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A Structurally-Characterized NbCl₅–NHC AdductMarco Bortoluzzi,^a Eleonora Ferretti,^b Fabio Marchetti*,^b Guido Pampaloni,^b and Stefano Zacchini^c

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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.^{5a}

It should be remarked also that the chemistry of NHCs was 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}OCl₄ afforded an intractable product whose controlled hydrolysis allowed the isolation and the full characterization of the more stable W^{VI}O₂Cl₂–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.

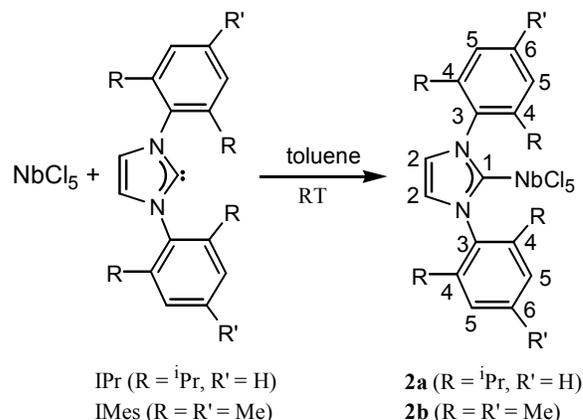
In the framework of our interest in the coordination chemistry of group 5 pentahalides,^{4,7} we present herein the synthesis and the characterization of two NbCl₅ coordination compounds with bulky monodentate NHC ligands. The reactions of NbCl₅, **1**,⁸ with equimolar amounts of NHC compounds⁹ were conducted in toluene at room temperature and afforded, after work up, the products NbCl₅(NHC), **2a–b**, in good yields (Scheme 1).

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† Electronic Supporting Information (ESI) available: Experimental details, NMR spectra, DFT structures and their relevant data.



Scheme 1. Synthesis of NHC complexes of NbCl₅.

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 C₆D₆ 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.

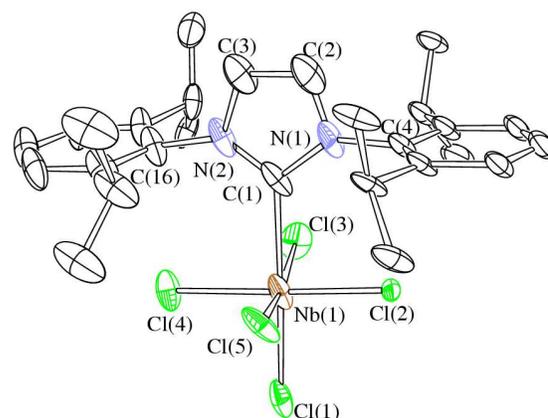


Figure 1. ORTEP drawing of **2a**. Displacement ellipsoids are at the 30% probability level. Only the min images of the disordered groups are represented. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Nb(1)–C(1) 2.396(12), Nb(1)–Cl(1) 2.362(4), Nb(1)–Cl(2) 2.236(6), 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),
 70 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 approximate octahedral coordination, and is slightly displaced [0.145 Å towards the
 75 apical Cl(1)] from the plane individuated by the four equatorial chlorides. This configuration is common with other NbCl₅L
 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 [C(1)–N(1)–C(4) angle is 139.6(15)°].
 80 plane [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 moieties¹¹ and even classical Nb(V)–
 alkyl σ-bonds,¹² for instance, the Nb–C_{eq} distances in NbCl₂Me₃
 measure 2.133(5) Å.^{12a} Interestingly, the Nb(III)–C lengths in the
 85 chelating NHC adduct [(C–N–C')NbCl₃(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
 90 atoms [sum = 3.45 Å].¹³ Analogous situation was previously
 observed in a range of d⁰ transition metal-chloride NHC
 complexes,⁶ including VOCl₃(IMes)¹⁴ and TiCl₄(IPr)₂,¹⁵ and was
 attributed to some π interaction between the Cl-lone pairs and the
 95 *p*-orbital of the carbenic carbon. Such an interaction has been
 considered as 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 into structural aspects, we carried out a
 DFT study. Thus the structure of **2a** was optimised without
 100 symmetry constrains by restricted DFT calculations (EDF2 and
 PBE functionals).¹⁶ 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
 105 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).

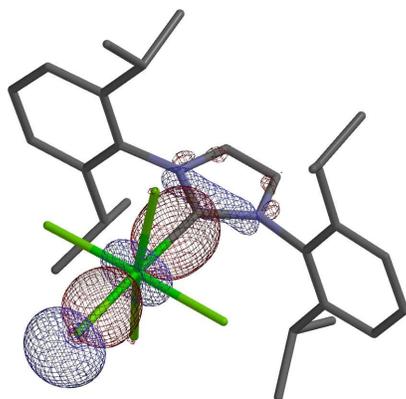
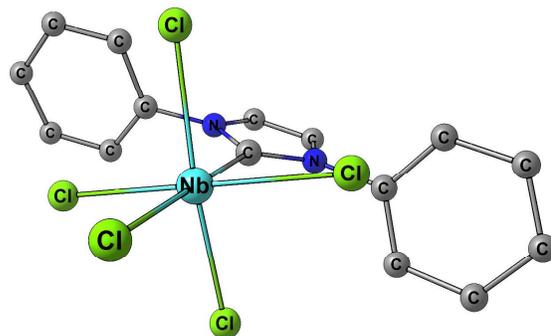


Figure 2. Isosurface of C–Nb–Cl σ-bonding orbital in **2a** (isovalue 0.05
 e^{1/2}bohr^{-3/2}). H-atoms have been omitted for clarity.

115 The computational analysis on the hypothetical NbCl₅ adduct of
 1,3-diphenylimidazol-2-ylidene, **3** (Figure 3), was helpful in the
 understanding of the niobium-NHC π bonding system of **2a**.



120 **Figure 3.** DFT-calculated structure of NbCl₅[CN(Ph)CHCHN(Ph)], **3**
 (hydrogen atoms omitted for clarity).

The formal replacement of the isopropyl groups in **2a** with
 125 hydrogen atoms, giving **3**, determines a twisting of the NbCl₅
 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
 130 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 NbCl₅ frame around
 135 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
 140 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 NbCl₅(1,3-
 145 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
 150 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.¹⁴

155 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)
 160 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.

dichloromethane were added to PBE calculations. References are reported in the Supplementary file.

Notes and references

- 1 A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361-363.
- 2 (a) T. Zou, C. Tung Lum, S. Sin-Yin Chui and C.-M. Che, *Angew. Chem. Int. Ed.*, 2013, **52**, 2930-2933; (b) S. J. Hock, L.-A. Schaper, W. A. Herrmann and F. E. Kühn, *Chem. Soc. Rev.*, 2013, **42**, 5073-5089; (c) L.-A. Schaper, S. J. Hock, W. A. Herrmann and F. E. Kühn, *Angew. Chem. Int. Ed.*, 2013, **52**, 270-289; (d) L. Oehninger, R. Rubbiani and I. Ott, *Dalton Trans.*, 2013, 3269-3284; (e) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354-396; (f) H. Jacobsena, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687-703; (g) C. Lorber and L. Vendier, *Dalton Trans.*, 2009, 6972-6984; (h) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978-4008; (i) W. A. Herrmann and C. Köcher, *Angew. Chem. Int. Ed.*, 1997, **36**, 2162-2187; (j) M. J. Ingleson and R. A. Layfield, *Chem. Commun.*, 2012, **48**, 3579-3589.
- 3 See for instance: (a) J. Broggi, V. Jurčik, O. Songis, A. Poater, L. Cavallo, A. M. Z. Slawin and C. S. J. Cazin, *J. Am. Chem. Soc.*, 2013, **135**, 4588-4591; (b) J. DePasquale, M. Kumar, M. Zeller and E. T. Papish, *Organometallics*, 2013, **32**, 966-979; (c) S. De Sarkar, A. Biswas, R. C. Samantha and A. Studer, *Chem. Eur. J.*, 2013, **19**, 4664-4678; (d) H. Diaz Velazquez and F. Verpoort, *Chem. Soc. Rev.*, 2012, **41**, 7032-7060; (e) K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Chem. Rev.*, 2009, **109**, 3859-3884.
- 4 F. Marchetti and G. Pampaloni, *Chem. Commun.*, 2012, **48**, 635-653, and references therein.
- 5 (a) D. Pugh, J. A. Wright, S. Freeman and A. A. Danopoulos, *Dalton Trans.*, 2006, 775-782; (b) W. A. Herrmann, K. Öfele, M. Elison, F. E. Kühn and P. W. Roesky, *J. Organomet. Chem.*, 1994, **480**, C7-C9.
- 6 C. A. Dodds, M. D. Spicer and T. Tuttle, *Organometallics*, 2011, **30**, 6262-6269.
- 7 F. Marchetti, G. Pampaloni and C. Pinzino, *Chem. Eur. J.*, 2013, **19**, 13962-13969.
- 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.
- 9 (a) A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523-14534; (b) L. Hintermann, *Beilst. J. Org. Chem.*, 2007, **3**, doi:10.1186/1860-5397-3-22.
- 10 (a) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2007, **38**, 4343-4351; (b) F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2008, **47**, 365-372; (c) F. Marchetti, G. Pampaloni and S. Zacchini, *Eur. J. Inorg. Chem.*, 2010, **5**, 767-774; (d) M. Jura, W. Levason, R. Ratnani, G. Reid and M. Webster, *Dalton Trans.*, 2010, **39**, 883-891.
- 11 K. F. Hirsekorn, A. S. Veige, M. P. Marshak, Y. Koldobskaya, P. T. Wolczanski, T. R. Cundari and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 2005, **127**, 4809-4830.
- 12 (a) G. S. McGrady, A. Haaland, H. P. Verne, H. V. Volden, A. J. Downs, D. Shorokhov, G. Eickerling and W. Scherer, *Chem. Eur. J.*, 2005, **11**, 4921-4934; (b) N. C. Tomson, J. Arnold and R. G. Bergman, *Organometallics*, 2010, **29**, 2926-2942; (c) M. Schormann, S. P. Varkey, H. W. Roesky and M. Noltemeyer, *J. Organomet. Chem.*, 2001, **621**, 310-316.
- 13 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.
- 14 C. D. Abernethy, G. M. Codd, M. D. Spicer and M. K. Taylor, *J. Am. Chem. Soc.*, 2003, **125**, 1128-1129. IMes = 1,3-dimesitylimidazol-2-ylidene.
- 15 A. Doddi, C. Gemel, R. W. Seidel, M. Winter and R. A. Fischer, *Polyhedron*, 2013, **52**, 1103-1108.
- 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

