Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Modifying Bis(Triflimide) Ionic Liquids by Dissolving Early Transition Metal Carbamates

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SUPPORTING INFORMATION

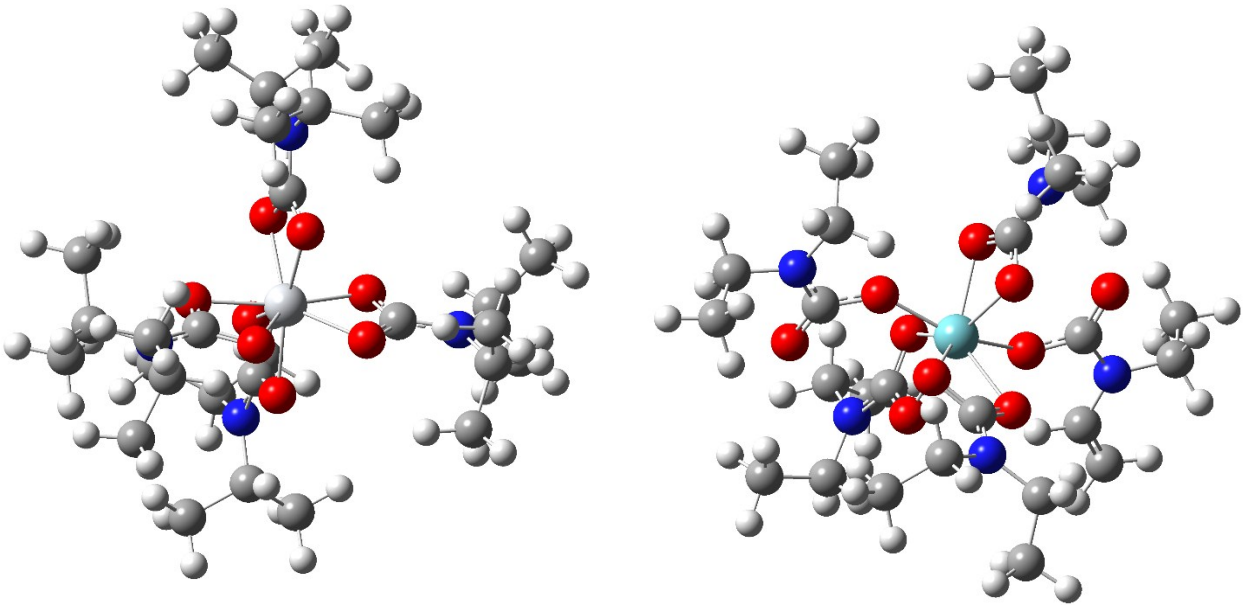

Figure S1. DFT-optimized structures of $Ti(O_2CN^iPr_2)_4$ (left) and $Nb(O_2CNEt_2)_5$ (right).

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

Compound	IR[a]: ν(CO_2) / cm^{-1}	NMR: δ(CO_2) / ppm		R(M-O)/Å	
	calculated	calculated	experimental [a]	calculated	experimental [b]
$Ti(O_2CN^iPr_2)_4$	1532, 1563, 1568, 1576	174.6-174.8	170.6	2.08-2.11	2.033- 2.110
$Zr(O_2CNEt_2)_4$	1530, 1540, 1580	177.4	170.4	2.23-2.24	2.180-2.276
$Zr(O_2CN^iPr_2)_4$	1482, 1509, 1516, 1521	177.8-178.9	170.3	2.23-2.24	---
$Nb(O_2CNEt_2)_5$	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)
$NbO(O_2CNEt_2)_3$	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)
$Ta(O_2CNEt_2)_5$	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: $Ti(O_2CN^iPr_2)_4$: D. Belli Dell'Amico, F. Calderazzo, S. Ianelli, L. Labella, F. Marchetti, G. Pelizzi, J. Chem. Soc., Dalton Trans. 2000, 4339. $Zr(O_2CNEt_2)_4$: 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. $Nb(O_2CNEt_2)_5$ and $NbO(O_2CNEt_2)_3$: M. Bortoluzzi, F. Ghini, M. Hayatifar, F. Marchetti, G. Pampaloni, S. Zacchini *Eur. J. Inorg. Chem.* 2013, 3112–3118. $Ta(O_2CNEt_2)_5$: 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 $Ti(O_2CNEt_2)_4$ in $[bmim][Tf_2N]$

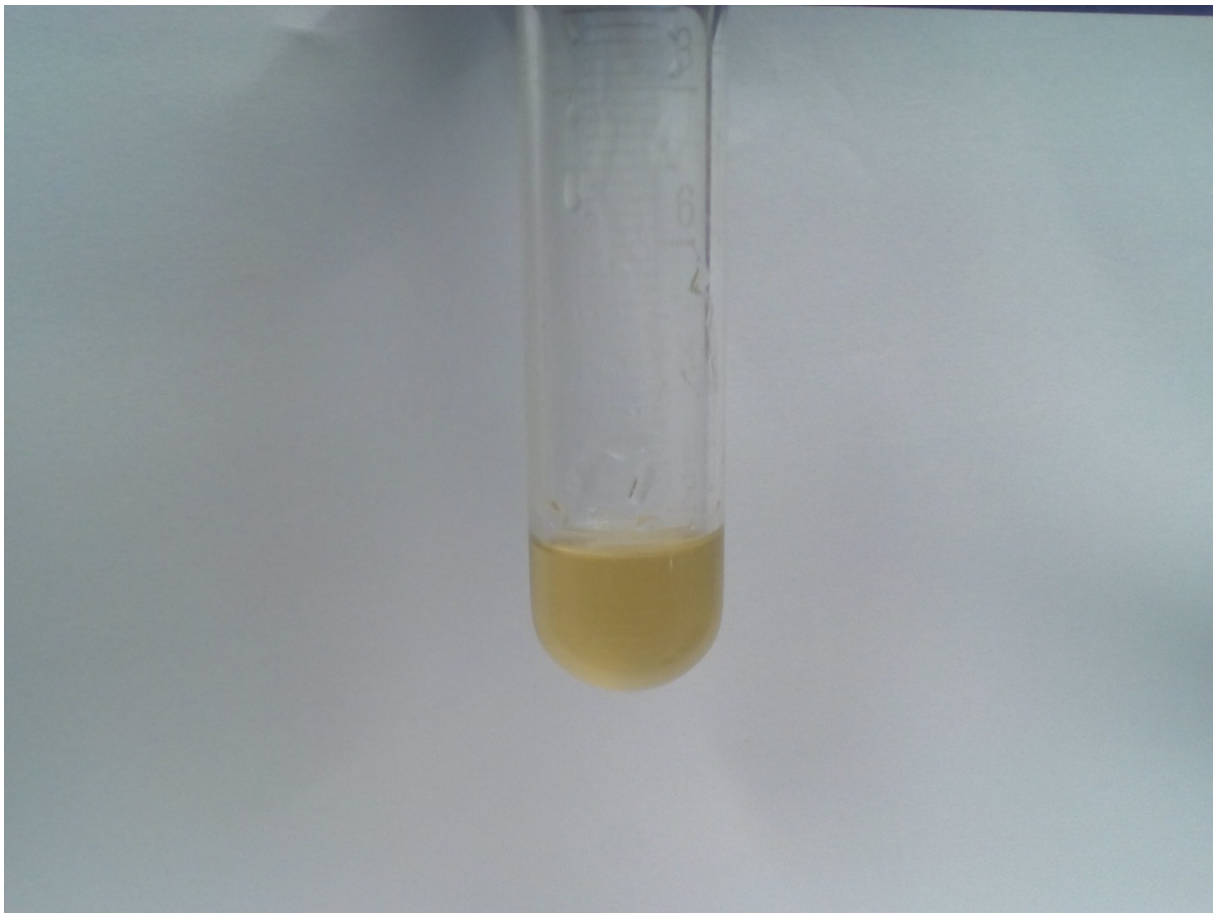

Figure S3. Solution of $Zr(O_2CNEt_2)_4$ in $[bmim][Tf_2N]$

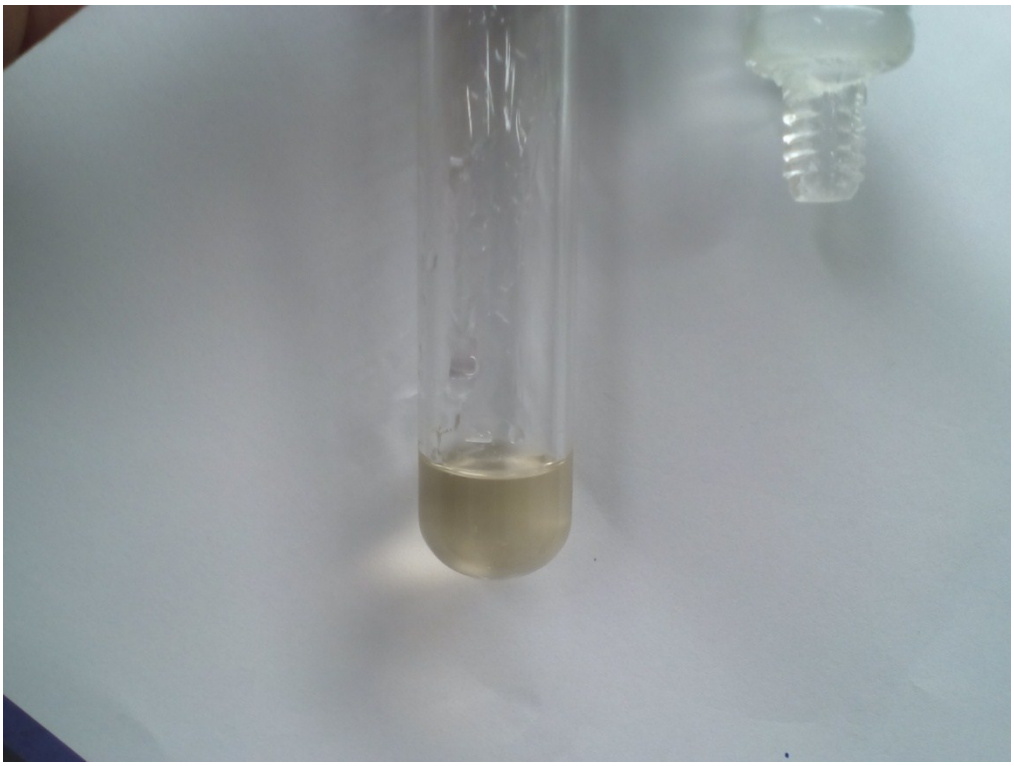

Figure S4. Solution of $Zr(O_2CN^iPr_2)_4$ in $[bmim][Tf_2N]$

Figure S5. Solution of $Hf(O_2CNEt_2)_4$ in [bmim][Tf_2N]

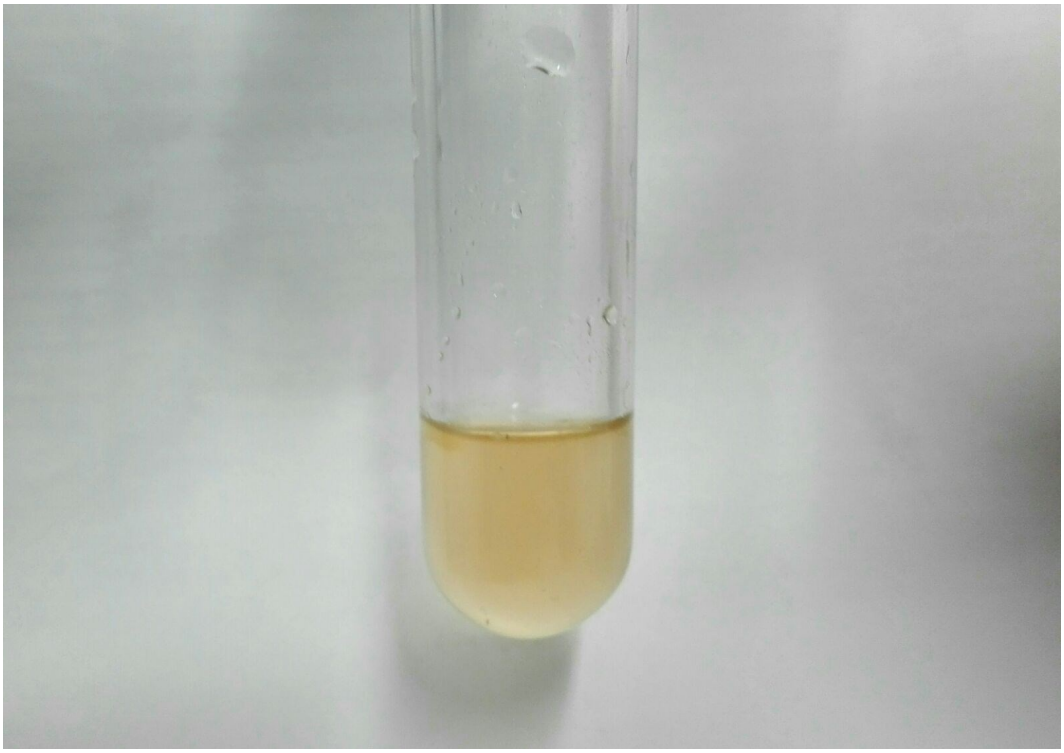

Figure S6. Solution of NbF_5 in [bmim][Tf_2N]

Figure S7. Solution of $NbCl_5$ in [bmim][Tf_2N]

Figure S8. Solution of $Nb(O_2CNEt_2)_5$ in [bmim][Tf_2N]

Figure S9. Solution of $NbO(O_2CNEt_2)_3$ in [bmim][Tf_2N]

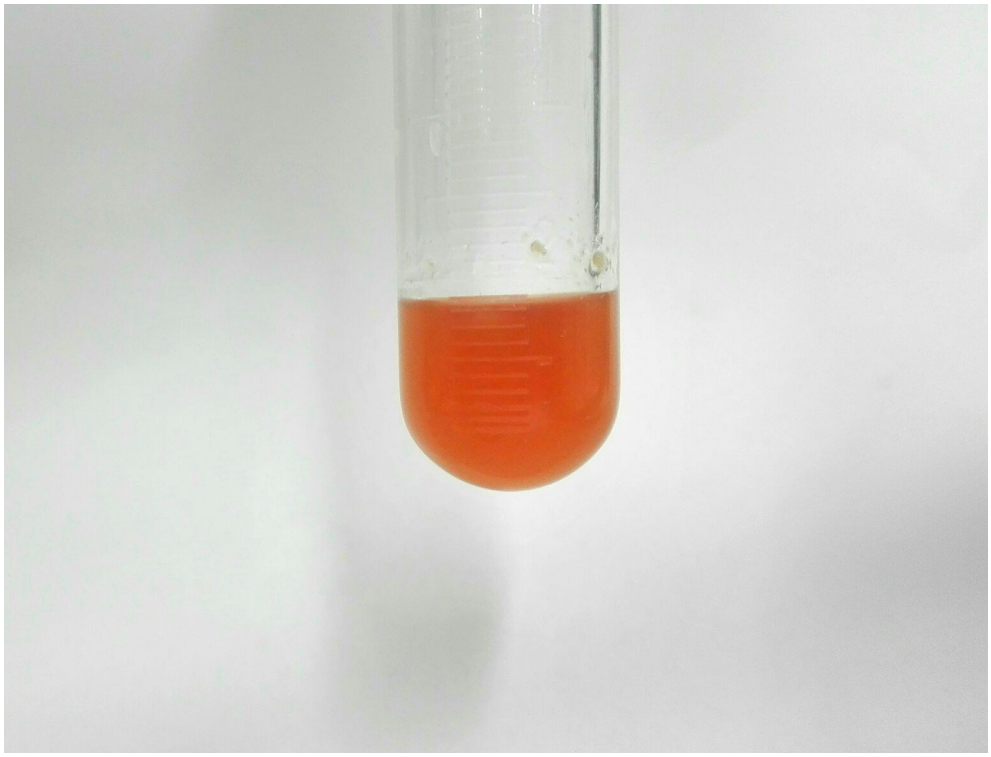

Figure S10. Solution of $Ta(O_2CNEt_2)_5$ in [bmim][Tf_2N]