

Supporting Information for the Paper Entitled:

**The Niobaziridine–Hydride Functional Group:
Synthesis and Divergent Reactivity**

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S1. Synthesis and spectroscopic data for all new compounds

S2. Crystallographic structure determinations.

Supporting Information

S1.1 General Synthetic Considerations

All manipulations were carried out under an atmosphere of dry dinitrogen using a Vacuum Atmospheres glove box or Schlenk techniques at room temperature unless otherwise stated. After purification, all solvents were stored in the glove box over 4 Å molecular sieves prior to use. Diethyl ether, n-pentane, n-hexane, tetrahydrofuran and toluene were obtained anhydrous from commercial sources and further purified by the method of Grubbs,¹ except tetrahydrofuran, which was distilled under dinitrogen from sodium-benzophenone ketyl. Benzene-d₆ (Cambridge Isotope Laboratories) was degassed and stored in the glove box over 4 Å molecular sieves for at least 3 d prior to use. Celite 435 (EM Science) and 4 Å molecular sieves (Aldrich) were dried under vacuum at 250 °C overnight and stored under dinitrogen. n-Butyl lithium was purchased from Aldrich as a 1.6 M solution in hexanes and used as received. Benzaldehyde and *tert*-butylnitrile were purchased from Aldrich and distilled from CaH₂ prior to use. 2,4,6-trimethylbenzonitrile (Aldrich) was recrystallized from n-hexane and dried *in vacuo* prior to use. Nitrous oxide (N₂O) was obtained from BOC Gases and passed through a 1 ft column of P₂O₅ before being introduced to the reaction vessel via a Schlenk line. The compounds Mg(THF)₃(anthracene),² *mer,cis*-Nb(Cl)₃(THF)₂(PhCCPh)³ and (P)Mo(N[ⁱPr]Ar)₃⁴ were prepared according to literature procedures. All other reagents were obtained from commercial sources and used as received. All glassware was oven-dried at a temperature of 230 °C prior to use.

Solution NMR spectra were recorded using Varian Unity-300 MHz, Varian XL-300 MHz and Varian INOVA 500 MHz spectrometers. ¹H and ¹³C chemical shifts are reported referenced to the residual C₆D₆ solvent resonances of 7.16 ppm (¹H) and 128.3 (t) ppm (¹³C) relative to TMS. ³¹P chemical shifts are reported referenced to the external standard H₃PO₄ (0.0 ppm). Solution IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. All spectra were recorded in C₆D₆ using a KBr plated solution cell. Solvent peaks were digitally subtracted from all spectra using an authentic spectrum obtained immediately prior to that of the sample. Combustion analyses were carried out by H. Kolbe Microanalytisches, Mülheim an der Ruhr, Germany.

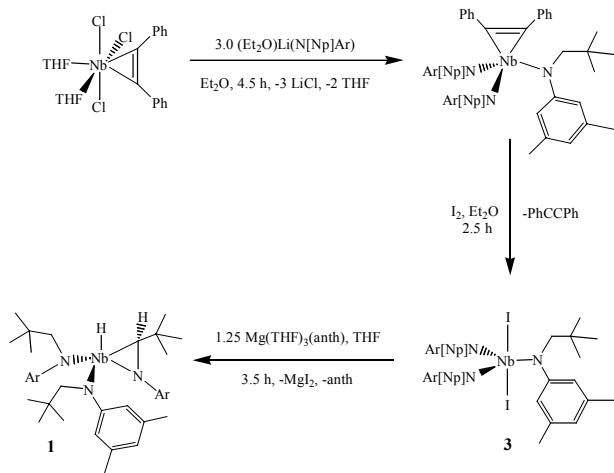


Figure S1: Synthetic scheme for the formation of Nb(H)(η^2 -tBu(H)C=N(Ar))(N[Np]Ar)₂ (**1**) (Np = neopentyl, Ar = 3,5-Me₂C₆H₃, anth = anthracene).

S1.2 Synthesis of HN(Np)Ar

Aniline HN(Np)Ar was prepared by modifying a literature procedure for the synthesis of N-alkylanilines,⁵ here, employing pivaldehyde as the carbonyl-containing source. The product was typically obtained in 60% yield after distillation *in vacuo* starting with 50 mL of pivaldehyde (460 mmol) and 36 mL of 3,5-dimethylaniline (287 mmol). ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 6.38 (s, 1H, p-Ar), 6.19 (s, 2H, o-Ar), 3.22 (b, 1H, NH), 2.73 (s, 2H, N-CH₂), 2.24 (s, 6H, Ar-CH₃), 0.84 (s, 9H, ^tBu); ¹³C{¹H} NMR (75.46 MHz, C₆D₆, 23 °C): δ 149.9 (aryl ipso), 138.7 (m-Ar), 119.8 (p-Ar), 111.6 (o-Ar), 56.2 (N-CH₂), 32.3 (C(CH₃)₃), 28.0 (C(CH₃)₃), 22.1 (Ar-CH₃); FTIR (KBr windows, C₆D₆ solution): ν(N-H) 3426 cm⁻¹ also 3022, 2960, 2870, 1596, 1519, 1497 1190, 690 cm⁻¹. Anal. Calcd. for C₁₃H₂₁N: C, 81.61; H, 11.06; N, 7.32. Found: C, 81.56; H, 10.98; N, 7.28.

S1.3 Synthesis of (Et₂O)Li(N[Np]Ar)

To a thawing n-pentane solution of HN(Np)Ar (20.0 g, 104 mmol, 75 mL) was added a hexanes solution of n-butyl lithium (1.6 M, 78 mL, 125 mmol) dropwise over 30 min. The viscous, pale yellow reaction mixture was allowed to stir for an additional 40 min. At this point, 25 mL of diethyl ether were added to the mixture concomitant with precipitation of (Et₂O)Li(N[Np]Ar). The solvent was reduced to a volume of 40 mL *in vacuo*. The resulting pale yellow slurry was filtered through a sintered glass frit, affording (Et₂O)Li(N[Np]Ar) as a white solid in 88 % yield (24.90 g) after washing with 40 mL of n-pentane and thorough drying under vacuum. ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 6.39 (s, 2H, o-Ar), 6.13 (s, 1H, p-Ar), 3.38 (s, 2H, N-CH₂), 3.10 (q, 4H, J = 6 Hz, O-CH₂-CH₃), 2.36 (s, 6H, Ar-CH₃), 1.15 (s, 9H, ^tBu), 0.83 (t, 6H, J = 6 Hz, O-CH₂-CH₃); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 161.5 (aryl ipso), 139.3 (m-Ar), 113.2 (o-Ar), 111.1 (p-Ar), 65.8 (N-CH₂), 60.3 (O-CH₂-CH₃), 36.5 (C(CH₃)₃), 29.8 (C(CH₃)₃), 22.9 (Ar-CH₃), 14.8 (O-CH₂-CH₃); Anal. Calcd. for C₁₇H₃₀NOLi: C, 75.24; H, 11.14; N, 5.16; Found: C, 74.29; H, 11.59; N, 5.21.

S1.4 Synthesis of Nb(PhCCPh)(N[Np]Ar)₃

To a diethyl ether slurry of *mer,cis*-Nb(Cl)₃(THF)₂(PhCCPh) (25.0 g, 47.9 mmol, 150 mL) at room temperature was added solid (Et₂O)Li(N[Np]Ar) (39.0 g, 143.7 mmol) in 3 g portions over the course of 1.5 h. After approximately 40 min, the mixture became dark brown and homogeneous and was allowed to stir for an additional time of 3 h. At this point, the solvent was removed *in vacuo* and the resulting dark brown residue was then extracted with two 50 mL portions of n-pentane and filtered through a sintered glass frit padded with approximately 4 cm of Celite in order to remove LiCl. The brown filtrate was evaporated to dryness *in vacuo* leaving a dark brown cake. The mixture was then slurried in 50 mL of n-pentane and filtered into a clean frit whereupon a yellow solid was obtained and washed with 10 mL of cold n-pentane. It has been our experience that this lipophilic material is not easily recrystallized from hydrocarbon or ethereal solvents and the material obtained by simple collection from the crude reaction mixture is of sufficient purity to be used in subsequent reactions. Yield: 35% based on Nb. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ 7.75 (d, 4 H, J = 7.5 Hz, o-Ph), 7.31 (t, 4 H, J = 7.5 Hz, m-Ph), 7.08 (t, 2 H, J = 7.5 Hz, p-Ph), 6.80 (s, 6 H, o-Ar), 6.59 (s, 3 H, p-Ar), 3.82 (s, 6 H, , N-CH₂), 2.19 (s, 18 H, Ar-CH₃), 0.74 (s, 27 H, ^tBu); ¹³C{¹H} NMR (125.66 MHz, C₆D₆,

23 °C): δ 200.0 (Ph-CC-Ph), 153.1 (aryl ipso), 143.4 (phenyl ipso), 138.8 (m-Ar), 129.2 (p-Ar), 128.5 (m-Ph), 127.4 (p-Ph), 126.0 (o-Ph), 122.8 (o-Ar), 67.1 (N-CH₂), 35.5 (C(CH₃)), 29.4 (C(CH₃)), 22.0 (Ar-CH₃). Satisfactory combustion analysis of this material has not been obtained.

S1.5 Synthesis of Nb(I)₂(N[Np]Ar)₃ (3)

A solution of Nb(PhCCPh)(N[Np]Ar)₃ (10.0 g, 11.8 mmol) in diethyl ether (75 mL) was stirred at room temperature for 5 min. whereupon a diethyl ether solution of I₂ (3.164 g, 12.4 mmol, 10 mL) was added dropwise over 5 min. The dark yellow solution gradually became dark orange over the course of 10 min. The reaction mixture was allowed to stir for 2.5 h, after which the solvent was removed *in vacuo*. n-Pentane (30 mL) was added to the residue and the mixture was stirred for 5 min in order to extract liberated PhCCPh. Isolation of the Nb containing product was afforded by filtration of the dark orange mixture through a sintered glass frit with subsequent washing of the bright orange solid with cold n-pentane followed by thorough drying *in vacuo*. For instances where isolated Nb(I)₂(N[Np]Ar)₃ is contaminated with free PhCCPh, the orange solid may be allowed to precipitate from diethyl ether (~1mL/g) in the freezer (-35 °C) overnight before being collected, washed and dried again. Yield: 7.080g, 65%. ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 8.04 (s, 6 H, o-Ar), 6.61 (s, 3 H, p-Ar), 3.60 (s, 6 H, N-CH₂), 2.14 (s, 18 H, Ar-CH₃), 0.585 (s, 27 H, ^tBu); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 150.1 (aryl ipso), 139.9 (m-Ar), 130.4 (p-Ar), 124.8 (o-Ar), 76.4 (N-CH₂), 36.3 (C(CH₃)₃), 29.1 (C(CH₃)₃), 21.6 (Ar-CH₃); Anal. Calc. for C₃₉H₆₀N₃I₂Nb: C, 51.05; H, 6.59; N, 4.58. Found: C, 50.61; H, 6.42; N, 4.56.

S1.6 Synthesis of Nb(H)(η²-^tBu(H)C=N(Ar))(N[Np]Ar)₂ (1)

To a thawing THF solution of Nb(I)₂(N[Np]Ar)₃ (6.0 g, 6.53 mmol, 75 ml), 300 mg portions of Mg(THF)₃(anthracene) (3.418 g, 8.16 mmol) were added over a period of 10 min. The reaction mixture gradually changed in color from orange to deep purple and back to orange while being allowed to stir for a total of 3.5 h. At this point the solvent was removed *in vacuo* and the resulting orange-brown solid was extracted with two 30 mL portions of n-pentane and filtered through a 4 cm pad of Celite to remove salts and anthracene. The pentane filtrate was then concentrated to a volume of 10 mL, frozen and filtered while thawing through another pad of Celite in order to remove any residual anthracene. The filtrate was then dried, diethyl ether (~1mL/g) added and cooled to -35° C for 24 h whereupon large orange blocks of pure Nb(H)(^tBu(H)C=N(Ar))(N[Np]Ar)₂ were obtained and collected by vacuum filtration. Yield: 2.170 g, 52 % in two crops. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ 9.25 (b, 1 H, Nb-H), 7.07 (s, 2 H, o-Ar), 7.02 (s, 2 H, o-Ar), 6.63 (s, 1 H, p-Ar), 6.59 (s, 1 H, p-Ar), 6.57 (s, 1 H, p-Ar), 6.11 (s, 2 H, o-Ar), 4.14, (s, 2 H, N-CH₂), 2.83, (d, 1H, J = 8 Hz, N-CH₂), 2.74 (d, 1H, J = 8 Hz, N-CH₂), 2.36 (s, 1 H, , ^tBu (H)C=N), 2.35 (s, 6 H, Ar-CH₃), 2.14 (s, 6 H, Ar-CH₃), 2.13 (s, 6 H, Ar-CH₃), 1.41 (s, 9 H, ^tBu), 0.77 (s, 9 H, ^tBu), 0.46 (s, 9 H, ^tBu); ¹³C{¹H} NMR (125.66 MHz, C₆D₆, 23° C): δ 155.8 (aryl ipso), 144.4 (aryl ipso), 141.3 (p-Ar), 140.3 (p-Ar), 138.6 (m-Ar), 138.2 (aryl ipso), 129.0 (m-Ar), 127.7 (m-Ar), 122.9 (p-Ar), 118.4 (o-Ar), 116.7 (o-Ar), 116.5 (o-Ar), 81.9 (^tBu (H)C=N), 68.3, (N-CH₂), 57.5 (N-CH₂), 36.4, (C(CH₃)₃), 35.0 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.7 (C(CH₃)₃), 29.3 (C(CH₃)₃), 28.6 (C(CH₃)₃), 22.2 (Ar-CH₃), 21.9 (Ar-CH₃), 21.8 (Ar-CH₃); FTIR (KBr windows, C₆D₆

solution): ν (Nb-H) 1701 cm⁻¹ also 1585, 1475, 1213, 1091, 1004, 689 cm⁻¹. Anal. Calcd. for C₃₉H₆₀N₃Nb: C, 70.56; H, 9.11; N, 6.33. Found: C, 70.60; H, 9.12; N, 6.30.

S1.7 Thermolysis of Nb(H)(η^2 -^tBu(H)C=N(Ar))(N[Np]Ar)₂: Synthesis of Nb(Ar)(NNp)(N[Np]Ar)₂ (**4**)

A toluene solution of **1** (200 mg, 0.30 mmol, 3 mL) was heated in a Schlenk tube at 100 °C for 1 h under an atmosphere of dinitrogen. Over this time the color of the reaction mixture changed from orange to light brown. The Schlenk tube was then transferred to the glove box where all volatile materials were removed *in vacuo*. The resulting brown residue was extracted with 2 mL of n-pentane and filtered through Celite. The filtrate was dried under vacuum to leave an oily brown residue which did not crystallize readily from hydrocarbon or ethereal solvents after numerous attempts. ¹H NMR indicated that the reaction had proceeded with complete consumption of complex **1** with no additional species produced besides **4**. ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 7.78 (s, 2H, M-Ar-ortho), 6.89 (s, 1H, M-Ar-para), 6.79 (s, 4H, o-Ar), 6.48 (s, 2H, p-Ar), 4.18 (d, 2H, J = 13 Hz, N-CH₂ amido), 3.86 (s, 2H, N-CH₂ imido), 3.84 (d, 2H, J = 13 Hz, N-CH₂ amido), 2.34 (s, 6H, M-Ar-CH₃), 2.07 (s, 12H, Ar-CH₃), 1.06 (s, 9H, ^tBu imido), 0.94 (s, 18H, ^tBu); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 150.8 (amide aryl ipso), 139.7 (amide m-Ar), 136.3 (m-Ar), 135.9 (amide p-Ar), 129.9 (p-Ar), 126.0 (o-Ar), 120.3 (amide o-Ar), 77.3 (imido N-CH₂), 70.0 (amide N-CH₂), 35.9 (amide C(CH₃)₃), 35.0 (imido C(CH₃)₃), 29.0 (amide C(CH₃)₃), 28.4 (imido C(CH₃)₃), 22.1 (Ar-CH₃), 21.7 (amide Ar-CH₃). The physical properties of **4** (i.e. oily nature and lack of crystallinity) prevented adequate purification and combustion analysis.

S1.8 Synthesis of (O)Nb(N[Np]Ar)₃ (**5**)

An atmosphere of dry N₂O was introduced to a partially evacuated 50 mL Schlenk tube containing an diethyl ether solution of **1** (88 mg, 0.093 mmol, 3 mL). The color of solution gradually became light brown over the course of 6 h at which point the solvent was removed *in vacuo*. The resulting yellow-brown residue was extracted with 1.5 mL n-pentane and filtered through Celite. The filtrate was then evaporated to dryness in vacuo. Diethyl ether (1 mL) was added to the residue and the solution chilled at -35 °C for 1 d whereupon yellow crystals were obtained. Yield: 0.063 g, 70% in two crops. ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 6.50 (s, 3H, p-Ar), 6.39 (s, 6H, o-Ar), 4.45 (s, 6H, N-CH₂), 2.00 (s, 18H, Ar-CH₃), 1.03 (s, 27H, ^tBu); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 153.7 (aryl ipso), 138.8 (m-Ar), 125.9 (p-Ar), 122.2 (o-Ar), 75.0 (N-CH₂), 35.7 (C(CH₃)₃), 32.0 (C(CH₃)₃), 21.9 (Ar-CH₃); Anal. Calcd for C₃₉H₆₀N₃NbO: C, 68.90; H, 8.90; N, 6.18. Found: C, 68.28; H, 8.72; N, 6.14.

S1.9 Deoxygenation of Triphenylphosphineoxide by

Nb(H)(^tBu(H)C=N(Ar))(N[Np]Ar)₂: Alternate Synthesis of (O)Nb(N[Np]Ar)₃ (**5**)

To a benzene-d₆ solution of **1** (50 mg, 0.075 mmol, 2 mL) was added a solution of triphenylphosphineoxide in benzene-d₆ (22.0 mg, 0.079 mmol, 1 mL). The reaction was monitored by ¹H NMR and was determined to be complete after 10 h. The resulting ¹H NMR spectrum contained only the signature resonances for compound **5** and triphenylphosphine. The presence of triphenylphosphine was confirmed by a signal at -4.8 ppm in the ³¹P NMR spectrum of the reaction mixture.

S1.10 Synthesis of (S)Nb(N[Np]Ar)₃ (6)

A diethyl ether solution of **1** (200 mg, 0.301 mmol, 2 mL) was added over the course of 30 min. to a slurry of trimethylphosphine sulfide (SPMe₃, 0.225 g, 2.11 mmol, 7 equiv) in diethyl ether (8 mL). After 10 min. the solution became emerald green and was allowed to stir for 2.5 h, at which point all volatile materials were removed *in vacuo*. The residue was extracted with n-pentane (2 mL) and filtered through Celite twice, before being dried in *vacuo* again. The resulting light green solid was dissolved in diethyl ether (2 mL) and chilled to -35 °C for 18 h whereupon yellow orange single crystals were obtained and collected. Yield: 0.088 g, 42%. ¹H NMR (300 MHz, C₆D₆, 23 °C): δ 6.51 (s, 3H, p-Ar), 6.44 (s, 6H, o-Ar), 4.47 (s, 6H, N-CH₂), 2.05 (s, 18H, Ar-CH₃), 1.09 (s, 27H, ^tBu); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 152.3 (aryl ipso), 138.6 (m-Ar), 126.5 (p-Ar), 123.4 (o-Ar), 76.9 (N-CH₂), 37.0 (C(CH₃)₃), 29.9 (C(CH₃)₃), 22.0 (Ar-CH₃); Anal. Calc. for C₃₉H₆₀N₃SNb: C, 67.31; H, 8.69; N, 6.04. Found: C, 67.30; H, 8.79; N, 6.08.

S1.11 Synthesis of (Se)Nb(N[Np]Ar)₃ (7)

To a slurry of selenium powder in benzene (45.0 mg, 0.569 mmol, 4 equiv., 3 mL) was added a benzene solution of **1** (0.100 g, 0.150 mmol, 2 mL) over the course of 5 min. The reaction mixture was allowed to stir for 5 h while gradually darkening in color to a dark orange-red. All volatile materials were removed in *vacuo* and the resulting dark orange residue extracted with n-pentane, filtered through Celite and dried again. The resulting residue was redissolved in diethyl ether (1.5 mL) and chilled to -35 °C overnight, whereupon red single crystals were obtained and collected. Yield: 0.078 g, 70% in two crops. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ 6.52 (s, 3H, p-Ar), 6.38 (s, 6H, o-Ar), 4.49 (s, 6H, N-CH₂), 2.04 (s, 18H, Ar-CH₃), 1.11 (s, 27H, ^tBu); ¹³C{¹H} NMR (75.0 MHz, C₆D₆, 23 °C): δ 151.7 (aryl-ipso), 138.6 (m-Ar), 126.6 (p-Ar), 123.5 (o-Ar), 76.5 (N-CH₂), 37.3 (C(CH₃)₃), 30.1 (C(CH₃)₃), 22.0 (Ar-CH₃); Anal. Calc. for C₃₉H₆₀N₃SeNb: C, 63.06; H, 8.14; N, 5.66. Found: C, 62.76; H, 8.06; N, 5.74.

S1.12 Synthesis of (Te)Nb(N[Np]Ar)₃ (8)

Compound **8** was prepared analogously to compound **7** by substituting tellurium powder for selenium powder. The reaction was allowed to stir for 24 h resulting in a dark red-brown solution. After filtration, the resulting red-brown residue was dissolved in 1 mL diethyl ether and chilled at -35° C overnight whereupon dark red crystals were obtained. Yield: 0.071 g, 60% in two crops. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ 6.53 (s, 3H, p-Ar), 6.36 (s, 6H, o-Ar), 4.49 (s, 6H, N-CH₂), 2.05 (s, 18H, Ar-CH₃), 1.14 (s, 27H, ^tBu); ¹³C{¹H} NMR (125.66 MHz, C₆D₆, 23 °C): δ 150.6 (aryl-ipso), 138.7 (m-Ar), 126.7 (p-Ar), 123.4 (o-Ar), 75.2 (N-CH₂), 37.4 (C(CH₃)₃), 30.4 (C(CH₃)₃), 21.7 (Ar-CH₃); Anal. Calc. for C₃₉H₆₀N₃TeNb: C, 59.19; H, 7.64; N, 5.31. Found: C, 59.25; H, 7.58; N, 5.28.

S1.13 Synthesis of (Ar[Np]N)₃Nb(μ-P)Mo(N*i*Pr]Ar)₃ (9)

A diethyl ether solution of (P)Mo(N*i*Pr]Ar)₃ (115 mg, 0.188 mmol, 2.5 mL) was added dropwise over 5 min to a diethyl ether solution of **1** (125 mg, 0.188 mmol, 2.5 mL). The color of the reaction mixture changed to a deep purple-red upon addition. The mixture

was allowed to stir for 2 h, after which, the solvent was removed *in vacuo*. The resulting purple residue was extracted with 1.5 mL n-pentane and filtered through Celite. The filtrate was evaporated to dryness, redissolved in 1.5 mL n-hexane and allowed to sit at room temperature for 3 d whereupon a purple, microcrystalline solid was obtained and collected. Yield: 0.108 g, 45 % one crop. ^1H NMR (300 MHz, C_6D_6 , 23 °C): δ 6.75 (s, 6H, o-Ar), 6.54 (s, 3H, p-Ar), 6.53 (s, 6H, o-Ar), 6.53 (s, 3H, p-Ar), 4.96 (sp, 3H, J = 6 Hz, N-CH(CH₃)₂), 2.22 (s, 18H, Ar-CH₃), 2.15 (s, 18H, Ar-CH₃), 1.57 (d, 18H, J = 6 Hz, N-CH(CH₃)₂), 1.09 (s, 27H, ^tBu); $^{13}\text{C}\{\text{H}\}$ NMR (75.0 MHz, C_6D_6 , 23 °C): δ 159.3 (aryl ipso), 158.3 (aryl ipso), 138.6 (m-Ar), 137.8 (m-Ar), 127.2 (p-Ar), 125.6 (o-Ar), 125.5 (p-Ar), 121.1 (o-Ar), 82.1 (N-CH(CH₃)₂), 72.0 (N-CH₂), 36.5 (C(CH₃)₃), 30.3 (C(CH₃)₃), 25.0 (C(CH₃)₂), 22.1 (Ar-CH₃), 21.9 (Ar-CH₃); ^{31}P NMR (121.4 MHz, C_6D_6 , 23 °C): δ 666.6 (bs); Anal. Calcd for $\text{C}_{72}\text{H}_{108}\text{N}_6\text{PMoNb}$: C, 67.69; H, 8.52; N, 6.58. Found: C, 67.48; H, 8.38; N, 6.34.

S1.14 Synthesis of ($\mu_2:\eta^2,\eta^2\text{-P}_2$)[Nb(N[Np]Ar)₃]₂ (10)

A benzene solution of **1** (300 mg, 0.452 mmol, 5.0 mL) was added over the course of 5 min. to a benzene solution of white phosphorus (16.8 mg, 0.135 mmol, 0.3 equiv., 5.0 mL). The reaction mixture turned dark green upon mixing and was allowed to stir for an additional 1.5 h. at which point all volatile materials were removed *in vacuo*. The resulting dark green residue was extracted with diethyl ether (6 mL), filtered through Celite and dried again *in vacuo*. The residue was redissolved in diethyl ether (3 mL) and chilled to -35 °C for one week whereupon small, dark green single crystals were obtained and collected. Yield: 0.375 g, 60 %. ^1H NMR (500 MHz, C_6D_6 , 23 °C): δ 6.98 (bs, 12H, o-Ar), 6.59 (s, 6H, p-Ar), 4.23 (bs, 12H, N-CH₂), 2.25 (s, 36H, Ar-CH₃), 0.97 (s, 54H, ^tBu); $^{13}\text{C}\{\text{H}\}$ NMR (125.66 MHz, C_6D_6 , 23 °C): δ 154.2 (aryl ipso), 138.1 (m-Ar), 126.6 (o-Ar), 124.4 (p-Ar), 73.4 (N-CH₂), 37.3 (C(CH₃)₃), 30.5 C(CH₃)₃), 22.1 (Ar-CH₃); ^{31}P NMR (202.6 MHz, C_6D_6 , 23 °C): δ 399.3 (bs); FTIR (KBr windows, C_6D_6 solution): 2951, 1600, 1586, 1475, 1365, 1062, 1001, 686 cm⁻¹. Anal. Calcd for $\text{C}_{78}\text{H}_{120}\text{N}_6\text{P}_2\text{Nb}_2$: C, 67.42; H, 8.70; N, 6.05. Found: C, 67.21; H, 8.58; N, 5.87.

S1.15 Synthesis of Nb(η^2 -(2,4,6-trimethylbenzonitrile))(N[Np]Ar)₃ (Nb(η^2 -MesCN)(N[Np]Ar)₃) (11)

To a diethyl ether solution of **1** (100 mg, 0.150 mmol, 2 mL) were added 1.05 equivalents of mesitylnitrile (23.0 mg, 0.158 mmol) in 0.5 mL of diethyl ether. A dark orange-brown solution was obtained upon addition. After filtration through Celite, the residue was dissolved in 1 mL n-hexane and allowed to sit at room temperature for 2 d whereupon large orange blocks were obtained and collected. Yield: 0.070 g, 55% one crop. ^1H NMR (300 MHz, C_6D_6 , 23 °C): δ 6.98 (s, 2H, m-Mes), 6.78 (s, 6H, o-Ar), 6.54 (s, 3H, p-Ar), 3.90 (s, 6H, N-CH₂), 3.01 (s, 6H, Mes-o-Me), 2.18 (s, 3H, Mes-p-Me), 2.15 (s, 18H, Ar-CH₃), 0.78 (s, 27H, ^tBu); $^{13}\text{C}\{\text{H}\}$ NMR (75.0 MHz, C_6D_6): δ 153.2 (aryl ipso), 140.4 (m-Mes), 140.3 (Mes ipso), 138.8 (m-Ar), 132.8 (p-Mes), 130.3 (o-Mes), 126.1 (p-Ar), 121.8 (o-Ar), 65.2 (N-CH₂), 35.9 (C(CH₃)₃), 29.4 (C(CH₃)₃), 23.3 (Mes-o-CH₃), 21.9 (Ar-CH₃), 21.6 (Mes-p-CH₃); FTIR (KBr windows, C_6D_6 solution): 2951, 1587, 1475, 999 cm⁻¹. Anal. Calcd for $\text{C}_{49}\text{H}_{71}\text{N}_4\text{Nb}$: C, 72.75; H, 8.85; N, 6.93. Found: C, 72.35; H, 9.22; N, 6.97.

S1.16 Synthesis of $\text{Nb}(\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu})(\eta^2\text{-}{}^{\text{t}}\text{Bu}(\text{H})\text{C}=\text{N}(\text{Ar}))(\text{N}[\text{Np}]\text{Ar})_2$ (12)

Compound **12** was prepared analogously to compound **11** by substituting *tert*-butylnitrile for mesitylnitrile. The solution became blood red upon addition and was allowed to stir for 4.5 h. After filtration, the resulting red-orange residue was dissolved in 1 mL diethyl ether and chilled at -35 °C overnight whereupon red-orange crystals were obtained.

Yield: 0.084 g, 75% in two crops. ^1H NMR (300 MHz, C_6D_6 , 23 °C): δ 8.87 (s, 1H, $\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$ ketimide), 6.94 (s, 2H, o-Ar), 6.89 (s, 2H, o-Ar), 6.67 (s, 1H, p-Ar), 6.50 (s, 1H, p-Ar), 6.46 (s, 1H, p-Ar), 6.26 (s, 2H, o-Ar), 4.33 (s, 2H, $\text{N}-\text{CH}_2$), 3.38 (d, 1H, $J = 14$ Hz, $\text{N}-\text{CH}_2$), 3.32 (d, 1H, $J = 14$ Hz, $\text{N}-\text{CH}_2$), 3.22 (s, 1H, $\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$ aziridine), 2.30 (s, 6H, Ar- CH_3), 2.27 (s, 6H, Ar- CH_3), 2.09 (s, 6H, Ar- CH_3), 1.35 (s, 9H, ${}^{\text{t}}\text{Bu}$), 1.11 (s, 9H, ${}^{\text{t}}\text{Bu}$), 0.83 (s, 9H, ${}^{\text{t}}\text{Bu}$), 0.55 (s, 9H, ${}^{\text{t}}\text{Bu}$); $^{13}\text{C}\{{}^1\text{H}\}$ NMR (75.0 MHz, C_6D_6 , 23 °C): δ 179.8 ($\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$ ketimide), 155.3 (aryl ipso), 150.0 (aryl ipso), 149.7 (aryl ipso), 139.2 (m-Ar), 137.8 (m-Ar), 137.7 (m-Ar), 125.7 (p-Ar), 125.4 (p-Ar), 122.3 (o-Ar), 121.2 (p-Ar), 119.8 (o-Ar), 117.1 (o-Ar), 77.9 ($\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$ imine), 68.9 ($\text{N}-\text{CH}_2$), 64.4 ($\text{N}-\text{CH}_2$), 40.0 ($\text{C}(\text{CH}_3)_3$), 38.0 ($\text{C}(\text{CH}_3)_3$), 35.0 ($\text{C}(\text{CH}_3)_3$), 34.4 ($\text{C}(\text{CH}_3)_3$), 31.1 ($\text{C}(\text{CH}_3)_3$), 29.2 ($\text{C}(\text{CH}_3)_3$), 28.4 ($\text{C}(\text{CH}_3)_3$), 26.6 ($\text{C}(\text{CH}_3)_3$), 21.7 (Ar- CH_3), 21.5 (Ar- CH_3), 21.3 (Ar- CH_3); FTIR (KBr windows, C_6D_6 solution): $\nu(\text{CN})$ 1667 cm^{-1} also 2951, 2867, 1586, 1475, 1208, 1003, 688 cm^{-1} . Anal. Calcd for $\text{C}_{44}\text{H}_{69}\text{N}_4\text{Nb}$: C, 70.75; H, 9.31; N, 7.50. Found: C, 70.61; H, 9.58; N, 7.48.

S1.17 Synthesis of $\text{Nb}(\text{OCH}_2\text{Ph})(\eta^2\text{-}{}^{\text{t}}\text{Bu}(\text{H})\text{C}=\text{N}(\text{Ar}))(\text{N}[\text{Np}]\text{Ar})_2$ (13)

Compound **13** was prepared analogously to compound **11** by substituting benzaldehyde for mesitylnitrile. The solution became bright yellow upon addition and was allowed to stir for 1.0 h. After filtration, the resulting light orange residue was dissolved in 1 mL diethyl ether and chilled at -35 °C overnight whereupon yellow crystals were obtained.

Yield: 0.080 g, 55%. ^1H NMR (300 MHz, C_6D_6 , 23 °C): δ 7.50 (d, 2H, $J = 7.0$ Hz, o-Ph), 7.28, (t, 2H, $J = 7.0$ Hz, m-Ph), 7.16 (t, 1H, $J = 7.0$ Hz, p-Ph), 6.79 (s, 2H, o-Ar), 6.75 (s, 2H, o-Ar), 6.61 (s, 3H, o-Ar and p-Ar), 6.53 (s, 1H, p-Ar), 6.51 (s, 1H, p-Ar), 5.70 (d, 1H, $J = 13$ Hz, $\text{N}-\text{CH}_2$), 5.59 (d, 1H, $J = 13$ Hz, $\text{N}-\text{CH}_2$), 4.08 (s, 2H, O- CH_2 -Ph), 3.39 (d, 1H, $J = 14$ Hz, $\text{N}-\text{CH}_2$), 3.27 (d, 1H, $J = 14$ Hz, $\text{N}-\text{CH}_2$), 3.15 (s, 1H, $\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$ aziridine), 2.26 (s, 6H, Ar- CH_3), 2.19 (s, 6H, Ar- CH_3), 2.15 (s, 6H, Ar- CH_3), 1.34 (s, 9H, ${}^{\text{t}}\text{Bu}$), 0.83 (s, 9H, ${}^{\text{t}}\text{Bu}$), 0.59 (s, 9H, ${}^{\text{t}}\text{Bu}$); $^{13}\text{C}\{{}^1\text{H}\}$ NMR (75.0 MHz, C_6D_6 , 23 °C): δ 154.6 (aryl-ipso), 154.4 (aryl-ipso), 151.5 (aryl-ipso), 151.1 (Ph-ipso), 142.2 (m-Ph), 138.9 (m-Ar), 138.8 (m-Ar), 137.9 (m-Ar), 129.1 (o-Ph), 128.4 (p-Ph), 125.7 (p-Ar), 125.6 (p-Ar), 123.4 (p-Ar), 121.7 (o-Ar), 121.2 (o-Ar), 118.2 (o-Ar), 80.4 (O- CH_2 -Ph), 77.7 ($\text{N}=\text{C}(\text{H})^{\text{t}}\text{Bu}$), 67.9 ($\text{N}-\text{CH}_2$), 66.6 ($\text{N}-\text{CH}_2$), 38.3 ($\text{C}(\text{CH}_3)_3$), 35.9 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 29.5 ($\text{C}(\text{CH}_3)_3$), 28.9 ($\text{C}(\text{CH}_3)_3$), 22.0 (Ar- CH_3), 21.9 (Ar- CH_3), 21.8 (Ar- CH_3); Anal. Calc. for $\text{C}_{46}\text{H}_{66}\text{N}_3\text{NbO}$: C, 71.76; H, 8.64; N, 5.46. Found: C, 71.68; H, 8.58; N, 5.31.

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S2. Single Crystal X-ray Structure Determination

S2.1 General Considerations

X-ray data collections were obtained using a Siemens Platform three-circle diffractometer equipped with either a CCD or APEX-CCD detector and low temperature aperture. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used for all data collections. The data were processed utilizing the program SAINT supplied by Siemens Industrial Automation, Inc.

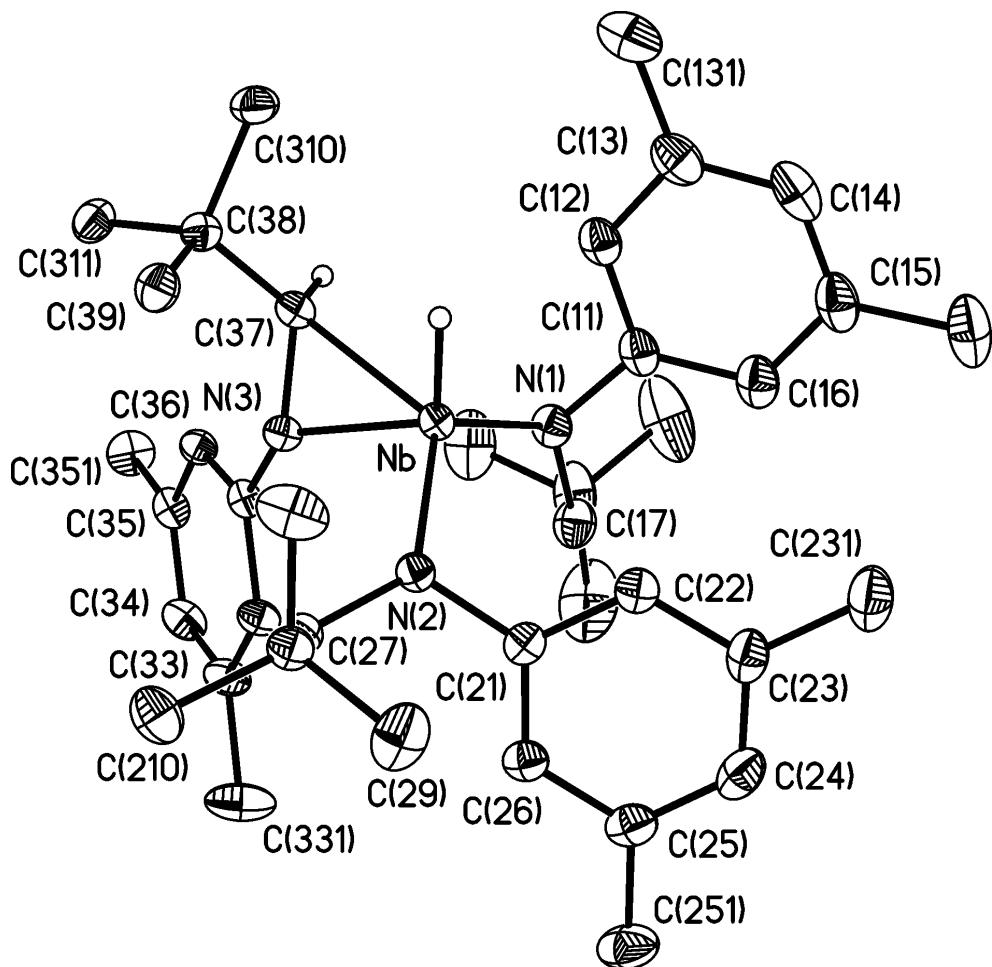


Figure S2. ORTEP diagram of $\text{Nb}(\text{H})(\eta^2\text{-tBu(H)C=NAr})(\text{N}[\text{Np}]\text{Ar})_2$ (**1**) with thermal ellipsoids at the 30% probability level.

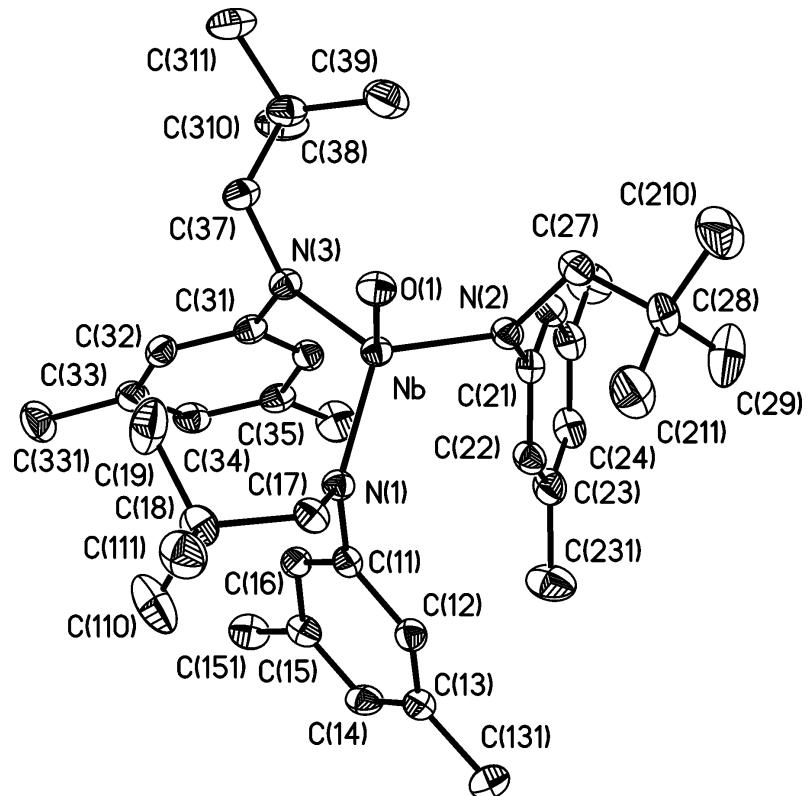


Figure S3. ORTEP diagram of $(\text{O})\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$ (**5**) with thermal ellipsoids at the 30% probability level.

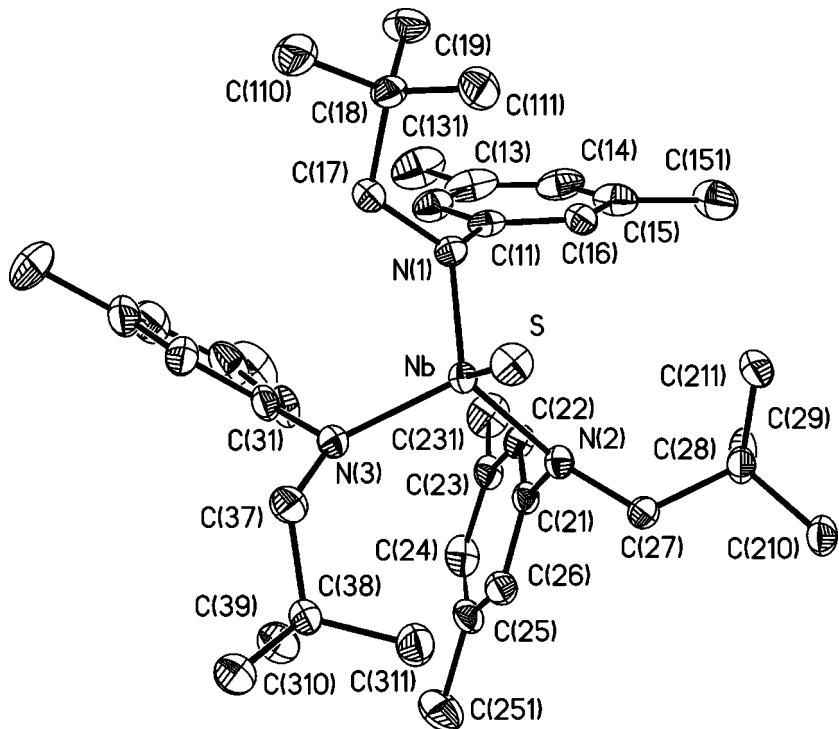


Figure S4. ORTEP diagram of $(\text{S})\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$ (**6**) with thermal ellipsoids at the 30% probability level.

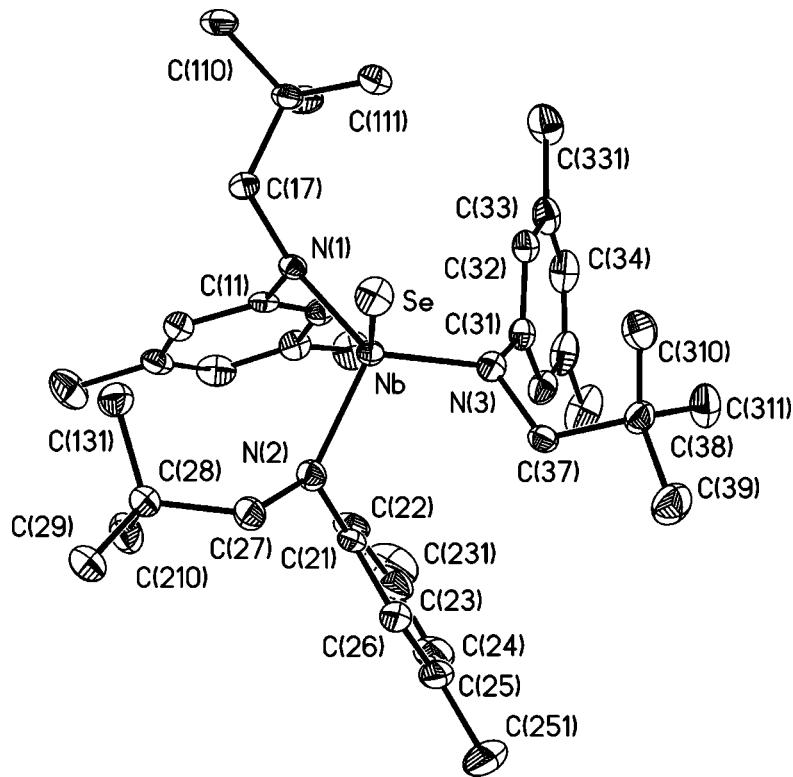


Figure S5. ORTEP diagram of (Se)Nb(N[Np]Ar)₃ (**7**) with thermal ellipsoids at the 30% probability level.

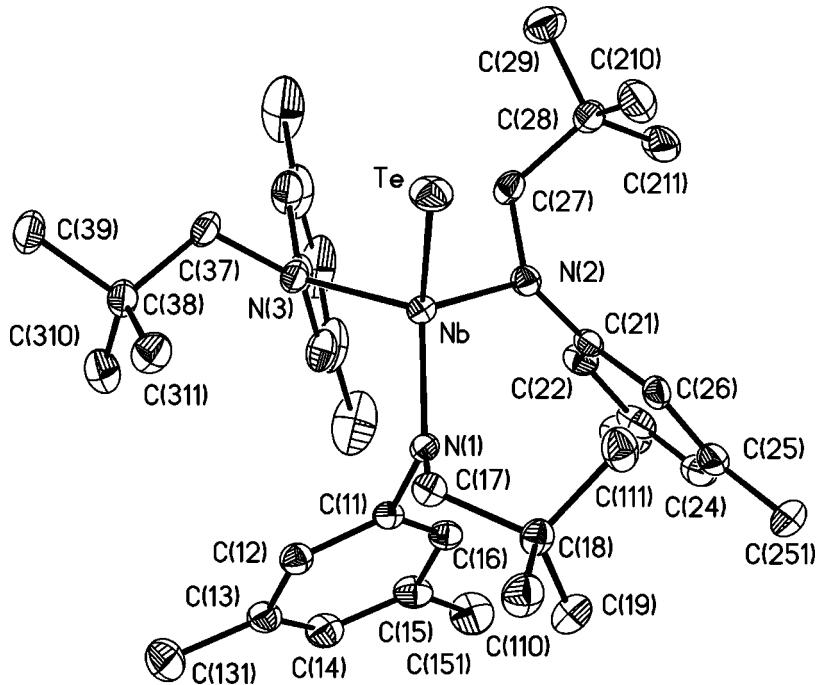


Figure S6. ORTEP diagram of (Te)Nb(N[Np]Ar)₃ (**8**) with thermal ellipsoids at the 30% probability level.

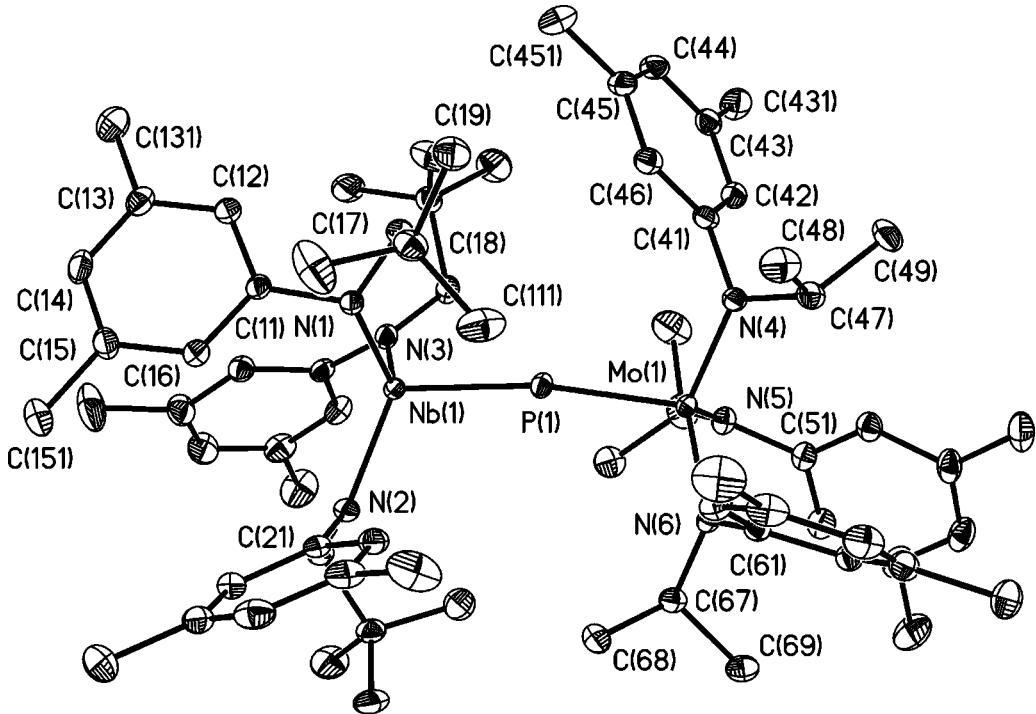


Figure S7. ORTEP diagram of $(\text{Ar}[\text{Np}] \text{N})_3 \text{Nb}(\mu\text{-P})\text{Mo}(\text{N}[\text{iPr}] \text{Ar})_3$ (**9**) with thermal ellipsoids at the 30% probability level. The TMS_2O molecule of solvation has been omitted for clarity.

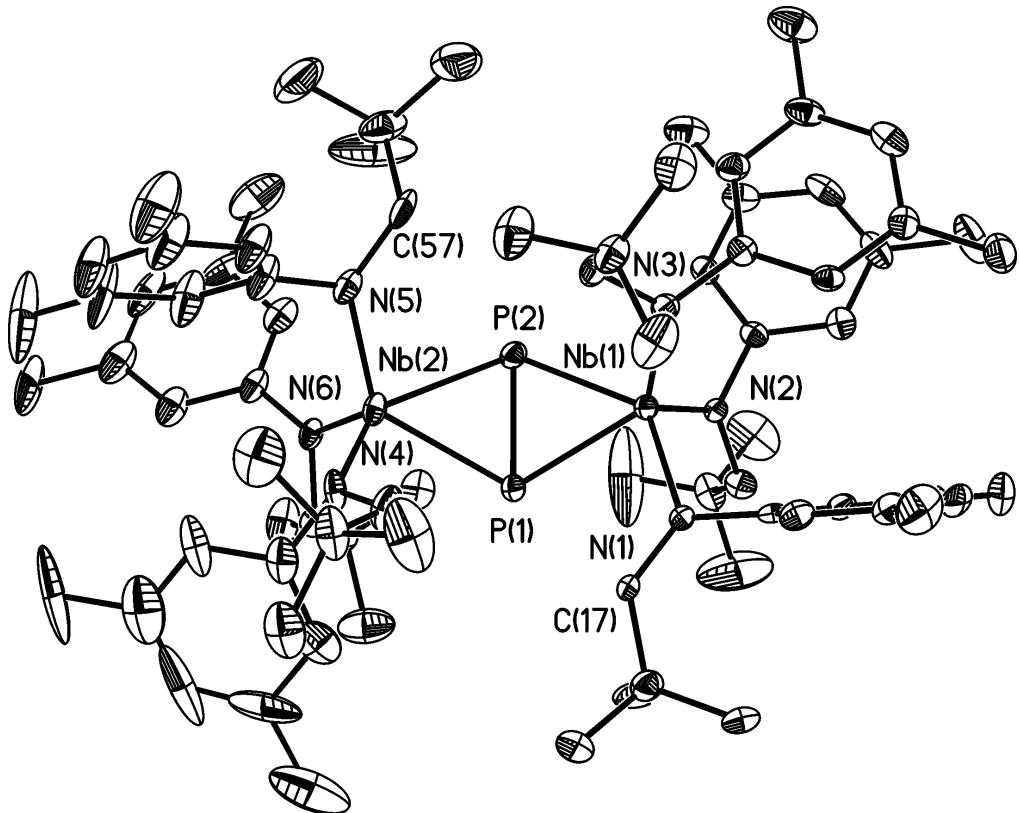


Figure S8. ORTEP diagram $(\mu_2:\eta^2,\eta^2-\text{P}_2)[\text{Nb}(\text{N}[\text{Np}] \text{Ar})_3]_2$ (**10**) with thermal ellipsoids at the 30% probability level.

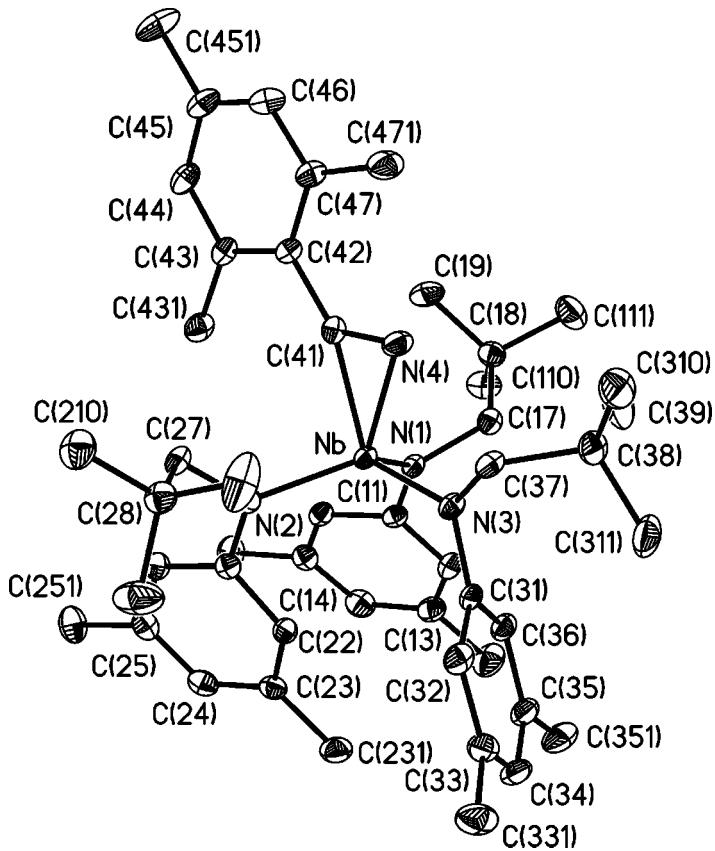


Figure S9. ORTEP diagram of $\text{Nb}(\eta^2\text{-MesCN})(\text{N}[\text{Np}]\text{Ar})_3$ (**11**) with thermal ellipsoids at the 30% probability level.

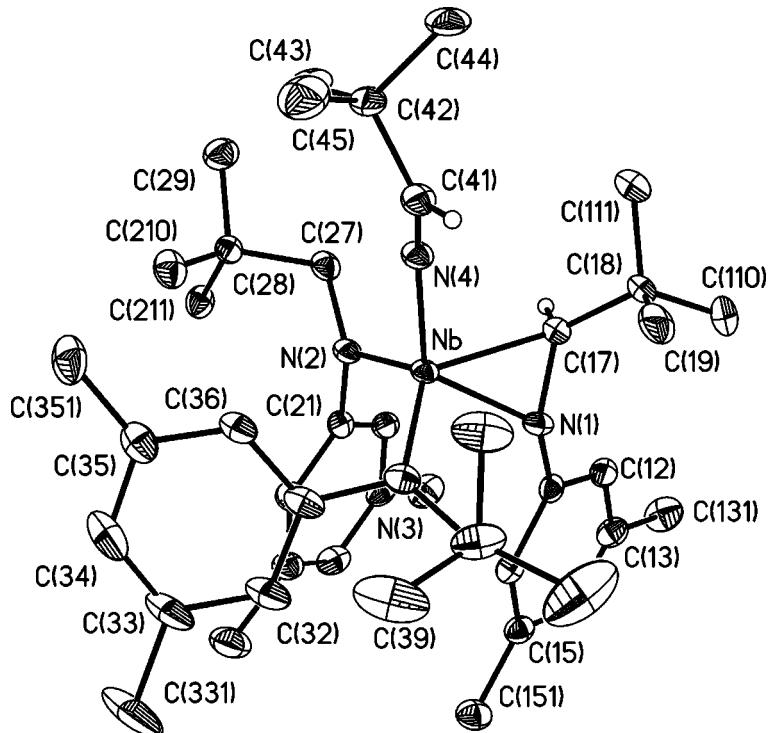


Figure S10. ORTEP diagram of $\text{Nb}(\text{N}=\text{C}(\text{H})^3\text{Bu})(\eta^2\text{-}^3\text{Bu}(\text{H})\text{C}=\text{NAr})(\text{N}[\text{Np}]\text{Ar})_2$ (**12**) with thermal ellipsoids at the 30% probability level.

S2.2 X-ray Crystal structure of Nb(H)(^tBu(H)C=N(Ar))(N[Np]Ar)₂ (**1**)

Orange crystals of **1** obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.62 x 0.42 x 0.26 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 7646 reflections (-11 ≤ h ≤ 12, -10 ≤ k ≤ 12, -19 ≤ l ≤ 14) were collected at 183 (2) K in the θ range 2.37° to 23.28°, of which 5394 ($R_{\text{int}} = 0.0617$) were unique. The structure was solved using the Patterson method (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the electron density map and refined isotropically, except H33a, H33b and H33c, which were placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.821 and -1.165 e.Å⁻³, respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.9165 and 0.8163, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0403$, $wR_2 = 0.1076$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.042$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C₃₉H₆₀N₃Nb, space group P-1, $a = 11.0193(7) \text{ \AA}$, $b = 11.2042(7) \text{ \AA}$, $c = 17.2591(4) \text{ \AA}$, $\alpha = 79.092(1)^\circ$, $\beta = 84.314(1)^\circ$, $\gamma = 66.605(1)^\circ$, $V = 1919.7(2) \text{ \AA}^3$, $Z = 2$, $\mu = 0.341 \text{ mm}^{-1}$, $\rho(\text{calc}) = 1.148 \text{ g/cm}^{-3}$, $F(000) = 712$, R_1 (based on F) = 0.0418, wR_2 (based on F^2) = 0.1092.

Table S1. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb	2813(1)	13710(1)	2154(1)	26(1)
N(2)	3026(2)	12268(2)	1562(1)	30(1)
N(3)	4258(2)	14144(2)	1582(1)	29(1)
C(21)	2976(3)	11166(3)	2109(2)	31(1)
C(37)	3350(3)	15398(3)	1708(2)	29(1)
C(38)	2795(3)	16498(3)	1007(2)	33(1)
N(1)	3289(3)	13233(3)	3302(1)	37(1)
C(34)	8345(3)	12432(3)	1844(2)	40(1)
C(33)	7675(3)	11657(3)	1730(2)	41(1)
C(35)	7690(3)	13764(3)	1865(2)	35(1)
C(27)	3504(3)	12070(3)	750(2)	32(1)
C(31)	5638(3)	13587(3)	1650(2)	28(1)
C(26)	4023(3)	9932(3)	2197(2)	37(1)
C(36)	6338(3)	14340(3)	1753(2)	31(1)
C(25)	3945(4)	8889(3)	2740(2)	45(1)
C(351)	8422(4)	14582(4)	2015(3)	49(1)
C(211)	1292(4)	13325(4)	113(3)	58(1)

C(311)	3845(4)	17064(4)	680(2)	43(1)
C(310)	1571(3)	17584(3)	1296(2)	45(1)
C(32)	6321(3)	12242(3)	1639(2)	34(1)
C(39)	2429(4)	15993(4)	346(2)	41(1)
C(22)	1852(3)	11336(3)	2596(2)	36(1)
C(16)	1449(4)	12962(4)	4202(2)	48(1)
C(28)	2496(3)	12043(3)	202(2)	35(1)
C(23)	1751(4)	10295(3)	3152(2)	44(1)
C(210)	3193(4)	11866(5)	-601(2)	51(1)
C(17)	4370(4)	12062(4)	3659(2)	49(1)
C(12)	1216(3)	15004(3)	3343(2)	42(1)
C(24)	2807(4)	9080(4)	3210(2)	51(1)
C(11)	2013(3)	13705(3)	3651(2)	38(1)
C(13)	-135(4)	15552(4)	3546(2)	52(1)
C(231)	492(5)	10491(6)	3636(3)	65(1)
C(29)	2062(6)	10896(5)	499(3)	62(1)
C(15)	135(4)	13514(4)	4435(2)	54(1)
C(18)	5218(4)	12328(5)	4214(2)	66(1)
C(14)	-643(4)	14795(5)	4090(2)	59(1)
C(331)	8408(4)	10210(4)	1700(3)	70(1)
C(251)	5090(6)	7567(4)	2823(3)	66(1)
C(131)	-960(5)	16926(5)	3178(3)	71(1)
C(111)	5770(7)	13309(8)	3782(3)	79(2)
C(110)	6357(7)	11009(10)	4468(5)	114(3)
C(151)	-473(6)	12748(7)	5049(3)	73(1)
C(19)	4395(7)			

Table S2. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	25(1)	31(1)	26(1)	-8(1)	-2(1)	-13(1)
N(2)	31(1)	32(1)	29(1)	-9(1)	-1(1)	-15(1)
N(3)	25(1)	29(1)	34(1)	-9(1)	-2(1)	-11(1)
C(21)	35(2)	35(2)	28(1)	-6(1)	-10(1)	-18(1)
C(37)	26(1)	33(2)	33(2)	-12(1)	-2(1)	-13(1)
C(38)	29(2)	32(2)	37(2)	-7(1)	-2(1)	-12(1)
N(1)	43(2)	43(1)	28(1)	-8(1)	-4(1)	-19(1)
C(34)	21(2)	52(2)	44(2)	-15(2)	-6(1)	-6(1)
C(33)	33(2)	41(2)	45(2)	-16(1)	-8(1)	-6(1)
C(35)	30(2)	47(2)	31(2)	-9(1)	-3(1)	-16(1)
C(27)	33(2)	34(2)	32(2)	-8(1)	1(1)	-14(2)
C(31)	25(1)	36(2)	25(1)	-6(1)	-2(1)	-13(1)
C(26)	42(2)	36(2)	33(2)	-8(1)	-8(1)	-13(1)

C(36)	30(2)	33(2)	32(2)	-9(1)	-2(1)	-11(1)
C(25)	64(2)	38(2)	33(2)	-8(1)	-14(2)	-16(2)
C(351)	36(2)	55(2)	63(2)	-11(2)	-13(2)	-22(2)
C(211)	43(2)	66(3)	64(3)	-28(2)	-20(2)	-8(2)
C(311)	42(2)	37(2)	48(2)	2(2)	-2(2)	-17(2)
C(310)	38(2)	31(2)	59(2)	-5(2)	1(2)	-6(2)
C(32)	32(2)	35(2)	39(2)	-16(1)	-3(1)	-13(1)
C(39)	44(2)	44(2)	36(2)	-3(2)	-6(2)	-18(2)
C(22)	39(2)	40(2)	35(2)	-9(1)	-5(1)	-19(2)
C(16)	61(2)	62(2)	34(2)	-15(2)	3(2)	-36(2)
C(28)	40(2)	36(2)	34(2)	-11(1)	-3(1)	-18(1)
C(23)	57(2)	56(2)	32(2)	-7(1)	-1(1)	-35(2)
C(210)	59(2)	65(2)	35(2)	-18(2)	-2(2)	-25(2)
C(17)	51(2)	54(2)	39(2)	0(2)	-7(2)	-21(2)
C(12)	49(2)	52(2)	35(2)	-19(2)	5(1)	-26(2)
C(24)	83(3)	47(2)	34(2)	-1(2)	-10(2)	-36(2)
C(11)	46(2)	54(2)	26(1)	-16(1)	1(1)	-27(2)
C(13)	48(2)	66(2)	50(2)	-27(2)	3(2)	-22(2)
C(231)	76(3)	79(3)	56(3)	-8(2)	11(2)	-50(3)
C(29)	90(3)	72(3)	48(2)	-9(2)	-14(2)	-56(3)
C(15)	65(2)	80(3)	38(2)	-25(2)	11(2)	-45(2)
C(18)	57(2)	110(3)	32(2)	7(2)	-14(2)	-38(2)
C(14)	46(2)	88(3)	54(2)	-34(2)	14(2)	-32(2)
C(331)	47(2)	47(2)	110(3)	-36(2)	-25(2)	2(2)
C(251)	94(3)	39(2)	50(2)	-3(2)	-18(2)	-8(2)
C(131)	54(3)	68(3)	79(3)	-27(2)	2(2)	-6(2)
C(111)	82(4)	124(5)	55(3)	-8(3)	-19(3)	-64(4)
C(110)	72(4)	158(7)	89(5)	43(5)	-48(4)	-40(4)
C(151)	85(3)	115(4)	50(2)	-27(3)	21(2)	-69(4)
C(19)	86(4)	217(9)	41(3)	-37(4)	-5(3)	-78(6)

S2.3 X-ray Crystal Structure of (O)Nb(N[Np]Ar)₃ (**5**)

Yellow crystals of **5** obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.33 x 0.32 x 0.05 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 15470 reflections (-21 ≤ h ≤ 21, -13 ≤ k ≤ 13, -35 ≤ l ≤ 24) were collected at 183 (2) K in the θ range 2.22° to 23.28°, of which 5587 ($R_{\text{int}} = 0.0563$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All non-methyl hydrogen atoms were located in the electron density map and refined isotropically. All methyl hydrogens were placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.385 and -0.593 e.Å⁻³, respectively. An empirical absorption correction (psi-scans) was applied

with maximum and minimum transmissions equal to 0.3030 and 0.2476, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0450$, $wR_2 = 0.1396$ based upon $I > 2\sigma(I)$ and GOF = 1.070 based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{39}H_{60}N_3NbO$, space group C2/c, $a = 19.7802(18)$ Å, $b = 12.6057(11)$ Å, $c = 31.987(3)$ Å, $\alpha = 90.0^\circ$, $\beta = 99.542(2)^\circ$, $\gamma = 90.0^\circ$, $V = 4865.4(12)$ Å³, $Z = 8$, $\mu = 0.336$ mm⁻¹, $\rho(\text{calc}) = 1.148$ g/cm⁻³, $F(000) = 2912$, R_1 (based on F) = 0.0550, wR_2 (based on F^2) = 0.1458.

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb	1698(1)	1955(1)	796(1)	31(1)
O(1)	1911(1)	1810(2)	307(1)	40(1)
N(1)	1660(2)	472(2)	1020(1)	33(1)
C(21)	470(2)	3106(3)	1012(1)	37(1)
C(31)	2564(2)	2863(3)	1558(1)	36(1)
N(3)	2454(2)	2846(2)	1107(1)	35(1)
C(35)	2126(2)	3243(3)	2208(1)	43(1)
C(36)	2047(2)	3252(3)	1769(1)	39(1)
C(11)	1369(2)	181(3)	1387(1)	35(1)
N(2)	806(2)	2753(2)	678(1)	36(1)
C(26)	393(2)	4180(4)	1095(2)	45(1)
C(28)	-97(2)	2621(4)	7(1)	49(1)
C(23)	-99(2)	2694(4)	1604(1)	51(1)
C(27)	537(2)	3179(3)	249(1)	43(1)
C(15)	1403(2)	229(3)	2148(1)	39(1)
C(16)	1671(2)	512(3)	1790(1)	36(1)
C(111)	2617(3)	-1805(4)	579(2)	62(1)
C(331)	3876(3)	1928(4)	2493(2)	64(1)
C(12)	772(2)	-426(3)	1347(1)	37(1)
C(14)	808(2)	-384(3)	2094(2)	44(1)
C(211)	15(3)	1437(4)	-4(2)	75(2)
C(34)	2726(2)	2820(3)	2438(2)	48(1)
C(32)	3153(2)	2454(3)	1800(1)	39(1)
C(38)	2869(2)	4549(3)	797(1)	46(1)
C(13)	485(2)	-709(3)	1696(1)	45(1)
C(24)	-174(2)	3763(4)	1673(1)	50(1)
C(33)	3241(2)	2417(3)	2238(1)	44(1)
C(22)	225(2)	2372(3)	1274(1)	42(1)
C(17)	1829(2)	-443(3)	765(1)	36(1)
C(37)	2989(2)	3357(3)	902(1)	43(1)
C(25)	76(2)	4520(4)	1422(1)	48(1)

C(18)	2542(2)	-932(3)	897(1)	46(1)
C(151)	1749(2)	540(4)	2584(1)	52(1)
C(131)	-170(2)	-1346(4)	1646(2)	59(1)
C(231)	-383(3)	1871(4)	1877(2)	76(2)
C(251)	-9(3)	5687(4)	1509(2)	73(2)
C(110)	2641(3)	-1396(5)	1337(2)	79(2)
C(351)	1575(3)	3668(4)	2427(2)	66(1)
C(311)	3474(2)	4922(4)	592(2)	64(1)
C(210)	-197(3)	3043(4)	-446(2)	82(2)
C(310)	2851(3)	5192(4)	1202(2)	70(2)
C(29)	-719(3)	2882(5)	198(2)	87(2)
C(19)	3093(2)	-89(4)	871(2)	73(2)
C(39)	2210(3)	4698(4)	484(2)	67(1)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	34(1)	33(1)	28(1)	0(1)	6(1)	-1(1)
O(1)	49(2)	43(2)	32(2)	-1(1)	13(1)	-1(1)
N(1)	36(2)	33(2)	29(2)	1(1)	5(1)	-1(1)
C(21)	32(2)	40(2)	38(2)	-2(2)	3(2)	3(2)
C(31)	39(2)	30(2)	39(2)	-4(2)	7(2)	-8(2)
N(3)	36(2)	37(2)	32(2)	-1(1)	7(1)	-3(1)
C(35)	48(2)	46(2)	38(2)	0(2)	14(2)	-10(2)
C(36)	40(2)	34(2)	42(2)	1(2)	1(2)	-2(2)
C(11)	33(2)	33(2)	38(2)	4(2)	5(2)	5(2)
N(2)	39(2)	38(2)	32(2)	3(1)	6(1)	1(1)
C(26)	48(3)	41(3)	43(3)	3(2)	1(2)	3(2)
C(28)	46(3)	55(3)	42(2)	2(2)	-6(2)	7(2)
C(23)	44(2)	58(3)	52(3)	7(2)	16(2)	13(2)
C(27)	47(3)	43(3)	39(3)	6(2)	9(2)	6(2)
C(15)	49(2)	35(2)	35(2)	0(2)	14(2)	8(2)
C(16)	34(2)	32(2)	41(2)	0(2)	7(2)	1(2)
C(111)	68(3)	53(3)	69(3)	-1(2)	20(3)	15(2)
C(331)	62(3)	62(3)	58(3)	7(2)	-15(3)	4(2)
C(12)	37(2)	36(2)	37(2)	1(2)	2(2)	0(2)
C(14)	51(3)	41(2)	44(3)	7(2)	22(2)	1(2)
C(211)	85(4)	54(3)	76(4)	-12(3)	-20(3)	-1(3)
C(34)	60(3)	49(3)	33(2)	3(2)	1(2)	-13(2)
C(32)	34(2)	35(2)	48(3)	-3(2)	9(2)	-2(2)
C(38)	58(3)	45(2)	35(2)	2(2)	9(2)	-11(2)
C(13)	38(2)	39(2)	58(3)	12(2)	9(2)	3(2)
C(24)	50(3)	64(3)	37(3)	-3(2)	8(2)	16(2)
C(33)	46(2)	40(2)	43(3)	3(2)	-2(2)	-8(2)

C(22)	43(2)	38(2)	45(3)	4(2)	11(2)	10(2)
C(17)	44(2)	34(2)	30(2)	-1(2)	4(2)	4(2)
C(37)	43(3)	45(2)	41(3)	2(2)	11(2)	-10(2)
C(25)	50(3)	49(3)	43(3)	-8(2)	0(2)	8(2)
C(18)	50(3)	45(2)	43(2)	-3(2)	8(2)	8(2)
C(151)	69(3)	53(3)	37(2)	-3(2)	14(2)	-2(2)
C(131)	48(3)	61(3)	70(3)	14(2)	16(2)	-12(2)
C(231)	94(4)	69(4)	78(4)	18(3)	53(3)	14(3)
C(251)	98(4)	55(3)	67(4)	-12(3)	17(3)	5(3)
C(110)	98(4)	87(4)	54(3)	10(3)	12(3)	54(3)
C(351)	71(3)	81(4)	49(3)	-3(3)	23(2)	10(3)
C(311)	77(3)	64(3)	53(3)	7(2)	18(3)	-28(3)
C(210)	99(4)	96(4)	44(3)	4(3)	-13(3)	-6(3)
C(310)	111(4)	48(3)	56(3)	-4(2)	25(3)	-19(3)
C(29)	49(3)	138(6)	69(4)	-24(3)	-3(3)	10(3)
C(19)	42(3)	74(4)	102(4)	-20(3)	7(3)	9(2)
C(39)	81(4)	61(3)	57(3)	12(2)	3(3)	-5(3)

S2.4 X-ray Crystal Structure of (S)Nb(N[Np]Ar)₃ (**6**)

Orange crystals of **6** obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.70 x 0.30 x 0.10 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 15225 reflections (-10 ≤ h ≤ 12, -9 ≤ k ≤ 11, -35 ≤ l ≤ 37) were collected at 183 (2) K in the θ range 2.26° to 23.26°, of which 5617 ($R_{\text{int}} = 0.0582$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All non-methyl hydrogen atoms were located in the electron density map and refined isotropically. All methyl hydrogens were placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.630 and -1.879 e.Å⁻³, respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.3144 and 0.1936, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0624$, $wR_2 = 0.2329$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.990$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C₃₉H₆₀N₃NbS, space group P2₁/c, $a = 11.0383(9) \text{ \AA}$, $b = 10.6757(9) \text{ \AA}$, $c = 33.434(3) \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 90.000(2)^\circ$, $\gamma = 90.0^\circ$, $V = 3939.9(6) \text{ \AA}^3$, $Z = 4$, $\mu = 0.386 \text{ mm}^{-1}$, $\rho(\text{calc}) = 1.173 \text{ g/cm}^{-3}$, $F(000) = 1488$, R_1 (based on F) = 0.0641, wR_2 (based on F^2) = 0.2339.

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Nb	1489(1)	3072(1)	1196(1)	29(1)
S	-352(1)	2339(2)	1165(1)	46(1)
N(2)	2354(4)	1871(3)	1552(1)	33(1)
C(21)	3640(5)	1955(4)	1516(2)	33(1)
N(3)	2080(5)	2964(4)	631(1)	38(1)
C(22)	4247(5)	2981(5)	1678(2)	37(1)
N(1)	1503(4)	4850(4)	1383(1)	35(1)
C(27)	1906(5)	714(5)	1741(2)	33(1)
C(11)	2188(5)	5419(5)	1685(2)	39(1)
C(37)	1598(6)	2146(6)	305(2)	47(1)
C(28)	1613(5)	832(5)	2196(2)	40(1)
C(26)	4314(5)	1040(6)	1323(2)	42(1)
C(38)	2248(6)	883(5)	254(2)	46(1)
C(16)	2015(5)	5024(5)	2081(2)	38(1)
C(13)	3769(6)	6804(6)	1923(3)	66(2)
C(18)	-147(5)	6487(5)	1199(2)	41(1)
C(12)	3079(5)	6322(5)	1610(2)	51(1)
C(17)	934(5)	5668(5)	1072(2)	41(1)
C(211)	552(7)	1672(6)	2275(2)	59(2)
C(111)	-1078(6)	5717(7)	1429(2)	59(2)
C(311)	1929(6)	5(6)	600(2)	56(2)
C(15)	2727(6)	5493(6)	2392(2)	53(2)
C(210)	1316(6)	-498(5)	2340(2)	47(1)
C(110)	-714(8)	7003(6)	816(2)	65(2)
C(29)	2729(6)	1324(7)	2412(2)	57(2)
C(14)	3588(6)	6359(6)	2311(2)	61(2)
C(151)	2545(7)	4988(8)	2818(2)	74(2)
C(131)	4727(8)	7778(8)	1848(3)	86(3)
C(310)	1784(8)	330(6)	-138(2)	68(2)
C(19)	275(6)	7606(6)	1455(2)	60(2)

C(39)	3611(6)	1078(7)	231(2)	65(2)
C(31)	2764(5)	4025(5)	494(1)	40(1)
C(25)	5518(5)	3110(5)	1644(2)	40(1)
C(32)	2318(7)	4804(6)	191(2)	57(2)
C(24)	6135(6)	2211(7)	1433(2)	48(2)
C(36)	3863(6)	4337(6)	681(2)	51(2)
C(23)	5582(5)	1163(6)	1279(2)	45(1)
C(33)	2942(10)	5868(7)	78(2)	80(3)
C(251)	6143(6)	4186(7)	1843(2)	66(2)
C(35)	4443(7)	5436(7)	574(2)	67(2)
C(231)	6290(6)	171(8)	1059(2)	72(2)
C(34)	3990(9)	6163(7)	268(2)	78(2)
C(331)	2440(16)	6689(8)	-257(3)	139(6)
C(351)	5642(8)	5764(10)	784(3)	100(3)

Table S6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	28(1)	31(1)	27(1)	1(1)	0(1)	-2(1)
S	32(1)	52(1)	55(1)	1(1)	-4(1)	-4(1)
N(2)	30(2)	37(3)	31(2)	3(2)	2(2)	-2(2)
C(21)	28(3)	39(3)	32(3)	7(2)	6(2)	1(2)
N(3)	50(3)	35(3)	29(2)	-1(2)	0(2)	1(2)
C(22)	33(3)	38(3)	41(3)	6(2)	-3(2)	-7(2)
N(1)	39(2)	29(2)	37(2)	-1(2)	1(2)	-1(2)
C(27)	33(3)	31(3)	36(3)	0(2)	2(2)	-5(2)
C(11)	34(3)	28(3)	56(3)	-3(2)	1(2)	5(2)
C(37)	59(4)	45(3)	36(3)	-8(2)	-5(3)	2(3)
C(28)	48(3)	40(3)	31(3)	4(2)	5(2)	-7(3)
C(26)	40(3)	47(3)	38(3)	3(2)	1(2)	6(3)
C(38)	67(4)	38(3)	33(3)	-1(2)	10(2)	-1(3)
C(16)	37(3)	42(3)	35(3)	-4(2)	0(2)	4(3)
C(13)	38(4)	40(4)	121(7)	-11(3)	-19(4)	-1(3)

C(18)	42(3)	39(3)	43(3)	2(2)	-3(2)	9(3)
C(12)	39(3)	40(3)	73(4)	4(3)	1(3)	1(3)
C(17)	47(3)	39(3)	36(3)	-2(2)	6(2)	2(3)
C(211)	76(5)	48(3)	53(4)	1(3)	32(3)	1(3)
C(111)	42(3)	71(4)	63(4)	10(3)	15(3)	6(3)
C(311)	76(4)	49(4)	43(3)	-1(3)	3(3)	-9(3)
C(15)	48(3)	55(4)	57(4)	-20(3)	-18(3)	10(3)
C(210)	55(3)	46(3)	40(3)	6(2)	11(2)	-9(3)
C(110)	78(5)	66(5)	52(4)	1(3)	-14(4)	21(3)
C(29)	68(4)	73(4)	32(3)	11(3)	-2(3)	-29(4)
C(14)	55(4)	47(4)	80(5)	-15(3)	-28(4)	12(3)
C(151)	88(5)	92(5)	43(3)	-13(3)	-18(3)	30(4)
C(131)	64(5)	58(4)	136(8)	0(5)	-18(5)	-14(4)
C(310)	109(6)	50(4)	44(3)	-8(3)	-2(3)	5(4)
C(19)	68(4)	49(4)	63(4)	-16(3)	-6(3)	12(3)
C(39)	65(4)	69(5)	61(4)	-1(3)	16(3)	12(4)
C(31)	50(3)	43(3)	28(2)	1(2)	10(2)	-4(3)
C(25)	27(3)	50(4)	43(3)	8(2)	7(2)	-2(2)
C(32)	86(5)	46(3)	38(3)	5(3)	2(3)	4(3)
C(24)	14(3)	71(4)	57(4)	10(3)	5(3)	-9(3)
C(36)	56(4)	64(4)	32(3)	2(3)	9(2)	-10(3)
C(23)	40(3)	59(4)	37(3)	5(3)	10(2)	15(3)
C(33)	148(8)	48(4)	44(4)	6(3)	29(5)	5(5)
C(251)	40(3)	71(4)	88(5)	1(4)	-8(3)	-27(3)
C(35)	71(4)	71(5)	58(4)	-17(4)	22(3)	-24(4)
C(231)	53(4)	93(6)	71(4)	-12(4)	16(3)	16(4)
C(34)	120(7)	46(4)	68(5)	-2(3)	40(5)	-22(4)
C(331)	263(18)	56(5)	98(8)	42(5)	38(9)	44(8)
C(351)	79(6)	122(8)	99(6)	-31(6)	23(5)	-51(6)

S2.5 X-ray Crystal Structure of (Se)Nb(N[Np]Ar)₃ (7)

Red crystals of 7 obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.38 x 0.34 x 0.28 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 15365 reflections (-12 ≤ h ≤ 9, -10 ≤ k ≤

11, -36 \leq ℓ \leq 36) were collected at 183 (2) K in the θ range 2.28° to 23.30°, of which 5626 ($R_{\text{int}} = 0.0421$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All non-methyl hydrogen atoms were located in the electron density map and refined isotropically. All methyl hydrogens were placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.573 and -0.954 e. \AA^{-3} , respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.2757 and 0.2147, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0651$, $wR_2 = 0.1322$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.387$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{39}H_{60}N_3NbSe$, space group $P2_1/c$, $a = 11.1454(8) \text{ \AA}$, $b = 10.6072(8) \text{ \AA}$, $c = 33.260(3) \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 90.000(1)^\circ$, $\gamma = 90.0^\circ$, $V = 3932.0(5) \text{ \AA}^3$, $Z = 4$, $\mu = 1.260 \text{ mm}^{-1}$, $\rho(\text{calc}) = 1.255 \text{ g/cm}^{-3}$, $F(000) = 1560$, R_1 (based on F) = 0.0655, wR_2 (based on F^2) = 0.1323.

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Nb	8522(1)	3014(1)	6199(1)	25(1)
Se	10451(1)	2224(1)	6165(1)	42(1)
N(1)	7675(4)	1802(5)	6555(1)	27(1)
N(2)	7940(5)	2912(5)	5629(2)	34(1)
N(3)	8511(4)	4798(5)	6381(2)	32(1)
C(11)	6387(5)	1894(6)	6522(2)	29(1)
C(12)	5722(5)	955(6)	6327(2)	34(2)
C(13)	4484(6)	1095(7)	6277(2)	41(2)
C(14)	3909(6)	2157(7)	6432(2)	47(2)
C(15)	4557(6)	3063(7)	6639(2)	42(2)
C(16)	5784(6)	2930(6)	6682(2)	34(1)
C(17)	8114(5)	645(6)	6754(2)	30(1)
C(18)	8361(6)	760(6)	7211(2)	33(2)
C(19)	7256(7)	1270(7)	7428(2)	48(2)
C(21)	7256(6)	3979(6)	5499(2)	37(2)
C(22)	6177(7)	4276(7)	5687(2)	46(2)
C(23)	5549(8)	5366(9)	5577(3)	67(3)
C(24)	6015(11)	6125(9)	5280(3)	79(3)
C(25)	7060(11)	5842(8)	5084(2)	71(3)
C(26)	7690(8)	4775(7)	5198(2)	51(2)
C(27)	8404(6)	2103(6)	5303(2)	39(2)
C(28)	7742(7)	844(6)	5247(2)	41(2)
C(29)	8206(8)	276(8)	4850(2)	59(2)

C(31)	7830(5)	5374(6)	6696(2)	32(2)
C(32)	8017(6)	4974(6)	7089(2)	36(2)
C(33)	7319(6)	5425(7)	7407(2)	45(2)
C(34)	6438(7)	6301(7)	7322(3)	53(2)
C(35)	6260(7)	6744(7)	6942(3)	54(2)
C(36)	6950(6)	6270(6)	6622(2)	44(2)
C(37)	9065(6)	5616(6)	6078(2)	32(1)
C(38)	10129(6)	6456(6)	6205(2)	39(2)
C(39)	10689(8)	6967(8)	5812(2)	62(2)
C(110)	8647(7)	-572(7)	7353(2)	43(2)
C(111)	9431(7)	1609(7)	7284(2)	48(2)
C(131)	3800(7)	82(9)	6052(3)	66(2)
C(151)	3909(7)	4172(8)	6831(3)	62(2)
C(210)	6407(7)	1053(8)	5219(2)	58(2)
C(211)	8052(7)	-60(7)	5586(2)	46(2)
C(231)	4373(10)	5685(11)	5786(3)	99(4)
C(251)	7566(13)	6687(9)	4759(3)	113(5)
C(310)	11064(7)	5701(8)	6435(2)	56(2)
C(311)	9707(7)	7577(7)	6454(2)	55(2)
C(331)	7502(8)	4928(9)	7826(2)	64(2)
C(351)	5298(8)	7725(8)	6846(3)	79(3)

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 7. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^{*} b^{*} U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	25(1)	28(1)	23(1)	1(1)	2(1)	1(1)
Se	28(1)	47(1)	53(1)	0(1)	5(1)	4(1)
N(1)	24(3)	31(3)	25(3)	-1(2)	-3(2)	5(2)
N(2)	39(3)	35(3)	29(3)	-4(2)	4(2)	-2(2)
N(3)	26(3)	33(3)	38(3)	1(2)	-1(2)	1(2)
C(11)	28(3)	38(4)	20(3)	7(3)	-2(2)	2(3)
C(12)	29(4)	39(4)	33(3)	0(3)	4(3)	-1(3)
C(13)	35(4)	58(5)	29(3)	11(3)	-5(3)	-18(3)
C(14)	21(3)	68(5)	52(4)	6(4)	0(3)	18(4)
C(15)	33(4)	46(4)	45(4)	4(3)	2(3)	1(3)
C(16)	31(3)	37(4)	33(3)	5(3)	3(3)	-1(3)
C(17)	27(3)	32(3)	30(3)	3(3)	1(3)	4(3)
C(18)	37(4)	36(4)	26(3)	0(3)	-6(3)	6(3)
C(19)	56(5)	56(5)	32(4)	3(3)	2(3)	19(4)
C(21)	59(5)	31(4)	21(3)	0(3)	-11(3)	-1(3)
C(22)	54(5)	53(5)	31(4)	-2(3)	-12(3)	12(4)
C(23)	78(6)	67(6)	55(5)	-14(5)	-32(5)	26(5)
C(24)	132(10)	46(5)	58(6)	-4(5)	-39(6)	28(6)
C(25)	139(9)	35(5)	38(5)	5(4)	-23(5)	-3(5)

C(26)	78(6)	40(4)	34(4)	2(3)	-6(4)	-10(4)
C(27)	51(4)	37(4)	29(3)	-7(3)	8(3)	-1(3)
C(28)	55(4)	37(4)	31(4)	-2(3)	-2(3)	-3(3)
C(29)	90(6)	53(5)	34(4)	-8(4)	-5(4)	-8(4)
C(31)	24(3)	32(3)	41(4)	-3(3)	3(3)	-3(3)
C(32)	35(4)	33(4)	39(4)	-5(3)	3(3)	-2(3)
C(33)	38(4)	48(4)	48(4)	-12(4)	11(3)	-11(3)
C(34)	44(5)	46(5)	68(6)	-15(4)	23(4)	-7(4)
C(35)	39(4)	35(4)	89(6)	-11(4)	15(4)	0(3)
C(36)	37(4)	37(4)	57(5)	5(3)	0(3)	-4(3)
C(37)	37(4)	34(4)	26(3)	-2(3)	-4(3)	2(3)
C(38)	48(4)	34(4)	35(4)	1(3)	7(3)	-6(3)
C(39)	73(6)	59(5)	56(5)	7(4)	15(4)	-15(5)
C(110)	52(4)	50(4)	28(4)	6(3)	-5(3)	8(3)
C(111)	58(5)	43(4)	43(4)	0(3)	-20(4)	1(4)
C(131)	44(5)	91(7)	62(5)	-13(5)	-9(4)	-18(5)
C(151)	38(4)	67(6)	80(6)	-6(5)	3(4)	17(4)
C(210)	57(5)	54(5)	62(5)	-11(4)	-18(4)	-6(4)
C(211)	57(5)	41(4)	39(4)	1(3)	2(3)	2(3)
C(231)	94(8)	112(9)	92(8)	-20(7)	-23(6)	65(7)
C(251)	221(15)	53(6)	66(7)	25(5)	-18(8)	-22(8)
C(310)	47(5)	59(5)	61(5)	5(4)	-13(4)	-15(4)
C(311)	58(5)	47(5)	61(5)	-14(4)	10(4)	-13(4)
C(331)	76(6)	79(6)	37(4)	-14(4)	18(4)	-22(5)
C(351)	50(5)	49(5)	137(9)	3(5)	27(6)	11(4)

S2.6 X-ray Crystal Structure of (Te)Nb(N[Np]Ar)₃ (**8**)

Red crystals of **8** obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.23 x 0.23 x 0.23 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 15761 reflections (-12 ≤ h ≤ 11, -11 ≤ k ≤ 11, -36 ≤ l ≤ 34) were collected at 183 (2) K in the θ range 2.16° to 23.26°, of which 5737 ($R_{\text{int}} = 0.0431$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions and placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ Å}$). The residual peak and hole electron density were 0.429 and -0.599 e.Å⁻³, respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.2876 and 0.2211, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0464$, $wR_2 = 0.0907$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.117$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C₃₉H₆₀N₃NbTe, space group P2₁/c, $a = 11.4215(5) \text{ Å}$, $b = 10.5624(5) \text{ Å}$, $c = 33.1624(16) \text{ Å}$, $\alpha = 90.0^\circ$, $\beta = 90.0440(10)^\circ$, $\gamma = 90.0^\circ$, $V = 4000.7(3) \text{ Å}^3$, $Z = 4$, $\mu = 1.043 \text{ mm}^{-1}$,

$\rho(\text{calc}) = 1.314 \text{ g/cm}^{-3}$, $F(000) = 1632$, R_1 (based on F) = 0.0553, wR_2 (based on F^2) = 0.0941.

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb	3504(1)	2955(1)	3796(1)	27(1)
Te	5566(1)	2077(1)	3837(1)	45(1)
N(1)	2687(3)	1739(4)	3431(1)	26(1)
N(2)	3506(3)	4749(4)	3609(1)	32(1)
N(3)	2927(4)	2862(4)	4368(1)	34(1)
C(11)	1423(4)	1831(5)	3473(1)	27(1)
C(12)	790(4)	893(5)	3672(1)	34(1)
C(13)	-407(4)	986(6)	3722(2)	40(1)
C(14)	-975(5)	2049(6)	3565(2)	45(1)
C(15)	-368(4)	2986(5)	3353(2)	42(1)
C(16)	838(4)	2860(5)	3310(1)	33(1)
C(17)	3113(4)	585(5)	3230(1)	31(1)
C(18)	3334(4)	687(5)	2772(1)	33(1)
C(19)	2258(5)	1212(6)	2557(2)	46(1)
C(21)	2844(4)	5320(5)	3293(2)	31(1)
C(22)	1961(5)	6201(5)	3368(2)	43(1)
C(23)	1280(5)	6671(5)	3048(2)	47(2)
C(24)	1481(5)	6221(6)	2663(2)	49(2)
C(25)	2353(5)	5351(5)	2579(2)	43(1)
C(26)	3033(4)	4924(5)	2899(1)	35(1)
C(27)	4039(5)	5563(5)	3922(2)	37(1)
C(28)	5044(5)	6436(5)	3800(2)	40(1)
C(29)	5579(6)	6919(6)	4198(2)	65(2)
C(31)	2245(5)	3922(5)	4492(1)	38(1)
C(32)	1186(5)	4188(6)	4304(2)	46(2)
C(33)	539(7)	5268(7)	4402(2)	68(2)
C(34)	970(9)	6046(7)	4702(2)	86(3)
C(35)	2007(9)	5808(6)	4898(2)	76(2)
C(36)	2645(6)	4746(6)	4791(2)	55(2)
C(37)	3371(5)	2057(5)	4705(1)	40(1)
C(38)	2737(5)	794(5)	4771(2)	39(1)
C(39)	3205(6)	257(6)	5170(2)	51(2)
C(110)	3606(5)	-656(5)	2623(2)	45(1)
C(111)	4384(5)	1538(5)	2690(2)	45(1)
C(131)	-1074(5)	-6(7)	3951(2)	62(2)
C(151)	-1019(5)	4072(6)	3163(2)	62(2)
C(210)	5988(5)	5721(6)	3565(2)	59(2)

C(211)	4619(5)	7569(6)	3557(2)	59(2)
C(231)	326(6)	7629(6)	3137(2)	77(2)
C(251)	2553(6)	4868(7)	2153(2)	59(2)
C(310)	1420(5)	1000(6)	4795(2)	56(2)
C(311)	3038(5)	-123(5)	4430(2)	48(2)
C(331)	-596(7)	5555(9)	4191(2)	103(3)
C(351)	2452(10)	6686(7)	5223(2)	123(4)

Table S10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	28(1)	29(1)	25(1)	0(1)	-2(1)	0(1)
Te	28(1)	52(1)	56(1)	2(1)	-6(1)	4(1)
N(1)	26(2)	28(2)	23(2)	0(2)	-1(2)	0(2)
N(2)	34(2)	27(2)	34(2)	1(2)	-1(2)	-2(2)
N(3)	43(2)	33(2)	26(2)	4(2)	-3(2)	-2(2)
C(11)	22(2)	34(3)	25(2)	-7(2)	4(2)	-1(2)
C(12)	31(3)	37(3)	32(3)	-1(2)	-1(2)	0(2)
C(13)	30(3)	56(4)	34(3)	-5(3)	3(2)	-8(3)
C(14)	28(3)	61(4)	45(3)	-5(3)	3(2)	2(3)
C(15)	27(3)	48(3)	50(3)	-7(3)	-2(2)	5(3)
C(16)	32(3)	31(3)	35(3)	-6(2)	-1(2)	1(2)
C(17)	31(3)	30(3)	34(3)	-3(2)	2(2)	2(2)
C(18)	38(3)	31(3)	29(3)	-3(2)	3(2)	3(2)
C(19)	53(4)	49(4)	34(3)	-3(3)	-5(3)	6(3)
C(21)	26(3)	28(3)	38(3)	5(2)	-3(2)	-5(2)
C(22)	40(3)	36(3)	52(3)	0(3)	-3(3)	-5(3)
C(23)	31(3)	30(3)	80(5)	10(3)	-8(3)	-1(2)
C(24)	45(3)	41(3)	61(4)	18(3)	-18(3)	-9(3)
C(25)	42(3)	41(3)	44(3)	11(3)	-6(3)	-12(3)
C(26)	34(3)	33(3)	36(3)	11(2)	0(2)	-3(2)
C(27)	52(3)	29(3)	29(3)	2(2)	-6(2)	2(3)
C(28)	54(3)	31(3)	34(3)	2(2)	-7(2)	-7(3)
C(29)	81(5)	61(4)	52(4)	-1(3)	-20(3)	-14(4)
C(31)	58(4)	32(3)	25(3)	-1(2)	13(2)	-3(3)
C(32)	55(4)	51(4)	33(3)	4(3)	13(3)	13(3)
C(33)	86(5)	65(5)	53(4)	11(4)	31(4)	30(4)
C(34)	151(9)	46(4)	61(5)	5(4)	40(5)	35(5)
C(35)	149(8)	33(4)	45(4)	-12(3)	25(5)	-9(4)
C(36)	88(5)	39(4)	37(3)	1(3)	6(3)	-8(3)
C(37)	51(3)	42(3)	26(3)	7(2)	-7(2)	-2(3)
C(38)	50(3)	35(3)	32(3)	5(2)	2(2)	-3(3)

C(39)	77(4)	44(4)	33(3)	9(3)	-3(3)	-7(3)
C(110)	56(4)	41(3)	39(3)	-7(3)	5(3)	2(3)
C(111)	51(3)	41(3)	43(3)	-3(3)	14(3)	-2(3)
C(131)	44(4)	80(5)	62(4)	9(4)	9(3)	-12(3)
C(151)	39(3)	68(5)	78(5)	7(4)	-4(3)	18(3)
C(210)	60(4)	57(4)	61(4)	0(3)	11(3)	-14(3)
C(211)	62(4)	41(4)	72(4)	17(3)	-14(3)	-16(3)
C(231)	55(4)	50(4)	124(7)	2(4)	-19(4)	14(3)
C(251)	67(4)	74(5)	35(3)	9(3)	-12(3)	-14(4)
C(310)	60(4)	54(4)	55(4)	7(3)	12(3)	-7(3)
C(311)	57(4)	43(3)	43(3)	-2(3)	-4(3)	4(3)
C(331)	85(6)	126(8)	97(6)	30(6)	31(5)	67(6)
C(351)	258(13)	44(5)	68(5)	-20(4)	24(7)	-29(6)

S2.7 X-ray Crystal Structure of ($\text{Ar}[\text{Np}] \text{N}_3 \text{Nb}(\mu\text{-P}) \text{Mo}(\text{N}[\text{iPr}] \text{Ar})_3$) (9)

Purple crystals of **9** obtained from a saturated hexamethyldisiloxane/diethyl ether (5 : 2) solution stored at -35°C for two weeks were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions $0.10 \times 0.07 \times 0.07 \text{ mm}^3$ was selected and mounted with wax on the end of a glass fiber. A total of 33539 reflections ($-15 \leq h \leq 15, -16 \leq k \leq 16, -39 \leq l \leq 39$) were collected at 188 (2) K in the θ range 1.36° to 28.31° , of which 17174 ($R_{\text{int}} = 0.0219$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions and placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). One molecule of hexamethyldisiloxane co-crystallized within the unit cell, of which, the oxygen atom (O1) was disordered over the inversion center and was modeled as such.

The residual peak and hole electron density were 1.152 and $-0.576 \text{ e.\AA}^{-3}$, respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.6204 and 0.3890, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0392$, $wR_2 = 0.0951$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.063$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $\text{C}_{75} \text{H}_{117} \text{Mo N}_6 \text{Nb O}_{0.50} \text{P Si}$, space group P-1, $a = 12.011(5) \text{ \AA}$, $b = 12.111(8) \text{ \AA}$, $c = 29.970(12) \text{ \AA}$, $\alpha = 84.99(3)^\circ$, $\beta = 88.69(4)^\circ$, $\gamma = 61.0(5)^\circ$, $V = 3799(3) \text{ \AA}^3$, $Z = 2$, $\mu = 0.396 \text{ mm}^{-1}$, $\rho(\text{calc}) = 1.188 \text{ g/cm}^{-3}$, $F(000) = 1450$, R_1 (based on F) = 0.0501, wR_2 (based on F^2) = 0.1028.

Table S11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo(1)	2946(1)	5286(1)	1447(1)	19(1)
Nb(1)	2885(1)	4322(1)	2943(1)	20(1)
P(1)	2997(1)	4634(1)	2181(1)	24(1)
N(1)	2147(2)	3130(2)	3005(1)	24(1)
O(1)	394(6)	58(8)	4891(3)	124(3)
Si(1)	-1119(2)	1191(1)	4738(1)	89(1)
N(2)	1844(2)	5980(2)	3224(1)	27(1)
N(3)	4766(2)	3364(2)	3102(1)	26(1)
N(4)	2974(2)	3939(2)	1128(1)	24(1)
N(5)	4465(2)	5495(2)	1333(1)	27(1)
N(6)	1593(2)	7004(2)	1358(1)	22(1)
C(11)	2191(2)	2681(2)	3467(1)	25(1)
C(12)	3089(2)	1457(2)	3635(1)	30(1)
C(13)	3201(3)	1084(2)	4092(1)	34(1)
C(14)	2384(3)	1934(3)	4381(1)	39(1)
C(15)	1472(3)	3144(3)	4225(1)	37(1)
C(16)	1383(2)	3508(2)	3767(1)	31(1)
C(17)	2022(2)	2346(2)	2682(1)	28(1)
C(18)	650(3)	2751(3)	2526(1)	35(1)
C(19)	699(3)	1720(3)	2254(1)	43(1)
C(21)	522(2)	6476(2)	3277(1)	28(1)
C(22)	-73(3)	6834(2)	3687(1)	34(1)
C(23)	-1363(3)	7247(2)	3733(1)	39(1)
C(24)	-2075(3)	7306(3)	3364(1)	43(1)
C(25)	-1522(3)	6973(2)	2952(1)	40(1)
C(26)	-231(2)	6564(2)	2912(1)	31(1)
C(27)	2475(2)	6514(2)	3479(1)	30(1)
C(28)	2349(3)	7790(2)	3282(1)	34(1)
C(29)	3015(4)	8172(3)	3617(1)	57(1)
C(31)	5047(2)	3650(2)	3520(1)	27(1)
C(32)	5820(3)	4215(2)	3555(1)	36(1)
C(33)	5965(3)	4622(3)	3954(1)	42(1)
C(34)	5332(3)	4471(3)	4326(1)	48(1)
C(35)	4578(3)	3904(3)	4308(1)	43(1)
C(36)	4459(2)	3477(2)	3905(1)	31(1)
C(37)	5854(2)	2716(2)	2808(1)	32(1)
C(38)	6531(2)	1263(2)	2872(1)	33(1)
C(39)	7655(3)	766(3)	2558(1)	55(1)
C(41)	3920(2)	2651(2)	1253(1)	26(1)
C(42)	5179(2)	2241(2)	1142(1)	30(1)

C(43)	6126(2)	1010(2)	1260(1)	32(1)
C(44)	5782(3)	181(2)	1488(1)	36(1)
C(45)	4532(3)	555(2)	1605(1)	34(1)
C(46)	3602(2)	1799(2)	1488(1)	30(1)
C(47)	2190(2)	4152(2)	721(1)	31(1)
C(48)	1143(3)	3802(3)	816(1)	46(1)
C(49)	2989(3)	3460(3)	329(1)	45(1)
C(51)	4310(2)	6234(2)	924(1)	28(1)
C(52)	3830(2)	5985(2)	548(1)	32(1)
C(53)	3523(2)	6761(3)	149(1)	38(1)
C(54)	3731(3)	7793(3)	125(1)	42(1)
C(55)	4228(3)	8059(3)	489(1)	41(1)
C(56)	4513(2)	7281(3)	884(1)	34(1)
C(57)	5619(2)	5176(3)	1603(1)	44(1)
C(58)	5339(3)	5768(3)	2038(1)	42(1)
C(59)	6525(3)	3818(3)	1639(1)	62(1)
C(61)	542(2)	7259(2)	1075(1)	23(1)
C(62)	-324(2)	6869(2)	1221(1)	31(1)
C(63)	-1323(2)	7056(3)	939(1)	40(1)
C(64)	-1447(3)	7669(3)	516(1)	43(1)
C(65)	-598(2)	8074(2)	362(1)	36(1)
C(66)	404(2)	7853(2)	643(1)	28(1)
C(67)	1534(2)	8056(2)	1597(1)	27(1)
C(68)	539(3)	8412(3)	1957(1)	39(1)
C(69)	1309(3)	9205(2)	1282(1)	36(1)
C(91)	-1607(6)	2543(5)	5073(2)	114(2)
C(92)	-596(5)	1506(5)	4189(2)	108(2)
C(93)	-2453(6)	885(6)	4655(2)	127(2)
C(110)	-215(3)	2918(4)	2924(1)	66(1)
C(111)	118(3)	3981(3)	2219(1)	55(1)
C(131)	4233(3)	-208(3)	4267(1)	53(1)
C(151)	574(4)	4065(3)	4540(1)	58(1)
C(210)	3032(3)	7607(3)	2837(1)	47(1)
C(211)	958(3)	8820(2)	3218(1)	47(1)
C(231)	-1979(3)	7619(3)	4181(1)	59(1)
C(251)	-2322(3)	7098(3)	2547(1)	64(1)
C(310)	5613(3)	817(3)	2741(1)	57(1)
C(311)	7003(4)	786(3)	3354(1)	63(1)
C(331)	6772(4)	5260(4)	3981(1)	65(1)
C(351)	3950(4)	3692(4)	4723(1)	75(1)
C(431)	7499(3)	592(3)	1151(1)	45(1)
C(451)	4193(3)	-363(3)	1864(1)	49(1)
C(531)	2980(3)	6460(3)	-238(1)	49(1)
C(551)	4440(4)	9192(3)	458(1)	62(1)
C(631)	-2231(3)	6588(4)	1100(1)	61(1)
C(651)	-748(3)	8737(3)	-101(1)	53(1)

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*{}^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Mo(1)	20(1)	19(1)	17(1)	1(1)	-2(1)	-8(1)
Nb(1)	25(1)	18(1)	18(1)	-1(1)	-1(1)	-11(1)
P(1)	29(1)	26(1)	20(1)	1(1)	-3(1)	-15(1)
N(1)	30(1)	23(1)	22(1)	-3(1)	1(1)	-15(1)
O(1)	79(6)	114(5)	132(7)	67(5)	-30(5)	-20(5)
Si(1)	109(1)	57(1)	74(1)	12(1)	-35(1)	-19(1)
N(2)	32(1)	22(1)	26(1)	-4(1)	0(1)	-13(1)
N(3)	26(1)	26(1)	23(1)	1(1)	-2(1)	-11(1)
N(4)	25(1)	21(1)	23(1)	-2(1)	-3(1)	-9(1)
N(5)	20(1)	32(1)	26(1)	2(1)	-4(1)	-11(1)
N(6)	18(1)	22(1)	22(1)	1(1)	-3(1)	-8(1)
C(11)	33(1)	25(1)	25(1)	-2(1)	2(1)	-19(1)
C(12)	36(1)	28(1)	30(1)	-4(1)	4(1)	-19(1)
C(13)	41(2)	34(1)	33(1)	3(1)	-4(1)	-24(1)
C(14)	56(2)	46(2)	25(1)	3(1)	2(1)	-34(1)
C(15)	49(2)	42(2)	27(1)	-8(1)	9(1)	-27(1)
C(16)	40(1)	27(1)	28(1)	-2(1)	4(1)	-18(1)
C(17)	36(1)	26(1)	27(1)	-5(1)	2(1)	-17(1)
C(18)	36(1)	37(1)	40(2)	-10(1)	1(1)	-22(1)
C(19)	53(2)	44(2)	44(2)	-10(1)	-1(1)	-32(1)
C(21)	33(1)	18(1)	31(1)	-2(1)	2(1)	-12(1)
C(22)	38(1)	27(1)	31(1)	-3(1)	3(1)	-11(1)
C(23)	40(2)	26(1)	43(2)	-2(1)	11(1)	-12(1)
C(24)	31(1)	30(1)	65(2)	-4(1)	4(1)	-12(1)
C(25)	37(2)	28(1)	53(2)	-4(1)	-9(1)	-14(1)
C(26)	35(1)	25(1)	33(1)	-3(1)	-2(1)	-13(1)
C(27)	36(1)	24(1)	30(1)	-3(1)	-4(1)	-13(1)
C(28)	43(2)	25(1)	37(1)	-4(1)	-2(1)	-18(1)
C(29)	81(2)	49(2)	61(2)	-10(2)	-11(2)	-44(2)
C(31)	29(1)	22(1)	28(1)	3(1)	-5(1)	-11(1)
C(32)	36(1)	37(1)	37(1)	7(1)	-4(1)	-21(1)
C(33)	46(2)	41(2)	49(2)	1(1)	-10(1)	-29(1)
C(34)	66(2)	53(2)	40(2)	-11(1)	-3(1)	-40(2)
C(35)	60(2)	50(2)	34(2)	-10(1)	4(1)	-36(2)
C(36)	39(1)	32(1)	31(1)	-2(1)	-1(1)	-23(1)
C(37)	29(1)	34(1)	28(1)	2(1)	2(1)	-11(1)
C(38)	30(1)	31(1)	31(1)	-5(1)	0(1)	-10(1)
C(39)	36(2)	51(2)	65(2)	-11(2)	14(2)	-10(1)
C(41)	26(1)	22(1)	25(1)	-6(1)	-3(1)	-8(1)
C(42)	29(1)	28(1)	28(1)	-3(1)	2(1)	-11(1)
C(43)	31(1)	30(1)	29(1)	-5(1)	-1(1)	-8(1)

C(44)	40(2)	21(1)	35(1)	-2(1)	-6(1)	-5(1)
C(45)	44(2)	25(1)	33(1)	-3(1)	-4(1)	-17(1)
C(46)	30(1)	28(1)	31(1)	-5(1)	-1(1)	-14(1)
C(47)	33(1)	28(1)	29(1)	-4(1)	-9(1)	-11(1)
C(48)	39(2)	44(2)	58(2)	-5(1)	-14(1)	-20(1)
C(49)	56(2)	43(2)	31(1)	-14(1)	-5(1)	-18(1)
C(51)	17(1)	35(1)	28(1)	0(1)	4(1)	-11(1)
C(52)	28(1)	36(1)	29(1)	-3(1)	5(1)	-14(1)
C(53)	29(1)	50(2)	26(1)	1(1)	6(1)	-13(1)
C(54)	35(2)	48(2)	34(2)	9(1)	7(1)	-16(1)
C(55)	32(1)	42(2)	47(2)	6(1)	8(1)	-19(1)
C(56)	26(1)	42(1)	38(1)	-1(1)	3(1)	-19(1)
C(57)	24(1)	57(2)	43(2)	-4(1)	-9(1)	-13(1)
C(58)	42(2)	47(2)	43(2)	-5(1)	-11(1)	-25(1)
C(59)	41(2)	56(2)	66(2)	-15(2)	-22(2)	-2(2)
C(61)	19(1)	19(1)	25(1)	-3(1)	-3(1)	-6(1)
C(62)	24(1)	28(1)	38(1)	-2(1)	0(1)	-11(1)
C(63)	26(1)	37(1)	60(2)	-11(1)	-2(1)	-17(1)
C(64)	32(1)	40(2)	52(2)	-9(1)	-18(1)	-11(1)
C(65)	33(1)	32(1)	31(1)	-5(1)	-10(1)	-6(1)
C(66)	27(1)	26(1)	26(1)	-4(1)	-1(1)	-9(1)
C(67)	25(1)	25(1)	29(1)	-3(1)	-5(1)	-10(1)
C(68)	44(2)	35(1)	29(1)	-7(1)	2(1)	-13(1)
C(69)	37(1)	28(1)	44(2)	-4(1)	-1(1)	-18(1)
C(91)	172(6)	124(4)	56(3)	-11(3)	2(3)	-79(4)
C(92)	89(4)	139(5)	119(4)	-67(4)	29(3)	-65(4)
C(93)	190(7)	113(4)	119(5)	-4(4)	32(4)	-109(5)
C(110)	52(2)	110(3)	60(2)	-38(2)	19(2)	-54(2)
C(111)	54(2)	38(2)	73(2)	-1(2)	-26(2)	-20(2)
C(131)	60(2)	44(2)	43(2)	10(1)	-8(2)	-17(2)
C(151)	75(2)	55(2)	34(2)	-9(1)	19(2)	-23(2)
C(210)	54(2)	45(2)	49(2)	-4(1)	8(1)	-30(2)
C(211)	54(2)	23(1)	58(2)	-2(1)	5(2)	-15(1)
C(231)	53(2)	53(2)	55(2)	-9(2)	24(2)	-14(2)
C(251)	40(2)	60(2)	84(3)	-26(2)	-16(2)	-14(2)
C(310)	47(2)	50(2)	78(2)	-29(2)	17(2)	-25(2)
C(311)	85(3)	31(2)	43(2)	5(1)	-16(2)	-4(2)
C(331)	76(3)	76(2)	72(2)	1(2)	-14(2)	-59(2)
C(351)	115(3)	121(3)	40(2)	-33(2)	27(2)	-94(3)
C(431)	32(1)	38(2)	47(2)	2(1)	1(1)	-4(1)
C(451)	56(2)	31(1)	60(2)	5(1)	-2(2)	-23(1)
C(531)	49(2)	64(2)	27(1)	0(1)	-1(1)	-22(2)
C(551)	64(2)	56(2)	74(2)	14(2)	4(2)	-39(2)
C(631)	38(2)	68(2)	90(3)	-13(2)	-1(2)	-36(2)
C(651)	59(2)	51(2)	35(2)	3(1)	-20(1)	-16(2)

S2.8 X-ray Crystal Structure of (μ_2 : η^2 , η^2 -P₂)[Nb(N[Np]Ar)₃]₂ (**10**)

Forest green crystals of **10** obtained from a saturated diethyl ether solution stored at -35 °C for one week were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.10 x 0.08 x 0.05 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 31335 reflections (-15 ≤ h ≤ 13, -11 ≤ k ≤ 17, -33 ≤ l ≤ 37) were collected at 188 (2) K in the θ range 1.18° to 22.50°, of which 10395 ($R_{\text{int}} = 0.0682$) were unique. The structure was solved using the Patterson method (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions and placed in calculated positions ($d_{\text{CH}} = 0.96$ Å). The residual peak and hole electron density were 0.511 and -0.361 e.Å⁻³, respectively. An empirical absorption correction using SADABS was applied with maximum and minimum transmissions equal to 0.2687 and 0.2321, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0523$, $wR_2 = 0.0939$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.208$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C₇₈H₁₂₀N₆Nb₂P₂, space group P2₁/c, $a = 13.931(2)$ Å, $b = 16.519(3)$ Å, $c = 34.582(5)$ Å, $\alpha = 90.0^\circ$, $\beta = 92.088(3)^\circ$, $\gamma = 90.0^\circ$, $V = 7953(2)$ Å³, $Z = 4$, $\mu = 0.371$ mm⁻¹, $\rho(\text{calc}) = 1.161$ g/cm³, $F(000) = 2968$, R_1 (based on F) = 0.0880, wR_2 (based on F^2) = 0.1162.

Table S13. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **10**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb(1)	7627(1)	735(1)	1644(1)	25(1)
Nb(2)	7651(1)	2927(1)	1026(1)	31(1)
P(1)	8400(1)	2091(1)	1564(1)	29(1)
P(2)	6849(1)	2106(1)	1531(1)	32(1)
N(1)	8981(3)	250(3)	1592(1)	27(1)
N(6)	7648(3)	4041(3)	1238(1)	33(1)
N(2)	7354(3)	670(3)	2198(1)	27(1)
C(27)	8040(4)	788(4)	2533(2)	40(2)
C(18)	10782(4)	594(4)	1603(2)	41(2)
N(4)	8780(4)	2770(3)	683(1)	39(1)
C(11)	9010(4)	-609(4)	1663(2)	30(2)
N(3)	6829(3)	68(3)	1272(1)	30(1)
C(36)	6581(4)	-1288(4)	1541(2)	31(2)
C(16)	8793(4)	-890(4)	2031(2)	34(2)
C(31)	6213(4)	-554(4)	1412(2)	31(2)
C(22)	5612(4)	836(4)	2207(2)	34(2)
C(21)	6429(4)	374(4)	2295(2)	29(2)
C(17)	9815(4)	521(4)	1378(2)	32(2)

N(5)	6488(4)	2733(3)	664(1)	40(1)
C(33)	4621(4)	-1040(4)	1534(2)	44(2)
C(25)	5417(5)	-662(5)	2562(2)	49(2)
C(14)	9017(4)	-2251(4)	1824(2)	50(2)
C(12)	9245(4)	-1178(4)	1386(2)	36(2)
C(51)	6566(5)	3093(4)	288(2)	52(2)
C(34)	5011(5)	-1772(4)	1658(2)	44(2)
C(41)	9464(6)	3407(5)	722(2)	52(2)
C(15)	8788(4)	-1722(4)	2115(2)	41(2)
C(32)	5223(4)	-439(4)	1412(2)	40(2)
C(26)	6320(4)	-379(4)	2471(2)	38(2)
C(57)	5709(6)	2137(5)	663(2)	50(2)
C(110)	10704(4)	1138(5)	1942(2)	74(3)
C(23)	4702(4)	553(5)	2298(2)	43(2)
C(35)	5991(5)	-1906(4)	1669(2)	37(2)
C(310)	6763(5)	143(4)	162(2)	66(2)
C(411)	10586(5)	2333(5)	148(2)	70(2)
C(311)	6029(5)	-973(4)	523(2)	65(2)
C(13)	9253(4)	-1998(5)	1459(2)	45(2)
C(39)	7780(5)	-717(5)	598(2)	70(2)
C(231)	3830(4)	1065(5)	2189(2)	66(2)
C(19)	11178(4)	-224(4)	1738(2)	52(2)
C(331)	3547(4)	-897(5)	1538(2)	72(2)
C(351)	6395(5)	-2699(4)	1811(2)	53(2)
C(37)	6638(5)	299(4)	867(2)	36(2)
C(38)	6813(5)	-329(4)	545(2)	42(2)
C(47)	9150(7)	1981(5)	564(2)	53(2)
C(48)	9623(6)	1908(4)	165(2)	58(2)
C(410)	8938(5)	2233(5)	-143(2)	87(3)
C(151)	8554(5)	-2000(4)	2521(2)	62(2)
C(42)	10289(6)	3322(5)	959(2)	67(2)
C(45)	9910(9)	4822(9)	596(3)	107(5)
C(24)	4633(5)	-185(5)	2478(2)	52(2)
C(49)	9789(6)	999(5)	108(2)	103(3)
C(43)	10923(6)	3999(9)	1009(3)	107(4)
C(131)	9497(5)	-2599(4)	1150(2)	65(2)
C(44)	10686(12)	4702(8)	822(4)	134(7)
C(46)	9292(7)	4142(5)	546(2)	71(3)
C(67)	8562(4)	4272(4)	1443(2)	36(2)
C(61)	6992(5)	4690(4)	1174(2)	37(2)
C(68)	8517(4)	4576(4)	1863(2)	35(2)
C(66)	6065(5)	4615(4)	1290(2)	48(2)
C(52)	6566(5)	2630(4)	-47(2)	59(2)
C(28)	7887(5)	1487(4)	2813(2)	46(2)
C(610)	7872(5)	4056(4)	2094(2)	56(2)
C(62)	7250(5)	5387(4)	980(2)	53(2)

C(53)	6669(6)	2971(5)	-400(2)	70(2)
C(58)	4656(5)	2449(5)	678(2)	70(3)
C(65)	5404(6)	5245(6)	1213(2)	68(3)
C(63)	6637(7)	6022(5)	906(2)	66(2)
C(64)	5714(8)	5924(5)	1019(2)	75(3)
C(56)	6674(6)	3922(5)	253(2)	75(3)
C(55)	6795(7)	4285(5)	-101(2)	97(3)
C(69)	8193(5)	5448(4)	1887(2)	70(2)
C(251)	5320(5)	-1492(5)	2746(2)	80(3)
C(54)	6795(6)	3804(5)	-422(2)	82(3)
C(111)	11506(4)	942(5)	1311(2)	79(3)
C(531)	6668(6)	2457(5)	-756(2)	105(3)
C(631)	6919(7)	6789(4)	700(2)	105(3)
C(29)	7064(6)	1313(6)	3079(2)	105(3)
C(611)	9534(5)	4519(6)	2030(2)	94(3)
C(451)	9727(9)	5619(5)	414(3)	169(6)
C(59)	4029(5)	1700(6)	721(3)	101(3)
C(511)	4337(6)	2822(6)	285(3)	125(4)
C(211)	8729(6)	1531(7)	3099(3)	149(5)
C(651)	4405(6)	5137(6)	1346(2)	115(4)
C(510)	4552(5)	3051(7)	978(3)	159(6)
C(551)	6902(9)	5201(5)	-132(2)	161(5)
C(210)	7694(10)	2238(5)	2619(2)	201(7)
C(431)	11784(7)	3844(7)	1269(3)	158(5)

Table S14. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb(1)	25(1)	21(1)	29(1)	0(1)	-1(1)	0(1)
Nb(2)	45(1)	21(1)	27(1)	0(1)	-1(1)	7(1)
P(1)	31(1)	23(1)	33(1)	3(1)	-1(1)	-1(1)
P(2)	30(1)	28(1)	37(1)	2(1)	-2(1)	5(1)
N(1)	22(3)	24(3)	34(3)	3(3)	1(2)	4(2)
N(6)	45(3)	18(3)	34(3)	1(3)	-4(2)	7(3)
N(2)	24(3)	23(3)	35(3)	4(3)	-1(2)	2(2)
C(27)	38(4)	43(5)	39(4)	-4(4)	3(3)	-3(4)
C(18)	36(4)	34(5)	53(5)	-2(4)	-2(3)	6(4)
N(4)	60(4)	17(3)	41(3)	7(3)	14(3)	2(3)
C(11)	15(3)	36(4)	37(4)	3(4)	-6(3)	0(3)
N(3)	31(3)	24(3)	34(3)	-4(3)	-5(2)	0(3)
C(36)	27(4)	32(4)	32(4)	-9(3)	-3(3)	-1(3)
C(16)	27(4)	29(4)	46(4)	-1(3)	-6(3)	4(3)
C(31)	37(4)	24(4)	31(4)	-9(3)	0(3)	1(3)
C(22)	34(4)	37(4)	31(4)	-1(3)	6(3)	-4(4)

C(21)	31(4)	33(4)	24(4)	-5(3)	1(3)	-6(3)
C(17)	23(4)	29(4)	44(4)	16(4)	-2(3)	3(3)
N(5)	53(4)	29(4)	35(3)	1(3)	-12(3)	10(3)
C(33)	27(4)	44(5)	63(5)	-18(4)	5(3)	-1(4)
C(25)	58(5)	41(5)	49(5)	-4(4)	19(4)	-17(5)
C(14)	41(4)	18(4)	89(6)	-5(4)	-16(4)	12(4)
C(12)	30(4)	41(5)	38(4)	-3(4)	1(3)	7(4)
C(51)	90(6)	32(5)	31(4)	-4(4)	-18(4)	17(4)
C(34)	46(5)	47(5)	39(4)	-11(4)	11(3)	-16(4)
C(41)	74(6)	46(6)	36(5)	3(4)	30(4)	14(5)
C(15)	32(4)	36(5)	52(5)	20(4)	-10(3)	1(4)
C(32)	33(4)	33(4)	52(4)	-8(4)	-6(3)	4(4)
C(26)	44(4)	38(5)	33(4)	-1(3)	5(3)	0(4)
C(57)	71(6)	32(5)	45(5)	11(4)	-23(4)	14(5)
C(110)	39(4)	69(6)	111(7)	-21(6)	-34(4)	1(4)
C(23)	34(4)	52(5)	42(4)	-17(4)	5(3)	2(4)
C(35)	48(5)	32(5)	31(4)	-5(3)	-4(3)	-2(4)
C(310)	108(6)	55(5)	35(4)	-4(4)	-10(4)	6(5)
C(411)	96(6)	57(6)	61(5)	-1(4)	42(5)	10(5)
C(311)	102(6)	45(5)	47(5)	-14(4)	-22(4)	-6(5)
C(13)	36(4)	42(5)	55(5)	2(4)	-8(4)	5(4)
C(39)	88(6)	74(6)	49(5)	-4(5)	12(4)	34(5)
C(231)	41(4)	75(6)	83(6)	-19(5)	3(4)	-2(4)
C(19)	25(4)	61(6)	70(5)	11(4)	-5(3)	6(4)
C(331)	41(5)	71(6)	104(6)	-24(5)	14(4)	-2(4)
C(351)	65(5)	45(5)	50(5)	8(4)	-3(4)	-11(4)
C(37)	43(5)	32(4)	33(4)	4(4)	-8(3)	4(4)
C(38)	56(5)	37(4)	33(4)	-6(4)	-9(3)	9(4)
C(47)	70(7)	39(5)	50(5)	7(4)	5(5)	21(5)
C(48)	87(6)	35(5)	54(5)	3(4)	37(5)	14(5)
C(410)	117(7)	102(8)	45(5)	-11(5)	20(5)	13(6)
C(151)	75(5)	43(5)	68(5)	24(4)	-3(4)	1(4)
C(42)	63(6)	65(6)	74(6)	-15(5)	33(5)	0(5)
C(45)	173(13)	87(10)	67(8)	-1(8)	66(7)	10(10)
C(24)	45(5)	61(6)	52(5)	-14(4)	18(4)	-25(5)
C(49)	155(8)	46(6)	114(8)	-17(5)	79(6)	9(6)
C(43)	34(6)	200(14)	91(8)	-72(9)	35(5)	-28(8)
C(131)	77(5)	45(5)	71(5)	-23(4)	3(4)	20(4)
C(44)	234(19)	49(8)	129(13)	-14(9)	138(12)	-43(11)
C(46)	137(8)	28(5)	50(5)	-4(4)	51(5)	-9(6)
C(67)	41(4)	36(4)	32(4)	-6(4)	3(3)	8(4)
C(61)	57(5)	25(4)	29(4)	-6(3)	-11(3)	11(4)
C(68)	36(4)	32(4)	37(4)	5(3)	-6(3)	-1(3)
C(66)	64(5)	43(5)	35(4)	-12(4)	-10(4)	13(4)
C(52)	101(6)	38(5)	35(5)	-6(4)	-22(4)	19(4)
C(28)	67(5)	41(5)	31(4)	-8(4)	10(4)	-8(4)

C(610)	79(5)	47(5)	41(4)	-11(4)	3(4)	5(4)
C(62)	78(6)	30(5)	48(5)	-7(4)	-15(4)	10(4)
C(53)	124(7)	59(6)	25(5)	-14(5)	-16(4)	30(6)
C(58)	59(6)	49(5)	100(7)	-24(5)	-37(5)	11(5)
C(65)	52(5)	90(8)	61(6)	-25(5)	-21(4)	42(6)
C(63)	98(7)	43(6)	55(5)	-10(4)	-27(5)	20(6)
C(64)	126(9)	38(6)	58(6)	-10(5)	-42(6)	39(6)
C(56)	152(8)	37(5)	35(5)	-7(4)	-27(5)	7(5)
C(55)	209(10)	42(5)	36(5)	13(5)	-34(6)	21(7)
C(69)	128(7)	36(5)	45(5)	-12(4)	-10(4)	4(5)
C(251)	98(6)	52(6)	92(6)	8(5)	34(5)	-26(5)
C(54)	149(8)	65(7)	32(5)	12(5)	-14(5)	18(6)
C(111)	35(4)	91(7)	112(7)	48(6)	4(4)	-10(5)
C(531)	181(9)	87(7)	45(5)	-8(5)	-17(6)	43(7)
C(631)	197(10)	25(5)	88(7)	22(5)	-42(7)	5(6)
C(29)	116(7)	104(9)	96(7)	-41(6)	37(6)	-17(7)
C(611)	62(6)	144(10)	77(6)	-38(6)	-12(5)	2(6)
C(451)	372(18)	25(5)	121(9)	11(6)	152(10)	-17(9)
C(59)	61(6)	91(8)	150(9)	6(7)	-23(6)	4(6)
C(511)	111(8)	96(8)	163(10)	35(8)	-75(7)	16(7)
C(211)	94(7)	188(13)	161(10)	-122(10)	-57(7)	19(8)
C(651)	93(7)	134(10)	117(8)	-13(7)	-13(6)	70(7)
C(510)	42(5)	195(13)	239(13)	-134(11)	-17(7)	34(7)
C(551)	380(17)	43(6)	59(6)	22(5)	-18(8)	-1(9)
C(210)	520(20)	36(6)	53(7)	-19(5)	25(10)	-9(10)
C(431)	83(8)	193(14)	202(12)	-86(11)	67(8)	-50(8)

S2.9 X-ray Crystal Structure of Nb(η^2 -MesCN)(N[Np]Ar)₃ (**11**)

Orange crystals of **11** obtained from a saturated n-hexane solution stored at room temperature were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.40 x 0.33 x 0.20 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 9197 reflections (-11 ≤ h ≤ 10, -13 ≤ k ≤ 13, -21 ≤ l ≤ 15) were collected at 183 (2) K in the θ range 2.69° to 23.29°, of which 6445 ($R_{\text{int}} = 0.0633$) were unique. The structure was solved using direct methods (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All non-methyl hydrogen atoms were located in the electron density map and refined isotropically. All methyl hydrogens were placed in calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.540 and -0.447 e.Å⁻³, respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.4353 and 0.3078, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0416$, $wR_2 = 0.1346$ based upon $I > 2\sigma(I)$ and $\text{GOF} = 1.203$ based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C₄₉H₇₁N₄Nb, space group P-1, $a = 10.7225(6) \text{ \AA}$, $b = 11.9653(7) \text{ \AA}$, $c = 19.3710(11) \text{ \AA}$, $\alpha = 86.526(1)^\circ$, $\beta =$

$77.2120(1)^\circ$, $\gamma = 72.101(1)^\circ$, $V = 2306.2(6)$ Å 3 , $Z = 2$, $\mu = 0.296$ mm $^{-1}$, $\rho(\text{calc}) = 1.165$ g/cm $^{-3}$, $F(000) = 868$, R_1 (based on F) = 0.0435, wR_2 (based on F^2) = 0.1371.

Table S15. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $^2 \times 10^3$) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb	3259(1)	7859(1)	2790(1)	23(1)
N(2)	1405(2)	8330(2)	3399(1)	27(1)
N(3)	3476(2)	6506(2)	2122(1)	26(1)
N(1)	4048(2)	9038(2)	2246(1)	26(1)
N(4)	4667(3)	6583(2)	3198(1)	36(1)
C(41)	4235(3)	7424(2)	3635(1)	27(1)
C(11)	3446(3)	10194(2)	2010(1)	26(1)
C(31)	2750(3)	6777(2)	1565(1)	28(1)
C(32)	1818(3)	6215(2)	1494(2)	34(1)
C(47)	5537(3)	6592(3)	4568(2)	36(1)
C(22)	540(3)	9438(2)	2431(2)	28(1)
C(36)	2992(3)	7605(3)	1059(2)	31(1)
C(12)	3634(3)	10482(3)	1294(2)	33(1)
C(23)	-140(3)	10481(3)	2139(2)	31(1)
C(21)	556(3)	9354(2)	3156(1)	27(1)
C(13)	3065(3)	11615(3)	1073(2)	37(1)
C(42)	4611(3)	7527(2)	4313(1)	27(1)
C(17)	5485(3)	8493(3)	1924(2)	30(1)
C(18)	6503(3)	8980(3)	2154(2)	33(1)
C(28)	202(3)	6981(3)	4138(2)	38(1)
C(27)	928(3)	7901(3)	4113(1)	32(1)
C(431)	3022(3)	9620(3)	4467(2)	39(1)
C(37)	4082(3)	5230(2)	2204(2)	30(1)
C(44)	4409(3)	8670(3)	5338(2)	38(1)
C(16)	2646(3)	11063(2)	2504(2)	29(1)
C(14)	2301(3)	12455(3)	1579(2)	41(1)
C(231)	-59(3)	10572(3)	1354(2)	43(1)
C(24)	-879(3)	11422(3)	2592(2)	36(1)
C(34)	1451(3)	7280(3)	432(2)	43(1)
C(33)	1188(3)	6442(3)	927(2)	39(1)
C(26)	-201(3)	10340(2)	3590(2)	31(1)
C(43)	4036(3)	8586(2)	4708(1)	31(1)
C(38)	5346(3)	4613(2)	1634(2)	38(1)
C(15)	2079(3)	12196(2)	2293(2)	33(1)
C(35)	2340(3)	7874(3)	498(2)	38(1)
C(25)	-936(3)	11359(2)	3310(2)	35(1)
C(251)	-1768(3)	12407(3)	3782(2)	49(1)

C(45)	5310(3)	7742(3)	5603(2)	41(1)
C(46)	5864(3)	6716(3)	5206(2)	42(1)
C(471)	6226(4)	5442(3)	4173(2)	51(1)
C(210)	-265(4)	6708(3)	4908(2)	51(1)
C(111)	7896(3)	8193(3)	1819(2)	54(1)
C(151)	1262(4)	13154(3)	2826(2)	47(1)
C(351)	2655(4)	8749(3)	-54(2)	52(1)
C(110)	6375(3)	10243(3)	1905(2)	46(1)
C(131)	3277(4)	11919(3)	295(2)	58(1)
C(19)	6348(3)	8952(3)	2953(2)	43(1)
C(311)	4987(4)	4497(3)	925(2)	64(1)
C(310)	5881(4)	3377(3)	1902(2)	58(1)
C(451)	5672(5)	7812(4)	6304(2)	66(1)
C(39)	6386(4)	5238(4)	1540(3)	78(2)
C(29)	1118(5)	5885(3)	3758(2)	73(1)
C(331)	265(4)	5755(3)	827(2)	55(1)
C(211)	-1040(5)	7494(4)	3817(2)	73(1)

Table S16. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^{*} b^{*} U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	28(1)	21(1)	19(1)	-1(1)	-7(1)	-7(1)
N(2)	28(1)	28(1)	23(1)	0(1)	-5(1)	-7(1)
N(3)	36(1)	22(1)	22(1)	0(1)	-8(1)	-9(1)
N(1)	29(1)	27(1)	20(1)	-1(1)	-5(1)	-8(1)
N(4)	44(2)	31(1)	32(1)	-5(1)	-18(1)	-4(1)
C(41)	31(2)	22(1)	27(1)	-1(1)	-3(1)	-9(1)
C(11)	30(2)	26(1)	26(1)	2(1)	-9(1)	-14(1)
C(31)	31(2)	28(1)	23(1)	-10(1)	-6(1)	-4(1)
C(32)	44(2)	23(1)	35(2)	-7(1)	-10(1)	-8(1)
C(47)	42(2)	38(2)	31(2)	0(1)	-15(1)	-14(1)
C(22)	29(2)	27(2)	28(2)	-4(1)	-6(1)	-7(1)
C(36)	37(2)	32(2)	26(2)	-6(1)	-7(1)	-9(1)
C(12)	38(2)	34(2)	27(2)	-5(1)	-5(1)	-12(1)
C(23)	27(2)	36(2)	35(2)	4(1)	-10(1)	-12(1)
C(21)	27(1)	26(1)	29(1)	1(1)	-6(1)	-12(1)
C(13)	42(2)	38(2)	33(2)	8(1)	-12(1)	-14(1)
C(42)	33(2)	27(1)	24(1)	2(1)	-8(1)	-12(1)
C(17)	34(2)	26(2)	29(2)	-1(1)	-6(1)	-8(1)
C(18)	31(2)	35(2)	36(2)	2(1)	-9(1)	-12(1)
C(28)	42(2)	38(2)	35(2)	8(1)	-8(1)	-17(1)
C(27)	40(2)	35(2)	20(1)	1(1)	-4(1)	-11(1)
C(431)	52(2)	31(2)	35(2)	-7(1)	-13(1)	-8(1)
C(37)	43(2)	24(1)	24(2)	0(1)	-13(1)	-8(1)

C(44)	56(2)	38(2)	26(2)	-3(1)	-8(1)	-21(2)
C(16)	32(2)	35(2)	25(2)	0(1)	-6(1)	-18(1)
C(14)	43(2)	31(2)	48(2)	9(2)	-13(2)	-9(2)
C(231)	43(2)	51(2)	38(2)	11(2)	-18(1)	-13(2)
C(24)	31(2)	32(2)	47(2)	6(1)	-13(1)	-9(1)
C(34)	47(2)	49(2)	31(2)	-7(2)	-20(2)	-2(2)
C(33)	37(2)	32(2)	47(2)	-15(1)	-16(1)	-2(1)
C(26)	33(2)	27(2)	31(2)	-2(1)	-4(1)	-9(1)
C(43)	38(2)	32(2)	25(1)	0(1)	-5(1)	-16(1)
C(38)	44(2)	26(2)	40(2)	-8(1)	-7(1)	-3(1)
C(15)	31(2)	31(2)	38(2)	-1(1)	-7(1)	-13(1)
C(35)	45(2)	40(2)	26(2)	-3(1)	-13(1)	-3(2)
C(25)	30(2)	31(2)	44(2)	-6(1)	-4(1)	-10(1)
C(251)	47(2)	34(2)	57(2)	-9(2)	2(2)	-6(2)
C(45)	56(2)	51(2)	28(2)	4(2)	-16(2)	-28(2)
C(46)	50(2)	44(2)	41(2)	9(2)	-24(2)	-17(2)
C(471)	62(2)	35(2)	48(2)	-4(2)	-27(2)	7(2)
C(210)	59(2)	49(2)	44(2)	12(2)	-6(2)	-21(2)
C(111)	34(2)	58(2)	68(2)	-8(2)	-6(2)	-10(2)
C(151)	55(2)	34(2)	47(2)	-9(1)	-3(2)	-11(2)
C(351)	71(2)	53(2)	34(2)	8(2)	-23(2)	-17(2)
C(110)	47(2)	43(2)	55(2)	14(2)	-20(2)	-24(2)
C(131)	78(3)	51(2)	37(2)	11(2)	-14(2)	-10(2)
C(19)	49(2)	53(2)	42(2)	7(2)	-23(2)	-26(2)
C(311)	76(3)	54(2)	36(2)	-14(2)	-4(2)	15(2)
C(310)	66(2)	38(2)	56(2)	-3(2)	-14(2)	6(2)
C(451)	106(3)	71(3)	39(2)	6(2)	-40(2)	-35(2)
C(39)	56(3)	53(2)	110(4)	-34(2)	18(2)	-15(2)
C(29)	120(4)	41(2)	50(2)	-6(2)	14(2)	-34(2)
C(331)	52(2)	45(2)	74(3)	-17(2)	-32(2)	-10(2)
C(211)	70(3)	103(3)	74(3)	39(3)	-38(2)	-57(3)

S2.10 X-ray Crystal Structure of Nb(N=C(H)^tBu)(η²-^tBu(H)C=N(Ar))(N[Np]Ar)₂ (12)

Red crystals of **12** obtained from a saturated diethyl ether solution stored at -35 °C were coated with Paratone N oil (an Exxon product) and placed on a microscope slide. A crystal of approximate dimensions 0.40 x 0.20 x 0.10 mm³ was selected and mounted with wax on the end of a glass fiber. A total of 17271 reflections (-16 ≤ h ≤ 22, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24) were collected at 183 (2) K in the θ range 2.13° to 23.29°, of which 6298 ($R_{int} = 0.0576$) were unique. The structure was solved using the Patterson method (SHELXTL V5.10, G. M. Sheldrick and Siemens Industrial Automation, Inc.) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All non-methyl hydrogen atoms were located in the electron density map and refined isotropically. All methyl hydrogens were placed in calculated positions ($d_{CH} = 0.96 \text{ \AA}$). The residual peak and hole electron density were 0.434 and -

1.213 e. \AA^{-3} , respectively. An empirical absorption correction (psi-scans) was applied with maximum and minimum transmissions equal to 0.5175 and 0.3941, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0526$, $wR_2 = 0.1487$ based upon $I > 2\sigma(I)$ and GOF = 1.182 based upon F^2 . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{44}H_{69}N_4Nb$, space group P2(1)/n, $a = 19.9926(16)$ \AA , $b = 10.8813(9)$ \AA , $c = 22.5023(18)$ \AA , $\alpha = 90.0^\circ$, $\beta = 116.247(1)^\circ$, $\gamma = 90.0^\circ$, $V = 4390.5(6)$ \AA^3 , $Z = 4$, $\mu = 0.306 \text{ mm}^{-1}$, $\rho(\text{calc}) = 1.130 \text{ g/cm}^{-3}$, $F(000) = 1608$, R_1 (based on F) = 0.0622, wR_2 (based on F^2) = 0.1548.

Table S17. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb	5402(1)	4629(1)	7714(1)	25(1)
N(4)	6236(2)	5370(3)	8473(2)	33(1)
N(3)	4807(2)	3677(3)	8095(2)	34(1)
C(21)	4305(2)	5655(3)	6483(2)	29(1)
C(22)	4338(2)	5463(3)	5884(2)	34(1)
C(16)	4275(2)	2434(3)	6463(2)	30(1)
C(25)	2996(2)	5088(4)	5952(2)	41(1)
N(1)	5489(2)	3214(3)	7190(2)	31(1)
C(41)	6695(2)	5512(4)	9071(2)	38(1)
N(2)	4962(2)	5989(3)	7074(2)	31(1)
C(17)	6180(2)	3814(4)	7373(2)	33(1)
C(31)	4253(2)	4401(4)	8162(2)	38(1)
C(12)	5211(2)	2491(4)	6068(2)	35(1)
C(26)	3633(2)	5467(4)	6517(2)	35(1)
C(27)	5355(2)	7114(4)	7020(2)	35(1)
C(36)	4457(2)	5569(4)	8451(2)	38(1)
C(14)	3989(3)	1768(4)	5364(2)	41(1)
C(13)	4715(2)	2017(4)	5474(2)	39(1)
C(28)	4972(2)	8346(3)	7013(2)	31(1)
C(211)	4296(3)	8579(5)	6350(2)	41(1)
C(11)	4998(2)	2710(3)	6581(2)	29(1)
C(33)	2990(3)	4834(6)	7993(3)	63(2)
C(15)	3760(2)	1966(3)	5863(2)	34(1)
C(24)	3048(3)	4917(4)	5365(2)	44(1)
C(231)	3749(3)	4890(4)	4675(2)	54(1)
C(23)	3712(2)	5096(4)	5325(2)	37(1)
C(37)	4827(3)	2359(4)	8242(2)	43(1)
C(42)	7094(2)	6685(4)	9403(2)	41(1)
C(210)	4730(3)	8393(5)	7558(3)	48(1)
C(310)	5810(3)	2708(5)	9411(2)	66(2)
C(39)	4516(3)	2248(7)	9222(2)	89(2)

C(45)	6820(3)	7767(4)	8930(3)	67(2)
C(151)	2978(2)	1686(4)	5741(2)	46(1)
C(29)	5553(3)	9358(5)	7126(3)	52(1)
C(32)	3511(3)	4052(6)	7931(2)	52(1)
C(38)	5095(3)	2023(4)	8978(2)	54(1)
C(34)	3215(3)	5979(7)	8264(3)	65(2)
C(35)	3944(2)	6380(4)	8499(2)	46(1)
C(111)	7545(3)	4071(5)	8037(3)	57(1)
C(110)	7056(3)	2230(5)	7317(4)	64(2)
C(351)	4185(3)	7623(5)	8813(2)	61(1)
C(19)	6898(3)	2441(5)	8347(3)	58(1)
C(18)	6918(2)	3144(4)	7774(2)	42(1)
C(44)	7931(3)	6496(5)	9612(3)	58(1)
C(331)	2183(3)	4413(8)	7751(4)	111(3)
C(131)	4948(3)	1793(4)	4922(2)	56(1)
C(251)	2271(3)	4925(5)	6005(3)	63(1)
C(43)	6970(3)	6886(6)	10021(3)	76(2)
C(311)	5282(5)	643(5)	9036(3)	115(3)

Table S18. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Nb	18(1)	29(1)	23(1)	0(1)	3(1)	-2(1)
N(4)	24(2)	36(2)	30(2)	-1(1)	5(2)	-1(1)
N(3)	29(2)	43(2)	25(2)	1(2)	7(2)	-4(2)
C(21)	24(2)	27(2)	28(2)	6(2)	3(2)	6(2)
C(22)	28(2)	28(2)	38(2)	2(2)	6(2)	2(2)
C(16)	36(2)	27(2)	27(2)	1(2)	15(2)	1(2)
C(25)	30(2)	35(2)	49(3)	5(2)	9(2)	0(2)
N(1)	23(2)	33(2)	31(2)	-2(1)	8(2)	-6(1)
C(41)	29(2)	37(2)	36(3)	4(2)	4(2)	2(2)
N(2)	20(2)	31(2)	36(2)	1(2)	6(2)	0(1)
C(17)	26(2)	32(2)	41(2)	-1(2)	15(2)	-1(2)
C(31)	27(2)	61(3)	21(2)	2(2)	8(2)	-7(2)
C(12)	37(2)	32(2)	41(2)	-1(2)	20(2)	0(2)
C(26)	30(2)	35(2)	33(2)	3(2)	7(2)	2(2)
C(27)	27(2)	43(2)	31(2)	-1(2)	8(2)	3(2)
C(36)	27(2)	57(3)	29(2)	-4(2)	12(2)	-6(2)
C(14)	50(3)	37(2)	27(2)	-5(2)	8(2)	-5(2)
C(13)	50(3)	35(2)	36(2)	-4(2)	21(2)	-5(2)
C(28)	26(2)	34(2)	27(2)	2(2)	6(2)	4(2)
C(211)	42(3)	36(3)	39(3)	3(2)	13(2)	8(2)
C(11)	30(2)	24(2)	29(2)	2(2)	9(2)	5(2)
C(33)	26(3)	114(5)	49(3)	-12(3)	16(2)	-14(3)

C(15)	34(2)	29(2)	32(2)	2(2)	9(2)	-2(2)
C(24)	36(3)	34(2)	39(3)	6(2)	-3(2)	-1(2)
C(231)	60(3)	50(3)	37(3)	-3(2)	8(2)	-3(2)
C(23)	40(3)	25(2)	34(2)	2(2)	5(2)	-1(2)
C(37)	48(3)	41(3)	34(2)	-2(2)	12(2)	-15(2)
C(42)	30(2)	42(2)	40(2)	-8(2)	4(2)	-6(2)
C(210)	42(3)	58(3)	37(3)	1(2)	10(2)	13(3)
C(310)	57(3)	92(4)	36(3)	9(3)	7(2)	-22(3)
C(39)	76(4)	151(6)	39(3)	17(3)	23(3)	-39(4)
C(45)	51(3)	39(3)	66(3)	2(2)	-15(3)	-6(2)
C(151)	34(2)	52(3)	41(2)	-4(2)	7(2)	-6(2)
C(29)	46(3)	39(3)	59(3)	2(3)	13(3)	-1(2)
C(32)	33(3)	83(4)	43(3)	-13(3)	18(2)	-18(3)
C(38)	63(3)	58(3)	34(2)	4(2)	15(2)	-24(3)
C(34)	39(3)	111(5)	48(3)	-2(3)	23(3)	15(3)
C(35)	40(3)	68(3)	33(2)	0(2)	18(2)	6(2)
C(111)	31(3)	55(3)	82(4)	-4(3)	22(3)	-2(2)
C(110)	42(3)	50(3)	95(5)	-7(3)	27(3)	16(3)
C(351)	64(3)	74(3)	50(3)	-13(3)	29(3)	14(3)
C(19)	34(3)	54(3)	71(4)	19(3)	9(3)	15(3)
C(18)	22(2)	37(2)	63(3)	-1(2)	16(2)	1(2)
C(44)	34(3)	49(3)	61(3)	-6(3)	-8(2)	-11(2)
C(331)	32(3)	208(9)	97(5)	-35(5)	32(3)	-26(4)
C(131)	72(4)	57(3)	44(3)	-10(2)	31(3)	-11(3)
C(251)	36(3)	69(3)	75(4)	2(3)	18(3)	-9(3)
C(43)	76(4)	84(4)	65(4)	-29(3)	28(3)	-18(3)
C(311)	198(9)	63(4)	54(4)	20(3)	30(5)	-22(5)