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Modifying Bis(Triflimide) Ionic Liquids with Early Transition Metal Carbamates

Journal:	<i>Physical Chemistry Chemical Physics</i>
Manuscript ID	Draft
Article Type:	Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Pampaloni, Guido; Universita di Pisa, Dipartimento di Chimica e Chimica Industriale Biancalana, Lorenzo; Universita' di Pisa, Dipartimento di Chimica e Chimica Industriale Bresciani, Giulio; Universita di Pisa, Dipartimento di Chimica e Chimica Industriale Chiappe, Cinzia; University of Pisa Marchetti, Fabio; Universita' di Pisa, Chimica e Chimica Industriale Pomelli, Christian; Universita degli Studi di Pisa, Pharmacy
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To the Editor
Phys. Chem. Chem. Phys., PCCP

Pisa, 2017 October 27

Dear Editor,

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Modifying Bis(Triflimide) Ionic Liquids with Early Transition Metal Carbamates

by

Lorenzo Biancalana, Giulio Bresciani, Cinzia Chiappe, Fabio Marchetti, Guido Pampaloni,
Christian Silvio Pomelli

that we would like to be considered for publication in *Phys. Chem. Chem. Phys.* as a regular paper.

Ionic liquids (ILs) have aroused a huge interest embracing an impressive range of application fields. The development of novel metal-based ionic liquid systems exploring the possible use of convenient but non typical metal sources, which could supply unusual features to the resulting solutions, is highly desirable.

Homoleptic metal carbamates constitute an intriguing class of inorganic compounds, that are easily accessible from cost effective halide precursors by CO₂ fixation and that have found applications in chemical vapour deposition processes, homogeneous catalysis and material chemistry.

The authors report the unprecedented modification of ionic liquids with homoleptic metal carbamates. Thus, the study of the dissolution of a selection of early transition metal carbamates in two ionic liquids (i.e., [bmim][Tf₂N] and [P(oct)₄][Tf₂N]) was investigated by spectroscopic techniques. Moreover, extensive DFT calculations were carried out in order to elucidate the interaction between the metal species and the solvent. According to the DFT results, the structure of the metal complex presents pockets, whose size and electrostatic features are presumably involved in the interaction with the solvent cation. This modality suggests an explanation to the fact that the dissolved metal compounds, surprisingly, preserve their coordination sphere, i.e. they do not release any of their original ligands.

With my best regards,

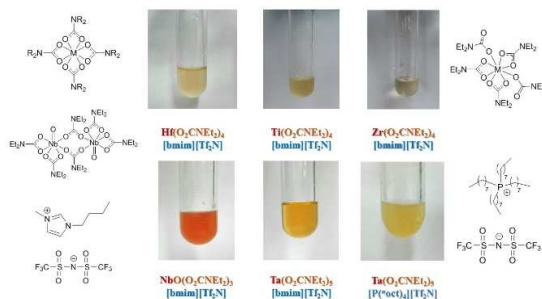
Guido Pampaloni

Graphical Abstract

Modifying Bis(Triflimide) Ionic Liquids with Early Transition Metal Carbamates

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Bis(triflimide) ionic liquids have been modified by dissolution of *N,N*-dialkylcarbamates of early transition metals, the solubilities generally exceeding 0.15 M with the maximum value (1.46 M) reached with $\text{Nb}(\text{O}_2\text{CNEt}_2)_3$. The solutions contain the intact metal complexes, presumably undergoing preferential electrostatic interaction with the solvent cation.



Modifying Bis(Triflimide) Ionic Liquids with Early Transition Metal Carbamates

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The authors report the first modification of ionic liquids with metal carbamates. A selection of homoleptic *N,N*-dialkylcarbamates carbamates of groups 4 and 5 metals, $M(O_2CNR_2)_n$, were dissolved in bis(trifluoromethylsulfonyl)imide-based ionic liquids, *i.e.* [bmim][Tf₂N] and [P(Oct)₄][Tf₂N], at 291 K. The resulting solutions were characterized by means of IR, UV and NMR spectroscopy, and the data were compared to those of the respective metal compounds. Notably, the dissolution process did not proceed with release of any of the original carbamate ligands, thus preserving the intact coordination frame around the metal centre. The solvation process of $Ti(O_2CN^iPr)_4$, as a model species, in [bmim][Tf₂N] was rationalized by DFT calculations. As a comparative study, solutions of NbF₅ and MCl₅ (M = Nb, Ta) in [bmim][Tf₂N] were also investigated, revealing the possible occurrence of solvent anion coordination to the metal centres.

Introduction

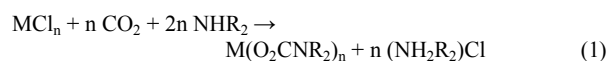
Ionic liquids (ILs) are low-melting-point compounds (the melting point being generally lower than 100 °C), composed by a bulky organic cation and an organic or inorganic anion, which have aroused a huge interest embracing an impressive range of application fields.¹ A vast number of different ILs can be prepared with the possibility of finely tuning their physical, chemical and biological properties, by modifying the molecular structure of the cation and/or the anion.² As an alternative approach to modulate the properties of ILs, the dissolution of transition metal salts to ILs having appropriate structure has been widely investigated. When highly concentrated solutions of metal salts in ILs are prepared, new liquid media can be obtained which combine the properties of organic ILs with magnetic, photophysical/optical, electrochemical and catalytic features of the incorporated metal ions.³ In particular, ILs containing late transition elements (such as iron, ruthenium, nickel, palladium, platinum, gold, copper or zinc) have been used in a broad range of metal-catalysed processes.⁴ Moreover, metal ions can be electro-reduced from concentrated ionic liquid solutions to afford metallic deposits (thin films, nanostructures and so on) with characteristics that are not easily achievable from aqueous solutions.⁵

The dissolution of transition metals in ILs has been achieved using a variety of well defined compounds,⁶ and most frequently halides or pseudo-halides.^{3a,7} In several cases, the interaction of the metal cation with the solvent anion results in the formation of adducts that facilitate the dissolution process.⁸ On the other hand, in order to enhance the solubility of the metal species, task-specific ILs have been designed, incorporating functional groups that can behave as ligands towards the metal centre.⁹ Metal salts having the anion in common with the solvent have been employed to the same purpose.¹⁰

The development of novel metal-based ionic liquid systems exploring the possible use of convenient but non-typical metal sources, which could supply unusual features to the resulting solutions, is highly desirable. Metal carbamates, *i.e.* molecular compounds of general formula $M(O_2CNR_2)_n$, are intriguing materials that, being well soluble in both polar and non polar organic solvents, have revealed to be convenient precursors for

chemical vapour deposition processes,¹¹ homogeneous catalysis¹² and material chemistry.¹³

They can be easily synthesized from commercial, cost effective metal chlorides by a CO₂ fixation process in the presence of secondary amines (Eq. 1).¹⁴



To the best of our knowledge, the modification of ionic liquids by dissolution of metal carbamates of any type is unprecedented. In the framework of the research of some of us on the chemistry of high valent molecular compounds of groups 4 and 5 elements,¹⁵ herein we report a review on the dissolution of a series of metal carbamates, $M(O_2CNR_2)_n$ (M = group 4-5 metal, n = 3-5), in [bmim][Tf₂N] and [P(Oct)₄][Tf₂N]. Spectroscopic and DFT results will be discussed.

Results and Discussion

The homoleptic metal carbamates $M(O_2CNR_2)_4$ (M = Ti, Zr, Hf; R = Me, Et, ⁱPr), $M(O_2CNEt_2)_5$ (M = Nb, Ta) and $Nb(O_2CNEt_2)_3$ were dissolved in [bmim][Tf₂N] at 293 K; $Ti(O_2CNEt_2)_4$ and $Ta(O_2CNEt_2)_5$ were also dissolved in [P(Oct)₄][Tf₂N] (Fig. 1).

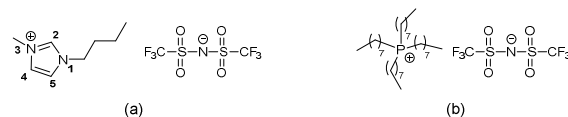


Figure 1. Structures of (a): [bmim][Tf₂N]; (b): [P(Oct)₄][Tf₂N].

Given the sensitivity of the metal complexes towards water and the hygroscopic nature of [Tf₂N]-based ionic liquids,¹⁶ all the operations were carried out in a strictly anhydrous atmosphere and the ILs were pre-dried by heating under vacuum in the presence of P₄O₁₀. When possible, the metal compound was added until saturation and the solubility was calculated via ¹H NMR with

respect to an internal standard. The resulting solutions were investigated by means of IR, UV and NMR techniques. In the case of paramagnetic metal carbamates, the molar concentration refers to the amount of material dissolved in the ionic liquid for a non-saturated solution.

Metal carbamates solutions in $R'[\text{Tf}_2\text{N}]$, $R' = [\text{bmim}]^+$, $[\text{P}(\text{oct})_4]^+$: solubility and spectroscopic investigation.

Metal N,N -dialkylcarbamates dissolved into $R'[\text{Tf}_2\text{N}]$ ($R' = [\text{bmim}]^+$, $[\text{P}(\text{oct})_4]^+$) ionic liquids affording colourless to pale yellow solutions (Figure 2 and Figures S2-S4 and S7-S9 in the Supporting Information; UV-Vis absorptions are in between 240 and 300 nm). The solubility of most of the metal carbamates in $[\text{bmim}][\text{Tf}_2\text{N}]$ exceeded 0.15 M, with the exception of $\text{Ti}(\text{O}_2\text{CNMe}_2)_n$ ($n = 3, 4$), being almost insoluble. Remarkably, high solubility values were observed with $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$ ($0.75 \text{ mol}\cdot\text{L}^{-1}$), $\text{Zr}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ ($0.85 \text{ mol}\cdot\text{L}^{-1}$) and $\text{Nb}(\text{O}_2\text{CNEt}_2)_3$ ($1.46 \text{ mol}\cdot\text{L}^{-1}$).



Figure 2. Solution of $\text{Zr}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ (0.85 M) in $[\text{bmim}][\text{Tf}_2\text{N}]$.

Spectroscopic data collected for $\text{M}(\text{O}_2\text{CNR}_2)_n / R'[\text{Tf}_2\text{N}]$ solutions were compared to those relative to the corresponding, isolated metal carbamates in the solid state and in solution of non-protic, neutral organic solvents (see Table 1). It is known that the molecular structures of various group 4 and 5 metal carbamates, as determined in the solid state by single crystal X-ray diffraction, are usually preserved in solution of hydrocarbons (benzene, toluene) or halogenated solvents (dichloromethane, chloroform).^{14c} More precisely, Titanium(IV), Zirconium(IV) and Hafnium(IV) N,N -dialkylcarbamates display a square anti-prismatic coordination given by four bidentate chelating ligands (Fig. 3a).^{14c} The CO_2 moiety in $\text{M}(\kappa^2\text{O}-\text{O}_2\text{CNR}_2)_4$ complexes ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; \text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$) gives rise to a sharp ^{13}C -NMR resonance around 169-170 ppm and a strong IR absorption in the $1535\text{-}1565 \text{ cm}^{-1}$ region.^{14c,17} On the other hand, Niobium(V) and Tantalum(V) N,N -diethylcarbamates show three bidentate chelating- and two monodentate ligands (Fig. 3b).^{14c,17b,18} Therefore, two strong IR absorptions at 1660 cm^{-1} ($\kappa\text{O}-\text{O}_2\text{CNEt}_2$) and 1570 cm^{-1} ($\kappa^2\text{O}-\text{O}_2\text{CNEt}_2$) are displayed by these compounds in the solid state. However, a fast, intramolecular ligand exchange occurs in solution and a single resonance at *ca.* 162 ppm appears in the ^{13}C spectrum.¹⁹ The niobyl derivative $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$ is instead a dinuclear compound with two bidentate chelating and one bidentate bridging diethylcarbamato group (Fig. 3c); it is characterized by two IR absorptions in the $1580\text{-}1550 \text{ cm}^{-1}$ range and two ^{13}C resonances (chelating: 168 ppm, bridging: 162 ppm) accounting for the CO_2 moieties.²⁰

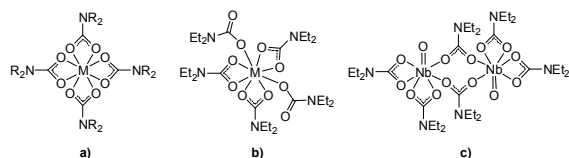


Figure 3. Structures of a): $\text{M}(\text{O}_2\text{CNR}_2)_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; \text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$); b): $\text{M}(\text{O}_2\text{CNEt}_2)_5$ ($\text{M} = \text{Nb}, \text{Ta}$); c): $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$.

$^1\text{H}/^{13}\text{C}$ NMR spectra of $\text{M}(\text{O}_2\text{CNR}_2)_n / R'[\text{Tf}_2\text{N}]$ solutions generally show a single set of signals due to the carbamato ligand, with chemical shifts belonging to the same region as observed in reference organic solvents (C_6D_6 , toluene- d_8 , CDCl_3). A single set of signals was also observed for solvent ions ($[\text{bmim}]^+$, $[\text{P}(\text{oct})_4]^+$ and $[\text{Tf}_2\text{N}]^-$) in all solutions. NMR resonances in both ionic liquids were generally broad and devoid of multiplicity, this effect being likely a consequence of the high viscosity of the medium.²¹ On the other hand, solutions of $\text{M}(\text{O}_2\text{CNR}_2)_4$ ($\text{M} = \text{Ti}, \text{R} = ^i\text{Pr}; \text{M} = \text{Ta}, \text{R} = \text{Et}$) and $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$ in $[\text{bmim}][\text{Tf}_2\text{N}]$ were characterized by two sets of $^1\text{H}/^{13}\text{C}$ signals with different intensity within the chemical shift regions typical of the other compounds. Most notably, the ^{13}C carbonyl resonance was detected around 168-169 ppm for group 4 metal carbamates and around 162 ppm for group 5 carbamates (see Table 1). The solution of $\text{Ti}(\text{O}_2\text{CNMe}_2)_4$ in $[\text{bmim}][\text{Tf}_2\text{N}]$ displayed several set of ^1H and ^{13}C resonances but its poor solubility prevented a satisfying characterization.

Table 1 about here

IR stretching vibrations of the carbamato groups related to $\text{M}(\text{O}_2\text{CNR}_2)_n / R'[\text{Tf}_2\text{N}]$ solutions were partially overlapped by solvent absorptions; relevant data are compiled in Table 1. A single absorption around $1525\text{-}1600 \text{ cm}^{-1}$ was observed for group 4 carbamates dissolved in $R'[\text{Tf}_2\text{N}]$. Once again, these data are not too dissimilar from those collected for the metal compounds in the solid state, being indicative of a bidentate chelating coordination. The solution of $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$ was characterized by two IR absorptions at 1576 cm^{-1} (chelating ligands) and 1558 cm^{-1} (bridging ligands) respectively, showing only a minor shift with respect to the solid state data ($1569 / 1535 \text{ cm}^{-1}$).²⁰ The IR spectrum of $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$ dissolved in $[\text{bmim}][\text{Tf}_2\text{N}]$ showed one absorption at 1604 cm^{-1} due to monodentate N,N -diethylcarbamate ligands, the absorption relative to the bidentate ligands being covered by the solvent (1574 cm^{-1}). In fact, two absorptions were recognized (1597 and 1573 cm^{-1}) when the same compound was dissolved in $[\text{P}(\text{oct})_4][\text{Tf}_2\text{N}]$.

Combined IR and NMR results indicate that no $[\text{R}_2\text{NCO}_2]^- / [\text{Tf}_2\text{N}]^-$ ligand exchange occurred when metal N,N -dialkylcarbamates were dissolved in $R'[\text{Tf}_2\text{N}]$ ($R' = [\text{bmim}]^+$, $[\text{P}(\text{oct})_4]^+$). This result was not anticipated, in view of the high affinity of group 4 and 5 metals in their high oxidation state^{15a,22} for oxygen ligands. Indeed a number of complexes having the bis(trifluoromethylsulfonyl)imide anion as a O,O' -chelating ligand have been reported.^{10,23}

Metal carbamates solutions in $R'[\text{Tf}_2\text{N}]$ ($R' = \text{bmim}^+$, $\text{P}(\text{oct})_4^+$): DFT calculations and solvent NMR analysis

A DFT study was carried out to elucidate the solvation process of carbamates in $[\text{bmim}][\text{Tf}_2\text{N}]$. We optimized the structures of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$,²⁴ $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$,²⁵ $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$,²⁶ $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$,²⁶ $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$,¹⁸ starting from the available X-ray data. The calculated structures of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ and $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$ and a selection of computed geometric and spectroscopic data are given as Supporting Information, Figure S1 and Table S1, respectively. A general good agreement between calculated and experimental structures was found, the differences being related to the conformation of the side chains and probably arising from crystal packing effects.

A comparative view of the structures of metal carbamates reveals that: i) The metallic centres are practically buried by the ligands, thus resulting isolated from the environment (solvent, for example). This may explain the low reactivity of metal N,N -dialkylcarbamates unless reagents prone to directly attack the ligand are used.^{14c} ii) Pockets are present within the structure, whose inner parts correspond to a region, nearby the oxygen atoms, displaying a negative electrostatic potential, thus able to interact with positively charged species. iii) Within the pockets, the oxygen atoms belonging to the (carbamato) carboxylic groups appear

sterically accessible, while the NR_2 units are probably more hindered.

Two isodensity plots of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$, mapped with the molecular electrostatic potential, are reported in Figure 4. Both views are focused on the two large and deep pockets located between the four ligands on opposite sides of the complex.

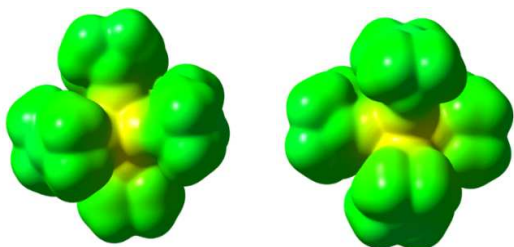


Figure 4. Isodensity plot of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ mapped with molecular electrostatic potential (MEP). The two different views show the two large pockets in the structure. Colour range from yellow to red indicates a negative MEP while green to blue a positive one. Isodensity value is 0.004 a.u.

Aiming to rationalize the solubility of metal carbamates in $[\text{bmim}][\text{Tf}_2\text{N}]$, we decided to focus on the interaction between $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$, as a model compound, and solvent ions, in the gas phase (eq. 2 and 3). The choice of the isopropyl carbamate complex ensured to consider the most sterically encumbered situation.

The isodensity plots, mapped with the molecular electrostatic potential, of the two charged species $\{\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4[\text{bmim}]\}^+$ and $\{\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4[\text{Tf}_2\text{N}]\}^-$ are reported in Figure 5. The pocket inside the structure of the complex (see above) has a suitable size to accommodate the aromatic ring of the $[\text{bmim}]^+$ cation. The interaction between the C2 hydrogen of the imidazolium ring and two oxygen atoms belonging to different carbamate ligands appears electrostatically favourable. The calculated distances between titanium, the two oxygen atoms and the imidazolium C2 hydrogen atom are 3.43, 2.02 and 2.41 Å, respectively. Despite bearing a partial positive charge, this hydrogen is not acidic enough to protonate the carbamate ligand.²⁷ It is worthy to remark that the $[\text{O}_2\text{CNR}_2]^-$ ligand is usually highly reactive towards protic species.^{14c}

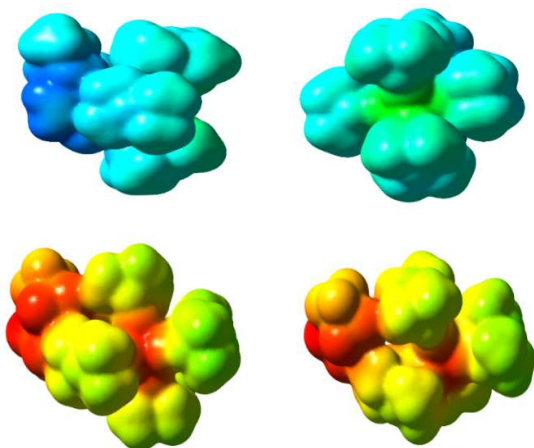
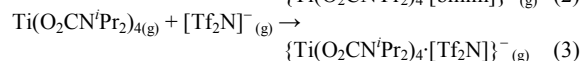
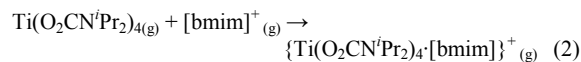


Figure 5. Top, left: Isodensity plot of the $[\text{bmim}]^+ / \text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ interaction mapped with molecular electrostatic potential (MEP). Top, right: effect of the neat charge of the cation (inversion of the sign of the MEP on the other big pocket). Bottom: Isodensity plot of the $[\text{Tf}_2\text{N}]^- / \text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ species mapped with MEP. Isodensity value is 0.004 a.u. The false colour scale is coherent with the one used in Figure 4.

In addition, the neat positive charge of $[\text{bmim}]^+$ within the $\{\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4[\text{bmim}]\}^+$ adduct should balance the formal negative electrostatic potential at the inner part of the opposite pocket.

The sterically hindered $[\text{Tf}_2\text{N}]^-$ anion, although able to interact electrostatically with the partial positive charges of the nitrogen atoms of the carbamate ligands, is too large to get inside the pocket. This reflects on the distance between the $[\text{Tf}_2\text{N}]^-$ nitrogen atom and the nearest carbamate nitrogen, being 5.76 Å, and the shortest distance between titanium and the anion fluorides (6.48 Å). By contrast, the higher penetrating $[\text{bmim}]^+$ is much closer to titanium ($\text{Ti} \cdots \text{H} \cdots \text{C}_2$ distance = 3.43 Å). The stronger interaction of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ with the cation is documented by the stabilization energies of the two species with respect to their constituents: these are -91.49 kJ/mol for the $[\text{bmim}]^+ / \text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ adduct (Eq. 2) and -24.84 kJ/mol for the $[\text{Tf}_2\text{N}]^- / \text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ adduct (Eq. 3).



A possible experimental evidence that enhanced interactions are established between N,N -dialkyl metal carbamates and the $[\text{bmim}]^+$ cation comes from NMR data. Figure 6 displays the $^1\text{H}/^{13}\text{C}/^{19}\text{F}$ chemical shift variation ($\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure IL}}$) of solvent ions ($[\text{bmim}]^+$, $[\text{Tf}_2\text{N}]^-$) with respect to the pure ionic liquid as a function of the concentration of $\text{M}(\text{O}_2\text{CNR}_2)_n/[\text{bmim}][\text{Tf}_2\text{N}]$ solutions. As shown in the Figure, an increase in concentration is correlated to an increase of $\Delta\delta$ for the $[\text{bmim}]^+$ cation (^1H : violet line, ^{13}C : red line). Otherwise, the $[\text{Tf}_2\text{N}]^-$ anion shows a weaker (^{13}C : green line) or absent (^{19}F : light blue line) correlation between concentration and chemical shift variation ($\Delta\delta$).

Data about the $\text{NbCl}_5/[\text{bmim}][\text{Tf}_2\text{N}]$ solution have been also included in the plot (Figure 6, point h): in this case, marked $\Delta\delta$ variations are noticeable for the $[\text{Tf}_2\text{N}]^-$ anion (^{13}C : -0.11 ppm; ^{19}F : $+0.45$ ppm), in addition to those of $[\text{bmim}]^+$. This fact is probably ascribable to the formation of chlorido-bistriflimido complexes (*vide infra*).

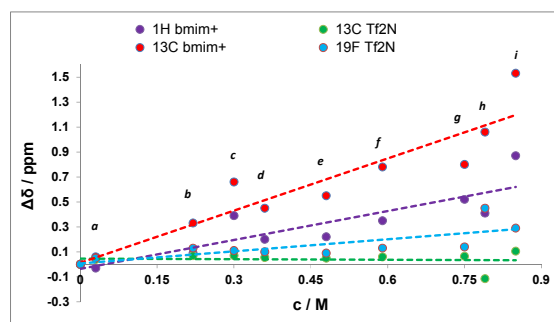


Figure 6. Variation of NMR chemical shifts of solvent ions ($[\text{bmim}]^+$ and $[\text{Tf}_2\text{N}]^-$) with respect to the pure ionic liquid ($\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure IL}}$) and molar concentration of a) $\text{Ti}(\text{O}_2\text{CNMe}_2)_4$, b) $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$, c) $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$, d) $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$, e) $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$, f) $\text{Hf}(\text{O}_2\text{CNEt}_2)_4$, g) $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$, h) NbCl_5 , i) $\text{Zr}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ solutions.

Metal carbamates solutions in $[\text{bmim}][\text{Tf}_2\text{N}]$: thermal and moisture stability

With just few exceptions,^{28,29} metal N,N -dialkylcarbamates are thermally robust compounds which are stable in common organic solvents. In order to test the thermal stability in $[\text{bmim}][\text{Tf}_2\text{N}]$ solutions were heated at 55°C for 24 hours. No variation was observed in the $^1\text{H}/^{13}\text{C}$ NMR spectra after the thermal treatment, thus indicating the thermal stability of carbamate complexes even

in an ionic liquid medium. Noteworthy is the result with $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$, which is quickly (1h, 100 %) converted into niobium(IV) derivative when heated in nonpolar solvents such as toluene or heptane.³⁰ The high dipole moment and polarizability calculated for $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$,²⁸ due to the presence of mono- and bidentate ligands, may favour solvation by the ionic solvent, resulting in an increase of the stability of the niobium(V) species.

It is well documented that *N,N*-dialkylcarbamato ligands undergo decomposition in the presence of protic species (see above), leading to the formation of the relevant dialkylamine and CO_2 .^{14c}³¹ The treatment of metal carbamates with controlled amounts of water in toluene or 1,2-dimethoxyethane does not generally proceed to the complete decomposition (formation of metal oxide), but affords mixed μ -oxo/carbamato derivatives.^{14c}³² Moreover, carbamato complexes undergo slow hydrolysis even when exposed to air, both in solution and in the solid state.

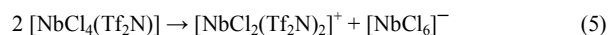
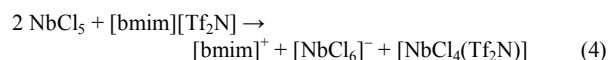
Solutions of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ and $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$ in either CDCl_3 or $[\text{bmim}][\text{Tf}_2\text{N}]$ were then exposed to air, and the decomposition process was monitored by ^1H spectroscopy with the assistance of an internal standard. We observed that the percentage of decomposition of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ and $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$ in CDCl_3 overcame 50% after 24 hours and reached 88% after 4 days, with concomitant precipitation of a colourless solid in the case of the tantalum compound. Surprisingly, solutions of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ and $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$ in $[\text{bmim}][\text{Tf}_2\text{N}]$ revealed more stable to decomposition than solutions in CDCl_3 . In fact, no formation of diethylamine was detected after 24 hours, while a decomposition rate around 10% was estimated in 4 days. This outcome is not trivial, since ionic liquids, unlike chloroform, are hygroscopic and capable to dissolve considerable amounts of water (≈ 0.3 mol fraction at saturation for $[\text{bmim}][\text{Tf}_2\text{N}]$)¹⁶. However, water in $[\text{bmim}][\text{Tf}_2\text{N}]$ is not homogeneously mixed with the IL but forms aggregates and clusters, whose size and connection increase on increasing the water content.³³ Moreover, water molecules are hydrogen-bonded to $[\text{Tf}_2\text{N}]^-$ anions, so giving pore wall richer in the anion than in the cation.³³ These structural features may slow down the diffusion of water and the contact between the metal compound and water, thus providing some inertness towards hydrolysis.

Metal halides solutions in $[\text{bmim}][\text{Tf}_2\text{N}]$

The study of the solubility in $[\text{bmim}][\text{Tf}_2\text{N}]$ was extended to NbF_5 , NbCl_5 and TaCl_5 . The dissolution process of these halides in ionic liquids was previously investigated, although the identity of the metal species in the resulting solutions was not fully ascertained.³⁴

In the solid state, niobium and tantalum pentahalides are featured by an octahedral coordination around the metal centre, with four terminal and two bridging halogenido ligands. Thus, NbF_5 is a tetramer, $[\text{NbF}_4(\mu\text{-F})_4]$, while NbCl_5 and TaCl_5 are dimers, $[\text{MCl}_4(\mu\text{-Cl})_2]$.³⁵

The pentachlorides NbCl_5 and TaCl_5 easily afforded 0.8 M solutions in $[\text{bmim}][\text{Tf}_2\text{N}]$, while NbF_5 was almost insoluble. The ^{93}Nb NMR spectrum of the $\text{NbCl}_5/[\text{bmim}][\text{Tf}_2\text{N}]$ solution displayed an intense signal around -6 ppm, indicative of the formation of $[\text{NbCl}_6]^-$,³⁶ and a broad and less intense signal at -128 ppm, presumably ascribable to some $[\text{NbCl}_4]^+$ derivative. The ^{19}F NMR spectrum of NbCl_5 in $[\text{bmim}][\text{Tf}_2\text{N}]$ showed three signals (-71.6 , -73.4 and -74.2 ppm) other than that of the solvent, thus suggesting the formation of mixed chlorido-bis(trifluoromethylsulfonyl)imido complexes such as $[\text{NbCl}_4(\text{Tf}_2\text{N})]$ or $[\text{NbCl}_2(\text{Tf}_2\text{N})_2]^+$. Therefore, the dissolution of NbCl_5 in $[\text{bmim}][\text{Tf}_2\text{N}]$ involves the unsymmetrical cleavage of the $\mu\text{-Cl}$ dimer and $[\text{Tf}_2\text{N}]^-$ coordination, with possible reactions indicated in eq. 4 and 5. Formation of $[\text{NbCl}_4\text{L}_2]^+$ and $[\text{NbCl}_6]^-$ has been reported upon reaction of NbCl_5 with a number of O,O and O,N-donor ligands.^{15a,36,37}



A similar mechanism seems to be operating with the dissolution of NbF_5 in $[\text{bmim}][\text{Tf}_2\text{N}]$. In fact, the formation of $[\text{NbF}_6]^-$ was clearly established by ^{19}F (decet at ≈ 100 ppm) and ^{93}Nb (heptet at -1551 ppm) NMR spectra.^{22a,38} The low solubility of NbF_5 prevented further characterization of the solution.

Conclusions

Ionic liquids are largely investigated materials, and especially those based on the bis-triflimide anion, $[\text{Tf}_2\text{N}]^-$, are prominent in view of attracting properties.³⁹ The modification of ionic liquids by dissolution of metal compounds is an intensively investigated field of research, and metal halides have been frequently employed to this purpose being easily available materials. Homoleptic metal carbamates constitute a class of coordination compounds which can be encountered throughout almost all the periodic table,^{14c} and that can be accessible by simple synthetic procedures from cost effective precursors. Herein, we have reported the unprecedented dissolution of a selection of homoleptic metal carbamates, based on high valent early transition metals, in bis-triflimide ionic liquids. The resulting solutions, some of them reaching relatively high concentrations, have been characterized by spectroscopic techniques. The dissolution process does not involve the loss of any carbamato ligand and leaves the coordination sphere of the metal centres substantially unvaried. This result is surprising in view of the facile disruption of the carbamato frame, usually promoted even by water traces.⁴⁰ According to DFT studies carried out on a model compound, the metal complex exhibits pockets allowing a preferential electrostatic interaction with the solvent cation, this interaction being presumably crucial for the dissolution. The dissolution into the ionic liquid supplies some inertness to the metal carbamates towards hydrolysis, and also evidence for enhanced thermal stability has been collected in the case of $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$. The incorporation of carbamato complexes, which possess previously documented interesting properties, into ionic liquids might represent a new platform for the future development of effective catalytic systems.

Experimental

Except otherwise noted, all the operations were carried out under an atmosphere of prepurified nitrogen or argon with standard Schlenk techniques. The Schlenk flasks and NMR tubes were oven dried at 140°C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. Metal halides were commercial products (Strem) stored under Ar as received. Metal carbamates,^{17,18,24,25,26} 1-butyl-3-methylimidazolium bistriflylimide ($[\text{bmim}][\text{Tf}_2\text{N}]$)⁴¹ and tetra-*n*-octylphosphonium bistriflylimide ($[\text{P}(\text{oct})_4][\text{Tf}_2\text{N}]$)⁴² were prepared according to literature methods. The ionic liquids were then dried under vacuum at 80°C over P_4O_{10} for 4 hours and stored under nitrogen. UV-Vis spectra were recorded on a Ultraspec 2100 Pro spectrophotometer with 0.1 cm quartz cuvettes. Infrared spectra were recorded at 298 K on a FTIR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. Chemical shifts were referenced to internal (^1H , ^{13}C to C_6D_6 in a sealed capillary tube) or to external (^{19}F to CFCl_3 , ^{31}P to 85% H_3PO_4 , ^{93}Nb to NbOCl_3) standards. ^1H and ^{13}C resonances were assigned with the assistance of ^1H - ^1H COSY and ^1H - ^{13}C HSQC correlation experiments.⁴³

Solutions of metal carbamates and halides in R[Tf₂N] (R = [bmim]⁺, [P(Oct)₄]⁺): preparation and characterization

General procedure: The selected metal compound was added until saturation to a weighted amount of ionic liquid (ca. 2 mL) into a Schlenk tube and the resulting opalescent solution or suspension was stirred for 14 hours at 293 K. Toluene or CH₂Cl₂ (40 μL) was added to [bmim][Tf₂N] or [P(Oct)₄][Tf₂N] solutions, respectively, as standard for ¹H NMR spectroscopy. Therefore, an aliquot of the resulting solution (ca. 0.4 mL) was transferred into a sealed NMR tube. The solutions were characterized by UV-Vis, IR and NMR spectroscopy then stored in sealed tubes under nitrogen. Dilution up to ca. 10⁻³ M was performed before collecting UV-Vis spectra. Molar concentrations of diamagnetic metal carbamates were calculated via ¹H NMR with respect to the internal standard (toluene in [bmim][Tf₂N]: δ/ppm = 2.27 (s, 3H); CH₂Cl₂ in [P(Oct)₄][Tf₂N]: δ/ppm = 5.51 (s, 2H)). Molar concentration of metal halides and paramagnetic metal carbamates refers to the amount of material dissolved in the ionic liquid for a non-saturated solution. NMR data of solvent ions ([bmim]⁺, [P(Oct)₄]⁺ and [Tf₂N]⁻) are given as chemical shift differences (Δδ) with respect to the pure ionic liquid (Δδ = δ_{solution} - δ_{solvent}); in the case of ¹³C and ¹H nuclei, an average value is given (Δδ = Σδ_{solution} - Σδ_{solvent}).

Ti(O₂CNEt₂)₃ in [bmim][Tf₂N]. Light violet solution; the compound is poorly soluble. NMR: silent (paramagnetic).

Ti(O₂CNMe₂)₄ in [bmim][Tf₂N]. Pale yellow solution; c = 0.03 M. UV-Vis: λ/nm = 268. IR: ν/cm⁻¹ = 1598sh (ν_{C=O}), 1497, 1274. ¹H NMR: δ/ppm = 2.92, 2.88, 2.77 and 2.49 (s-br, CH₃); Δδ/ppm = -0.03 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 169.2 (C=O), 34.6 and 33.3 (CH₃); Δδ/ppm = 0.06 (bmim⁺), 0.04 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.05 (Tf₂N⁻).

Ti(O₂CNEt₂)₄ in [bmim][Tf₂N]. Yellow solution; c = 0.30 M. UV-Vis: λ/nm = 250-300br. IR: ν/cm⁻¹ = 1527 (ν_{C=O}), 1496, 1434, 979. ¹H NMR: δ/ppm = δ 3.20 (s-br, 2H, CH₂), 1.05 (s-br, 3H, CH₃); Δδ/ppm = 0.39 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 168.8 (C=O), 39.4 (CH₂), 12.8 (CH₃); Δδ/ppm = 0.66 (bmim⁺), 0.07 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.11 (Tf₂N⁻).

Ti(O₂CNEt₂)₄ in [P(Oct)₄][Tf₂N]. Yellow solution, c = 0.14 M. UV-Vis: λ/nm = 240-300. IR: ν/cm⁻¹ = 1558 (ν_{C=O}), 1501, 1264, 981, 938. ¹H NMR: δ/ppm = 3.45 (s-br, CH₂), 1.30 (s-br, CH₃); Δδ/ppm = 0.29 (P(Oct)₄⁺). ¹³C{¹H} NMR: δ/ppm = 168.5 (CO), 39.6 (CH₂), 13.4 (CH₃); Δδ/ppm = 0.91 (P(Oct)₄⁺), 0.08 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.02 (Tf₂N⁻). ³¹P{¹H} NMR: Δδ/ppm = 0.03 (P(Oct)₄⁺).

Ti(O₂CNⁱPr₂)₄ in [bmim][Tf₂N]. Yellow solution; c = 0.22 M. UV-Vis: λ/nm = 250-300br. IR: ν/cm⁻¹ = 2376, 2361, 2341, 1555 (ν_{C=O}), 1497, 814. ¹H NMR: δ/ppm = 3.75 (m, 1H, CH), 2.97 and 2.76 (s-br, 1H, CH⁺), 1.16 (s-br, 6H, CH₃), 1.04 (s-br, 6H, CH₃); Δδ/ppm = 0.09 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 168.9 (C=O), 45.4 (CH), 45.0 (CH⁺), 21.8 (CH₃⁺), 19.9 (CH₃); Δδ/ppm = 0.33 (bmim⁺), 0.07 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.13 (Tf₂N⁻).

Zr(O₂CNEt₂)₄ in [bmim][Tf₂N]. Pale yellow solution; c = 0.36 M. UV-Vis: λ/nm = 261, 268. IR: ν/cm⁻¹ = 1550-1530 (ν_{C=O}), 1498, 1445, 980. ¹H NMR: δ/ppm = 3.21 (s-br, 2H, CH₂), 1.04 (s-br, 3H, CH₃); Δδ/ppm = 0.20 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 168.6 (CO), 39.8 (CH₂), 12.7 (CH₃); Δδ/ppm = 0.45 (bmim⁺), 0.06 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.10 (Tf₂N⁻).

Zr(O₂CNⁱPr₂)₄ in [bmim][Tf₂N]. Colourless solution; c = 0.85 M. UV-Vis: λ/nm = 260, 268. IR: ν/cm⁻¹ = 1544 (ν_{C=O}), 1491, 1463, 1386, 814. ¹H NMR: δ/ppm = 3.82 (s-br, 1H, CH), 1.21 (s-br, 6H, CH₃); Δδ/ppm = 0.87 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 168.5 (CO), 45.2 (CH), 19.9 (CH₃); Δδ/ppm = 1.53 (bmim⁺), 0.11 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.29 (Tf₂N⁻).

Hf(O₂CNEt₂)₄ in [bmim][Tf₂N]. Pale pink solution; c = 0.59 M. UV-Vis: λ/nm = 260, 268. IR: ν/cm⁻¹ = 1567 (ν_{C=O}), 1503, 1447, 979. ¹H NMR: δ/ppm = δ 3.21 (s-br, 2H, CH₂), 1.05 (s-br, 3H, CH₃); Δδ/ppm = 0.35 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 168.2 (CO), 39.9 (CH₂), 12.7 (CH₃); Δδ/ppm = 0.78 (bmim⁺), 0.06 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.13 (Tf₂N⁻).

Nb(O₂CNEt₂)₃ in [bmim][Tf₂N]. Dark red solution; c = 1.46 M.

¹H NMR spectrum displays very broad resonances (paramagnetic). **Nb(O₂CNMe₂)₄ in [bmim][Tf₂N].** Pale yellow solution; c = 0.15 M. NMR: silent (paramagnetic).

Nb(O₂CNEt₂)₅ in [bmim][Tf₂N]. Pale yellow solution; c = 0.16 M. UV-Vis: λ/nm = 250-280. IR ν/cm⁻¹ = 1260, 823. ¹H NMR: δ/ppm = 3.27 (s-br, 2H, CH₂), 1.10 (s-br, 3H, CH₃). ¹³C{¹H} NMR: δ/ppm = 161.3 (C=O), 40.6 (CH₂), 13.5 (CH₃).

NbO(O₂CNEt₂)₃ in [bmim][Tf₂N]. Orange solution; c = 0.75 M. UV-Vis: λ/nm = 250-280. IR ν/cm⁻¹ = 1569 (ν_{C=O}), 1535 (ν_{C=O}), 1484, 982, 917, 840. ¹H NMR: δ/ppm = 3.35 and 3.12 (s-br, 2H, CH₂), 1.13 (s-br, 3H, CH₃); Δδ/ppm = 0.52 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 167.8 (C=O), 162.4-161.2 (m, C=O), 42.5-41.4 (m, CH₂), 40.3-38.8 (m, CH₃), 13.3-12.8 (m, CH₃); Δδ/ppm = 0.80 (bmim⁺), 0.07 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.14 (Tf₂N⁻). ⁹³Nb{¹H} NMR: no signal.

Ta(O₂CNEt₂)₅ in [bmim][Tf₂N]. Yellow-orange solution; c = 0.48 M. UV-Vis: λ/nm = 250-270. IR: ν/cm⁻¹ = 1604 (ν_{C=O}), 1267, 973. ¹H NMR: δ/ppm = δ 3.26 (s-br, 2H, a-CH₂), 2.86 (s-br, 2H, b-CH₂), 1.18 (sh, b-CH₃), 1.09 (s-br, 3H, a-CH₃); a/b ratio = 88:12; Δδ/ppm = 0.22 (bmim⁺). ¹³C{¹H} NMR: δ/ppm = 163.3-160.7 (m, C=O), 41.9 (b-CH₂), 40.5 (a-CH₂), 12.8 (a-CH₃), 11.6 (b-CH₃); Δδ/ppm = 0.55 (bmim⁺), 0.05 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = 0.09 (Tf₂N⁻).

Ta(O₂CNEt₂)₅ in [P(Oct)₄][Tf₂N]. Yellow solution, c = 0.43 M. UV-Vis: λ/nm = 240-260. IR: ν/cm⁻¹ = 1597 (ν_{C=O}), 1573 (ν_{C=O}), 1271, 1100, 938, 873, 846. ¹H NMR: δ/ppm = 3.42 (s-br, 2H, CH₂), 1.26 (s-br, 3H, CH₃); Δδ/ppm = 0.06 (P(Oct)₄⁺). ¹³C{¹H} NMR: δ/ppm = 163.2-160.7 (m, C=O), 40.6 (CH₂), 13.4 (CH₃); Δδ/ppm = 0.37 (P(Oct)₄⁺), 0.02 (Tf₂N⁻). ¹⁹F{¹H} NMR: Δδ/ppm = -0.02 (Tf₂N⁻). ³¹P{¹H} NMR: Δδ/ppm = -0.01 (P(Oct)₄⁺).

NbF₅ in [bmim][Tf₂N]. Colourless solution; the compound is poorly soluble. UV-Vis: λ/nm = 250-300br. ¹H NMR: Δδ/ppm = -0.01 (bmim⁺). ¹³C{¹H} NMR: Δδ/ppm = -0.04 (bmim⁺), 0 (Tf₂N⁻). ¹⁹F{¹H} NMR: δ/ppm = 107.6 - 98.7 (m); Δδ/ppm = 0.02 (Tf₂N⁻). ⁹³Nb{¹H} NMR: δ/ppm = -1551 (hept, ¹J_{FNb} = 320 Hz).

NbCl₅ in [bmim][Tf₂N]. Golden yellow solution; c = 0.79 M. UV-Vis: λ/nm = 285, 320sh. IR: ν/cm⁻¹ = 3500-3200br, 1439, 878. ¹H NMR: δ/ppm = δ 11.3 (s, 1H), 5.39 (s, 0.25H), 2.65 (s, 1H); Δδ/ppm = 0.41 (bmim⁺). ¹³C{¹H} NMR: Δδ/ppm = 1.06 (bmim⁺), -0.11 (Tf₂N⁻). ¹⁹F{¹H} NMR: δ/ppm = -71.6, -73.4, -74.2; Δδ/ppm = 0.45 (Tf₂N⁻). ⁹³Nb{¹H} NMR: δ/ppm = -6.0 (s, Δν_{1/2} = 950 Hz), -128.7 (br).

TaCl₅ in [bmim][Tf₂N]. Golden yellow solution; c = 0.79 M.

Solutions of metal carbamates in R[Tf₂N] (R = [bmim]⁺, [P(Oct)₄]⁺): thermal and moisture stability tests.

Thermal stability tests: Sealed NMR tubes containing the solutions described in the previous section were kept at 293 K for 1 week then heated at 328 K for 24 hours without any appreciable variation in their appearance and ¹H NMR spectra.

Moisture stability tests: An aliquot of Ti(O₂CNEt₂)₄ and Ta(O₂CNEt₂)₅ solutions in [bmim][Tf₂N] was transferred in NMR tubes under a non-inert atmosphere. Before every analysis, NMR tubes were opened for 1 hour to favour the contact of solutions with moisture. The concentration of metal carbamates was evaluated after 16 hours, 24 hours and 4 days by ¹H NMR using toluene as internal standard. Parallel experiments were performed with solutions of Ti(O₂CNEt₂)₄ and Ta(O₂CNEt₂)₅ in CDCl₃ (CH₂Cl₂ as internal standard). The % of decomposition was calculated with respect to the initial concentration.

Ti(O₂CNEt₂)₄ in [bmim][Tf₂N]. t = 0, 16h, 24h: c = 0.30 mol/L, %_{decomp} = 0. t = 4 days: c = 0.26 mol/L, %_{decomp} = 13.

Ti(O₂CNEt₂)₄ in CDCl₃. ¹H NMR: δ/ppm = 3.34 (q, CH₂ carbamate), 3.20* (m), 2.64 (br, CH₂ diethylamine), 1.12-1.03 (m, CH₃ carbamate + CH₃ diethylamine). Carbamate:amine molar ratio = 4:1, %_{decomp} = 20 (t = 16 h); 65:100, %_{decomp} = 60 (t = 24 h); ca. 1:7, %_{decomp} = 88 (t = 4 d). *Signal observed after 24 h. A

broadening of carbamate NMR signals over time was observed, as already reported for other hydrolysis experiments.⁴⁴

Ta(O₂CNEt₂)₅ in [bmim][Tf₂N]. t = 0, 16h, 24h: c = 0.48 mol/L, %_{decomp} = 0. t = 4 days: c = 0.43 mol/L, %_{decomp} = 10.

Ta(O₂CNEt₂)₅ in CDCl₃. ¹H NMR: δ/ppm = 3.33 (q, CH₂ carbamate), 2.98 (br), 2.67 (q, CH₂ diethylamine), 1.12 (m, CH₃ carbamate + CH₃ diethylamine). Carbamate:amine molar ratio = 16:10, %_{decomp} = 38 (t = 16 h); 4:10, %_{decomp} = 71 (t = 24 h); 5:100, %_{decomp} = 95 (t = 4 days). A broadening of carbamate NMR signals over time was observed, as already reported for other hydrolysis experiments.⁴⁴ The formation of a colourless precipitate was observed after 4 days.

Metal carbamates and ionic liquids: reference data.

[bmim][Tf₂N]. Colourless liquid. Density (295 K): 1.429 g·mL^{-1.45} UV-Vis: λ/nm = 240 (cutoff). IR (liquid film): ν/cm⁻¹ = 3158w, 3122w, 3104w, 2968w, 2941w, 2880w, 1574w, 1468w, 1432w, 1347s, 1330s, 1226m-sh, 1178s, 1133s, 1052s, 843w, 789m, 761m, 750m-sh, 740m, 655w. ¹H NMR: δ/ppm = 8.55 (s, 1H), 7.46 (s, 1H), 7.38 (s, 1H), 4.16 (t, J = 7.2 Hz, 2H), 3.89 (s, 3H), 1.88–1.79 (m, 2H), 1.38–1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR: δ/ppm = δ 136.0, 123.4, 122.2, 119.8 (q, ¹J_{CF} = 321 Hz), 49.4, 35.5, 31.5, 18.9, 12.4. ¹⁹F{¹H} NMR: δ/ppm = -80.2.

[P(Oct)₄][Tf₂N]. Colourless liquid. Density (273 K): 1.071 g·mL^{-1.42} UV-Vis: λ/nm = 230 (cutoff), 340. IR (liquid film): ν/cm⁻¹ = 2956w, 2928m, 2858m, 1466w, 1413w, 1349s, 1225m, 1182s, 1136s, 1055s, 787w, 761w, 739w, 723w, 654w. ¹H NMR: δ/ppm = δ 2.27 (s-br, 2H), 1.65 and 1.59 (s-br, 4H), 1.42 (s-br, 8H), 1.02 (s-br, 3H). ¹³C{¹H} NMR: δ/ppm = 120.1 (q, ¹J_{CF} = 322 Hz), 31.8, 30.5 (d, J = 14.7 Hz), 29.0, 28.6, 22.6, 21.3, 18.4 (d, J = 47.5 Hz), 13.8. ¹⁹F{¹H} NMR: δ/ppm = -79.1. ³¹P{¹H} NMR: δ/ppm = 33.0.

Ti(O₂CNMe₂)₄. UV-Vis (CH₂Cl₂, c = 3.5·10⁻³ M): λ/nm (ε/M⁻¹·cm⁻¹) = 220-250, 297 (8.1·10³). IR (solid state): ν/cm⁻¹ = 2937w-br, 1588vs (ν_{C=O}), 1531m, 1455w-m, 1405s, 1268s, 1042w, 866w, 843vw, 787vs. ¹H NMR (CDCl₃): δ/ppm = 2.91 (s, CH₃). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 169.6 (C=O), 34.4 (CH₃).

Ti(O₂CNEt₂)₄. UV-Vis (CH₂Cl₂, c = 3.3·10⁻³ M): λ/nm (ε/M⁻¹·cm⁻¹) = 220-250, 305 (6.5·10³). IR²⁵ (Nujol and poly(chlorotrifluoroethylene) mulls): ν/cm⁻¹ = 2990m, 2980m, 2940mw, 1560vs (ν_{C=O}), 1505s, 1460m, 1320s, 1210m, 1100w, 1080m, 975w, 940w, 835s, 790s, 635s, 450s. ¹H NMR (CDCl₃): δ/ppm = 3.24 (q, ³J_{HH} = 7.1 Hz, 2H, CH₂), 0.96 (t, ³J_{HH} = 7.1 Hz, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 169.0 (C=O), 38.5 (CH₂), 13.5 (CH₃).

Ti(O₂CNⁱPr₂)₄. IR (Nujol and poly(chlorotrifluoroethylene) mulls) ²⁴: ν/cm⁻¹ = 2970ms, 2940m, 2880mw, 1550vs (ν_{C=O}), 1500s, 1460m, 1320vs, 1200m, 1160m, 1140m, 1060m, 1030mw, 900w, 815s, 790s, 615s, 530s, 510m and 415s. ¹H NMR (C₆D₆): δ/ppm = 3.76 (hept, ³J_{HH} = 7.0 Hz, 1H, CH), 1.05 (d, ³J_{HH} = 7.0 Hz, 6H, CH₃). ¹³C{¹H} NMR (C₆D₆): δ/ppm = 170.6 (C=O), 45.5 (CH), 21.5 (CH₃).

Zr(O₂CNEt₂)₄. UV-Vis (CH₂Cl₂, c = 3.0·10⁻³ M): λ/nm = 220-230. IR²⁵ (Nujol and poly(chlorotrifluoroethylene) mulls): ν/cm⁻¹ = 2990m, 2980m, 2940mw, 1565vs (ν_{C=O}), 1505vs, 1450s, 1380m, 1325 s, 1220m, 1100m, 1080m, 1070m, 975m, 940w, 835ms, 795ms, 640s, 435s. ¹H NMR²⁵ (C₆D₆): δ/ppm = 2.97 (q, ³J_{HH} = 7.0 Hz, 2H, CH₂), 0.78 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃). ¹³C{¹H} NMR²⁵ (C₆D₆): δ/ppm = 170.4 (CO), 40.3 (CH₂), 14.3 (CH₃).

Zr(O₂CNⁱPr₂)₄. UV-Vis (CH₂Cl₂, c = 3.1·10⁻³ M): λ/nm = 220-230. IR (Nujol and poly(chlorotrifluoroethylene) mulls): ν/cm⁻¹ = 2970ms, 2940m, 2880w, 1535vs (ν_{C=O}), 1500vs, 1380s, 1360 s, 1200m, 1160ms, 1140m, 1060ms, 810s, 795s, 620m, 515s. ¹H NMR (C₆D₆): δ/ppm = 3.73 (hept, ³J_{HH} = 7.0 Hz, 1H, CH), 1.00 (d, ³J_{HH} = 7.0 Hz, 6H, CH₃). ¹³C{¹H} NMR (C₆D₆): δ/ppm = 170.3 (CO), 45.7 (CH), 21.3 (CH₃).

Hf(O₂CNEt₂)₄. UV-Vis (CH₂Cl₂, c = 2.5·10⁻³ M): no absorptions in the solvent window. IR¹⁷ (Nujol and poly(chlorotrifluoroethylene) mulls): ν/cm⁻¹ = 2990m, 2980ms,

2940m, 2880w, 1565vs (ν_{C=O}), 1508vs, 1485mw, 1440s, 1380m, 1325s, 1230m, 1100w, 1090m, 1080m, 970w, 840m, 795m, 640s, 525m. ¹H NMR¹⁷ (C₆D₆): δ/ppm = 2.98 (q, ³J_{HH} = 7.0 Hz, 2H, CH₂), 1.05 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃). ¹³C{¹H} NMR¹⁷ (C₆D₆): δ/ppm = 170.2 (C=O), 40.5 (CH₂), 12.3 (CH₃).

Nb(O₂CNEt₂)₅. UV-Vis (CH₂Cl₂, c = 1.9·10⁻³ M): λ/nm (ε/M⁻¹·cm⁻¹) = 220-265. IR²⁶ (poly(chlorotrifluoroethylene) mull): ν/cm⁻¹ = 2970vs, 2933s, 2874s, 1666vs (ν_{C=O}), 1590vs (ν_{C=O}), 1494s, 1440vs, 1406s, 1380s, 1325vs. ¹H NMR (C₆D₆): δ/ppm = 3.16 (q, ³J_{HH} = 7.0 Hz, 2H, CH₂), 0.97 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃). ¹³C{¹H} NMR²⁶ (C₆D₆): δ/ppm = 162.3 (C=O), 40.7 (CH₂), 13.8 (CH₃). ²⁶ ⁹³Nb NMR²⁶ (C₆D₆): δ/ppm = -1049 (w_{1/2} = 7443 Hz).

NbO(O₂CNEt₂)₃. UV-Vis (CH₂Cl₂, c = 2.8·10⁻³ M): λ/nm = 220-265. IR¹⁸ (solid state): ν/cm⁻¹ = 2974w, 2935w, 2876w, 1620m, 1576s (ν_{C=O}), 1558s (ν_{C=O}), 1484s, 1433vs, 1380m, 1321s, 1301s, 1209m, 1100w-m, 1074m, 1022w, 977w-m, 929vs, 840s, 782s. ¹H NMR¹⁸ (toluene-d₈): δ/ppm = 3.03 (m, 2H, CH₂), 0.86 (m, 3H, CH₃). ¹³C{¹H} NMR¹⁸ (toluene-d₈): δ/ppm = 168.1, 162.0 (C=O), 39.5, 41.7 (CH₂), 12.1, 13.1 (CH₃).

Ta(O₂CNEt₂)₅. UV-Vis (CH₂Cl₂, c = 1.4·10⁻³ M): λ/nm = 220-260. IR¹⁸ (poly(chlorotrifluoroethylene) mull): ν/cm⁻¹ = 2976m, 2934m, 2876w, 2728m-w, 1651s (ν_{C=O}), 1587vs (ν_{C=O}), 1494vs, 1473vs, 1461vs, 1440vs, 1412s, 1380m, 1349w, 1324m, 1278vs. ¹H NMR¹⁸ (C₆D₆): δ/ppm = 3.18 (q, ³J_{HH} = 7.0 Hz, 2H, CH₂), 0.98 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃). ¹³C{¹H} NMR¹⁸ (C₆D₆): δ/ppm = 161.8 (CO), 40.5 (CH₂), 13.5 (CH₃).

Computational Details

All calculations have been carried out using the Gaussian09 package⁴⁶ and the B3LYP functional. Furthermore, the all-electrons triple zeta basis set 6-311+G(d,p) has been employed for the first and second row elements. The transition metal atoms have been described using the effective core electron potential basis set LANL2TZ(f)⁴⁷, expressly designed for application with 6-311+G(d,p). Two identical Workstation equipped with Xeon E5-1660 CPU, 32Gb of ECC-Registered RAM, SATA3 HD and with Linux Opensuse 12.3 O.S. has been used.

Acknowledgements

We gratefully thank the University of Pisa for financial support.

Supplementary Material

Figure S1 [DFT-optimized structures of Ti(O₂CNⁱPr₂)₄ and Nb(O₂CNEt₂)₅], Table S1 (Selection of computed geometric and spectroscopic data for metal N,N-dialkylcarbamates), Figures S2-S9 [Photos of solutions of metal N,N-dialkylcarbamates) in [bmim][Tf₂N] / [P(Oct)₄][Tf₂N]]. Cartesian coordinates of all DFT-optimized compounds are collected in separated .xyz files.

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Table 1. Selected spectroscopic data for metal carbamates in ionic liquids, and comparison with corresponding data in the solid state or in solution of common organic solvents.

Compound	IR: $\nu_{\text{asym}}(\text{CO}_2) / \text{cm}^{-1}$		^{13}C NMR: $\delta(\text{CO}_2) / \text{ppm}$		UV-Vis: λ / nm	
	<i>Solid state</i>	<i>R' [Tf₂N] solution^[a]</i>	<i>CDCl₃ / C₆D₆ / toluene-d₈ solution</i>	<i>R' [Tf₂N] solution^[a]</i>	<i>CH₂Cl₂ solution</i>	<i>R' [Tf₂N] solution^[a]</i>
Ti(O₂CNMe₂)₄	1558	1598	169.9	169.2	220-250	268
Ti(O₂CNEt₂)₄	1560	1527; 1558 ^[b]	169.0	168.8; 168.5 ^[c]	220-250	250-300; 240-300 ^[c]
Ti(O₂CNⁱPr₂)₄	1550	1555	170.6	168.9		250-300
Zr(O₂CNEt₂)₄	1565	1550-1530	170.4	168.6	220-230	261, 268
Zr(O₂CNⁱPr₂)₄	1535	1544	170.3	168.5	220-230	260, 268
Hf(O₂CNEt₂)₄	1565	1567	170.2	168.2	^[d]	260, 268
Nb(O₂CNEt₂)₅	1666 1590	^[e]	162.3	161.3	220-265	250-280
NbO(O₂CNEt₂)₃	1576 1558	1569 1535	168.1 162.0	167.8 162.4-161.2	220-265	250-280
Ta(O₂CNEt₂)₅	1651 1587	1604 ^[c] , 1597 ^[b] , 1537 ^[b]	161.7	163.3-160.7; 163.2- 160.7 ^[c]	220-260	250-270; 240-260 ^[c]

[a] R' = bmim⁺ except otherwise noted. [b] R' = P(oct)₄⁺. [c] The absorption at lower wavenumbers is covered by the solvent. [d] No absorption in the solvent window. [e] Both the absorptions are covered by the solvent (1574 cm⁻¹).

Modifying Bis(Triflimide) Ionic Liquids with Early Transition Metal Carbamates

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SUPPORTING INFORMATION

Figure S1. DFT-optimized structures of $\text{Ti}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ (left) and $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$ (right)	2
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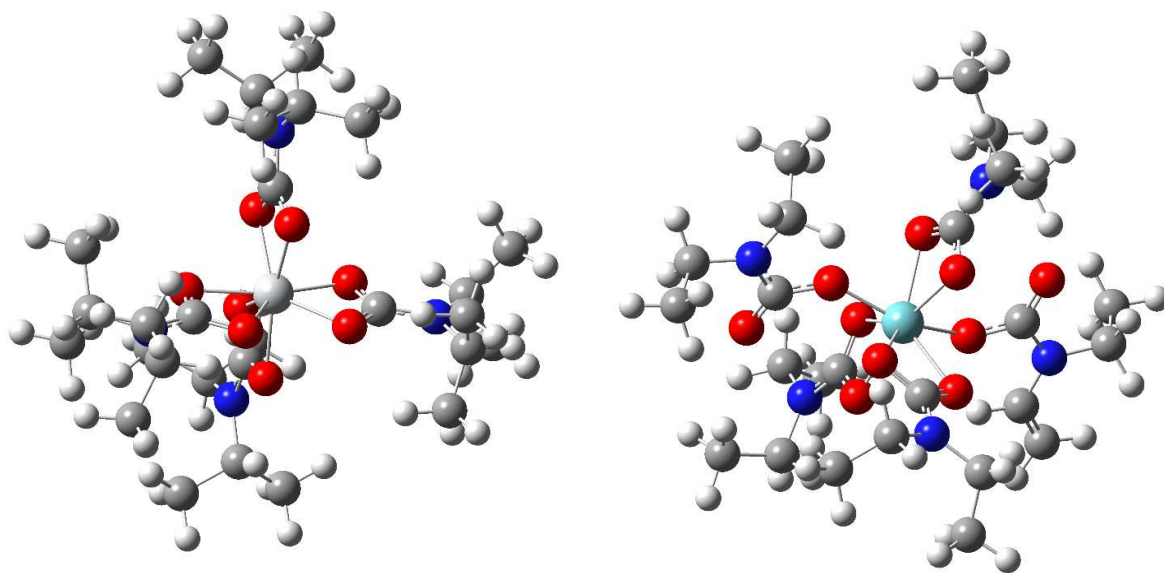


Figure S1. DFT-optimized structures of $\text{Ti}(\text{O}_2\text{CN}^t\text{Pr}_2)_4$ (left) and $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$ (right).

Table S1. Selection of computed and experimental geometric data and computed spectroscopic data for metal *N,N*-dialkylcarbamates.

Compound	IR ^a : $\nu(\text{CO}_2)$ / cm^{-1} calculated	NMR: $\delta(\text{CO}_2)$ / ppm		R(M-O)/Å	
		calculated	experimental ^[a]	calculated	experimental ^[b]
Ti(O₂CNⁱPr₂)₄	1532, 1563, 1568, 1576	174.6-174.8	170.6	2.08-2.11	2.033- 2.110
Zr(O₂CNEt₂)₄	1530, 1540, 1580	177.4	170.4	2.23-2.24	2.180-2.276
Zr(O₂CNⁱPr₂)₄	1482, 1509, 1516, 1521	177.8-178.9	170.3	2.23-2.24	---
Nb(O₂CNEt₂)₅	1566, 1585, 1617, 1646, 1650	158.6-161.2 176.1-178.7	162.3	2.13 -2.20 (chelate) 1.97 -2.01 (monodentate)	2.103-2.154 (chelate) 1.972 (monodentate)
NbO(O₂CNEt₂)₃	1471, 1475, 1476,, 1531 1532, 1545, 1592	175.8 165.2-165.3	168.1, 162.0	1.71 (Nb=O) 2.18–2.21(chelate) 2.17(bridge)	1.710 (Nb=O) 2.149 (chelate) 2.161 (bridge)
Ta(O₂CNEt₂)₅	1569, 1642	177.1-177.5 160.3- 160.6	161.8	2.10–2.18 (chelate) 1.968 (monodentate)	2.093-2.147(chelate) 1.9688 (monodentate)

[a] References are given in the main text.

[b] X-ray structures: Ti(O₂CNⁱPr₂)₄: D. Belli Dell'Amico, F. Calderazzo, S. Ianelli, L. Labella, F. Marchetti, G. Pelizzi, J. Chem. Soc., Dalton Trans. 2000, 4339. Zr(O₂CNEt₂)₄: F. Calderazzo, U. Englert, C. Maichle-Mössmer, F. Marchetti, G. Pampaloni, D. Petroni, C. Pinzino, J. Strähle, G. Tripepi, Inorg. Chim. Acta 270, 1998, 177-188. Nb(O₂CNEt₂)₅ and NbO(O₂CNEt₂)₃: M. Bortoluzzi, F. Ghini, M. Hayatifar, F. Marchetti, G. Pampaloni, S. Zacchini Eur. J. Inorg. Chem. 2013, 3112–3118. Ta(O₂CNEt₂)₅: P. B. Arimondo, F. Calderazzo, U. Englert, C. Maichle-Mössmer, G. Pampaloni, J. Strähle, J. Chem. Soc., Dalton Trans., 1996, 311-319.

Figure S2. Solution of $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$ in $[\text{bmim}][\text{Tf}_2\text{N}]$

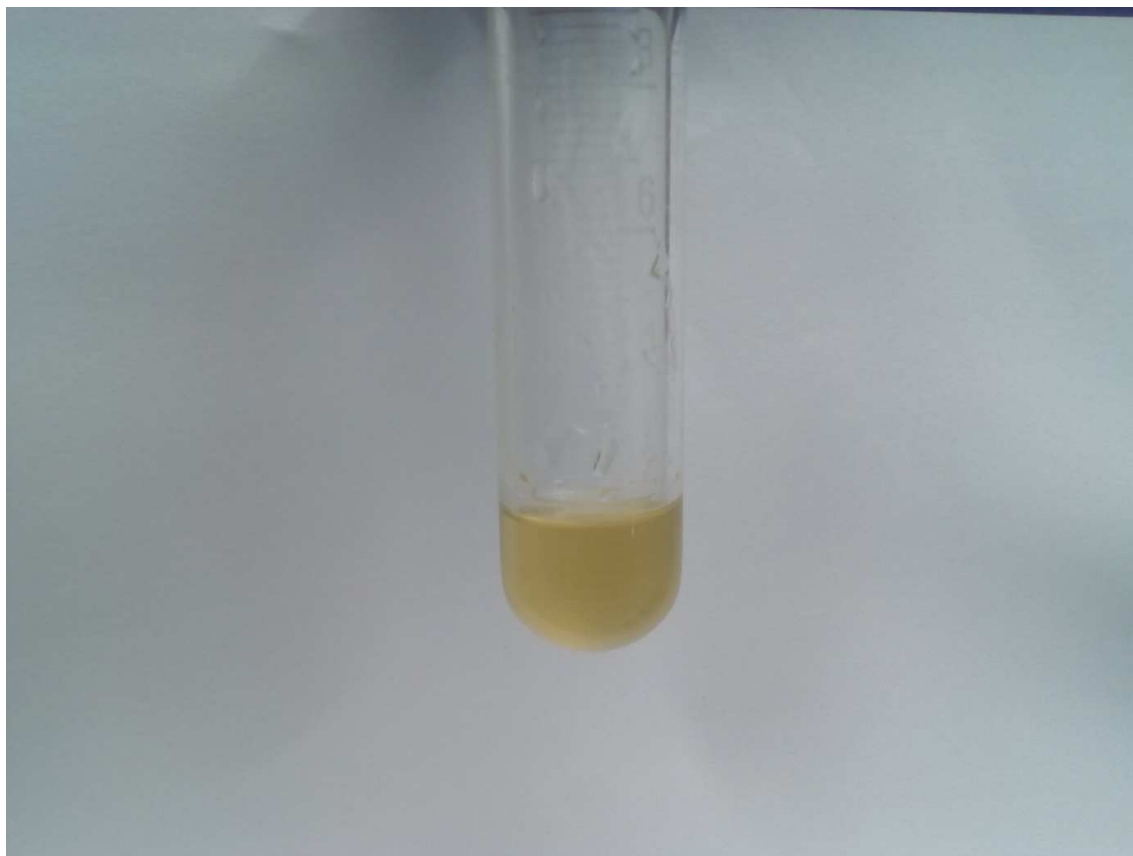


Figure S3. Solution of $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$ in $[\text{bmim}][\text{Tf}_2\text{N}]$



Figure S4. Solution of $\text{Hf}(\text{O}_2\text{CNEt}_2)_4$ in $[\text{bmim}][\text{Tf}_2\text{N}]$

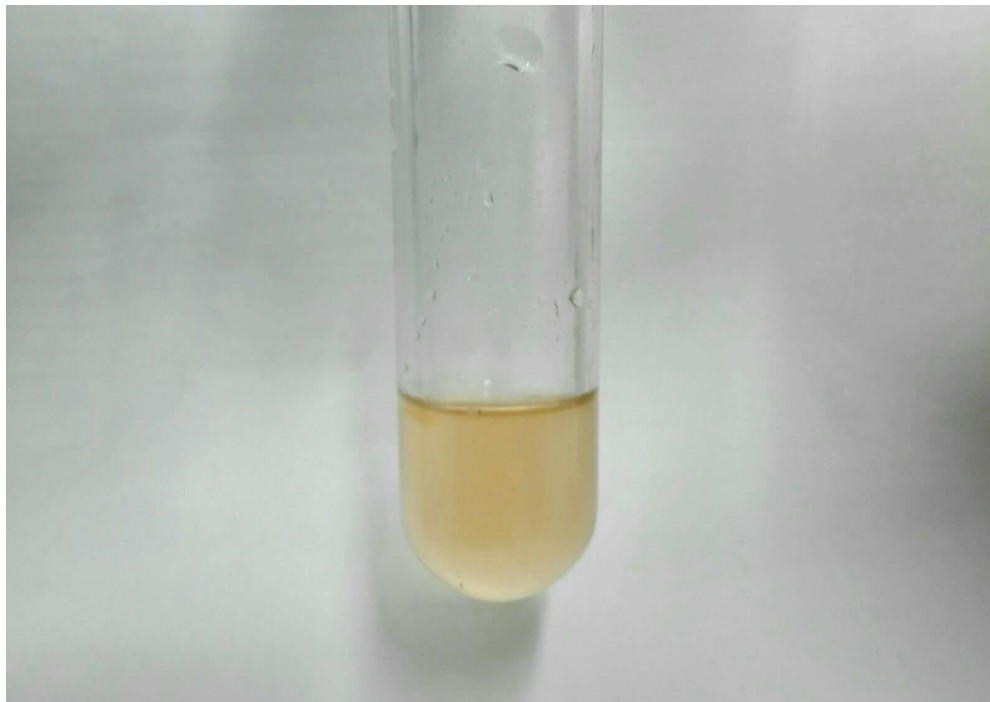


Figure S5. Solution of NbF_5 in $[\text{bmim}][\text{Tf}_2\text{N}]$



Figure S6. Solution of NbCl_5 in $[\text{bmim}][\text{Tf}_2\text{N}]$



Figure S7. Solution of $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$ in $[\text{bmim}][\text{Tf}_2\text{N}]$



Figure S8. Solution of $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$ in $[\text{bmim}][\text{Tf}_2\text{N}]$



Figure S9. Solution of $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$ in $[\text{bmim}][\text{Tf}_2\text{N}]$

