

Supporting Information

Reduction of carbon monoxide by a tetrakis(aryloxy) diniobium having four bridging hydrides

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Fig. S1 Molecular structure of 1.

Experimental Section

General procedure

All manipulations were carried out using standard Schlenk techniques or in a glove-box under argon atmosphere. Anhydrous hexane, pentane and toluene were dried by passage through two columns of activated alumina and a Q-5 column, while anhydrous THF was dried by passage through two columns of activated alumina. Anhydrous benzene and deuterated benzene (benzene- d_6) were dried and degassed over a potassium mirror prior to use. Deuterated toluene (toluene- d_8) was distilled from calcium hydride prior to use. The lithium salt of 2,6-diadamantyl-*p*-cresol (ArOH) and $\text{NbCl}_4(\text{thf})_2$ were prepared by the literature procedure.^{1,2} ^1H and ^{13}C NMR spectra were recorded on JEOL ECX-400 spectrometer. All spectra were referenced to residual protiosolvent (^1H , $\text{C}_6\text{D}_5\text{H}$ in C_6D_6 , ^1H (δ) = 7.15; $\text{C}_7\text{D}_7\text{H}$ in toluene- d_8 , ^1H (δ) = 2.08, 6.97, 7.01, 7.09), solvent (^{13}C). Infrared samples were recorded between KBr Plates using a JASCO FT/IR-410 spectrometer. Elemental analyses (C and H) were carried out on an Elementar VarioMicroCube. Solid-state magnetic susceptibilities were measured on a Sherwood Scientific MSB-AUTO at ambient temperature. Corrections were applied for diamagnetism calculated for Pascal constants.

Synthesis of $(\text{ArO})_2\text{NbCl}_2$ (**1**)

A solid of $\text{NbCl}_4(\text{thf})_2$ (572 mg, 1.51 mmol) was added in portions to a stirring solution of $\text{ArOLi}(\text{thf})_2$ (1.59 g, 3.02 mmol) in THF (40 mL) at room temperature, giving a yellow-brown slurry. The mixture was stirred for 18 h, during which time the solution became green in color and homogeneous. After removal of volatiles under vacuum, the green residue was extracted with toluene (100 mL) and centrifuged to remove an insoluble material. The green supernatant was evaporated to dryness, and the residue was washed with hexane to afford an olive green powder of **1** (834 mg, 912 μmol , 60%).

^1H NMR (400 MHz, C_6D_6): δ -0.84 (br), 1.87 (br), 2.58 (br), 4.73 (br). Anal. Calcd for $\text{C}_{54}\text{H}_{70}\text{Cl}_2\text{O}_2\text{Nb}_2$: C, 70.89; H, 7.71. Found: C, 70.92; H, 8.01. $\mu_{\text{eff}} = 1.75 \mu_{\text{B}}$.

Synthesis of $[(^{\text{Ad}}\text{ArO})_2\text{Nb}]_2(\mu\text{-H})_4$ (**2**)

A THF solution of KBHET_3 (1.0 M, 2.35 mL, 2.35 mmol) was added dropwise to **1** (1.01 g, 1.10 mmol) in THF (30 mL) at -78°C . The mixture was allowed to warm to room temperature and

the color of the mixture gradually changed from green to yellow-brown. After stirring for additional 18 h at room temperature, all volatiles were removed in vacuo to leave a yellow-brown solid. The residue was extracted with toluene (10 mL) and centrifuged to remove an insoluble material. Evaporation of toluene and washing the resulting solid with hexane afforded a yellow-brown powder of **2** (763 mg, 451 μmol , 82%).

^1H NMR (400 MHz, C_6D_6): δ 1.63 (br, 24H, Ad), 1.76 (br, 24H, Ad), 1.99 (br, 24H, Ad), 2.18 (br, 6H, Ad), 2.21 (br, 6H, Ad), 2.32 (s, 12H, *p*Me), 2.36 (br, 48H, Ad), 7.00 (s, 4H, *m*H), 7.02 (s, 4H, *m*H), 9.16 (br, 4H, NbH). ^{13}C NMR (100 MHz, C_6D_6): δ 21.0, 22.7 (*p*Me), 29.2, 29.6, 36.7, 37.2, 39.0 - 44.0 (Ad), 127.0 - 129.7, 137.1, 139.9, 161.3 (Ar). Anal. Calcd for $\text{C}_{108}\text{H}_{144}\text{O}_4\text{Nb}_2$: C, 76.66; H, 8.58. Found: C, 76.75; H, 8.77.

The reaction of **2** with ^{13}CO monitored by NMR spectroscopy

A J. Young valve NMR tube was charged with **2** (35 mg, 21 μmol) and toluene- d_8 (0.5 mL). The headspace was evacuated and an atmosphere of ^{13}CO (1 atm) was introduced. The mixture was allowed to stand at room temperature. After 1 h, the mixture turned from yellow-brown to red-brown along with a brown precipitate, and its NMR spectra displayed formation of $[(\text{ArO})_2\text{Nb}][(\text{ArO})\text{Nb}(\text{O})][\mu\text{-C}=\text{C}(\text{H})\text{-ArO}](\mu\text{-O})$ (**3**) and $[(\text{ArO})_2\text{Nb}]_2(\mu\text{-CH}_2)(\mu\text{-O})$ (**4**). After 24h, the resonances due to **4** disappeared, and **3** was observed as a sole product.

^1H NMR (400 MHz, toluene- d_8 , selected data): δ 5.10 (d, $^1J_{\text{CH}} = 120$ Hz, NbCH₂ of **4**), 9.18 (d, $^1J_{\text{CH}} = 156$ Hz, C=C(*H*)-Ar of **3**). ^{13}C NMR (100 MHz, toluene- d_8 , selected data): δ 159.5 (br, NbCH₂ of **4**), 157.6 (d, $^1J_{\text{CC}} = 54$ Hz, C=C(*H*)-Ar of **3**), 281.9 (br d, C=C(*H*)-Ar of **3**). Selected ^1H , ^{13}C HMQC NMR chemical shifts (400 MHz, THF- d_8 , -30 °C): δ ^1H (δ ^{13}C) 5.10 (159.5), 9.18 (157.6).

Synthesis of $[(\text{ArO})_2\text{Nb}][(\text{ArO})\text{Nb}(\text{O})][\mu\text{-C}=\text{C}(\text{H})\text{-ArO}](\mu\text{-O})$ (**3**)

A 50 mL flask was charged with **4** (120 mg, 69.8 μmol) and toluene (20 mL). The headspace was evacuated, and an atmosphere of CO (1 atm) was introduced. The brown suspension was stirred at room temperature for 24 h, producing a homogeneous red-wine solution. The reaction mixture was evaporated to dryness, extracted with pentane (5 mL), and then filtered with a PTFE

membrane filter (0.45 μm). Upon standing the filtrate at -30°C for 24 h, a red-brown powder of **3** precipitated (57.7 mg, 35.8 μmol , 52%).

^1H NMR (400 MHz, toluene- d_8): δ 1.33 (br, 3H, Ad), 1.40 (br, 3H, Ad), 1.51 (br, 3H, Ad), 1.61, 1.71, 1.78, 2.01, 2.08, 2.27, 2.34 (overlapped, *p*Me, Ad and toluene- d_8), 2.67 (br, 3H, Ad), 2.72 (br, 3H, Ad), 6.88, 6.97, 7.01, 7.09, 7.16, 7.22 (overlapped, *m*H and toluene- d_8), 9.18 (s, 1H, *m*H), 7.08 (s, 2H, *m*H), 7.19 (s, 1H, C=C(*H*)-Ar). ^{13}C NMR (100 MHz, toluene- d_8): δ 19.8 – 20.9 (*p*Me and toluene- d_8), 29.5, 29.6, 29.7, 30.2, 32.0, 37.1, 37.4, 39.0, 41.8, 42.1, 43.2, 43.9 (Ad), 124.9 – 129.1 (Ar and toluene- d_8). Anal. Calcd for $\text{C}_{100}\text{H}_{126}\text{O}_6\text{Nb}_2$: C, 74.61; H, 7.89. found: C, 74.61; H, 7.80. IR (KBr) / cm^{-1} ; 748 (Nb-O-Nb), 943 (Nb=O).

Synthesis of $[(\text{ArO})_2\text{Nb}]_2(\mu\text{-CH}_2)(\mu\text{-O})$ (**4**)

A 50 mL flask was charged with **2** (350 mg, 207 μmol) and benzene (20 mL). The headspace was evacuated, and an atmosphere of CO (1 atm) was introduced. The yellow-brown solution was stirred at room temperature for 1h, during which time a brown precipitate formed. The precipitate was collected by centrifugation and washed with hexane to give **4** as a red-brown powder (197 mg, 115 μmol , 56%).

^1H NMR (400 MHz, C_6D_6): δ 1.22 (br, 6H, Ad), 1.53, 1.71, 1.76, 1.81, 1.87, 1.90, 1.94, 1.98, 2.08, 2.14, 2.20, 2.24, 2.30, 2.32, 2.33, 2.36 (overlapped, *p*Me and Ad), 2.91 (br, 6H, Ad), 2.94 (br, 6H, Ad), 2.97 (br, 3H, Ad), 3.00 (br, 3H, Ad), 3.11 (br, 3H, Ad), 3.13 (br, 3H, Ad), 5.10 (s, 2H, NbCH₂), 6.96 (s, 2H, *m*H), 7.02 (s, 2H, *m*H), 7.08 (s, 2H, *m*H), 7.19 (s, 2H, *m*H). Anal. Calcd for $\text{C}_{109}\text{H}_{142}\text{O}_5\text{Nb}_2$: C, 76.20; H, 8.33. found: C, 76.44; H, 8.18. Solubility constraints prevent us from acquiring the ^{13}C NMR spectrum of **4**. IR (KBr) / cm^{-1} ; 674 (Nb-O-Nb-O).

X-ray crystallographic analysis

Crystallographic data for **1**, **2**, **3** and **4** are summarized Table S1. Single crystals of **1**, **2**, **3** and **4** were obtained from THF/hexane, benzene/pentane, benzene/hexane and toluene, respectively. Crystals of these complexes were immersed in mineral oil on nylon loop and transferred to a Rigaku Saturn CCD system for **2** and **4**, and to a Rigaku Mercury CCD system for **1** and **3** equipped with a Rigaku GNNP low-temperature device. Data were collected under cold nitrogen stream (123 K) using graphite-monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). Equivalent reflections were

merged, and the images were processed with the CrystalClear (Rigaku) Program. Corrections for Lorentz-polarization effects and absorption were performed.

All calculations were performed using SHELXS³ and SHELXL⁴. The structures were solved by Patterson and Fourier transform methods. For **1**, three sites occupied by THF were identified in the asymmetric unit. Two of these sites were fully occupied by 1.5 THF molecules. The other site contains considerably disordered THF molecules and was treated by SQUEEZE as a diffuse contribution.^{5,6} In the void space, a contribution of 52 e⁻ per unit cell was found and taken to represent 0.5 THF molecules for each Nb complex, giving a total of 2 THF in the asymmetric unit. For **2**, three of adamantyl groups were rotationally disordered with typical fashion and one of benzene molecule was fixed with a rigid group model. For **4**, niobium centers were disordered over two positions and one of adamantyl group was rotationally disordered with typical fashion. Six sites occupied by toluene were identified in the asymmetric unit. Two of these sites were fully occupied by two toluene molecules. The other sites contain considerably disordered toluene molecules and were treated by SQUEEZE again. In the void space, a contribution of 288 e⁻ per unit cell was found and taken to represent 1.5 toluene molecules for each Nb₂ complex, giving a total of 3.5 toluene in the asymmetric unit. All non-hydrogen atoms are refined anisotropically, with exception of disordered atoms that were refined isotropically. All carbon-bound hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. In the case of metal-bound hydrides and the proton of the vinyl unit, the positions of these atoms were found in the Fourier map.

These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disorder of adamantyl groups and crystal solvents. The large values of the second parameter on the SHELXL weighting are due to the poor quality of crystals.

References

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Table S1. Crystallographic Data for **1**, **2**, **3** and **4**.

	1	2	3
Formula	C ₆₂ H ₈₆ O ₄ Cl ₂ Nb	C ₁₁₉ H ₁₆₂ O ₄ Nb ₂	C ₁₂₁ H ₁₆₇ O ₆ Nb ₂
<i>M</i>	1059.12	1842.31	1903.37
<i>T</i> /K	123(2)	123(2)	123(2)
Color	green	yellow	red
Crystal size/mm ³	0.12 x 0.11 x 0.02	0.12 x 0.09 x 0.04	0.11 x 0.04 x 0.03
Crystal system	<i>Monoclinic</i>	<i>Monoclinic</i>	<i>Triclinic</i>
Space group	<i>P2/a</i> (No. 13)	<i>P2₁/a</i> (No. 14)	<i>P-1</i> (No. 2)
<i>a</i> /Å	21.571(8)	14.635(2)	17.793(7)
<i>b</i> /Å	10.906(4)	17.948(3)	17.972(7)
<i>c</i> /Å	24.181(9)	35.657(5)	18.964(7)
α /°	90	90	58.272(11)
β /°	110.853(3)	93.768(3)	74.032(18)
γ /°	90	90	83.67(2)
<i>V</i> /Å ³	5316(3)	9584(2)	4955(3)
<i>Z</i>	4	4	2
<i>D_c</i> /g cm ⁻³	1.323	1.277	1.276
μ /mm ⁻¹	0.375	0.295	0.289
Reflections collected	52911	79045	53106
Independent reflections (<i>R</i> _{int})	12181 (0.1129)	21925 (0.0585)	22676 (0.1109)
Refined parameters	598	1067	1052
Goodness-of-fit on <i>F</i> ²	1.073	1.070	1.055
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0770	0.0780	0.0848
w <i>R</i> ₂ (all data) ^b	0.2170	0.2166	0.2435
Largest diff. peak and hole/e Å ⁻³	1.386 and -0.809	1.794 and -1.085	1.347 and -1.098

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$

Table S1. Crystallographic Data for **1**, **2**, **3** and **4**. (Cont.)

4	
Formula	C _{133.5} H ₁₇₀ O ₅ Nb ₂
<i>M</i>	2040.52
<i>T</i> /K	123(2)
Color	brown
Crystal size/mm ³	0.11 x 0.09 x 0.05
Crystal system	<i>Monoclinic</i>
Space group	<i>C2/c</i> (No. 15)
<i>a</i> /Å	20.333(3)
<i>b</i> /Å	25.833(5)
<i>c</i> /Å	21.541(4)
α /°	90
β /°	90.185(3)
γ /°	90
<i>V</i> /Å ³	11314(3)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.198
μ /mm ⁻¹	0.257
Reflections collected	69689
Independent reflections (<i>R</i> _{int})	12895 (0.0735)
Refined parameters	759
Goodness-of-fit on <i>F</i> ²	1.070
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0803
w <i>R</i> ₂ (all data) ^b	0.2148
Largest diff. peak and hole/e Å ⁻³	0.881 and -0.740

^a $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, ^b $wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{0.5}$

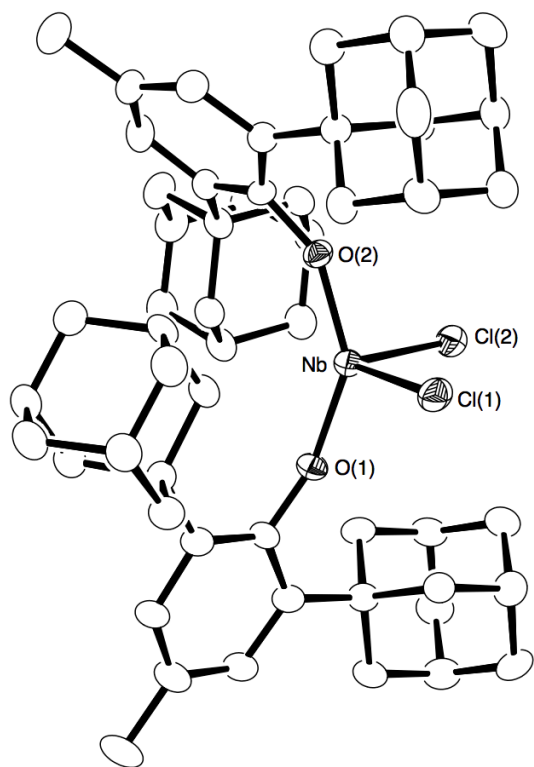


Fig. S1 Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected metric parameters (\AA , $^\circ$): Nb–O(1), 1.868(3); Nb–O(2), 1.879(3); Nb–Cl(1), 2.3411(14); Nb–Cl(2), 2.3493(15); O(1)–Nb–O(2), 145.30(13); Cl(1)–Nb–Cl(2), 95.23(10); Nb–O(1)–C(1), 158.6(3); Nb–O(2)–C(28), 153.0(3).