Electronic Supplementary Material (ESI) for Dalton Transactions.

Stable Coordination Complexes of α-Diimines with Nb(V) and Ta(V) Halides

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Figure SI-1. DFT-optimized geometry of $[NbF_4(\mathbf{DAD}^{Mes})_2]^+$ (C-PCM/ωB97X, dichloromethane as continuous medium). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Nb-F 1.889, 1.889, 1.889, 1.889; Nb-N 2.401, 2.401, 2.401, 2.401; C=N 1.271, 1.271, 1.271, 1.271. Selected angles (°): N-Nb-N (chelate) 67.6, 67.6; F-Nb-F (trans) 145.2, 145.2. Inset: polyhedron around the metal centre.

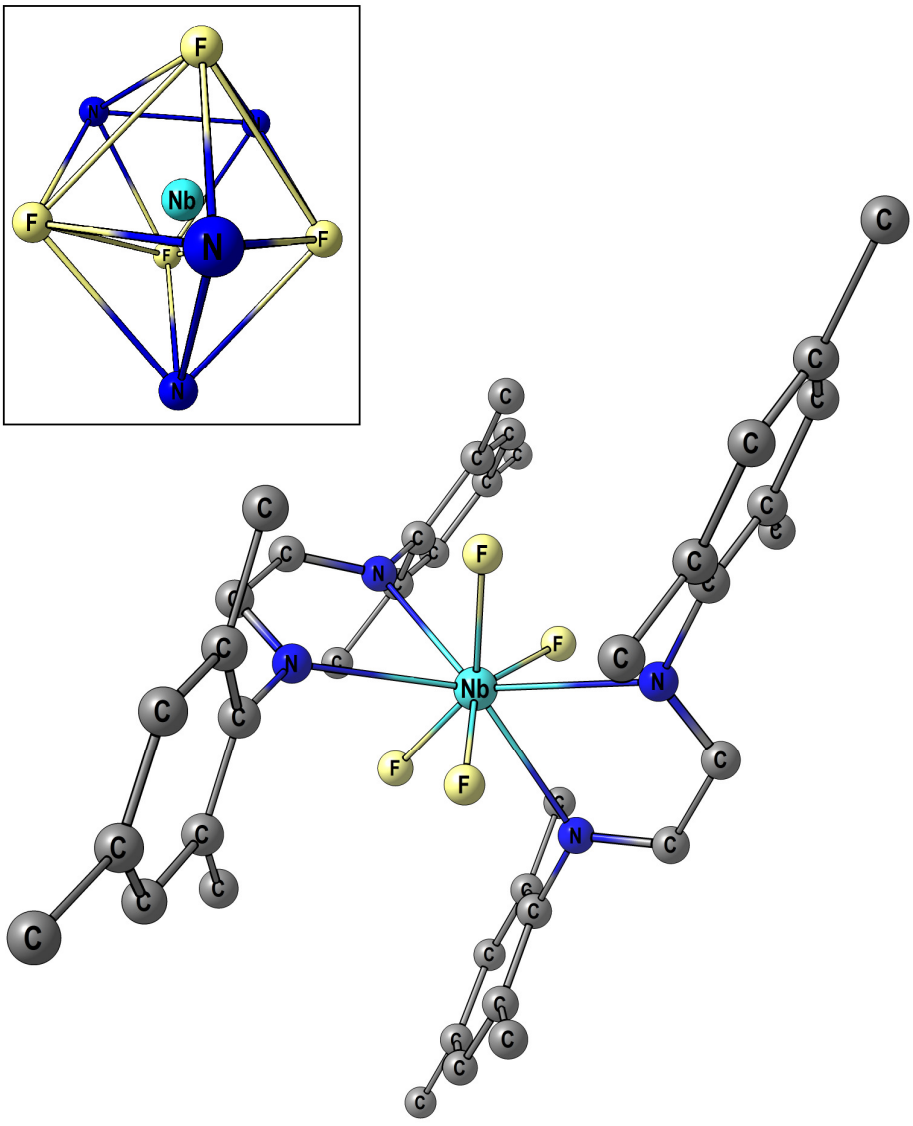


Figure SI-2. DFT-optimized geometry of $[NbF_4(\mathbf{DAD}^{Dip})_2]^+$ (C-PCM/ωB97X, dichloromethane as continuous medium). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Nb-F 1.885, 1.885, 1.886, 1.886; Nb-N 2.434, 2.434, 2.438, 2.438; C=N 1.272, 1.272, 1.272, 1.272. Selected angles (°): N-Nb-N (chelate) 67.0, 67.0; F-Nb-F (trans) 146.1, 146.1. Inset: planes crossing the DAD^{Ipr} donor moieties.

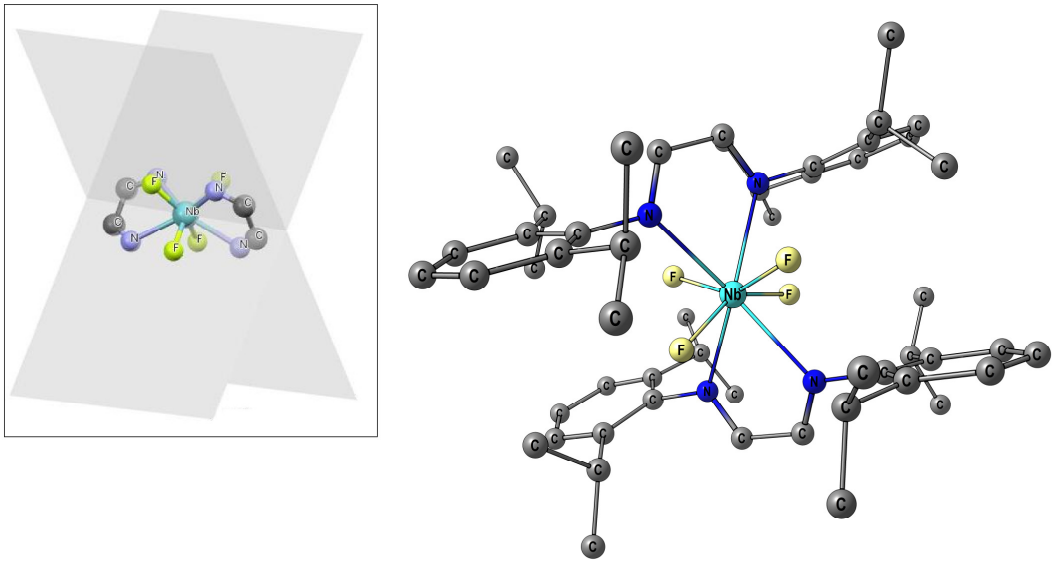


Figure SI-3. ORTEP drawing of [{2,6-$C_6H_3(CHMe_2)_2$}$N(CH)_2NCC(CHMe_2)(CH)_3C$][$NbCl_6$], **2**. Displacement ellipsoids are at the 50% probability level.

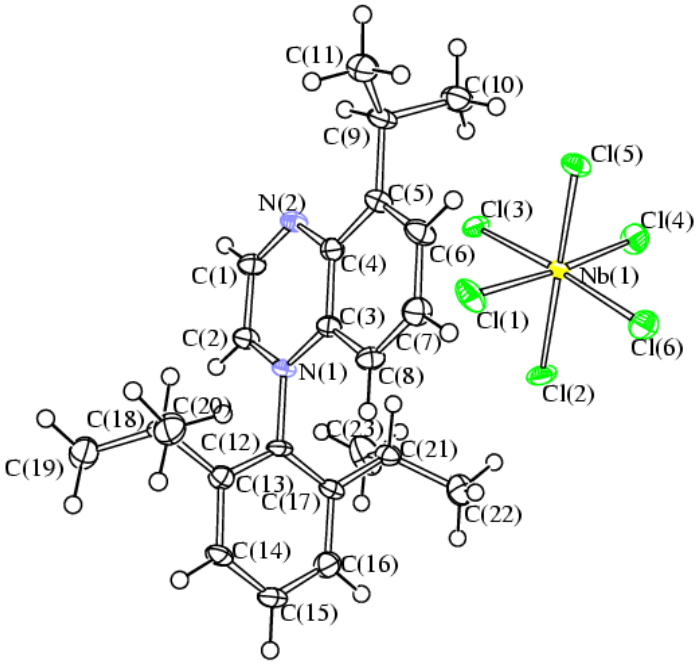


Table SI-1. Selected bond lengths (Å) and angles (deg) for **2**.

Nb(1)-Cl(1)	2.3676(11)	Nb(1)-Cl(2)	2.3814(11)
Nb(1)-Cl(3)	2.3598(10)	Nb(1)-Cl(4)	2.3096(11)
Nb(1)-Cl(5)	2.3284(10)	Nb(1)-Cl(6)	2.3270(11)
C(1)-C(2)	1.406(5)	C(3)-C(4)	1.427(5)
C(1)-N(2)	1.316(4)	C(4)-N(2)	1.354(4)
C(2)-N(1)	1.323(4)	C(3)-N(1)	1.383(4)
C(4)-C(5)	1.425(5)	C(5)-C(6)	1.366(5)
C(6)-C(7)	1.412(5)	C(7)-C(8)	1.371(5)
C(8)-C(3)	1.390(5)	N(1)-C(12)	1.475(4)
Cl(1)-Nb(1)-Cl(4)	174.99(4)	Cl(2)-Nb(1)-Cl(5)	177.89(4)
Cl(3)-Nb(1)-Cl(6)	174.67(4)	C(2)-C(1)-N(2)	122.7(3)
C(1)-N(2)-C(4)	118.3(3)	N(2)-C(4)-C(3)	121.6(3)
C(4)-C(3)-N(1)	116.9(3)	C(3)-N(1)-C(2)	121.2(3)
N(1)-C(2)-C(1)	119.2(3)	C(3)-C(4)-C(5)	119.1(3)
C(4)-C(5)-C(6)	117.3(3)	C(5)-C(6)-C(7)	122.7(3)
C(6)-C(7)-C(8)	121.2(3)	C(7)-C(8)-C(3)	117.7(3)
C(8)-C(3)-C(4)	122.0(3)		

Figure SI-4. ORTEP drawing of $NbCl_4$(**DAD**^{Dip}), **3**. Displacement ellipsoids are at the 50% probability level.

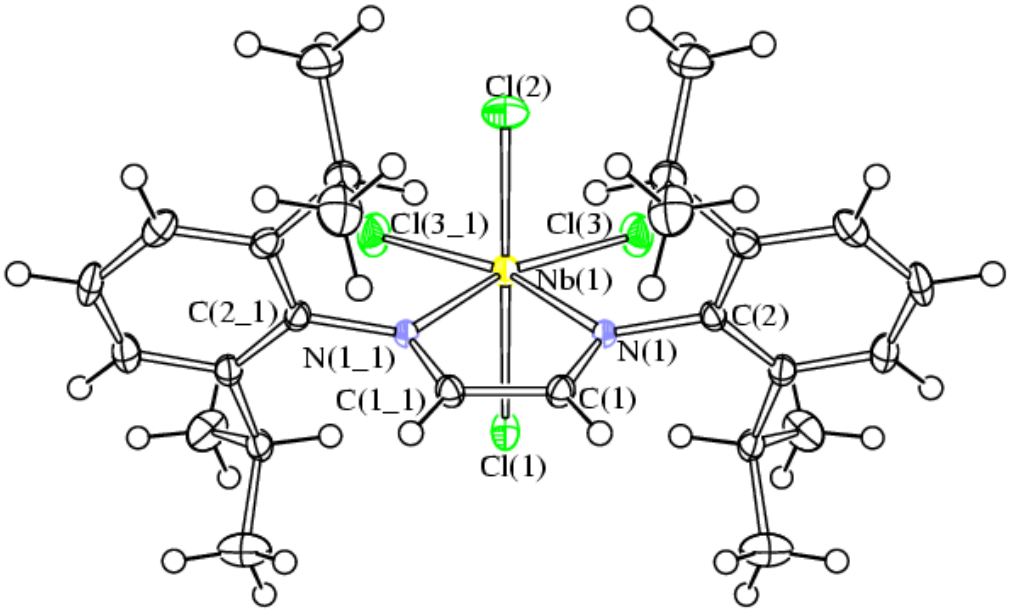


Table SI-2. Selected bond lengths (Å) and angles (deg) for **3**.

Nb(1)-Cl(1)	2.4194(8)	Nb(1)-Cl(2)	2.3306(9)
Nb(1)-Cl(3)	2.3088(6)	Nb(1)-N(1)	2.2211(17)
N(1)-C(1)	1.296(3)	C(1)-C(1_1)	1.444(4)
Cl(1)-Nb(1)-Cl(2)	178.28(3)	Cl(3)-Nb(1)-N(1_1)	162.51(5)
N(1)-Nb(1)-N(1_1)	73.01(9)	Cl(3)-Nb(1)-Cl(3_1)	106.93(3)
Nb(1)-N(1)-C(1)	114.99(14)	Nb(1)-N(1)-C(2)	129.27(13)
C(1)-N(1)-C(2)	115.59(17)	N(1)-C(1)-C(1_1)	117.54(12)

Figure SI-5. ORTEP drawing of [**DAD**^{Dip}(H)][$NbCl_6$], **4a**. Displacement ellipsoids are at the 50% probability level.

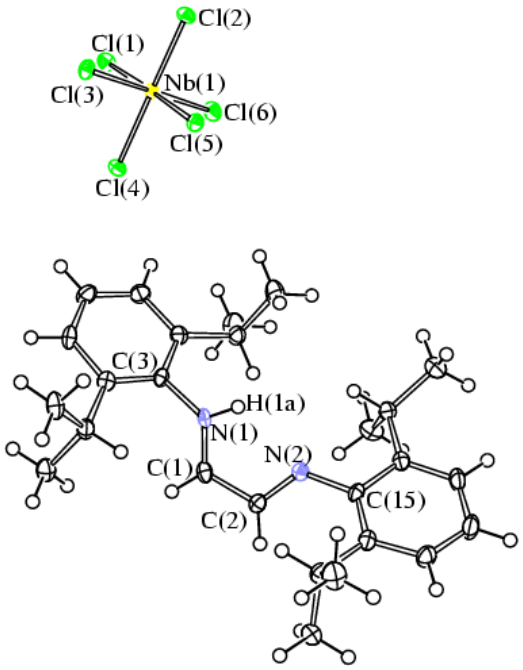


Table SI-3. Selected bond lengths (Å) and angles (deg) for **4a**.

Nb(1)-Cl(1)	2.3319(9)	Nb(1)-Cl(2)	2.3380(9)
Nb(1)-Cl(3)	2.3779(9)	Nb(1)-Cl(4)	2.3684(9)
Nb(1)-Cl(5)	2.3769(9)	Nb(1)-Cl(6)	2.3125(9)
N(1)-C(1)	1.275(4)	N(2)-C(2)	1.274(4)
C(1)-C(2)	1.473(5)	N(1)-C(3)	1.441(4)
N(2)-C(15)	1.414(4)		
Cl(1)-Nb(1)-Cl(5)	176.71(3)	Cl(2)-Nb(1)-Cl(4)	177.67(3)
Cl(3)-Nb(1)-Cl(6)	179.66(4)	N(1)-C(1)-C(2)	117.9(3)
C(1)-C(2)-N(2)	114.8(3)	C(2)-N(2)-C(15)	124.4(3)
C(1)-N(1)-C(3)	130.1(3)		

Table SI-3B. Hydrogen bonds (Å and deg) for **4a**.

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(DHA)**
N(1)-H(1A) ··N(2)	0.881(18)	2.11(3)	2.606(4)	115(3)

Figure SI-6. ORTEP drawing of [**DAD**^{Dip}(H)][$TaCl_6$], **4b**. Displacement ellipsoids are at the 50% probability level.

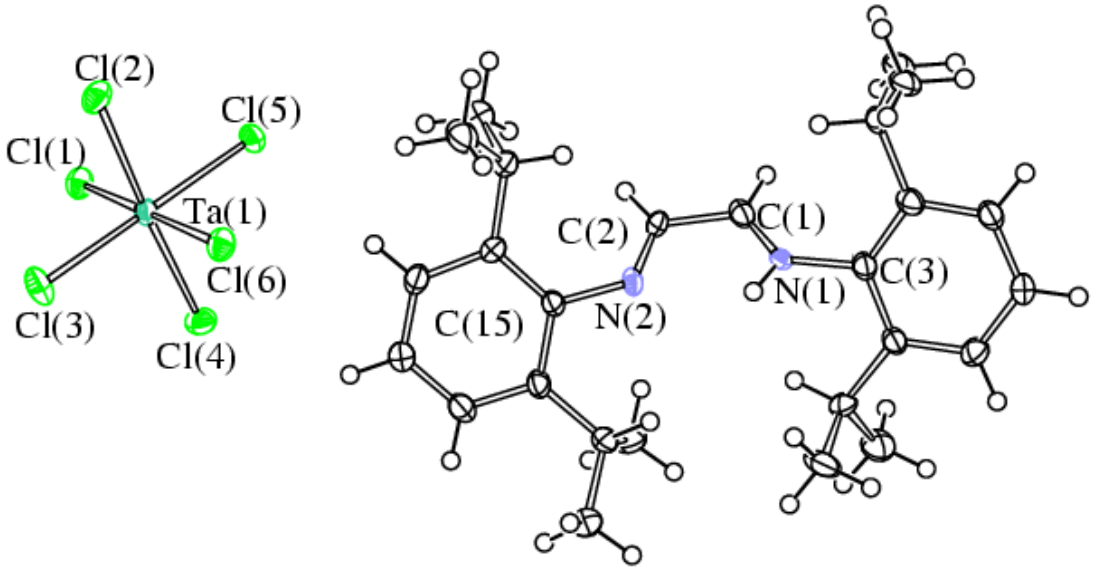


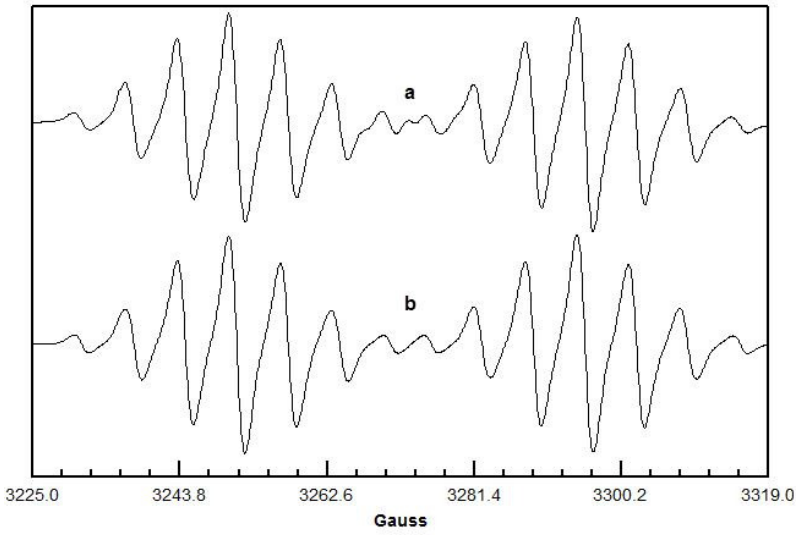
Table SI-4. Selected bond lengths (Å) and angles (deg) for **4b**.

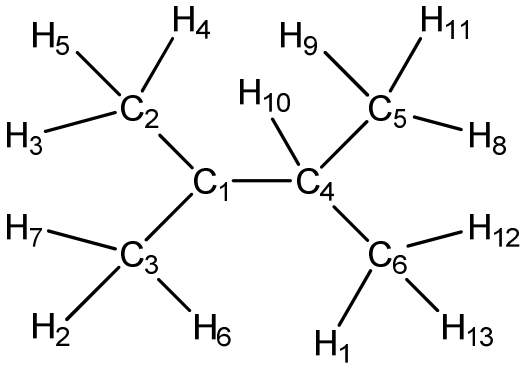
Ta(1)-Cl(1)	2.345(2)	Ta(1)-Cl(2)	2.3446(19)
Ta(1)-Cl(3)	2.324(2)	Ta(1)-Cl(4)	2.3832(19)
Ta(1)-Cl(5)	2.3802(19)	Ta(1)-Cl(6)	2.371(2)
N(1)-C(1)	1.275(10)	N(2)-C(2)	1.267(9)
C(1)-C(2)	1.496(10)	N(1)-C(3)	1.448(9)
N(2)-C(15)	1.428(8)		
Cl(1)-Ta(1)-Cl(6)	177.92(6)	Cl(2)-Ta(1)-Cl(4)	177.09(7)
Cl(3)-Ta(1)-Cl(5)	179.83(7)	N(1)-C(1)-C(2)	117.9(7)
C(1)-C(2)-N(2)	113.7(7)	C(2)-N(2)-C(15)	123.9(6)
C(1)-N(1)-C(3)	129.6(6)		

EPR analysis of the mixture $NbCl_5$/DAD^{Dip}.

A suspension of $NbCl_5$ (0.4 mmol) in CH_2Cl_2 (2 mL) was cooled to −90 °C and then treated with **DAD^{Dip}** (0.4 mmol). An aliquot of the resulting mixture was analyzed by EPR spectroscopy as a function of temperature and time.

Figure SI-7. EPR spectrum of the mixture $NbCl_5$/**DAD^{Dip}**: a) experimental (CH_2Cl_2, 213 K), b) calculated.





$(CH_3)_2CCH(CH_3)_2$, not rotating around C1–C4 (relative concentration = 100.00%)

Line width = 1.150 G; Lorentzian = 38.00%; g_{iso} = 2.00145

Hyperfine coupling constant

Set	*Spin*	*Number*	*Coupling (G), exp.*	*Coupling (G), DFT*
1	0.5	1 H	44.500	44.337 (H_{10})
2	0.5	3 H	6.810	7.300 (H_3 H_4 H_5)
3	0.5	3 H	6.360	7.300 (H_2 H_6 H_7)

Figure SI-8. DFT calculated spin density surface (0.002 electron/au^3) of $(CH_3)_2CHC(CH_3)_2$ at T = 213 K. Red: negative spin density; Green: positive spin density.

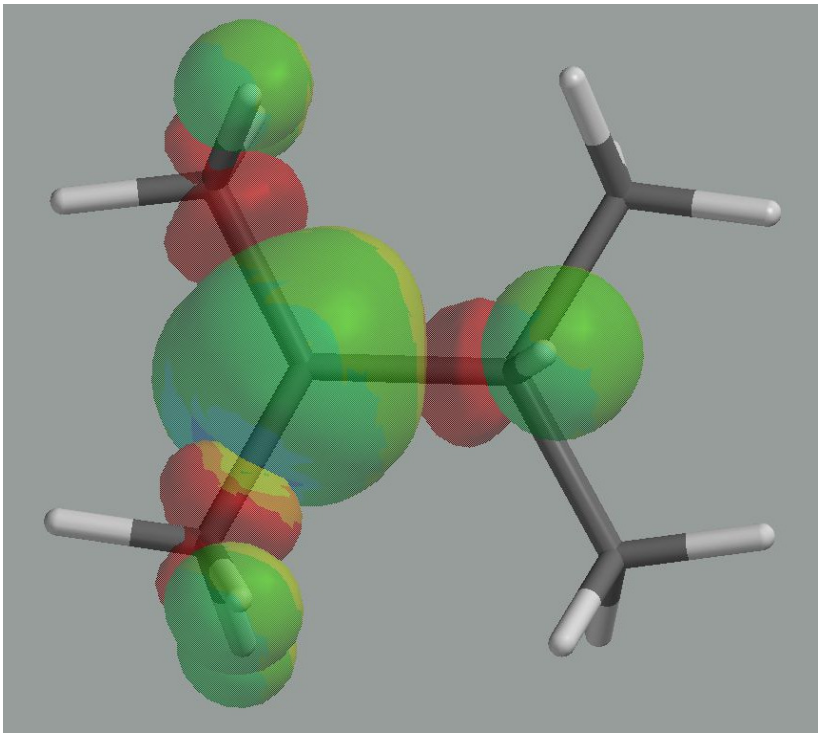


Figure SI-9. ORTEP drawing of [(2,6-$C_6H_3Me_2$)NCHCHN(2,6-$C_6H_3Me_2$)CCHN(2,6-$C_6H_3Me_2$)][$NbCl_6$], **5**. Displacement ellipsoids are at the 50% probability level.

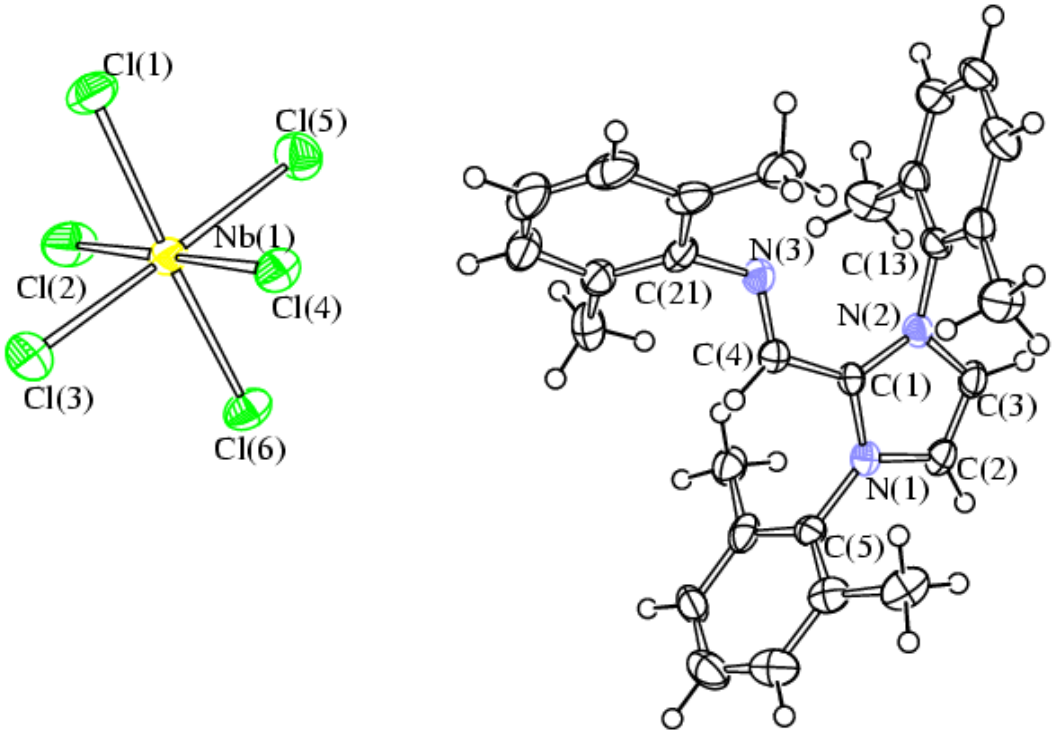


Table SI-5. Selected bond distances (Å) and angles (°) for **5**.

Nb(1)-Cl(1)	2.3547(17)	Nb(1)-Cl(2)	2.3470(18)
Nb(1)-Cl(3)	2.3247(19)	Nb(1)-Cl(4)	2.3634(17)
Nb(1)-Cl(5)	2.3500(18)	Nb(1)-Cl(6)	2.3483(17)
C(1)-N(1)	1.360(8)	N(1)-C(2)	1.379(8)
C(2)-C(3)	1.349(10)	C(3)-N(2)	1.370(9)
N(2)-C(1)	1.348(8)	C(1)-C(4)	1.462(9)
C(4)-N(3)	1.270(8)	N(3)-C(21)	1.429(9)
N(1)-C(5)	1.441(8)	N(2)-C(13)	1.445(8)
Cl(1)-Nb(1)-Cl(6)	177.41(7)	Cl(2)-Nb(1)-Cl(4)	178.95(7)
Cl(3)-Nb(1)-Cl(5)	178.51(7)	C(1)-N(1)-C(2)	108.6(5)
N(1)-C(2)-C(3)	107.2(6)	C(2)-C(3)-N(2)	108.0(6)
C(3)-N(2)-C(1)	109.0(5)	N(2)-C(1)-N(1)	107.2(5)
N(1)-C(1)-C(4)	123.1(5)	N(2)-C(1)-C(4)	129.6(6)
C(1)-C(4)-N(3)	119.9(6)	C(4)-N(3)-C(21)	118.5(6)

Figure SI-10. DFT-optimized structures of the isomers of $NbOCl_3(DAD^{Dip})$, **6**, and relative Gibbs energies. Hydrogen atoms are omitted for clarity.