Supplementary Information

Facile access to mid-valent Group 5 and 6 metal synthons

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Species specific observations during the preparation of MCl_4

$NbCl_4$. The addition of bright yellow $NbCl_5$ to toluene results in a dark, orange-red solution. Addition of dimethylphenylsilane does not result in rapid observable elimination of H_2. After stirring overnight, a fine, chocolate brown precipitate is recovered via vacuum filtration with a clear (or pale orange if an incomplete reduction occurs) filtrate.

$TaCl_4$. The addition of white, crystalline $TaCl_5$ to toluene results in a bright yellow solution. Addition of dimethylphenylsilane does not result in rapid observable elimination of H_2. After stirring overnight, a fine, olive-green precipitate is recovered via vacuum filtration with a clear (or pale yellow if an incomplete reduction occurs) filtrate.

$MoCl_4$. The addition of $MoCl_5$ to toluene results in a dark, yellow-brown solution/suspension. Upon addition of dimethylphenylsilane to the suspension, evolution of H_2 is immediate and vigorous. At the end of the experiment, when stirring is ceased, a clear supernatant is visible with insoluble, black $MoCl_4$ deposited at the bottom of the vial.

WCl_4. The addition of WCl_6 to toluene results in a deep, royal blue solution. Evolution of H_2 is noticeable upon the addition of dimethylphenylsilane, but much less pronounced than in the $MoCl_4$ reaction. Upon completion, the reaction appears to be a suspension of a fine, grey powder that resembles amorphous WCl_4 prepared via the $W(CO)_6$ reduction of WCl_6.[1] When left to sit, this suspension persists and upon filtering, a clear toluene filtrate is obtained.

Table S1. Crystal Data and structure refinement for $NbCl_4(dme)$.

Empirical formula	$C_4H_{10}Cl_4NbO_2$
Formula weight	324.83
Temperature/K	100.00(16)
Crystal system	monoclinic
Space group	Cc
a, b, c	8.11655(12), 11.38883(17), 11.79824(19)
α, β, γ	90, 90.2289(14), 90
Volume/Å^3	1090.60(3)
Z	4
ρ_{calc}g/cm^3	1.978
μ/mm^{-1}	2.039
F(000)	636.0
Crystal size/mm^3	0.303 × 0.1 × 0.063
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.164 to 67.522
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	34712
Independent reflections	4052 [R_{int} = 0.0594, R_{sigma} = 0.0269]
Data/restraints/parameters	4052/2/103
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1113
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1122
Largest diff. peak/hole / e Å^{-3}	3.20/-0.81

Flack parameter	0.01(4)

Table S2: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $NbCl_4(dme)$. U(eq) is defined as one third of the trace of the orthogonalized U^{IJ} tensor.

Atom	x	y	z	U(eq)
Nb1	5719.1(6)	7646.0(4)	5016.0(6)	17.21(12)
Cl1	7249(3)	9221.1(17)	5774.6(17)	34.4(4)
Cl2	8059(2)	6518.7(19)	4564.8(17)	29.4(3)
Cl3	5361(2)	6673.4(13)	6763.7(12)	22.3(3)
Cl4	5456(2)	8561.4(15)	3231.3(13)	24.8(3)
O1	3287(7)	8364(4)	5416(4)	22.2(9)
O2	4007(6)	6376(4)	4309(4)	18.2(8)
C1	1966(9)	7529(7)	5224(8)	26.5(15)
C2	2335(8)	6838(7)	4173(7)	24.6(12)
C3	2987(14)	9082(8)	6399(7)	37.1(18)
C4	4394(9)	5525(6)	3444(6)	26.3(13)

Table S3: Bond lengths (Å) and angles (°) for $NbCl_4(dme)$.

Bond Lengths (Å)		Angles (°)			
Nb1-Cl1	2.3565(18)	Cl1-Nb1-Cl3	95.28(6)	O2-Nb1-Cl3	86.68(14)
Nb1-Cl2	2.3551(19)	Cl1-Nb1-Cl4	92.76(6)	O2-Nb1-Cl4	84.03(14)

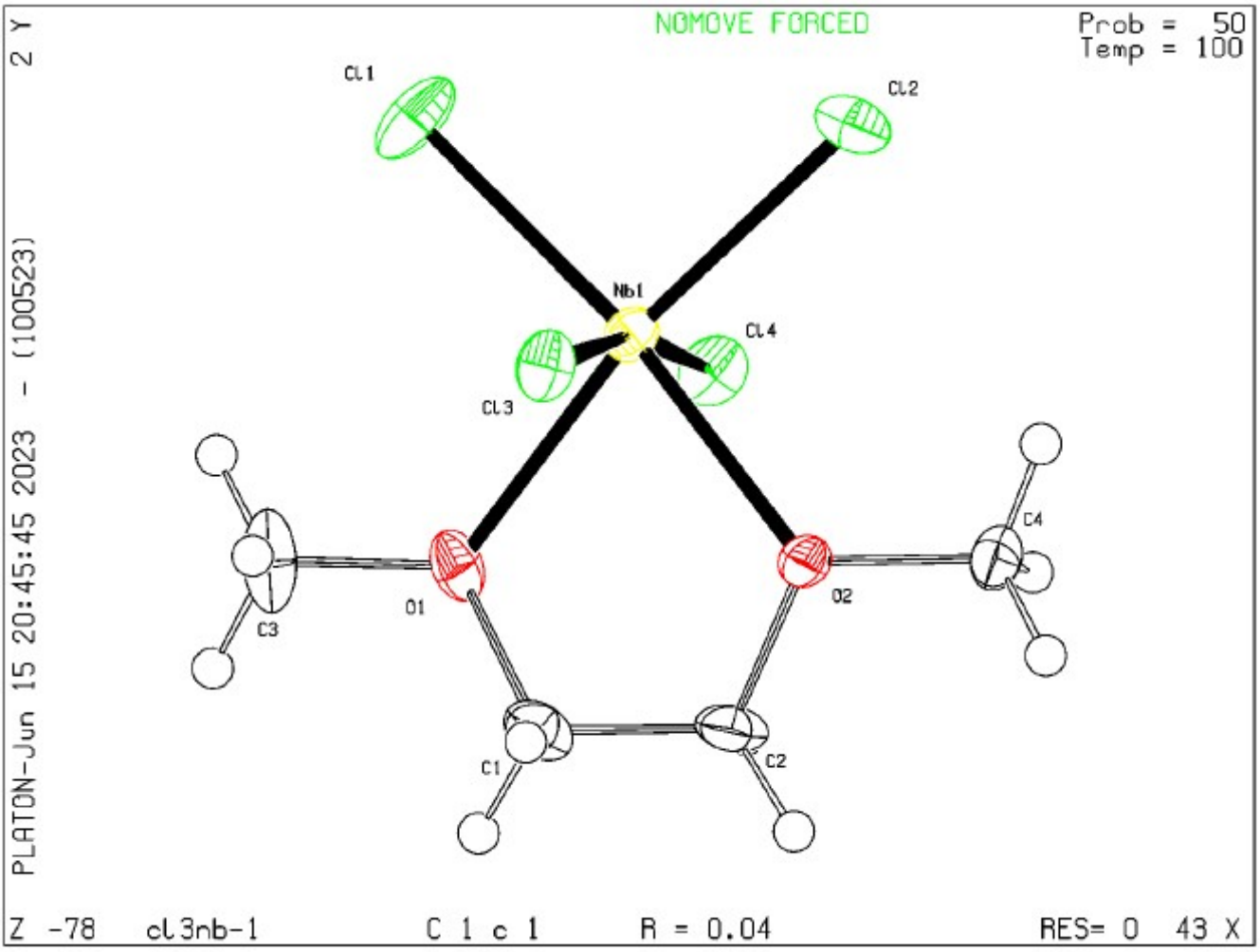
Nb1-Cl3	2.3596(15)	Cl2-Nb1-Cl1	94.39(9)	O2-Nb1-O1	75.86(19)
Nb1-Cl4	2.3585(15)	Cl2-Nb1-Cl3	92.52(7)	C1-O1-Nb1	112.8(4)
Nb1-O1	2.190(5)	Cl2-Nb1-Cl4	96.27(7)	C3-O1-Nb1	122.7(6)
Nb1-O2	2.170(4)	Cl4-Nb1-Cl3	167.59(6)	C3-O1-C1	111.7(6)
O1-C1	1.451(10)	O1-Nb1-Cl1	96.20(16)	C2-O2-Nb1	113.2(4)
O1-C3	1.440(9)	O1-Nb1-Cl2	168.74(15)	C4-O2-Nb1	125.4(4)
O2-C2	1.465(8)	O1-Nb1-Cl3	82.70(14)	C4-O2-C2	111.6(5)
O2-C4	1.442(8)	O1-Nb1-Cl4	87.06(14)	O1-C1-C2	108.9(6)
C1-C2	1.500(12)	O2-Nb1-Cl1	171.54(14)	O2-C2-C1	106.6(6)
		O2-Nb1-Cl2	93.74(14)		

Table S4: Anisotropic displacement parameters ($Å^2×10^3$) for $NbCl_4$(dme). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb1	18.60(19)	13.41(19)	19.62(18)	0.76(19)	0.13(18)	-3.1(2)
Cl1	49.0(11)	22.4(7)	31.8(8)	1.4(6)	-9.3(7)	-18.8(7)
Cl2	17.2(6)	36.4(9)	34.6(8)	1.1(7)	2.4(5)	3.2(6)
Cl3	31.3(7)	15.0(6)	20.6(6)	2.4(4)	0.1(5)	-0.9(5)
Cl4	30.7(8)	21.0(6)	22.7(6)	5.6(5)	0.3(5)	-5.1(6)
O1	27(2)	13.8(19)	26(2)	1.3(15)	6.2(17)	5.7(17)
O2	16.7(18)	12.1(18)	26(2)	-2.4(15)	0.5(15)	-2.4(14)
C1	19(3)	20(3)	40(5)	2(2)	6(3)	2(2)
C2	12(2)	23(3)	39(3)	2(2)	-1(2)	1(2)
C3	61(5)	23(3)	27(3)	-5(3)	12(3)	5(4)
C4	26(3)	24(3)	28(3)	-11(2)	4(2)	-5(2)

Table S5: Hydrogen atom coordinates ($Å×10^4$) and isotropic displacement parameters ($Å^2×10^3$) for $NbCl_4$(dme).

Atom	x	y	z	U(eq)
H1A	906.47	7949.14	5133.98	32
H1B	1874.46	6992.69	5881.56	32
H2A	1536.1	6187.47	4082.87	30
H2B	2266.47	7349.39	3495.55	30



H3A	3037.14	8592.5	7081.7	56
H3B	1894.2	9441.77	6337.23	56
H3C	3826.83	9698.23	6447.1	56
H4A	4295.53	5893.2	2695.45	39
H4B	3625.39	4863.85	3493.63	39
H4C	5522.87	5241.48	3553.92	39

Figure S1. ORTEP plot of $NbCl_4$(dme)

Table S6: Crystal data and structure refinement for $NbCl_4(Et_2O)_2$

Empirical formula	$C_8H_{20}Cl_4NbO_2$
Formula weight	191.47
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, b, c	7.6027(2), 11.3827(3), 8.9641(3)
α, β, γ	90, 107.012(3), 90
Volume/Å^3	741.80(4)
Z	2
ρ_{calc}g/cm^3	1.714
μ/mm^{-1}	1.513
F(000)	386.0
Crystal size/mm^3	0.217 × 0.155 × 0.112
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.95 to 54.956
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -10 ≤ l ≤ 11
Reflections collected	6073
Independent reflections	1677 [R_{int} = 0.0280, R_{sigma} = 0.0319]
Data/restraints/parameters	1677/0/72

Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0255, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0668
Largest diff. Peak/hole / e $Å^{-3}$	0.86/-0.90

Table S7: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $NbCl_4(Et_2O)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{IJ} tensor.

Atom	x	y	z	U(eq)
Nb1	5000	5000	5000	12.3(1)
Cl2	4950.1(7)	6305.6(5)	2907.3(6)	19.85(14)
Cl3	8171.3(7)	5408.1(5)	6242.3(6)	20.53(14)
O4	4240.5(18)	6405.2(12)	6242.6(17)	15.6(3)
C5	2755(3)	6297(2)	6987(3)	19.0(5)
C7	5149(3)	7563.9(18)	6446(3)	19.4(5)
C6	3449(3)	6435(2)	8735(3)	25.7(5)
C8	3874(3)	8527(2)	5636(3)	25.6(5)

Table S8: Bond lengths (Å) and angles (°) for $NbCl_4(Et_2O)_2$.

Bond Lengths (Å)		Angles (°)			
Nb1-Cl2	2.3848(5)	Cl2-Nb1-Cl2^{1}	180.0	O4^{1}-Nb1-Cl3	89.93(4)
Nb1-Cl2^{1}	2.3848(5)	Cl2^{1}-Nb1-Cl3^{1}	91.556(19)	O4^{1}-Nb1-Cl3^{1}	90.07(4)
Nb1-Cl3^{1}	2.3870(5)	Cl2^{1}-Nb1-Cl3	88.444(19)	O4-Nb1-Cl3^{1}	89.93(4)
Nb1-Cl3	2.3870(5)	Cl2-Nb1-Cl3^{1}	88.444(19)	O4-Nb1-Cl3	90.07(4)
Nb1-O4	2.1235(14)	Cl2-Nb1-Cl3	91.556(19)	O4^{1}-Nb1-O4	180.0
Nb1-O4^{1}	2.1235(14)	Cl3-Nb1-Cl3^{1}	180.0	C5-O4-Nb1	122.39(12)
O4-C5	1.475(2)	O4-Nb1-Cl2	89.95(4)	C5-O4-C7	114.32(15)
O4-C7	1.475(2)	O4^{1}-Nb1-Cl2	90.05(4)	C7-O4-Nb1	123.29(11)
C5-C6	1.509(3)	O4-Nb1-Cl2^{1}	90.06(4)	O4-C5-C6	112.34(17)
C7-C8	1.503(3)	O4^{1}-Nb1-Cl2^{1}	89.95(4)	O4-C7-C8	112.34(17)

Symmetry transformations used to generate equivalent atoms: (1) 1-X, 1-Y, 1-Z

Table S9: Anisotropic displacement parameters (Å^{2}×10^{3}) for $NbCl_4(Oet_2O)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb1	9.16(15)	15.38(16)	10.93(16)	0.57(10)	0.71(10)	-0.64(9)
Cl2	22.2(3)	21.2(3)	16.2(3)	4.4(2)	5.7(2)	0.8(2)
Cl3	11.0(2)	27.1(3)	20.6(3)	-2.2(2)	-0.04(19)	-1.9(2)
O4	12.1(7)	16.7(7)	17.9(8)	-1.9(6)	4.0(6)	-2.8(6)
C5	13.8(10)	22.5(11)	22.0(12)	-1.3(9)	7.3(9)	-0.4(8)
C7	18.5(11)	16.7(11)	20.9(11)	-1.9(9)	2.7(9)	-4.6(8)
C6	29.0(12)	32.5(14)	18.4(12)	-0.7(10)	11.2(10)	-0.3(10)
C8	27.9(12)	19.0(11)	27.0(14)	1.4(10)	3.5(10)	-1.6(9)

Table S10: Hydrogen atom coordinates (Å×10^{4}) and isotropic displacement parameters (Å^{2}×10^{3}) for $NbCl_4(Et_2O)_2$.

Atom	x	y	z	U(eq)
H5A	2176.86	5533.14	6739.72	23
H5B	1829.71	6890.92	6562.43	23

H7A	6195.87	7533.55	6035.74	23
H7B	5604.96	7742.29	7550.51	23
H6A	3800.76	7236.95	8988.85	39
H6B	4494.2	5932.93	9144.29	39
H6C	2492.99	6221.85	9185.91	39
H8A	3376.56	8337.99	4550.04	38
H8B	4540.65	9253.6	5741.85	38
H8C	2889.45	8605.35	6098.62	38

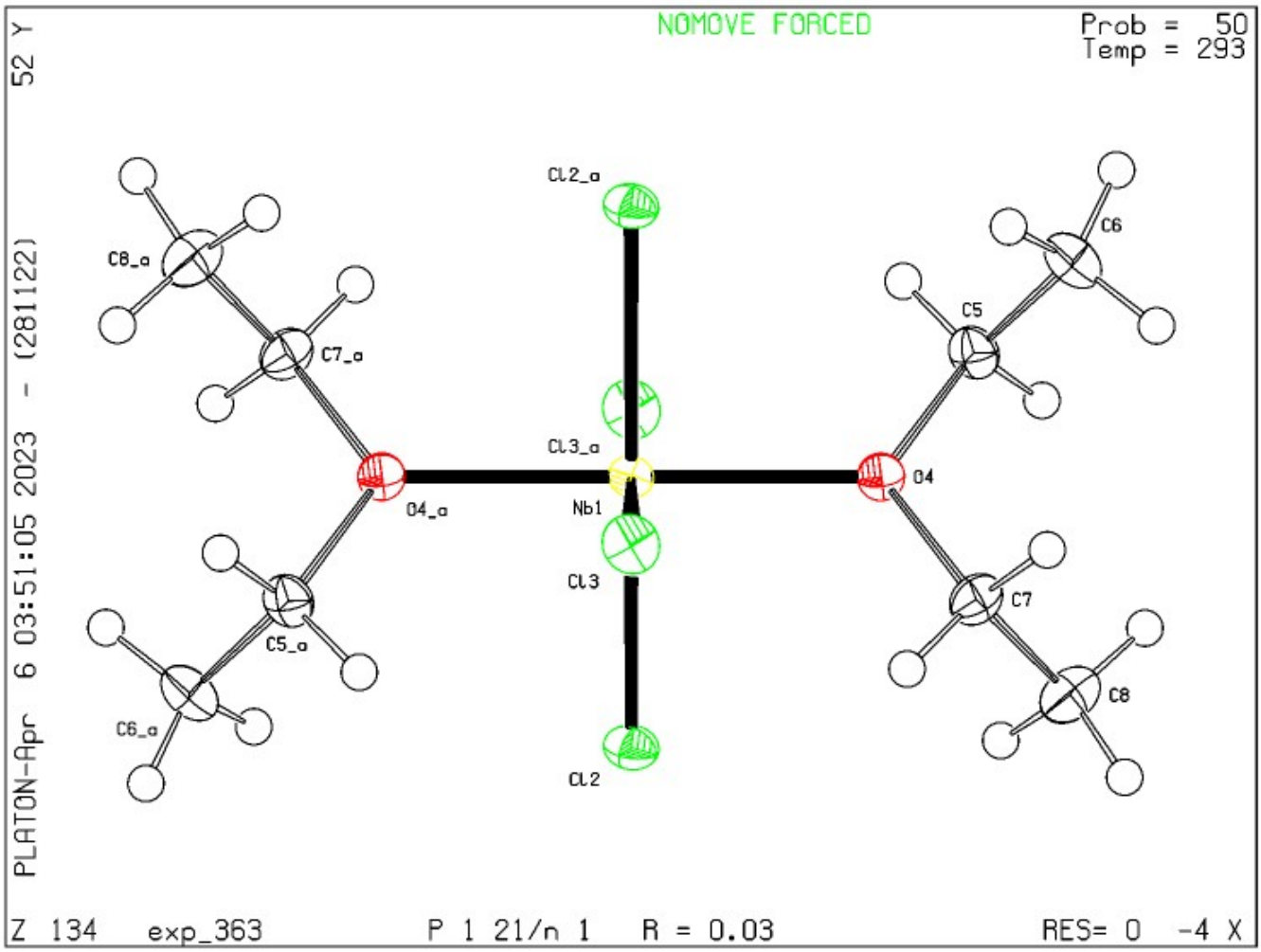


Figure S2. ORTEP plot of $NbCl_4(Et_2O)_2$.

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Table S11: Crystal data and structure refinement for $TaCl_4(Et_2O)_2$.

Empirical formula	$C_8H_{20}Cl_4O_2Ta$
Formula weight	470.99
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, b, c	7.6010(3), 11.3893(3), 8.9865(3)
α, β, γ	90, 107.050(4), 90
Volume/Å^3	743.77(4)
Z	2
ρ_{calc}g/cm^3	2.103
μ/mm^{-1}	8.089
F(000)	450.0
Crystal size/mm^3	0.523 × 0.086 × 0.044
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.94 to 61.28
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 15, -11 ≤ l ≤ 12
Reflections collected	6261

Independent reflections	2188 [R_{int} = 0.0254, R_{sigma} = 0.0278]
Data/restraints/parameters	2188/0/72
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0190, wR_2 = 0.0391
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0409
Largest diff. Peak/hole / e $Å^{-3}$	1.54/-0.92

Table S12: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $TaCl_4(Et_2O)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{IJ} tensor.

Atom	x	y	z	U(eq)
Ta1	5000	5000	5000	10.28(4)
Cl3	4952.2(8)	6304.6(5)	2910.4(7)	17.76(12)
Cl1	8170.2(8)	5404.6(6)	6244.4(7)	18.20(12)
O1	4249(2)	6401.0(15)	6234.9(19)	14.5(3)
C1	5152(3)	7562(2)	6438(3)	17.3(5)
C2	2758(3)	6292(2)	6984(3)	16.9(5)
C3	3870(4)	8527(2)	5636(3)	22.8(6)
C4	3449(4)	6438(2)	8723(3)	23.5(6)

Table S13: Bond lengths (Å) and angles (°) for $TaCl_4(Et_2O)_2$.

Bond Lengths (Å)		Angles (°)			
Ta1-Cl3^{1}	2.3865(6)	Cl3-Ta1-Cl3^{1}	180.0	O1^{1}-Ta1-Cl1^{1}	89.95(5)
Ta1-Cl3	2.3865(6)	Cl1^{1}-Ta1-Cl3	88.35(2)	O1^{1}-Ta1-Cl1	90.05(5)
Ta1-Cl1	2.3852(6)	Cl1^{1}-Ta1-Cl3^{1}	91.65(2)	O1-Ta1-Cl1^{1}	90.05(5)
Ta1-Cl1^{1}	2.3852(6)	Cl1-Ta1-Cl3^{1}	88.35(2)	O1-Ta1-Cl1	89.95(5)
Ta1-O1^{1}	2.1153(17)	Cl1-Ta1-Cl3	91.65(2)	O1^{1}-Ta1-O1	180.0
Ta1-O1	2.1153(17)	Cl1^{1}-Ta1-Cl1	180.0	C1-O1-Ta1	123.61(13)
O1-C1	1.476(3)	O1^{1}-Ta1-Cl3	90.06(5)	C1-O1-C2	114.07(18)
O1-C2	1.483(3)	O1-Ta1-Cl3	89.94(5)	C2-O1-Ta1	122.32(14)
C1-C3	1.505(3)	O1-Ta1-Cl3^{1}	90.06(5)	O1-C1-C3	112.5(2)
C2-C4	1.505(3)	O1^{1}-Ta1-Cl3^{1}	89.94(5)	O1-C2-C4	112.45(19)

Symmetry transformations used to generate equivalent atoms: (1) 1-X, 1-Y, 1-Z

Table S14: Anisotropic displacement parameters (Å^{2}×10^{3}) for $TaCl_4(Et_2O)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	x	y	z	U(eq)
Ta1	9.49(6)	10.26(7)	11.55(7)	0.48(5)
Cl3	22.1(3)	15.9(3)	17.1(3)	4.3(2)
Cl1	10.6(2)	20.9(3)	21.9(3)	-2.7(3)
O1	15.0(8)	12.6(8)	18.3(8)	-0.5(7)
C1	18.8(12)	11.5(11)	21.4(12)	-2.5(10)
C2	14.0(11)	16.9(12)	22.8(12)	-2.0(10)
C3	26.2(13)	12.9(12)	28.7(14)	0.8(11)
C4	27.4(14)	25.4(15)	19.9(13)	-0.5(11)

Table S15: Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $TaCl_4(Et_2O)_2$.

Atom	x	y	z	U(eq)
H1A	6195.49	7535.02	6024.75	21
H1B	5612.5	7738.1	7540.15	21
H2A	2184.68	5527.29	6743.04	20
H2B	1828.07	6882.79	6555.25	20
H3A	3386.12	8347.54	4548.32	34
H3B	4530.62	9256.05	5759.99	34
H3C	2876.26	8592.18	6088.33	34
H4A	3802.35	7240.28	8969.89	35
H4B	4493.35	5936.37	9136.69	35
H4C	2491.19	6229.75	9172.69	35

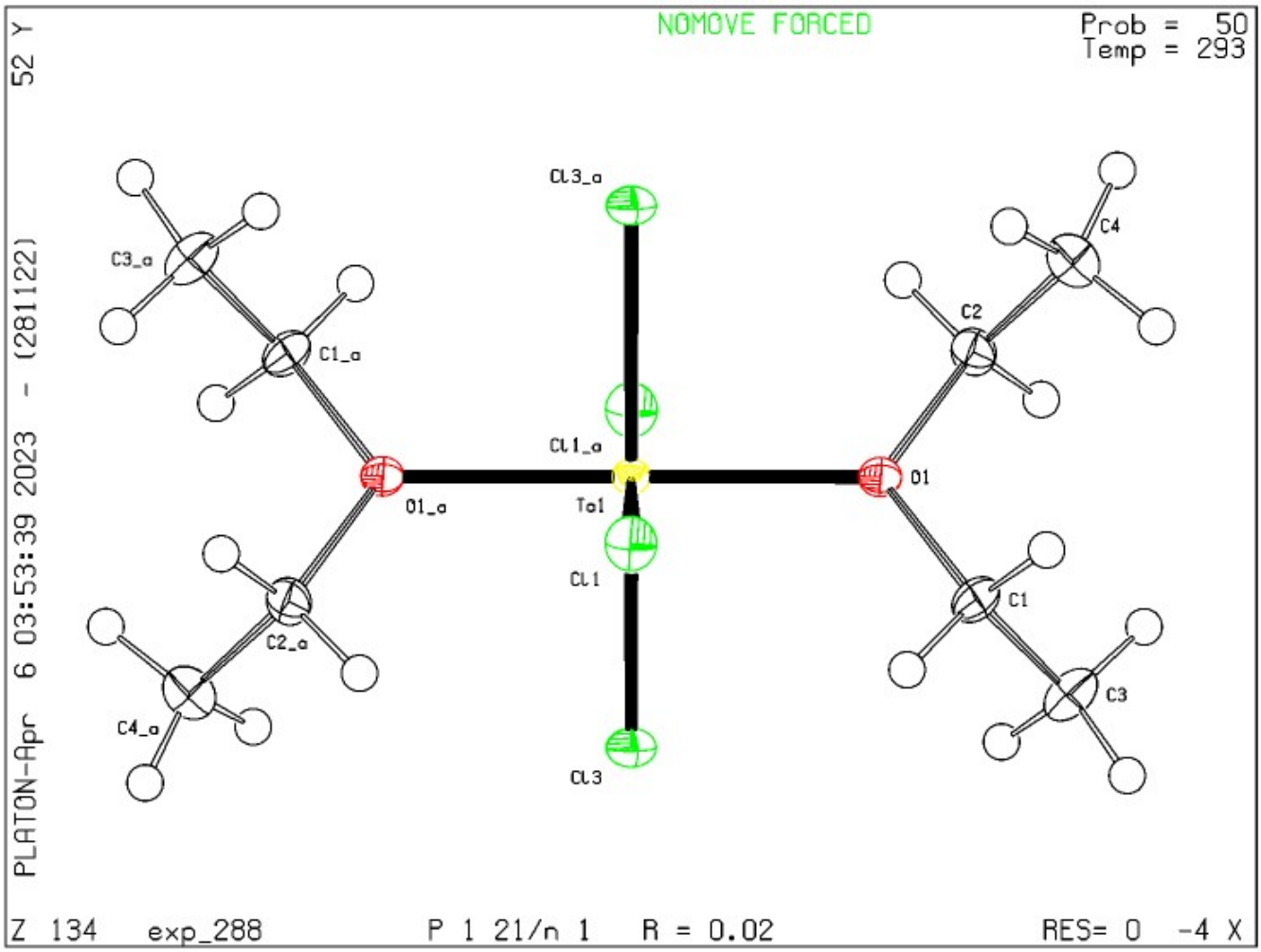

Figure S3. ORTEP plot of $TaCl_4(Et_2O)_2$.

Table S16: Crystal data and structure refinement for $Ta_2Cl_8(Et_2O)_2$.

Empirical formula	$C_8H_{20}Cl_8O_2Ta_2$
Formula weight	793.74
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, b, c	7.8857(2), 11.5388(4), 11.4054(4)
α, β, γ	90, 103.223(3), 90
Volume/Å^3	1010.28(6)
Z	2
ρ_{calc}g/cm^3	2.609
μ/mm^{-1}	11.877
F(000)	732.0
Crystal size/mm^3	0.29 × 0.125 × 0.08
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	5.72 to 61.228
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	9991
Independent reflections	2996 [R_{int} = 0.0395, R_{sigma} = 0.0526]
Data/restraints/parameters	2996/12/130
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0725
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.0767
Largest diff. Peak/hole / e $Å^{-3}$	2.05/-1.45

Table S17: Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$×10^3) for $Ta_2Cl_8(Et_2O)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{IJ} tensor.

Atom	x	y	z	U(eq)
Ta1	5022.6(5)	4556.8(4)	6273.6(3)	14.49(11)
Cl2	2037.6(17)	4837.4(14)	5996.3(14)	21.6(3)
Cl3	5584.0(18)	6500.5(12)	5678.8(13)	22.6(3)
Cl4	7870.4(18)	3892.3(14)	6625.2(14)	21.2(3)
Cl1	5571(2)	5392.7(16)	8229.7(17)	22.7(3)
O1	4470(5)	2896(3)	7036(3)	20.6(9)

C2	3302(10)	2013(7)	6413(7)	42.6(19)
C3	3777(11)	2878(7)	9025(7)	47(2)
C4	4223(11)	1012(6)	6019(7)	45(2)
C5	5067(10)	2615(7)	8346(7)	46(2)
Ta2	5562(14)	4132(9)	6017(8)	38(3)
Cl5	2640(40)	4660(20)	5210(30)	31(6)
Cl6	8370(40)	3470(30)	7050(30)	30(6)
Cl7	5510(50)	5290(30)	7630(40)	49(12)

Table S18: Bond lengths (Å) and angles (°) for $Ta_2Cl_8(Et_2O)_2$.

Bond Lengths (Å)		Angles (°)			
Ta1-Ta1^1	3.0725(6)	Cl2-Ta1-Ta1^1	91.87(4)	C5-O1-Ta2	127.8(4)
Ta1-Cl2	2.3249(14)	Cl2-Ta1-Cl3	94.44(5)	O1-C2-C4	113.3(6)
Ta1-Cl3	2.4132(15)	Cl2-Ta1-Cl3^1	88.00(5)	C3-C5-O1	113.0(6)
Ta1-Cl3^1	2.4876(15)	Cl2-Ta1-Cl1	91.85(6)	Cl3^1-Ta2-Cl3	103.5(2)
Ta1-Cl4	2.3195(15)	Cl3^1-Ta1-Ta1^1	50.10(4)	Cl3^1-Ta2-O1	97.4(3)
Ta1-Cl1	2.3776(19)	Cl3-Ta1-Ta1^1	52.26(4)	Cl3-Ta2-Ta2^1	41.5(3)

Ta1-O1	2.189(4)	Cl3-Ta1-Cl3^{1}	102.37(4)	Cl3^{1}-Ta2-Ta2^{1}	62.0(3)
Cl3-Ta2	2.761(9)	Cl4-Ta1-Ta1^{1}	94.29(5)	Cl3^{1}-Ta2-Cl5^{1}	82.0(7)
Cl3-Ta2^{1}	2.072(9)	Cl4-Ta1-Cl2	168.43(6)	Cl3^{1}-Ta2-Cl5	63.3(8)
Cl3-Cl5^{1}	2.34(3)	Cl4-Ta1-Cl3	97.08(5)	Cl3^{1}-Ta2-Cl6	120.4(10)
O1-C2	1.447(7)	Cl4-Ta1-Cl3^{1}	88.45(5)	Cl3^{1}-Ta2-Cl7	151.1(10)
O1-C5	1.496(8)	Cl4-Ta1-Cl1	90.62(6)	O1-Ta2-Cl3	138.7(8)
O1-Ta2	2.141(8)	Cl1-Ta1-Ta1^{1}	135.43(5)	O1-Ta2-Ta2^{1}	140.4(6)
C2-C4	1.488(10)	Cl1-Ta1-Cl3	83.17(6)	O1-Ta2-Cl5^{1}	168.8(10)
C3-C5	1.445(10)	Cl1-Ta1-Cl3^{1}	174.46(6)	O1-Ta2-Cl5	84.6(8)
Ta2-Ta2^{1}	3.040(12)	O1-Ta1-Ta1^{1}	134.97(11)	O1-Ta2-Cl6	87.8(8)
Ta2-Cl5^{1}	2.61(3)	O1-Ta1-Cl2	83.61(10)	O1-Ta2-Cl7	82.5(13)
Ta2-Cl5	2.36(3)	O1-Ta1-Cl3^{1}	84.92(11)	Cl5^{1}-Ta2-Cl3	51.5(6)
Ta2-Cl6	2.38(3)	O1-Ta1-Cl3	172.42(11)	Cl5-Ta2-Cl3	74.0(7)
Ta2-Cl7	2.28(4)	O1-Ta1-Cl4	85.11(11)	Cl5-Ta2-Cl5^{1}	104.9(9)
		O1-Ta1-Cl1	89.56(11)	Cl5-Ta2-Cl6	171.9(12)
		Ta1-Cl3-Ta1^{1}	77.63(4)	Cl6-Ta2-Cl3	110.6(8)
		Ta2^{1}-Cl3-Ta2	76.5(2)	Cl6-Ta2-Cl5^{1}	83.0(11)
		Ta2^{1}-Cl3-Cl5^{1}	64.4(8)	Cl7-Ta2-Cl3	62.3(13)
		Cl5^{1}-Cl3-Ta2	61.0(8)	Cl7-Ta2-Cl5^{1}	103.5(15)
		C2-O1-Ta1	125.7(4)	Cl7-Ta2-Cl5	88.1(12)
		C2-O1-C5	110.9(5)	Cl7-Ta2-Cl6	88.5(10)
		C2-O1-Ta2	119.5(4)	Cl3^{1}-Cl5-Ta2^{1}	67.5(9)

C5-O1-Ta1	122.7(4)	$Cl3^{1-}$Cl5-Ta2	52.3(7)

Symmetry transformations used to generate equivalent atoms: (1) 1-X, 1-Y, 1-Z

Table S19: Anisotropic displacement parameters ($Å^2×10^3$) for $Ta_2Cl_8(Et_2O)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta1	13.40(13)	15.16(19)	14.79(13)	-1.23(12)	2.98(9)	-1.56(12)
Cl2	14.2(6)	25.0(8)	26.1(8)	2.2(6)	5.7(6)	0.5(5)
Cl3	26.0(6)	20.9(7)	21.0(7)	-3.0(6)	5.5(5)	-6.0(5)
Cl4	14.8(6)	25.0(8)	22.9(8)	-0.5(7)	2.1(6)	1.3(6)
Cl1	27.8(8)	23.6(8)	16.3(8)	-4.0(8)	4.1(7)	-0.9(7)
O1	20.3(18)	21(2)	20(2)	4.3(17)	2.6(16)	-5.3(16)
C2	43(4)	45(5)	37(4)	3(4)	3(3)	-15(4)
C3	74(6)	41(5)	37(4)	-8(4)	35(4)	-21(4)
C4	71(5)	26(4)	35(4)	-2(3)	4(4)	11(4)
C5	52(5)	42(5)	37(4)	4(4)	-5(4)	-6(4)
Ta2	43(4)	25(4)	35(4)	7(3)	-13(3)	-9(4)
Cl5	32(7)	28(7)	32(8)	0(5)	6(5)	-3(5)
Cl6	29(7)	30(8)	29(8)	0(5)	1(5)	-2(5)
Cl7	40(17)	40(20)	40(20)	-32(18)	-29(17)	28(15)

Table S20: Hydrogen atom coordinates ($Å×10^4$) and isotropic displacement parameters ($Å^2×10^3$) for $Ta_2Cl_8(Et_2O)_2$.

Atom	x	y	z	U(eq)
H2A	2533.57	2356.43	5712.95	51
H2B	2586.07	1734.28	6941.92	51
H3A	2697.11	2507.34	8655.44	71
H3B	3604.96	3701.67	9035.44	71
H3C	4170.59	2601.21	9835.4	71
H4A	5025.81	1288.67	5564.58	68
H4B	3388.7	506.05	5525.17	68
H4C	4848.32	596.12	6712.98	68
H5A	5352.71	1797	8432.58	56

H5B	6120.19	3049.53	8679.67	56

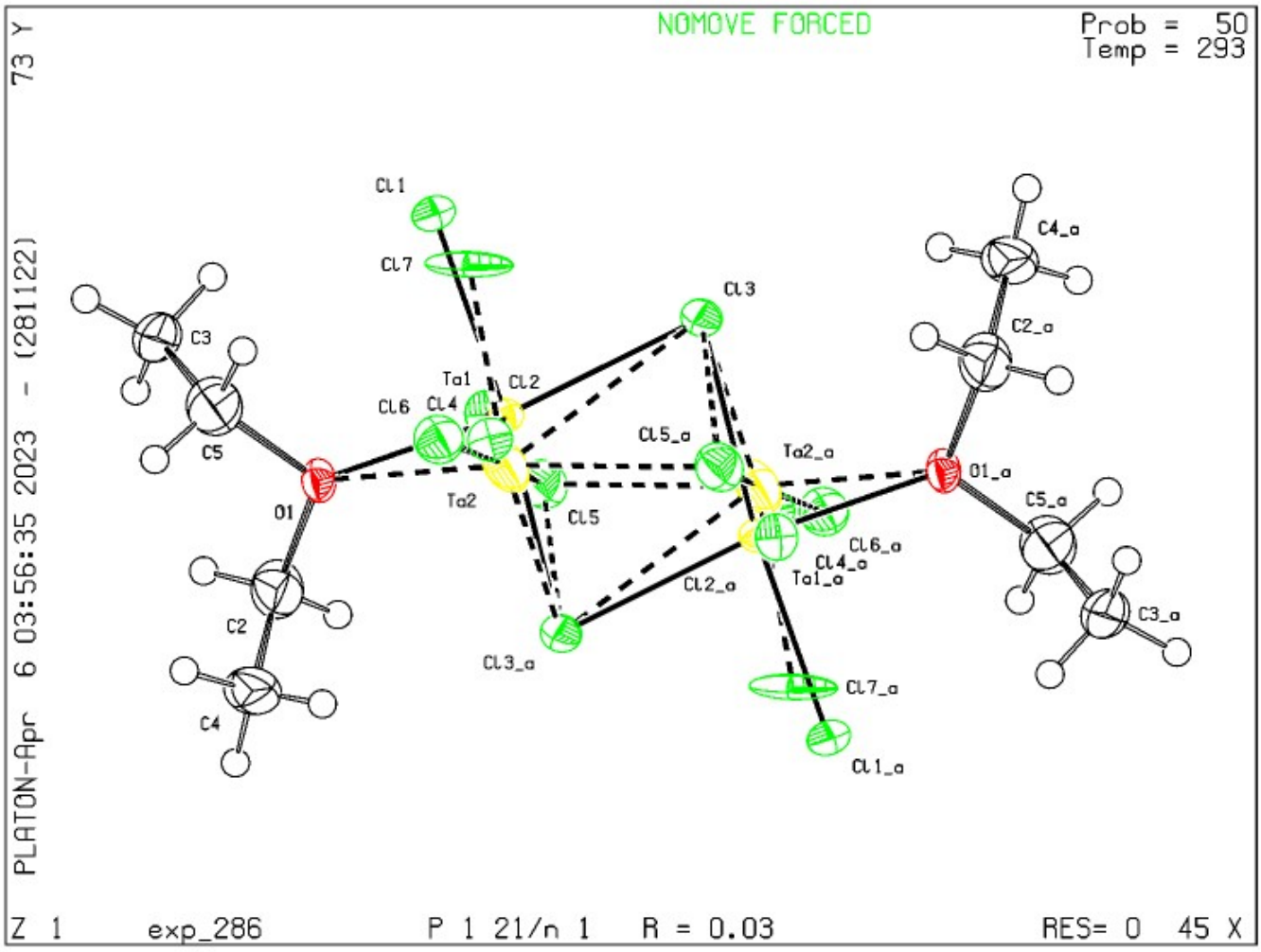

Figure S4. ORTEP plot of $Ta_2Cl_8(Et_2O)_2$.

Table S21: Crystal data and structure refinement for $[Ta_2Cl_6(dme)_2][TaCl_6]$.

Empirical formula	$C_8H_{20}Cl_{12}O_4Ta_3$
Formula weight	1148.49
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.0261(6)
b/Å	7.2740(5)
c/Å	13.2064(5)
α/°	85.923(5)
β/°	85.482(6)
γ/°	81.744(7)
Volume/Å^3	664.66(8)
Z	1
ρ_{calc}g/cm^3	2.869
μ/mm^{-1}	13.536
F(000)	523.0
Crystal size/mm^3	0.234 × 0.153 × 0.076
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	5.67 to 54.948
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 9$, $-16 \le l \le 16$
Reflections collected	6551
Independent reflections	2864 [R_{int} = 0.0782, R_{sigma} = 0.0903]
Data/restraints/parameters	2864/0/126
Goodness-of-fit on F^2	0.956
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0607, wR_2 = 0.0990
Largest diff. peak/hole / e $Å^{-3}$	3.00/-2.56

Table S22: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Ta_2Cl_6(dme)_2][TaCl_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{IJ} tensor.

Atom	x	y	z	U(eq)
Ta1	906.7(5)	5261.5(5)	873.3(3)	15.30(13)
Ta2	5000	10000	5000	18.58(16)
Cl3	-1270(3)	3007(3)	747.0(17)	19.1(5)
Cl4	3678(3)	3122(3)	550.4(18)	19.8(5)
Cl5	-1514(3)	7532(3)	1557.6(19)	25.5(6)
Cl6	4784(4)	8779(4)	6695.6(18)	29.0(6)
Cl7	6941(4)	7238(4)	4510(2)	34.7(7)
Cl8	2247(4)	8736(4)	4672(2)	33.6(6)
O9	1135(9)	4208(9)	2457(5)	22.1(15)

O12	2889(9)	6946(9)	1400(5)	21.5(16)
C13	2911(14)	8912(12)	1259(7)	22(2)
C14	-200(13)	3201(13)	3112(7)	24(2)
C10	2021(14)	5443(14)	3024(7)	24(2)
C11	3672(14)	6119(14)	2360(7)	25(2)

Table S23: Bond lengths (Å) and angles (°) for $[Ta_2Cl_6(dme)_2][TaCl_6]$.

Bond Lengths (Å)		Angles (°)			
Ta1-Ta1^1	2.7956(7)	Cl3^1-Ta1-Ta1^1	54.72(6)	Cl6^2-Ta2-Cl7	89.68(9)
Ta1-Cl3	2.420(2)	Cl3-Ta1-Ta1^1	54.70(5)	Cl6^2-Ta2-Cl7^2	90.33(9)
Ta1-Cl3^1	2.419(2)	Cl3^1-Ta1-Cl3	109.42(6)	Cl6-Ta2-Cl7^2	89.68(9)
Ta1-Cl4	2.343(2)	Cl4-Ta1-Ta1^1	96.76(6)	Cl7-Ta2-Cl7^2	180.00(15)
Ta1-Cl5	2.366(2)	Cl4-Ta1-Cl3	93.81(8)	Cl8-Ta2-Cl6	90.50(10)
Ta1-O9	2.186(6)	Cl4-Ta1-Cl3^1	93.99(8)	Cl8^2-Ta2-Cl6	89.50(10)
Ta1-O12	2.165(6)	Cl4-Ta1-Cl5	166.01(8)	Cl8-Ta2-Cl7^2	89.50(10)
Ta2-Cl6^2	2.351(2)	Cl5-Ta1-Ta1^1	97.23(6)	Cl8^2-Ta2-Cl6^2	90.50(10)
Ta2-Cl6	2.351(2)	Cl5-Ta1-Cl3	94.33(8)	Cl8-Ta2-Cl7^2	90.25(10)

Ta2-Cl7^{2}	2.361(2)	Cl5-Ta1-Cl3^{1}	94.01(8)	Cl8^{2}-Ta2-Cl7	90.25(10)
Ta2-Cl7	2.361(2)	O9-Ta1-Ta1^{1}	141.41(18)	Cl8-Ta2-Cl7	89.75(10)
Ta2-Cl8	2.340(3)	O9-Ta1-Cl3^{1}	163.87(19)	Cl8^{2}-Ta2-Cl7^{2}	89.75(10)
Ta2-Cl8^{2}	2.340(3)	O9-Ta1-Cl3	86.71(18)	Cl8-Ta2-Cl8^{2}	180.0
O9-C14	1.465(10)	O9-Ta1-Cl4	84.72(17)	Ta1^{1}-Cl3-Ta1	70.58(6)
O9-C10	1.444(11)	O9-Ta1-Cl5	84.41(17)	C14-O9-TA1	128.8(5)
O12-C13	1.431(10)	O12-Ta1-Ta1^{1}	140.75(17)	C10-O9-Ta1	111.1(5)
O12-C11	1.476(10)	O12-Ta1-Cl3	164.54(17)	C10-O9-C14	111.6(7)
C10-C11	1.516(13)	O12-Ta1-Cl3^{1}	86.04(17)	C13-O12-Ta1	129.4(5)
		O12-Ta1-Cl4	84.51(17)	C13-O12-C11	113.6(7)
		O12-Ta1-Cl5	84.61(18)	C11-O12-Ta1	110.9(5)
		O12-Ta1-O9	77.8(2)	O9-C10-C11	108.5(7)
		Cl6-Ta2-Cl6^{2}	180.0	O12-C11-C10	107.5(7)
		Cl6-Ta2-Cl7	90.32(9)		

Symmetry transformations used to generate equivalent atoms: (1) -X, 1-Y, -Z; (2) 1-X, 2-Y, 1-Z

Table S24: Anisotropic displacement parameters (Å^{2}×10^{3}) for $[Ta_2Cl_6(dme)_2][TaCl_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta1	12.7(2)	14.2(2)	18.2(2)	0.03(15)	-0.04(16)	0.03(15)
Ta2	18.5(3)	20.1(3)	15.9(3)	-2.9(2)	0.3(2)	1.7(2)
Cl3	18.0(11)	18.6(12)	20.1(13)	4.4(9)	-1.6(10)	-3.5(9)
Cl4	14.2(11)	16.7(12)	26.7(13)	-1.6(10)	-0.2(10)	3.6(9)
Cl5	20.3(12)	27.0(14)	26.5(14)	-8.4(10)	-0.2(11)	8.3(10)
Cl6	35.6(15)	31.2(15)	17.5(13)	-0.6(11)	-0.1(11)	2.8(12)
Cl7	44.6(17)	27.9(15)	26.3(15)	-6.3(11)	-3.1(13)	15.5(13)

Cl8	26.5(14)	44.3(17)	31.7(16)	-9.3(13)	2.1(12)	-9.8(12)
O9	21(4)	26(4)	18(4)	-1(3)	-3(3)	2(3)
O12	18(3)	21(4)	28(4)	2(3)	-8(3)	-7(3)
C13	36(6)	9(5)	20(5)	-1(4)	-4(5)	-4(4)
C14	26(5)	21(6)	24(6)	6(4)	9(4)	-11(4)
C10	30(6)	36(6)	6(5)	-3(4)	-1(4)	-1(5)
C11	25(5)	34(6)	13(5)	-3(4)	-3(4)	5(5)

Table S25: Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $[Ta_2Cl_6(dme)_2][TaCl_6]$.

Atom	x	y	z	U(eq)
H13A	2466.15	9347.95	603.75	32
H13B	4201.14	9178.94	1297.57	32
H13C	2079.54	9527.98	1780.33	32
H14A	-1250.95	4068.78	3375.5	36
H14B	465.52	2546.14	3666.4	36
H14C	-690.02	2327.73	2724.04	36
H10A	2498.73	4791.38	3639.74	29
H10B	1080.17	6493.72	3216.21	29
H11A	4216.81	7041.46	2699.89	29
H11B	4677.63	5088.52	2224.89	29

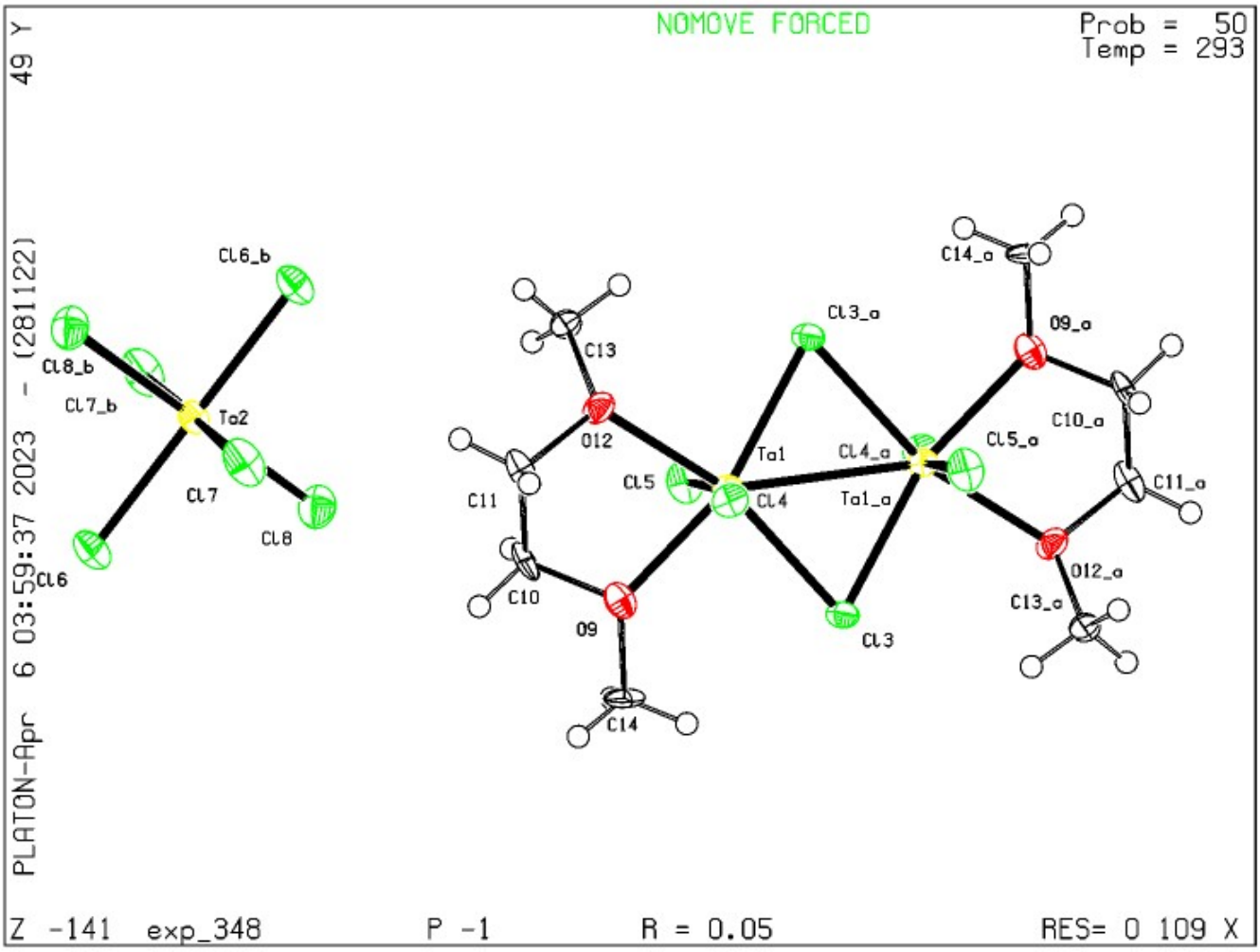

Figure S5. ORTEP plot of $[Ta_2Cl_6(dme)_2][TaCl_6]$.

References

1. D. J. Santure, A. P. Sattelberger, *Inorg. Synth.*, 1989, **26**, 219-225.