

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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Figure S1. ORTEP drawing of $[\text{TMGH}]_6[\text{TiCl}_6]\text{Cl}_4 \cdot 2\text{MeCN}$, **3**, with key atoms labelled. Displacement ellipsoids are at the 50 % probability level. The asymmetric unit of the unit cell is represented which contains: half of a $[\text{TiCl}_6]^{2-}$ anion (the whole anion is represented), two Cl^- anions, one MeCN molecule. Symmetry transformations used to generate equivalent atoms: $-x+1, -y, -z+1$

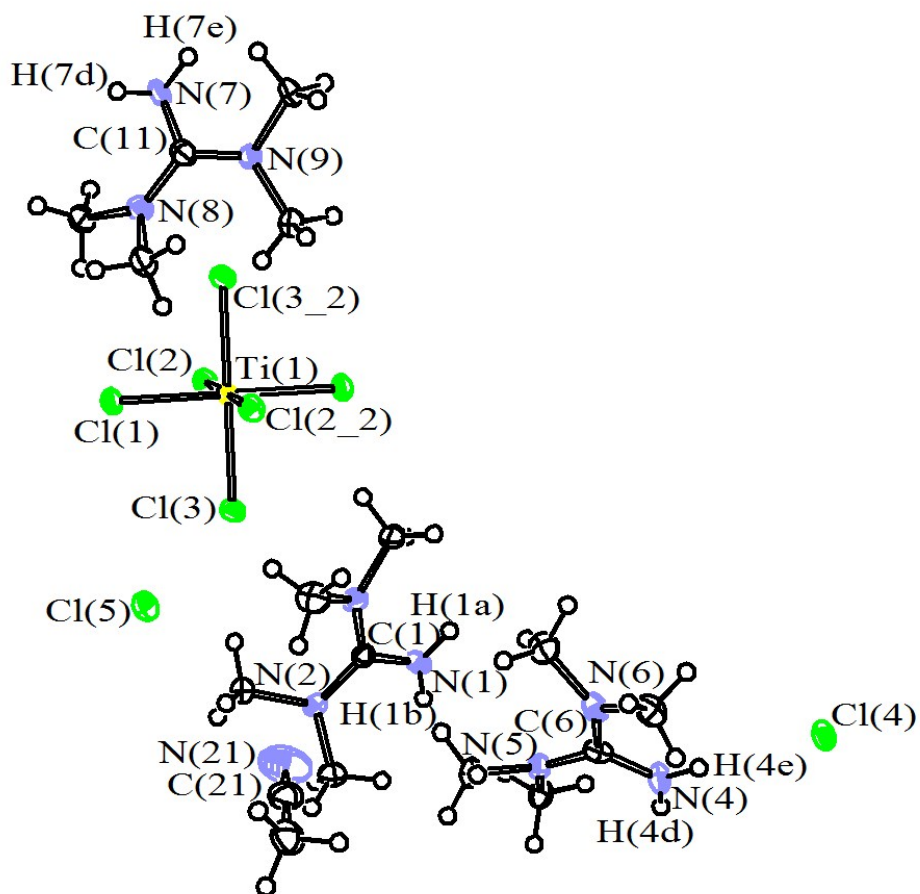


Table S1

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**

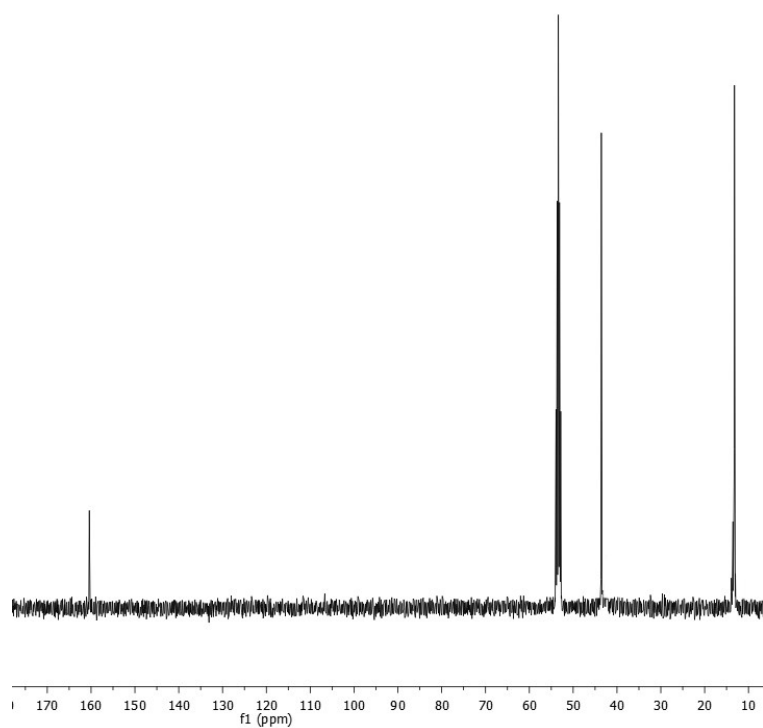


Figure S3. ^{13}C NMR spectrum (CDCl_3) of $\text{Ti}(\text{O}_2\text{CNet}_2)_4$

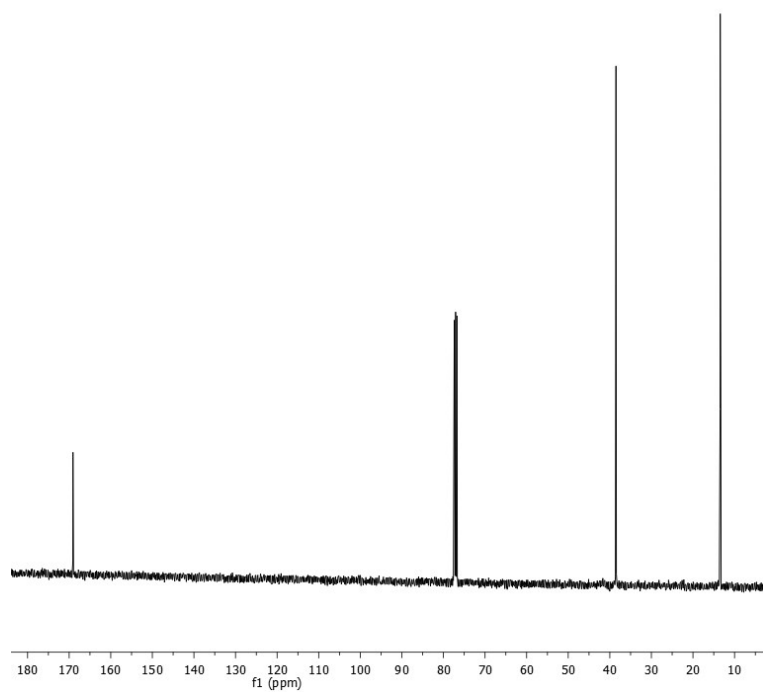


Figure S4. ^{13}C NMR spectrum (CD_2Cl_2) of **6**

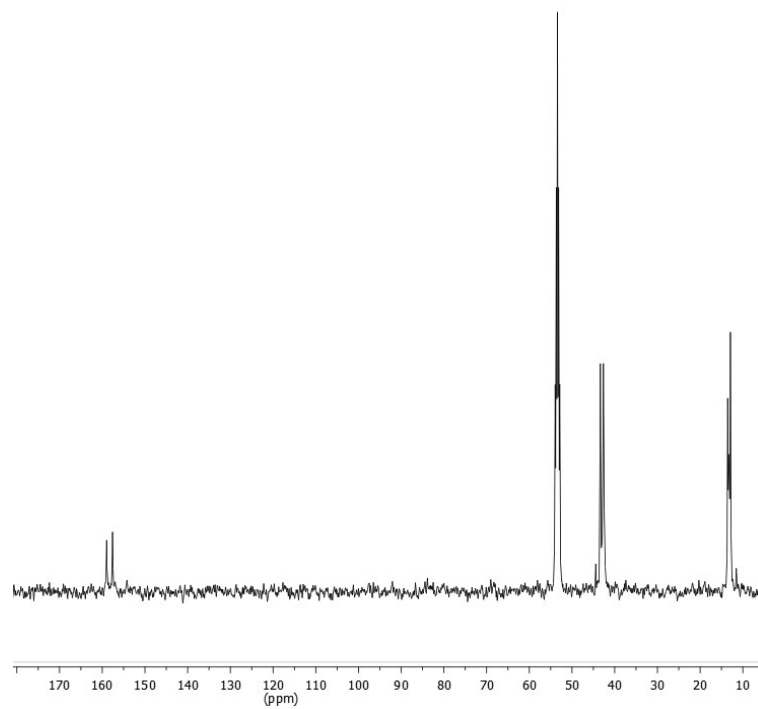


Figure S5. ^{13}C NMR spectrum (CD_2Cl_2) of **7**

