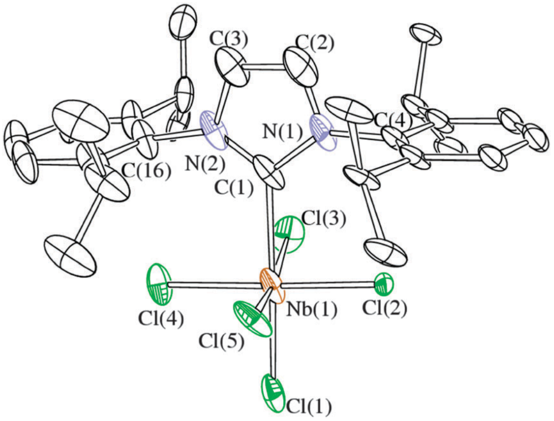

Fig. 1 ORTEP drawing of **2a**. Displacement ellipsoids are at the 30% probability level. Only the min images of the disordered groups are represented. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Nb(1)–C(1) 2.396(12), Nb(1)–Cl(1) 2.362(4), Nb(1)–Cl(2) 2.236(6), Nb(1)–Cl(3) 2.336(2), Nb(1)–Cl(4) 2.304(3), Nb(1)–Cl(5) 2.326(2), C(1)–N(1) 1.387(11), C(1)–N(2) 1.343(14), C(2)–N(1) 1.362(16), C(3)–N(2) 1.371(14), C(2)–C(3) 1.328(16), N(1)–C(1)–N(2) 104.1(10), C(1)–N(1)–C(2) 110.3(10), N(1)–C(2)–C(3) 106.9(10), C(2)–C(3)–N(2) 108.2(13), C(3)–N(2)–C(1) 110.5(9), C(1)–N(1)–C(4) 139.6(15), C(1)–N(2)–C(16) 132.0(10).

The Nb(1) centre displays approximately 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 $NbCl_5L$ complexes (L = monodentate organic ligand).[10] The steric effect of the chloride ligands on the NHC unit is evident in that especially one C6-ring is forced away from the Cl-equatorial plane [the C(1)–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[11] and even classical Nb(V)–alkyl σ-bonds;[12] for instance, the longest $Nb–C_{eq}$ distance in $NbCl_2Me_3$ measures 2.152(4) Å.[12a] Interestingly, the Nb(III)–C lengths in the chelating NHC adduct $[(C–N–C')NbCl_3(thf)]$, C–N–C′ = 2,6-bis(imidazolylidene)pyridine, were found to be around 2.20 Å.[5a]

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].[13] An analogous situation was previously observed in a range of d^0 transition metal–chloride NHC complexes,[6] including $VOCl_3(IMes)$[14] and $TiCl_4(IPr)_2$,[15] and was attributed to some π interaction between the Cl-lone pairs and the p-orbital of the carbenic carbon. Such an interaction has been considered to be a form of 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 onto the structural aspects, we carried out a DFT study. Thus the structure of **2a** was optimised without symmetry constraints using restricted DFT calculations (EDF2 and PBE functionals).[16] The calculated structure of **2a** is provided in the ESI† (Fig. S5), together with relevant bonding parameters (Table S1, ESI†). The latter are in good agreement with the corresponding data obtained using the X-ray diffraction study.

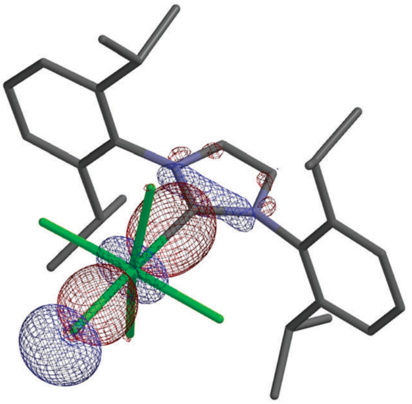

Fig. 2 Isosurface of C–Nb–Cl σ-bonding orbital in **2a** (isovalue 0.05 $e^{1/2}$ $bohr^{-3/2}$). H-atoms have been omitted for clarity.

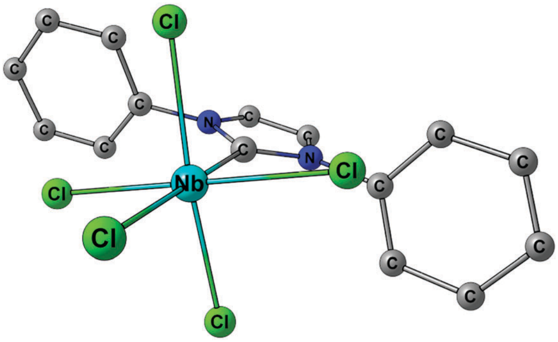

Fig. 3 DFT-calculated structure of $NbCl_5[\overline{CN(Ph)CHCHN}(Ph)]$, **3** (hydrogen atoms omitted for clarity).

The computational analysis suggests that the C–Nb bond essentially consists of a σ-donation from the carbon to a niobium d-type orbital; the relevant molecular orbital includes the axial Cl–Nb bond (see Fig. 2).

The computational analysis of the hypothetical $NbCl_5$ adduct of 1,3-diphenylimidazol-2-ylidene, **3** (Fig. 3), was helpful in the understanding of the niobium–NHC π bonding system of **2a**.

The formal replacement of the isopropyl groups in **2a** with hydrogen atoms, giving **3**, determines a twisting of the $NbCl_5$ frame respect to the imidazole ring, by about 24° (see Fig. 3 and compare Tables S1 and S2, ESI†). A molecular orbital possible candidate for the π interaction in **2a** receives a 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 the *trans* position with respect to the carbene (Fig. S7A, ESI†). The contribution of the NHC moiety appears to be nearly absent in the corresponding orbital calculated for **3**; this seems reasonable because the rotation of the $NbCl_5$ frame around the Nb–C axis inhibits overlapping of the Cl and NHC orbitals, respectively (Fig. S7B, ESI†). It may be concluded that no π interaction exists in **3**. Upon considering that the Nb–C distance does not vary substantially in **3** with respect to **2a** (Tables S1 and S2, ESI†), the Nb–NHC bond in **2a** should be envisaged as an essentially 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, ESI†). With reference to the Nb–C bond, it is noteworthy that computer simulation of the hypothetical complex $NbCl_5$(1,3-methylimidazol-2-ylidene), **4** (Fig. S8, ESI†), has pointed out that the Nb–C distance is negligibly shortened upon replacing the hindered aromatic N-substituents (compounds **2a**, **3**) with methyl groups (Table S3, ESI†).

The computational analysis of the charge distribution of **2a** has revealed some deficiency of electron density on the carbene carbon (the Mulliken charge resulted to be 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.[14]

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 stable NHC 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 π contribution, in contrast to what was previously reported for a series of d^0 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.

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