The Reactions of α-Amino Acids and α-Amino Esters with High Valent Transition Metal Halides: Synthesis of Coordination Complexes, Activation Processes and Stabilization of α-Ammonium Acylchloride Cations

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Supporting Information

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Scheme S1. Proposed pathway to the formation of complex 3. M06 calculations, C-PCM implicit salvation model for dichloromethane. Relative Gibbs energies are referred to $Nb_2Cl_9(L\text{-prolinate})$, A (G = 0 kcal mol^{-1}). The Gibbs energy variations associated with side-reactions (e.g. $NbOCl_3$ polymerisation, interaction of HCl with bases) are not considered.   S10

Figure S1. DFT-optimized geometries of the possible isomers of **1b** (C-PCM/ωB97X calculations) and relative Gibbs energies (kcal mol^{-1}), referred to the [TiCl$_4$(phenylalanine)] unit.

| 0 | 4.1 | 0.7 |
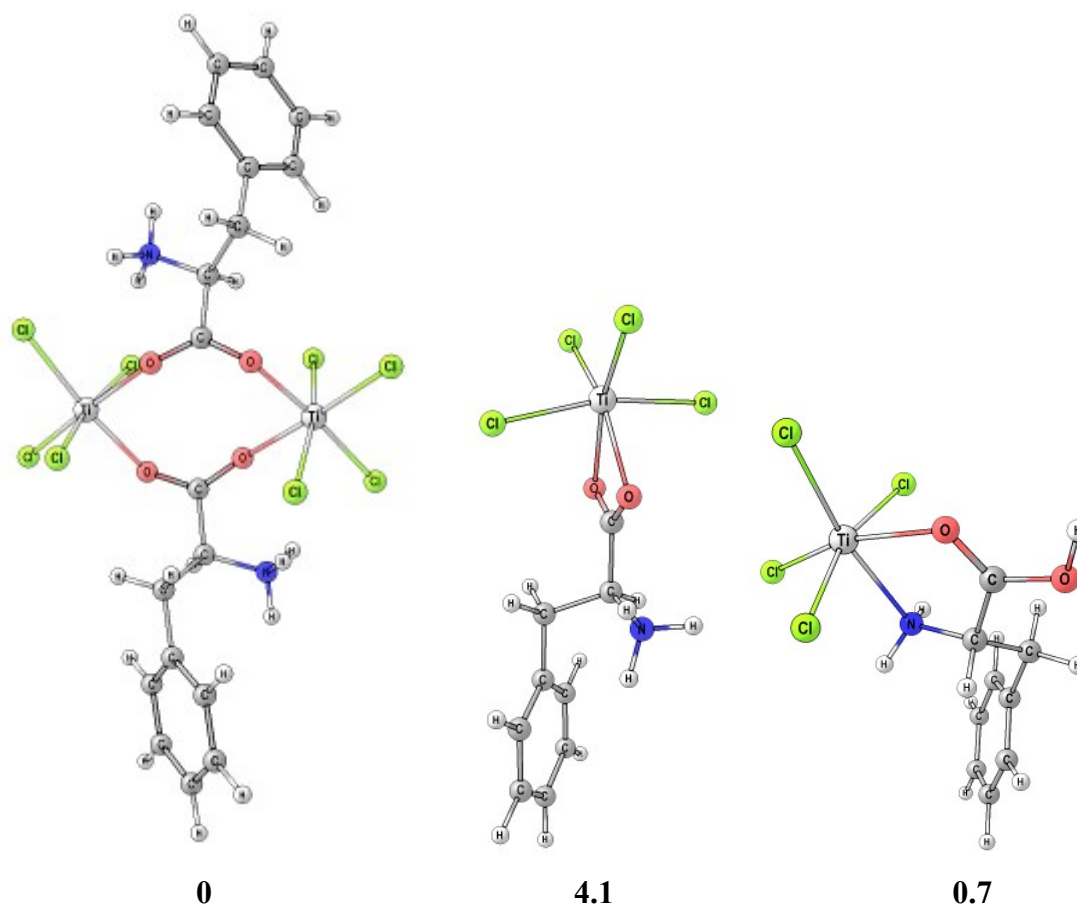
Figure S2. DFT-optimized anions of **2a** and **2b** (EDF2 functional) and relative Gibbs energies (kcal mol^{-1}), referred to the [TiCl$_4$(amino acidate)]$^-$ units.
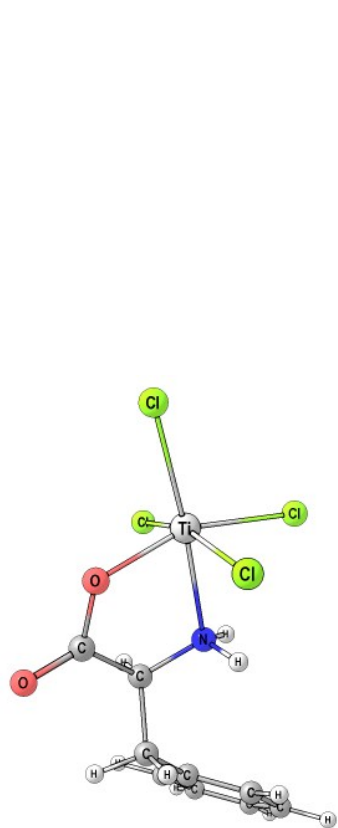
2a   0   33.3

2b   0   43.1

Figure S3. ORTEP drawing of [NH$_2$^{i}Pr$_2$][NbCl$_6$], **4**. Displacement ellipsoids are at the 50% probability level.
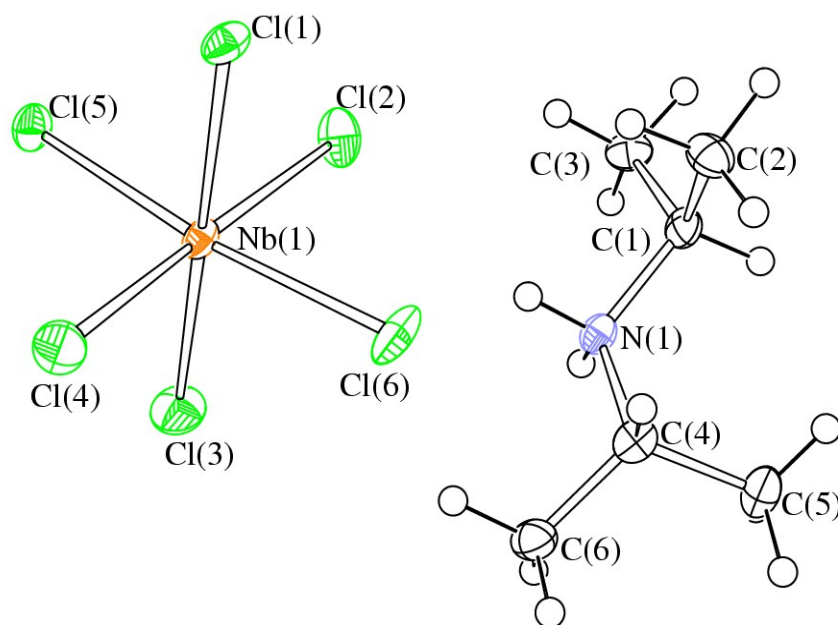
Table S1A. Selected bond lengths (Å) and angles (deg) for **4**.

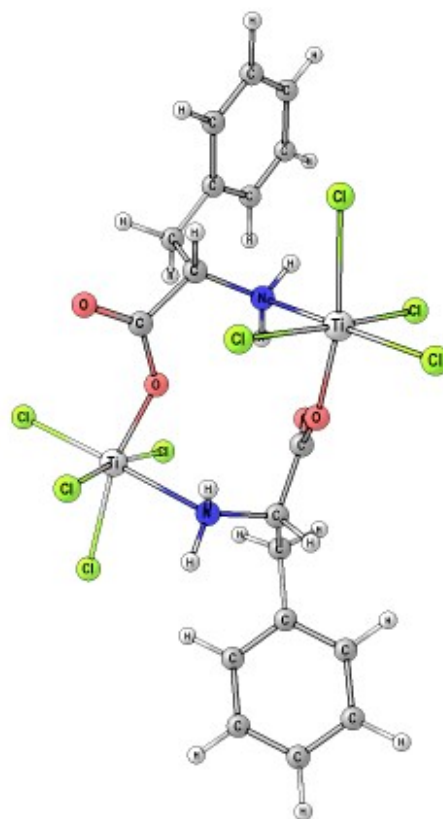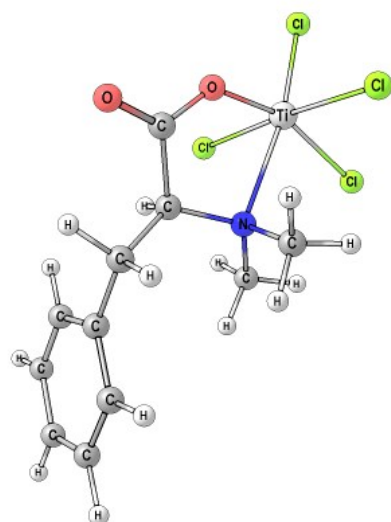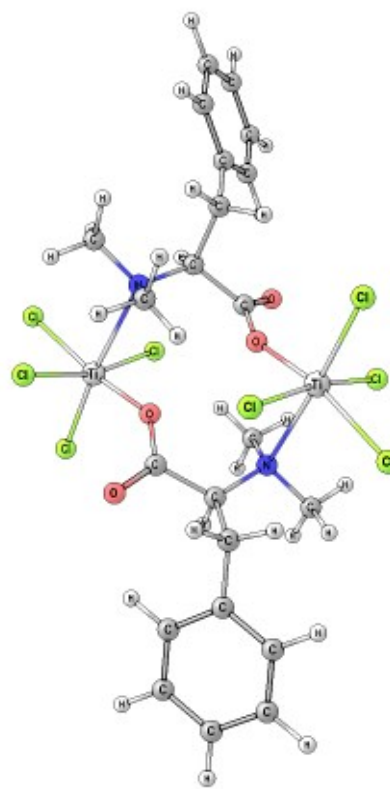| Nb(1)–Cl(1)	2.3927(12)	Nb(1)–Cl(2)	2.3944(13)
Nb(1)–Cl(3)	2.3145(13)	Nb(1)–Cl(4)	2.3082(13)
Nb(1)–Cl(5)	2.3299(12)	Nb(1)–Cl(6)	2.3663(13)
N(1)–C(1)	1.512(5)	N(1)–C(4)	1.518(5)
C(1)–C(2)	1.512(6)	C(1)–C(3)	1.514(6)
C(4)–C(5)	1.526(6)	C(4)–C(6)	1.509(6)
Cl(1)–Nb(1)–Cl(3)	179.70(5)	Cl(2)–Nb(1)–Cl(4)	176.93(4)
Cl(5)–Nb(1)–Cl(6)	173.45(4)	C(1)–N(1)–C(4)	119.0(3)

Table S1B. Hydrogen bonds (Å and deg) for **4**.

D-H⋯A	d(D–A)	d(H⋯A)	d(D⋯A)	<(DHA)
N(1)–H(12)⋯Cl(1)#1	0.920(19)	2.47(2)	3.358(4)	162(4)
N(1)–H(12)⋯Cl(6)#1	0.920(19)	2.84(4)	3.412(4)	121(3)
N(1)–H(11)⋯Cl(2)	0.919(19)	2.71(2)	3.618(4)	168(4)

Symmetry transformations used to generate equivalent atoms: #1 x,–y+1/2,z–1/2

Figure S4. DFT-optimized cations of **9** (EDF2 functional) and relative Gibbs energies (kcal mol^{-1}).

0   32.2   35.5

Figure S5. DFT-optimized isomers (EDF2 functional) of NbF$_5$(Me$_2$CHCH$_2$CHNH$_2$CO$_2$Me) and relative Gibbs energies (kcal mol^{-1}).

0   1.8
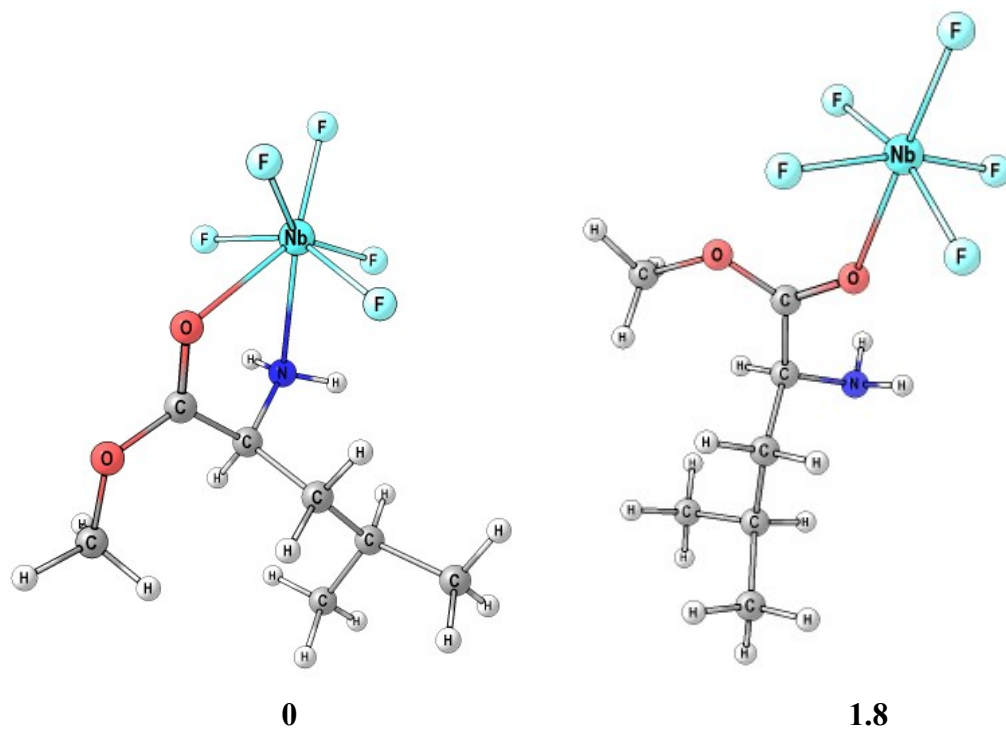
Figure S6. ORTEP drawing of of the [NbCl$_6$]$^-$ anion in**12**. Displacement ellipsoids are at the 50% probability level.
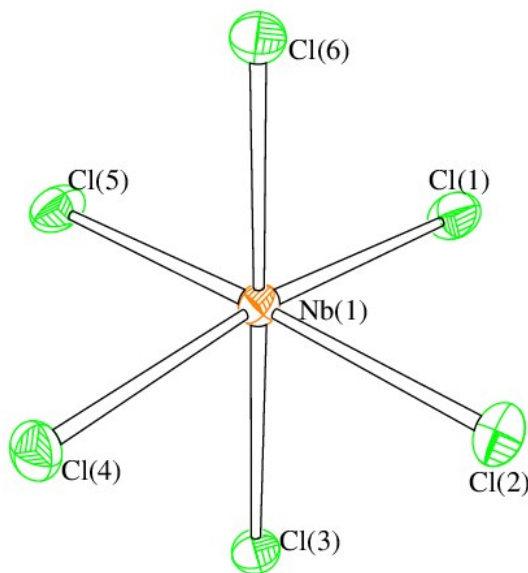
Table S2A. . Selected bond lengths (Å) and angles (deg) for the [NbCl$_6$]$^-$ anion of **12**.

Nb(1)–Cl(1)	2.3526(9)	Nb(1)–Cl(2)	2.3591(9)
Nb(1)–Cl(3)	2.4307(9)	Nb(1)–Cl(4)	2.3670(9)
Nb(1)–Cl(5)	2.3388(9)	Nb(1)–Cl(6)	2.2825(9)
Cl(1)–Nb(1)–Cl(4)	172.60(3)	Cl(2)–Nb(1)–Cl(5)	176.49(3)
Cl(3)–Nb(1)–Cl(6)	179.07(4)		

Table S2B. Hydrogen bonds (Å and deg) for **12**.

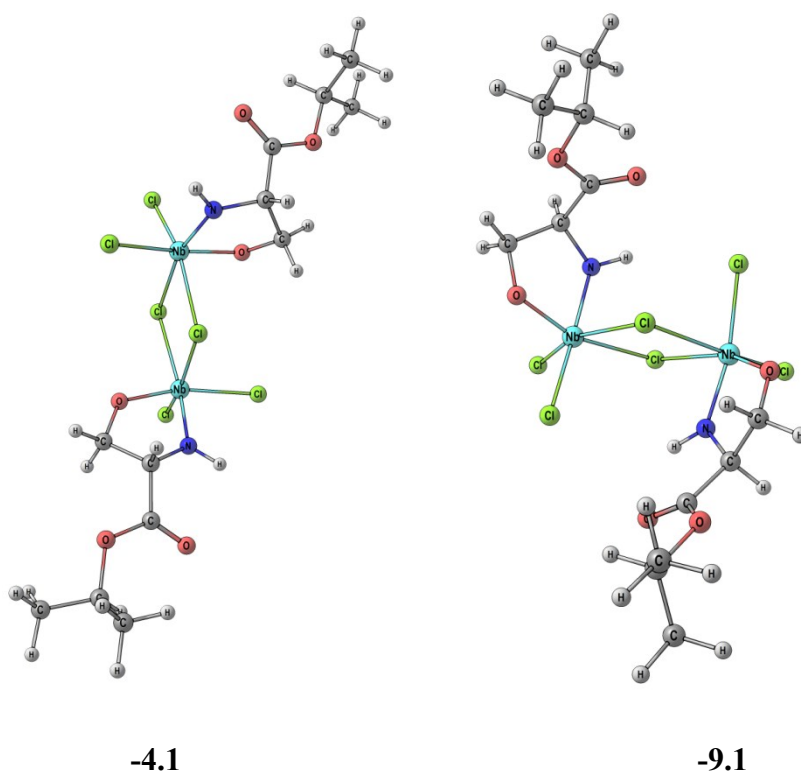| D-H···A	d(D–A)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1A)···Cl(4)#1	0.915(18)	2.555(19)	3.461(3)	171(3)
N(1)–H(1B)···Cl(1)#2	0.913(17)	2.46(2)	3.296(3)	153(3)
N(1)–H(1B)···Cl(2)#2	0.913(17)	2.89(3)	3.335(3)	111(2)
N(1)–H(1C)···Cl(3)#3	0.892(18)	2.50(2)	3.366(3)	163(3)

Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1   #2 –x+1,y-1/2,–z+1   #3 –x+1,y+1/2,-z+1

Figure S7. DFT-optimized isomers of **13** (M06 functional) and relative Gibbs energies (kcal mol^{-1}) referred to the mononuclear stoichiometry.

0   **3.5**
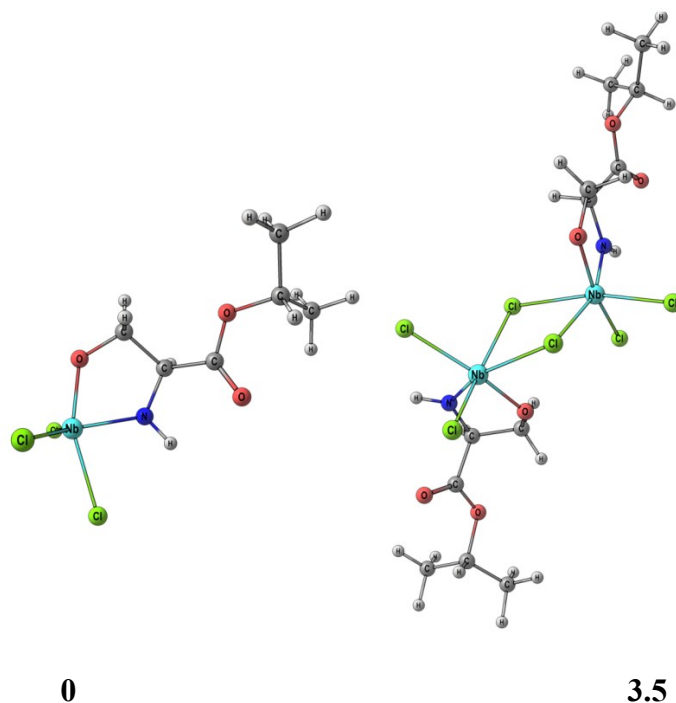
Figure S8. DFT-optimized dinuclear isomers of **13** (EDF2 functional) and relative Gibbs energies (kcal mol^{-1}) referred to the mononuclear stoichiometry. The EDF2-optimized mononuclear complex was taken as zero. Other dinuclear isomers resulted unstable towards dissociation to mononuclear complexes.

-4.1   **-9.1**

Scheme S1. Proposed pathway to the formation of complex **3**. M06 calculations, C-PCM implicit salvation model for dichloromethane. Relative Gibbs energies are referred to Nb_2Cl_9(*L*-prolinate), **A** ($G = 0$ kcal mol^{-1}). The Gibbs energy variations associated with side-reactions (e.g. $NbOCl_3$ polymerisation, interaction of HCl with bases) are not considered.