Supporting Information

The Niobium Oxoazides $[NbO(N_3)_3]$, $[NbO(N_3)_3\cdot 2CH_3CN]$, $[(bipy)NbO(N_3)_3]$, $Cs_2[NbO(N_3)_5]$ and $[PPh_4]_2[NbO(N_3)_5]$

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Experimental Details

General

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. Because of the high energy content and the high detonation velocity of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory. **Ignoring safety precautions can lead to serious injuries!**

***Materials and apparatus**:* All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a grease-less Pyrex glass vacuum lines equipped with Kontes® HI-VAC® valves. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. $NbOF_3$ was prepared from NbF_5 (Alfa Aesar) and SiO_2 in anhydrous HF (Galaxy Chemicals). Me_3SiN_3 (95%, TCI America) was purified by fractional condensation. SO_2 (Aldrich) was dried over CaH_2. Acetonitrile (Aldrich) was dried over molecular sieves and freshly distilled prior to use. PPh_4N_3 was prepared according to a literature procedure[1] and 2,2'-bipyridine (Aldrich) was used without further purification. The NMR spectra were recorded at 298 K on a Bruker AMX-500 spectrometer. Spectra were externally referenced to neat nitromethane for ^{14}N NMR spectra. Raman spectra were recorded in 5mm J. Young nmr tubes in the range 4000–80 cm^{-1} on Bruker Equinox 55 FT-RA or Vertex 70/RAM II spectrophotometer, using Nd-YAG lasers at 1064 nm. Infrared spectra were recorded in the range 4000-400 cm^{-1} on Bruker Alpha, Bruker Vertex 70, or Bruker Tensor FT-IR spectrometers using KBr pellets. The pellets were prepared inside the glove box using an Econo Press (Thermo Scientific) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment, which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample. Neat grinding of the friction sensitive polyazides must be avoided. The azides were added to the finely powdered KBr and blended into the KBr using a non-metallic spatula. DTA curves were recorded with a purge of dry nitrogen gas on an OZM Research DTA552-Ex instrument with the Meavy 2.2.0 software. The heating rate was 5 °C/min and the sample size was 5-25 mg. The impact and friction sensitivity data were determined on an OZM Research BAM Fall Hammer BFH-10 and an OZM Research BAM Friction apparatus FSKM-10, respectively. Both instruments were calibrated using RDX.

Crystal Structure determinations

The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The frames were integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[2] The absorption correction was performed using the SADABS program.[3, 4] The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[5-8] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[9] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1419751-1419753.

Preparation of $[NbO(N_3)_3 \cdot 2CH_3CN]$

A sample of $[NbOF_3]$ (133 mg; 0.80 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of CH_3CN (1.2 mL) and Me_3SiN_3 (402 mg, 3.50 mmol) *in vacuo* at -196 °C. The mixture was warmed to -20 °C. After 2 hours, a light yellow solution was obtained and all volatile materials were pumped off, first at -20 °C and then later at ambient temperature, leaving behind yellow solid $[NbO(N_3)_3 \cdot 2CH_3CN]$ (243 mg; weight expected for 0.80 mmol $[NbO(N_3)_3 \cdot 2CH_3CN]$: 254 mg). DTA: 131 °C (onset, explosion); impact sensitivity: <1 J, friction sensitivity: <5 N; ^{14}N NMR (SO_2, 25 °C) δ = -135 ppm (CH_3CN), -145 ppm ($\Delta\nu_{½}$ = 50 Hz) (N_β), -207 ppm ($\Delta\nu_{½}$ = 90 Hz) (N_γ), -313 ppm ($\Delta\nu_{½}$ = 700 Hz) (N_α); Raman (20 °C, 20 mW) $\bar{\nu}$ = 2940 (6.2); 2268 (2.2); 2157 (10.0); 2125 (6.7); 2058 (2.2); 1371 (1.5); 1267 (0.6); 961 (0.6); 875 (0.8); 725 (2.0); 689 (2.7); 608 (2.1); 531 (1.0); 456 (5.3); 390 (1.2); 273 (0.5); 224 (0.8) cm^{-1}; IR (KBr) $\bar{\nu}$ = 2998 (vw); 2931 (w); 2312 (vw); 2288 (w); 2252 (vw); 2135 (vs); 2087 (vs); 1361 (s); 1258 (s); 1182 (m); 1033 (w); 919 (m sh); 773 (s sh); 704 (s); 674 (s); 616 (s); 576 (m sh) cm^{-1}.

Preparation of $[NbO(N_3)_3]$

A sample of $[NbOF_3]$ (133 mg; 0.80 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of SO_2 (1.0 mL) and Me_3SiN_3 (402 mg, 3.50 mmol) *in vacuo* at -196 °C. The mixture was warmed to -20 °C. After 2 hours, a light yellow solution was obtained and all volatile materials were pumped off, first at -20 °C and then later at ambient temperature, leaving behind pale yellow solid $[NbO(N_3)_3]$ (185 mg; weight expected for 0.80 mmol $[NbO(N_3)_3]$: 188 mg). DTA: 104 °C (onset, explosion); impact sensitivity: <1 J, friction sensitivity: <5 N; ^{14}N NMR (acetone-d_6, 25°C) δ = -135 ppm ($\Delta\nu_{½}$ = 40 Hz) (N_β), -206 ppm ($\Delta\nu_{½}$ = 60 Hz) (N_γ), -316 ppm ($\Delta\nu_{½}$ = 300 Hz) (N_α); Raman (-80 °C, 20 mW) $\tilde{\nu}$ = 2136 (8.6); 2114 (8.9); 2082 (5.4); 1364 (4.2); 945 (5.2); 788 (5.7); 638 (7.8); 448 (10.0) cm^{-1}; IR (KBr) $\tilde{\nu}$ = 2183 (m); 2149 (d); 2037 (w); 1751 (m); 1638 (m); 1522 (vw); 1431 (w); 1400 (w); 1257 (w); 1183 (m); 1033 (w); 856 (s sh); 663 (vs); 619 (s sh) cm^{-1}.

Preparation of $[(bipy)NbO(N_3)_3]$

A solution of $[NbO(N_3)_3]$ (117 mg; 0.50 mmol) in CH_3CN (1.0 mL) was added to a solution of 2,2'-bipyridine (78 mg; 0.50 mmol) in CH_3CN (1.5 mL). After about 15 minutes, the solution was cooled to -20°C and the solvent slowly pumped off, leaving behind a crystalline yellow solid of $[(bipy)NbO(N_3)_3]$ (191 mg; weight expected for 0.50 mmol $[(bipy)NbO(N_3)_3]$: 196 mg). DTA: 172 °C (onset, exotherm); impact sensitivity: <1 J, friction sensitivity: 80 N; ^{14}N NMR (SO_2, 25 °C) δ = -144 ppm ($\Delta\nu_{½}$ = 30 Hz) (N_β), -206 ppm ($\Delta\nu_{½}$ = 50 Hz) (N_γ), -236 ppm ($\Delta\nu_{½}$ = 400 Hz) (N_α); Raman (20 °C, 20 mW) $\tilde{\nu}$ = 3090 (0.5); 3064 (0.5); 2131 (3.7); 2073 (0.5); 1669 (0.2); 1608 (1.0); 1600 (7.1); 1591 (1.9); 1573 (1.6); 1563 (2.9); 1494 (2.5); 1484 (0.6); 1448 (0.9); 1408 (0.5); 1350 (0.8); 1343 (1.3); 1313 (7.9); 1303 (0.9); 1267 (1.3); 1246 (0.3); 1237 (0.6); 1174 (0.4); 1159 (0.9); 1064 (1.2); 1047 (0.4); 1027 (6.1); 1009 (0.3); 995 (1.7); 928 (10.0); 903 (0.3); 812 (0.2); 767 (1.5); 737 (0.2); 657 (0.2); 637 (0.6); 634 (0.7); 616 (0.3); 549 (0.1); 464 (0.2); 403 (3.3); 356 (0.5); 267 (0.7); 230 (1.4); 213 (1.2); 177 (0.7); 149 (1.8); 108 (7.7); 92 (7.3) cm^{-1}; IR (KBr) $\tilde{\nu}$ = 3111 (vw); 3071 (vw); 3061 (vw); 3036 (vw); 2126 (s); 2084 (vs); 2068 (vs); 2038 (s); 1600 (m); 1572 (vw); 1562 (w); 1543 (vw); 1528 (vw); 1509 (vw); 1496 (w); 1474 (m); 1459 (vw); 1442 (m); 1422 (vw); 1378 (m); 1348 (s); 1325 (s); 1281 (vw); 1268 (vw); 1243 (vw); 1224 (vw); 1177 (vw); 1157 (m);

1104 (w); 1063 (w); 1025 (m); 1015 (w); 921 (s); 897 (m); 767 (s); 734 (m); 700 (vw); 655 (m); 635 (w); 622 (m); 592 (w); 414 (m) cm^{-1}.

Preparation of $Cs_2[NbO(N_3)_5]$

To a frozen solution of $[NbOF_3]$ (83 mg; 0.50 mmol) and CsF (152 mg; 1.0 mmol) in SO_2 (1.0 mL), Me_3SiN_3 (288 mg, 2.50 mmol) was added *in vacuo* at -196 °C. The mixture was allowed to warm to ambient temperature. After about 15 minutes, the solution was cooled to -20°C and the volatile materials slowly pumped off, leaving behind a crystalline yellow-orange solid of $Cs_2[NbO(N_3)_5]$ (289 mg; weight expected for 0.50 mmol $Cs_2[NbO(N_3)_5]$: 292 mg). DTA: 134 °C (onset, explosion); impact sensitivity: 2 J, friction sensitivity: <5 N; ^{14}N NMR (SO_2, 25 °C) δ = -135 ppm ($\Delta\nu_{½}$ = 50 Hz) (N_β), -223 ppm ($\Delta\nu_{½}$ = 100 Hz) (N_γ), -310 ppm ($\Delta\nu_{½}$ = 300 Hz) (N_α); Raman (-70 °C, 30 mW) $\tilde{\nu}$ = 2039 (1.8); 2016 (3.1); 1379 (0.6); 1331 (0.7); 1273 (1.9); 1188 (1.2); 1077 (10.0); 1048 (0.8); 539 (0.9); 424 (1.7); 384 (0.4); 312 (4.5); 264 (9.8); 172 (2.6); 98 (7.8) cm^{-1}; IR (KBr); $\tilde{\nu}$ = 2145 (w); 2032 (s sh); 2010 (vs); 1251 (w); 1179 (s sh); 1074 (m); 1049 (w); 962 (m); 889 (vw); 847 (vw); 754 (vw); 653 (w); 637 (m); 615 (m); 558 (w); 549 (w); 517 (w); 499 (w); 442 (w); 433 (vw sh) cm^{-1}.

Preparation of $[TPP]_2[NbO(N_3)_5]$

A solution of $[NbO(N_3)_3]$ (117 mg; 0.50 mmol) in CH_3CN (1.0 mL) was added to a solution of tetraphenylphosphonium azide (381 mg; 1.00 mmol) in CH_3CN (2.5 mL). After about 15 minutes, the solution was cooled to -20 °C and the solvent slowly pumped off, leaving behind a crystalline yellow solid of $[TPP]_2[NbO(N_3)_5]$ (469 mg; weight expected for 0.50 mmol $[TPP]_2[NbO(N_3)_5]$: 478 mg). DTA: 200 °C (onset, exotherm); impact sensitivity: 50 J, friction sensitivity: >360 N; ^{14}N NMR (acetone-d_6, 25 °C) δ = -133 ppm ($\Delta\nu_{½}$ = 40 Hz) (N_β), -170 ppm ($\Delta\nu_{½}$ = 80 Hz) (N_γ), -225 ppm ($\Delta\nu_{½}$ = 600 Hz) (N_α); Raman (-80 °C, 20 mW)) $\tilde{\nu}$ = 3174 (0.7); 3145 (0.8); 3063 (9.9); 3027 (0.9); 3011 (0.9); 2993 (0.6); 2986 (0.5); 2964 (0.5); 2956 (0.5); 2118 (2.9); 2111 (7.8); 2080 (1.2); 2064 (0.9); 2053 (0.7); 1588 (6.6); 1577 (1.8); 1484 (0.5); 1436 (0.4); 1363 (0.9); 1353 (0.9); 1342 (1.4); 1315 (1.7); 1242 (0.4); 1187 (1.2); 1165 (1.0); 1112 (1.5); 1100 (2.8); 1075 (0.4); 1028 (4.6); 1001 (12.8); 988 (0.7); 930 (0.5); 907 (4.9); 733 (1.1); 680 (2.9); 629 (0.5); 616 (1.9); 413 (4.6); 383 (0.8); 358 (0.9); 332 (1.3); 291 (1.1); 285 (1.5); 252 (3.3); 245 (2.4); 222 (1.6); 206 (2.0); 198 (2.5); 108 (11.8); 95 (11.0); 85 (10.3) cm^{-1}; IR (KBr)) $\tilde{\nu}$ = 3091 (vw); 3062 (w); 3050 (w); 3006 (vw); 2205 (vw); 2117 (w); 2067 (s sh); 2059 (s sh); 1985 (vw); 1585 (m); 1482 (s sh); 1438 (vs); 1336 (m); 1320 (m sh); 1273 (vw); 1186 (w); 1167 (w); 1108 (vs); 1027 (w); 996 (m); 930 (vw); 909 (m); 856 (w); 754 (s); 723 (vs); 690 (vs); 628 (w); 614 (vw); 527 (vs); 459 (vw); 447 (vw); 419 (vw) cm^{-1}.

Crystallographic Details

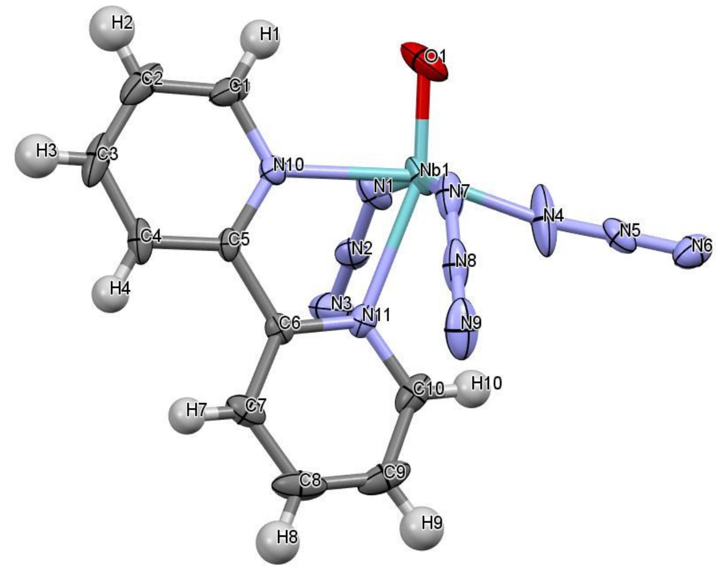


Figure S1. Asymmetric unit in the crystal structure of [(bipy)NbO(N_3)$_3$].

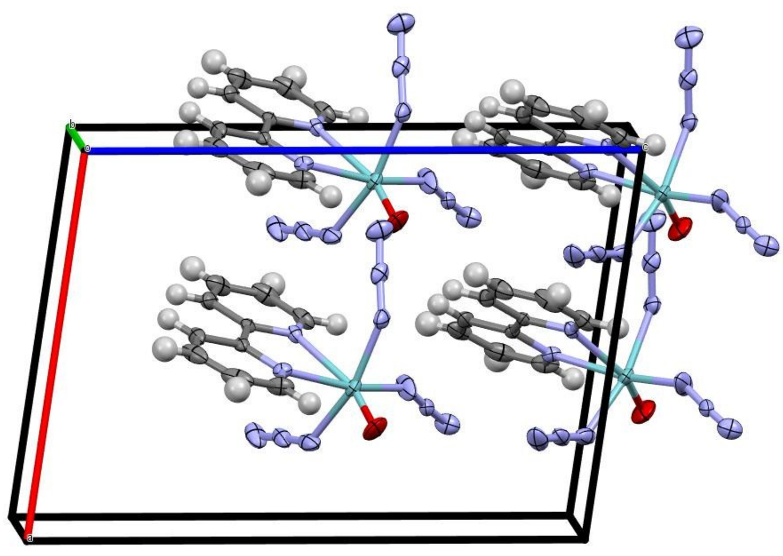


Figure S2. The unit cell in the crystal structure of [(bipy)NbO(N_3)$_3$].

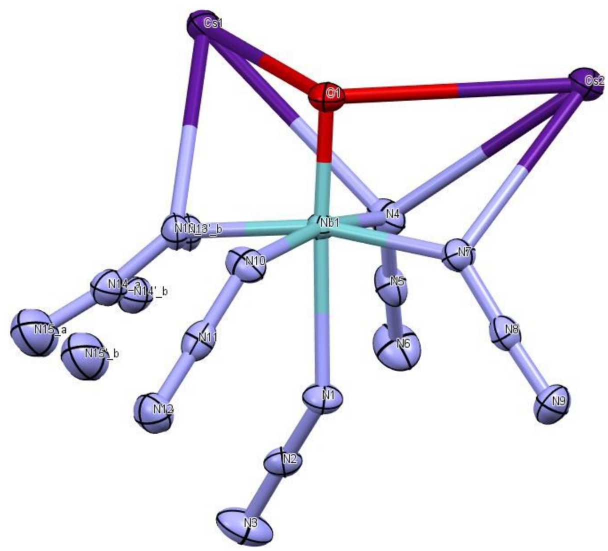


Figure S3. Asymmetric unit in the crystal structure of $Cs_2[NbO(N_3)_5]$.

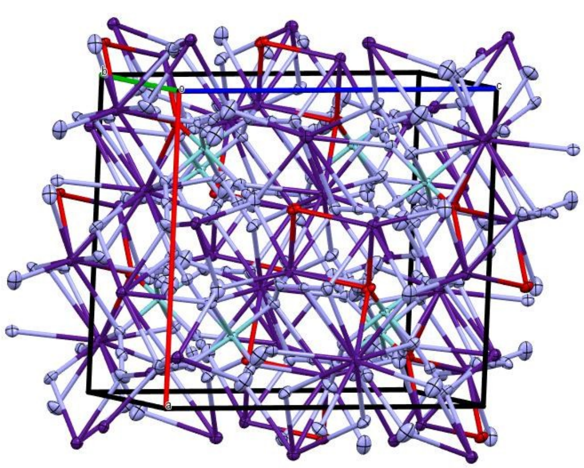


Figure S4. The unit cell in the crystal structure of $Cs_2[NbO(N_3)_5]$.

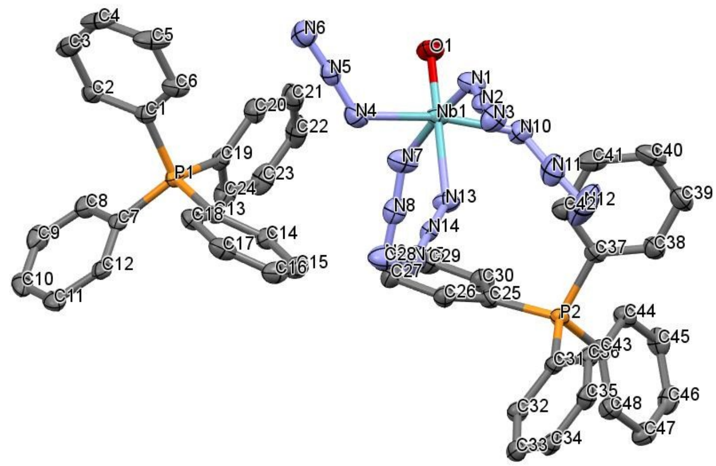


Figure S5. Asymmetric unit in the crystal structure of $[PPh_4]_2[NbO(N_3)_5]$.

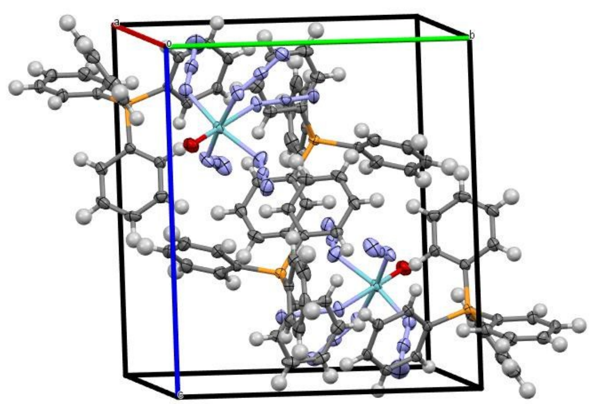


Figure S6. The unit cell in the crystal structure of $[PPh_4]_2[NbO(N_3)_5]$.

Table S1. Sample and crystal data for $[(bipy)NbO(N_3)_3]$.

Identification code	NbON9bipy	
Chemical formula	$C_{10}H_8N_{11}NbO$	
Formula weight	391.18 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.148 x 0.177 x 0.451 mm	
Crystal habit	yellow prism	
Crystal system	monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 10.2393(8) Å	α = 90°
	b = 9.8720(7) Å	β = 98.4600(10)°
	c = 14.4784(11) Å	γ = 90°
Volume	1447.59(19) $Å^3$	
Z	4	
Density (calculated)	1.795 g/cm^3	
Absorption coefficient	0.856 mm^{-1}	
F(000)	776	

Table S2. Data collection and structure refinement for [(bipy)NbO$(N_3)_3$].

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.85 to 30.55°
Index ranges	-14<=h<=14, -14<=k<=13, -20<=l<=20
Reflections collected	13714
Independent reflections	4321 [R(int) = 0.0210]
Coverage of independent reflections	99.3%
Absorption correction	multi-scan
Max. and min. transmission	0.8840 and 0.6990
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4321 / 2 / 208
Goodness-of-fit on F^2	1.094
Final R indices	4097 data; I>2σ(I) R1 = 0.0233, wR2 = 0.0500
	all data R1 = 0.0264, wR2 = 0.0518
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0157P)^2+1.4433P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.652 and -0.929 eÅ^{-3}
R.M.S. deviation from mean	0.060 eÅ^{-3}

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for [(bipy)NbO(N_3)$_3$].

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.6076(3)	0.0428(3)	0.4148(3)	0.0319(7)
C2	0.5823(3)	0.9684(3)	0.3334(3)	0.0413(9)
C3	0.5231(3)	0.0312(4)	0.2526(3)	0.0391(9)
C4	0.4866(3)	0.1659(3)	0.2559(2)	0.0283(6)
C5	0.5124(3)	0.2357(3)	0.34061(18)	0.0178(5)
C6	0.4721(2)	0.3776(3)	0.35181(18)	0.0174(5)
C7	0.4131(3)	0.4572(3)	0.2781(2)	0.0273(6)
C8	0.3819(3)	0.5906(4)	0.2955(3)	0.0384(8)
C9	0.4090(4)	0.6413(3)	0.3842(3)	0.0390(8)
C10	0.4657(3)	0.5562(3)	0.4553(2)	0.0291(6)
N1	0.4469(3)	0.2276(3)	0.58490(18)	0.0283(5)
N2	0.3331(3)	0.2661(3)	0.57043(19)	0.0273(5)
N3	0.2248(3)	0.2976(3)	0.5599(3)	0.0421(7)
N4	0.6364(4)	0.4405(5)	0.6544(2)	0.0581(11)
N5	0.6925(2)	0.5296(3)	0.69924(17)	0.0255(5)
N6	0.7410(3)	0.6151(3)	0.7438(2)	0.0327(6)
N7	0.7732(3)	0.3923(3)	0.4935(2)	0.0361(7)
N8	0.7679(3)	0.4966(4)	0.4467(2)	0.0354(7)
N9	0.7673(3)	0.5922(4)	0.4024(2)	0.0462(9)
N10	0.5752(2)	0.1751(2)	0.41873(18)	0.0213(5)
N11	0.4974(2)	0.4268(2)	0.43987(16)	0.0199(4)
Nb1	0.62665(2)	0.29359(3)	0.55434(2)	0.02723(7)
O1	0.7244(3)	0.1615(4)	0.5998(2)	0.0513(7)

Table S4. Bond lengths (Å) for [(bipy)NbO$(N_3)_3$].

C1-N10	1.350(4)	C1-C2	1.381(5)
C1-H1	0.95	C2-C3	1.383(6)
C2-H2	0.95	C3-C4	1.384(5)
C3-H3	0.95	C4-C5	1.397(4)
C4-H4	0.95	C5-N10	1.355(4)
C5-C6	1.476(4)	C6-N11	1.353(3)
C6-C7	1.390(4)	C7-C8	1.387(5)
C7-H7	0.95	C8-C9	1.368(6)
C8-H8	0.95	C9-C10	1.389(5)
C9-H9	0.95	C10-N11	1.345(4)
C10-H10	0.95	N1-N2	1.214(4)
N1-Nb1	2.061(3)	N2-N3	1.139(4)
N4-N5	1.189(4)	N4-Nb1	2.042(3)
N5-N6	1.132(4)	N7-N8	1.229(5)
N7-Nb1	2.090(3)	N8-N9	1.141(5)
N10-Nb1	2.280(2)	N11-Nb1	2.362(2)
Nb1-O1	1.715(3)		

Table S5. Bond angles (°) for [(bipy)NbO(N_3)$_3$].

N10-C1-C2	122.3(3)	N10-C1-H1	118.9
C2-C1-H1	118.9	C1-C2-C3	119.2(3)
C1-C2-H2	120.4	C3-C2-H2	120.4
C2-C3-C4	119.2(3)	C2-C3-H3	120.4
C4-C3-H3	120.4	C3-C4-C5	119.2(3)
C3-C4-H4	120.4	C5-C4-H4	120.4
N10-C5-C4	121.3(3)	N10-C5-C6	115.7(2)
C4-C5-C6	123.0(3)	N11-C6-C7	121.5(3)
N11-C6-C5	115.2(2)	C7-C6-C5	123.3(3)
C8-C7-C6	118.9(3)	C8-C7-H7	120.6
C6-C7-H7	120.6	C9-C8-C7	119.9(3)
C9-C8-H8	120.1	C7-C8-H8	120.1
C8-C9-C10	118.6(3)	C8-C9-H9	120.7
C10-C9-H9	120.7	N11-C10-C9	122.5(3)
N11-C10-H10	118.8	C9-C10-H10	118.8
N2-N1-Nb1	136.7(2)	N3-N2-N1	176.6(3)
N5-N4-Nb1	151.9(3)	N6-N5-N4	176.9(3)
N8-N7-Nb1	130.3(2)	N9-N8-N7	177.5(4)
C1-N10-C5	118.8(3)	C1-N10-Nb1	120.3(2)
C5-N10-Nb1	120.90(18)	C10-N11-C6	118.7(3)
C10-N11-Nb1	122.4(2)	C6-N11-Nb1	118.12(18)
O1-Nb1-N4	107.66(17)	O1-Nb1-N1	99.60(13)
N4-Nb1-N1	91.41(12)	O1-Nb1-N7	95.81(14)
N4-Nb1-N7	90.26(13)	N1-Nb1-N7	163.20(11)
O1-Nb1-N10	89.31(12)	N4-Nb1-N10	163.03(14)
N1-Nb1-N10	85.53(10)	N7-Nb1-N10	88.02(10)
O1-Nb1-N11	158.00(12)	N4-Nb1-N11	93.79(15)
N1-Nb1-N11	84.30(9)	N7-Nb1-N11	78.91(10)
N10-Nb1-N11	69.31(8)		

Table S6. Torsion angles (°) for [(bipy)NbO(N_3)$_3$].

N10-C1-C2-C3	0.8(5)	C1-C2-C3-C4	-2.2(5)
C2-C3-C4-C5	1.0(5)	C3-C4-C5-N10	1.6(4)
C3-C4-C5-C6	-177.3(3)	N10-C5-C6-N11	-3.1(3)
C4-C5-C6-N11	175.9(2)	N10-C5-C6-C7	176.5(3)
C4-C5-C6-C7	-4.5(4)	N11-C6-C7-C8	1.2(4)
C5-C6-C7-C8	-178.4(3)	C6-C7-C8-C9	-0.3(5)
C7-C8-C9-C10	-1.0(5)	C8-C9-C10-N11	1.4(5)
C2-C1-N10-C5	1.8(4)	C2-C1-N10-Nb1	-177.8(2)
C4-C5-N10-C1	-3.0(4)	C6-C5-N10-C1	176.0(3)
C4-C5-N10-Nb1	176.6(2)	C6-C5-N10-Nb1	-4.3(3)
C9-C10-N11-C6	-0.5(4)	C9-C10-N11-Nb1	169.1(2)
C7-C6-N11-C10	-0.9(4)	C5-C6-N11-C10	178.8(2)
C7-C6-N11-Nb1	-170.9(2)	C5-C6-N11-Nb1	8.8(3)

Table S7. Anisotropic atomic displacement parameters (Å^2) for [(bipy)NbO(N_3)$_3$].

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0240(14)	0.0175(13)	0.054(2)	0.0021(13)	0.0059(14)	0.0013(10)
C2	0.0273(15)	0.0229(15)	0.077(3)	-0.0164(16)	0.0189(17)	-0.0054(12)
C3	0.0281(16)	0.0416(18)	0.051(2)	-0.0301(17)	0.0174(15)	-0.0162(14)
C4	0.0229(13)	0.0396(16)	0.0231(14)	-0.0125(12)	0.0055(11)	-0.0123(12)
C5	0.0156(11)	0.0213(12)	0.0169(12)	-0.0038(9)	0.0032(9)	-0.0051(9)
C6	0.0156(11)	0.0209(11)	0.0162(11)	0.0026(9)	0.0044(9)	-0.0047(9)
C7	0.0217(13)	0.0358(16)	0.0246(14)	0.0104(12)	0.0044(11)	0.0000(11)
C8	0.0315(16)	0.0345(16)	0.053(2)	0.0246(16)	0.0175(15)	0.0079(13)
C9	0.0388(18)	0.0196(14)	0.065(2)	0.0082(15)	0.0283(17)	0.0038(12)
C10	0.0312(15)	0.0219(13)	0.0385(17)	-0.0076(12)	0.0190(13)	-0.0064(11)
N1	0.0282(13)	0.0365(14)	0.0194(11)	0.0100(10)	0.0005(9)	-0.0041(11)
N2	0.0346(14)	0.0211(11)	0.0248(12)	0.0069(9)	-0.0002(10)	-0.0030(10)
N3	0.0380(16)	0.0337(15)	0.0518(19)	0.0087(13)	-0.0030(14)	0.0069(12)
N4	0.0437(18)	0.101(3)	0.0320(17)	-0.0381(19)	0.0132(14)	-0.032(2)
N5	0.0207(11)	0.0405(14)	0.0156(11)	0.0041(10)	0.0039(9)	0.0019(10)
N6	0.0307(13)	0.0235(12)	0.0450(17)	-0.0006(12)	0.0089(12)	-0.0007(10)
N7	0.0213(12)	0.0523(18)	0.0348(15)	-0.0207(14)	0.0039(11)	-0.0080(12)
N8	0.0263(13)	0.0535(19)	0.0280(14)	-0.0186(14)	0.0095(11)	-0.0195(12)
N9	0.0437(18)	0.062(2)	0.0357(16)	-0.0132(16)	0.0162(14)	-0.0335(16)
N10	0.0168(10)	0.0217(11)	0.0247(12)	-0.0006(9)	0.0007(9)	-0.0009(8)
N11	0.0219(11)	0.0199(10)	0.0193(11)	-0.0020(8)	0.0077(8)	-0.0040(8)
Nb1	0.02273(10)	0.04216(13)	0.01484(9)	-0.00124(15)	-0.00373(7)	-0.00247(15)
O1	0.0402(14)	0.073(2)	0.0353(14)	0.0121(14)	-0.0126(12)	0.0152(14)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for [(bipy)NbO$(N_3)_3$].

	x/a	y/b	z/c	U(eq)
H1	0.6493	-0.0005	0.4700	0.038
H2	0.6053	-0.1248	0.3329	0.05
H3	0.5076	-0.0176	0.1955	0.047
H4	0.4445	0.2104	0.2014	0.034
H7	0.3944	0.4208	0.2168	0.033
H8	0.3418	0.6466	0.2460	0.046
H9	0.3894	0.7329	0.3969	0.047
H10	0.4828	0.5906	0.5172	0.035

Table S9. Sample and crystal data for $Cs_2[NbO(N_3)_5]$.

Identification code	Cs2NbON15	
Chemical formula	$Cs_2N_{15}NbO$	
Formula weight	584.88	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal size	0.090 x 0.150 x 0.170 mm	
Crystal habit	yellow prism	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 12.5793(15) Å	α = 90°
	b = 16.4373(19) Å	β = 92.433(2)°
	c = 12.8012(15) Å	γ = 90°
Volume	2644.5(5) $Å^3$	
Z	8	
Density (calculated)	2.938 g/cm^3	
Absorption coefficient	6.358 mm^{-1}	
F(000)	2112	

Table S10. Data collection and structure refinement for $Cs_2[NbO(N_3)_5]$.

Diffractometer	Bruker SMART APEX	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	2.04 to 28.72°	
Index ranges	-11<=h<=16, -21<=k<=21, -17<=l<=14	
Reflections collected	8376	
Independent reflections	3157 [R(int) = 0.0213]	
Coverage of independent reflections	92.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5980 and 0.4110	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2013/6 (Sheldrick, 2013)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3157 / 39 / 182	
Goodness-of-fit on F^2	1.053	
Δ/σ_{max}	0.001	
Final R indices	2931 data; I>2σ(I)	R1 = 0.0200, wR2 = 0.0442
	all data	R1 = 0.0226, wR2 = 0.0450
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0169P)^2+4.2919P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.625 and -0.772 eÅ^{-3}	
R.M.S. deviation from mean	0.130 eÅ^{-3}	

Table S11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $Cs_2[NbO(N_3)_5]$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cs1	0.07691(2)	0.38598(2)	0.90181(2)	0.02238(6)
Cs2	0.34604(2)	0.62577(2)	0.06078(2)	0.02510(6)
N1	0.3140(2)	0.34738(15)	0.2886(2)	0.0246(5)
N2	0.3395(2)	0.27840(15)	0.29288(18)	0.0210(5)
N3	0.3653(3)	0.21076(17)	0.3000(2)	0.0404(8)
N4	0.3077(2)	0.41863(15)	0.0712(2)	0.0259(5)
N5	0.3759(2)	0.36650(15)	0.0662(2)	0.0262(6)
N6	0.4409(2)	0.31847(17)	0.0581(2)	0.0377(7)
N7	0.3001(2)	0.52140(15)	0.26627(19)	0.0244(5)
N8	0.3786(2)	0.51415(14)	0.32361(19)	0.0216(5)
N9	0.4533(2)	0.51024(16)	0.3769(2)	0.0313(6)
N10	0.1125(2)	0.42707(15)	0.3282(2)	0.0268(6)
N11	0.11502(19)	0.37121(15)	0.3884(2)	0.0219(5)
N12	0.1159(2)	0.31907(17)	0.4482(2)	0.0311(6)
N13_a	0.1186(10)	0.3279(6)	0.1467(11)	0.0205(17)
N14_a	0.1029(5)	0.2628(4)	0.1773(5)	0.0261(11)
N15_a	0.0707(6)	0.2024(4)	0.2093(5)	0.0530(13)
N13'_b	0.1371(12)	0.3276(7)	0.1319(14)	0.0205(17)
N14'_b	0.1418(6)	0.2597(5)	0.1533(6)	0.0261(11)
N15'_b	0.1534(7)	0.1911(4)	0.1659(6)	0.0530(13)
Nb1	0.20361(2)	0.43388(2)	0.19315(2)	0.01592(6)
O1	0.12599(17)	0.50311(12)	0.12205(17)	0.0257(5)

Table S12. Bond lengths (Å) for $Cs_2[NbO(N_3)_5]$.

Cs1-O1	3.141(2)	Cs1-N3	3.145(3)
Cs1-N13'_b	3.159(16)	Cs1-N10	3.251(3)
Cs1-N13_a	3.297(13)	Cs1-N3	3.319(3)
Cs1-N12	3.343(3)	Cs1-N6	3.408(3)
Cs1-O1	3.448(2)	Cs1-N4	3.589(3)
Cs1-N7	3.691(3)	Cs1-N11	3.695(2)
Cs2-N7	3.213(3)	Cs2-N12	3.216(3)
Cs2-N9	3.232(3)	Cs2-N6	3.268(3)
Cs2-N12	3.305(3)	Cs2-N15_a	3.329(6)
Cs2-N4	3.442(3)	Cs2-N1	3.519(3)
Cs2-O1	3.539(2)	Cs2-N3	3.549(3)
Cs2-N9	3.554(3)	Cs2-N15_a	3.568(6)
N1-N2	1.179(3)	N1-Nb1	2.302(2)
N1-Cs2	3.519(3)	N2-N3	1.161(3)
N2-Cs2	3.772(2)	N3-Cs1	3.145(3)
N3-Cs1	3.319(3)	N3-Cs2	3.549(3)
N4-N5	1.216(4)	N4-Nb1	2.095(2)
N5-N6	1.145(4)	N6-Cs2	3.268(3)
N6-Cs1	3.408(3)	N7-N8	1.211(3)
N7-Nb1	2.079(2)	N7-Cs1	3.691(3)
N8-N9	1.139(4)	N8-Cs2	3.845(2)
N9-Cs2	3.232(3)	N9-Cs2	3.554(3)
N10-N11	1.198(3)	N10-Nb1	2.118(3)
N10-Cs1	3.251(3)	N11-N12	1.149(3)
N11-Cs2	3.574(2)	N11-Cs1	3.695(2)
N12-Cs2	3.216(3)	N12-Cs2	3.305(3)
N12-Cs1	3.343(3)	N13_a-N14_a	1.159(9)
N13_a-Nb1	2.116(12)	N14_a-N15_a	1.155(7)
N15_a-Cs2	3.329(6)	N15_a-Cs2	3.568(6)
N13'_b-N14'_b	1.150(11)	N13'_b-Nb1	2.076(15)
N14'_b-N15'_b	1.149(9)	N15'_b-Cs2	3.660(8)
N15'_b-Cs1	3.757(9)	Nb1-O1	1.732(2)
Nb1-Cs1	4.3364(4)	O1-Cs1	3.141(2)

Table S13. Bond angles (°) for $Cs_2[NbO(N_3)_5]$.

O1-Cs1-N3	115.38(7)	O1-Cs1-N13'_b	115.4(3)
N3-Cs1-N13'_b	123.9(3)	O1-Cs1-N10	62.89(6)
N3-Cs1-N10	101.56(7)	N13'_b-Cs1-N10	121.8(3)
O1-Cs1-N13_a	110.9(2)	N3-Cs1-N13_a	127.0(2)
N10-Cs1-N13_a	122.1(2)	O1-Cs1-N3	66.74(7)
N3-Cs1-N3	69.18(11)	N13'_b-Cs1-N3	112.2(3)
N10-Cs1-N3	117.20(7)	N13_a-Cs1-N3	109.1(2)
O1-Cs1-N12	68.92(6)	N3-Cs1-N12	120.26(8)
N13'_b-Cs1-N12	61.0(3)	N10-Cs1-N12	126.12(7)
N13_a-Cs1-N12	56.6(2)	N3-Cs1-N12	58.56(7)
O1-Cs1-N6	121.90(6)	N3-Cs1-N6	69.17(7)
N13'_b-Cs1-N6	64.8(3)	N10-Cs1-N6	170.58(7)
N13_a-Cs1-N6	65.2(2)	N3-Cs1-N6	61.96(7)
N12-Cs1-N6	62.29(7)	O1-Cs1-O1	82.64(5)
N3-Cs1-O1	156.13(7)	N13'_b-Cs1-O1	51.7(3)
N10-Cs1-O1	71.76(6)	N13_a-Cs1-O1	50.9(2)
N3-Cs1-O1	134.53(7)	N12-Cs1-O1	79.82(6)
N6-Cs1-O1	115.97(6)	O1-Cs1-N4	127.23(6)
N3-Cs1-N4	111.27(7)	N13'_b-Cs1-N4	47.7(3)
N10-Cs1-N4	85.18(6)	N13_a-Cs1-N4	51.5(2)
N3-Cs1-N4	157.42(7)	N12-Cs1-N4	106.88(6)
N6-Cs1-N4	96.50(7)	O1-Cs1-N4	46.40(5)
O1-Cs1-N7	110.24(5)	N3-Cs1-N7	67.39(7)
N13'_b-Cs1-N7	114.0(3)	N10-Cs1-N7	49.99(6)
N13_a-Cs1-N7	118.2(2)	N3-Cs1-N7	128.78(7)
N12-Cs1-N7	172.15(6)	N6-Cs1-N7	122.27(6)
O1-Cs1-N7	92.33(5)	N4-Cs1-N7	67.07(5)
O1-Cs1-N11	63.60(5)	N3-Cs1-N11	138.14(7)
N13'_b-Cs1-N11	56.0(3)	N10-Cs1-N11	112.02(6)
N13_a-Cs1-N11	51.1(2)	N3-Cs1-N11	73.50(7)
N12-Cs1-N11	17.91(6)	N6-Cs1-N11	77.08(6)
O1-Cs1-N11	62.75(5)	N4-Cs1-N11	96.17(6)
N7-Cs1-N11	154.47(6)	N7-Cs2-N12	126.09(6)
N7-Cs2-N9	69.50(7)	N12-Cs2-N9	118.27(7)
N7-Cs2-N6	135.26(7)	N12-Cs2-N6	65.17(7)
N9-Cs2-N6	68.44(7)	N7-Cs2-N12	108.59(7)
N12-Cs2-N12	80.92(8)	N9-Cs2-N12	158.33(7)
N6-Cs2-N12	116.13(7)	N7-Cs2-N15_a	62.55(13)
N12-Cs2-N15_a	67.44(12)	N9-Cs2-N15_a	77.92(12)
N6-Cs2-N15_a	94.12(15)	N12-Cs2-N15_a	121.24(12)
N7-Cs2-N4	53.84(6)	N12-Cs2-N4	179.49(7)
N9-Cs2-N4	61.22(7)	N6-Cs2-N4	114.48(6)
N12-Cs2-N4	99.58(7)	N15_a-Cs2-N4	112.30(11)
N7-Cs2-N1	149.39(6)	N12-Cs2-N1	81.46(6)
N9-Cs2-N1	111.94(7)	N6-Cs2-N1	64.24(7)
N12-Cs2-N1	58.17(6)	N15_a-Cs2-N1	147.84(12)
N4-Cs2-N1	98.74(6)	N7-Cs2-O1	49.08(5)
N12-Cs2-O1	133.61(6)	N9-Cs2-O1	102.74(6)

N6-Cs2-O1	158.02(6)	N12-Cs2-O1	64.79(6)
N15_a-Cs2-O1	103.85(14)	N4-Cs2-O1	46.82(5)
N1-Cs2-O1	103.49(5)	N7-Cs2-N3	68.57(7)
N12-Cs2-N3	75.22(7)	N9-Cs2-N3	134.52(7)
N6-Cs2-N3	140.33(7)	N12-Cs2-N3	56.63(7)
N15_a-Cs2-N3	67.78(14)	N4-Cs2-N3	105.11(6)
N1-Cs2-N3	113.03(7)	O1-Cs2-N3	60.23(6)
N7-Cs2-N9	107.03(6)	N12-Cs2-N9	122.44(7)
N9-Cs2-N9	58.63(8)	N6-Cs2-N9	61.72(7)
N12-Cs2-N9	103.53(6)	N15_a-Cs2-N9	135.19(12)
N4-Cs2-N9	57.39(6)	N1-Cs2-N9	56.87(6)
O1-Cs2-N9	96.37(6)	N3-Cs2-N9	153.34(7)
N7-Cs2-N15_a	85.30(11)	N12-Cs2-N15_a	63.56(11)
N9-Cs2-N15_a	58.88(11)	N6-Cs2-N15_a	60.17(13)
N12-Cs2-N15_a	142.63(11)	N15_a-Cs2-N15_a	35.2(3)
N4-Cs2-N15_a	115.96(11)	N1-Cs2-N15_a	122.56(12)
O1-Cs2-N15_a	133.80(11)	N3-Cs2-N15_a	100.77(13)
N9-Cs2-N15_a	105.11(13)	N2-N1-Nb1	140.8(2)
N2-N1-Cs2	93.14(17)	Nb1-N1-Cs2	119.28(9)
N3-N2-N1	178.1(3)	N3-N2-Cs2	109.5(2)
N1-N2-Cs2	68.67(16)	N2-N3-Cs1	119.6(2)
N2-N3-Cs1	135.0(2)	Cs1-N3-Cs1	82.58(7)
N2-N3-Cs2	101.7(2)	Cs1-N3-Cs2	114.68(9)
Cs1-N3-Cs2	102.69(7)	N5-N4-Nb1	126.0(2)
N5-N4-Cs2	126.5(2)	Nb1-N4-Cs2	90.20(8)
N5-N4-Cs1	114.7(2)	Nb1-N4-Cs1	87.32(8)
Cs2-N4-Cs1	103.64(7)	N6-N5-N4	177.5(3)
N5-N6-Cs2	116.9(2)	N5-N6-Cs1	127.9(2)
Cs2-N6-Cs1	114.03(8)	N8-N7-Nb1	130.6(2)
N8-N7-Cs2	112.24(19)	Nb1-N7-Cs2	97.05(8)
N8-N7-Cs1	111.87(18)	Nb1-N7-Cs1	93.20(8)
Cs2-N7-Cs1	109.35(7)	N9-N8-N7	177.5(3)
N9-N8-Cs2	127.3(2)	N7-N8-Cs2	50.79(16)
N9-N8-Cs2	66.83(19)	N7-N8-Cs2	115.22(18)
Cs2-N8-Cs2	165.26(7)	N8-N9-Cs2	136.9(2)
N8-N9-Cs2	96.0(2)	Cs2-N9-Cs2	121.37(8)
N11-N10-Nb1	124.4(2)	N11-N10-Cs1	122.58(19)
Nb1-N10-Cs1	105.81(9)	N12-N11-N10	177.9(3)
N12-N11-Cs2	67.28(18)	N10-N11-Cs2	112.66(19)
N12-N11-Cs1	63.44(18)	N10-N11-Cs1	114.61(18)
Cs2-N11-Cs1	95.14(6)	N11-N12-Cs2	135.2(2)
N11-N12-Cs2	94.01(19)	Cs2-N12-Cs2	99.08(8)
N11-N12-Cs1	98.7(2)	Cs2-N12-Cs1	117.28(8)
Cs2-N12-Cs1	107.64(8)	N14_a-N13_a-Nb1	139.1(11)
N14_a-N13_a-Cs1	124.5(9)	Nb1-N13_a-Cs1	95.0(3)
N15_a-N14_a-N13_a	169.0(9)	N14_a-N15_a-Cs2	122.5(5)
N14_a-N15_a-Cs2	113.4(5)	Cs2-N15_a-Cs2	123.37(18)
N14'_b-N13'_b-Nb1	135.3(13)	N14'_b-N13'_b-Cs1	121.6(12)
Nb1-N13'_b-Cs1	100.0(4)	N15'_b-N14'_b-N13'_b	172.7(12)

N14'_b-N15'_b-Cs2	114.7(6)	N14'_b-N15'_b-Cs1	114.2(6)
Cs2-N15'_b-Cs1	99.01(18)	O1-Nb1-N13'_b	98.3(4)
O1-Nb1-N7	95.01(10)	N13'_b-Nb1-N7	166.0(4)
O1-Nb1-N4	92.47(10)	N13'_b-Nb1-N4	82.7(4)
N7-Nb1-N4	92.70(10)	O1-Nb1-N13_a	97.3(3)
N7-Nb1-N13_a	167.0(3)	N4-Nb1-N13_a	90.9(3)
O1-Nb1-N10	98.69(10)	N13'_b-Nb1-N10	92.3(4)
N7-Nb1-N10	89.71(10)	N4-Nb1-N10	168.34(10)
N13_a-Nb1-N10	84.3(3)	O1-Nb1-N1	176.80(10)
N13'_b-Nb1-N1	84.6(4)	N7-Nb1-N1	82.00(9)
N4-Nb1-N1	86.53(10)	N13_a-Nb1-N1	85.8(3)
N10-Nb1-N1	82.50(9)	O1-Nb1-Cs1	70.21(7)
N13'_b-Nb1-Cs1	130.9(4)	N7-Nb1-Cs1	58.20(7)
N4-Nb1-Cs1	142.99(7)	N13_a-Nb1-Cs1	122.7(3)
N10-Nb1-Cs1	46.16(7)	N1-Nb1-Cs1	108.92(6)
Nb1-O1-Cs1	150.45(11)	Nb1-O1-Cs1	98.06(8)
Cs1-O1-Cs1	97.36(5)	Nb1-O1-Cs2	93.55(8)
Cs1-O1-Cs2	106.72(6)	Cs1-O1-Cs2	104.57(6)

Table S14. Anisotropic atomic displacement parameters (Å^2) for $Cs_2[NbO(N_3)_5]$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Cs1	0.02702(10)	0.01916(9)	0.02071(10)	0.00047(6)	-0.00192(7)	-0.00093(7)
Cs2	0.02556(11)	0.02148(10)	0.02818(11)	0.00469(7)	0.00021(8)	0.00096(7)
N1	0.0248(13)	0.0201(12)	0.0290(14)	0.0018(10)	0.0000(10)	0.0063(10)
N2	0.0230(13)	0.0243(13)	0.0155(12)	0.0006(9)	-0.0015(9)	0.0028(10)
N3	0.062(2)	0.0234(14)	0.0355(17)	0.0025(12)	0.0017(15)	0.0140(14)
N4	0.0265(14)	0.0250(13)	0.0266(14)	0.0036(11)	0.0073(10)	0.0039(11)
N5	0.0278(14)	0.0231(13)	0.0284(14)	0.0009(11)	0.0081(11)	-0.0049(12)
N6	0.0377(17)	0.0303(15)	0.0463(18)	-0.0024(13)	0.0153(14)	0.0072(13)
N7	0.0268(14)	0.0170(12)	0.0288(14)	-0.0004(10)	-0.0069(11)	-0.0006(10)
N8	0.0251(13)	0.0167(11)	0.0231(13)	-0.0009(10)	0.0020(10)	-0.0021(10)
N9	0.0292(15)	0.0314(14)	0.0322(15)	-0.0020(12)	-0.0103(12)	-0.0049(12)
N10	0.0253(13)	0.0246(13)	0.0311(15)	0.0056(11)	0.0092(11)	0.0059(11)
N11	0.0166(12)	0.0271(13)	0.0220(13)	-0.0094(11)	0.0025(10)	-0.0001(10)
N12	0.0317(15)	0.0325(15)	0.0296(15)	0.0062(12)	0.0050(11)	-0.0010(12)
N13_a	0.020(4)	0.0212(12)	0.021(3)	0.0006(14)	0.002(2)	-0.0069(16)
N14_a	0.029(3)	0.0229(15)	0.026(2)	-0.0024(16)	-0.006(2)	-0.001(2)
N15_a	0.068(3)	0.035(2)	0.054(2)	0.0048(19)	-0.017(2)	-0.011(2)
N13'_b	0.020(4)	0.0212(12)	0.021(3)	0.0006(14)	0.002(2)	-0.0069(16)
N14'_b	0.029(3)	0.0229(15)	0.026(2)	-0.0024(16)	-0.006(2)	-0.001(2)
N15'_b	0.068(3)	0.035(2)	0.054(2)	0.0048(19)	-0.017(2)	-0.011(2)
Nb1	0.01473(12)	0.01369(12)	0.01917(13)	0.00037(9)	-0.00147(9)	0.00117(9)
O1	0.0230(11)	0.0210(10)	0.0325(12)	0.0054(9)	-0.0056(9)	0.0027(9)

Table S15. Sample and crystal data for $[PPh_4]_2[NbO(N_3)_5]$.

Identification code	TPP2NbON15	
Chemical formula	$C_{48}H_{40}N_{15}NbOP_2$	
Formula weight	997.80	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.380 x 0.600 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.9621(12) Å	α = 86.124(2)°
	b = 13.2840(12) Å	β = 85.660(2)°
	c = 14.0506(13) Å	γ = 73.9850(10)°
Volume	2316.0(4) $Å^3$	
Z	2	
Density (calculated)	1.431 g/cm^3	
Absorption coefficient	0.385 mm^{-1}	
F(000)	1024	

Table S16. Data collection and structure refinement for $[PPh_4]_2[NbO(N_3)_5]$.

Diffractometer	Bruker SMART APEX
Radiation source	fine-focus tube, MoKα
Theta range for data collection	1.60 to 28.73°
Index ranges	-16<=h<=17, -16<=k<=17, -18<=l<=12
Reflections collected	13718
Independent reflections	9499 [R(int) = 0.0192]
Coverage of independent reflections	79.2%
Absorption correction	multi-scan
Max. and min. transmission	0.9810 and 0.8020
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/6 (Sheldrick, 2013)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XLMP 2014/1 (Bruker AXS, 2013)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9499 / 0 / 604
Goodness-of-fit on F^2	1.054
Δ/σ_{max}	0.001
Final R indices	7512 data; I>2σ(I) R1 = 0.0361, wR2 = 0.0887
	all data R1 = 0.0503, wR2 = 0.0929
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0491P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.585 and -0.363 eÅ^{-3}
R.M.S. deviation from mean	0.062 eÅ^{-3}

Table S17. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for $[PPh_4]_2[NbO(N_3)_5]$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Nb1	0.32283(2)	0.21944(2)	0.25635(2)	0.02543(7)
P1	0.29071(4)	0.40133(4)	0.67499(4)	0.02065(13)
P2	0.93202(4)	0.02303(4)	0.22139(4)	0.02083(13)
O1	0.27334(14)	0.11767(13)	0.30136(12)	0.0398(4)
N1	0.20893(16)	0.26532(15)	0.15173(15)	0.0341(5)
N2	0.18388(15)	0.34008(15)	0.09626(14)	0.0292(4)
N3	0.15487(17)	0.40773(17)	0.04171(16)	0.0419(5)
N4	0.21692(18)	0.33454(17)	0.34351(16)	0.0410(5)
N5	0.13146(17)	0.32705(14)	0.37867(14)	0.0314(5)
N6	0.04936(18)	0.32511(17)	0.41297(17)	0.0441(6)
N7	0.44103(17)	0.19571(16)	0.35456(15)	0.0388(5)
N8	0.51084(16)	0.23658(15)	0.36654(14)	0.0306(5)
N9	0.57759(18)	0.27228(18)	0.38258(18)	0.0488(6)
N10	0.43376(16)	0.13311(15)	0.15523(15)	0.0365(5)
N11	0.48786(19)	0.16352(17)	0.09260(17)	0.0460(6)
N12	0.5397(3)	0.1886(2)	0.0319(2)	0.0917(11)
N13	0.38382(15)	0.35567(14)	0.19671(14)	0.0314(5)
N14	0.36147(14)	0.44852(14)	0.18697(12)	0.0249(4)
N15	0.34266(17)	0.53829(15)	0.17576(15)	0.0411(5)
C1	0.15210(16)	0.40382(15)	0.70220(16)	0.0223(5)
C2	0.11247(18)	0.39771(16)	0.79712(17)	0.0282(5)
C3	0.0040(2)	0.40642(18)	0.8161(2)	0.0398(6)
C4	0.93657(19)	0.41949(18)	0.7423(2)	0.0446(7)
C5	0.9760(2)	0.4218(2)	0.6492(2)	0.0443(7)
C6	0.08434(19)	0.41360(18)	0.62788(18)	0.0323(6)
C7	0.34000(16)	0.45273(17)	0.77115(15)	0.0223(5)
C8	0.35917(18)	0.39545(19)	0.85813(16)	0.0300(5)
C9	0.38541(18)	0.4409(2)	0.93534(17)	0.0364(6)
C10	0.39321(18)	0.5427(2)	0.92604(18)	0.0353(6)
C11	0.37754(17)	0.59885(19)	0.83985(17)	0.0303(5)
C12	0.35023(16)	0.55446(17)	0.76246(16)	0.0248(5)
C13	0.29659(17)	0.48183(16)	0.56812(15)	0.0226(5)
C14	0.37776(18)	0.44908(18)	0.49795(16)	0.0280(5)
C15	0.38243(19)	0.5123(2)	0.41611(17)	0.0348(6)
C16	0.3074(2)	0.6076(2)	0.40498(17)	0.0349(6)
C17	0.22676(19)	0.64074(18)	0.47495(17)	0.0320(5)
C18	0.21985(18)	0.57849(17)	0.55707(16)	0.0271(5)
C19	0.36950(17)	0.26970(16)	0.65497(15)	0.0249(5)
C20	0.3255(2)	0.20394(18)	0.60902(17)	0.0326(5)
C21	0.3871(2)	0.10364(19)	0.58955(18)	0.0408(6)
C22	0.4918(2)	0.0692(2)	0.61647(18)	0.0432(7)
C23	0.5354(2)	0.1347(2)	0.66205(18)	0.0401(6)
C24	0.47531(18)	0.23559(19)	0.68130(17)	0.0335(6)
C25	0.89359(17)	0.02195(16)	0.34659(15)	0.0237(5)
C26	0.81393(18)	0.10527(17)	0.38416(16)	0.0270(5)

	x/a	y/b	z/c	U(eq)
C27	0.77680(19)	0.09918(19)	0.47963(16)	0.0326(5)
C28	0.8200(2)	0.0109(2)	0.53591(17)	0.0360(6)
C29	0.8988(2)	0.92801(19)	0.49954(17)	0.0373(6)
C30	0.93600(19)	0.93256(18)	0.40493(17)	0.0312(5)
C31	0.91456(16)	0.15540(16)	0.17574(15)	0.0214(5)
C32	0.95393(17)	0.22407(16)	0.22460(16)	0.0245(5)
C33	0.94766(17)	0.32373(16)	0.18545(16)	0.0268(5)
C34	0.90303(18)	0.35563(17)	0.09910(16)	0.0284(5)
C35	0.86261(18)	0.28843(17)	0.05062(16)	0.0294(5)
C36	0.86777(17)	0.18839(17)	0.08823(15)	0.0247(5)
C37	0.84803(17)	0.96326(16)	0.16161(15)	0.0237(5)
C38	0.8880(2)	0.90649(18)	0.08096(17)	0.0330(5)
C39	0.8227(2)	0.8623(2)	0.03447(18)	0.0393(6)
C40	0.7171(2)	0.8760(2)	0.06644(19)	0.0420(7)
C41	0.6757(2)	0.9343(2)	0.14579(19)	0.0407(6)
C42	0.74109(19)	0.97713(18)	0.19391(18)	0.0330(6)
C43	0.06948(17)	0.95000(16)	0.19910(15)	0.0239(5)
C44	0.09661(18)	0.84003(17)	0.20317(16)	0.0296(5)
C45	0.20235(19)	0.78334(18)	0.18266(17)	0.0332(6)
C46	0.27996(19)	0.83569(19)	0.15781(17)	0.0348(6)
C47	0.25474(19)	0.94331(19)	0.15559(17)	0.0343(6)
C48	0.14911(17)	0.00096(18)	0.17640(16)	0.0280(5)

Table S18. Bond lengths (Å) for $[PPh_4]_2[NbO(N_3)_5]$.

Nb1-O1	1.7147(15)	Nb1-N7	2.085(2)
Nb1-N10	2.098(2)	Nb1-N1	2.1030(19)
Nb1-N4	2.136(2)	Nb1-N13	2.2553(18)
P1-C7	1.788(2)	P1-C13	1.793(2)
P1-C19	1.794(2)	P1-C1	1.800(2)
P2-C31	1.790(2)	P2-C25	1.792(2)
P2-C43	1.794(2)	P2-C37	1.796(2)
N1-N2	1.206(3)	N2-N3	1.140(3)
N4-N5	1.205(3)	N5-N6	1.141(3)
N7-N8	1.204(3)	N8-N9	1.138(3)
N10-N11	1.202(3)	N11-N12	1.135(3)
N13-N14	1.187(2)	N14-N15	1.152(2)
C1-C6	1.392(3)	C1-C2	1.398(3)
C2-C3	1.385(3)	C2-H2	0.95
C3-C4	1.379(4)	C3-H3	0.95
C4-C5	1.368(4)	C4-H4	0.95
C5-C6	1.390(3)	C5-H5	0.95
C6-H6	0.95	C7-C12	1.390(3)
C7-C8	1.396(3)	C8-C9	1.384(3)
C8-H8	0.95	C9-C10	1.380(4)
C9-H9	0.95	C10-C11	1.377(3)
C10-H10	0.95	C11-C12	1.384(3)
C11-H11	0.95	C12-H12	0.95
C13-C14	1.384(3)	C13-C18	1.398(3)
C14-C15	1.385(3)	C14-H14	0.95
C15-C16	1.375(3)	C15-H15	0.95
C16-C17	1.379(3)	C16-H16	0.95
C17-C18	1.386(3)	C17-H17	0.95
C18-H18	0.95	C19-C20	1.383(3)
C19-C24	1.391(3)	C20-C21	1.385(3)
C20-H20	0.95	C21-C22	1.380(4)
C21-H21	0.95	C22-C23	1.375(4)
C22-H22	0.95	C23-C24	1.384(3)
C23-H23	0.95	C24-H24	0.95
C25-C26	1.391(3)	C25-C30	1.400(3)
C26-C27	1.395(3)	C26-H26	0.95
C27-C28	1.376(3)	C27-H27	0.95
C28-C29	1.376(4)	C28-H28	0.95
C29-C30	1.383(3)	C29-H29	0.95
C30-H30	0.95	C31-C32	1.400(3)
C31-C36	1.402(3)	C32-C33	1.382(3)
C32-H32	0.95	C33-C34	1.374(3)
C33-H33	0.95	C34-C35	1.389(3)
C34-H34	0.95	C35-C36	1.383(3)
C35-H35	0.95	C36-H36	0.95
C37-C38	1.390(3)	C37-C42	1.392(3)
C38-C39	1.377(3)	C38-H38	0.95
C39-C40	1.374(4)	C39-H39	0.95

C40-C41	1.388(4)	C40-H40	0.95
C41-C42	1.380(3)	C41-H41	0.95
C42-H42	0.95	C43-C48	1.390(3)
C43-C44	1.403(3)	C44-C45	1.389(3)
C44-H44	0.95	C45-C46	1.385(3)
C45-H45	0.95	C46-C47	1.374(3)
C46-H46	0.95	C47-C48	1.392(3)
C47-H47	0.95	C48-H48	0.95

Table S19. Bond angles (°) for $[PPh_4]_2[NbO(N_3)_5]$.

O1-Nb1-N7	95.34(8)	O1-Nb1-N10	96.15(8)
N7-Nb1-N10	91.27(9)	O1-Nb1-N1	93.22(8)
N7-Nb1-N1	171.24(7)	N10-Nb1-N1	89.61(8)
O1-Nb1-N4	95.36(8)	N7-Nb1-N4	90.19(9)
N10-Nb1-N4	168.21(8)	N1-Nb1-N4	87.20(8)
O1-Nb1-N13	178.62(8)	N7-Nb1-N13	85.70(7)
N10-Nb1-N13	84.73(7)	N1-Nb1-N13	85.71(7)
N4-Nb1-N13	83.72(8)	C7-P1-C13	109.76(10)
C7-P1-C19	110.43(10)	C13-P1-C19	109.35(10)
C7-P1-C1	109.72(10)	C13-P1-C1	107.57(10)
C19-P1-C1	109.96(10)	C31-P2-C25	109.64(10)
C31-P2-C43	109.27(10)	C25-P2-C43	111.24(10)
C31-P2-C37	109.78(10)	C25-P2-C37	108.42(10)
C43-P2-C37	108.47(10)	N2-N1-Nb1	134.05(16)
N3-N2-N1	175.2(2)	N5-N4-Nb1	123.82(16)
N6-N5-N4	176.6(2)	N8-N7-Nb1	134.53(16)
N9-N8-N7	176.2(2)	N11-N10-Nb1	129.15(17)
N12-N11-N10	177.4(3)	N14-N13-Nb1	143.97(16)
N15-N14-N13	177.9(2)	C6-C1-C2	120.3(2)
C6-C1-P1	119.37(17)	C2-C1-P1	120.32(17)
C3-C2-C1	119.1(2)	C3-C2-H2	120.5
C1-C2-H2	120.5	C4-C3-C2	120.3(2)
C4-C3-H3	119.8	C2-C3-H3	119.8
C5-C4-C3	120.6(2)	C5-C4-H4	119.7
C3-C4-H4	119.7	C4-C5-C6	120.4(2)
C4-C5-H5	119.8	C6-C5-H5	119.8
C5-C6-C1	119.2(2)	C5-C6-H6	120.4
C1-C6-H6	120.4	C12-C7-C8	119.4(2)
C12-C7-P1	119.69(16)	C8-C7-P1	120.70(17)
C9-C8-C7	120.0(2)	C9-C8-H8	120.0
C7-C8-H8	120.0	C10-C9-C8	119.9(2)
C10-C9-H9	120.1	C8-C9-H9	120.1
C11-C10-C9	120.6(2)	C11-C10-H10	119.7
C9-C10-H10	119.7	C10-C11-C12	119.9(2)
C10-C11-H11	120.0	C12-C11-H11	120.0
C11-C12-C7	120.2(2)	C11-C12-H12	119.9
C7-C12-H12	119.9	C14-C13-C18	120.4(2)
C14-C13-P1	120.09(16)	C18-C13-P1	119.50(17)
C13-C14-C15	119.7(2)	C13-C14-H14	120.1
C15-C14-H14	120.1	C16-C15-C14	120.2(2)
C16-C15-H15	119.9	C14-C15-H15	119.9
C15-C16-C17	120.3(2)	C15-C16-H16	119.9
C17-C16-H16	119.9	C16-C17-C18	120.6(2)
C16-C17-H17	119.7	C18-C17-H17	119.7
C17-C18-C13	118.8(2)	C17-C18-H18	120.6
C13-C18-H18	120.6	C20-C19-C24	120.3(2)
C20-C19-P1	119.22(17)	C24-C19-P1	120.44(18)
C19-C20-C21	119.7(2)	C19-C20-H20	120.1

C21-C20-H20	120.1	C22-C21-C20	120.2(2)
C22-C21-H21	119.9	C20-C21-H21	119.9
C23-C22-C21	120.0(2)	C23-C22-H22	120.0
C21-C22-H22	120.0	C22-C23-C24	120.6(2)
C22-C23-H23	119.7	C24-C23-H23	119.7
C23-C24-C19	119.2(2)	C23-C24-H24	120.4
C19-C24-H24	120.4	C26-C25-C30	119.7(2)
C26-C25-P2	120.17(16)	C30-C25-P2	119.79(17)
C25-C26-C27	119.8(2)	C25-C26-H26	120.1
C27-C26-H26	120.1	C28-C27-C26	119.5(2)
C28-C27-H27	120.2	C26-C27-H27	120.2
C29-C28-C27	121.2(2)	C29-C28-H28	119.4
C27-C28-H28	119.4	C28-C29-C30	120.0(2)
C28-C29-H29	120.0	C30-C29-H29	120.0
C29-C30-C25	119.7(2)	C29-C30-H30	120.1
C25-C30-H30	120.1	C32-C31-C36	119.94(19)
C32-C31-P2	119.79(16)	C36-C31-P2	120.14(16)
C33-C32-C31	119.6(2)	C33-C32-H32	120.2
C31-C32-H32	120.2	C34-C33-C32	120.4(2)
C34-C33-H33	119.8	C32-C33-H33	119.8
C33-C34-C35	120.3(2)	C33-C34-H34	119.8
C35-C34-H34	119.8	C36-C35-C34	120.4(2)
C36-C35-H35	119.8	C34-C35-H35	119.8
C35-C36-C31	119.2(2)	C35-C36-H36	120.4
C31-C36-H36	120.4	C38-C37-C42	119.6(2)
C38-C37-P2	120.42(18)	C42-C37-P2	119.89(17)
C39-C38-C37	120.2(2)	C39-C38-H38	119.9
C37-C38-H38	119.9	C40-C39-C38	120.1(2)
C40-C39-H39	119.9	C38-C39-H39	119.9
C39-C40-C41	120.2(2)	C39-C40-H40	119.9
C41-C40-H40	119.9	C42-C41-C40	120.0(3)
C42-C41-H41	120.0	C40-C41-H41	120.0
C41-C42-C37	119.8(2)	C41-C42-H42	120.1
C37-C42-H42	120.1	C48-C43-C44	119.6(2)
C48-C43-P2	120.84(16)	C44-C43-P2	119.53(17)
C45-C44-C43	119.7(2)	C45-C44-H44	120.2
C43-C44-H44	120.2	C46-C45-C44	119.8(2)
C46-C45-H45	120.1	C44-C45-H45	120.1
C47-C46-C45	121.0(2)	C47-C46-H46	119.5
C45-C46-H46	119.5	C46-C47-C48	119.7(2)
C46-C47-H47	120.2	C48-C47-H47	120.2
C43-C48-C47	120.2(2)	C43-C48-H48	119.9
C47-C48-H48	119.9		

Table S20. Anisotropic atomic displacement parameters (Å^2) for $[PPh_4]_2[NbO(N_3)_5]$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Nb1	0.02905(12)	0.02087(11)	0.02772(13)	0.00334(8)	-0.00275(8)	-0.00985(8)
P1	0.0206(3)	0.0218(3)	0.0198(3)	-0.0001(2)	-0.0018(2)	-0.0062(2)
P2	0.0247(3)	0.0160(3)	0.0214(3)	0.0001(2)	0.0004(2)	-0.0056(2)
O1	0.0535(11)	0.0360(10)	0.0372(10)	0.0053(8)	-0.0003(8)	-0.0264(8)
N1	0.0353(12)	0.0297(11)	0.0406(13)	0.0022(9)	-0.0119(9)	-0.0128(9)
N2	0.0249(10)	0.0362(12)	0.0281(11)	-0.0064(9)	0.0001(8)	-0.0102(9)
N3	0.0429(13)	0.0427(13)	0.0365(13)	0.0083(10)	-0.0024(10)	-0.0081(10)
N4	0.0416(13)	0.0360(12)	0.0489(14)	-0.0126(10)	0.0038(11)	-0.0158(10)
N5	0.0395(13)	0.0243(10)	0.0288(11)	-0.0045(8)	-0.0022(10)	-0.0051(9)
N6	0.0416(13)	0.0341(12)	0.0534(15)	-0.0058(10)	0.0092(11)	-0.0071(10)
N7	0.0469(13)	0.0347(12)	0.0391(13)	0.0128(10)	-0.0174(10)	-0.0177(10)
N8	0.0313(11)	0.0256(10)	0.0283(11)	0.0061(8)	-0.0029(9)	0.0016(9)
N9	0.0384(13)	0.0499(14)	0.0612(16)	0.0105(12)	-0.0147(12)	-0.0171(11)
N10	0.0354(12)	0.0299(11)	0.0415(13)	0.0002(9)	0.0052(10)	-0.0068(9)
N11	0.0491(14)	0.0341(12)	0.0459(15)	-0.0040(11)	0.0074(12)	0.0015(10)
N12	0.113(3)	0.068(2)	0.078(2)	0.0031(17)	0.059(2)	-0.0167(18)
N13	0.0313(11)	0.0221(10)	0.0419(12)	0.0040(9)	-0.0025(9)	-0.0101(8)
N14	0.0245(10)	0.0282(11)	0.0203(10)	0.0008(8)	0.0037(7)	-0.0064(8)
N15	0.0514(14)	0.0211(11)	0.0426(13)	0.0012(9)	0.0135(10)	-0.0010(9)
C1	0.0202(11)	0.0163(10)	0.0302(12)	-0.0013(9)	-0.0021(9)	-0.0042(8)
C2	0.0290(12)	0.0217(11)	0.0348(14)	-0.0046(10)	0.0038(10)	-0.0094(9)
C3	0.0355(14)	0.0264(13)	0.0578(18)	-0.0061(12)	0.0176(13)	-0.0132(11)
C4	0.0190(12)	0.0246(13)	0.090(2)	0.0056(13)	0.0026(14)	-0.0090(10)
C5	0.0316(14)	0.0368(15)	0.070(2)	0.0147(14)	-0.0204(14)	-0.0180(12)
C6	0.0335(13)	0.0313(13)	0.0364(14)	0.0057(11)	-0.0105(11)	-0.0154(10)
C7	0.0185(10)	0.0309(12)	0.0191(11)	-0.0030(9)	-0.0012(8)	-0.0090(9)
C8	0.0293(12)	0.0366(13)	0.0254(13)	0.0027(10)	-0.0042(10)	-0.0117(10)
C9	0.0283(13)	0.0577(17)	0.0230(13)	0.0027(12)	-0.0053(10)	-0.0113(12)
C10	0.0222(12)	0.0556(17)	0.0305(14)	-0.0151(12)	-0.0028(10)	-0.0111(11)
C11	0.0203(11)	0.0356(13)	0.0372(14)	-0.0097(11)	-0.0009(10)	-0.0094(10)
C12	0.0186(11)	0.0319(12)	0.0248(12)	-0.0012(10)	0.0008(9)	-0.0089(9)
C13	0.0268(11)	0.0244(11)	0.0202(11)	-0.0001(9)	-0.0063(9)	-0.0119(9)
C14	0.0272(12)	0.0323(12)	0.0256(12)	0.0002(10)	-0.0026(9)	-0.0098(10)
C15	0.0330(13)	0.0502(16)	0.0249(13)	0.0011(11)	-0.0005(10)	-0.0187(12)
C16	0.0409(14)	0.0437(15)	0.0266(13)	0.0104(11)	-0.0114(11)	-0.0227(12)
C17	0.0379(14)	0.0253(12)	0.0360(14)	0.0057(10)	-0.0162(11)	-0.0120(10)
C18	0.0286(12)	0.0265(12)	0.0273(13)	-0.0019(10)	-0.0063(10)	-0.0078(9)
C19	0.0260(12)	0.0224(11)	0.0229(12)	0.0024(9)	0.0035(9)	-0.0029(9)
C20	0.0350(13)	0.0318(13)	0.0299(13)	-0.0053(10)	0.0005(10)	-0.0070(10)
C21	0.0597(18)	0.0284(13)	0.0340(15)	-0.0086(11)	0.0045(12)	-0.0120(12)
C22	0.0614(19)	0.0240(13)	0.0330(15)	0.0003(11)	0.0101(13)	0.0032(12)
C23	0.0329(14)	0.0388(15)	0.0367(15)	0.0054(12)	0.0037(11)	0.0069(11)
C24	0.0303(13)	0.0375(14)	0.0294(13)	-0.0002(11)	0.0006(10)	-0.0049(11)
C25	0.0294(12)	0.0211(11)	0.0218(12)	0.0023(9)	-0.0020(9)	-0.0097(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	0.0331(13)	0.0227(11)	0.0253(12)	0.0000(9)	0.0010(10)	-0.0085(10)
C27	0.0374(14)	0.0357(14)	0.0267(13)	-0.0038(10)	0.0058(10)	-0.0151(11)
C28	0.0460(15)	0.0478(16)	0.0212(13)	0.0018(11)	0.0029(11)	-0.0266(13)
C29	0.0483(16)	0.0348(14)	0.0295(14)	0.0119(11)	-0.0070(11)	-0.0143(12)
C30	0.0380(13)	0.0241(12)	0.0304(13)	0.0030(10)	-0.0032(10)	-0.0074(10)
C31	0.0236(11)	0.0170(10)	0.0216(11)	0.0004(8)	0.0036(9)	-0.0039(8)
C32	0.0282(12)	0.0210(11)	0.0233(12)	0.0017(9)	-0.0006(9)	-0.0060(9)
C33	0.0276(12)	0.0199(11)	0.0316(13)	-0.0037(9)	0.0053(10)	-0.0058(9)
C34	0.0330(13)	0.0194(11)	0.0290(13)	0.0023(9)	0.0086(10)	-0.0046(9)
C35	0.0351(13)	0.0254(12)	0.0223(12)	0.0039(10)	0.0030(10)	-0.0016(10)
C36	0.0251(11)	0.0231(11)	0.0241(12)	-0.0015(9)	0.0019(9)	-0.0043(9)
C37	0.0294(12)	0.0174(10)	0.0244(12)	0.0038(9)	-0.0041(9)	-0.0068(9)
C38	0.0421(14)	0.0310(13)	0.0285(13)	-0.0017(10)	-0.0018(11)	-0.0141(11)
C39	0.0606(18)	0.0358(14)	0.0285(14)	-0.0039(11)	-0.0058(12)	-0.0231(13)
C40	0.0590(18)	0.0395(15)	0.0387(16)	0.0090(12)	-0.0220(13)	-0.0297(13)
C41	0.0366(14)	0.0467(16)	0.0450(16)	0.0085(13)	-0.0102(12)	-0.0223(12)
C42	0.0340(13)	0.0316(13)	0.0345(14)	0.0010(11)	-0.0017(11)	-0.0116(10)
C43	0.0257(11)	0.0200(11)	0.0243(12)	-0.0008(9)	-0.0030(9)	-0.0033(9)
C44	0.0337(13)	0.0208(11)	0.0329(14)	0.0001(10)	-0.0006(10)	-0.0059(10)
C45	0.0384(14)	0.0239(12)	0.0314(14)	-0.0012(10)	-0.0058(11)	0.0025(10)
C46	0.0292(13)	0.0395(14)	0.0288(13)	-0.0022(11)	-0.0004(10)	0.0019(11)
C47	0.0278(13)	0.0391(14)	0.0352(14)	0.0024(11)	-0.0009(10)	-0.0088(11)
C48	0.0283(12)	0.0243(12)	0.0300(13)	0.0014(10)	-0.0011(10)	-0.0057(9)

Table S21. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $[PPh_4]_2[NbO(N_3)_5]$.

	x/a	y/b	z/c	U(eq)
H2	0.1593	0.3877	0.8479	0.034
H3	-0.0240	0.4034	0.8804	0.048
H4	-0.1380	0.4269	0.7561	0.054
H5	-0.0710	0.4291	0.5990	0.053
H6	0.1118	0.4146	0.5633	0.039
H8	0.3542	0.3253	0.8643	0.036
H9	0.3980	0.4022	0.9946	0.044
H10	0.4095	0.5742	0.9796	0.042
H11	0.3855	0.6680	0.8335	0.036
H12	0.3385	0.5936	0.7033	0.03
H14	0.4300	0.3835	0.5059	0.034
H15	0.4376	0.4897	0.3675	0.042
H16	0.3111	0.6508	0.3488	0.042
H17	0.1755	0.7069	0.4668	0.038
H18	0.1639	0.6011	0.6050	0.033
H20	0.2533	0.2275	0.5909	0.039
H21	0.3573	0.0584	0.5576	0.049
H22	0.5337	0.0001	0.6035	0.052
H23	0.6075	0.1106	0.6805	0.048
H24	0.5060	0.2810	0.7121	0.04
H26	0.7849	0.1661	0.3449	0.032
H27	0.7221	0.1556	0.5056	0.039
H28	0.7949	0.0071	0.6010	0.043
H29	0.9276	-0.1324	0.5394	0.045
H30	0.9901	-0.1247	0.3796	0.037
H32	0.9848	0.2023	0.2843	0.029
H33	0.9744	0.3705	0.2185	0.032
H34	0.8998	0.4240	0.0724	0.034
H35	0.8312	0.3114	-0.0087	0.035
H36	0.8399	0.1425	0.0552	0.03
H38	0.9605	-0.1019	0.0579	0.04
H39	0.8507	-0.1777	-0.0198	0.047
H40	0.6723	-0.1545	0.0341	0.05
H41	0.6024	-0.0553	0.1670	0.049
H42	0.7132	0.0160	0.2489	0.04
H44	1.0429	-0.1954	0.2199	0.035
H45	1.2214	-0.2911	0.1857	0.04
H46	1.3518	-0.2034	0.1421	0.042
H47	1.3091	-0.0218	0.1399	0.041
H48	1.1314	0.0753	0.1751	0.034

Computational Optimized Coordinates

Table S22. Geometry parameters: selective bond lengths in angstroms.

Molecule	No	functional	Nb-O	Nb-N_3
[NbO$(N_3)_3$]	1	B3LYP	1.708	1.995
		SVWN5	1.708	1.968
[NbO$(N_3)_4$]$^-$	3(A)	B3LYP	1.717	2.088 (ave)
	3(C)	SVWN5	1.722	2.058
[NbO$(N_3)_5$]$^{2-}$	4(A)	B3LYP	1.733	2.145 (eq) 2.252 (ax)
		SVWN5	1.744	2.093 (ave,eq) 2.201 (ax)
	4(B)	B3LYP	1.735	2.142 (ave,eq) 2.266 (ax)
		SVWN5	1.747	2.094 (ave,eq) 2.202 (ax)
	4(C)	B3LYP	1.737	2.137 (ave,eq) 2.274 (ax)
	4(D)	B3LYP	1.737	2.133 (eq) 2.272 (ax)
		SVWN5	1.749	2.082 (eq) 2.210 (ax)

Table S23. Selected Frequencies (v) (cm^{-1}), IR Intensities (km/mol) for the N_3 groups and Nb-O.

Molecule	functional	v(Nb-O)	IR I	$\nu_{sym}(N_3)$	IR I	$\nu_{as}(N_3)$	IR I
$[NbO(N_3)_3]$ (1)	B3LYP	1013.9	155.6	1395.4(a)	656.3	2219.2(a)	1730.2
				1395.6(a)	655.7	2219.4(a)	1727.5
				1416.9(s)	0.2	2245.3(s)	37.3
	SVWN5	1005.3	137.8	1426.2(a)	396.2	2237.0(a)	1431.4
				1426.9(a)	397.1	2237.3(a)	1434.2
				1441.2(s)	1.1	2257.1(s)	10.2
$[NbO(N_3)_4]^-$	B3LYP [3(A)]	988.9	238.0	1401.2(a)	334.6	2169.9(a)	637.5
				1402.9(a)	46.0	2175.4(a)	1553.7
				1405.5(a)	390.4	2189.0(a)	2968.9
				1419.2(s)	26.4	2220.0(s)	201.3
	SVWN5 [3(C)]	966.3	228.9	1440.7(a)	201.3	2216.6(a)	0.0
				1440.7(a)	201.3	2233.8(a)	1978.3
				1441.1(a)	0.0	2233.8(a)	1978.4
				1455.8(s)	22.0	2267.5(s)	508.1
$[NbO(N_3)_5]^{2-}$ 4(A)	B3LYP	948.9	290.7	1400.1	228.9	2136.1	0.0
				1400.1	228.8	2151.5	2648.1
				1401.4	0.0	2151.5	2647.8
				1411.2	52.0	2161.3	2943.6
				1427.3(s)	46.0	2203.1(s)	35.2
	SVWN5	921.4	272.5	1408.7	72.5	2190.2	67.4
				1409.9	60.0	2195.7	1978.0
				1410.0	118.3	2202.1	2342.8
				1414.5	28.4	2203.3	2284.8
				1423.6(s)	4.7	2240.2(s)	56.6
$[NbO(N_3)_5]^{2-}$ 4(B)	B3LYP	946.0	329.9	1393.2	177.0	2143.0	758.8
				1404.1	111.8	2146.8	1597.1
				1408.9	209.1	2153.5	3015.5
				1410.9	19.2	2161.9	2242.5
				1418.7(s)	28.7	2202.4(s)	294.6
	SVWN5	919.1	294.6	1396.5	74.0	2184.4	395.3
				1400.4	45.3	2188.6	1681.3
				1412.1	102.5	2202.3	2046.6
				1414.9	27.4	2204.7	1896.4
				1421.8(s)	16.9	2237.7(s)	235.3
$[NbO(N_3)_5]^{2-}$ 4(D)	B3LYP	943.5	420.1	1415.0	36.8	2144.5	0.0
				1415.1	212.0	2148.9	454.7
				1415.1	211.8	2163.7	2460.5
				1416.3	0.0	2163.8	2460.4
				1427.9(s)	18.3	2215.4(s)	1284.7
	SVWN5	911.9	352.5	1402.8	28.5	2186.6	593.4
				1422.0	102.6	2198.6	1.3
				1422.9	101.8	2212.9	2237.0
				1425.0	0.6	2213.9	2268.3
				1433.9(s)	2.3	2250.2(s)	600.4

(s) = symmetric coupling. (a) = antisymmetric coupling

Table S24. Reaction energies in kcal/mol.

Reaction	B3LYP/ DZVP2/D-PP		SVWN5/ DZVP2/D-PP		MP2/aD/aD-PP[a]				
	ΔH_{0K}	ΔH_{298K}	ΔH_{0K}	ΔH_{298K}	ΔH_{0K}	ΔH_{298K}	ΔG_{298K}	ΔG_{solv}[b]	ΔG_{sol}[c]
$[NbO(N_3)_3] + N_3^- \rightarrow [NbO(N_3)_4]^-$	-62.7	-61.6	-74.7	-74.4	-61.8	-60.8	-54.4	33.5	-20.9
$[NbO(N_3)_4]^- + N_3^- \rightarrow [NbO(N_3)_5]^{2-}$	23.5	23.6	13.2	13.1	12.2	12.3	22.2	-35.4	-13.2
$[NbO(N_3)_3] + CH_3CN \rightarrow [NbO(N_3)_3 \cdot CH_3CN]$	-13.4	-12.1	-24.4	-24.3	-18.6	-17.4	-11.5	2.8	-8.7
$[NbO(N_3)_3 \cdot CH_3CN] + CH_3CN \rightarrow [NbO(N_3)_3 \cdot 2CH_3CN]$	-9.1	-8.8	-19.8	-19.7	-19.6	-19.2	-9.7	1.8	-7.9
$[NbO(N_3)_3]$ + bipy $\rightarrow$ [(bipy)$NbO(N_3)_3$]	-26.0	-25.0	-48.6	-48.7	-62.5	-61.5	-50.9	1.9	-49.0

[a]MP2/aug-cc-pVDZ/aug-cc-pVDZ-PP at SVWN5 optimized geometries

Table S25. Frequencies (cm^{-1}), IR Intensities (km/mol) and Raman Activities (Å^4/amu).

[$NbO(N_3)_3$], C_{3v}

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
34.0	0.2	17.0	34.6	0.2	18.1
34.6	0.2	17.1	35.2	0.2	18.2
44.8	0.3	2.6	40.4	0.3	1.3
72.0	0.4	9.5	68.2	0.4	11.1
72.0	0.4	9.5	68.4	0.4	11.2
95.1	0.0	0.0	100.1	0.0	0.0
175.3	0.4	1.7	169.7	2.1	8.9
175.5	0.4	1.8	171.4	0.2	2.0
176.7	2.6	10.9	171.6	0.2	2.0
260.7	3.7	4.7	251.7	3.0	3.3
260.7	3.7	4.7	251.8	3.1	3.4
440.3	11.3	44.5	437.5	7.2	46.3
476.9	177.7	6.9	482.2	126.2	8.4
477.0	178.0	6.9	482.5	125.4	8.4
558.1	2.6	0.0	549.4	2.5	0.0
558.7	20.0	0.0	550.0	19.4	0.0
558.8	22.1	0.0	550.2	21.8	0.0
581.3	37.9	1.1	568.1	33.3	7.6
581.4	38.3	1.1	569.2	34.4	2.1
582.7	37.6	6.3	569.7	35.8	2.3
1013.9	155.6	34.3	1005.3	137.8	34.4
1395.4	656.3	7.4	1426.2	396.2	15.1
1395.6	655.7	7.4	1426.9	397.1	15.2
1416.9	0.2	8.8	1441.2	1.1	38.2
2219.2	1730.2	189.6	2237.0	1431.4	195.6
2219.4	1727.5	190.2	2237.3	1434.2	196.0
2245.3	37.3	738.4	2257.1	10.2	734.5

[$NbO(N_3)_4$]$^-$, C_2

B3LYP [3(A)]			SVWN5 [3(B)]		
Freq	IR	Raman	Freq	IR	Raman
17.6	1.0	3.6	7.6	1.9	3.0
22.5	2.0	7.4	7.6	1.9	3.0
23.4	0.2	10.7	9.5	0.0	11.3
29.4	0.0	14.8	25.6	1.9	25.7
38.4	0.6	18.5	28.6	0.0	29.7
55.4	1.1	11.5	42.7	0.9	3.5
59.7	0.1	10.6	42.7	0.9	3.5
78.8	1.0	2.3	42.9	0.0	0.0

89.4	0.0	13.4	72.7	0.0	0.3
200.6	15.2	3.0	220.8	1.7	5.3
206.0	2.6	5.9	222.3	1.7	2.5
215.2	18.0	1.8	222.3	1.7	2.5
243.1	7.0	4.3	245.0	12.1	3.5
260.2	18.5	2.1	245.0	12.1	3.5
266.6	0.8	13.6	282.3	0.0	12.0
328.5	2.4	4.0	317.2	0.0	3.1
404.6	11.0	40.2	378.5	10.8	45.6
409.7	346.3	1.6	422.6	308.1	0.7
418.4	357.2	1.2	422.6	308.1	0.7
570.7	18.0	0.1	554.2	14.5	0.0
572.5	5.1	2.1	554.2	14.5	0.0
580.6	14.4	0.1	558.0	0.0	0.0
582.5	0.5	0.8	559.6	0.0	0.8
591.1	11.3	1.2	560.4	0.0	0.1
592.4	17.4	1.3	563.5	9.4	0.4
598.6	45.3	1.1	563.5	9.4	0.4
599.8	0.0	0.7	564.3	12.5	0.3
988.9	238.0	82.6	966.3	228.9	108.1
1401.2	334.6	14.4	1440.7	201.3	17.2
1402.9	46.0	59.0	1440.7	201.3	17.2
1405.5	390.4	0.6	1441.1	0.0	73.2
1419.2	26.4	57.1	1455.8	22.0	121.5
2169.9	637.5	108.2	2216.6	0.0	179.5
2175.4	1553.7	88.4	2233.8	1978.3	48.6
2189.0	2968.9	16.1	2233.8	1978.4	48.6
2220.0	201.3	516.9	2267.5	508.1	557.7

$[NbO(N_3)_5]^{2-}$ [4(A)], C_s

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
21.5	1.5	18.3	20.7	0.1	15.7
21.5	1.5	18.3	20.9	0.1	15.7
29.7	4.6	0.0	21.9	0.0	7.9
29.7	4.6	0.0	28.9	6.8	4.0
34.0	0.0	9.0	29.0	6.7	4.5
35.6	0.0	28.3	32.8	0.1	32.4
46.9	2.8	24.2	32.9	3.9	19.2
58.6	0.0	0.0	43.5	0.7	4.4
69.6	3.7	0.4	44.0	0.6	2.9
69.6	3.7	0.4	72.1	0.0	0.0

140.6	0.0	13.5	142.4	0.0	17.0
149.9	0.1	9.6	155.2	1.6	7.4
149.9	0.1	9.6	155.3	1.6	7.5
192.3	0.1	1.0	196.3	0.0	0.5
192.4	0.1	1.0	196.4	0.0	0.5
197.6	0.9	17.8	199.8	0.0	20.0
237.3	0.0	8.0	237.1	0.0	12.5
246.4	172.5	1.5	267.7	140.3	2.0
290.7	58.4	0.9	277.9	32.0	0.1
290.7	58.6	0.9	278.2	32.7	0.1
309.5	0.0	8.2	319.9	1.1	0.7
351.6	434.8	0.7	369.0	102.7	24.7
351.6	434.9	0.7	372.6	386.4	0.4
370.8	21.0	36.2	373.0	303.1	7.7
588.7	0.0	0.0	574.8	6.9	0.1
590.7	15.1	0.2	575.8	13.2	0.1
590.7	15.1	0.2	576.2	4.5	0.1
592.8	0.0	0.9	578.1	1.5	0.3
604.8	5.1	0.3	579.7	4.7	0.8
604.8	5.1	0.3	583.8	7.6	0.8
606.8	0.0	0.6	584.6	11.7	1.5
611.2	22.5	2.0	587.0	13.4	0.9
611.2	22.5	2.0	594.3	9.2	0.9
612.0	18.0	0.5	594.4	9.2	0.9
948.9	290.7	138.4	921.4	272.5	130.5
1400.1	228.9	19.3	1408.7	72.5	53.6
1400.1	228.8	19.3	1409.9	60.0	67.4
1401.4	0.0	87.2	1410.0	118.3	26.4
1411.2	52.0	71.9	1414.5	28.4	93.4
1427.3	46.0	130.2	1423.6	4.7	205.8
2136.1	0.0	28.5	2190.2	67.4	99.2
2151.5	2648.1	50.6	2195.7	1978.0	101.3
2151.5	2647.8	50.6	2202.1	2342.8	30.9
2161.3	2943.6	81.7	2203.3	2284.8	31.9
2203.1	35.2	407.9	2240.2	56.6	476.2

$[NbO(N_3)_5]^{2-}$ [4(B)], C_s

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
16.9	0.1	4.5	14.0	0.1	5.7
25.3	3.1	6.9	24.4	2.6	8.2

28.8	0.0	24.3	25.8	0.4	16.2
31.9	4.0	13.6	29.4	2.7	12.1
37.9	0.3	19.2	30.2	0.1	22.5
38.8	1.0	9.3	32.5	3.8	21.4
45.2	1.5	16.0	33.7	0.3	12.7
60.4	3.5	0.1	51.4	8.4	0.5
75.3	2.3	0.5	55.8	0.6	2.1
76.9	5.8	0.4	76.2	0.7	0.7
137.8	0.4	13.1	135.8	0.6	15.4
147.9	0.3	9.9	147.2	1.9	9.7
153.7	0.1	18.0	157.9	0.4	14.8
196.9	3.2	6.1	199.4	0.4	8.5
218.5	6.5	3.1	219.7	6.4	3.6
225.4	17.6	2.2	224.2	4.5	0.7
233.0	0.0	8.2	227.9	5.3	7.5
244.5	108.7	5.8	245.0	9.5	6.5
250.8	11.0	1.7	257.9	58.0	6.1
277.3	72.2	5.3	282.8	72.7	1.1
304.8	29.3	12.0	321.5	28.8	3.9
352.4	407.8	0.2	369.3	132.2	18.8
363.4	388.9	0.0	377.2	242.6	12.4
365.5	11.3	33.3	386.4	323.9	0.5
588.4	3.7	0.2	572.7	9.3	0.2
588.5	13.9	0.2	573.0	2.8	0.1
590.4	3.4	0.1	574.5	8.1	0.4
595.3	6.6	0.3	581.1	12.2	1.0
601.8	18.1	0.4	582.4	0.3	1.2
603.3	5.7	0.9	582.8	10.0	0.0
604.1	12.7	1.0	584.4	14.8	0.3
604.9	8.1	1.0	589.1	2.5	0.6
610.6	14.7	2.2	593.3	11.6	2.4
616.8	15.3	2.2	596.3	13.6	1.7
946.0	329.9	133.3	919.1	294.6	129.4
1393.2	177.0	46.7	1396.5	74.0	55.1
1404.1	111.8	62.1	1400.4	45.3	54.6
1408.9	209.1	27.5	1412.1	102.5	27.9
1410.9	19.2	59.1	1414.9	27.4	86.4
1418.7	28.7	99.7	1421.8	16.9	167.1
2143.0	758.8	21.5	2184.4	395.3	67.5
2146.8	1597.1	90.1	2188.6	1681.3	94.7
2153.5	3015.5	30.9	2202.3	2046.6	51.6
2161.9	2242.5	46.8	2204.7	1896.4	48.5
2202.4	294.6	420.3	2237.7	235.3	425.5

$[NbO(N_3)_5]^{2-}$ [4(D)], C_1

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
19.0	0.4	0.0	15.2	0.0	11.3
19.1	0.4	0.0	17.2	0.4	0.0
32.2	0.0	12.4	17.2	0.3	0.0
34.1	0.0	27.5	25.7	1.6	21.9
39.6	0.3	12.1	26.4	0.7	15.5
39.6	0.3	12.1	27.4	0.6	14.8
42.9	0.4	25.8	32.1	0.0	33.0
50.7	0.0	0.0	44.3	8.8	2.3
60.8	10.6	0.2	44.7	9.0	2.1
60.8	10.6	0.2	69.6	0.0	0.0
149.9	0.0	11.1	156.8	0.0	10.6
163.8	0.9	0.4	168.5	4.0	2.4
163.9	0.9	0.4	168.6	3.9	2.4
207.3	22.4	6.9	217.9	2.1	15.6
233.6	4.2	0.8	227.8	4.0	2.7
233.6	4.3	0.8	228.4	4.8	2.9
237.7	76.1	11.9	236.8	9.9	3.3
238.7	0.0	9.7	237.3	11.0	3.3
239.7	24.3	6.8	240.5	0.0	14.6
239.8	24.3	6.8	257.1	84.0	1.4
284.9	0.0	5.2	300.5	0.0	0.0
345.4	9.9	33.1	349.8	15.0	33.6
353.8	412.2	0.1	373.1	364.2	0.5
353.8	412.2	0.1	373.9	361.0	0.5
587.4	14.9	0.0	568.2	0.9	0.3
587.4	14.9	0.0	569.1	11.9	0.1
587.6	0.0	0.0	570.0	14.0	0.2
591.5	0.0	0.1	570.9	13.9	1.5
595.4	0.0	0.2	572.2	7.6	0.0
596.4	20.8	0.1	572.4	8.7	0.0
596.5	20.8	0.1	574.7	0.0	0.0
599.5	19.3	0.7	576.5	0.0	0.0
599.9	0.5	0.5	587.5	4.5	0.5
600.0	0.4	0.5	587.5	4.4	0.5
943.5	420.1	173.4	911.9	352.5	180.3
1415.0	36.8	46.2	1402.8	28.5	57.7
1415.1	212.0	8.5	1422.0	102.6	6.0
1415.1	211.8	8.6	1422.9	101.8	5.6
1416.3	0.0	85.6	1425.0	0.6	108.3

1427.9	18.3	91.2	1433.9	2.3	182.2
2144.5	0.0	31.6	2186.6	593.4	80.7
2148.9	454.7	75.1	2198.6	1.3	113.7
2163.7	2460.5	28.5	2212.9	2237.0	15.7
2163.8	2460.4	28.5	2213.9	2268.3	14.4
2215.4	1284.7	371.6	2250.2	600.4	447.3

[(bipy)NbO(N_3)$_3$] [2(A)], C_s

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
13.2	2.2	3.0	25.0	0.2	6.3
24.2	0.2	20.1	28.0	3.1	4.1
28.0	0.0	3.1	34.3	0.2	11.3
40.2	0.1	10.6	36.3	0.1	10.8
40.8	0.6	3.4	48.2	1.4	1.1
55.6	1.3	18.6	65.7	1.5	17.2
72.2	0.4	1.2	74.0	2.3	2.0
81.3	1.3	2.7	82.6	0.8	4.6
97.2	0.8	11.2	94.5	1.0	9.8
112.6	0.3	0.7	115.0	0.1	8.8
121.8	0.1	0.8	132.6	0.9	0.9
127.4	0.3	2.6	138.8	1.6	1.6
155.7	0.1	1.6	169.6	0.9	4.2
203.0	2.0	2.5	200.7	0.2	3.3
207.7	6.3	2.5	202.4	0.8	0.7
214.0	10.7	3.4	210.6	2.4	2.3
228.3	2.0	5.2	220.5	0.5	2.0
229.5	1.5	1.9	230.4	13.5	2.1
246.8	6.7	1.5	233.0	2.2	1.3
261.2	0.5	3.1	260.0	0.0	2.6
274.4	31.0	2.0	275.4	11.7	1.1
350.7	0.6	3.4	353.4	0.6	7.0
383.6	53.8	14.5	413.6	14.4	0.4
421.1	167.4	32.7	415.7	5.9	27.5
421.6	230.5	2.2	427.3	4.3	0.1
433.0	22.8	0.0	428.8	168.8	12.3
438.0	19.7	0.8	445.5	42.3	0.5
457.8	2.3	0.4	450.8	91.1	6.7
462.9	4.5	2.7	463.0	9.0	3.5
562.2	0.2	0.1	541.5	0.3	0.6
566.9	8.1	0.2	560.0	3.9	0.4
578.2	13.3	0.3	560.1	0.5	0.5
579.9	1.6	0.7	562.7	5.8	0.2

591.8	22.7	0.4	573.0	20.0	0.2
600.1	41.1	0.6	598.3	70.0	2.3
600.2	5.6	1.8	600.3	0.9	1.1
639.4	7.0	8.7	622.3	5.1	9.1
659.4	9.7	3.4	639.9	3.4	0.1
660.8	8.7	1.0	643.8	11.2	3.5
749.8	1.1	0.3	718.5	2.2	0.3
760.4	28.2	0.2	735.4	125.1	0.2
773.8	91.6	0.1	746.6	5.3	0.6
779.8	1.6	15.8	768.9	1.0	13.8
829.1	0.1	1.3	800.6	0.0	1.7
895.6	0.1	0.3	856.2	0.0	0.2
905.2	0.0	0.5	865.6	0.6	0.2
978.6	226.3	75.2	944.8	0.1	0.3
993.3	0.0	0.4	947.5	200.9	68.0
1000.5	0.2	0.1	955.4	0.2	0.1
1013.7	0.0	0.7	968.5	0.1	0.4
1018.3	0.2	0.6	980.0	0.5	0.6
1026.4	4.0	4.7	1008.9	4.1	3.3
1034.1	21.0	115.5	1018.6	17.1	81.2
1053.6	2.2	3.6	1039.4	1.1	10.5
1082.0	8.8	44.3	1056.9	6.2	21.4
1094.4	4.2	1.0	1059.1	8.0	42.7
1129.0	9.2	1.7	1099.1	12.6	3.4
1142.9	0.4	0.4	1114.0	0.2	0.5
1178.1	8.3	10.2	1126.8	3.3	7.4
1192.6	6.7	3.5	1139.2	5.7	6.0
1303.6	9.6	10.9	1252.8	3.1	11.9
1308.1	1.4	30.0	1269.2	3.9	8.3
1318.4	1.5	185.3	1320.1	1.8	204.1
1343.2	8.3	42.5	1384.7	2.6	7.7
1347.2	17.7	38.5	1390.9	94.7	34.5
1392.9	307.6	19.6	1397.2	66.8	14.8
1398.1	300.2	20.1	1398.4	26.0	8.7
1412.9	134.0	22.7	1419.2	2.3	43.2
1459.9	9.7	25.0	1434.6	207.4	51.2
1473.5	70.0	0.9	1445.5	82.3	0.8
1507.3	40.0	1.7	1458.1	43.3	2.1
1526.3	8.0	170.1	1508.0	2.3	173.5
1615.9	14.6	140.0	1600.9	7.1	145.7
1629.5	14.9	1.0	1618.1	14.5	0.6
1646.0	32.2	318.4	1635.9	21.5	335.7

1657.9	25.4	11.7	1646.6	21.6	11.8
2176.5	1407.2	68.4	2196.8	686.1	38.4
2183.0	1136.0	130.1	2203.1	952.4	76.2
2222.8	967.2	422.9	2243.8	940.6	415.3
3212.8	3.5	40.7	3100.3	17.1	32.3
3215.9	4.3	100.6	3106.3	5.5	40.2
3219.9	0.7	73.9	3138.4	0.7	110.3
3227.5	3.2	33.9	3139.4	0.1	38.0
3239.5	2.6	43.4	3153.7	0.1	14.0
3241.7	1.8	322.2	3157.0	0.0	107.0
3244.2	0.4	18.0	3160.7	0.7	57.2
3255.6	3.1	173.0	3161.3	0.1	448.7

[(bipy)NbO(N_3)$_3$] [2(B)]

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
18.0	1.9	7.3	22.2	0.2	7.3
23.8	0.4	7.9	23.4	3.1	4.2
27.2	0.5	12.2	33.1	0.2	10.0
36.1	0.1	7.6	35.1	0.1	10.8
39.3	0.2	8.3	48.1	1.4	1.5
48.1	1.9	2.3	64.3	1.5	17.1
72.1	0.3	9.2	74.3	2.0	2.2
74.2	0.3	8.6	82.5	1.1	3.7
95.3	0.6	9.9	96.4	1.0	10.0
102.1	0.7	3.8	115.3	0.1	9.3
122.2	0.5	2.0	133.0	0.8	1.0
130.2	0.2	0.3	138.6	1.6	1.6
155.2	0.0	1.4	169.4	0.9	4.2
182.2	3.7	2.8	203.0	0.4	2.4
193.5	3.5	4.0	203.0	1.0	1.0
208.3	6.3	1.7	209.2	2.1	2.4
223.0	2.6	2.8	220.6	1.4	2.0
232.7	2.5	0.6	232.3	12.0	2.3
257.2	4.3	6.4	232.3	2.3	1.4
267.7	7.9	3.4	258.6	0.0	2.5
274.1	26.2	2.0	276.9	11.7	1.0
351.0	0.8	3.8	352.8	0.6	6.9
390.5	87.9	15.1	414.7	13.5	0.4
420.1	228.8	4.6	415.6	6.0	27.4
424.1	167.3	29.7	426.8	3.8	0.1
431.7	39.4	0.5	429.0	168.8	12.4
437.3	5.6	0.7	445.4	40.6	0.5

458.1	4.2	0.5	450.8	94.2	6.7
463.6	5.4	2.5	462.7	8.7	3.5
561.4	0.1	0.2	541.5	0.3	0.6
566.9	8.3	0.2	559.9	4.0	0.4
572.8	8.3	1.4	559.9	0.5	0.5
574.7	2.8	0.3	562.4	5.7	0.2
591.1	22.1	0.3	573.0	20.2	0.2
598.8	23.8	1.6	597.9	70.3	2.3
606.9	28.8	2.3	599.8	1.0	1.1
640.4	7.2	8.7	622.1	5.1	9.1
660.0	11.3	2.3	639.6	3.5	0.1
661.0	8.4	1.5	643.5	11.3	3.4
749.6	1.0	0.2	718.9	1.9	0.3
759.8	28.9	0.1	735.5	126.1	0.2
773.5	92.7	0.0	747.1	4.5	0.6
780.0	1.8	16.4	768.8	1.0	13.9
828.8	0.0	1.4	800.1	0.0	1.7
895.1	0.0	0.3	856.6	0.0	0.2
904.7	0.1	0.5	865.3	0.5	0.2
979.5	187.9	66.5	945.0	0.1	0.4
992.0	0.1	0.4	948.6	200.6	67.8
998.8	0.1	0.2	955.8	0.2	0.1
1012.4	0.0	0.9	968.0	0.1	0.4
1016.5	0.1	0.5	981.4	0.5	0.6
1027.6	4.9	4.5	1009.1	4.1	2.6
1034.5	21.0	115.8	1018.8	16.9	82.4
1053.7	2.5	4.9	1039.6	1.0	10.5
1082.0	9.4	46.7	1057.9	5.4	48.4
1094.5	3.8	1.1	1060.5	9.3	15.7
1129.2	9.9	1.6	1099.1	12.4	3.1
1142.8	0.5	0.4	1113.9	0.2	0.6
1177.8	8.5	10.7	1127.7	3.1	7.2
1192.8	7.2	3.2	1140.0	5.9	5.8
1304.1	7.7	12.7	1253.8	2.6	12.2
1308.0	2.9	21.5	1269.8	4.7	7.8
1318.8	1.4	199.9	1320.6	1.9	203.8
1343.4	10.8	43.8	1383.7	2.6	8.2
1346.2	12.6	36.9	1390.8	95.2	34.3
1377.4	312.8	12.6	1397.0	58.8	14.2
1400.2	318.1	24.8	1398.1	33.7	9.6
1413.9	182.9	26.3	1418.7	2.5	42.8
1459.8	9.6	25.9	1434.0	205.7	51.1

1473.6	69.0	0.7	1444.8	84.6	0.8
1507.3	40.6	2.5	1458.1	42.5	1.7
1526.7	8.3	168.5	1507.5	2.3	174.2
1616.1	15.3	137.5	1600.3	7.1	147.8
1630.2	16.1	1.9	1617.7	14.4	0.9
1646.2	31.5	341.1	1635.6	21.6	333.4
1657.8	25.9	12.0	1646.2	21.5	12.1
2178.9	1761.4	52.6	2196.7	688.2	38.7
2187.2	996.5	221.9	2203.0	950.4	76.6
2223.5	979.0	468.4	2243.6	939.7	414.1
3213.0	4.8	50.9	3101.1	17.4	31.7
3216.6	4.1	101.7	3106.4	5.7	40.5
3218.9	0.4	64.7	3138.6	0.6	100.5
3226.9	2.6	33.6	3139.9	0.2	46.8
3239.2	2.8	94.1	3154.3	0.1	7.2
3241.9	1.9	280.3	3157.0	0.0	110.9
3244.6	0.1	9.5	3160.8	0.7	97.1
3256.3	3.3	172.1	3161.4	0.2	413.3

[$NbO(N_3)_3 \cdot CH_3CN$]

B3LYP [5(A)]			SVWN5 [5(B)]		
Freq	IR	Raman	Freq	IR	Raman
13.2	0.4	0.3	18.3	0.7	10.8
23.0	1.0	0.8	26.7	1.5	4.4
26.3	0.9	17.1	34.7	0.2	11.6
29.1	3.4	4.2	39.4	2.8	1.7
33.0	0.0	13.1	57.1	0.0	1.8
45.3	1.3	3.5	66.2	2.4	8.3
65.7	0.5	9.1	68.8	1.5	7.8
79.2	2.1	10.7	77.0	5.6	11.9
98.9	2.3	3.4	113.8	1.3	1.0
107.9	0.9	0.9	140.1	0.3	8.5
176.8	5.6	0.9	189.7	2.3	6.6
178.8	2.9	3.0	195.7	1.5	2.9
189.4	2.6	9.9	224.6	0.1	1.3
226.1	4.2	5.6	228.9	3.0	4.7
228.9	0.1	0.1	238.9	1.6	2.7
260.8	1.9	2.5	259.8	2.1	1.0
278.7	16.9	5.8	265.9	7.7	1.4
418.5	51.3	25.1	413.4	5.2	2.3
422.7	3.5	3.1	415.5	6.3	8.2
425.0	0.7	1.0	431.2	26.5	38.6
448.2	207.9	33.9	445.5	182.0	16.0

458.3	256.9	0.5	472.1	161.5	0.7
562.9	6.3	0.5	552.5	10.5	1.0
567.7	8.3	0.9	554.8	7.7	0.3
568.1	13.3	0.2	558.3	8.5	0.7
580.3	25.8	1.5	562.9	5.4	0.7
588.0	51.5	2.7	579.0	53.8	2.9
591.8	29.7	2.3	594.3	38.7	3.1
945.1	8.9	8.5	980.4	11.5	3.7
999.2	165.4	45.6	980.9	64.3	55.0
1053.8	4.8	0.1	987.1	83.3	17.4
1054.0	2.0	0.1	989.8	9.7	0.2
1400.6	470.0	19.0	1317.1	37.8	15.5
1403.2	63.8	13.9	1370.8	24.4	12.4
1407.3	351.5	12.7	1379.2	16.8	7.1
1428.2	177.9	9.2	1401.8	112.5	28.3
1462.2	13.4	8.0	1422.8	183.3	24.6
1462.8	13.7	7.1	1466.0	244.7	29.2
2202.4	1725.8	114.4	2216.9	977.9	88.1
2208.0	1762.8	133.2	2231.3	1326.0	137.0
2233.9	216.7	639.5	2255.5	555.3	603.8
2396.3	82.7	207.6	2336.3	105.1	268.1
3079.6	0.4	209.2	2994.7	7.6	279.4
3168.0	0.0	63.6	3090.9	4.8	60.6
3169.4	0.1	51.7	3095.1	4.1	80.7

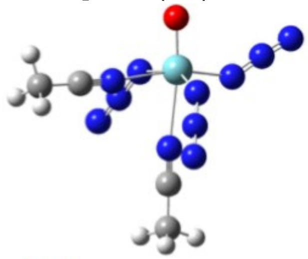
[$NbO(N_3)_3 \cdot 2CH_3CN$] [6(A)], C_1

B3LYP			SVWN5		
Freq	IR	Raman	Freq	IR	Raman
19.9	3.0	7.9	22.9	0.9	15.8
20.8	0.2	6.9	24.7	0.2	8.2
23.2	0.1	0.0	33.2	1.0	11.0
30.5	2.4	1.5	36.3	1.8	2.8
31.5	0.9	10.4	43.4	2.4	2.2
32.6	3.6	4.1	65.4	0.5	3.9
32.8	1.9	1.0	70.8	0.2	1.6
34.9	1.0	5.6	74.6	0.3	0.9
58.2	1.3	16.5	87.9	8.9	0.2
81.1	0.4	9.3	92.4	6.0	4.9
82.7	1.8	0.8	116.9	3.1	8.7
113.3	0.0	3.8	125.0	9.6	4.7
117.9	6.3	1.0	148.6	0.8	6.8
136.4	0.1	2.1	159.8	0.9	2.0

148.7	2.8	3.4	180.4	0.4	5.0
173.8	0.0	1.7	184.1	2.0	1.1
188.3	4.2	1.5	199.4	7.0	4.7
214.2	5.3	0.5	217.3	0.9	3.2
218.3	9.0	3.5	220.1	2.5	1.6
222.4	10.9	4.5	224.5	4.3	3.6
235.9	0.3	1.0	235.5	5.0	1.8
246.1	6.4	1.2	248.4	10.0	1.1
273.8	38.3	9.0	271.9	15.0	2.1
395.2	63.7	11.6	382.5	1.8	1.1
398.5	2.7	2.6	390.8	0.5	1.8
404.8	1.1	0.6	404.8	10.4	1.9
413.3	2.1	3.3	407.7	4.7	6.9
421.5	0.6	3.1	427.2	8.9	18.3
438.1	254.5	0.7	436.3	193.5	29.6
439.4	185.8	37.5	451.6	179.3	2.5
567.4	8.7	0.3	559.3	4.2	0.9
577.1	14.4	0.2	561.3	6.9	0.3
578.8	1.1	0.2	561.7	19.8	0.8
593.2	34.6	1.1	568.4	6.9	0.3
605.4	3.2	2.0	597.0	37.9	3.1
605.5	54.6	0.4	598.6	35.4	1.0
942.0	14.5	7.0	966.4	105.1	73.9
948.7	10.4	11.6	975.6	81.8	34.2
998.1	240.7	68.1	980.8	10.1	1.4
1052.8	4.4	0.4	983.0	5.0	2.0
1054.3	3.5	0.1	983.2	38.8	3.2
1054.6	1.8	0.4	991.6	4.4	0.6
1055.0	3.3	0.2	994.3	4.4	0.2
1393.2	274.7	23.3	1314.0	42.8	9.2
1396.7	407.7	15.0	1314.6	41.0	12.8
1403.1	14.6	8.7	1371.3	27.1	16.3
1403.8	1.0	17.6	1374.0	18.0	11.7
1412.4	91.0	15.4	1382.6	15.9	7.2
1463.2	13.3	8.9	1385.5	15.8	5.6
1463.5	12.1	3.9	1398.2	79.3	24.0
1464.4	13.4	10.2	1407.1	66.3	30.8
1465.2	14.8	6.6	1454.9	220.8	29.7
2179.7	1253.1	88.0	2205.7	935.7	75.9
2187.5	1808.1	79.9	2214.7	1082.9	84.0
2219.6	563.9	499.5	2248.5	780.7	504.5
2389.8	73.7	141.1	2326.4	84.9	203.9

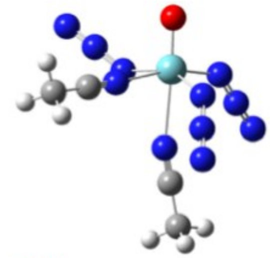
2402.6	74.7	303.3	2338.6	94.0	301.4
3078.8	0.1	231.1	2992.7	2.5	208.1
3079.4	0.0	185.4	2993.0	3.6	328.8
3166.7	0.0	51.8	3087.3	3.6	53.0
3166.9	0.1	73.5	3088.3	4.5	67.2
3167.6	0.0	53.5	3095.3	2.5	81.6
3169.0	0.0	48.0	3096.4	1.6	71.6

Figure S7: $[NbO(N_3)_3{\cdot}2CH_3CN]$ structures.

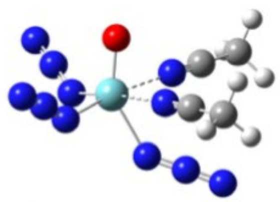


6(A) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 0.0 kcal/mol

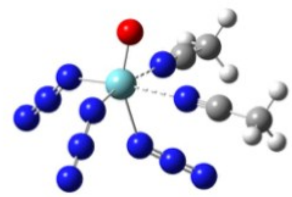
6(B) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 0.5 kcal/mol



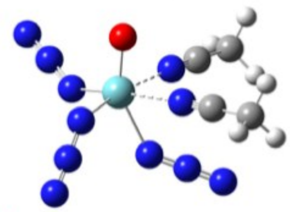
6(C) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 1.0 kcal/mol



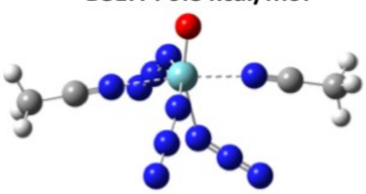
6(D) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 6.8 kcal/mol



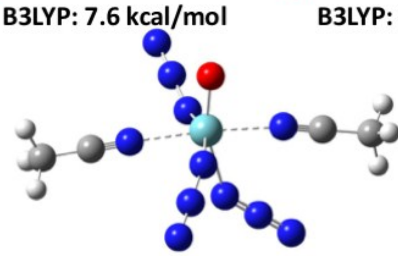
6(E) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 7.6 kcal/mol



6(F) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 8.6 kcal/mol

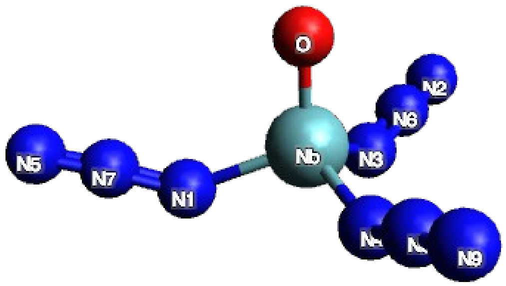


6(G) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 12.3 kcal/mol



6(H) $[NbO(N_3)_3{\cdot}2CH_3CN]$
B3LYP: 13.0 kcal/mol

Figure S8: Optimized structure of $[NbO(N_3)_3]$.



Cartesian Coordinates

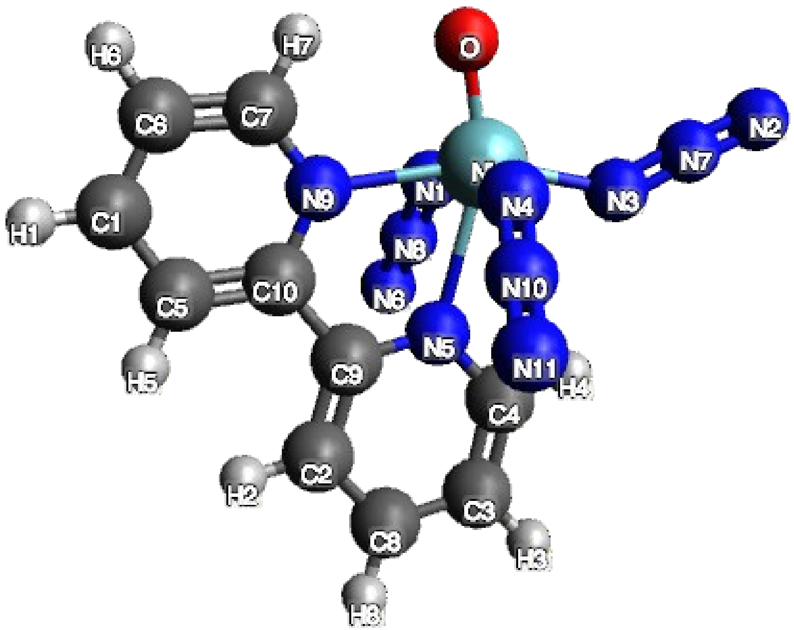
B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	1.529210	-0.907016	0.000000
N	-0.988581	-0.506603	1.629625
N	2.151648	3.583352	0.000000
N	0.453292	1.920318	0.000000
N	-0.988581	-0.506603	-1.629625
N	-1.056484	-1.805988	3.618757
N	1.358448	2.752545	0.000000
N	-0.988581	-1.193373	2.649467
N	-0.988581	-1.193373	-2.649467
N	-1.056484	-1.805988	-3.618757
NB	0.060821	-0.035460	0.000000

SVWN5/DZVP2/cc-pVDZ-PP
0 1

O	1.739006	-0.521515	0.000000
N	-0.774598	-0.739152	1.612718
N	1.128928	4.046344	0.000000
N	0.031354	1.936099	0.000000
N	-0.774598	-0.739152	-1.612718
N	-0.706251	-1.982058	3.639464
N	0.625509	3.003636	0.000000
N	-0.706251	-1.384030	2.647944
N	-0.706251	-1.384030	-2.647944
N	-0.706251	-1.982058	-3.639464
NB	0.102605	-0.030660	0.000000

Figure S9: Optimized structure of [(bipy)NbO$(N_3)_3$] 2(A).



Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

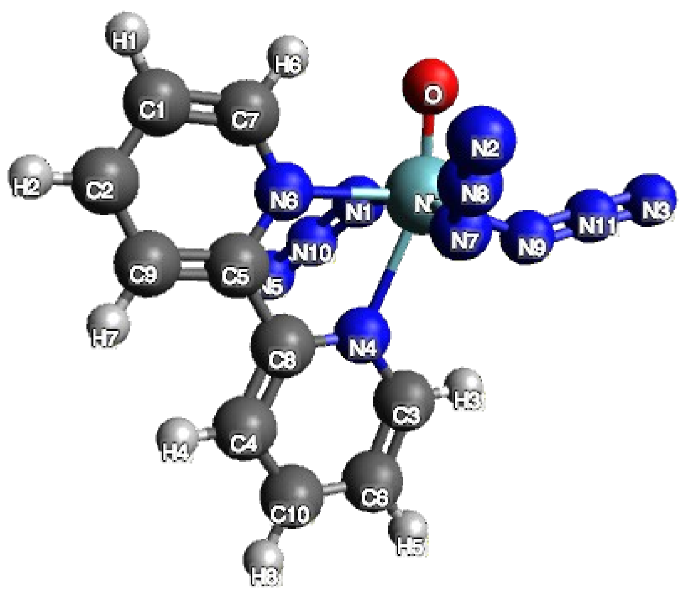
O	0.088444	-2.816050	0.000000
N	0.435895	-0.813943	2.040927
N	4.607390	-2.389662	0.000000
N	2.627629	-1.078563	0.000000
N	0.435895	-0.813943	-2.040927
N	0.310048	1.272589	0.000000
N	0.424623	0.995100	3.581879
N	3.628244	-1.780548	0.000000
N	0.435895	0.131962	2.808258
N	-1.680914	-0.501111	0.000000
C	-4.379647	0.185119	0.000000
H	-5.430147	0.458954	0.000000
C	-1.141223	3.178886	0.000000
H	-2.141255	3.593174	0.000000
C	1.247710	3.482058	0.000000
H	2.133505	4.107291	0.000000
C	1.371585	2.092295	0.000000
H	2.344707	1.609746	0.000000
N	0.435895	0.131962	-2.808258
C	-3.394811	1.174315	0.000000
H	-3.680850	2.218241	0.000000
C	-3.990769	-1.156543	0.000000
H	-4.718852	-1.959931	0.000000
N	0.424623	0.995100	-3.581879
C	-2.628011	-1.453705	0.000000
H	-2.263813	-2.475911	0.000000
C	-0.036514	4.032453	0.000000
H	-0.177237	5.108768	0.000000

C	-0.935101	1.793972	0.000000
C	-2.045060	0.802742	0.000000
NB	0.590753	-1.169856	0.000000

SVWN5/DZVP2/cc-pVDZ-PP
0 1

O	-1.322380	-2.458033	0.000000
N	0.012698	-0.856301	1.993583
N	3.066154	-4.321248	0.000000
N	1.741297	-2.348025	0.000000
N	0.012698	-0.856301	-1.993583
N	0.993322	0.790421	0.000000
N	-0.000598	1.201010	3.194098
N	2.398545	-3.370474	0.000000
N	0.012698	0.196965	2.597492
N	-1.569673	0.310887	0.000000
C	-3.538683	2.267354	0.000000
H	-4.315992	3.040466	0.000000
C	0.767415	3.169774	0.000000
H	0.119863	4.052669	0.000000
C	2.947642	2.161548	0.000000
H	4.040873	2.226328	0.000000
C	2.324557	0.918714	0.000000
H	2.892199	-0.023320	0.000000
N	0.012698	0.196965	-2.597492
C	-2.194343	2.620832	0.000000
H	-1.894742	3.673873	0.000000
C	-3.880522	0.914549	0.000000
H	-4.926150	0.588806	0.000000
N	-0.000598	1.201010	-3.194098
C	-2.864483	-0.033821	0.000000
H	-3.047806	-1.119055	0.000000
C	2.150074	3.307698	0.000000
H	2.607629	4.303827	0.000000
C	0.216504	1.887805	0.000000
C	-1.226581	1.616589	0.000000
NB	0.003390	-1.343413	0.000000

Figure S10: Optimized structure of [(bipy)NbO(N_3)$_3$] 2(B).



Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

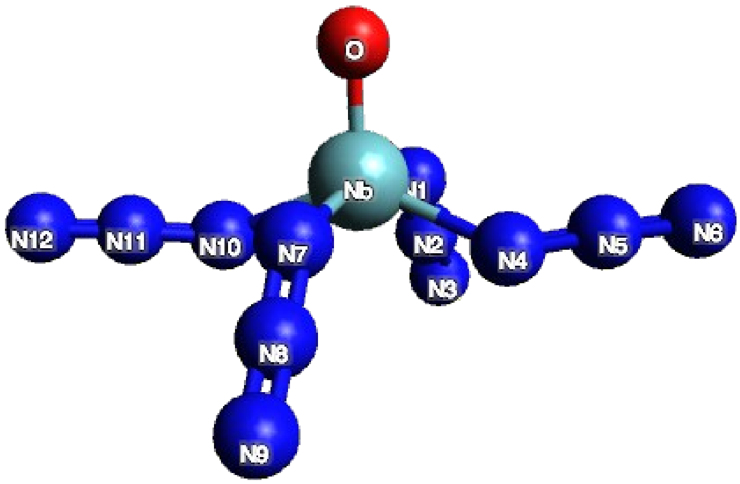
O	1.489318	-2.032161	0.866932
N	0.599017	0.441533	2.097792
N	0.630200	-2.966087	-2.935034
N	5.176453	0.536532	0.173300
N	-0.357277	1.343749	-0.518910
N	-0.856648	2.073170	3.027217
N	-1.201824	-1.038208	0.344462
N	0.855644	-0.930119	-1.726547
N	0.745870	-1.997589	-2.314594
N	2.807954	0.603476	0.021799
N	-0.152577	1.283404	2.551236
N	4.025138	0.538154	0.110292
C	-2.882401	-2.668213	0.879933
H	-3.117154	-3.656021	1.260232
C	-3.881588	-1.789942	0.454115
H	-4.927817	-2.076405	0.496215
C	0.157023	2.504720	-0.946622
H	1.236623	2.600513	-0.876613
C	-2.551362	2.125510	-1.073742
H	-3.620418	1.961100	-1.117302
C	-2.161176	-0.178693	-0.073730
C	-0.635246	3.533471	-1.457951
H	-0.178265	4.457751	-1.793471
C	-1.554167	-2.248722	0.808888
H	-0.735345	-2.885849	1.127145
C	-1.689582	1.141774	-0.572530
C	-3.515006	-0.531920	-0.026842
H	-4.278276	0.161601	-0.355332
C	-2.017153	3.335009	-1.521955

H	-2.669936	4.109318	-1.912783
NB	1.094057	-0.462653	0.282975

SVWN5/DZVP2/cc-pVDZ-PP
0 1

O	1.293094	-2.474205	0.000208
N	0.715161	-0.472152	1.994059
N	-0.984434	0.684949	-3.195338
N	5.294377	0.114830	-0.000528
N	-0.099227	1.263448	0.000103
N	-0.985850	0.684544	3.195140
N	-1.138941	-1.126338	-0.000162
N	0.715933	-0.472031	-1.993611
N	-0.150726	0.125807	-2.598294
N	2.917600	0.129140	0.000399
N	-0.151791	0.125553	2.598451
N	4.132766	0.097301	-0.000094
C	-2.932403	-2.703167	-0.000540
H	-3.248256	-3.751827	-0.000641
C	-3.861702	-1.662279	-0.000650
H	-4.937525	-1.873409	-0.000846
C	0.541260	2.437445	0.000218
H	1.639561	2.378447	0.000364
C	-2.195661	2.411098	-0.000157
H	-3.289810	2.370590	-0.000295
C	-2.028207	-0.110784	-0.000256
C	-0.138013	3.650511	0.000155
H	0.421824	4.591752	0.000251
C	-1.577739	-2.392212	-0.000298
H	-0.780693	-3.151248	-0.000207
C	-1.443475	1.235984	-0.000096
C	-3.402226	-0.350280	-0.000507
H	-4.107137	0.487446	-0.000596
C	-1.534253	3.633230	-0.000028
H	-2.102271	4.570786	-0.000073
NB	1.113171	-0.751501	0.000303

Figure S11: Optimized structure of $[NbO(N_3)_4]^-$ 3(A).

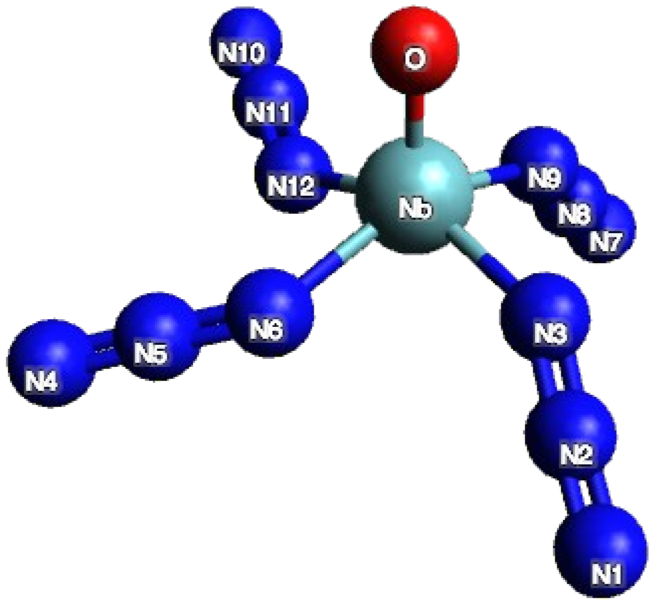


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
-1 1

O	0.000000	0.000000	2.218869
N	0.000000	2.056570	0.152970
N	-0.092744	2.840803	-0.770526
N	-0.183144	3.642683	-1.606089
N	1.933465	-0.017709	-0.292142
N	3.008030	0.532650	-0.153020
N	4.059713	1.017232	-0.069213
N	0.000000	-2.056570	0.152970
N	0.092744	-2.840803	-0.770526
N	0.183144	-3.642683	-1.606089
N	-1.933465	0.017709	-0.292142
N	-3.008030	-0.532650	-0.153020
N	-4.059713	-1.017232	-0.069213
NB	0.000000	0.000000	0.501984

Figure S12: Optimized structure of $[NbO(N_3)_4]^-$ 3(B).



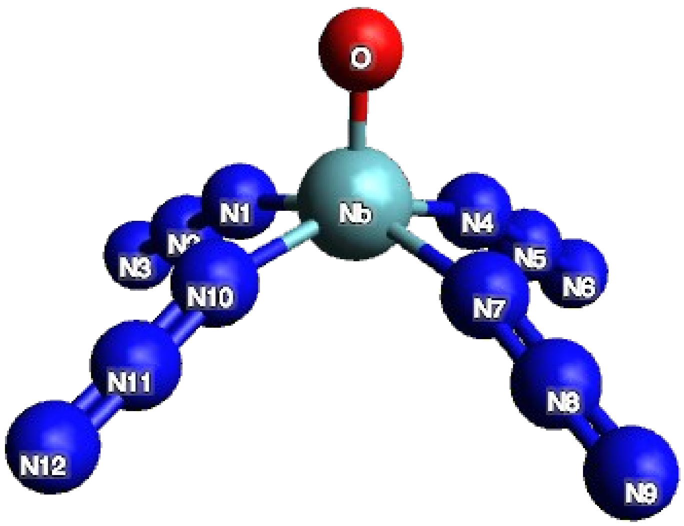
Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP

-1 1

O	0.193587	0.223218	2.209230
N	-4.006178	-0.894279	-0.890936
N	-3.025751	-0.825245	-0.271650
N	-2.031538	-0.782880	0.422780
N	-0.361445	3.819218	-1.198379
N	-0.621642	2.801407	-0.705923
N	-0.957736	1.753224	-0.191750
N	1.332087	-3.502852	-1.424176
N	0.999968	-2.705430	-0.647018
N	0.663427	-1.919786	0.215080
N	3.963284	0.681377	-0.206291
N	2.806234	0.673592	-0.294341
N	1.600105	0.706191	-0.451066
NB	-0.099376	-0.010183	0.532484

Figure S13: Optimized structure of $[NbO(N_3)_4]^-$ 3(C).



Cartesian Coordinates

SVWN5/DZVP2/cc-pVDZ-PP
-1 1

O	0.000000	0.000000	2.327209
N	1.976470	-0.000001	0.116644
N	2.990639	0.000001	-0.533906
N	3.997222	0.000003	-1.133177
N	0.000000	-1.976471	0.116647
N	0.000000	-2.990628	-0.533922
N	0.000000	-3.997201	-1.133209
N	-1.976470	0.000001	0.116644
N	-2.990639	-0.000001	-0.533906
N	-3.997222	-0.000003	-1.133177
N	0.000000	1.976471	0.116647
N	0.000000	2.990628	-0.533922
N	0.000000	3.997201	-1.133209
NB	0.000000	0.000000	0.604762

Figure S14: Optimized structure of $[NbO(N_3)_5]^{2-}$ 4(A).

Cartesian Coordinates

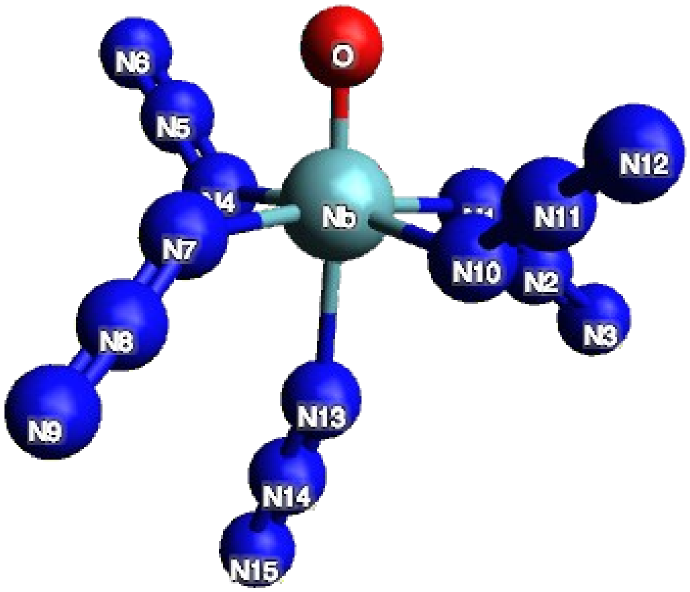
B3LYP/DZVP2/cc-pVDZ-PP
-2 1

N	0.000064	0.079556	-2.136984
N	0.000080	-0.640021	-3.105888
N	0.000080	-1.272388	-4.090991
N	-2.137043	0.079534	0.000000
N	-3.105921	-0.640058	0.000000
N	-4.091013	-1.272458	0.000000
N	0.000064	0.079556	2.136984
N	0.000080	-0.640021	3.105888
N	0.000080	-1.272388	4.090991
N	0.000536	2.150940	0.000000
N	0.000042	3.345379	0.000000
N	-0.000404	4.524781	0.000000
O	-0.000245	-1.834214	0.000000
N	4.090684	-1.273512	0.000000
N	3.105751	-0.640878	0.000000
N	2.137037	0.078944	0.000000
NB	0.000028	-0.100856	0.000000

SVWN5/DZVP2/cc-pVDZ-PP
-2 1

N	0.001313	-0.004637	2.086424
N	0.002131	-0.566229	3.149641
N	0.002131	-1.057835	4.220568
N	2.093735	0.066821	0.000000
N	3.163340	-0.483791	0.000000
N	4.240995	-0.960161	0.000000
N	0.001313	-0.004637	-2.086424
N	0.002131	-0.566229	-3.149641
N	0.002131	-1.057835	-4.220568
N	-0.043638	2.023017	0.000000
N	-0.074315	3.219391	0.000000
N	-0.105466	4.403355	0.000000
O	0.079159	-1.919874	0.000000
N	-4.227724	-1.089003	0.000000
N	-3.148519	-0.614674	0.000000
N	-2.074867	-0.075933	0.000000
NB	0.012777	-0.177131	0.000000

Figure S15: Optimized structure of $[NbO(N_3)_5]^{2-}$ 4(B).



Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP

-2 1

O	0.387893	0.000018	-2.173765
N	0.130760	-2.125654	-0.293164
N	0.195770	-3.006794	0.528836
N	0.262374	-3.914997	1.262429
N	-2.038601	-0.000104	-0.724107
N	-2.785283	-0.000096	-1.673901
N	-3.569818	0.000023	-2.542644
N	0.130583	2.125622	-0.293129
N	0.195454	3.006755	0.528890
N	0.261932	3.914880	1.262592
N	2.149674	0.000059	0.175126
N	3.246378	0.000183	-0.326697
N	4.339854	0.000403	-0.746210
N	-0.450952	-0.000062	1.735574
N	-1.193493	-0.000085	2.678444
N	-1.898270	-0.000057	3.620935
NB	0.099081	-0.000017	-0.462456

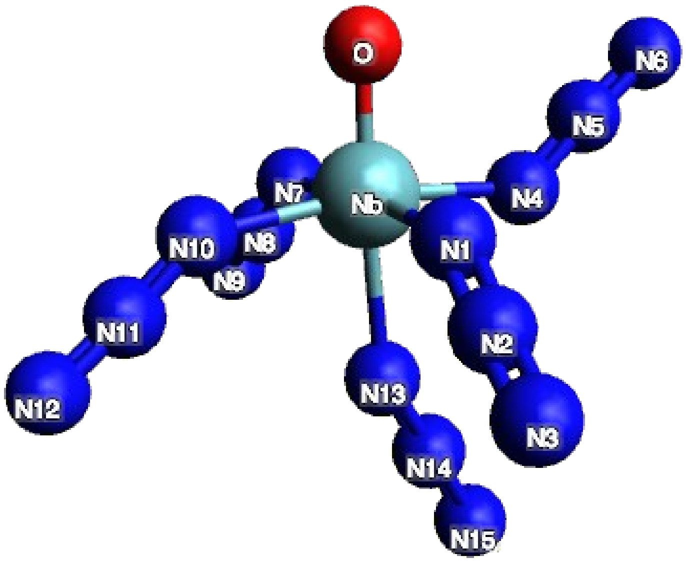
SVWN5/DZVP2/cc-pVDZ-PP

-2 1

O	0.174564	-0.000859	-2.222940
N	0.118542	-2.076356	-0.282098
N	0.265070	-3.010059	0.462710
N	0.405216	-3.966523	1.134780
N	-2.047483	-0.004648	-0.575898
N	-2.924505	-0.007062	-1.402974
N	-3.830607	-0.009459	-2.155193
N	0.110289	2.076448	-0.285021
N	0.252252	3.011610	0.458863

N	0.387894	3.969461	1.129870
N	2.105149	0.003837	-0.040585
N	3.246769	0.005604	-0.413955
N	4.383053	0.007403	-0.728380
N	-0.348744	0.000585	1.684389
N	-1.014062	0.000644	2.684733
N	-1.648739	0.000691	3.681986
NB	0.058118	-0.000204	-0.480221

Figure S16. Optimized structure of $[NbO(N_3)_5]^{2-}$ 4(C).

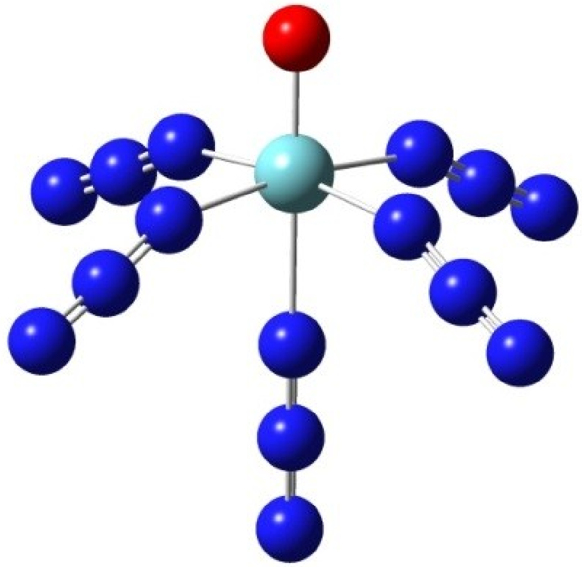


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
-2 1

O	0.965295	-0.000354	-2.193861
N	0.120698	2.126680	-0.503433
N	-0.278679	3.046483	0.166335
N	-0.635277	3.991035	0.757407
N	2.086657	-0.000270	0.415906
N	3.244270	-0.000466	0.068469
N	4.386327	-0.000638	-0.186437
N	0.120132	-2.126850	-0.503012
N	-0.279537	-3.046415	0.166909
N	-0.636696	-3.990747	0.757992
N	-1.815115	0.000087	-1.309813
N	-2.969276	0.000285	-0.961396
N	-4.109976	0.000538	-0.700010
N	-0.626458	0.000217	1.484834
N	-0.515540	0.000362	2.681257
N	-0.438065	0.000744	3.855206
NB	0.212278	-0.000109	-0.628795

Figure S17: Optimized structure of $[NbO(N_3)_5]^{2-}$ 4(D)



Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
-2 1

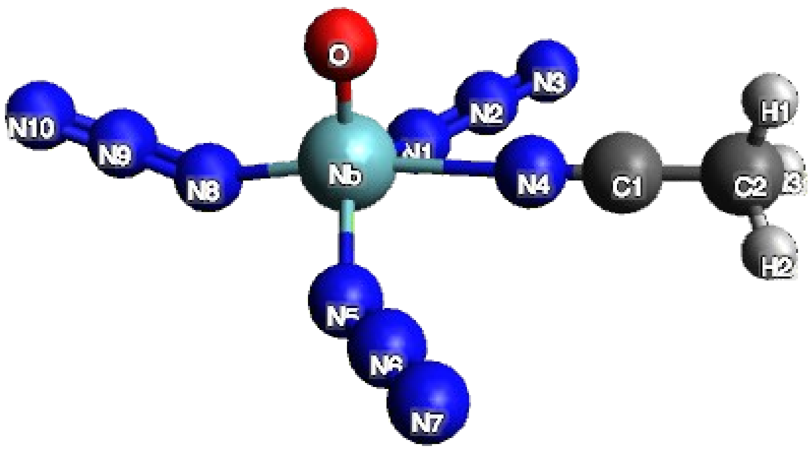
O	0.000738	0.000040	-2.596837
N	1.763027	1.191228	-0.708171
N	2.541715	1.717744	0.046087
N	3.339834	2.257047	0.710922
N	1.191426	-1.762543	-0.707634
N	1.717348	-2.541517	0.046736
N	2.256330	-3.339753	0.711683
N	-1.762290	-1.191264	-0.708504
N	-2.541180	-1.717633	0.045647
N	-3.339321	-2.257116	0.710297
N	-1.190956	1.762638	-0.708552
N	-1.718529	2.540701	0.045634
N	-2.259008	3.337772	0.710732
N	-0.000239	0.000293	1.411772
N	-0.000283	0.000783	2.611617
N	-0.000457	0.001199	3.788433
NB	0.000297	0.000064	-0.860297

SVWN5/DZVP2/cc-pVDZ-PP
-2 1

O	-0.004172	-0.004168	-2.526921
N	-0.019612	-2.076699	-0.604273
N	-0.032763	-3.117037	-0.005419
N	-0.045837	-4.169106	0.526222
N	-2.075023	0.018559	-0.602734
N	-3.123438	0.037619	-0.018933
N	-4.182314	0.056007	0.499180
N	0.018777	2.073842	-0.609107
N	0.031797	3.112660	-0.007402
N	0.044676	4.163540	0.526465
N	2.074595	-0.019818	-0.611726

N	3.121859	-0.026692	-0.025347
N	4.180045	-0.034254	0.494322
N	0.004498	0.000731	1.432145
N	0.005383	-0.001383	2.632787
N	0.006329	-0.003325	3.815640
NB	-0.000717	-0.001687	-0.777497

Figure S18: Optimized structure of [$NbO(N_3)_3 \cdot CH_3CN$] 5(A).

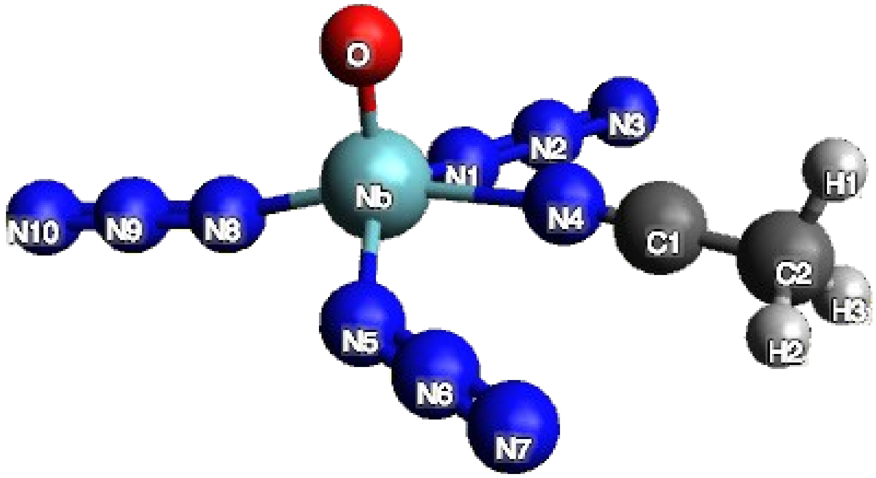


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	-0.485255	-0.000289	1.788178
N	-0.079939	1.828658	-0.707361
N	0.693896	2.764752	-0.571752
N	1.407075	3.669163	-0.497237
N	1.865214	0.000241	0.203149
N	-0.079267	-1.828642	-0.707723
N	0.695626	-2.763869	-0.572008
N	1.409805	-3.667478	-0.497376
N	-2.462618	-0.000510	-0.387771
N	-3.616312	-0.000831	0.017356
N	-4.722792	-0.001133	0.335891
C	3.017920	0.000275	0.316261
C	4.469554	0.000294	0.466042
H	4.725322	0.000038	1.529071
H	4.886846	-0.892448	-0.007260
H	4.886747	0.893353	-0.006743
NB	-0.519916	-0.000110	0.077549

Figure S19: Optimized structure of [$NbO(N_3)_3 \cdot CH_3CN$] 5(B).

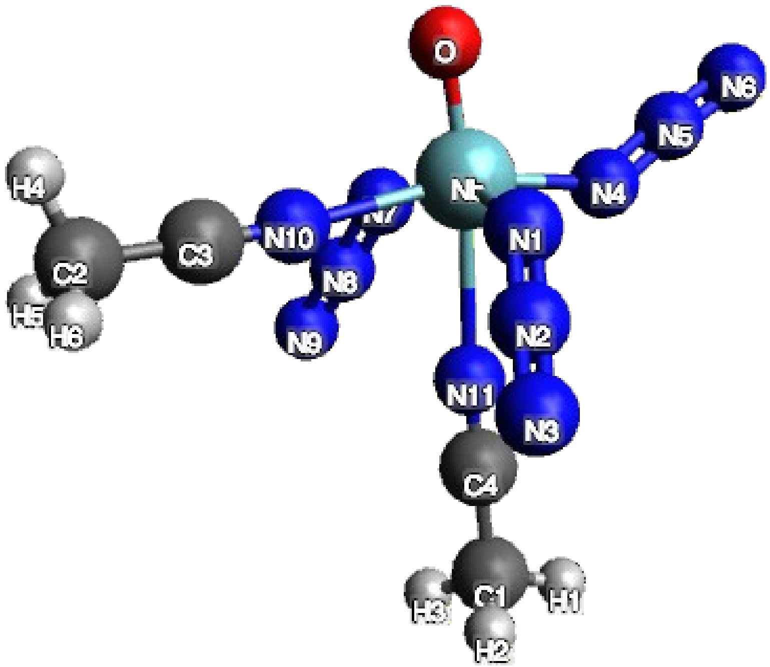


Cartesian Coordinates

SVWN5/DZVP2/cc-pVDZ-PP
0 1

O	-0.507448	0.045379	1.946012
N	-0.314057	1.874328	-0.454549
N	0.428733	2.837848	-0.474218
N	1.110962	3.777255	-0.531494
N	1.689842	0.163420	0.176695
N	0.096237	-1.836737	-0.392149
N	1.177955	-2.379745	-0.489666
N	2.222315	-2.886444	-0.595704
N	-2.421256	-0.259221	-0.265695
N	-3.615099	-0.464314	-0.315987
N	-4.757734	-0.657338	-0.391652
C	2.845520	0.009908	0.111993
C	4.267082	-0.185507	0.043822
H	4.725349	0.057061	1.018520
H	4.466694	-1.243392	-0.205084
H	4.703151	0.466182	-0.733083
NB	-0.532598	0.005545	0.233112

Figure S20: Optimized structure of [$NbO(N_3)_3 \cdot 2CH_3CN$] 6(A).

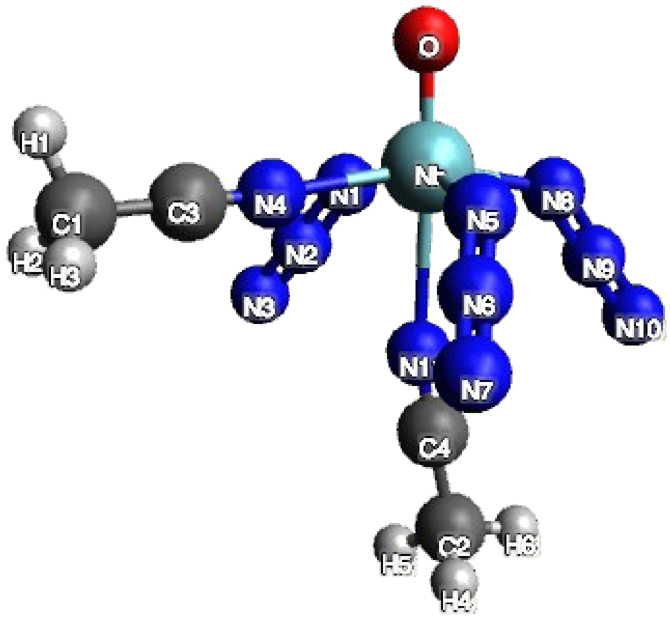


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	1.042181	-2.322512	-0.000242
N	0.169394	-0.404237	-2.010771
N	-0.498530	0.364611	-2.678858
N	-1.121685	1.064339	-3.361072
N	2.372418	0.283913	-0.000031
N	3.570765	0.039777	0.000013
N	4.713197	-0.116273	0.000050
N	0.169512	-0.404630	2.010695
N	-0.498396	0.364145	2.678886
N	-1.121540	1.063782	3.361205
N	-1.713635	-1.201541	-0.000053
N	-0.424894	1.669261	0.000162
C	-1.241222	4.157649	0.000315
H	-0.373359	4.822560	0.002244
H	-1.839552	4.348962	-0.894334
H	-1.842645	4.347862	0.893124
C	-4.194375	-2.033743	-0.000010
H	-4.204309	-3.127106	-0.003168
H	-4.707533	-1.670637	0.894446
H	-4.709310	-1.665477	-0.891331
C	-2.812778	-1.563905	-0.000033
C	-0.790044	2.769101	0.000236
NB	0.591550	-0.671042	-0.000090

Figure S21: Optimized structure of [$NbO(N_3)_3 \cdot 2CH_3CN$] 6(B).

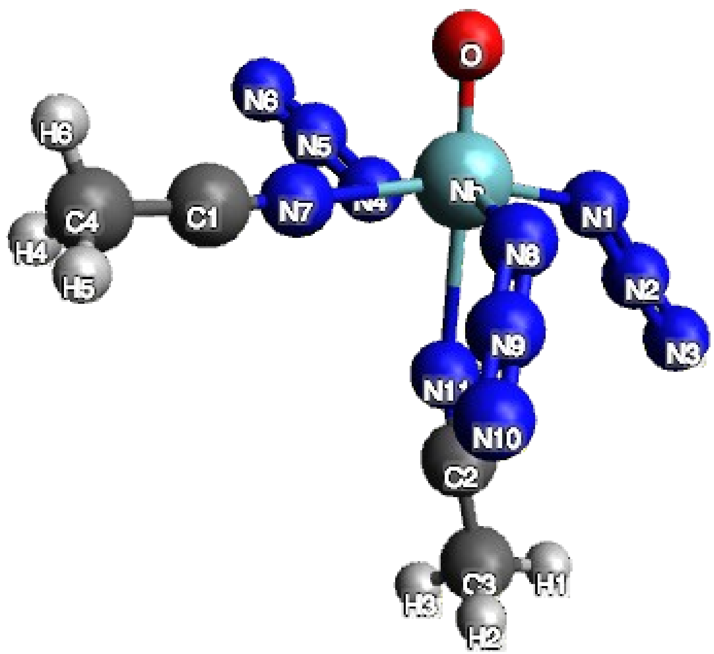


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	-0.895996	-2.629169	-0.041336
N	-0.257706	-0.644212	1.999189
N	-0.256781	0.363807	2.684207
N	-0.267236	1.288310	3.382454
N	-2.109159	0.128690	0.001062
N	-0.255001	-0.580920	-2.017520
N	-0.253414	0.447861	-2.670862
N	-0.262916	1.393617	-3.340078
N	1.839607	-1.601027	-0.023114
N	2.898662	-0.996576	-0.012737
N	3.929654	-0.471157	-0.003499
N	0.843242	1.283999	0.020674
C	-4.412920	1.367370	0.018957
H	-5.217630	0.627211	0.034157
H	-4.485545	1.999177	0.908229
H	-4.506581	1.985555	-0.877886
C	2.400464	3.390550	0.048164
H	2.215561	3.999399	-0.840680
H	2.207075	3.982652	0.946510
H	3.441965	3.057999	0.050091
C	-3.126340	0.680216	0.009070
C	1.526405	2.221201	0.032926
NB	-0.140371	-1.094181	-0.016655

Figure S22: Optimized structure of [$NbO(N_3)_3·2CH_3CN$] 6(C).

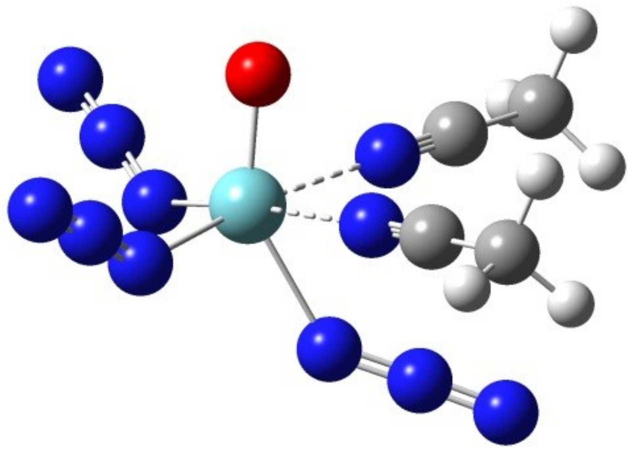


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	-1.214613	-1.321142	-1.825103
N	1.555295	-1.587233	-0.932888
N	2.685299	-1.519151	-0.479118
N	3.771598	-1.495876	-0.082096
N	-0.794896	-1.542799	1.067825
N	-1.771617	-2.206410	1.386533
N	-2.666560	-2.832269	1.763615
N	-1.862480	0.875036	0.058118
N	0.361779	1.154259	-1.653521
N	0.677628	2.291141	-1.354270
N	0.980875	3.385271	-1.117067
N	1.179770	0.624813	1.127402
C	-2.729551	1.580924	0.356221
C	2.025081	1.101610	1.761864
C	3.102484	1.689349	2.553415
H	4.029850	1.145462	2.354734
H	3.231831	2.738404	2.274658
H	2.862507	1.619865	3.617659
C	-3.828677	2.466462	0.724858
H	-4.109118	2.292470	1.767115
H	-3.520301	3.507581	0.597534
H	-4.688319	2.262635	0.080588
NB	-0.202985	-0.586703	-0.657594

Figure S23: Optimized structure of [$NbO(N_3)_3\cdot 2CH_3CN$] 6(D).

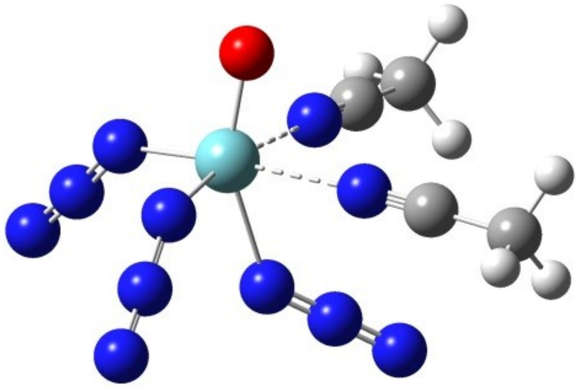


Cartesian Coordinates

B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	-0.008103	0.763756	-1.675536
N	1.507492	1.742044	0.654781
N	2.376765	2.447628	0.160448
N	3.223960	3.124656	-0.232336
N	1.737447	-1.028485	-0.508168
N	-1.723389	-1.054607	-0.505066
N	-1.533521	1.718397	0.658296
N	-2.415376	2.410099	0.166716
N	-3.274388	3.073633	-0.223441
N	0.007995	-0.824348	1.671396
N	0.019790	-2.028367	1.831645
N	0.031218	-3.177383	2.011130
C	3.615718	-2.775639	-1.031471
H	4.583300	-2.370541	-0.722941
H	3.419919	-3.699041	-0.480102
H	3.639332	-2.987895	-2.103588
C	-3.573576	-2.829251	-1.035829
H	-3.586187	-3.045423	-2.107350
H	-3.369173	-3.748011	-0.479848
H	-4.548985	-2.436554	-0.736032
C	-2.539664	-1.840643	-0.743144
C	2.566032	-1.802517	-0.743061
NB	-0.004644	0.557143	0.037985

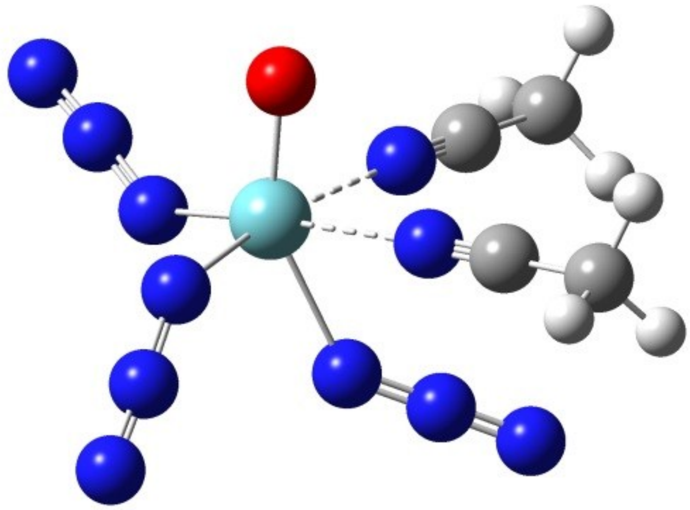
Figure S24: Optimized structure of [$NbO(N_3)_3 \cdot 2CH_3CN$] 6(E).



Cartesian Coordinates
B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	0.596149	-0.228587	-1.994473
N	0.782683	1.853755	-0.169613
N	2.233963	-0.724104	0.397879
N	3.374042	-0.701018	-0.049307
N	4.474160	-0.689889	-0.394242
N	-0.274904	-2.389037	-0.226758
N	-0.708022	-3.163050	0.617920
N	-1.126171	-3.947126	1.353212
N	-1.907332	0.112377	-0.857481
N	-0.533608	0.108630	1.578272
N	-1.228650	1.014473	1.992215
N	-1.891364	1.877750	2.404414
C	0.969109	2.988663	-0.038218
C	-3.008095	0.377489	-1.098948
C	1.210237	4.417340	0.137030
H	0.469134	4.830224	0.826471
H	2.210892	4.569042	0.550897
H	1.137851	4.926268	-0.827774
C	-4.400356	0.699404	-1.397861
H	-4.992881	-0.219552	-1.402780
H	-4.792265	1.375791	-0.633728
H	-4.467892	1.176592	-2.379088
NB	0.357976	-0.468204	-0.300385

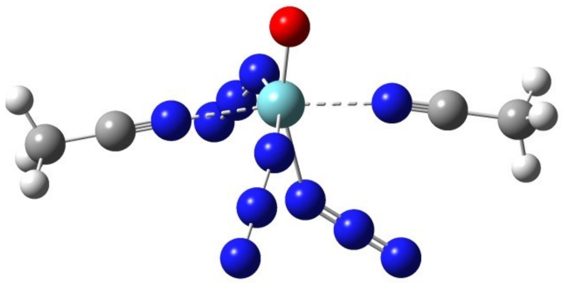
Figure S25: Optimized structure of [$NbO(N_3)_3·2CH_3CN$] 6(F).



Cartesian Coordinates
B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	0.085649	-0.000044	-2.333875
N	1.782250	-1.556478	-0.525182
N	2.358367	-2.185345	0.353850
N	2.929280	-2.827814	1.123099
N	-1.244772	-1.584559	-0.474493
N	-1.229875	1.596284	-0.473848
N	1.796730	1.539683	-0.524451
N	2.379001	2.163468	0.354093
N	2.956171	2.800795	1.122962
N	0.012406	-0.000528	1.464949
N	-0.999109	0.003477	2.137569
N	-1.962717	0.007265	2.790701
C	-3.124679	-3.372220	-0.131630
H	-2.665983	-4.358706	-0.021489
H	-3.692964	-3.136816	0.772056
H	-3.794677	-3.380462	-0.995423
C	-3.091943	3.402422	-0.130431
H	-3.767614	3.410784	-0.989792
H	-3.656200	3.177856	0.778518
H	-2.624042	4.385608	-0.029929
C	-2.057520	2.391524	-0.324623
C	-2.080272	-2.371586	-0.325499
NB	0.492650	-0.002256	-0.654014

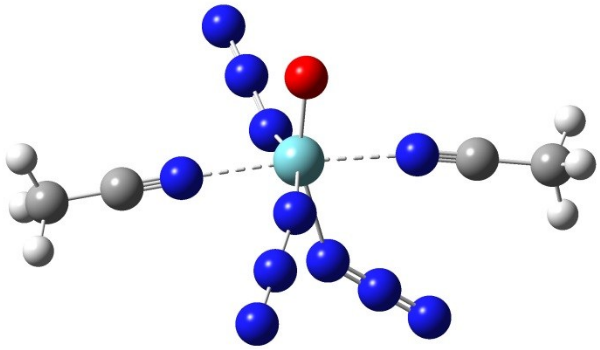
Figure S26: Optimized structure of [$NbO(N_3)_3 \cdot 2CH_3CN$] 6(G).



Cartesian Coordinates
B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	-0.009202	-0.000741	-2.413942
N	0.340703	-2.034383	-0.474409
N	0.701810	-2.767957	0.436176
N	1.044746	-3.516793	1.247079
N	-2.203313	0.000381	-0.776247
N	0.342654	2.033476	-0.475577
N	0.705461	2.766597	0.434628
N	1.050358	3.514809	1.245348
N	2.291537	-0.000948	-0.261663
N	-0.561501	0.000558	1.417688
N	-1.596249	0.001930	2.050156
N	-2.597709	0.003193	2.645685
C	-3.354372	0.001014	-0.653229
C	3.418115	-0.000761	0.002533
C	4.836774	-0.000104	0.337119
H	5.425580	0.111276	-0.577541
H	5.051826	0.833222	1.011511
H	5.097809	-0.942540	0.825984
C	-4.802928	0.001711	-0.486176
H	-5.224707	0.894341	-0.956136
H	-5.225788	-0.889636	-0.957593
H	-5.036719	0.001043	0.581406
NB	0.067576	-0.000463	-0.688771

Figure S27: Optimized structure of $[NbO(N_3)_3{\cdot}2CH_3CN]$ 6(H).



Cartesian Coordinates
B3LYP/DZVP2/cc-pVDZ-PP
0 1

O	0.137650	0.963737	-1.932951
N	-2.178729	0.298394	-0.650143
N	0.347544	1.872263	0.749773
N	0.794455	2.985809	0.501455
N	1.206086	4.054468	0.349164
N	2.288815	-0.058879	0.048782
N	0.371982	-1.745596	-1.114987
N	0.732883	-2.813785	-0.643007
N	1.079414	-3.849388	-0.260955
N	-0.724787	-0.735684	1.412996
N	-1.797215	-0.930571	1.943653
N	-2.832341	-1.115481	2.444506
C	-4.793986	0.285139	-0.606044
H	-5.128217	-0.113381	0.355133
H	-5.169385	1.303989	-0.734597
H	-5.171173	-0.344320	-1.416675
C	4.820120	-0.398665	0.608572
H	5.426737	-0.075543	-0.241913
H	5.083195	0.194006	1.488876
H	5.010957	-1.456340	0.809430
C	-3.336188	0.294398	-0.635252
C	3.408992	-0.209827	0.295870
NB	0.078934	0.176209	-0.396199

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