Unexpected Formation of (Dimethylaminomethylene)methylamide Complexes from the Reactions between Metal Chlorides and Lithium Dimethylamide

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Supporting Information

Complete list of Reference 16.

Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford, CT, 2004.

Additional Experimental

Analyses by X-ray Photoelectron Spectroscopy (XPS). XPS analyses of solids of **1b**, $Ta(NMe_2)_5$ and a mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ were carried out on an upgraded Perkin Elmer Phi 5000 Series ESCA/SAM system using a standard Mg K_α excitation. Base pressure in the XPS chamber was 10^{-9} torr. The composition was determined according to the XPS multiplex spectrum. Solid of each sample was ground into powders in a glovebox, and then put on a Scotch tape. The tape was then placed into the XPS chamber for analysis. The XPS spectra of **1b**, $Ta(NMe_2)_5$ and $W(NMe_2)_6$ [containing a small amount of $W_2(NMe_2)_6$][S1] are given in Figures S1-S3. The Ta and W $4f_{5/2}$ and $4f_{7/2}$ peaks were not resolved in the spectra. However, the $4f_{5/2}$-$4f_{7/2}$ peaks for **1b**, $Ta(NMe_2)_5$ and $W(NMe_2)_6$ are at 30.7, 29.6 and 38.7 eV, respectively.[S2] Although these spectra for the volatile samples are not high resolution, they show that the chemical shifts of the $4f_{5/2}$-$4f_{7/2}$ peaks in **1b** and $Ta(NMe_2)_5$ are close to each other (and are close to those of other Ta samples)[S3] but are ca. 8.0 eV less than that of the tungsten sample. The XPS spectra suggest that **1b** contains Ta but not W. These results are consistent with other analyses of **1b**.

XPS analyses of the residue after sublimation of $Ta(NMe_2)_5$ (**1b**) and $Ta(NMe_2)_4(MeNCH_2NMe_2)$ (**2b**) were carried out on a Perkin Elmer PHI 5500 Multi-Technique System using a standard Al K_α excitation source. Base pressure in the XPS chamber was 10^{-9} torr. The Ta $4f_{5/2}$-$4f_{7/2}$ peaks at >27.3 eV are closed to those of Ta(V) species, suggesting that there are unlikely Ta(0) species in the residue.

Additional References

(S1) $W(NMe_2)_6$ prepared from WCl_6 is usually contaminated with $W_2(NMe_2)_6$.[8b]

(S2) The chemical shifts in XPS spectra are not calibrated. Thus the relative values are significant.

(S3) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. *Handbook of X-ray Photoelectron Spectroscopy.* Perkin-Elmer Corporation: Minnesota, 1979.

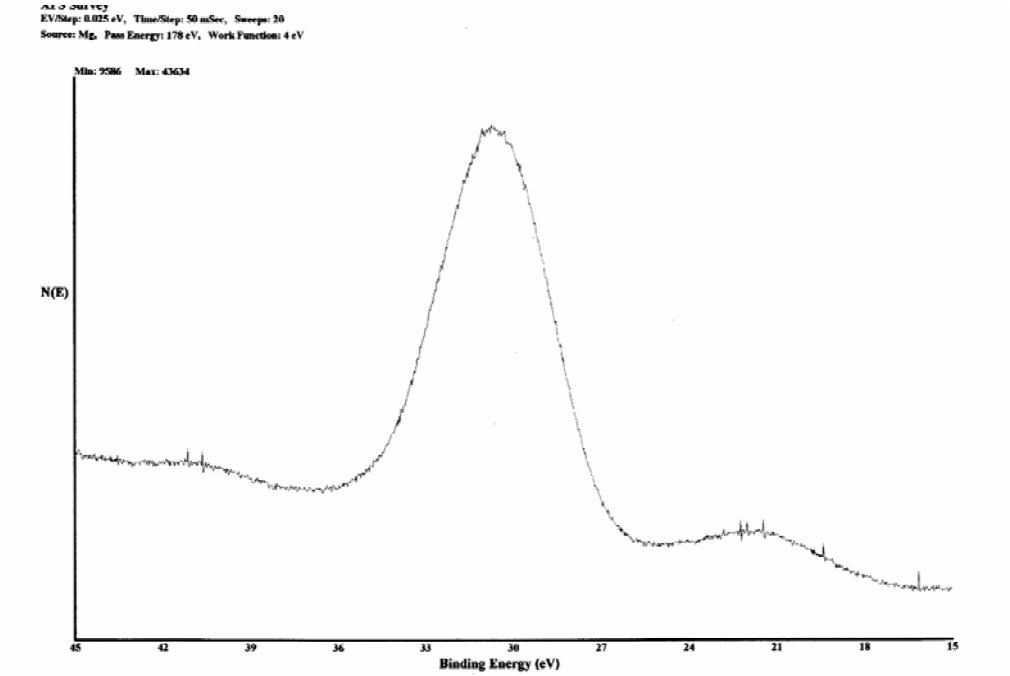


Figure S1. XPS spectrum of $Ta(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (**2b**).

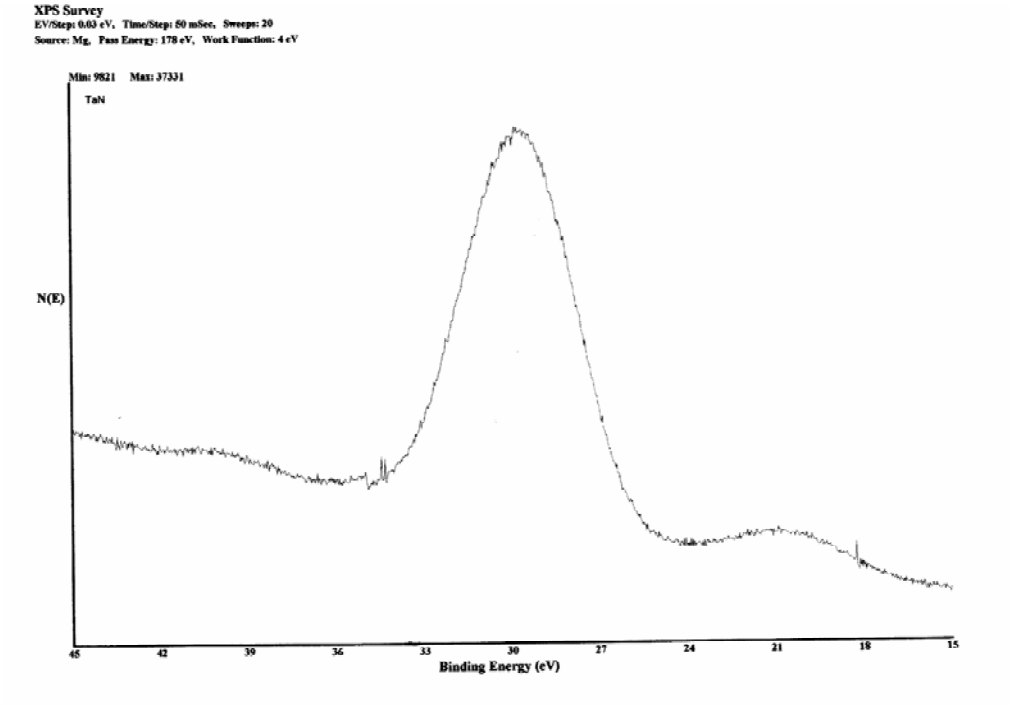


Figure S2. XPS spectrum of $Ta(NMe_2)_5$ (**1b**).

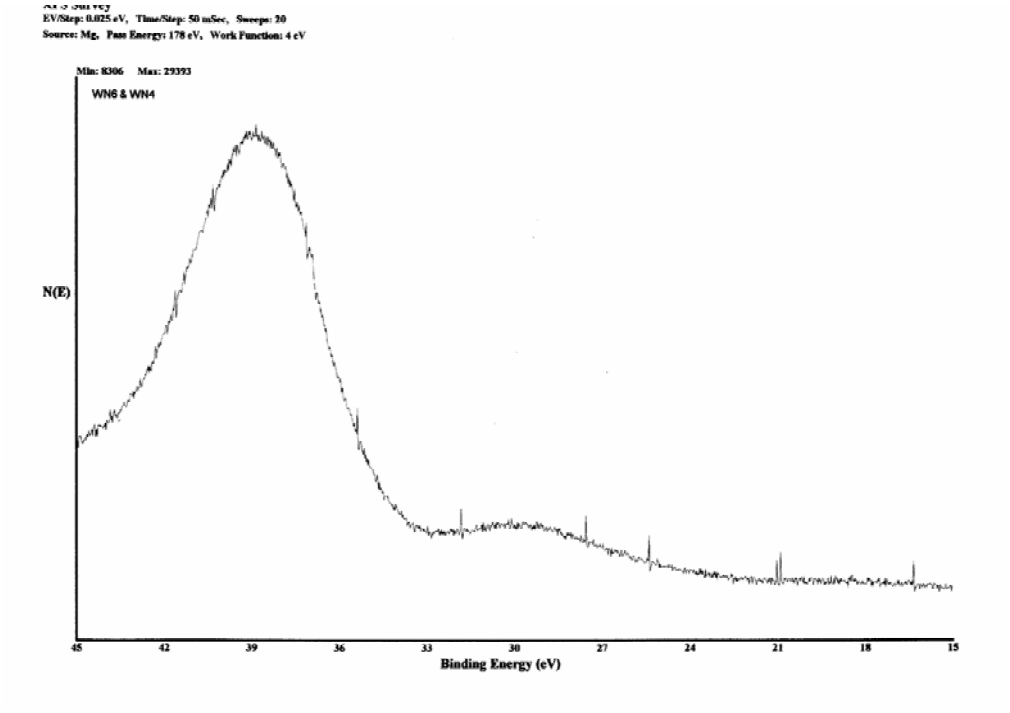


Figure S3. XPS spectrum of a mixture of $W(NMe_2)_6$ [containing a small amount of $W_2(NMe_2)_6$].

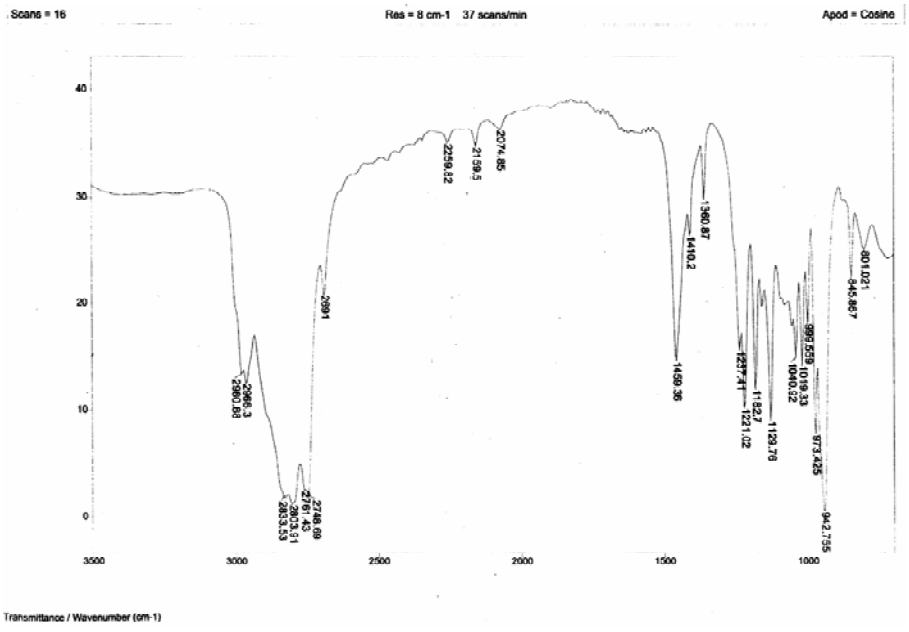


Figure S4. IR spectrum of $Ta(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (**2b**, KBr pellet).

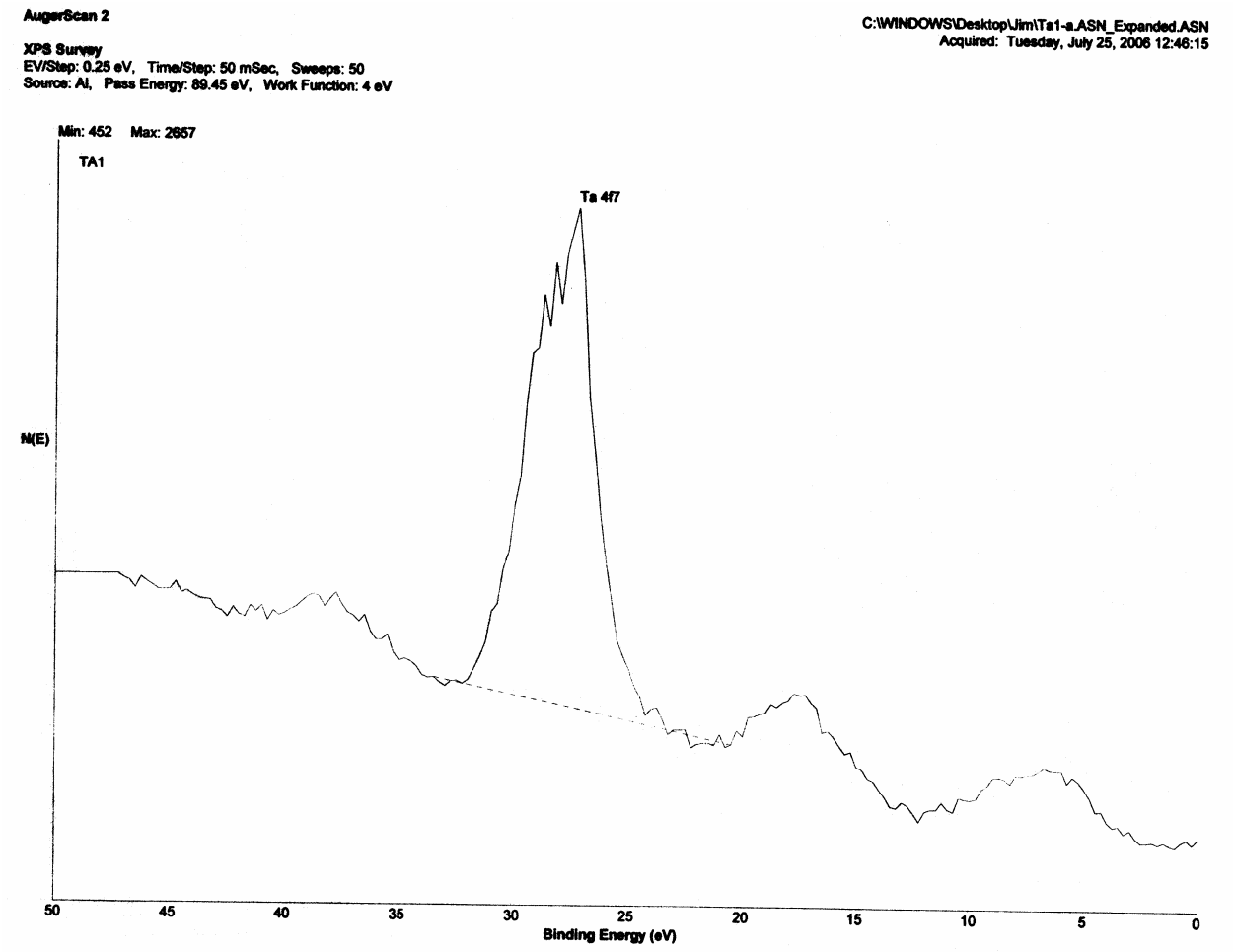
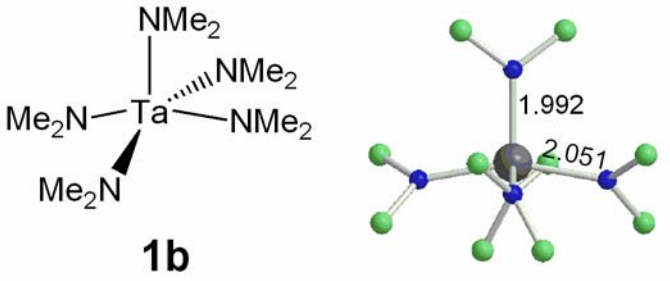


Figure S5. XPS spectrum of the residue after the sublimation of **1b** and **2b**.

Table S1. Calculated total energies, energies with zero-point energy corrections, and free energies of the structures in the text.

	E (Hartree)	E (with ZPE) (Hartree)	Free energies (Hartree)
CH_2=NCH_3	-133.9393776	-133.8707726	-133.8954956
1b	-730.7837507	-730.3707027	-730.4232487
2b	-864.7504827	-864.2624877	-864.3191237
2b-TS	-864.6909138	-864.2056048	-864.2600868
3b	-864.7256077	-864.2399667	-864.2956337
3b-TS	-864.7228574	-864.2387544	-864.2955704

The Calculated Geometries with Cartesian coordinates



1b

Ta	0.00002900	-0.00001100	0.0193690
N	-0.00010000	-0.00077600	2.0119190
N	-1.96140100	0.47916400	-0.3433600
N	-0.47007900	-1.85830000	-0.6495520
N	1.96163300	-0.47859400	-0.3434640
N	0.47005600	1.85879000	-0.6484440
C	1.18994500	0.15089100	2.8474150
C	-1.19036600	-0.15300900	2.8470110
C	-2.50365200	1.72833200	0.1905160
C	-2.92659000	-0.09999600	-1.2652100
C	-1.46235800	-2.70058400	0.0042910
C	0.02844400	-2.49453500	-1.8572160
C	2.50383900	-1.72796400	0.1900090
C	2.92657300	0.10056000	-1.2655480
C	1.46242900	2.70060000	0.0058240
C	-0.02853000	2.49563200	-1.8557350
H	1.11381200	1.05025500	3.4803620
H	1.31208900	-0.71422600	3.5196610
H	2.08690000	0.23605800	2.2321230
H	-1.31256900	0.71157500	3.5199310
H	-1.11447600	-1.05289200	3.4792490
H	-2.08717500	-0.23755300	2.2314250
H	-1.79733400	2.20601400	0.8738460
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H	-3.44036100	1.54059600	0.7419540
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H	-3.86707500	-0.37008700	-0.7540620
H	-2.51938000	-0.99347000	-1.7386840
H	-1.86773200	-2.21340700	0.8950400
H	-2.31200300	-2.94435500	-0.6570410
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H	-0.76536100	-2.61516100	-2.6162850
H	0.42314100	-3.50330000	-1.6460500
H	0.83231500	-1.90172700	-2.3028550
H	1.79754900	-2.20579800	0.8732750
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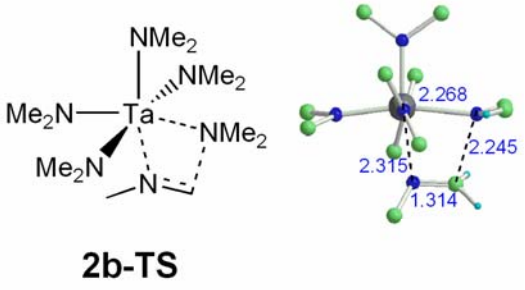
H	3.44063800	-1.54049000	0.7413840
H	3.19577800	-0.61519300	-2.0628090
H	3.86743100	0.37005500	-0.7547700
H	2.51950800	0.99440400	-1.7384450
H	2.31238200	2.94428900	-0.6551480
H	1.01173900	3.65787800	0.3186790
H	1.86734300	2.21310700	0.8966120
H	0.76514300	2.61642500	-2.6149270
H	-0.42298500	3.50439700	-1.6441000
H	-0.83260300	1.90315600	-2.3014610

2b



2b-TS

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N	0.24481400	2.07342300	0.16250700
N	0.52389300	-0.14496900	1.98846400
N	-0.92621300	0.17261400	-1.69136300
C	-2.99973300	1.35501600	0.62720400
C	-3.11740100	-1.05515800	0.65763000
C	2.91224400	1.06094500	-1.12444700
C	0.74995500	2.83149300	1.30220100
C	-0.45350800	0.00635500	3.04980100
C	-2.32058100	0.10071200	-1.35801400
C	-0.13068200	3.03710000	-0.86669200
C	1.83813300	-0.42169000	2.56348200
C	-0.65465500	0.29201300	-3.10795300
C	2.78182800	-1.31240900	-1.17865300
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H	-4.17947700	-1.03803100	0.36214400
H	-3.06555800	-1.05501400	1.75036100
H	-2.65156800	-1.97042600	0.29144500
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H	3.87295800	0.98732900	-0.58906800
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H	1.64129800	3.42771400	1.03058000
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H	-1.43576600	0.25602800	2.64627100
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H	-0.16796400	0.80940000	3.75205300
H	-2.79669300	-0.81963300	-1.74287800
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H	-0.57749400	2.53729400	-1.72546500
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H	2.17525200	0.40976700	3.20819700
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H	0.39136900	-3.55419100	-1.54558100
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N	1.29706300	-1.27541900	0.9507730
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N	1.19576100	-0.17014500	-1.8724660
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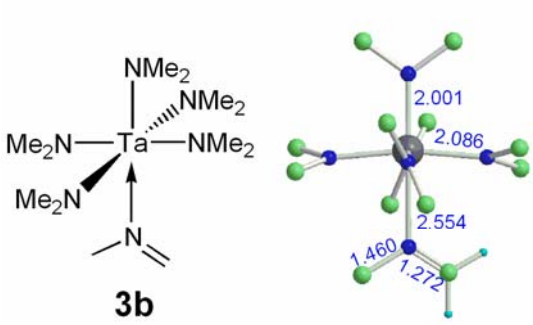
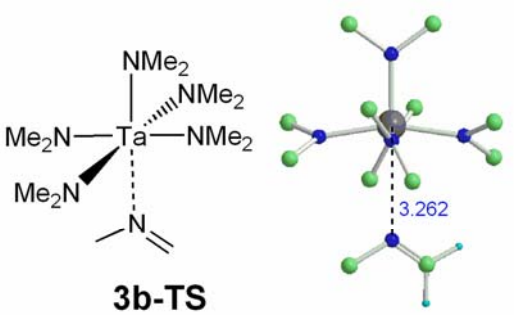


3b



3b-TS

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Ta	0.14245400	-0.06391700	-0.0048700
N	0.20132800	0.54222500	1.9641900
C	-0.89380400	0.86786500	2.8613490
N	-0.95928700	-1.72785700	0.5954090
C	-0.93593000	-2.29837500	1.9403950
N	-0.43067400	-0.40529400	-1.9582980
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N	1.90393600	-1.01289300	-0.0552980
C	2.11739300	-2.42795500	0.2468870
N	-2.09533600	1.16584600	0.0444070
C	-3.34187600	0.40678500	0.0835140
C	-1.83799800	-2.56261600	-0.2148670
C	0.08736500	-1.55839000	-2.6931080
C	3.19395000	-0.41126600	-0.3890480
C	-2.17091300	2.43512500	0.0488590
C	1.46122700	0.70779700	2.6853130
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H	2.41983800	2.37759300	-1.9788400
H	0.80137900	2.98735300	-2.3425970
H	0.82156200	3.86290700	-0.1535250
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H	-1.96809800	-2.14280900	-1.2114980
H	-1.44015300	-3.58850300	-0.3208760
H	-2.83649500	-2.66854700	0.2483800
H	0.71258400	-2.18598400	-2.0574720
H	-0.72545600	-2.18863100	-3.0960280
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H	3.91524400	-0.55132300	0.4344610
H	3.63194200	-0.88910000	-1.2812870
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H	-1.25719700	3.01816500	0.0015210
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H	2.59852900	-2.94137700	-0.6032500
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C	-0.64659900	2.32352500	2.0232090
N	-0.19378900	1.92886000	0.6907580
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Ta	-0.31854900	-0.01317100	-0.0049750
N	0.09045400	0.68106700	-1.8847050
C	1.26375800	0.44312400	-2.7054960
N	0.16818600	-1.90397000	-0.6781970
C	-0.14228000	-2.37625300	-2.0263830
N	0.09819000	-0.64226000	1.8953740
C	1.18920500	-0.23640900	2.7630320
N	-2.29959600	-0.17535300	-0.0562860
C	-3.03841500	-1.41002300	-0.3170390
N	2.93079000	0.26366800	0.0607580
C	3.74392500	-0.94287800	0.0751610
C	0.85171700	-2.97830400	0.0290300
C	-0.72022000	-1.64440100	2.5682660
C	-3.24385200	0.92002400	0.1596190
C	3.53514700	1.37825300	0.0112340
C	-0.83402900	1.56309100	-2.5880130
H	-1.06166600	1.47042300	2.5617710
H	-1.42555700	3.10374100	1.9587040
H	0.17562300	2.74874400	2.6249200
H	1.12851200	3.59003000	0.6454430
H	-0.42852400	3.87640400	-0.1360430
H	0.78156200	2.84519200	-0.9349600
H	1.18625200	-2.64434900	1.0103660
H	0.19569600	-3.85715400	0.1636620
H	1.73243300	-3.33360700	-0.5349620
H	-1.54087300	-1.98217500	1.9317210
H	-0.13499500	-2.53409300	2.8612040
H	-1.15863400	-1.23187400	3.4941460
H	-2.71943300	1.86097200	0.3223790
H	-3.90898400	1.03780300	-0.7122430
H	-3.88579000	0.71952800	1.0332140
H	4.63112100	1.46578500	-0.0219370
H	2.95751000	2.30035500	0.0005650
H	1.75437100	0.58195100	2.3160490
H	1.88928700	-1.06902100	2.9637070
H	0.81211600	0.09825000	3.7453600
H	-3.71200700	-1.64566500	0.5240080
H	-3.66660600	-1.30961100	-1.2174520
H	-2.35846200	-2.24916100	-0.4600460
H	3.45756100	-1.57528600	-0.7712700
H	3.52305300	-1.50834600	0.9861340
H	4.82549400	-0.74043500	0.0278800
H	-0.64961600	-1.60300300	-2.6049940
H	-0.79688700	-3.26493900	-1.9904430
H	0.76774600	-2.67945600	-2.5732180
H	-1.19827600	1.08841100	-3.5160720
H	-1.70198600	1.80211700	-1.9698970
H	-0.35964700	2.51619800	-2.8813450
H	1.90179600	-0.31878200	-2.2557590
H	0.97743100	0.10004800	-3.7150750
H	1.86957200	1.35754800	-2.8400390

Table S2. Crystal data and structure refinement for **2a**.

Empirical formula	C12 H35 N6 Nb	
Formula weight	356.35	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Im-3m	
Unit cell dimensions	a = 9.8520(11) Å	α = 90°
	b = 9.8520(11) Å	β = 90°
	c = 9.8520(11) Å	γ = 90°
Volume	956.25(18) $Å^3$	
Z	2	
Density (calculated)	1.241 Mg/m^3	
Absorption coefficient	0.629 mm^{-1}	
F(000)	382	
Crystal size	0.25 × 0.23 × 0.20 mm^3	
Theta range for data collection	2.92 to 28.41°	
Index ranges	$-12 \le h \le 13$, $-13 \le k \le 13$, $-13 \le l \le 12$	
Reflections collected	2686	
Independent reflections	143 [R(int) = 0.0678]	
Completeness to theta = 28.41°	96.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8845 and 0.8586	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	143 / 0 / 11	
Goodness-of-fit on F^2	1.192	
Final R indices [I > 2sigma(I)]	R1 = 0.0465, wR2 = 0.1123	
R indices (all data)	R1 = 0.0465, wR2 = 0.1123	
Largest diff. peak and hole	0.432 and -0.540 $e.Å^{-3}$	

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb(1)	0	0	0	52(1)
N	2142(6)	0	0	80(2)
C	3030(11)	1133(18)	0	152(8)

Table S4. Bond lengths (Å) and angles (°) for **2a**.

Nb(1)-N#1	2.110(6)	N-C	1.418(14)
Nb(1)-N#2	2.110(6)	N-C#6	1.418(14)
Nb(1)-N#3	2.110(6)	N-C#7	1.418(14)
Nb(1)-N#4	2.110(6)	N-C#8	1.418(14)
Nb(1)-N#5	2.110(6)	C-C#7	1.58(3)
Nb(1)-N	2.110(6)	C-C#6	1.58(3)
N#1-Nb(1)-N#2	180.0	N#2-Nb(1)-N	90.0
N#1-Nb(1)-N#3	90.0	N#3-Nb(1)-N	180.0
N#2-Nb(1)-N#3	90.0	N#4-Nb(1)-N	90.0
N#1-Nb(1)-N#4	90.0		
N#2-Nb(1)-N#4	90.0	N#5-Nb(1)-N	90.0
N#3-Nb(1)-N#4	90.0	C-N-C#6	67.6(7)
N#1-Nb(1)-N#5	90.0	C-N-C#7	67.6(7)
N#2-Nb(1)-N#5	90.0	C#6-N-C#7	103.8(14)
N#3-Nb(1)-N#5	90.0	C-N-C#8	103.8(14)
N#4-Nb(1)-N#5	180.0	C#6-N-C#8	67.6(7)
N#1-Nb(1)-N	90.0	C#7-N-C#8	67.6(7)

C-N-Nb(1)	128.1(7)	N-C-C#7	56.2(4)
C#6-N-Nb(1)	128.1(7)	N-C-C#6	56.2(4)
C#7-N-Nb(1)	128.1(7)	C#7-C-C#6	90.002(2)
C#8-N-Nb(1)	128.1(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -y,-z,-x #2 y,z,x #3 -x,-y,-z #4 z,x,y

#5 -z,-x,-y #6 x,z,y #7 x,z,-y #8 x,-y,z

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nb(1)	52(1)	52(1)	52(1)	0	0	0
N	48(3)	95(3)	95(3)	0	0	0
C	58(4)	137(13)	260(20)	0	0	-30(6)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2a**.

	x	y	z	U(eq)
H(0)	2902	2120	0	182

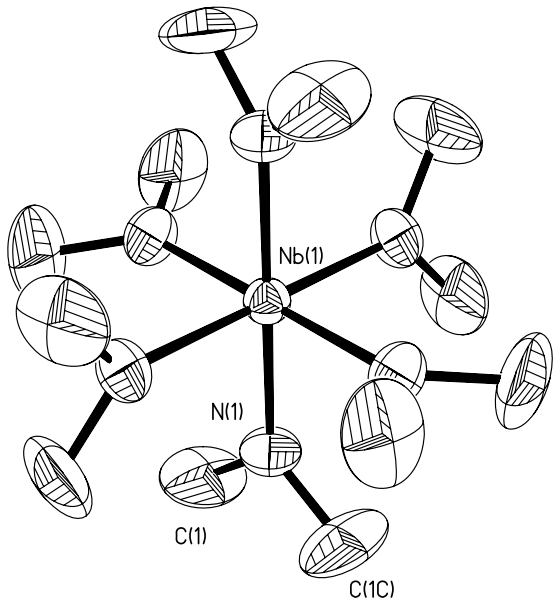

Figure S6. ORTEP of **2a** showing 30% probability thermal ellipsoids.

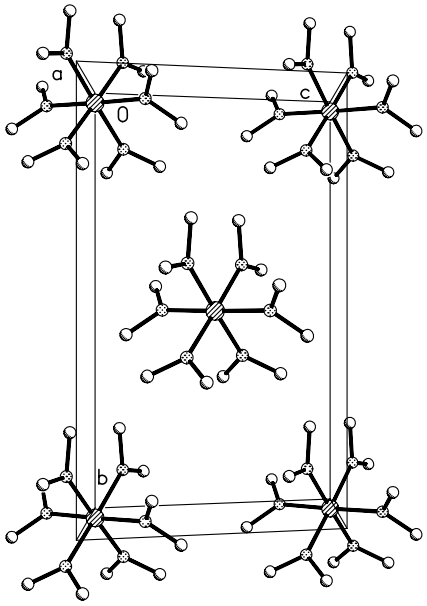

Figure S7. Packing diagram of **2a** along the a axis.

Table S7. Crystal data and structure refinement for **2b**.

Empirical formula	C12 H35 N6 Ta	
Formula weight	444.39	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Im-3m	
Unit cell dimensions	a = 9.835(3) Å	α = 90°
	b = 9.835(3) Å	β = 90°
	c = 9.835(3) Å	γ = 90°
Volume	951.2(5) $Å^3$	
Z	2	
Density (calculated)	1.555 g/cm^3	
Absorption coefficient	5.778 mm^{-1}	
F(000)	446	
Crystal size	0.19 × 0.12 × 0.10 mm^3	
Theta range for data collection	2.93 to 26.27°	
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-12 \le l \le 12$	
Reflections collected	4518	
Independent reflections	123 [R(int) = 0.0497]	
Completeness to theta = 26.27°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5958 and 0.4065	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	123 / 0 / 12	
Goodness-of-fit on F^2	1.147	
Final R indices [I>2sigma(I)]	R1 = 0.0143, wR2 = 0.0370	
R indices (all data)	R1 = 0.0143, wR2 = 0.0370	
Largest diff. peak and hole	0.219 and -0.274 $e.Å^{-3}$	

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ta	0	0	0	50(1)
N	0	2110(6)	0	81(2)
C(1)	0	3040(11)	1146(13)	164(7)

Table S9. Bond lengths (Å) and angles (°) for **2b**

Ta-N#1	2.075(6)	Ta-N	2.075(6)
Ta-N#2	2.075(6)	N-C(1)#6	1.451(11)
Ta-N#3	2.075(6)	N-C(1)	1.451(11)
Ta-N#4	2.075(6)	N-C(1)#7	1.451(11)
Ta-N#5	2.075(6)	N-C(1)#8	1.451(11)
N#1-Ta-N#2	180.0	N#4-Ta-N	90.0
N#1-Ta-N#3	90.0	N#5-Ta-N	90.0
N#2-Ta-N#3	90.0	C(1)#6-N-C(1)	66.6(6)
N#1-Ta-N#4	90.0	C(1)#6-N-C(1)#7	101.9(11)
N#2-Ta-N#4	90.0	C(1)-N-C(1)#7	66.6(6)
N#3-Ta-N#4	90.0	C(1)#6-N-C(1)#8	66.6(6)
N#1-Ta-N#5	90.0	C(1)-N-C(1)#8	101.9(11)
N#2-Ta-N#5	90.0	C(1)#7-N-C(1)#8	66.6(6)
N#3-Ta-N#5	90.0	C(1)#6-N-Ta	129.1(6)
N#4-Ta-N#5	180.0	C(1)-N-Ta	129.1(6)
N#1-Ta-N	90.0	C(1)#7-N-Ta	129.1(6)
N#2-Ta-N	90.0	C(1)#8-N-Ta	129.1(6)
N#3-Ta-N	180.0		

Symmetry transformations used to generate equivalent atoms:
#1 -y,-z,-x #2 y,z,x #3 -x,-y,-z #4 z,x,y
#5 -z,-x,-y #6 z,y,-x #7 -z,y,-x #8 x,y,-z

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta	50(1)	50(1)	50(1)	0	0	0
N	95(3)	52(3)	95(3)	0	0	0
C(1)	262(19)	69(5)	160(12)	-36(6)	0	0

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2b**.

	x	y	z	U(eq)
H(1A)	492	3849	909	246
H(1B)	428	2612	1912	246
H(1C)	-920	3274	1375	246

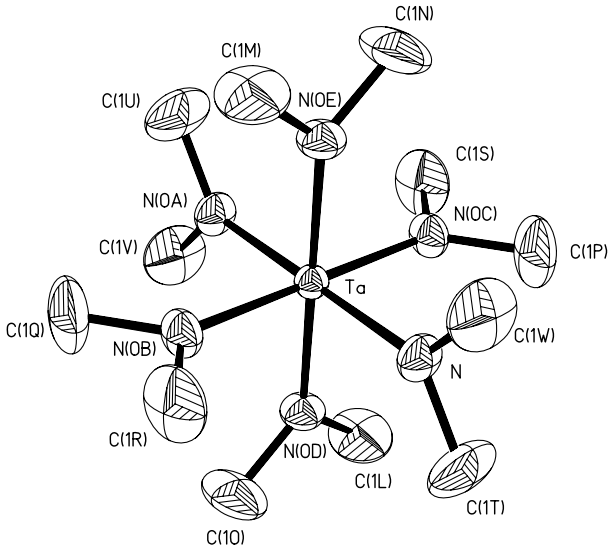

Figure S8. ORTEP of **2b** showing 5% probability thermal ellipsoids.