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of Unusual Tetrahydrofuran Activation**

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Synthesis and Structural Characterization of Mixed Halide - *N,N*-Diethylcarbamates of Group 4 Metals, Including a Case of Unusual Tetrahydrofuran Activation

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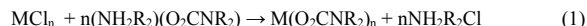
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The solid-state, thermally stable tetramethylguanidinium *N,N*-diethylcarbamate [TMGH][O₂CNEt₂] was prepared from tetramethylguanidine (TMG), *N,N*-diethylamine and carbon dioxide (1 atm). The reaction of [TMGH][O₂CNEt₂] with TiCl₄ in toluene afforded [TMGH]₂[TiCl₆] and TiCl₂(O₂CNEt₂)₂. The tetrachlorides of titanium, zirconium and hafnium were effectively converted into the respective mixed dichloride-dicarbamates, MCl₂(O₂CNEt₂)₂, by the reaction with either silver diethylcarbamate or the corresponding homoleptic metal *N,N*-diethylcarbamate, M(O₂CNEt₂)₄. The titanium and the hafnium derivatives are trinuclear in the solid state according to X-ray diffraction analysis (M = Ti) and DFT calculations (M = Hf). Instead, ZrCl₂(O₂CNEt₂)₄ was obtained as a mixture of two isomers presumably holding dinuclear and trinuclear structure, according to DFT calculations. The difluoride-dicarbamate TiF₂(O₂CNEt₂)₄ was prepared in a similar way as the homologous Cl-compound. All the products were characterized by analytical and spectroscopic methods, and by X-ray diffraction in the cases of [TMGH]₂[TiCl₆] and Ti₃Cl₆(μ-O₂CNEt₂)₆. The complex Hf₄Cl₄(O₂CNEt₂)₆[O(CH₂)₃CHO]₂ was isolated in low yield in crystalline form from a thf solution of HfCl₂(O₂CNEt₂)₂, and then X-ray characterized.

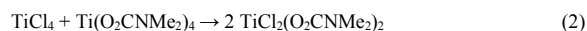
Introduction

Carbon dioxide is an abundant, cheap, non toxic and therefore appealing C1 building block in synthetic chemistry.¹ Its feasible incorporation into *N,N*-dialkylcarbamates, i.e. monoanionic oxygen donors of formula (O₂CNR₂)⁻,² allows the straightforward access to a variety of compounds of general formula M(O₂CNR₂)_n (M = non-transition or transition, d or f, element), see Eq. 1.³



The procedure described in Eq. 1 affords homoleptic metal carbamates, wherein the number of carbamate ligands corresponds to the oxidation state of the metal. This kind of compounds may exhibit interesting catalytic properties, and in particular homoleptic carbamates of group 4 and group 5 transition metals have been proposed as catalytic precursors for a variety of polymerization reactions.⁴

In the past years, non-homoleptic carbamates such as PdMe(O₂CNEt₂)(PPh₃)₂,⁵ Re(O₂CNEt₂)(CO)₂(PPh₃)₂,⁶ and W(NMe₂)₃(O₂CNMe₂)₃,⁷ have been synthesized by various synthetic routes.³ On the other hand, examples of well defined synthetic procedures leading to mixed halide-carbamates are relatively rare in the literature.⁸ The only targeted synthesis of a transition metal species refers to TiCl₂(O₂CNMe₂)₂, prepared by metathetical reaction between equimolar amounts of TiCl₄ and Ti(O₂CNMe₂)₄ in toluene (Eq. 2).⁹



Besides, some mixed chloride-carbamates have been fortuitously obtained as a result of partial chloride replacement in transition

metal chlorides by in situ generated (O₂CNR₂)⁻.¹⁰ For instance, Cr₂Cl(O₂CNⁱPr₂)₅ was obtained by treatment of CrCl₃ with an excess of NHⁱPr₂ in atmosphere of CO₂.¹⁰

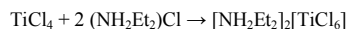
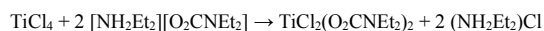
The interest in expanding the family of mixed metal halide-carbamates lies also in that such compounds may exhibit better performances in catalytic processes, compared to the corresponding homoleptic carbamates.⁹

In the framework of our research on early transition metal coordination compounds,¹¹ herein we present the preparation and the structural characterization of a series of group 4 dihalide-dicarbamates. The new compounds were fully characterized both in solution and in the solid state, and their structures were ascertained with the assistance of DFT calculations. Unusually, the hafnium derivative promoted C–H bond activation of tetrahydrofuran under mild conditions.

Results and Discussion

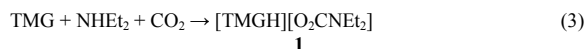
Titanium tetrachloride smoothly reacted with two equivalents of [NH₂Et₂][O₂CNEt₂] in toluene, affording a mixture of two compounds, i.e. TiCl₂(O₂CNEt₂)₂ and Ti(O₂CNEt₂)₄, according to NMR.¹² Due to partial overlapping of NMR resonances, the molar ratio between TiCl₂(O₂CNEt₂)₂ and Ti(O₂CNEt₂)₄ could be more clearly established to be 4:1 by elemental analysis. The reaction was accompanied by the precipitation of a ca. 4:1 molar mixture (based on elemental analysis) of NH₂Et₂Cl and [NH₂Et₂]₂[TiCl₆].

The identification of Ti(O₂CNEt₂)₄ and [NH₂Et₂]₂[TiCl₆] suggests that the Cl⁻ / (O₂CNEt₂)⁻ exchange might occur via the sequence of reactions reported in Scheme 1. This sequence includes the formation of the [TiCl₆]²⁻ anion by chloride transfer to unreacted TiCl₄ from the newly generated (NH₂Et₂)Cl.

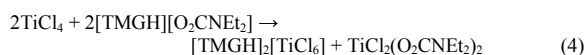


Scheme 1. Compounds involved in the reaction of TiCl_4 with $[\text{NH}_2\text{Et}_2][\text{O}_2\text{CNEt}_2]$.

The chloride / carbamate exchange was straightforwardly performed by using tetramethylguanidinium *N,N*-diethylcarbamate $[\text{TMGH}][\text{O}_2\text{CNEt}_2]$, **1**. This salt, recently obtained by some of us from $\text{TMG}/\text{NHEt}_2/\text{CO}_2$ (1 atm) as a room temperature, vacuum-stable solid (Eq. 3),¹³ is easier to use in stoichiometric amounts with respect to the liquid $[\text{NH}_2\text{Et}_2][\text{O}_2\text{CNEt}_2]$.



The reaction of **1** with TiCl_4 sluggishly proceeded in toluene affording pure $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$, which could be separated from $[\text{TMGH}]_2[\text{TiCl}_6]$ in view of the poor solubility of the latter in the reaction medium (Eq. 4).



The compound $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$ is not stable in air even for short periods of time and releases CO_2 upon treatment with diluted acids. It was fully characterized by means of IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structure was ascertained by X ray diffraction (Figure 1 and Table 1). The compound has a trinuclear structure corresponding to the formula $\text{Ti}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$, **2**. Within the crystals, $\text{Ti}(1)$ is located on an inversion centre. The molecule is composed of three octahedral $\text{Ti}(\text{IV})$ centres joined by six bridging carbamate ligands. The coordination of $\text{Ti}(2)$ is completed by three chlorides with a *fac* arrangement. All bonding parameters are as expected for $\text{Ti}(\text{IV})$ -carbamate complexes.^{9,14}

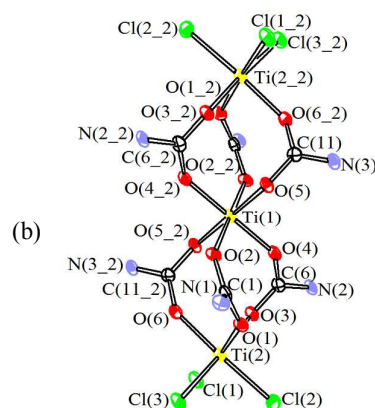
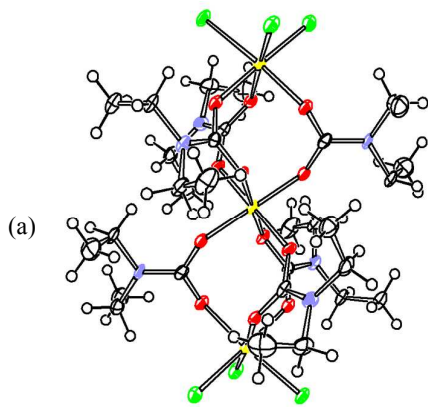


Figure 1. ORTEP drawing of $\text{Ti}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$, **2**. Displacement ellipsoids are at the 50 % probability level. (a) Complete molecule. (b) Labelling scheme (H atoms and Et groups have been omitted). Symmetry transformation used to generate equivalent atoms: $-x, -y+1, -z$

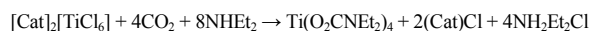
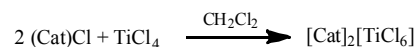
Table 1. Selected bond lengths (Å) and angles (deg) in **2**.

Ti(1)–O(2)	1.943(2)	Ti(1)–O(4)	1.929(2)
Ti(1)–O(5)	1.930(2)	Ti(2)–O(1)	1.980(2)
Ti(2)–O(3)	1.962(2)	Ti(2)–O(6)	1.971(2)
Ti(2)–Cl(1)	2.3054(11)	Ti(2)–Cl(2)	2.2805(11)
Ti(2)–Cl(3)	2.3033(10)	C(1)–N(1)	1.329(4)
C(1)–O(1)	1.279(4)	C(1)–O(2)	1.295(4)
C(6)–O(3)	1.288(4)	C(6)–O(4)	1.294(4)
C(6)–N(2)	1.325(4)	C(11)–N(3)	1.324(4)
C(11)–O(5)	1.303(4)	C(11)–O(6 ₂)	1.277(4)
Ti(1)–O(2)–C(1)	136.6(2)	O(2)–C(1)–O(1)	122.6(3)
C(1)–O(1)–Ti(2)	133.2(2)	Ti(1)–O(4)–C(6)	134.5(2)
O(4)–C(6)–O(3)	122.4(3)	C(6)–O(3)–Ti(2)	137.3(2)
Ti(1)–O(5)–C(11)	130.8(2)	O(5)–C(11)–O(6 ₂)	121.9(3)
C(11)–O(6 ₂)–Ti(2 ₂)	138.1(2)		

The salient IR feature found for **2** (solid state) regards the absorption due to the carbamate moieties, falling in the range $1600\text{--}1400\text{ cm}^{-1}$, in accordance with the bidentate coordination mode.^{3c}

The ^1H NMR spectrum of **2** shows the resonances typical of transition metal-bonded diethylcarbamates.^{3c} Particularly informative is the ^{13}C NMR spectrum, showing the resonance assigned to the carbonyl carbon at 160.8 ppm (Figure S2, Supporting Information), to be compared with the value 169.2 ppm observed in the spectrum of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ (Figure S3).

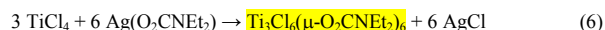
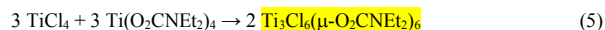
The anion $[\text{TiCl}_6]^{2-}$, which was prepared by Cl^- addition to TiCl_4 as reported in Scheme 2, was structurally characterized as the $[\text{TMGH}]^+$ salt **3** (See Figure S1 and Table S1). Moreover, $[\text{TiCl}_6]^{2-}$ reacted with $\text{CO}_2/\text{NHEt}_2$ affording $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ in good yields, Scheme 2. This result suggests that $[\text{TiCl}_6]^{2-}$ may act as an intermediate during the synthesis of the homoleptic titanium(IV) carbamate from TiCl_4 .



Scheme 2. Synthesis of $[\text{Cat}]_2[\text{TiCl}_6]$ and formation of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ from $[\text{Cat}]_2[\text{TiCl}_6]$ and $\text{CO}_2/\text{NHEt}_2$.

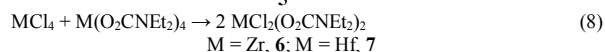
In order to improve the conversion of TiCl_4 into **2** (a maximum titanium conversion of 50% is expected according to Eq. 4), and in

view of the easy availability of both $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ ¹² and $\text{Ag}(\text{O}_2\text{CNEt}_2)$,¹⁵ the procedures reported in Equations 5 and 6 were adopted.



The first of the two preparations (Eq. 5) is more desirable in the light of the atom economy principle (i.e., all of the reagents are transformed into products), and of the easier manipulation of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ with respect to the silver carbamate.¹⁵

The metathetical reaction between tetrahalides and tetrakis(*N,N*-diethylcarbamates) was used for the preparation of $\text{TiF}_2(\text{O}_2\text{CNEt}_2)_2$, **5**, and $\text{MCl}_2(\text{O}_2\text{CNEt}_2)_2$ ($\text{M} = \text{Zr}$, **6**; Hf , **7**), Eq. 7-8.



At variance to TiF_4 , the analogous reaction with zirconium tetrafluoride afforded an inseparable mixture of non identified products. The reactions leading to **5-7** are slower than that involving liquid TiCl_4 , due to the low solubilities of TiF_4 and MCl_4 ($\text{M} = \text{Zr}$, Hf) in the reaction medium. The progress of these reactions is accompanied by a decrease of the amount of solid, and clean solutions are visible after ca. 18 h at room temperature. Likewise the titanium analogue, **5-7** are readily soluble in aromatic and chlorinated solvents, and are quickly decomposed by moisture with release of CO_2 and NHEt_2 .

The IR spectra of **5-7** are very similar to that of **2**, with a strong absorption in the region $1600\text{-}1400 \text{ cm}^{-1}$, suggesting a bidentate coordination of the carbamate groups.^{3c}

The ^1H and ^{13}C NMR spectra of **5** and **7** (as well as **2**, Figure S2) show only one set of resonances. Conversely, two sets of resonances are observed for **6**, see Figure S4. Noteworthy, all the spectra did not change on rising the temperature from $-60 \text{ }^\circ\text{C}$ (solvent: CD_2Cl_2) to $+80 \text{ }^\circ\text{C}$ (solvent: $\text{C}_2\text{H}_4\text{Cl}_2$ or toluene- d^8).

The relative Gibbs energies of compounds having general formula $\text{MX}_2(\text{O}_2\text{CNEt}_2)_2$ or $\text{M}_n\text{X}_{2n}(\mu\text{-O}_2\text{CNEt}_2)_{2n}$ ($n = 2, 3$; $\text{M} = \text{Ti}$, $\text{X} = \text{F}$, Cl ; $\text{M} = \text{Zr}$, Hf , $\text{X} = \text{Cl}$) were evaluated by means of DFT calculations (EDF2 functional). The Cartesian coordinates of the stationary points are collected in a separated .xyz file. The *cis* arrangement of the ligands in $\text{MX}_2(\text{O}_2\text{CNEt}_2)_2$ resulted always more stable than the *trans* one by $2\text{--}4 \text{ kcal mol}^{-1}$.

In all the cases, the trinuclear structures resulted more stable than the corresponding mono- and bimetallic frames; the relative stability of $\text{M}_3\text{X}_6(\mu\text{-O}_2\text{CNEt}_2)_6$ increases on increasing the atomic number of the metal centre (see Figure 2). It is however to be highlighted that, in the case of zirconium, the energy difference between the dinuclear and the trinuclear geometries is quite low (about $2.8 \text{ kcal mol}^{-1}$). Such energy gap is meaningfully higher on considering hafnium as a metal centre, $5.4 \text{ kcal mol}^{-1}$. The appearance of two sets of ^{13}C NMR resonances for **6** can be therefore tentatively explained on supposing the presence of both $\text{Zr}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$ and $\text{Zr}_2\text{Cl}_4(\mu\text{-O}_2\text{CNEt}_2)_4$.

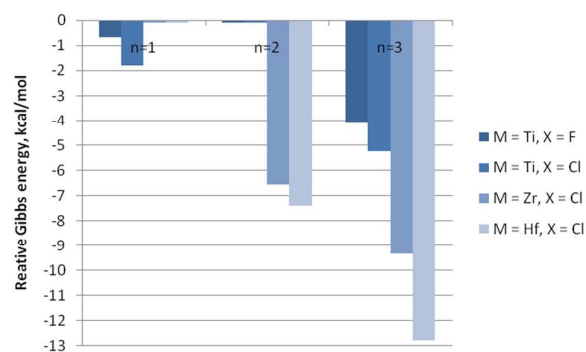


Figure 2. Relative Gibbs energies (EDF2 functional) of $\text{MX}_2(\text{O}_2\text{CNEt}_2)_2$ and $\text{M}_n\text{X}_{2n}(\mu\text{-O}_2\text{CNEt}_2)_{2n}$ ($n = 2, 3$) derivatives. Data are referred to the $\text{MX}_2(\text{O}_2\text{CNEt}_2)_2$ unit.

Further geometry optimizations of $\text{M}_3\text{X}_3(\mu\text{-O}_2\text{CNEt}_2)_6$ compounds and $\text{Zr}_2\text{Cl}_4(\mu\text{-O}_2\text{CNEt}_2)_4$ were carried out using the ωB97X DFT functional. The stationary points are depicted in Figures 3 and 4, while selected computed bond lengths are reported in Table 2. ωB97X calculations confirmed the comparable stability of the di- and tri-nuclear zirconium structures, providing relative energy values closely similar to those obtained with the EDF2 functional.

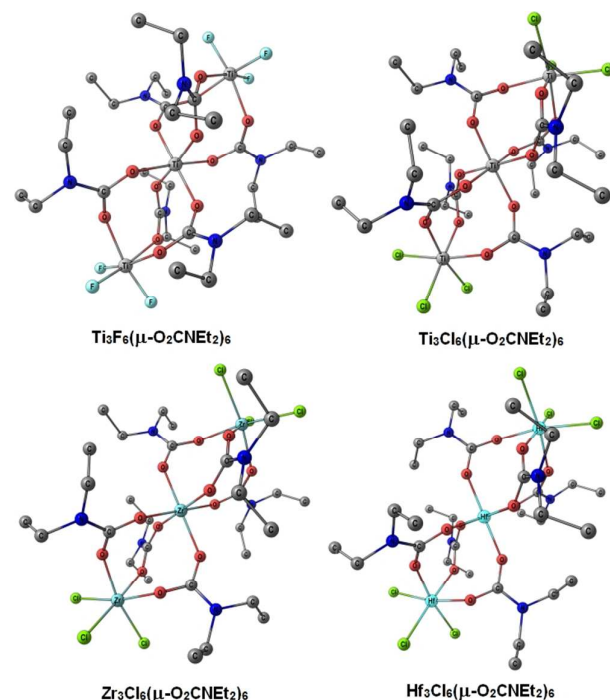


Figure 3. DFT-optimized geometries (ωB97X DFT functional) of $\text{Ti}_3\text{F}_3(\mu\text{-O}_2\text{CNEt}_2)_6$, $\text{Ti}_3\text{Cl}_3(\mu\text{-O}_2\text{CNEt}_2)_6$, $\text{Zr}_3\text{Cl}_3(\mu\text{-O}_2\text{CNEt}_2)_6$ and $\text{Hf}_3\text{Cl}_3(\mu\text{-O}_2\text{CNEt}_2)_6$. Hydrogen atoms have been omitted for clarity.

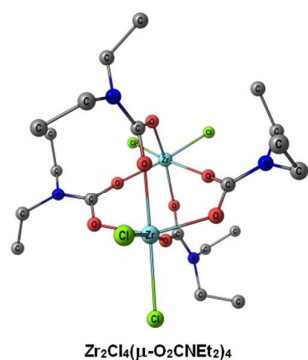


Figure 4. DFT-optimized geometry (ω B97X DFT functional) of $\text{Zr}_2\text{Cl}_2(\mu\text{-O}_2\text{CNET}_2)_4$. Hydrogen atoms have been omitted for clarity.

Table 2. Selected computed average bond lengths (Å) for $\text{Ti}_3\text{F}_6(\text{L})_6$, $\text{Ti}_3\text{Cl}_6(\text{L})_6$, $\text{Zr}_3\text{Cl}_6(\text{L})_6$, $\text{Zr}_2\text{Cl}_4(\text{L})_4$ and $\text{Hf}_3\text{Cl}_6(\text{L})_6$. L = $\mu\text{-O}_2\text{CNET}_2$.

	$\text{Ti}_3\text{F}_6(\text{L})_6$	$\text{Ti}_3\text{Cl}_6(\text{L})_6$	$\text{Zr}_3\text{Cl}_6(\text{L})_6$	$\text{Hf}_3\text{Cl}_6(\text{L})_6$
M-X	1.772	2.257	2.420	2.406
M(terminal)-O	2.068	2.012	2.139	2.085
M(central)-O	1.939	1.939	2.087	2.054
$\text{Zr}_2\text{Cl}_4(\text{L})_4$				
M-X			2.422	
M(terminal)-O			2.129	

During attempts to collect single crystals of **7** from thf/hexane mixtures, we isolated few large crystals of complex $\text{Hf}_4\text{Cl}_4(\text{O})_2(\text{O}_2\text{CNET}_2)_6[\text{O}(\text{CH}_2)_3\text{CHO}]_2$, **8** which was then identified by X-ray diffractometry as its thf monosolvate (Figure 5 and Table 3). The molecule is located on an inversion centre and, thus, only half of it is present within the asymmetric unit of the unit cell. The tetranuclear complex contains two independent Hf(IV) centres, both displaying a distorted pentagonal bipyramidal coordination being bonded to six oxygens and one chlorine atom. The complex contains two $\mu_3\text{-O}$ oxo-ligands, four terminal chlorides (one per Hf atom), two carbamates acting as chelating ligands on Hf(2), four edge bridging carbamates, and two $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ ligands. Each $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ ligand is coordinated to Hf(1) with both endo-cyclic O(9) and exo-cyclic O(8) oxygen atoms, and O(8) is also bonded to Hf(2). This observed coordination mode of $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ is unprecedented for transition metals.^{16,17} There is only a related example, in which the $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ ligand is coordinated in the same way to one Cu and one Na. Conversely, $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ has been found to act either as a terminal ligand *via* the exo-cyclic oxygen,¹⁸ or a bridging ligand between three metal atoms, one *via* the endo-cyclic oxygen and two *via* the exo-cyclic oxygen. The $\text{Hf}_2(\mu_3\text{-O})_2$ core-diamond of **8** is almost planar, with O(1) showing an almost perfect sp^2 hybridization [sum angles $357.5(6)^\circ$], as already detected in related complexes.¹⁹

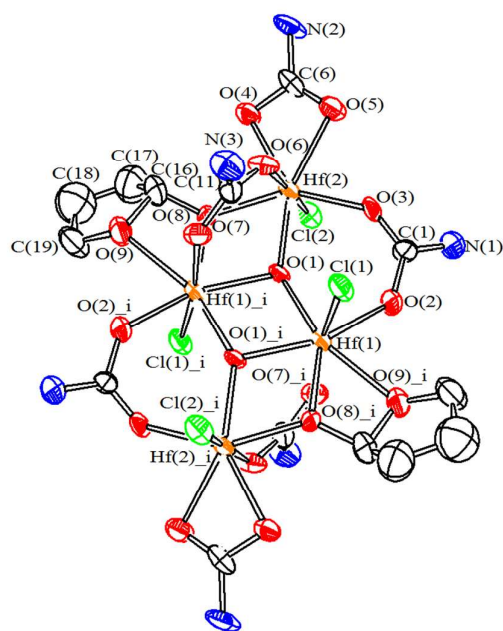


Figure 5. ORTEP drawing of $\text{Hf}_4\text{Cl}_4(\text{O})_2(\text{O}_2\text{CNET}_2)_6[\text{O}(\text{CH}_2)_3\text{CHO}]_2$, **8**. Displacement ellipsoids are at the 50 % probability level. Labelling scheme (H atoms and Et groups have been omitted). Symmetry transformation used to generate equivalent atoms: $-x+1, -y+1, -z+1$.

Table 3. Selected bond lengths (Å) and angles (deg) in **8**

Hf(1)–O(1)	2.044(8)	Hf(1)–O(2)	2.114(8)
Hf(1)–O(9) _i	2.334(9)	Hf(1)–O(8) _i	2.160(8)
Hf(1)–O(1) _i	2.084(8)	Hf(1)–O(7) _i	2.099(9)
Hf(1)–Cl(1)	2.430(3)	Hf(2)–Cl(2)	2.446(3)
Hf(2)–O(1)	2.067(7)	Hf(2)–O(3)	2.077(8)
Hf(2)–O(5)	2.194(9)	Hf(2)–O(4)	2.202(8)
Hf(2)–O(8)	2.129(8)	Hf(2)–O(6)	2.110(9)
C(1)–N(1)	1.310(16)	C(1)–O(2)	1.290(15)
C(1)–O(3)	1.263(15)	C(6)–N(2)	1.358(18)
C(6)–O(4)	1.324(15)	C(6)–O(5)	1.238(17)
C(11)–N(3)	1.320(18)	C(11)–O(6)	1.298(15)
C(11)–O(7)	1.280(16)	C(16)–C(17)	1.489(18)
C(17)–C(18)	1.527(19)	C(18)–C(19)	1.518(18)
C(19)–O(9)	1.452(13)	C(16)–O(9)	1.445(13)
C(16)–O(8)	1.377(16)		
O(1)–Hf(1)–O(1) _i	74.8(3)	Hf(1)–O(1)–Hf(1) _i	105.2(3)
Sum at O(1)	357.5(6)	Sum at C(1)	360(2)
Sum at C(6)	360(2)	Sum at C(11)	360(2)
Hf(2)–O(8)–Hf(1) _i	105.0(3)	Hf(2)–O(1)–Hf(1) _i	110.1(4)
O(8)–C(16)–O(9)	103.7(10)	C(16)–O(9)–Hf(1) _i	93.5(7)

It should be mentioned here that activation reactions of tetrahydrofuran by means of high valent metal halides are well known, however these usually proceed with the cleavage of either one²⁰ or two C–O bonds per thf unit.²¹ The former situation may ultimately lead to thf polymerization,^{20b,21a} while in the latter case metal-oxide species and 1,4-dihalobutanes are generally formed. In **8**, the $[\text{O}(\text{CH}_2)_3\text{CHO}]^-$ moieties are presumably generated via a metal-mediated C–H bond activation of thf in the presence of some oxygen,¹⁶ that is a unusual feature in the landscape of the chemistry of transition metal compounds. Instead, the presence of $\mu\text{-oxo}$ groups in **8** seems to be more properly ascribable to the presence of traces of 2-hydroxytetrahydrofuran or water (*N,N*-dialkylcarbamates of early transition metals are generally very sensitive to hydrolysis),^{3c} rather than to Cl/O exchange between

Hf and thf. Indeed NMR analyses on $\text{HfCl}_2(\text{O}_2\text{CNEt}_2)_2/\text{thf}$ mixtures did not reveal the formation of 1,4-dichlorobutane.

Conclusions

Mixed metal chloride carbamates are significantly more rare in the literature than the corresponding homoleptic carbamate compounds, basically due to the absence of convenient synthetic routes. In this paper, we have reported the synthesis and the structural characterization of dichloride-dicarbamates of group 4 elements, as best prepared by metathesis reaction of MCl_4 with $\text{M}(\text{O}_2\text{CNEt}_2)_4$. The products possess variable nuclearity depending on the metal. Thus, experimental and computational outcomes suggest the trinuclear structure $\text{M}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$ for $\text{M} = \text{Ti}, \text{Hf}$. Otherwise, DFT calculations showed that the zirconium species may exist as a mixture of dinuclear, $\text{Zr}_2\text{Cl}_4(\mu\text{-O}_2\text{CNEt}_2)_2$, and trinuclear, $\text{Zr}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$, forms. The homoleptic metal fluorides have revealed to be poorly prone to $\text{F}^-/(\text{O}_2\text{CNEt}_2)^-$ exchange. More in detail, $\text{TiF}_2(\text{O}_2\text{CNEt}_2)_2$ has been obtained only under forceful conditions, while the analogous reaction involving ZrF_4 give mixtures of unidentified products. The interaction of $\text{HfCl}_2(\text{O}_2\text{CNEt}_2)_2$ with thf has provided a possible case of uncommon thf activation, promoted by a transition metal chloride via C–H bond cleavage.

Experimental

General

Unless otherwise stated, all of the operations were carried out under an atmosphere of pre-purified nitrogen. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with nitrogen. TiCl_4 (Strem, 99%), ZrCl_4 (Strem, 99.6%), HfCl_4 (Strem, 98%), TiF_4 (Strem, 98%) were stored in sealed glass tubes under an argon atmosphere as received. 1,1,3,3-tetramethylguanidine (Aldrich) was used as received and stored in a Schlenk tube under a nitrogen atmosphere. $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$,¹² $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$,¹² $\text{Hf}(\text{O}_2\text{CNEt}_2)_4$,¹² $\text{Ag}(\text{O}_2\text{CNEt}_2)$ ¹⁵ were prepared according to literature procedures. Once isolated, the products were conserved in sealed glass tubes under nitrogen. Solvents and NH_2Et_2 (Sigma Aldrich) were distilled from appropriate drying agents before use. Infrared spectra were recorded at 298 K on a Perkin Elmer Spectrum One FTIR Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded on a Bruker Avance II DRX400 instrument equipped with BBFO broadband probe at 298 K. The ^1H and ^{13}C NMR spectra were assigned with assistance of DEPT experiments and ^1H , ^{13}C correlation measured through g_s -HSQC and g_s -HMBC experiments.²² Carbon, hydrogen, nitrogen and titanium analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Volhard method²³ on solutions prepared by dissolution of the solid in aqueous Na_2CO_3 at boiling temperature, followed by cooling down to room temperature and addition of H_2SO_4 up to acid pH. The metal content (Ti, Zr and Hf) of the compounds was determined by a ICP-OES Thermo Optek IRIS Advantage Duo instrument.

Reaction of $[\text{NH}_2\text{Et}_2][\text{O}_2\text{CNEt}_2]$ and TiCl_4 . NH_2Et_2 (2.19 mL, 21.2 mmol) in toluene (30 mL) was saturated with CO_2 . The resulting solution was dropped under CO_2 atmosphere into a round bottom flask containing a solution of TiCl_4 (0.58 mL, 5.3 mmol) in toluene (20 mL). The mixture was stirred for 20 hours at 298 K. A yellow solid (1.03 g) was recovered by filtration and dried in vacuo at room temperature, and identified as a ca. 4:1 mixture of $\text{NH}_2\text{Et}_2\text{Cl}$ and $[\text{NH}_2\text{Et}_2]_2[\text{TiCl}_6]$. Anal. Calc. for $\text{C}_{24}\text{H}_{72}\text{Cl}_{10}\text{N}_6\text{Ti}$: C, 34.02; H, 8.56; N, 9.91; Cl, 41.84; Ti, 5.65%. Found: C, 33.81; H, 7.96; N, 9.75; Cl, 41.25; Ti, 5.81%. IR (solid state): $\nu = 3125\text{w}, 2972\text{m}, 2913\text{vw}, 2866\text{vw}, 2821\text{s}, 2774\text{vs}, 2750\text{s}, 2550\text{vw}, 2481\text{m}, 2388\text{m-w}, 2339\text{w}, 1869\text{vw-br}, 1594\text{vw}, 1570\text{vw}, 1483\text{w-m},$

$1465\text{m}, 1454\text{m}, 1427\text{vw}, 1391\text{m}, 1376\text{m-w}, 1336\text{w}, 1208\text{vw}, 1159\text{m-w}, 1061\text{m-w}, 1049\text{m}, 918\text{vw}, 872\text{vw}, 806\text{m}, 764\text{w cm}^{-1}$. An orange solid (1.41 g) was recovered from the filtrate by the evaporation of the solvent in vacuo. The solid was identified as a 4:1 molar mixture of $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$ and $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$. Anal. Calc. for $\text{C}_{60}\text{H}_{120}\text{Cl}_8\text{N}_{12}\text{O}_{24}\text{Ti}_5$: C, 37.60; H, 6.31; N, 8.77; Cl, 14.79; Ti, 12.49%. Found: C, 37.25; H, 6.59; N, 9.02; Cl, 14.23; Ti, 12.75%. IR (solid state): $\nu = 2968\text{ w}, 2936\text{vw}, 2875\text{vw}, 1527\text{s}, 1416\text{vs}, 1387\text{m-s}, 1299\text{vs}, 1261\text{m}, 1208\text{m-s}, 1097\text{w-m}, 1073\text{m-s}, 977\text{m-s}, 941\text{w}, 838\text{vw}, 773\text{s}, 733\text{w cm}^{-1}$. ^1H NMR (C_6D_6): $\delta = 4.15, 3.00$ (m, 2 H, CH_2); 1.50, 0.84 (m, 3 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 169.9$ (C=O); 160.9 (C=O); 43.8 (CH_2); 39.6 (CH_2); 14.8 (CH_3), 12.7 (CH_3) ppm.

Syntheses

$[\text{TMGH}][\text{O}_2\text{CNEt}_2]$, **1.** 0.78 mL (7.54 mmol) of NH_2Et_2 were added to 0.95 mL (7.54 mmol) of TMG. A colourless solid formed upon introduction of carbon dioxide at atmospheric pressure. When the absorption ceased (ca. 20 minutes), the colourless mixture was dried in vacuo at room temperature. The colourless solid, sensitive to moisture, was identified as $[\text{TMGH}][\text{O}_2\text{CNEt}_2]$, **1** (1.260 g, 72% yield). The solid resulted stable at room temperature for limited periods of time, but it was preferentially stored at 277 K. Anal. Calc. for $\text{C}_{10}\text{H}_{24}\text{N}_4\text{O}_2$: C, 51.70; H, 10.41; N, 24.11%. Found: C, 51.49; H, 10.31; N, 24.01%. Melting point: 337-338 K; Decomposition temperature: 342-345 K. IR (solid state): $\nu = 2958\text{w-sh}, 2927\text{w}, 2868\text{w}, 2817\text{w}, 1594\text{vs}, 1540\text{vs}, 1464\text{m-s}, 1455\text{m-s}, 1434\text{m}, 1395\text{s}, 1291\text{s}, 1207\text{w}, 1106\text{w-m}, 1071\text{m-s}, 1049\text{m-s}, 1032\text{s}, 887\text{w}, 804\text{w-m}, 772\text{w}, 727\text{w cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 8.16$ (br, NH_2); 3.11 (br, CH_2); 2.69 (s, N- CH_3); 0.91 (br, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR + DEPT-135 (CDCl_3): $\delta = 165.2$ (C=O); 162.1 (C=N); 40.4 (–, CH_2); 39.3 (+, N- CH_3); 14.2 (+, CH_3) ppm.

$\text{Ti}_3\text{Cl}_6(\mu\text{-O}_2\text{CNEt}_2)_6$, **2.** TiCl_4 (0.17 mL, 1.55 mmol) was added to a solution of $[\text{TMGH}][\text{O}_2\text{CNEt}_2]$ (0.360 g, 1.55 mmol) in toluene (20 mL). The mixture was stirred for 20 h at the reflux temperature and then filtered. The yellow solid was washed with 20 mL of toluene (2×10 mL) and dried in vacuo affording 0.324 g (85% calculated on the amount of expected product) of $[\text{TMGH}]_2[\text{TiCl}_6]$, **3**, as an orange yellow, moisture sensitive microcrystalline solid. Anal. Calc. for $\text{C}_{10}\text{H}_{28}\text{N}_6\text{Cl}_6\text{Ti}$: Cl, 43.15; Ti, 9.71%. Found: Cl, 42.58; Ti, 10.01%. IR (solid state): $\nu = 3397\text{w-m}, 3323\text{w-m}, 3251\text{w}, 2964\text{w}, 1639\text{vs}, 1595\text{vs}, 1564\text{m-s}, 1454\text{w-m}, 1435\text{w}, 1408\text{s}, 1323\text{w}, 1254\text{w}, 1143\text{vw}, 1070\text{w-m}, 1054\text{m}, 1038\text{m}, 871\text{w-m cm}^{-1}$. ^1H NMR (CD_3CN): $\delta = 6.44$ (br, 2 H, NH_2); 2.90 (s, 12 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = 162.6$ (C=N); 40.7 (CH_3) ppm.

The filtrate was evaporated to dryness and the residue was treated with pentane. The solid was recovered by filtration and dried in vacuo at room temperature affording **2** (0.198 g, 73% yield calculated on the amount of expected product) as a moisture-sensitive yellow-green microcrystalline solid. Anal. Calc. for $\text{C}_{30}\text{H}_{60}\text{Cl}_6\text{N}_6\text{O}_{12}\text{Ti}_3$: C, 34.21; H, 5.74; N, 7.98; Cl, 20.20; Ti, 13.63%. Found: C, 33.85; H, 5.90; N, 7.71; Cl, 20.51; Ti, 13.92%. IR (solid state): $\nu = 2977\text{w}, 2938\text{w}, 2876\text{vw}, 1538\text{s}$ (C=O), 1473m, 1434s, 1379m-s, 1299vs, 1205m-s, 1098w-m, 1074m, 978m, 942w-m, 817vw, 772m, 656m cm^{-1} . ^1H NMR (CD_2Cl_2): $\delta = 3.88, 2.96$ (m, 2 H, CH_2); 1.43, 0.93 (m, 3 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 160.5$ (C=O); 44.2 (CH_2); 13.6 (CH_3) ppm.

$[\text{Cat}]_2[\text{TiCl}_6]$, Cat = TMGH, **3, NH_2Et_2 , **4**.** Only the preparation of $[\text{NH}_2\text{Et}_2]_2[\text{TiCl}_6]$, **4**, is described in detail, **3** being prepared in a similar way.

A solution of $\text{NH}_2\text{Et}_2\text{Cl}$ (1.03 g, 9.4 mmol) in CH_2Cl_2 (35 mL) was treated with TiCl_4 (0.52 mL, 4.7 mmol), and an abundant yellow precipitate suddenly formed. The mixture was stirred for 3

hours at 298 K. The solvent was removed in vacuo at room temperature affording **3** (1.81 g, 94% yield) as a moisture-sensitive yellow solid. Anal. Calc. for $C_8H_{24}Cl_6N_2Ti$: Cl, 52.02; Ti, 11.71%. Found: Cl, 51.79; Ti, 11.59%. IR (solid state): $\nu = 3125s, 3081m, 3005w-m, 2992w, 2970w, 1466s, 1428m-s, 1385m, 1375w, 1162m, 1065m, 1035s, 763vs\text{ cm}^{-1}$.

[TMGH]₂[TiCl₆], **4**: yellow solid, 85% yield. Calc. for $C_{10}H_{28}Cl_6N_6Ti$: Cl, 43.15; Ti, 9.71%. Found: Cl, 42.63; Ti, 10.14%. IR (solid state): $\nu = 3396w-m, 3322m, 3250w, 3197vw, 1638s, 1595vs, 1564s, 1453m-sh, 1435w, 1408s, 1254vw, 1238vw, 1143w-m, 1053m-s, 1038m-s, 871w-m\text{ cm}^{-1}$. ¹H NMR (CD₃CN): $\delta = 6.48$ (br, 2 H, NH₂); 2.94 (s, 12 H, CH₃). ¹³C{¹H} NMR (CD₃CN): $\delta = 162.2$ (C=N); 40.2 (CH₃) ppm.

Ti(O₂CNEt₂)₄ from [NH₂Et]₂[TiCl₆] and CO₂/NHET₂ 1.120 g of [NH₂Et]₂[TiCl₆] (2.7 mmol) were added to a solution of NHET₂ (2.8 mL, 27.1 mmol) in toluene 45 mL. The mixture was saturated with CO₂. When carbon dioxide was introduced into the system, an exothermic reaction took place with formation of a colourless solid. After stirring for 20 hours at room temperature, the reaction mixture was filtered and the solvent was removed in vacuo at 323K from the filtrate. The pale yellow residue was treated with pentane (15 mL). The solid was recovered by filtration and dried in vacuo at room temperature affording Ti(O₂CNEt₂)₄ (1.04 g, 75%) as a pale yellow microcrystalline solid. IR (solid state): $\nu = 2990m, 2980m, 2940mw, 1560vs, 1505s, 1460m, 1320vs, 1210m, 1100w, 1080m, 975w, 940w, 835s, 790s, 635s\text{ and }450s\text{ cm}^{-1}$. ¹H NMR (CDCl₃): $\delta = 3.32$ (q, 2 H, CH₂); 1.05 (t, 3 H, CH₃). ¹³C{¹H} NMR (CDCl₃): $\delta = 169.2$ (C=O); 38.6 (CH₂); 13.5 (CH₃) ppm.

Ti₃Cl₆(μ-O₂CNEt₂)₆, 2. a) From TiCl₄ and Ti(O₂CNEt₂)₄ A solution of Ti(O₂CNEt₂)₄ (0.785 g, 1.53 mmol) in CH₂Cl₂ (30 mL) was treated with TiCl₄ (0.17 mL, 1.55 mmol). The resulting solution was stirred for 4 hours at 298 K and for additional 2 hours at the reflux temperature. After cooling to room temperature, the solvent was removed in vacuo and the residue was treated with pentane. The solid was recovered by filtration and dried in vacuo at room temperature affording **2** (0.913 g, 85% yield) as a moisture-sensitive yellow-green microcrystalline solid. Anal. Calc. for $C_{30}H_{60}Cl_6N_6O_{12}Ti_3$: C, 34.21; H, 5.74; N, 7.98; Cl, 20.20; Ti, 13.63%. Found: C, 33.90; H, 5.90; N, 7.71; Cl, 20.63; Ti, 13.89%. IR (solid state): $\nu = 2977w, 2938w, 2876vw, 1538s$ (C=O), 1473m, 1434s, 1379m-s, 1299vs, 1205m-s, 1098w-m, 1074m, 978m, 942w-m, 817vw, 772m, 656m cm^{-1} . ¹H NMR (CD₂Cl₂): $\delta = 3.86, 2.98$ (m, 2 H, CH₂); 1.42, 0.95 (m, 3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 160.8$ (C=O); 44.0 (CH₂); 13.7 (CH₃) ppm.

b) From TiCl₄ with AgO₂CNEt₂ The reaction vessel was protected from light by covering it with an aluminium foil. A 0.221 M solution of TiCl₄ in heptane (2.3 mL, 0.51 mmol of TiCl₄) was dropped into a suspension of AgO₂CNEt₂ (0.231 g, 1.03 mmol) in toluene (15 mL). Immediate formation of a colourless solid was observed. The mixture was stirred for 18 h at room temperature, filtered and then the solvent was removed in vacuo from the filtrate. The residue was treated with pentane. The solid was recovered by filtration and dried in vacuo at room temperature affording **2** (0.143 g, 80% yield) as a moisture-sensitive yellow-green microcrystalline solid. ¹H NMR (CD₂Cl₂): $\delta = 3.87, 3.02$ (m, 2 H, CH₂); 1.39, 1.00 (m, 3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 160.7$ (C=O); 43.9 (CH₂); 13.6 (CH₃) ppm.

TiF₂(O₂CNEt₂)₂, 5. Solid TiF₄ (0.192 g, 1.55 mmol), Ti(O₂CNEt₂)₄ (0.794 g, 1.55 mmol) and CH₂Cl₂ (20 mL) were mixed in a Schlenk tube and the suspension was stirred for 24 hours at 298 K and for additional 6 hours at the reflux temperature. After cooling to room temperature, the solvent was

removed in vacuo and the residue was treated with pentane (15 mL). The solid was recovered by filtration and dried in vacuo affording **5** (0.650 g, 66% yield). Anal. Calc. for $C_{10}H_{20}F_2N_2O_4Ti$: C, 37.75; H, 6.33; N, 8.80; Ti, 15.04%. Found: C, 36.99; H, 5.95; N, 7.99; Ti, 15.89%. IR (solid state): $\nu = 2973m-w, 2935w, 2874vw, 1505s-br$ (C=O), 1432vs, 1378m, 1307s, 1213m, 1098w-m, 1073m, 978m, 939w, 839vw, 784m-s cm^{-1} . ¹H NMR (CD₂Cl₂): $\delta = 3.34$ (q, 2 H, CH₂); 1.14 (t, 3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 169.5$ (C=O); 40.1 (CH₂); 14.0 (CH₃); ppm.

MCl₂(O₂CNEt₂)₂ (M = Zr, 6; Hf, 7). Only the preparation of ZrCl₂(O₂CNEt₂)₂, **6**, is described in detail, **7** being prepared in a similar way. A solution of Zr(O₂CNEt₂)₄ (1.23 g, 2.21 mmol) in CH₂Cl₂ (50 mL) was treated with solid ZrCl₄ (0.516 g, 2.21 mmol). The solution was stirred for 18 hours at 298 K and for additional 3 hours at the reflux temperature. After cooling to room temperature, the solvent was removed in vacuo and the residue was treated with pentane. The suspension was filtered and the solid was dried in vacuo at room temperature affording ZrCl₂(O₂CNEt₂)₂, **6** (1.33 g, 76% yield), as a moisture-sensitive colourless microcrystalline solid. Anal. Calc. for $C_{10}H_{20}Cl_2N_2O_4Zr$: C, 30.4; H, 5.1; N, 7.1; Cl, 17.9; Zr, 23.1%. Found: C, 30.0; H, 5.4; N, 6.9; Cl, 17.5; Zr, 22.9%. IR (solid state): $\nu = 2976w-m, 2938w, 2898w, 1538s$ (C=O), 1435vs, 1381m, 1350w, 1315s, 1215m-s, 1098w-m, 1075m, 979m, 943w-m, 842vw, 775m-s, 661m-s cm^{-1} . ¹H NMR (CD₂Cl₂): $\delta = 3.60, 3.25$ (m, 2 H, CH₂); 1.39, 1.08 (m, 3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 159.6$ (C=O); 158.0 (C=O); 44.0 (CH₂); 43.3 (CH₂); 14.1 (CH₃); 13.5 (CH₃) ppm.

HfCl₂(O₂CNEt₂)₂, **7**: colourless solid, 69% yield. Calc. for $C_{10}H_{20}Cl_2N_2O_4Hf$: C, 24.9; H, 4.2; N, 5.8; Cl, 14.7; Hf, 37.0%. Found: C, 24.0; H, 4.3; N, 5.7; Cl, 14.5; Hf, 36.5%. IR (solid state): $\nu = 2966w, 2936vw, 2876vw, 1538vs$ (C=O), 1435vs, 1381w-m, 1317s, 1259m, 1218m, 1075m-s, 1015m, 981m, 941w-m, 778vs, 659m cm^{-1} . ¹H NMR (CD₂Cl₂): $\delta = 3.80, 2.95$ (m, 2 H, CH₂); 1.37, 0.83 (m, 3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 158.7$ (C=O); 43.0 (CH₂); 13.9 (CH₃) ppm.

Few crystals of **8**·thf were obtained from a thf solution of **7**, layered with hexane and stored at room temperature for two weeks. All the attempts to prepare **8** in larger amounts were not successful.

X-ray crystallographic studies

Crystal data and collection details for Ti₃Cl₆(O₂CNEt₂)₆·4CH₂Cl₂ (**2**·4CH₂Cl₂), [TMGH]₆[TiCl₆]Cl₄·2MeCN (**3**·2MeCN) and Hf₄Cl₄(O₂CNEt₂)₆[O(CH₂)₃CHO]₂ (**8**) are listed in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).²⁴ The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F².²⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold *U*_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold *U*_{iso} value of the parent C-atom.

The asymmetric unit of the unit cell of Ti₃Cl₆(O₂CNEt₂)₆·4CH₂Cl₂ contains half of Ti-complex (located on an inversion centre) and two CH₂Cl₂ molecules (located on general positions).

The asymmetric unit of the unit cell of [TMGH]₆[TiCl₆]Cl₄·2MeCN contains two halves of two complex anions (located on inversion centre), three [TMGH]⁺ cations, two Cl⁻ anions and one MeCN molecule (all located on general positions). The crystals are non-merohedrally twinned. The TwinRotMat routine of PLATON²⁵ was used to determine the twinning matrix and to write the reflection data file (.hkl) containing the

two twin components. Refinement was performed using the instruction HKLF 5 in SHELXL and one BASF parameter, that refined as 0.503(3).

The asymmetric unit of the unit cell of $\text{Hf}_4\text{Cl}_4(\text{O})_2(\text{O}_2\text{CNEt}_2)_6[\text{O}(\text{CH}_2)_3\text{CHO}]_2$ contains half of a Hf_4 -complex (located on an inversion centre). A total potential solvent accessible void of 152 \AA^3 (47 electrons) per formula unit remains

after refinement, corresponding to one solvent molecule per Hf_4 -complex. Due to disorder issues, it has not been possible to locate nor identify this solvent molecule. Thus, it has been treated using the SQUEEZE routine of PLATON.²⁶

Table 4. Crystal data and experimental details for $\text{Ti}_3\text{Cl}_6(\text{O}_2\text{CNEt}_2)_6 \cdot 4\text{CH}_2\text{Cl}_2$ (**2**·**4CH₂Cl₂**), $[\text{TMGH}]_6[\text{TiCl}_6]\text{Cl}_4 \cdot 2\text{MeCN}$ (**3**·**2MeCN**) and $\text{Hf}_4\text{Cl}_4(\text{O})_2(\text{O}_2\text{CNEt}_2)_6[\text{O}(\text{CH}_2)_3\text{CHO}]_2$ (**8**).

	2 · 4CH₂Cl₂	3 · 2MeCN	8
Formula	$\text{C}_{34}\text{H}_{68}\text{Cl}_{14}\text{N}_6\text{O}_{12}\text{Ti}_3$	$\text{C}_{34}\text{H}_{90}\text{Cl}_{10}\text{N}_{20}\text{Ti}$	$\text{C}_{38}\text{H}_{74}\text{Cl}_4\text{Hf}_4\text{N}_6\text{O}_{18}$
F_w	1392.94	1181.66	1758.79
λ , Å	0.71073	0.71073	0.71073
Temperature, K	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a , Å	10.7343(6)	8.6586(9)	11.5959(12)
b , Å	11.1683(6)	13.0597(14)	18.794(2)
c , Å	14.4997(12)	14.2197(15)	14.5380(16)
α [°]	106.064(5)	82.059(8)	90
β [°]	102.815(5)	76.615(7)	102.888(3)
γ [°]	104.401(4)	78.133(7)	90
Cell volume, Å ³	1537.03(17)	1523.9(3)	3088.5(6)
Z	1	1	2
D_c , g cm ⁻³	1.505	1.288	1.891
μ , mm ⁻¹	1.042	0.622	6.935
$F(000)$	714	626	1688
Crystal size	0.16×0.12×0.10	0.15×0.14×0.10	0.18×0.16×0.14
θ limits [°]	1.54–26.00	1.48–25.03	1.80–25.99
Reflections collected	22419	20858	28411
Independent reflections	6032 [R_{int} = 0.0753]	5269 [R_{int} = 0.0983]	6078 [R_{int} = 0.1059]
Data / restraints / parameters	6032 / 0 / 313	5269 / 0 / 309	6078 / 65 / 322
Goodness on fit on F^2	1.020	1.106	1.024
$R1$ ($> 2\sigma(I)$)	0.0428	0.0869	0.0635
$wR2$ (all data)	0.1075	0.2456	0.1701
Largest diff. peak and hole, e.Å ⁻³	0.461 / -0.776	1.076 / -0.970	3.759 / -1.917

Computational studies.

The computational geometry optimizations were carried out without symmetry constraints, initially using the hybrid-GGA EDF2 functional²⁷ in combination with the 6-31G** basis set (LANL2DZ on Zr and Hf).²⁸ Further geometry optimizations were performed with the range-separated DFT functional ω B97X²⁹ and the LANL2TZ(f) basis set on the metal centers.

The “restricted” formalism was always applied. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections ($T = 298.15 \text{ K}$) were obtained.³¹ Spartan '08³² and Gaussian '09³³ were used as software, running on x86-64 workstations based on Intel Xeon E5 v3 multicore processors.

Supplementary Material. Figure S1 and Tables S1-S2 report the ORTEP drawing of $[\text{TMGH}]_6[\text{TiCl}_6]\text{Cl}_4 \cdot 2\text{MeCN}$, **3**, and a selection of bond distances and angles. Figures S2-S5 show the ¹³C-NMR spectra of **2**, $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$, **6** and **7**.

CCDC reference numbers 1495489 (**2**·**4CH₂Cl₂**), 1495490 (**3**·**2MeCN**) and 1511415 (**8**) 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].

Acknowledgements

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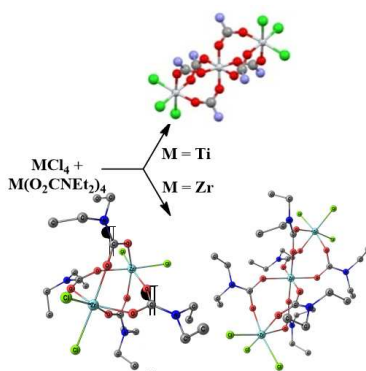
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Synthesis and Structural Characterization of Mixed Halide - *N,N*-Diethylcarbamates of Group 4 Metals, Including a Case of Unusual Tetrahydrofuran Activation

Marco Bortoluzzi, Giulio Bresciani, Fabio Marchetti, Guido Pampaloni, Stefano Zacchini

A straightforward synthesis of dichloride-dicarbamates of group 4 metals consists in the metathesis reaction of the respective tetrahalides with the tetracarbamates. The nuclearity of the new compounds has been elucidated, being dependant on the nature of the metal.



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and Stefano Zacchini*

Supporting Information

Figure S1. ORTEP drawing of 3	Page S2
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Figure S5. ¹³ C NMR spectrum (CD ₂ Cl ₂) of 7	Page S5

Table S1

Ti(1)–Cl(1)	2.3409(17)	Ti(1)–Cl(2)	2.3546(17)
Ti(1)–Cl(3)	2.3348(18)	C(1)–N(1)	1.318(9)
C(1)–N(2)	1.353(10)	C(1)–N(3)	1.333(9)
C(6)–N(4)	1.329(10)	C(6)–N(5)	1.340(9)
C(6)–N(6)	1.352(9)	C(11)–N(7)	1.334(10)
C(11)–N(8)	1.333(9)	C(11)–N(9)	1.345(9)
N(1)–C(1)–N(2)	119.5(7)	N(1)–C(1)–N(3)	120.0(7)
N(2)–C(1)–N(3)	120.5(6)	N(4)–C(6)–N(5)	121.4(7)
N(4)–C(6)–N(6)	119.6(6)	N(5)–C(6)–N(6)	119.0(7)
N(7)–C(11)–N(8)	119.1(7)	N(7)–C(11)–N(9)	120.0(7)
N(8)–C(11)–N(9)	120.9(7)		

Table S2

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1A)···Cl(5)#2	0.88	2.35	3.205(6)	162.7
N(1)–H(1B)···Cl(4)#3	0.88	2.47	3.220(6)	143.7
N(4)–H(4E)···Cl(4)	0.88	2.44	3.267(6)	157.6
N(4)–H(4D)···Cl(5)#4	0.88	2.33	3.186(7)	163.0
N(7)–H(7D)···Cl(4)#5	0.88	2.49	3.290(6)	151.2
N(7)–H(7E)···Cl(5)#6	0.88	2.42	3.238(6)	155.5

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+1$ #2 $-x+1, -y+1, -z+1$ #3 $-x+1, -y+1, -z+2$

#4 $x, y, z+1$ #5 $x, y-1, z-1$ #6 $x+1, y-1, z$

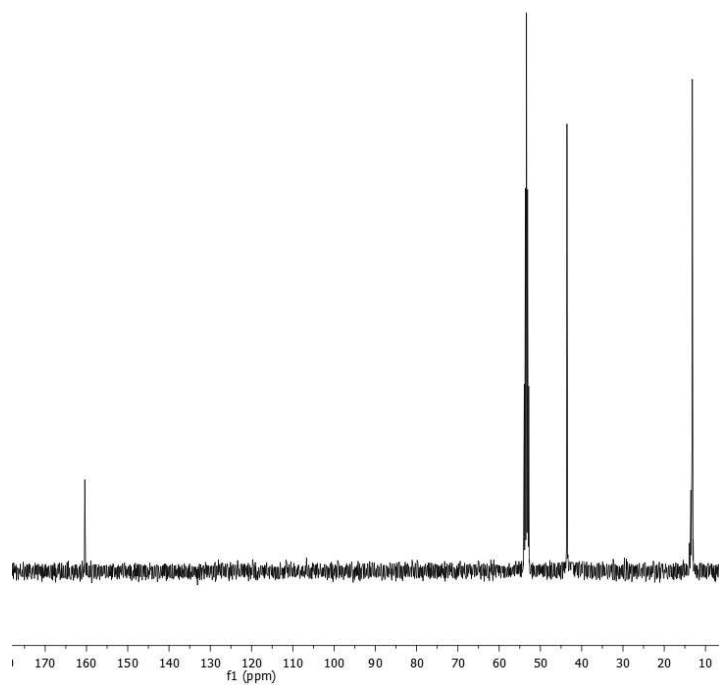
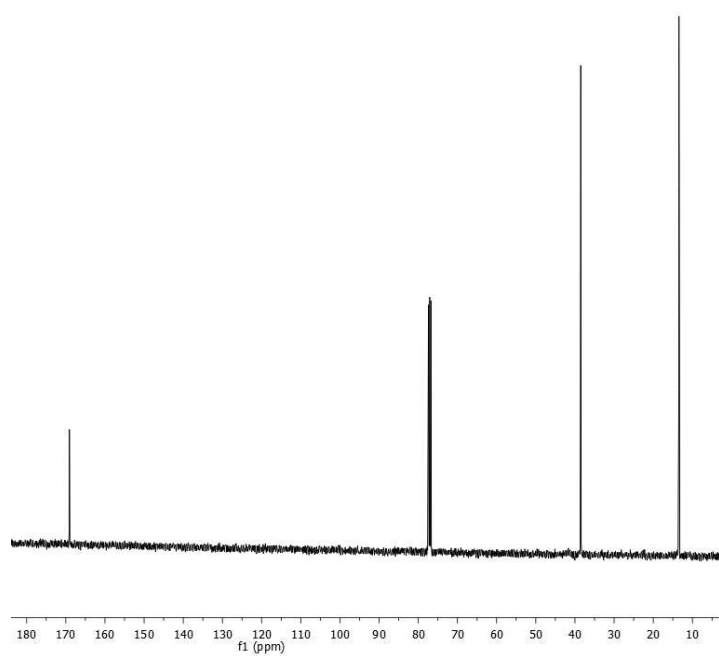
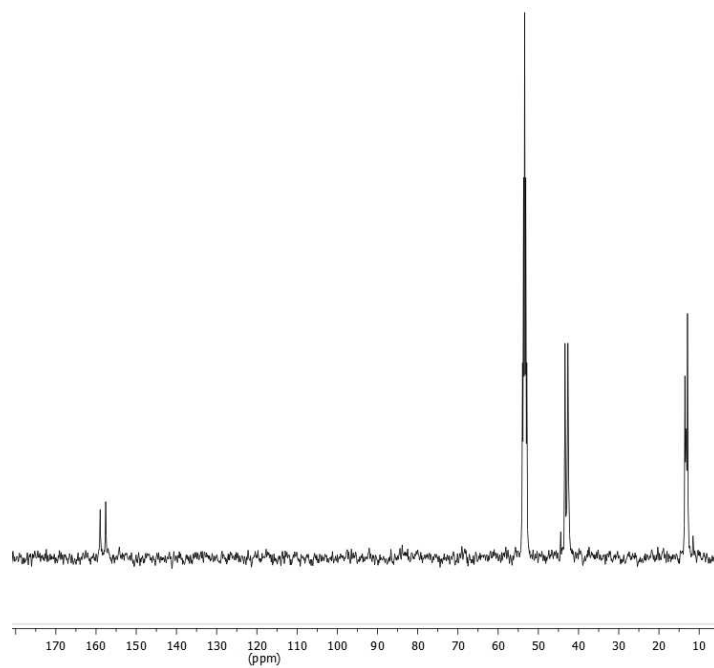
Figure S2. ^{13}C NMR spectrum (CD_2Cl_2) of **2****Figure S3.** ^{13}C NMR spectrum (CDCl_3) of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ 

Figure S4. ^{13}C NMR spectrum (CD_2Cl_2) of **6****Figure S5.** ^{13}C NMR spectrum (CD_2Cl_2) of **7**