# The solid state structure and reactivity of $NbCl_5$·(N,N′-dicyclohexylurea) in solution: evidence for co-ordinated urea dehydration to the relevant carbodiimide†‡

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$NbCl_5$·(N,N′-dicyclohexylurea) **1a** owns a distorted octahedral structure due to intramolecular NH · · · Cl bonding. The unit cell contains four units which are intermolecularly NH · · · Cl and NH · · · N bonded. An extended intramolecular network of H-bonding (N–H · · · Cl, CH · · · Cl, CH · · · N) causes the 3D self assembling of the units. Upon addition of base, the HCl release from **1a** is observed with the transfer to Nb of the O-atom of the carbonylic function of the starting urea which is converted into the relevant carbodiimide CyN=C=NCy **4**. The latter is quantitatively released by adding an excess of $NEt_3$ at 308 K (py and DBU are less efficient) with formation of the known $NbOCl_3(NEt_3)_2$, isolated in quantitative yield. Increasing the temperature leads to a loss in selectivity as the formed DCC undergoes further reactions. At 350 K, the isocyanate CyN=C=O has been isolated in 60% yield besides a mixture of Nb-complexes. DFT calculations have been coupled to IR and NMR experiments for characterizing possible reaction intermediates and the behaviour of **1a**. Several other $MCl_x$ species ($ScCl_3$,$YCl_3$,$LaCl_3$,$TiCl_4$, $TaCl_5$, $AlCl_3$, $SnCl_4$) have been shown to be able to co-ordinate DCU but not all of them promote the conversion of urea into DCC.

## Introduction

We have recently used DCC **4** as promoter (eqn (1)) of the direct carboxylation of alcohols to afford dialkylcarbonates.[1]

$$\begin{aligned} 2\mathrm{ROH} + \mathrm{CO_2} + \mathrm{CyN{=}C{=}NCy} &\rightarrow \mathrm{(RO)_2CO} \\ &+ \mathrm{CyHN{-}C(O){-}NHCy} \end{aligned} \tag{1}$$

$$\mathrm{R} = \mathrm{Me,\ Et,\ allyl}$$

Such reaction has high selectivity (>98%) and occurs under milder conditions (330 K and 0.2 MPa of $CO_2$) when compared to the transition metal catalyzed carboxylation of alcohols[2-5] that requires 410–470 K and 1–30 MPa of $CO_2$.

Fig. 1 shows that if DCU is converted back into DCC it would be possible to run a cyclic two-step catalytic carboxylation of alcohols using DCC, a technique useful for the production of either niche carbonates or carbonates bearing temperature sensitive substituents.

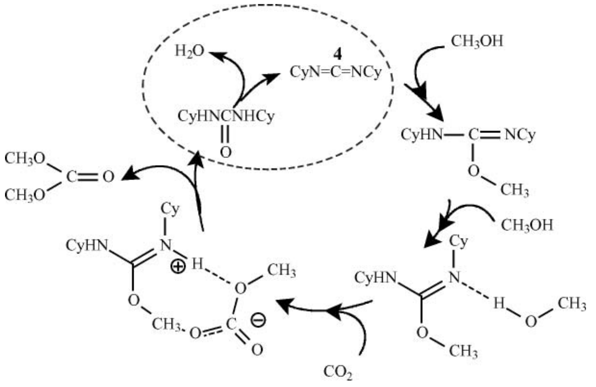

**Fig. 1** DCC as promoter of the direct carboxylation of alcohols and the recycling of the formed DCU.

Removal of water from *syn*-dialkyl-ureas is reported in the literature to occur with the use of toxic reagents such as phosgene[6-9] or $PCl_5$[7] or $SOCl_2$[8] (eqn (2a)–(c)) with low selectivity and a complex work-up of the reacting mixture.

$$\begin{aligned} \mathrm{CyHN{-}C(O){-}NHCy} + \mathrm{COCl_2} &\rightarrow \mathrm{CO_2} + 2\mathrm{HCl} \\ &+ \mathrm{CyN{=}C{=}NCy} \end{aligned} \tag{2a}$$

$$\begin{aligned} \mathrm{CyHN{-}C(O){-}NHCy} + \mathrm{PCl_5} &\rightarrow \mathrm{POCl_3} + 2\mathrm{HCl} \\ &+ \mathrm{CyN{=}C{=}NCy} \end{aligned} \tag{2b}$$

$$\begin{aligned} \mathrm{CyHN{-}C(O){-}NHCy} + \mathrm{SOCl_2} &\rightarrow \mathrm{SO_2Cl_2} + 2\mathrm{HCl} \\ &+ \mathrm{CyN{=}C{=}NCy} \end{aligned} \tag{2c}$$

In order to find more efficient, cleaner and safer alternative routes, we decided to investigate whether coordination of DCU

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† Electronic supplementary information (ESI) available: The asymmetric cell unit of **1a** (Fig. S1); representation of the unit cell of **1a** (Fig. S2); 3D architecture of **1a** (Fig. S3); D–H · · · A distances (Å) in the complex $NbCl_5$·DCU **1a** and the angles of the set of atoms (Table S1). CCDC reference number 743003. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001669a

‡ Dedicated to Prof. Antonio Tiripicchio.

to (transition) metal systems would promote its dehydration to DCC.

Ureas may act as ligands to transition metal systems[10] through the O- or the N-atoms: the $\eta^1$-O, $\eta^1$-N and $\eta^2$-N,N′ modes of bonding[11] have been demonstrated. “Hard” acids prefer a coordination at the oxygen atom, while more “soft” acids prefer N as a donor. Metal complexes containing 2, 4, 6 molecules of urea itself,[10,12] either O- or N-bonded have been described and a rare example of a chelate $\eta^2$-N,N′ mode of bonding has recently been described.[13] Metal complexes in which urea bridges two metal centres have also been characterized[14] and substituted ureas or thioureas have intensively been studied.[15-17] The renovated interest in metal complexes (Mn$^{II}$, Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$, lanthanides) with N,N′-dimethylurea-DMU, O-bonded to the metal, was due to their ability to form supramolecular **2D** structures.[18]

Despite such abundance of cases, very rare studies on the reactivity of co-ordinated ureas are available in the literature: Ti-urea complexes have been thermally decomposed to afford nanoparticles of $TiO_2$,[19] while Ni$^{II}$-urea complexes have been reported to show an urease-like action.[20] Reactions of the co-ordinated ureas selectively involving the carbonylic function and the N–H bonds have never been described.

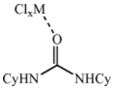
Very recently, the coordination of tetramethylureas (TMUs) to Group 4 (Ti) and 5 (Nb, Ta) metals in their highest oxidation state was for the first time investigated and the relevant complexes characterized by XRD.[21] TMU is reported to be O-bonded to the metal centers with no distortion around the Nb–O–C bond affording a symmetric molecule. Intra- or intermolecular H-bonds were not evident. Noteworthy, N,N′-dicyclohexylurea has never been used so far as a ligand.

In this paper we report the synthesis, characterization and reactivity of several metal-halide complexes with DCU. Among them, we detail the $NbCl_5$(N,N′-dicyclohexylurea) complex, describe its structure, discuss the unique mode of bonding of urea to Nb and show the presence of H-bonding in solid state which play a key role in: (*i*) determining the primary structure of the complex; (*ii*) promoting the association of four molecules in the unit cell; (*iii*) driving the supramolecular organization of the complex into an extended 3D architecture that influences the physical properties of the solid. We also show that among the metal complexes investigated in this work, Group 4 (Ti) and 5 (Nb, Ta) metal halides[22,23] in their highest oxidation state, perform quite easily the dehydration reaction of DCU to afford DCC under very mild conditions (300 K). In particular, $NbCl_5$ shows high conversion yield (> 98%) and selectivity (100%).

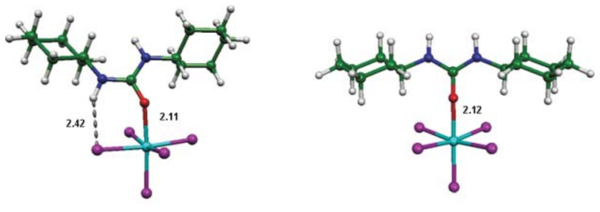
## Results and discussion

Transition metal halides with the metal (either transition metal or not) in the highest oxidation state afford solid 1 : 1 adducts with DCU. As it is shown in Table 1, the highest shift (28 cm$^{-1}$) of the $\nu$(CO) upon coordination is observed with $SnCl_4$, the lowest (7 cm$^{-1}$) with $TaCl_5$. Such shift is not diagnostic of the readiness of the metal-complexes to undergo further reactivity of the adducts, as we shall discuss later-on. A detailed analysis of the IR spectra has shown in all cases the insurgence of multiple bands in the region characteristic of N–H stretching, supporting a H-bonding formation.

**Table 1** Infrared $\nu$(CO) frequency and $^{13}$C NMR chemical shift for $\boldsymbol{C}$=O of various 1 : 1 metal-halides adducts with DCU

| $MCl_x$ | $\nu_{C=O}$ cm$^{-1}$ | $\delta_{C=O}$ | Product of the reaction of $MCl_x$·DCU with excess triethylamine |  |
|---|---|---|---|---|
| Free DCU | 1627 | 155.5 | | |
| $ScCl_3$ | 1610 | 158.2 | Free DCU + DCC traces | |
| $YCl_3$ | 1614 | 158.1 | Free DCU | |
| $LaCl_3$ | 1601 | 157.4 | Free DCU | |
| **$TiCl_4$** | **1603** | 158.9 | **DCC** | |
| **$NbCl_5$** | **1615** | 158.5 | **DCC** | |
| **$TaCl_5$** | **1620** | 158.4 | **DCC** | |
| $AlCl_3$ | 1614 | 157.8 | Free DCU + DCC traces | |
| $SnCl_4$ | 1599 | 157.6 | Free DCU | |

In the adduct of $NbCl_5$ with DCU, the IR spectrum of solid **1** in Nujol mull shows a $\nu$(C=O) at 1615 cm$^{-1}$ shifted by 12 cm$^{-1}$ towards lower energy with respect to the free urea: this supports the O-coordination to Nb. The $\nu$(N–H) region shows two bands at 3325 and 3290 cm$^{-1}$, which infer an involvement of the aminic hydrogen in H-bonding. This feature was confirmed by DFT calculations, which indicate that the most stable form of the $NbCl_5$(DCU) complex is characterized by intramolecular N–H···Cl type H-bonding (see **1a** in Fig. 2). The metal–ligand interaction in $NbCl_5$(DCU) is rather strong as the calculations predict $\Delta E$ = −30.3 kcal mol$^{-1}$ for the gas-phase binding free energy and $\Delta G_{solv}$ = −12.1 kcal mol$^{-1}$ for the solvent-corrected Gibbs free energy of complex formation. The stabilizing effect of the N–H···Cl bonding is clearly borne out by a comparison with a structural isomer without intramolecular H-bonding (see **1b** in Fig. 2), which is found to be 3.0 kcal mol$^{-1}$ less stable than **1a**.



**1a** **1b**

**Fig. 2** Equilibrium structures of two $NbCl_5$(DCU) isomers obtained from DFT calculations. Selected bond lengths are given in Å.

The calculated H···Cl distance (2.42 Å) is well within the value of “strong or classic” H-bonding.[24] Structure **1a** makes the two cyclohexyl rings non-equivalent. Instead, the $^1$H and $^{13}$C NMR spectra in $CD_2Cl_2$ show their equivalence, that can be explained invoking the fluxionality of **1** in solution at 298 K.

Already such features make complex **1** quite unique and different from $NbCl_5 \cdot [(Me_2N)_2CO]$[12] in which the urea is symmetrically bonded to the metal so that its molecular axis corresponds to the axis of the whole complex. A peculiarity of solid **1a** is that once crystallized it is scarcely soluble in the mother solution, that suggests a supramolecular architecture, either 2D or 3D. The single crystal XRD (Fig. 3) confirms that in the solid state, the DCU molecule is asymmetrically bonded to Nb.

The asymmetric cell unit is depicted in Fig. S1 (see ESI†) in which intramolecular H-bonding is represented with continuous black lines, while intermolecular H-bonding is represented by red

**Table 2** Selected bond lengths (Å) and angles (°) for the **A** molecule $NbCl_5 \cdot DCU$ in the unit cell

| Bond lengths | | | |
|---|---|---|---|
| Nb/A–Cl(1A) | 2.333(3) | Nb/A–Cl(2A) | 2.351(3) |
| Nb/A–Cl(3A) | 2.342(3) | Nb/A–Cl(4A) | 2.372(3) |
| Nb/A–Cl(5A) | 2.280(3) | Nb/A–O(A) | 2.007(5) |
| O/A–C(1A) | 1.321(9) | C(1A)–N(1A) | 1.327(10) |
| C(1A)–N(2A) | 1.294(10) | | |
| **Bond angles** | | | |
| Nb/A–O(A)–C(1A) | 139.96(5) | O/A–C(1A)–N(1A) | 118.56(7) |
| OA–C(1A)–N(2A) | 119.07(8) | N(1A)–C(1A)–N(2A) | 122.36(8) |

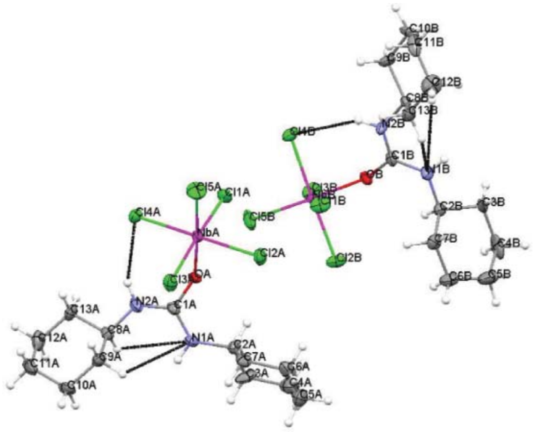


**Fig. 3** Two molecules of **1a** in the asymmetric unit. The thermal ellipsoids have a 30% probability level; H atoms are represented by circles of arbitrary radius. Intramolecular H-bonding is represented with black lines.

dotted lines. Fig. S2 (see ESI†) shows the unit cell of **1a** which crystallizes in the $P2_1$ spatial group with both cyclohexyl moieties having a "chair" conformation.

Table 2 summarizes the most important structural data. Crystallographic data are reported in Table 4 (Experimental).

The coordination of the carbonylic oxygen to Nb is coherent with the electron density at the oxygen with a NbOC angle of 140°: oxygen is using one of its lone-pair for coordination. The structure also shows the six-atom $-C-O^{-}-Nb-Cl^{-}-H-N-$ cyclic structure forced by the intramolecular NH···Cl bond. The fine analysis of crystal data has permitted the identification of two more intramolecular H-bonding in **1a**. In particular, N–H···Cl and CH···N bonds of two different intensities are clearly evident (Table 3).

In a "D–H⁻–A" system (D-donor, A-acceptor), "classic or strong" H-bonds are formed when both D and A have a high electronegativity, such as in N–H···X or O–H···X where X is N, O, F, Cl.[24a] On such basis, the N(2A)–H(2A1)···Cl(4A) (Table 3) is a "classic or strong" H-bonding. Besides such interactions, we have observed other H-bonding in which C–H bonds are involved that are characterized by a scarce polarization, called "weak or non-classic" H-bonding interactions.[24b,25,26] Such weak interactions, for which the most likely distance D–A is usually calculated on the basis of a statistic analysis of data contained in Cambridge Structural Database-CSD,[27] often play a key role in the stabilization of some peculiar molecular geometries or in the building-up of extended supramolecular 2D or 3D architectures.[28,29] In $NbCl_5 \cdot DCU$ they determine (Table 3) the 3D architecture (Fig. S3 in ESI†) and the physical properties: as mentioned above, the solid complex is very scarcely soluble in the solvent from which it is crystallized.

Table S1 (ESI†) reports the D–A distance and the D–H···A angles which confirm the existence of weak H-bonding.[27b,c] In fact, the directional properties of the C–H···X set of atoms is a key parameter in distinguishing a van der Waals interaction (such as in $R_3C-H \cdots H-CR_3$, which is linear without any preferential direction) from a weak hydrogen bonding which may have a marked direction.[27a] The "metal-assisted hydrogen bonding" effect[27a,30,31] may play a key role in the assembling of the supramolecular structure[27b] and the Nb–Cl system has, indeed, good acceptor properties.[32] Noteworthy, four out of the five chlorine atoms bonded to Nb are involved in H-bonding. The fifth (notably, $Cl_5$ in molecule **1a** in Fig. 3) is not involved and shows the shortest of the Nb–Cl distances (2.28 Å, compared to 2.33–2.37 of the other four Nb–Cl bonds). It is worth pointing out that the extended 3D association of **1a** units is undoubtedly driven by H-bonding and not by dipole-coupling forces. In fact, although the structure of $NbCl_5(DCU)$ is predicted by DFT calculations to have a relatively large dipole moment (10.7 D) aligned with the Cl–Nb···O molecular axis, the calculations carried out for a **1a**···**1a** dimer cut out from the crystal structure and involving an antiparallel arrangement of the monomers indicate only a very small interaction energy between the two monomers (–2.5 kcal $mol^{-1}$).

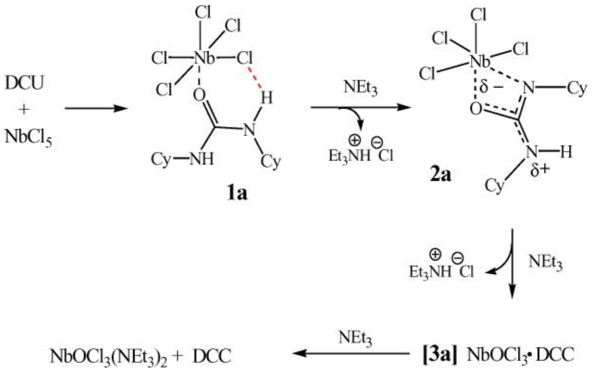
$NbCl_5 \cdot DCU$ represents, thus, a unique case, as in other urea-metal-complexes the strong N–H···Cl interactions were responsible for building at maximum a 2D structure[9] while in the recently described Nb-tetralkyl-urea complexes[12] H-bonding implying C–H···N bonds were not identified at all. The strong intramolecular H-bonding may also play an important role in determining the unusual observed reactivity of **1a**. In fact, when **1a** was treated with

**Table 3** Intramolecular H-bonding (Å) and D–H···A angles (°) in **1b**. *Weaker CH···N bonds are in italics*

| Donor-H···*Acceptor* | D–H | H···*Acceptor* | Donor···*Acceptor* | Donor-H···*Acceptor* |
|---|---|---|---|---|
| N(2A)–H(2A1)···Cl(4A)$^{(0)}$ | 0.860(9) | 2.473(3) | 3.260(9) | 152.58(45) |
| *C*(8A)–H(8A)··· N(1A)$^{(0)}$ | 0.980(7) | 2.734(6) | 2.931(11) | 91.66(41) |
| *C(9A)–H(9A2)···N(1A)*$^{(0)}$ | *0.970(11)* | *2.956(.7)* | *3.440(140)* | *112.07(79)* |
| N(2B)–H(2B1)···Cl(4B)$^{(0)}$ | 0.860(8) | 2.570(3) | 3.339(5) | 149.43(29) |
| C(8B)–H(8B)···N(1B)$^{(0)}$ | 0.980(6) | 2.677(7) | 2.892(11) | 92.59(38) |
| *C(13B)–H(13C)···N(1B)*$^{(0)}$ | *0.970(.13)* | *2.961(.8)* | *3.429(170)* | *110.90(80)* |

Symmetry code: (0) *x*, *y*, *z*.

an excess of base at 300 K, we observed the immediate formation of the dehydrated form of the urea, *i.e.* dicyclohexylcarbodiimide, and of $NbOCl_3(base)_2$ (Scheme 1).

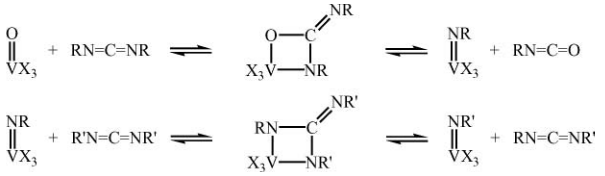


**Scheme 1** Step-by-step conversion of CyHNC(O)NHCy into CyN=C=NCy promoted by $NbCl_5$ and a base by progressive loss of HCl and transfer of the O-atom from C– to –Nb. Compounds **2a** was identified by multinuclear NMR.

We have observed that the yield of the reaction was dependent on the base used (Py < DBU < $NEt_3$) while the selectivity was governed by the temperature. In fact, above 325 K the reaction afforded a mixture of Nb-compounds and cyclohexylisocyanate ($\nu_{NCO}$ at 2260 $cm^{-1}$) that was determined by GC-MS (eqn (3)).

$$NbOCl_3 + CyN{=}C{=}NCy \rightarrow \text{Nb-species} + CyN{=}C{=}O \qquad (3)$$

Such reaction is reminiscent of the first step of the metathesis of carbodiimides promoted by oxo-complexes of vanadium(V) which have been proposed to co-ordinate the cumulene and form an imido-V complex and isocyanate.[33] The V=NR moiety would then promote the metathesis with a second carbodiimide R′N=C=NR′ to afford RN=C=NR′ and the V=NR′ moiety (Scheme 2).



**Scheme 2** Proposed mechanism for carbodiimide metathesis.

So far, we were not able to isolate the imido complex $CyN{=}NbCl_3$ as a pure compound as it was contaminated with other Nb-species difficult to separate.

The dehydration of DCU 300 K was followed by IR (Fig. 5) or NMR. Intermediate **2a** (Scheme 1) was obtained by addition of stoichiometric amounts (1 : 1) of the base to complex **1a** with mono-deprotonation of DCU. It was characterised *in situ* by IR and NMR. The formation of compound **2a** caused the insurgence of an intense IR absorption at 1651 $cm^{-1}$; the $^{13}C$ NMR of **2a** shows two equivalent cyclohexyl groups (see Experimental). DFT calculations suggest that the structure of such intermediate corresponds to a 4-membered ring involving the metal center and the NC=O moiety of the deprotonated DCU (**2a** in Fig. 4).

In **2a**, Nb reaches a hexa-coordinate configuration, which is more stable by 21.8 kcal $mol^{-1}$ than the penta-coordinated form **2b** (Fig. 4).

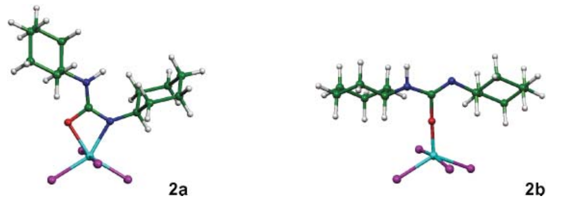


**Fig. 4** DFT calculated structures for intermediate **2** obtained upon single deprotonation of complex **1a**.

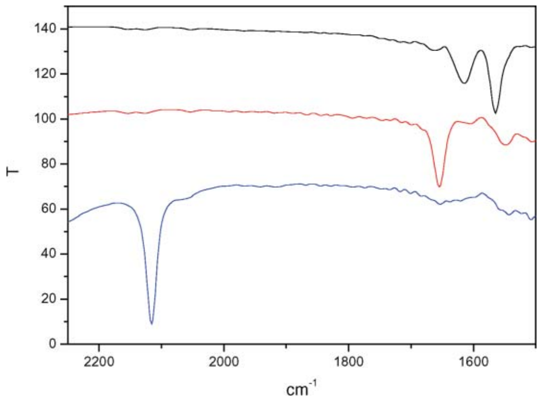
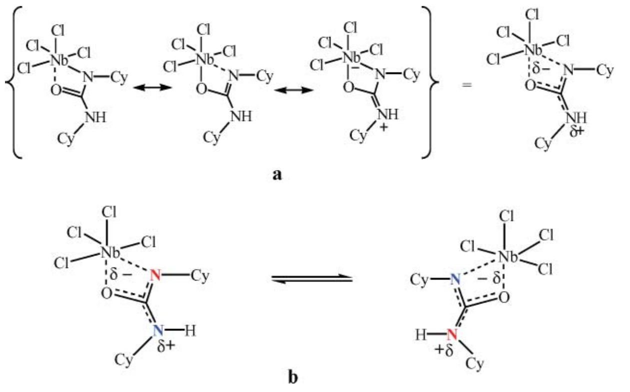


**Fig. 5** The effect of addition of $NEt_3$ to a solution of **1a** in $CH_2Cl_2$. *Black*: IR spectrum of starting compound **1a**: the band at 1615 $cm^{-1}$ is due to the $\nu$(C=O) of the co-ordinated urea. *Red*: The sample above after addition of two mol of base per mol $NbCl_5{\cdot}DCU$. The band at 1653 $cm^{-1}$ is most probably due to the carbodiimide co-ordinated to $NbOCl_3$. *Blue*: The above sample after the addition of an excess of $NEt_3$. The band at 2117 $cm^{-1}$ is due to free CyN=C=NCy.

Intermediate **2a** can be represented as the resonance hybrid of three different possible structures (Scheme 3). The chemical equivalence of the cyclohexyl groups in the $^{13}C$ NMR spectra can be, thus, explained by the fluxionality of the complex, with a rapid exchange of the two N atoms which co-ordinate to Nb and bind the proton. The addition of a second equivalent of base afforded a further change of the IR spectrum (Fig. 5) with formation of putative **3a** (band at 1653 $cm^{-1}$ due to the C=N stretching).



**Scheme 3** (a) Resonance structures; and (b) fluxionality equilibrium for intermediate **2a**.

After an excess of base was added, free DCC was formed (band at 2117 $cm^{-1}$) and isolated. The nature of **3a** was inferred on the basis of the fact that the same IR spectrum was observed when an authentic sample of $NbOCl_3$ was reacted with an equimolar amount of DCC (Fig. 6). Most interestingly, the $^{13}$C NMR of putative **3a** in solution shows a net change of the resonance of the original N=C=N carbon which is shifted from 140.0 ppm in the free DCC to 158.8 in the co-ordinated DCC. Such value recalls very close the resonance of the urea indicating a C–O interaction.

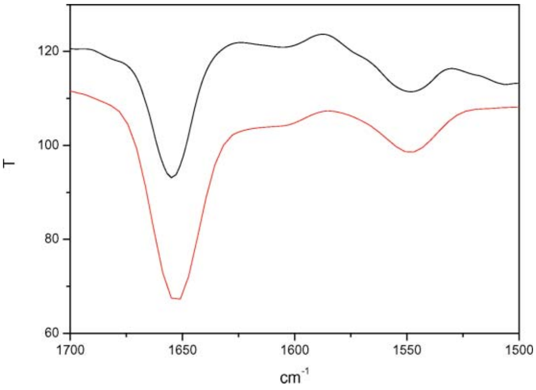


**Fig. 6** Comparison of the IR spectra of putative compound **3a** obtained from: (*black*) $NbCl_5{\cdot}DCU + 2NEt_3$; (*red*) the direct reaction of an authentic sample of $NbOCl_3$ with CyN=C=NCy.

Attempts to grow a mono-crystal of **3a** for its XRD characterization (that would allow the definition of the mode of bonding of DCC to $NbOCl_3$) failed so far as a fast precipitation produced nanocrystals not suited for XRD determination while a long permanence of **3a** in solution caused its conversion into a mixture of products. This was demonstrated by the IR spectrum of the isolated solid which shows the appearance of several new bands below 1650 cm$^{-1}$. Also, the powder-method did not give a good resolution of the structure.

The three bases used in this work were selected for their different properties and showed a different activity, as expected (py < DBU < $NEt_3$). With $NEt_3$, pure DCC was isolated from the reacting mixture with a yield of 98–99% and a selectivity of 100% at 300 K. DBU allowed to isolate DCC with a maximum yield of 70% and pyridine was the worst with a yield of only 50%. Such different behaviour can be explained in terms of both the proton-affinity and the coordination ability to $NbOCl_3$ of the three bases. Both such functions play a key role in the elimination of H–Cl and in the fast de-coordination from the metal of the formed DCC that prevents its further conversion. $NEt_3$ combines the best capacity in the two reactions, maximizing, thus, the yield.

It is worth emphasizing that among the metal halides-DCU complexes we have synthesized so far (Table 1), only the Nb derivative promotes the quantitative conversion of DCU into DCC (and $NbOCl_3$) upon treatment with $NEt_3$. The Ti(IV) and Ta(V) derivatives show an interesting but lower yield (> 90%), while the Al(III) and Sc(III) complexes afford only a limited conversion. Other adducts undergo a ligand substitution reaction (eqn (4)) more than a dehydration of the co-ordinated DCU.

$$MCl_x{\cdot}DCU + 2\,NEt_3 \rightarrow MCl_x{\cdot}(NEt_3)_2 + DCU \qquad (4)$$

We recall that there is no correlation between the low-energy shift of the C=O stretching and the reactivity of the adducts. The variation of the chemical shift of the co-ordinated carbonyl is not aligned with the low energy shift of the C=O stretching. A careful analysis of data shows that, anyway, the trend of reactivity for the most reactive Nb(V) > Ti(IV), Ta(V) species is some how parallel to the low-field shift of the $^{13}$C-resonance.

## Experimental

### General

All starting reagents and solvents were commercial products purchased by Aldrich. Solvents were dried, distilled,[34] and stored under dinitrogen. All manipulations were carried out under a dry dinitrogen atmosphere, due to the high sensitivity of $NbCl_5$ to moisture.

Nuclear magnetic resonance experiments were carried out with a 600 MHz Bruker Avance II Ultrashield Plus instrument using deuterated solvents. Infrared spectra were recorded with a FTIR Shimadzu Prestige 21 instrument. GC-MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; Agilent 19091J-433E HP5 5% phenyl methyl siloxane; Ø 0.25 mm, 0.25 μm film) coupled to a Shimadzu QP5050 A mass spectrometer.

Quantitative determinations on the reaction solutions were recorded using a Hewlett-Packard 6850 GC-FID (capillary column: 30 m; Phenomenex ZB-Wax; Ø 0.25 mm, 0.25 μm film). Elemental analyses on Nb were conducted colorimetrically[35] using a Shimadzu UV-1601 spectrophotometer. Other elements were determined using Atomic Absorption Spectrophotometer Shimadzu AA-6200.

### X-Ray data collection, structure solution, and refinement†

The structure of **1a** was determined by X-ray single-crystal diffraction data from a crystal mounted on a glass fibre. Because of the instability of the compound under ambient conditions, the crystalline sample was covered with a thin layer of glaze, to protect the compound for the time of experiments.

Single crystal X-ray data were collected on a Bruker-Nonius KappaCCD diffractometer equipped with a CCD area detector, a 0.35 mm capillary collimator optic (important to improve intensity of Mo radiation and to reduce the beam divergence), using Mo radiation ($\lambda_{K\alpha1} = 0.71073$ Å) and an adjustable graphite monochromator.

The structure was solved by direct methods using SIR2008[36] and refined by full-matrix least-squares on $F^2$ with SHELXL-97,[37] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

All H atoms were introduced into the geometrically calculated positions and then treated as riding-model in idealized positions on the corresponding parent atoms, with bond lengths C–H = 0.97 Å for methylene H-atoms and N–H = 0.86 Å, in spite of several of them were observed in a difference Fourier map. The H atoms of each group were assigned the same $U_{iso}$ (H) value, set at 1.2 $U_{eq}$ (carrier), which was refined isotropically. The absolute configuration was confirmed by the absolute structure determination by X-ray data indicated by the Flack parameter of $x = 0.17(8)$.

Crystallographic and experimental details of the structure are summarized in Table 4.

**Table 4** Summary of crystallographic data for **1a**

| | **1a** |
|---|---|
| Formula | $C_{13}H_{24}Cl_5N_2NbO$ |
| Fw | 494.50 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ (No. 4) |
| $T$/K | 298(2) |
| Mo-$\lambda_{K\alpha 1}$/Å | 0.71073 |
| $a$/Å | 10.623(4) |
| $b$/Å | 12.392(5) |
| $c$/Å | 15.881(4) |
| $\alpha$/° | 90 |
| $\beta$/° | 107.286(5) |
| $\gamma$/° | 90 |
| $V$/Å$^3$ | 1996.20(12) |
| $Z$ | 4 |
| $\mu$/mm$^{-1}$ | 1.274 |
| Crystal size/mm | max = 0.60, mid = 0.10, min = 0.06 |
| $\rho_c$/g cm$^{-3}$ | 1.645 |
| $S$ = GoF | 1.022 |
| θ range/° | 5.01–24.40 |
| $h,k,l$ ranges | −12 → 12<br>−13 → 14<br>−18 → 18 |
| $N(hkl)_{measured}$ | 18 159 |
| $N(hkl)_{unique}$ | 6417 [$R_{int}$ = 0.074] |
| $N(hkl)_{used}$ [$I_{obs}2\sigma(I_{obs})$] | 4866 |
| $N(param)_{refined}$ | 398 |
| $R[I_{obs}2\sigma(I_{obs})]$ | $R_1$ = 0.0449; w$R_2$ = 0.0992 |
| $R$[all data] | $R_1$ = 0.0688; w$R_2$ = 0.1106 |
| Absolute structure: Flack (1983) Flack parameter | 0.17(8) |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2002) | $T_{min}$ = 0.515, $T_{max}$ = 0.928 |

$R_1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$; w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

## Computational details

The DFT calculations in the present work were carried out at the B3LYP/SDDP level, where the B3LYP refers to the applied exchange–correlation functional[38–40] and SDDP denotes a basis set including the Stuttgart-Dresden relativistic small core ECP basis and the Dunning/Huzinaga DZ electron polarization basis set for the lighter atoms.[41–44] The structures of all investigated species have been fully optimized. Vibrational frequencies have been calculated to estimate the zero-point energy and thermal contributions to the gas phase Gibbs free energy of the reaction components. The effect of solvent ($CH_2Cl_2$) was included *via* the PSM methodology.[45] The thermal corrections were calculated for standard conditions ($T$ = 298 K and $P$ = 0.1 MPa). All these calculations were performed using the Gaussian 03 package.[46]

## Synthesis of NbCl$_5$·DCU

DCU (0.31 g, 1.37 mmol) was added to a suspension of $NbCl_5$ (0.36 g, 1.35 mmol) in dichloromethane (30 mL) with continuous stirring at 298 K until the starting precipitate was completely dissolved. FTIR and NMR analyses on the yellow solution showed the coordination of DCU to niobium chloride. The insoluble impurities were filtered off and the filtrate was layered with pentane at 298 K until prismatic yellow crystals were formed. The solvent was filtered off and the crystals were washed with pentane and dried under vacuum.

IR: 1615 cm$^{-1}$ ($\nu_{CO}$); 1568 cm$^{-1}$ ($\delta_{N-H} + \nu_{C=N}$).

$^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.5 ppm ($C$=O); 20–40 ppm ($C$-cyclohexyl rings).

Anal. Calcd for $C_{13}H_{24}Cl_5N_2NbO$: C 31.57, H 4.89, Cl 35.84, N 5.67, Nb 18.79%. Found: C 31.40, H 4.83, Cl 35.70, N 5.63, Nb 18.65%.

## Synthesis of other MCl$_x$·DCU complexes

All the complexes described below were synthesized by mixing equimolecular quantities of DCU and metal chloride and processing the mixture as reported above. In each case the $\nu$(C=O) and the carbonyl relevant $^{13}$C-chemical shift (see Table 1) indicate the coordination of DCU to the metal center.

**ScCl$_3$·(N,N′-dicyclohexylurea).** IR: 1610 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.2 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_3N_2OSc$ (M 375.66): C 41.56, H 6.44, Cl 28.31, N 7.46, Sc 11.97%. Found: C 41.62, H 6.60, Cl 28.28, N 7.48, Sc 11.93%.

**YCl$_3$·(N,N′-dicyclohexylurea).** IR: 1614 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.1 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_3N_2OY$ (M 419.61): C 37.21, H 5.77, Cl 25.35, N 6.68, Y 21.19%. Found: C 37.15, H 5.75, Cl 25.32, N 6.60, Y 21.25%.

**LaCl$_3$·(N,N′-dicyclohexylurea).** IR: 1601 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 157.4 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_3LaN_2O$ (M 469.61): C 33.25, H 5.15, Cl 22.65, La 29.58, N 5.97%. Found: C 33.37, H 5.22, Cl 22.73, La 29.62, N 5.90%.

**TiCl$_4$·(N,N′-dicyclohexylurea).** IR: 1603 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.9 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_4N_2OTi$ (M 414.02): C 37.71, H 5.84, Cl 34.25, N 6.77, Ti 11.56%. Found: C 37.65, H 5.82, Cl 34.29, N 6.68, Ti 11.58%.

**TaCl$_5$·(N,N′-dicyclohexylurea).** IR: 1620 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.4 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_5N_2OTa$ (M 582.55): C 26.80, H 4.15, Cl 30.43, N 4.81, Ta 31.06%. Found: C 26.85, H 4.19, Cl 30.55, N 4.78, Ta 31.14%.

**AlCl$_3$·(N,N′-dicyclohexylurea).** IR: 1614 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 157.8 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}AlCl_3N_2O$ (M 357.68): C 43.65, H 6.76, Al 7.54, Cl 29.74, N 7.83%. Found: C 43.77, H 6.85, Al 7.46, Cl 29.66, N 7.90%.

**SnCl$_4$·(N,N′-dicyclohexylurea).** IR: 1599 cm$^{-1}$ ($\nu_{CO}$); $^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 157.6 ppm ($C$=O). Anal. Calcd for $C_{13}H_{24}Cl_4N_2OSn$ (M 484.86): C 32.20, H 4.99, Cl 29.25, N 5.78, Sn 24.48%. Found: C 32.12, H 4.87, Cl 29.31, N 5.63, Sn 24.55%.

## Reaction of NbCl$_5$·DCU with NEt$_3$: formation of DCC

To a solution of $NbCl_5$·DCU in dichloromethane a large excess of triethylamine (8 : 1 molar ratio with respect to the starting DCU) was added at 298 K. The addition of the amine caused a change in color of the reaction mixture from yellow to red with the production of white vapors and formation of some precipitate. The reaction was followed by FTIR, GC and GC-MS analyses showing the complete conversion of DCU after few minutes and the formation of DCC (intense IR absorption at 2117 cm$^{-1}$). The solvent was evaporated under vacuum and the residue was repeatedly extracted with pentane (5 × 3 mL). The collected pentane fractions were evaporated under vacuum and DCC was obtained in high purity, as shown by FTIR and NMR analyses of the isolated product compared with those of an authentic sample. The yield of conversion of DCU into DCC was 98%.

$^{13}$C NMR ($CD_2Cl_2$, 150 MHz) for DCC: 140.0 ppm (N=*C*=N), 56.0, 35.4, 25.9 and 25.1 ppm (*C*-cyclohexyl rings).

### Step-by-step deprotonation of 1a

**Step 1.** To a solution of $NbCl_5\cdot DCU$ in $CH_2Cl_2$ a diluted solution of triethylamine in $CH_2Cl_2$ (1 : 10 v/v) in a 1 : 1 molar ratio respect to the starting complex was added dropwise. The resulting mixture was analyzed by FTIR and NMR. The IR analysis showed the disappearance of the band due to the coordinated DCU ($\nu_{C=O}$ at 1615 cm$^{-1}$) and the appearance of the C=N stretching at 1651 cm$^{-1}$. The formed $NEt_3\cdot HCl$ was isolated and monitored by $^{13}$C NMR (signals at 47.0 and 8.6 ppm due to the two C-atoms of the ethyl group, identical with those of an authentic samples).

The solution was monitored by $^{13}$C NMR that showed the equivalence of the two cyclohexyl rings (four sharp signals at 53 partially overlapping with the signal of the solvent, 34.9, 25.4, 24.8 ppm).

**Step 2.** The filtered solution was added with a further equivalent of $NEt_3$ which caused a slight change of the IR spectrum. The formation of putative **3a** is proposed on the basis of the fact that the IR and NMR spectra are identical with those of a compound isolated from the reaction of $NbOCl_3$ with DCC (see next paragraph).

**Step 3.** The addition of an excess of $NEt_3$ caused further change of the IR spectrum with the appearance of the typical band of free DCC (Fig. 5), quantitatively dosed by GC-MS, and the formation of $NbOCl_3(NEt_3)_2$ which was separated from the mother solution and was filtered off. DCC remained in solution and was separated by fractional crystallization. $NbOCl_3(NEt_3)_2$ was identified by comparison with an authentic sample[47] prepared from $NbOCl_3$ and $NEt_3$.

### Reaction of $NbOCl_3$ and DCC: formation of $NbOCl_3\cdot DCC$ 3a

To a suspension of $NbOCl_3$[48] (0.193 g, 0.90 mmol) in dichloromethane (15 mL) at room temperature a solution of DCC (0.185 g, 0.90 mmol) in the same solvent (5 mL) was added. The mixture was stirred at 300 K for 30 min with the slow dissolution of the starting solid. The filtered yellow solution was analyzed by FTIR, showing the absence of the N=C=N stretching of free carbodiimide and the presence of a C=N stretching at 1653 cm$^{-1}$. The solvent was evaporated under vacuum and the formed solid was crystallized as nanocrystals not suited for XRD determination. A slow crystallization by pentane layering caused the conversion of the compound into several other species.

IR: 1652 cm$^{-1}$ (N=C=N).

$^{13}$C NMR ($CD_2Cl_2$, 150 MHz): 158.8 ppm (N=*C*=N); 51.3, 33.2, 25.5, 21.1 ppm (*C*-cyclohexyl rings).

Anal. Calcd for $C_{13}H_{22}Cl_3N_2NbO$: C 37.02, H 5.26, Cl 25.26, N 6.64, Nb 22.03%. Found: C 36.90, H 5.23, Cl 25.17, N 6.63, Nb 21.85%.

### Reaction of $NbCl_5\cdot DCU$ with pyridine and DBU

To a solution of $NbCl_5\cdot DCU$ in dichloromethane was added a large excess of either base (in 8 : 1 molar ratio respect to the starting DCU). The color of the mixture turned to red and some precipitate and white vapors were formed. The reaction mixture was analyzed by FTIR and GC techniques. In both case DCC production was observed. It was quantified by GC and shown to be 40–50% of the theoretical amount with pyridine and 60–70% with DBU. In both cases the starting compound was present in the reaction mixture.

## Conclusions

In conclusion, N,N′-dicyclohexylurea gives unique complexes with Group 3, 4, 5, 13 and 14 metal halides.[22,23] In $NbCl_5\cdot DCU$ H-bondings of different intensity dictate the molecular structure and the **3D** architecture. Also, the intramolecular H-bonding prompts the easy elimination of HCl upon action of an external base and the formation of $NbOCl_3$ and free DCC.

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