Niobium-Nitride Dimers Derived from Atmospheric Nitrogen Splitting

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Experimental Details

General procedures: Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Benzene, pentane, tetrahydrofuran (THF), and toluene were purchased from Fisher Scientific. Solvents were sparged with nitrogen for 20 minutes and dried using a two-column solvent purification system where columns designated for benzene, pentane, and toluene were packed with Q5 and alumina respectively and columns designated for THF were packed with alumina. Deuterated benzene and dimethyl sulfoxide (DMSO) were purchased from Cambridge Isotope Laboratory (CIL). Deuterated benzene was degassed by freeze-pump-thaw cycles and stored over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Compounds HOAr (Ar = $2,6-(CHPh_2)_2-4-$ ^tBu-C₆H₂)¹ and $[Nb(CH_3)_2Cl_3]^2$ were prepared following the literature procedures. KC₈ was prepared by slight modification of a literature procedure.³ A Chemglass thick walled glass pressure reactor was charged with graphite dried in a vacuum oven at 150 °C for 1 week, small chunks of freshly cut potassium, and an iron stir bar. Teflon tape was wrapped around the threads of the Teflon reactor screw cap prior to sealing and after sealing, electrical tape was wrapped around the glass Teflon interface prior to removal from the glove box. The vessel was heated to 150 °C while maintaining vigorous stirring. Once the solid material had become bronze in color and all potassium chunks had been intercalated into the graphite, the reaction vessel was returned to the glove box and KC_8 was transferred to an appropriate storage container. All other chemicals were purchased from Strem Chemicals, Acros, Aldrich, or Alfa Aesar and used as received. ¹H and ¹³C NMR spectra were recorded on Bruker 500 or 400 MHz NMR spectrometers. ¹H and ¹³C NMR spectra recorded in C_6D_6 are reported with reference to residual ¹H solvent resonances of C₆D₆ at 7.16 and 128.06 ppm respectively. ¹H NMR spectrum recorded in DMSO-D₆ are reported with reference to residual ¹H solvent resonances of DMSO-D₆ at 2.50 ppm. EPR spectra were recorded using a Bruker Elexsys 500 X-band spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories.

Synthesis of $[(ArO)_2Nb(\mu-Cl)Cl_2]$ (1). A 500 mL round-bottom flask containing a 50 mL orange toluene solution of [Nb(CH₃)₂Cl₃] (1.002 g, 4.369 mmol) was added dropwise a white 100 mL toluene slurry of HOAr (4.206 g, 8.721 mmol) via a glass pipette, resulting in a fast color change to dark-red with effervescence occurring. After stirring for 12 hours at room temperature the reaction mixture was concentrated to approximately 10 mL and approximately 150 mL of pentane was added resulting in the precipitation of a dark-red solid. After stirring for 1 hour the solid was isolated on a medium porosity glass frit and rinsed with 20 mL of pentane. The resulting dark-red solid was dried under reduced pressure yielding 4.702 g of pure material (93% yield). Dark-red single crystals of 1 were grown from cooling a saturated toluene solution layered with pentane to $-37 \,^{\circ}\text{C}$ for three days. Yield = 93% (4.702 g, 2.022 mmol). ¹H NMR (25 °C, 500 MHz, C₆D₆): δ 7.21 (m, 40H, -Ar- H_{ortho} /-Ar- H_{meta}), 7.07 (t, J_{HH} = 7.51 Hz, 32H, -Ar- H_{meta}), 6.99 (t, J_{HH} = 7.51 Hz, 16H, -Ar- H_{para}), 6.57 (s, 8H, -CH(Ph)₂), 0.99 (s, 36H, -C(C H_3)₃). ¹³C {¹H} **NMR (25 °C, 126 MHz, C₆D₆):** δ 159.69 (s, -C_{Ar}), 148.63 (s, -C_{Ar}), 144.27 (s, -C_{Ar}), 135.69 (s, -C_{Ar}), 130.35 (s, -CH_{Ar}), 128.64 (s, -CH_{Ar}), 127.50 (s, -CH_{Ar}), 126.83 (s, -CH_{Ar}), 50.91 (s, -CH(Ph)₂), 34.74 (s, -C(CH₃)₃), 31.12 (s, -C(CH₃)₃). Anal. Calcd. For 1, C₁₄₄H₁₃₂Cl₆Nb₂O₂: C, 74.39; H, 5.72. Found: C, 74.20; H, 5.60.



Figure S1. ¹H NMR spectrum of 1 recorded in C_6D_6 (500 MHz, 25°C).



Figure S2. ¹³C {¹H} NMR spectrum of **1** recorded in C₆D₆ (126 MHz, 25°C).

Synthesis of $[(ArO)_2Nb(\mu-N)]_2$ (2). Method A: To a 20 mL scintillation vial containing a 14 mL dark-red toluene solution of 1 (500 mg, 0.215 mmol) was added 0.5 mL of THF followed by the dropwise addition of a 5 mL toluene suspension of KC_8 (175 mg, 1.295) mmol) via a glass pipette. Addition of KC₈ resulted in several color changes over a period of approximately 1.5 hours occurring in the sequence of dark-red, yellow, green, orange, yellow-brown, and finally to orange-brown. The resulting suspension was stirred for an additional 6.5 hours and then filtered through a celite plug supported on a medium porosity glass frit. All volatiles were removed from the red-purple filtrate under reduced pressure yielding a dark oily residue. Addition of 2 mL of toluene yielded a dark colored solution to which 18 mL of pentane was added. Addition of pentane resulted in the precipitation of a yellow powder. The mixture was stirred for 30 minutes and the yellow solid was collected on a medium porosity glass frit, rinsed with 10 mL of pentane, and dried under reduced pressure yielding 173 mg of pure material. Yellow single crystals of 2 were grown by layering a concentrated toluene solution with pentane and storing at -37°C for 4 days. Isolated yield = 38% (0.173 g, 0.081 mmol). * ¹H NMR spectral analysis of the remaining filtrate revealed the presence of additional 2, however the similar solubility of other co-products has hindered separation. *

Method B: To a 20 mL scintillation vial containing a 15 mL yellow toluene solution of 4 (500 mg, 0.393 mmol) was added dropwise a 5 ml toluene suspension of KC₈ (115 mg, 0.851 mmol) via a glass pipette, resulting in formation of an orange-brown suspension which slowly changed color to red-brown over the duration of 1 hour. After stirring the reaction mixture for an additional 8 hours the resulting red-brown suspension was filtered through a celite plug supported on a medium porosity glass frit. All volatiles were removed from the filtrate under reduced pressure. The oily residue was extracted into 1 mL of toluene and 19 mL of pentane was added to the reaction mixture resulting in the precipitation of a yellow solid. After stirring for 30 minutes the yellow solid was isolated on a medium porosity glass frit, washed with 10 mL of pentane and dried under reduced pressure yielding 150 mg of pure material. Isolated yield = 36% (0.150 g, 0.070 mmol). * ¹*H NMR analysis of the remaining filtrate revealed the presence of additional 2, however the similar solubility of other co-products has hindered separation.* *

Method C: To a J. Young NMR tube containing a 0.5 mL purple C_6D_6 solution of **3** (84 mg, 0.039 mmol) was added a 0.5 mL clear C_6D_6 solution of AgOTf (10 mg, 0.039 mmol) resulting in an immediate color change to yellow accompanied by the formation of insoluble material. After shaking the J. Young NMR tube for approximately 1 minute, all insoluble material was allowed to settle to the bottom of the NMR tube. ¹H NMR analysis indicated clean formation of **2**.

¹**H** NMR (**25** °C, **500** MHz, C₆D₆): δ 7.65 (br, 12H, -Ar-*H*), 7.30 (br, 8H, -Ar-*H*), 7.04 (br, -Ar-*H*), 6.96 (br, -Ar-*H*), 6.88 (br, -Ar-*H*), 6.80 (br, -Ar-*H*), 6.76 (br, -Ar-*H*), 6.69 (br, -Ar-*H*), 6.65 (br, -Ar-*H*), 6.61 (br, -Ar-*H*), 5.20 (br, 8H, -C*H*(Ph)2), 1.15 (s, 36H, -C(CH3)3). ¹³C {¹H} NMR (**25** °C, **126** MHz, C₆D₆): δ 157.12 (s, -CAr), 144.63 (br, -CAr), 144.50 (s, -CAr), 143.53 (br, -CAr), 143.41 (s, -CAr), 143.27 (br, -CAr), 142.00 (br, -CAr), 133.74 (br, -CAr), 133.58 (br, -CAr), 130.43 (br, -CAr), 130.21 (br, -CAr), 129.83 (s, -CAr), 129.41 (br, -CAr), 129.05 (br, -CAr), 128.77 (s, -CAr), 128.71 (br s, -CAr), 128.59 (s, -CAr), 127.52 (s, -CAr), 127.48 (s, -CAr), 127.12 (br, -CAr), 126.85 (s, -CAr), 126.73 (br, -CAr), 126.43 (br, -CAr), 126.10 (br, -CAr) 52.54 (s, -CH(Ph)2), 50.38 (s, -CH(Ph)2), 34.58 (s, -C(CH3)3), 31.53 (s, -C(CH3)3). Attempts to obtain satisfactorily combustion analysis failed. **Anal. Calcd. For 2:** C, 80.80; H, 6.22; N, 1.31. **Found:** C, 77.09; H, 6.47; N, 0.98.



Figure S3. ¹H NMR spectrum of 2 recorded in C_6D_6 (500 MHz, 25°C).



L65 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 ppm

Figure S4. ¹³C {¹H} NMR spectrum of 2 recorded in C_6D_6 (126 MHz, 25°C).

Synthesis of $K[(ArO)_2Nb(\mu-N)]_2$ (3). Method A: During the crystallization of 2 from methods A and B, small amounts of purple single crystals were obtained in varying amounts. The amount of 3 produced from the reaction mixtures is varying and optimization for the direct synthesis of 3 from 1, 4, and 5 is still under investigation. Method B: To a 20 mL scintillation vial containing a 10 mL yellow toluene solution of 2 (158 mg, 0.074 mmol) was added dropwise a 5 ml toluene suspension of KC_8 (10 mg, 0.073 mmol) via a glass pipette, resulting in slow progression to a dark purple suspension over the duration of 20 minutes. After stirring for an additional 40 minutes, the reaction mixture was filtered through a celite plug supported on a medium porosity glass frit and a purple filtrate was obtained. The filtrate was concentrated to approximately 2 mL, layered with pentane, and stored at -37 °C for 24 hours resulting in the formation of purple single crystals. The crystals were isolated on a medium porosity glass frit and dried under reduced pressure yielding 101 mg. The filtrate was concentrated to approximately 1 mL and a second recrystallization yielded an additional 34 mg of purple single crystals. Yield of 3 · toluene = 81% (0.134 g, 0.059 mmol). ¹H NMR (25 °C, 500 MHz, C_6D_6): δ 10.5 $(\Delta v_{1/2} = 394 \text{ Hz}), 9.4 (\Delta v_{1/2} = 593 \text{ Hz}), 6.8 (\Delta v_{1/2} = 127 \text{ Hz}), 1.2 (\Delta v_{1/2} = 35 \text{ Hz}). \mu_{\text{eff}} =$ 1.92 $\mu_{\rm B}$ (C₆D₆, 298 K, Evan's method). Attempts to obtain satisfactorily combustion analysis failed. Anal. Calcd. For 3: C, 79.35; H, 6.10; N, 1.29; N, 1.31. Found: C, C, 77.02; H, 6.18; N, 0.96.



Figure S5. ¹H NMR spectrum of 3 recorded in C₆D₆ (500 MHz, 25°C).



Figure S6. EPR spectrum recorded on a 0.1 mmol toluene solution of **3** at 25 °C (v = 9.4 GHz, MP = 100 mW, MF = 100 KHz, and MA = 20 G), $g_{iso} = 2.097$.

Synthesis of [trans-(ArO)₂NbCl₂(THF)₂] (4). Method A: To a 20 mL scintillation vial containing a dark red 15 mL THF solution of 1 (500 mg, 0.215 mmol) was added dropwise a 5 mL THF suspension of KC_8 (58 mg, 0.431 mmol) resulting in a color change to an orange-brown suspension over the duration of 20 minutes. The reaction was stirred for 1 hour followed by filtration through a celite plug supported on a medium porosity glass frit. All volatiles of the filtrate were removed under reduced pressure and the resulting orange-brown solid was extracted into 20 mL of toluene and filtered through a celite plug supported on a medium porosity glass frit. The filtrate was concentrated to approximately 4 mL and 16 mL of pentane was added, resulting in the precipitation of a yellow solid. After stirring for 1 hour, the solid was isolated on a medium porosity glass frit and washed with 20 mL of pentane. The resulting solid was dried under reduced pressure yielding 309 mg of yellow powder. Yellow single crystals of 4 were grown from layering a concentrated benzene solution with pentane stored at room temperature. Yield = 57% (0.309 g, 0.243 mmol). Method B: A 500 mL round-bottom flask containing a 50 mL yellow THF slurry of NbCl₄(THF)₂ (1.467 g, 3.871 mmol) was added dropwise a light yellow 150 mL THF solution of NaOAr (3.910 g, 7.748 mmol) via a glass pipette, resulting in a color change to an orange-brown suspension. After stirring for 8 hours all solvent was removed under reduced pressure. The resulting solid was extracted into 100 mL of toluene and filtered through a celite plug supported on a medium porosity glass frit. The filtrate was concentrated to approximately 40 mL and 160 mL of pentane was added, resulting in the precipitation of a yellow solid. After stirring for 1 hour, the yellow solid was isolated on a medium porosity glass frit and washed with 40 mL of pentane. The resulting solid was dried under reduced pressure yielding 3.706 g of yellow powder. The filtrate was further concentrated to approximately 10 mL and added 30 mL of pentane resulting in precipitation of yellow solid. After stirring for 30 minutes, the yellow solid was isolated on a medium porosity glass frit and rinsed with 20 mL of pentane. The yellow solid was dried under reduced pressure yielding an additional 0.674 g of product. Yield = 89% (4.380 g, 3.445 mmol). ¹H NMR (25 °C, 500 MHz, C_6D_6): δ 7.5 ($\Delta v_{1/2}$ = 296 Hz), 7.0 ($\Delta v_{1/2} = 49$ Hz), 4.0 ($\Delta v_{1/2} = 730$ Hz), 0.9 ($\Delta v_{1/2} = 17$ Hz). $\mu_{eff} = 1.87 \ \mu_{B}$ (C₆D₆, 298 K, Evan's method). Anal. Calcd. For 4, C₈₀H₈₂Cl₂NbO₄: C, 75.58; H, 6.50. Found: C, 75.29; H, 6.69.



Figure S7. ¹H NMR spectrum of 4 recorded in C₆D₆ (500 MHz, 25°C).



Figure S8. EPR spectrum recorded on a 1.0 mmol toluene solution of 4 at 25 °C (v = 9.4 GHz, P = 20 mW, MF = 100 KHz, and MA = 20 G), $g_{iso} = 1.984$.

Synthesis of $K_3[(ArO)_4Nb_2(\mu-Cl)_3Cl_2]$ (5). To a 20 mL scintillation vial containing a 15 mL dark red toluene solution of 1 (500 mg, 0.215 mmol) was added dropwise a 5 mL toluene suspension of KC₈ (116 mg, 0.860 mmol) via a glass pipette. During the addition, the dark red solution slowly progressed to a dark yellow suspension and finally to a dark green suspension after complete addition of KC₈. After stirring for 1 hour the reaction mixture was filtered through a celite plug supported on a medium porosity glass frit. The resulting green filtrate was concentrated to approximately 5 mL and stored at -37 °C for 12 hours. The solution was subsequently filtered through a medium porosity glass frit, separating a yellow solid from the green filtrate. The filtrate was concentrated to approximately 2 mL and 15 mL of pentane was added resulting in the precipitation of green microcrystalline material. After stirring for approximately 20 minutes the green solid was isolated on a medium porosity glass frit. The resulting solid was dried under reduced pressure yielding 309 mg of pure material (60 % yield). Green single crystals of 5 were obtained by layering a concentrated toluene solution with pentane and storing at room temperature for 5 hours. Yield = 60% (0.309 g, 0.128 mmol). ¹H NMR (25 °C, 500 **MHz**, C₆D₆): δ 8.47 (m, 1H, -Ar-H), 8.15 (m, 1H, -Ar-H), 8.02 (br, 1H, -Ar-H), 7.95 (br, 2H, -Ar-H), 7.89 (m, 2H, -Ar-H), 7.71 (m, 5H, -Ar-H), 7.50 (m, 5H, -Ar-H), 7.44 (br, 2H, -Ar-H), 7.43-7.17 (m, 22H, -Ar-H), 7.11-6.18 (m, 53H, -Ar-H), 6.10 (m, 2H, -Ar-H), 1.32 (s, 9H, -C(CH₃)₃), 1.23 (s, 9H, -C(CH₃)₃), 0.97 (s, 9H, -C(CH₃)₃), 0.99 (s, 9H, - $C(CH_3)_3$). ¹³C {¹H} NMR (25 °C, 126 MHz, C₆D₆): δ 173.34 (s, -CAr), 163.93 (s, -CAr), 162.72 (s, -CAr), 161.04 (s, -CAr), 158.92 (s, -CAr), 158.87 (s, -CAr), 158.01 (s, -CAr), 157.92 (s, -CAr), 156.04 (s, -CAr), 155.08 (s, -CAr), 154.43 (s, -CAr), 153.80 (s, -CAr), 150.32 (s, -CAr), 149.53 (s, -CAr), 149.45 (s, -CAr), 148.97 (s, -CAr), 148.78 (s, -CAr), 148.61 (s, -CAr), 147.60 (s, -CAr), 147.49 (s, -CAr), 147.42 (s, -CAr), 147.27 (s, -CAr), 146.63 (s, -CAr), 146.10 (s, -CAr), 146.06 (s, -CAr), 145.75 (s, -CAr), 145.19 (s, -CAr), 145.16 (s, -CAr), 143.41 (s, -CAr), 142.91 (s, -CAr), 139.68 (s, -CAr), 138.82 (s, -CAr), 137.70 (s, -CAr), 134.67 (s, -CAr), 133.77 (s, -CAr), 132.98 (s, -CAr), 132.33 (s, -CAr), 131.18 (s, -CAr), 130.94 (s, -CAr), 130.52 (s, -CAr), 130.03 (s, -CAr), 129.82 (s, -CAr), 129.17 (s, -CAr), 128.93 (s, -CAr), 128.82 (s, -CAr), 128.76 (s, -CAr), 128.61 (s, -CAr), 128.43 (s, -CAr), 127.67 (s, -CAr), 127.52 (s, -CAr), 127.49 (s, -CAr), 127.30 (s, -CAr), 127.21 (s, -CAr), 127.14 (s, -CAr), 127.07 (s, -CAr), 126.88 (s, -CAr), 126.61 (s, -CAr),

126.50 (s, -CAr), 126.04 (s, -CAr), 125.81 (s, -CAr), 125.47 (s, -CAr), 125.41 (s, -CAr), 125.30 (s, -CAr), 125.18 (s, -CAr), 124.66 (s, -CAr), 124.32 (s, -CAr), 123.97 (s, -CAr), 123.91 (s, -CAr), 121.78 (s, -CAr), 52.88 (s, -CH(Ph)₂), 51.38 (s, -CH(Ph)₂), 49.99 (s, -CH(Ph)₂), 48.92 (s, -CH(Ph)₂), 48.65 (s, -CH(Ph)₂), 48.41 (s, -CH(Ph)₂), 47.88 (s, -CH(Ph)₂), 46.20 (s, -CH(Ph)₂), 34.28 (s, -C(CH₃)₃), 34.24 (s, -C(CH₃)₃), 34.20 (s, -C(CH₃)₃), 32.24 (s, -C(CH₃)₃), 31.94 (s, -C(CH₃)₃), 31.62 (s, -C(CH₃)₃). Attempts to obtain satisfactorily combustion analysis failed. **Anal. Calcd. For 5:** C, 71.86; H, 5.53; N, 0.00; **Found:** C, 70.48; H 5.75; N, <0.02.



Figure S9. ¹H NMR spectrum of **5** recorded in C_6D_6 (500 MHz, 25°C).



Figure S10. ¹³C {¹H} NMR spectrum of 5 recorded in C_6D_6 (126 MHz, 25°C).

NH₄Cl Production from Complexes 2 and 3. A 20 mL toluene solution containing either 2 or 3 (0.050 g, 0.023 mmol) was transferred to a 100 mL Schlenk flask inside of a glove box. The flask was then connected to a schlenk line and using schlenk technique 100 equivalents of anhydrous 1 M HCl(OEt₂) in Et₂O was added via a syringe. Upon addition, the yellow and purple toluene solutions of 2 and 3, respectively, rapidly changed color to an orange-red solution. After stirring for 1 hour, all volatiles were removed under reduced pressure. The contents of the flask were then exposed to atmospheric conditions and approximately 0.5 mL of DMSO-D₆ was added to the flask resulting in a color change to greenish-yellow. ¹H NMR analysis of the reaction mixtures revealed formation of NH₄Cl and HOAr in a 1:2 ratio. ¹H NMR (25 °C, 500 MHz, DMSO-D₆): δ 8.39 (br, -O*H*), 7.49 (t, ¹J_{NH} = 50.5 Hz, 4H, -N*H*₄), 7.26 (t, J_{HH} = 7.13 Hz, 16H -Ar-*H_{meta}*) 7.16 (t, J_{HH} = 6.92 Hz, 8H -Ar-*H_{para}*), 7.04 (d, J_{HH} = 7.29 Hz, 16H, -Ar-*H_{ortho}*), 6.99 (s, 4H, -Ar-*H_{meta}*), 5.99 (s, 4H, -C*H*(Ph)₂), 0.95 (s, 18H, -C(CH₃)₃).



Figure S11. ¹H NMR spectrum of NH₄Cl and HOAr (1:2 ratio) produced from either 2 or 3 recorded in DMSO-D₆.

Crystallographic Details. Suitable crystals for analysis of complex 1 and 4 were placed onto the tip of a MiTeGen loop coated in NVH oil and mounted on an Apex Kappa Duo diffractometer. The data collection was carried out at 150 K using Mo Ka radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50° steps in ω and ϕ scans. Final cell constants were calculated from the xyz centroids of a particular number of strong reflections for each crystal from the actual data collection after integration using SAINT.⁴ The intensity data were corrected for absorption using SADABS.⁵ The space group was determined based on intensity statistics and systematic absences. The structures were solved using SIR-92⁶ and refined (fullmatrix-least squares) using either SHELXL-977 or Oxford University Crystals for Windows system.⁸ A direct-methods solution was calculated, which provided most nonhydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms. Suitable crystals for analysis of complexes 2, 3, and 5 were mounted on the end of a Cryoloop coated in NVH oil and data collection was performed using a Bruker APEXII CCD area detector employing Mo Kα radiation (graphite monochromator) at a temperature of 100 K. Rotation frames were integrated using SAINT,⁴ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL⁹ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS¹⁰ or SADABS.⁵ The structures were solved by direct methods using SHELXS-97.7 Refinement was by full-matrix least-squares based on F^2 using SHELXL-97.⁷ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

	1	2	3
molecular formula	$C_{165}H_{156}Cl_6Nb_2O_4$	$C_{151}H_{140}N_2Nb_2O_2$	$C_{144}H_{132}KN_2Nb_2O_4$
formula weight	2601.42	2232.47	2179.44
temp (K)	150	100	100
crystal system	monoclinic	orthorhombic	Cubic
space group	P2/c	Pbca	<i>I</i> 23
cell constants			
<i>a</i> (Å)	18.1297(8)	24.6450(6)	46.870(2)
<i>b</i> (Å)	15.6334(8)	25.8062(5)	46.870(2)
<i>c</i> (Å)	26.0900(12)	37.2338(8)	46.870(2)
α (deg)	90	90	90
β (deg)	93.396(3)	90	90
$\gamma(\text{deg})$	90	90	90
Ζ	2	8	24
V (Å ³)	7381.7(6)	23680.5(9)	102999(8)
abs coeff (mm ⁻¹)	0.266	0.252	0.196
calcd density (g/cm ³)	1.170	1.252	0.843
<i>F</i> (000)	2724	9392	27432
crystal dimensions	0.12x0.12x0.24	0.10x0.25x0.38	0.10x0.12x0.15
(mm)			
wavelength (Å)	0.71073	0.71073	0.71073
<i>h,k,l</i> ranges collected	$-20 \le h \le 18$	$-32 \le h \le 31$	$-46 \le h \le 42$
	$-16 \le k \le 17$	$-33 \le k \le 33$	$-27 \le k \le 60$
	$-28 \le l \le 29$	$-48 \le l \le 48$	$-37 \le l \le 60$
θ range for data	2.44 to 61.31	1.37 to 27.62	1.37 to 27.52
collection (deg)			
number of reflns collected	44783	407228	186663
number of unique reflns	11303	27382	39376

 Table S1. Crystallographic Parameters for Complexes 1-3

number of parameters	811	1430	1427
data to parameter ratio	11303/811	27382/1430	39376/1427
refinement method	Full-matrix	Full-matrix	Full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2
R_I^a	0.0645	0.0920	0.0828
wR_2^{b}	0.2116	0.3249	0.2154
Goodness-of-fit on F^{2c}	1.062	1.041	0.909
	4	5	
molecular formula	$C_{92}H_{94}Cl_2NbO_4$	$C_{149}H_{144}Cl_5K_3Nb_2O_4$	
formula weight	1427.57	2479.01	
temp (K)	150	100	
crystal system	monoclinic	triclinic	
space group	$P2_l/n$	<i>P</i> -1	
cell constants			
<i>a</i> (Å)	15.8132(5)	16.7009(14)	
<i>b</i> (Å)	14.3842(4)	17.9962(15)	
<i>c</i> (Å)	17.9828(5)	24.535(2)	
α (deg)	90	92.288(4)	
$\beta(\text{deg})$	111.412(2)	100.453(4)	
$\gamma(\text{deg})$	90	114.629(4)	
Ζ	2	2	
V (Å ³)	3808.3(2)	6536.7(9)	
abs coeff (mm ⁻¹)	0.280	0.426	
calcd density (g/cm ³)	1.245	1.260	
<i>F</i> (000)	1506	2588	
crystal dimensions	not measured	0.05x0.30x0.38	
(mm)			
wavelength (Å)	0.71073	0.71073	
<i>h</i> , <i>k</i> , <i>l</i> ranges collected	$-22 \le h \le 19$	$-21 \le h \le 21$	
	$-19 \le k \le 20$	$-22 \le k \le 23$	

	$-25 \le l \le 25$	$-31 \le l \le 32$	
θ range for data	1.47 to 30.09	1.37 to 27.73	
collection (deg)			
number of reflns	444469	161655	
collected			
number of unique reflns	11194	30335	
number of parameters	467	1483	
data to parameter ratio	11194/467	30335/1483	
refinement method	Full-matrix	Full-matrix	
	least-squares on F^2	least-squares on F^2	
R_I^a	0.0324	0.0415	
wR_2^b	0.0880	0.1301	
Goodness-of-fit on F^{2c}	1.054	1.050	

^{*a*} $R_1 = (|F_o| - |F_c|) / |F_o|$. ^{*b*} $wR_2 = [[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]]^{1/2}$. ^{*c*} Goodness-of-fit = $[[w(F_o^2 - F_c^2)^2]/N_{observns} N_{params})]^{1/2}$, all data.



Figure S12. Molecular structure of **1** with thermal ellipsoide at the 50% probability level. All hydrogens have been omitted for clarity.



Figure S13. Molecular structure of **4** with thermal ellipsoide at the 50% probability level. All hydrogens have been omitted for clarity.

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