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Reduction of (^{t}BuN$=$)NbCl$_3$(py)$_2$ in a Salt-Free Manner for Generating Nb(IV) Dinuclear Complexes and Their Reactivity toward Benzo[*c*]cinnoline

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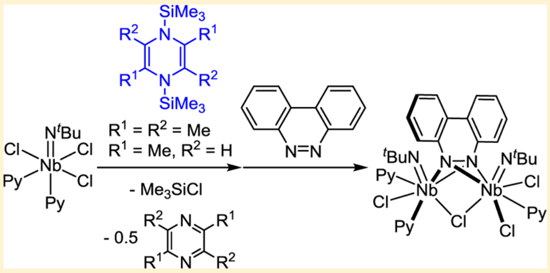
Supporting Information

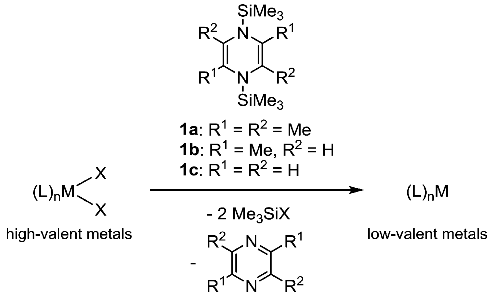
ABSTRACT: The organosilicon reducing reagent 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1a**) was used for the one-electron, salt-free reduction of (^{t}BuN$=$)NbCl$_3$(py)$_2$ (**2**), resulting in the formation of a neutral, triply chloride-bridged dinuclear niobium(IV) complex, [(^{t}BuN$=$)ClNb(py)](μ-Cl)$_3$[(^{t}BuN$=$)Nb(py)$_2$] (**3**) in moderately high yield. Heating **3** in toluene at 80 °C caused a unique intramolecular rearrangement of **3** to another neutral dinuclear complex, [Cl$_2$Nb(py)](μ-Cl)(μ-N^{t}Bu)$_2$[ClNb(py)$_2$] (**4**), in which two niobium(IV) atoms were bridged by one chloride atom and two imido ligands. Reaction of complex **3** with benzo[*c*]cinnoline produced a benzo[*c*]cinnoline-bridged dinuclear niobium(V) complex **7** by an overall two-electron reduction of benzo[*c*]cinnoline through a disproportionation of **3** into a mixture of a niobium(V) complex **2** and a niobium(III) complex, the latter of which efficiently reduced benzo[*c*]cinnoline.



INTRODUCTION

Low-valent early transition metal complexes bearing *N*-arylimido and *N*-alkylimido ligands have attracted continuing interest owing to their ability to activate small molecules due to the strongly electron-donating nature of the imido ligands.[1−3] Electron-rich Nb(III) species are capable of performing activation of alkynes, arenes, and white phosphorus as well as cleavage of carbon−nitrogen double bonds and carbon−fluorine bonds.[2d] However, since early transition metals favor a high oxidation state, reduction of high-valent (imido)metal complexes often requires strong reducing reagents containing alkali or alkaline earth metals; as a result, contamination by reductant-derived metal salts is often unavoidable and frequently hampers any isolation of the metal complexes in pure form.[4] While some methods of avoiding or separating salt-contact complexes of early transition metals, such as hydrogenolysis of metal bis(alkyl) complexes or removal of alkali metal ions with crown ethers, exist, these methods typically require additional synthetic steps, lowering yield and creating more waste. In this context, we recently developed a salt-free reduction method using organosilicon-based compounds for early transition metal halide complexes:[5] simple addition of 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1a**) and its derivative **1b** to group 4−6 metal halide complexes supported by Cp or phosphine ligands led to the formation of corresponding low-valent metal complexes (Scheme 1).[5d] Motivated by the success of these organosilicon reagents in reducing high-valent early transition metal complexes, we targeted the salt-free reduction of early transition metal halides supported by strongly donating imido ligands. Herein, we report a salt-free reduction of (*N-tert*-butylimido)niobium trichloride using organosilicon compounds **1a** and **1b** as reductants to form niobium(IV) complexes.

Scheme 1. Reduction of Early Transition Metal Species by Organosilicon Reductants 1



RESULTS AND DISCUSSION

Reaction of (^{t}BuN$=$)NbCl$_3$(py)$_2$ (**2**) with 0.5 equiv of **1a** in toluene at room temperature afforded the chloride-bridged dinuclear niobium(IV) complex **3** as a poorly soluble purple precipitate in 90% yield (eq 1). Under these reaction

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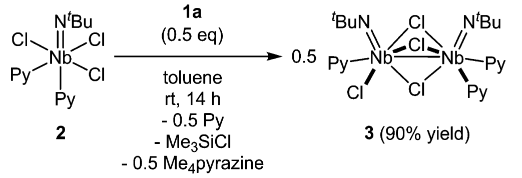
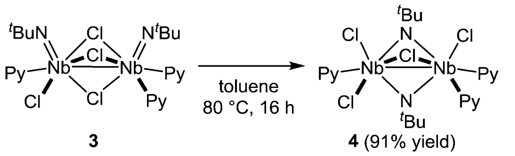
conditions, full consumption of **1a** was confirmed by the ^{1}H NMR spectrum, which showed 1 equiv of Me_3SiCl, 0.5 equiv of pyridine, and 0.5 equiv of 2,3,5,6-tetramethylpyrazine (Me_4pyrazine) relative to **2**. Similarly, the reaction of **2** with **1b** produced **3** in 85% yield, while the reaction of **2** with nonmethylated reductant **1c** did not give any conversion to **3** (*vide infra*). The ^{1}H NMR spectrum of complex **3** displayed two singlet resonances at 1.60 and 1.71 ppm due to two ^{t}Bu groups and three sets of resonances assignable to the three coordinating pyridine ligands based on the 2:3 molar ratio of the ^{t}Bu group and the coordinating pyridine. The structure of complex **3** could not be determined solely on the basis of NMR data; however, its asymmetric dinuclear structure was confirmed by a single crystal X-ray diffraction study.



(1)

The X-ray diffraction study of **3** clarified the connectivity of the overall structure, and the ORTEP drawing of **3** is shown in Supporting Information due to the low quality of the data. The niobium atoms are bridged by three chloride ligands to form a bifacial octahedral geometry. One niobium atom is coordinated by one terminal chloride ligand and one pyridine, while the other possesses two pyridine ligands without any terminal chlorides. Such an asymmetrical structure is in good accordance with its ^{1}H NMR spectrum. The distance between two niobium metal atoms (2.9657(13) Å) in **3** is longer than that of other chloride-bridged Nb(IV) dinuclear complexes that contain a Nb–Nb single bond such as $Nb_2(\mu\text{-}Cl)_4Cl_4(L)_2$ (L = PR_3, 2.7949–2.838 Å),[6] but is significantly shorter than that of chloride-bridged dinuclear Nb(V) complexes (4.096–4.132 Å);[7] these data imply that there is an electronic interaction between two Nb(IV) atoms of **3**.

Complex **3** was stable enough at room temperature in toluene to be isolated; however, prolonged heating of a suspension of **3** in toluene at 80 °C for 16 h resulted in a color change from purple to orange, followed by precipitation of complex **4** from the reaction mixture as an orange crystalline solid in 91% yield (eq 2). Complex **4** was insoluble in C_6D_6, toluene, THF, chloroform, dichloromethane, and acetonitrile, preventing characterization by solution NMR. Hence, characterization of **4** was limited to an X-ray diffraction study and combustion analysis.



(2)

Figure 1 shows the dinuclear structure of **4**, in which two niobium atoms are bridged by two imido ligands and one chloride. Selected bond distances and angles are summarized in Table 1. The doubly imido-bridged structure of **4** is clearly more thermodynamically stable than the chloride-bridged structure of **3**, while **3** is the kinetically preferred product of the reduction. The increased stability of **4** may be because two dianionic μ-imido bridging ligands contribute electrons to the low-valent niobium atoms in **4**, rather than having only monoanionic μ-chloride bridging ligands as in **3**. The bond distance between the two niobium atoms (2.5279(4) Å) is significantly shorter than not only that of **3** (2.955(2) Å) but also that of most other imido-bridged Nb(IV) dinuclear complexes (2.65–2.68 Å).[8] The bond distances of the four Nb–N_{imido} (1.9847(18)–2.0044(18) Å) lie within the range observed for typical Nb–N single bonds (1.984–2.045 Å).[9]

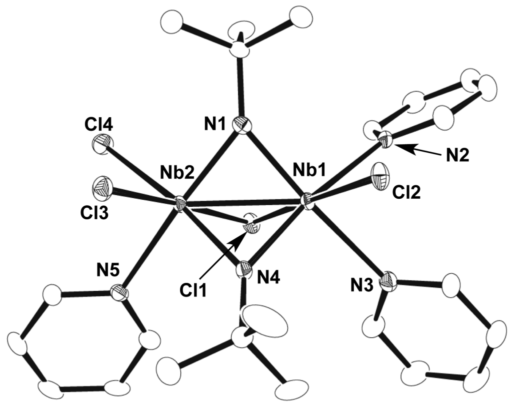


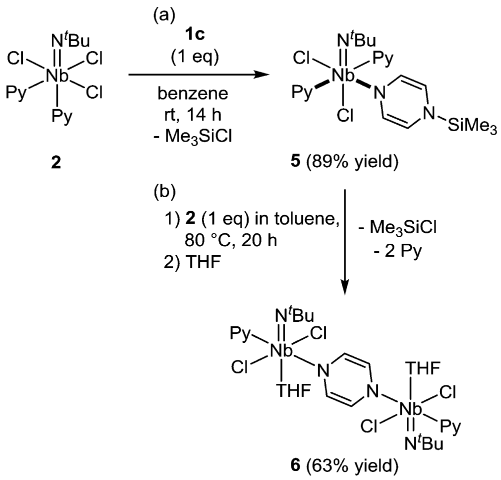
Figure 1. ORTEP drawing of complex **4** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Nb1–Nb2	2.5279(4)	Nb1–N1	1.9847(18)
Nb2–N1	1.9945(17)	Nb1–N4	1.9975(18)
Nb2–N4	2.0044(18)	Nb1–Cl1	2.5180(6)
Nb2–Cl1	2.5833(7)	Nb1–Cl2	2.4231(6)
Nb2–Cl3	2.4224(7)	Nb2–Cl4	2.5185(6)
Nb1–N1–Nb2	78.88(6)	Nb1–N4–Nb2	78.35(7)
Nb1–Cl1–Nb2	59.395(15)	sum of angles around N1	359.10(11)
sum of angles around N4	359.87(12)		

In contrast to the reaction of (^{t}BuN=)$NbCl_3(py)_2$ (**2**) with **1a** and **1b**, nonmethylated reductant **1c** gave a Nb(V) imido complex **5** in 89% yield along with the formation of 1 equiv of Me_3SiCl (Scheme 2a). The ^{1}H NMR spectrum of **5** in C_6D_5Br displayed one singlet at 0.12 ppm due to the TMS group and four doublets at 4.43, 4.83, 8.24, and 8.54 ppm assignable to the

Scheme 2. Reaction of Complex 2 with an Organosilicon Compound 1c



protons on the dihydropyrazine ring. Since **1c** is less sterically hindered around the nitrogen atom, the diazacyclohexadienyl moiety was able to attach to the niobium atom as a monoanionic ligand to form the Nb(V) complex **5**.[5d]

Treatment of complex **5** with 1 equiv of **2** at 80 °C for 20 h afforded a blue powder with release of 1 equiv of Me_3SiCl. Extraction with THF from the blue powder and evaporation of the solvent gave the dinuclear niobium(V) complex **6** in 63% yield (Scheme 2b). The ^{1}H NMR spectrum in THF-d_8 displayed one broad signal at 6.54 ppm for the pyrazine ring, suggested that complex **6** contained a two-electron reduced pyrazine ligand that bridged two niobium(V) atoms due to the significant upfield shift from the neutral pyrazine.

Upon recrystallization from a slow vapor diffusion of hexane into saturated THF solution of **6**, blue crystals suitable for a single crystal X-ray diffraction study were isolated. The solid-state structure of **6** is shown in Figure 2, and selected bond distances and angles are summarized in Table 2. Two niobium atoms are bridged by a two-electron reduced pyrazine ring, and each niobium atom possesses a pseudo-octahedral geometry. The long−short−long sequence of bonds in the pyrazine ring (longer C−N bonds, 1.399(5) and 1.404(6) Å; shorter C−C bonds, 1.323(6) Å) indicates that the pyrazine moiety is reduced to be a dianionic ligand that bridges two niobium(V) atoms, as is the same tendency of some dianions of dihydropyrazine derivatives (1.365−1.421 Å for C−N bonds; 1.322−1.338 Å for C−C bonds).[5d,10] The dianionic nature of the bridging pyrazine in the solid state is consistent with its characterization in solution by the ^{1}H NMR spectrum. The dianionic pyrazine ring for **6** is planar, and the sum of angles around the nitrogen atom N2 is 359.7°, the same as for both free **1c** and corresponding bis(trimethylgermyl) derivatives.[10]

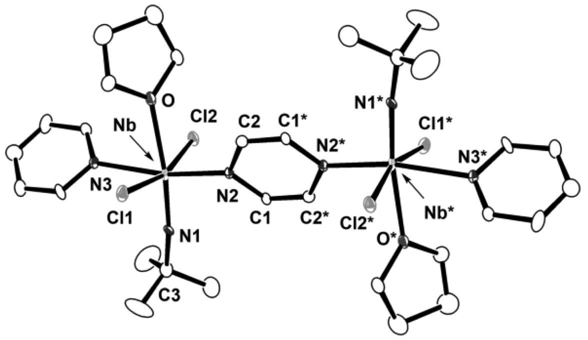


Figure 2. ORTEP drawing of complex **6** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. The complex **6** is centrosymmetric structure, and atoms generated by symmetry operation are labeled with *.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Nb−N1	1.791(4)	Nb−N2	2.057 (4)
Nb−N3	2.338(4)	N2−C1	1.399(5)
N2−C2	1.404(6)	C1−C2*	1.323(6)
N2−Nb−N3	169.63(14)	Nb−N1−C3	170.6(4)

With two isomorphous low-valent dinuclear niobium(IV) complexes **3** and **4** in hand, we compared the reducing ability of these two complexes toward substrates having an N=N double bond. Among substrates we examined, we successfully isolated complex **7** when **3** was treated with benzo[*c*]cinnoline. Reaction of complex **3** with benzo[*c*]cinnoline in C_6H_5Cl at room temperature for 24 h gave **7** in 70% yield (eq 3), while complex **4** did not react with benzo[*c*]cinnoline, probably because of its stable imido-bridged structure. In the ^{1}H NMR spectrum of **7**, two singlet signals due to inequivalent ^{t}Bu groups were observed at 0.55 and 0.75 ppm, and two sets of broad resonances attributed to three coordinating pyridines appeared, suggesting that all ligands of **3** remained in complex **7**. The asymmetric structure of **7** was determined by an X-ray diffraction analysis (Figure 3, Table 3), revealing that Nb1 has two terminal chloride ligands and one pyridine while Nb2 has one terminal chloride atom and two pyridine ligands. The two niobium atoms are bisected by a two-electron reduced benzo[*c*]cinnoline moiety and bridged by one chloride ligand. The N1−N2 bond distance (1.421(4) Å) is much longer than that of uncoordinated benzo[*c*]cinnoline (1.292(3) Å)[11] as a consequence of the reduction of the N=N bond of benzo[*c*]cinnoline,[12] while the two-electron reduced benzo[*c*]cinnoline moiety is planar despite significant elongation of the N−N bond.[12a] The lack of a direct bonding interaction between the two niobium atoms, as evidenced by the elongated Nb−Nb distance compared to that in complexes **3** and **4**, as well as the diamagnetic behavior of the complex, are clearly indicative of the two-electron reduction of benzo[*c*]cinnoline.

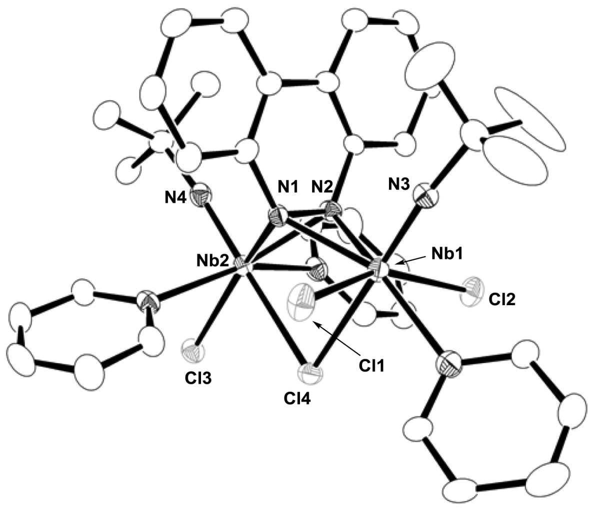
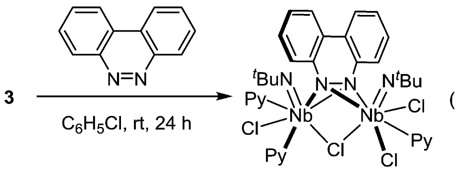


Figure 3. ORTEP drawing of complex **7** with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 7

N1−N2	1.421(4)	Nb1−Nb2	3.5651(5)
Nb1−N1	2.196(3)	Nb1−N2	2.183(3)
Nb2−N1	2.191(3)	Nb2−N2	2.160(3)
Nb1−N3	1.744(3)	Nb2−N4	1.756(3)
Nb1−Cl1	2.4855(11)	Nb1−Cl2	2.4942(11)
Nb1−Cl4	2.6964(11)	Nb2−Cl4	2.6728(10)
Nb2−Cl3	2.4863(11)		
Nb1−N1−Nb2	108.71(13)	Nb1−N2−Nb2	110.36(14)
Nb1−Cl4−Nb2	83.21(3)	Cl2−Nb1−Cl1	153.99(4)

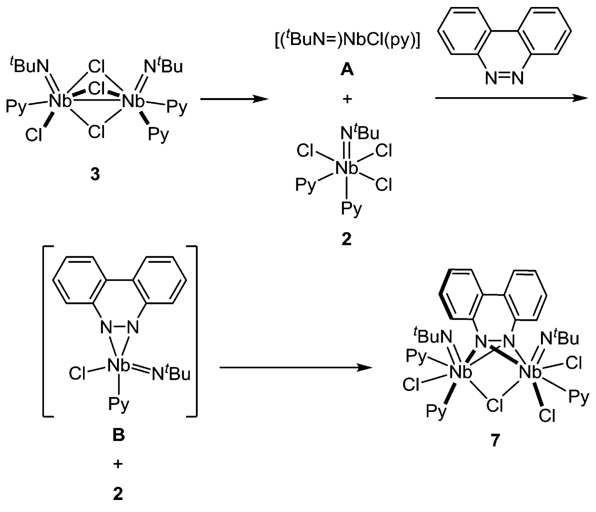


(3)

7 (70% yield)

Monitoring the formation of **7** in C_6D_6 by ^1H NMR measurements revealed one set of signals of **2** as soon as benzo[*c*]cinnoline was added (Supporting Information Figure S1). An explanation for this is that the chloride-bridged dinuclear complex **3** disproportionates to the Nb(V) complex **2** and a putative, low-valent Nb(III) species, (^{t}BuN=)NbCl(py) (**A**), the latter of which reacts with benzo[*c*]cinnoline via a two-electron reduction process to form a mononuclear Nb(V) intermediate **B** as outlined in Scheme 3.[13] In situ generated **2** is then trapped by this intermediate species to form complex **7**, which is assumed to be a relatively slow process because of the detection of **2** during the formation of **7**. We note that disproportionation of **3** might also be involved in the structural rearrangement of **3** to the doubly imido-bridged complex **4** (*vide supra*).

Scheme 3. Proposed Reaction of Complex 3 with Benzo[*c*]cinnoline



■ SUMMARY

We found that methylated pyrazine-based reductants **1a** and **1b** effectively reduced (^{t}BuN=)NbCl$_3$(py)$_2$ (**2**) to give two dinuclear niobium(IV) complexes **3** and **4**. In contrast, the reduction by nonmethylated pyrazine-based reductant **1c** afforded a mononuclear (imido)niobium(V) complex **5** bearing a monoanionic 1-trimethylsilyldiazacyclohexadienyl ligand and dinuclear pyrazine-bridged complex **6**. This differing reactivity can be ascribed to the coordination behavior of the diazacyclohexadienyl ligand: steric bulkiness around the nitrogen atom of the six-membered ring prevents the coordination of the pyridine derivatives to the metal center, leading to the formation of the reduced niobium species. The chloride-bridged dinuclear Nb(IV) complex **3** reacted with the N=N bond of benzo[*c*]cinnoline to produce dinuclear Nb(V) complex **7** bridged by a two-electron reduced benzo[*c*]cinnoline ligand, which is assumed to result from a disproportionation of **3** to two mononuclear Nb(III) and Nb(V) species. Further studies of the rich chemistry of low-valent niobium-imido fragments are ongoing in our laboratories.

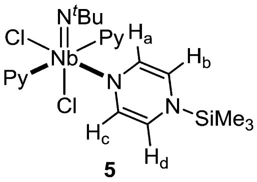
■ EXPERIMENTAL SECTION

General. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under N_2 or Ar using the standard Schlenk technique or N_2-filled or Ar-filled glovebox. 2,3,5,6-Tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1a**), 2,5-dimethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1b**), and 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1c**) were prepared according to the modified procedure of the literature by replacing potassium metal by sodium metal except for the synthesis of **1a** that needed the use of potassium.[14] (^{t}BuN=)NbCl$_3$(py)$_2$ was prepared according to the literature procedure.[15] Hexane, THF, toluene, and benzene were purified by passage through a column of activated alumina and were degassed prior to use. Benzo[*c*]cinnoline was used as received. Deuterated solvents were vacuum-transferred from either sodium/benzophenone and degassed with three freeze–pump–thaw cycles. NMR spectra were recorded on Bruker AVANCEIII-400, AV-300, AVQ- 400, AVB-400, DRX-500, AV-500, and AV-600 spectrometers. ^1H and $^{13}C\{^1H\}$ chemical shifts were measured relative to residual solvent peaks, which were calibrated with an external TMS standard set to 0.00 ppm. Proton and carbon NMR assignments were routinely confirmed by $^1H-^1H$ (COSY), $^1H-^{13}C$ (HSQC and HMBC), and/or NOESY experiments. Elemental analyses were carried out either at the College of Chemistry, University of California, Berkeley, or at the Faculty of Engineering Science, Osaka University. Samples for ultraviolet spectrometry were prepared in a Schlenk-adapted quartz cuvette and analyzed on a Shimadzu UV-3101PC scanning spectrophotometer. Uncorrected melting points were measured in sealed tubes under argon.

*Synthesis of [(^{t}BuN=)ClNb(py)](μ-Cl)$_3$[(^{t}BuN=)Nb(py)$_2$] (**3**).* To a solution of ^{t}BuN=NbCl$_3$(py)$_2$ (**2**) (500 mg, 1.17 mmol) in toluene (5 mL) at room temperature was added a solution of **1a** (167 mg, 0.592 mmol) in toluene (5 mL). The solution color immediately turned to purple. The reaction mixture was stirred for 14 h, resulting in formation of a purple precipitate. All volatiles were removed under reduced pressure. The residue was washed with hexane (3 × 5 mL) to afford **3** as a purple powder (372 mg, 90% yield), mp 120–121 °C (dec). Purple crystals of complex **3** suitable for X-ray crystallography were grown by vapor diffusion of hexane into the toluene solution of **3** at room temperature. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 1.60 (s, 9H, C(CH$_3$)$_3$), 1.71 (s, 9H, C(CH$_3$)$_3$), 6.24 (m, 2H, *m*-py), 6.35 (m, 2H, *m*-py), 6.46 (m, 2H, *m*-py), 6.54 (t, 1H, J = 8.0 Hz, *p*-py), 6.64 (t, 1H, J = 7.2 Hz, *p*-py), 6.75 (t, J = 7.2 Hz, 2H, *p*-py), 9.00 (d, 2H, J = 5.5 Hz, *o*-py), 9.01 (d, 2H, J = 5.5 Hz, *o*-py), 9.60 (d, 2H, J = 5.1 Hz, *o*-py). The low solubility of **3** in common organic solvents prevented further characterization by ^{13}C NMR spectroscopy. UV–vis (toluene) λ_{max}/nm (ε/M^{-1} cm^{-1}): 557 (5265). Anal. Calcd for $C_{23}H_{30}Cl_4N_5Nb_2$: C, 39.23; H, 4.29; N, 9.95. Found: C, 39.19; H, 4.56; N, 9.40.

*Synthesis of [Cl$_2$Nb(py)](μ-Cl)(μ-N^{t}Bu)$_2$[ClNb(py)$_2$] (**4**).* A purple suspension of complex **3** (100 mg, 0.284 mmol) in toluene (5 mL) was stirred at 80 °C for 16 h. The color of the suspension gradually changed to orange. All volatiles were removed under reduced pressure to give an orange solid, which was washed with hexane (3 × 5 mL) to afford **4** as an orange powder (91 mg, 91% yield), mp 130–132 °C (dec). Orange crystals of complex **4** suitable for X-ray crystallography were directly obtained from the reaction mixture at 80 °C. The low solubility of **4** in common organic solvents prevented characterization by NMR spectroscopy. Anal. Calcd for $C_{23}H_{30}Cl_4N_5Nb_2$: C, 39.23; H, 4.29; N, 9.95. Found: C, 39.11; H, 4.57; N, 9.52.

*Synthesis of ^{t}BuN=NbCl$_2$(py)$_2$(1-trimethylsilyldiazacyclohexadienyl) (**5**).* A solution of ^{t}BuN=NbCl$_3$(py)$_2$ (**2**) (100 mg, 0.233 mmol) in benzene (1 mL) was added to a solution of compound **1c** (52.8 mg, 0.233 mmol) in benzene (1 mL) at room temperature. The color of the mixture turned to purple. After the reaction mixture was stirred for 14 h, all volatiles were removed under reduced pressure, and a purple solid was obtained. The solid was washed with hexane (3 × 3 mL). After removal of all volatiles, complex **5** was obtained as purple microcrystals (105 mg, 89% yield), mp 179−180 °C (dec). ^{1}H NMR (400 MHz, C_6D_5Br, 30 °C): δ 0.12 (s, 9H, Si(CH$_3$)$_3$), 1.47 (s, 9H, C(CH$_3$)$_3$), 4.43 (d, ^3J = 6.0 Hz, ^4J = 1.8 Hz, 1H, CH$_c$=C*H*$_d$), 4.83 (d, ^3J = 5.7 Hz, ^4J = 1.7 Hz, 1H, CH$_a$=C*H*$_b$), 7.00 (t, J = 6.8 Hz, 4H, *m*-py), 7.33 (t, J = 7.6 Hz, 2H, *p*-py), 8.24 (d, ^3J = 5.7 Hz, ^4J = 1.7 Hz, 1H, C*H*$_a$═CH$_b$), 8.54 (d, ^3J = 6.0 Hz, ^4J = 1.8 Hz, 1H, C*H*$_c$═CH$_d$), 9.69 (d, J = 4.8 Hz, 4H, *o*-py). ^{13}C NMR (100 MHz, C_6D_5Br, 30 °C): δ −2.21 (Si(CH$_3$)$_3$), 30.7 (C(CH$_3$)$_3$), 65.4 (C(CH$_3$)$_3$), 115.1 (CH$_c$═CH$_d$), 115.2 (CH$_a$═CH$_b$), 123.1 (m-*py*), 129.9 (CH$_c$═CH$_d$), 132.2 (CH$_a$═CH$_b$), 137.2 (p-*py*), 150.1 (m-*py*). UV−vis (toluene) λ_{max}/nm (ε/M^{-1} cm^{-1}): 523 (3285). Anal. Calcd for $C_{21}H_{30}Cl_2N_5NbSi$: C, 46.33; H, 5.55; N, 12.86. Found: C, 46.10; H, 5.89; N, 13.22.



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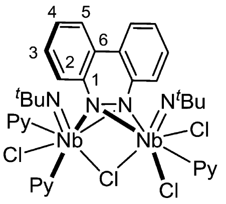
*Synthesis of {[^{t}BuN═NbCl$_2$(py)(THF)]$_2$(μ-pyrazine)} (**6**).* A solution of complex **5** (127 mg, 0.234 mmol) in toluene (5 mL) was added to a solution of ^{t}BuN═NbCl$_3$(py)$_2$ (**2**) (100 mg, 0.234 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred at 80 °C for 20 h to give a deep blue precipitate. All volatiles were removed under reduced pressure. The resulting residue was washed with a 1:1 mixture of toluene/hexane (5 × 5 mL) and extracted with THF. After evaporation of the solvent under vacuum, deep blue powder of **6** was isolated (98.0 mg, 63% yield), mp 180−182 °C (dec). Blue crystals of complex **6** suitable for X-ray crystallography were grown by vapor diffusion of hexane into a THF solution of **6** at room temperature. ^{1}H NMR (400 MHz, THF-d_8, 30 °C): δ 1.28 (s, 18H, C(CH$_3$)$_3$), 6.54 (br, 4H, CH═CH), 7.50 (br, 4H, *m*-py), 7.94 (br, 2H, *p*-py), 9.25 (br, 4H, *o*-py). The low solubility of **3** in common organic solvents prevented further characterization by ^{13}C NMR spectroscopy. UV−vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 433 (2819). Anal. Calcd for $C_{30}H_{48}Cl_4N_6Nb_2O_2$: C, 42.27; H, 5.68; N, 9.86. Found: C, 42.02; H, 5.83; N, 9.50.

*Synthesis of [(^{t}BuN═Nb)$_2$Cl$_3$(μ-Cl)(py)$_3$(benzo[c]cinnoline)] (**7**).* A solution of benzo[*c*]cinnoline (42.1 mg, 0.234 mmol) in C_6H_5Cl (10 mL) at room temperature was added to a solution of complex **3** (127 mg, 0.234 mmol) in C_6H_5Cl (5 mL). The reaction mixture was stirred at room temperature for 24 h to give a red solution. All volatiles were removed under reduced pressure, and the residue was washed with hexane (5 × 5 mL) to afford **7** as a red-purple powder (132 mg, 70% yield), mp 130−131 °C (dec). Red-purple crystals of complex **7** suitable for X-ray crystallography were grown in C_6D_6 solution of **7** at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C): δ 0.53 (s, 9H, C(CH$_3$)$_3$), 0.73 (s, 9H, C(CH$_3$)$_3$), 6.95 (t, 2H, J = 7.6 Hz, C^{3}H or C^{4}H), 7.02 (t, 2H, J = 7.6 Hz, C^{3}H or C^{4}H), 7.15 (d, 2H, J = 7.6 Hz, C^{2}H or C^{5}H), 7.35 (m, 2H, *m-py*), 7.53 (t, 4H, J = 6.8 Hz, *m-py*), 7.75 (d, 2H, J = 7.6 Hz, C^{2}H or C^{5}H), 7.76 (br s, 1H, *p*-py), 7.95 (t, 2H, J = 7.6 Hz, *p*-py), 9.35 (br s, 2H, *o*-py), 9.69 (d, J = 5.2 Hz, 4H, *o*-py). ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C): δ 29.0 (C(CH$_3$)$_3$), 29.7 (C(CH$_3$)$_3$), 69.4 (C(CH$_3$)$_3$), 69.9 (C(CH$_3$)$_3$), 117.9 (C^1 or C^6), 121.8 (C^2 or C^5), 122.7 (m-*py*), 123.3 (C^2 or C^5), 124.2 (m-*py*), 124.9 (C^3 or C^4), 128.3 (C^3 or C^4), 138.8 (p-*py*), 139.2 (p-*py*), 150.5 (C^1 or C^6), 152.9 (o-*py*), 155.2 (o-*py*). UV−vis (THF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 351 (5065). Anal. Calcd for $C_{35}H_{41}Cl_4N_7Nb_2$: C, 47.37; H, 4.66; N, 11.05. Found: C, 46.89; H, 4.62; N, 10.89.

X-ray Diffraction Study. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K (Osaka University) or were coated in Paratone-N oil, mounted on a Kaptan loop, and cooled to 100(1) K by a nitrogen flow low-temperature apparatus (CHEXRAY, University of California, Berkeley). The X-ray structural determinations were performed using a Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα (1.71075 Å) radiation (Osaka University) or a Bruker SMART APEX II Quazar diffractometer with a Bruker APEX CCD area detector. (CHEXRAY, University of California, Berkeley). Crystal data and structure refinement parameters are listed in Table S2 in Supporting Information.



The structures of **3**, **4**, **6**, and **7** were solved by direct methods (SHELXS-97),[16] and the structure was finally refined on F^2 by full-matrix least-squares method, using SHELXL-97.[16] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 and wR2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. ORTEP diagrams were created using the ORTEP-3 software package.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structure of **3**, ^{1}H NMR spectra for the conversion of **3** to **7**, crystal data and data collection parameters, and CIF file giving data for complexes **3**, **4**, **6**, and **7**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00812.

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Notes

The authors declare no competing financial interest.

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