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Synthesis, Characterization, and Reactions of Isolable (β -Diketiminato)Nb(III) Imido Complexes*

Neil C. Tomson, John Arnold*, and Robert G. Bergman*

University of California, Berkeley, California 94720

Abstract

We have investigated both the chemical reduction of (BDI)Nb(V) imido complexes (BDI = HC[C(Me)NAr]₂; Ar = 2,6-*i*Pr₂-C₆H₃) to the formal Nb(III) oxidation state and the ability of these Nb(III) complexes to behave as two-electron reductants. The reduction of the Nb(V) species was found to depend heavily on the nature of available supporting ligands, but the chemistry of the reduced compounds proceeded cleanly with a number of unsaturated organic reagents. Accordingly, the novel Nb(V) *bis*(imido) complexes supported by the monoazabutadiene (mad) ligand (mad)Nb(N^tBu)(NAr)(L') (L' = py, thf) were formed by either KC₈ reduction of (BDI)Nb(N^tBu)Cl₂(py) in the absence of strong π -acids or by H₂ reduction of the Nb(V) dimethyl complex (BDI)Nb(N^tBu)Me₂ in THF. These products are likely formed through an intramolecular, 2 e⁻ reductive C–N bond cleavage, as has been observed previously for related Group 4 systems, suggesting that transient Nb(III) intermediates were present in both cases. In the presence of 1,2-*bis*(dimethylphosphino)ethane (dmpe), KC₈ reduction of (BDI)Nb(N^tBu)Cl₂(py) was arrested at the Nb(IV) oxidation state to give (BDI)Nb(N^tBu)Cl(dmpe), which was characterized by solution-state EPR spectroscopy as a Nb-centered paramagnet with strong coupling to the two equivalent phosphorus nuclei ($A_{\text{iso}}\{^{93}\text{Nb}\} = 120.5 \times 10^{-4} \text{ cm}^{-1}$, $A_{\text{iso}}\{^{31}\text{P}\} = 31.0 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{iso}} = 1.9815$). When strong π -acids were used to intercept the thermally unstable Nb(III) complex (BDI)Nb(N^tBu)(py) prior to reductive cleavage of the ligand C–N bond, the thermally stable Nb(III) species (BDI)Nb(N^tBu)(CX)₂(L'') (X = O, L'' = py; X = NXyl, L'' = CNXyl; Xyl = 2,6-Me₂-C₆H₃) were obtained in good yields. The Nb(III) complexes (BDI)Nb(N^tBu)py, (BDI)Nb(N^tBu)(CO)₂(py) and (BDI)Nb(N^tBu)(CO)₂ were subsequently investigated for their ability to serve as two-electron reducing reagents for both metal-ligand multiple bond formation and for the reduction of organic π -systems. The reduction of mesityl azide by (BDI)Nb(N^tBu)(py) and diphenylsulfide by (BDI)Nb(N^tBu)(CO)₂ led to the monomeric *bis*(imido) and dimeric oxo complexes (BDI)Nb(N^tBu)(NMe)₂(py) and [(BDI)Nb(N^tBu)]₂(μ^2 -O)₂, respectively. MeLi addition to (BDI)Nb(N^tBu)(CO)₂(py) resulted in the formation of a Nb-acylate *via* methide addition to one of the carbonyl carbons. The acylate product was revealed to have a short Nb–C_{acylate} bond distance (2.059(4) Å), consistent with multiple Nb–C bond character resulting from Nb(III) back-bonding into the acylate carbon. The interaction of (BDI)Nb(N^tBu)(CO)₂ with two equivalents of 4,4'-dichlorobenzophenone resulted in the clean, quantitative formation of the corresponding pinacol coupling product, but introduction of the ketone in 1:1 molar ratios resulted in mixtures of the pinacol product and the starting material, suggesting that ketone coordination to the Nb(III) complex may be reversible. Relatedly, addition of 1-phenyl-1-propyne to (BDI)Nb(N^tBu)(CO)₂ formed a thermally unstable 1:1 Nb/alkyne complex, as characterized by

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arnold@berkeley.edu, rbergman@berkeley.edu.

Supporting Information Available. Complete crystallographic data for compounds **2•py**, **2•thf**, **5**, **6**, **7**, **10**, **11**, **12** (CIF). This information is available free of charge *via* the Internet at <http://www.pubs.acs.org>.

NMR and IR spectroscopies; reaction of this species with HCl/MeOH yielded a 2: 1 mixture of 1-phenyl-1-propene and the free alkyne, suggesting a high degree of covalency in the Nb–C bonds.

Introduction

Use of the reducing capability of early-metal complexes in the d^2 electronic state is a powerful tool in synthetic chemistry.^{1,2} From an organic perspective, the ability to form C–C bonds *via* the reductive coupling of unsaturated organic molecules (alkenes, alkynes, ketones, ketimines, *etc.*) has provided general routes to dienes, amino alcohols, diols, and bicyclic products. In a related sense, the formation of reactive multiple bonds between early-metals and *p*-block-based ligands can be effected through a number of two-electron reductions of organic substrates, leading variously to early-metal alkylidenes, imidos and oxos.

One area of early-metal d^2 chemistry that has enjoyed considerable attention for C–C bond forming reactivity is that of the Cp_2ML^n systems (Cp = cyclopentadienyl; M = Ti, Zr; L^n = neutral $2e^-$ donor).^{3–7} Mechanisms leading to the new C–C bonds from the d^2 metallocenes commonly involve the initial formation of a three-membered metallacycle by binding an unsaturated substrate to the metallocene with loss of the L-type ligands – formally a $2e^-$ reduction of the incoming ligand.^{8–11} Subsequent insertion of another unsaturated molecule into one of the newly formed M–C bonds results in a new C–C σ -bond as part of a five-membered metallacycle (Scheme 1).² Such metallacycles are often hydrolyzed to obtain the products of stoichiometric reductive coupling, but in certain cases the coupling reactions have been rendered catalytic by way of protonolysis/reductive elimination pathways or by dialkylation of electrophiles (CO, CNR) followed by ketone/imine dissociation.

Relatedly, the formation of multiple metal-ligand bonds *via* oxidation of early-metal d^2 complexes with cleavable $2e^-$ oxidants (*e.g.* M=NR from RN_3 , M=O from R_2SO , M=CR₂ from N_2CR_2 , *etc.*) can provide facile entry into reactive complexes while avoiding difficulties encountered with generating these species through redox-neutral substitution routes.^{13,14} Redox-based methods for the introduction of Y^{2-} (Y = NR, O, CR₂, *etc.*) ligands also have the advantage of creating generally innocuous and volatile by-products (*e.g.* N_2 , R_2S , *etc.*), which can aid in the isolation of what are often low-coordinate and electron-deficient complexes.

A common limitation to both the organic and transition-metal chemistry described so far is the formation of stable, d^2 early-metal complexes with available coordination sites. The Group 4 d^2 metallocenes have been studied extensively in this regard due to the stability of the metallocene framework toward reductive degradation, but recent interest in “post-metallocene” early-metal catalysts for olefin polymerization and selective bond activation has highlighted the utility of developing alternative ligand frameworks for the Group 4 and Group 5 metals.^{15–25} With this expanded scope of available ligands for early-metal complexes, we were interested in furthering the application of this “post-metallocene” strategy to niobium complexes in the d^2 electronic state.^{26–28}

Here we describe our efforts toward the investigation of reductive bond formation with the (BDI)Nb(N^tBu) system (BDI = $\text{HC}[\text{C}(\text{Me})\text{NAr}]_2$; Ar = 2,6- $\text{Pr}_2\text{-C}_6\text{H}_3$). Following initial observations of a known reductive ligand degradation pathway,^{29–32} we have found that the use of π -acids leads to (BDI)Nb(III) products that are indefinitely stable at room temperature. The chemistry of the previously reported³³ Nb(III) dicarbonyl complex, along with related Nb(III) complexes described below, has been explored with the aim of generating Nb=Y (Y = NR, CR₂, O) and C–C bonds.

Results and Discussion

Synthesis of Nb(V) *bis*(imido) and Nb(IV) *mono*(imido) complexes

Reduction of (BDI)Nb(N^tBu)Cl₂(py) with KC₈ in the absence of trapping ligands—Initial attempts to isolate a BDI-supported Nb(III) complex proceeded by chemical reduction of the dichloride complex (BDI)Nb(N^tBu)Cl₂(py), **1**. Addition of 2.0 equiv of KC₈ in Et₂O to a slurry of **1** in Et₂O at −72 °C quickly caused the solution to turn from red to dark blue. The consumption of KC₈ was checked visually (bronze to black), which indicated that the reaction was complete after 10 min at −72 °C. The color quickly turned dark yellow when this solution was allowed to warm to room temperature. The subsequent removal of solvent and extraction with pentane gave a clear yellow solution from which a bright yellow solid crystallized at −40 °C. A ¹H NMR spectrum indicated that the material was diamagnetic and that it lacked the symmetry expected for the proposed Nb(III) species (BDI)Nb(N^tBu)(py) (**3**, Scheme 2). Importantly, only three sets of resonances for the aryl ring *iso*-propyl groups (in a relative ratio of 1:1:2) were observed, indicating that one of the aryl rings is freely rotating on the NMR timescale while the other is locked in position. An X-ray crystal structure was obtained, revealing a monoazabutadiene (mad) *bis*(imido) complex (mad)Nb(N^tBu)(NAr)(py) (**2•py**, Scheme 2, Figure 1).

The route to this product likely involves reductive cleavage of one of the ligand N–C_{imine} bonds, in a manner analogous to that proposed by Mindiola,^{29,30} Stephan,³¹ and Tokitoh³² from their separate work on Group 4 β-diketiminato complexes. In those cases, reduction of the complexes (BDI)MCl_x (M = Ti, x = 2; M = Zr, Hf, x = 3) to the M^{II} oxidation state resulted in the formation of (mad)M(NAr)Cl. In related Ti chemistry, Roesky *et al.* reported that trans-metallation of a LiBDI salt with TiCl₃ resulted in the isolation of a (BDI)Ti(IV) imide (among other products), with the imido group originating from a section of a BDI ligand.³⁴

While the ligand degradation pathway prevented isolation of the Nb(III) complex, the formation of a *bis*(imido) complex is of interest considering both the rarity of this moiety on Group 5 metals and that complex **2•py** represents the first example of a Group 5 *bis*(imido) complex with unsymmetrically substituted imido groups. The arylimido ligand has a longer Nb–N bond length (Nb(1)–N(2) 1.821(5) Å) and a shorter N–C distance (N(2)–C(5) 1.386(7) Å) than the alkyl substituted imido group (Nb(1)–N(1) 1.803(5) Å, N(1)–C(1) 1.465(8) Å). This effect is well documented in the literature and can be attributed to N(*p*_π)–Ar(*p*_π) bonding, making the Nb(1)–N(2)–C(5) bonding angle (173.4(4)°) more linear than the analogous Nb(1)–N(1)–C(1) bond angle (161.2(4)°). Related Group 6 *bis*(imido) compounds with one alkylimido and one arylimido group related across a pseudo molecular mirror plane have a similar disparity in imido group bonding.

The bonding within the monoazabutadiene ligand reflects considerable double bond localization, with a short N(3)–C(30) distance (1.267(7) Å), long C(30)–C(31) bond (1.447(9) Å), and short C(31)–C(32) interaction (1.327(8) Å). The Nb–C bond length (Nb(1)–C(32) 2.213(7) Å) is typical for Nb(V)–C single bonds, and the Nb(1)–N(3) bond length (2.340(5) Å) is indicative of a neutral donor, on the order of a Nb–pyridine interaction. With a formally *d*⁰ metal center, the metallacycle has a four-electron non-aromatic π-system, consistent with the observed bond localization within the ring.

Reduction of (BDI)Nb(N^tBu)Me₂ with H₂—Reaction of a thawing THF solution of the dimethyl complex (BDI)Nb(N^tBu)Me₂³³ **4** with dihydrogen (1 atm) immediately caused the color of the solution to change from bright yellow to orange. The product isolated by crystallization was identified as the monoazabutadiene *bis*(imido) complex (mad)Nb(N^tBu)(NAr)(thf) (**2•thf**, Figure 2) formed *via* the reductive cleavage of the ligand N–C_{imine} bond.

Complex **2•thf** crystallizes in the same space group as **2•py** ($P2_12_12_1$), and the molecular structure is analogous to that for **2•py**; the molecular geometry of both structures is best described as pseudo-square pyramidal ($\tau(\mathbf{2}\cdot\mathbf{py}) = 0.42$; $\tau(\mathbf{2}\cdot\mathbf{thf}) = 0.46$).³⁵

While no intermediates leading to **2•thf** could be detected by NMR spectroscopy, the isolation of the product suggests the intermediacy of a Nb(III) complex. Hydrogen addition to early-metal alkyls is a well-known method for generating early metal hydrides, but the synthesis of early metal polyhydrides from MR_n ($n > 1$) complexes typically requires high pressures of H_2 to give clean conversions.³⁶ This is likely due to the facile reductive elimination of alkane products from R-M-H species, indicating that high pressures of H_2 are needed to out-compete C–H reductive elimination. In the present case, the low H_2 pressure used in the reaction would presumably yield a transient methyl hydride species $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})\text{Me}(\text{H})(\text{L})$ ($\text{L} = \square, \text{thf}$); reductive elimination of methane from this intermediate would give the Nb(III) complex $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{L})$, which would be capable of reductive ligand degradation (Figure 2). This hydrogenolysis pathway circumvents a Nb(IV) intermediate, indicating that the proposed Nb(III) complex **3**, formed by chemical reduction of the dichloride **1**, could be competent for forming **2•py**.

Unfortunately, we were unable to obtain spectroscopic data on **3** due to the heterogeneity of the mixture throughout the reaction and the thermal instability of the product. Still, we have assigned this Nb(III) intermediate as a pyridine adduct, $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{py})$ (**3**, Scheme 2), based on the following points: *i*) The pyridine-coordinated complexes **7** and **10** (see below) were synthesized directly from solutions of **3**, which had been synthesized as described above *via* KC_8 reduction of **1** at -72°C . *ii*) No intermediate Nb(III) species could be detected visually or by NMR spectroscopy at -70°C during the formation of **2•thf** with THF as the solvent, but the dark blue solution that we have assigned to **3** is stable for *ca.* 10 min at -72°C in Et_2O , suggesting that the nature and concentration of the neutral donor may have a significant effect on the stability of the intermediate Nb(III) species. *iii*) A color change from blue to yellow was observed following addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of the dark blue intermediate at -72°C . This color change could be attributed to a change in the metal's coordination number (and possibly oxidation state) following pyridine abstraction by the borane reagent to form $\text{py}\cdot\text{B}(\text{C}_6\text{F}_5)_3$.^{37–38}

Reduction of $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})$ with KC_8 in the presence of dmpe—

Considering the limitations toward exploratory Nb(III)-based reactivity imposed by the thermal instability of **3**, we sought to stabilize the Nb(III) complex by introducing suitable neutral donors. Addition of *bis*(dimethylphosphine)ethane (dmpe) into the slurry of **1** *before* the addition of KC_8 resulted in a new dmpe-containing product following chemical reduction. The color of the solution turned from blue to yellow-green while being maintained at -72°C . Allowing the flask to warm to room temperature and stirring the mixture for 12 h did not cause the color of the solution to change, and following workup, a product was isolated as yellow-green dichroic crystals from a saturated Et_2O solution. A ^1H NMR spectrum of the crystallized material revealed paramagnetically shifted and broadened peaks between -5 and 15 ppm. While most d^2 Nb systems are known to be diamagnetic, some paramagnetic Nb(III) phosphine complexes are known;³⁹ the crystallographically determined molecular structure of the product, however, was found to be that of a distorted-octahedral Nb(IV) complex $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})\text{Cl}(\text{dmpe})$ (**5**, Scheme 3, Figure 3), resulting from dmpe substitution for pyridine and a one-electron reduction to a Nb(IV) mono-chloride complex.

The stability of **5** in the presence of excess KC_8 was unexpected. Compound **5** can be synthesized in yields similar to those observed in the procedure given above using 1.0 equiv of KC_8 , and reducing **1** with 2.0 equiv of Na/Hg amalgam (0.5% by weight) in the presence

of dmpe results only in the isolation of **2•py**. Since we had previously reduced **1** to a Nb(III) complex using 2 equiv of KC_8 , it seems that phosphine coordination may be significantly affecting the reduction potential of the Nb(IV) complex. Attempts at forming related Nb(IV) complexes with monodentate phosphines (PMe_3 , PMe_2Ph , PMePh_2 , PPh_3) in the presence of two equivalents of KC_8 resulted only in the formation of **2•py**. When one equivalent of KC_8 was used to reduce **1** in the presence of the monodentate phosphines, mixtures of **1** and **2•py** were recovered.

Investigation of the electronic structure of **5** by EPR spectroscopy confirmed that the complex is a spin doublet with the unpaired electron localized largely on the Nb nucleus. The 298 K X-band (9.251 GHz) EPR spectrum of **5** in benzene revealed a decet of triplets corresponding to a niobium-centered radical coupling to two equivalent phosphorus nuclei; no superhyperfine coupling to either the nitrogen or chlorine centers could be discerned. Unexpectedly, the 34.326 GHz (Q-band) spectrum gave better line-width resolution; this higher field spectrum was thus used for modeling the spectral parameters, revealing $g_{\text{iso}} = 1.9815$ (Figure 4, bottom), with a strong $120.5 \times 10^{-4} \text{ cm}^{-1}$ hyperfine coupling to niobium (^{93}Nb , 100 %, $I = 9/2$) and a weaker $31.0 \times 10^{-4} \text{ cm}^{-1}$ superhyperfine coupling to the two equivalent phosphorus nuclei (^{31}P , 100 %, $I = 1/2$).

Forming stable Nb(III) complexes via π -acid coordination

Since the presence of phosphines were not found to yield stable Nb(III) adducts of **3**, we were interested in investigating whether the Nb(III) intermediate could be trapped with alternative neutral donors. As has been reported previously, the dicarbonyl compound $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CO})_2$ **9** can be prepared in moderate yields from carbonylation of the dimethyl complex, $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})\text{Me}_2$ **4**.³³ The stability of the Nb(III) dicarbonyl compared to **3** indicated that strong π -acids may be necessary for stabilizing a d^2 $(\text{BDI})\text{Nb}$ species. A full discussion of the synthesis and characterization of **9** will be given below, following the results of treating **3** with XylNC and CO .

Formation of a Nb(III) isocyanide complex—The addition of 3.0 equiv of solid XylNC ($\text{Xyl} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$) to a solution of **3** at -72°C (generated from the treatment of **1** with two equivalents of KC_8 at -72°C) resulted in a rapid color change from dark blue to dark red. Removing the cold bath and allowing the flask to warm to room temperature caused the solution to take on a blue-green color. The product $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CNXyl})_3$ (**6**, Scheme 4) was isolated as dark blue-purple dichroic crystals from a saturated Et_2O solution cooled to -40°C . Attempts at isolating the intermediate dark-red product by using sub-stoichiometric amounts of XylNC were unsuccessful, resulting only in isolation of **6**. Still, while we lack any explicit knowledge of the identity of the intermediate, our synthesis of the dark-red, pyridine-coordinated dicarbonyl species $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CO})_2(\text{py})$ (see below) would suggest that the intermediate in this reaction is the six-coordinate species $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CNXyl})_2(\text{py})$. The better σ -donor capability of XylNC over CO could account for the more facile pyridine loss when compared to the isolable pyridine adduct of the dicarbonyl complex. This dissociative process could then generate a transient five-coordinate bis(isocyanide) species, analogous to the isolable five-coordinate dicarbonyl complex $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CO})_2$ (see below). Coordination of a third XylNC to this species would lead to the formation of **6**.

The crystal structure of **6** (Figure 5) revealed that the isocyanides are meridionally distributed around the Nb atom, consistent with the ^tBu resonance in the ^1H NMR spectrum being shifted upfield due to its proximity to the flanking aryl ring of the BDI ligand. The Nb–C bond lengths (Nb(1)–C(1) 2.216(3) Å, Nb(1)–C(2) 2.183(2) Å, Nb(1)–C(3) 2.203(2) Å) are in

the range expected for Nb–C single bonds. This relatively short distance for a neutral donor is a result of the Nb-based back-bonding into the isocyanide π^* orbitals.

The differences between the bonding within the mutually *trans* isocyanides and the isocyanide *trans* to the BDI nitrogen match the trend observed by Royo and coworkers with the analogous Nb(III) complex $\text{Cp}^*\text{NbCl}_2(\text{CNXyl})_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$).⁴⁰ The latter complex has a distorted octahedral geometry with meridionally substituted isocyanide ligands and a $1\sigma, 2\pi$ ligand (Cp^*) located *cis* to all three isocyanides. The two chlorides are σ -donors analogous to the BDI ligand nitrogens in **6**. In the present case, we observe two longer Nb–C bond lengths (2.216(3) Å, 2.203(2) Å) for the mutually *trans* isocyanides compared to the shorter Nb(1)–C(2) distance (2.183(2) Å). A similar trend is observed by Royo, wherein the mutually *trans* isocyanides have notably longer Nb–C bond lengths than the isocyanide situated *cis* to each of them. The Nb–C–N bond angle for the isocyanide ligand *trans* to a chloride in $\text{Cp}^*\text{NbCl}_2(\text{CNXyl})_3$ is also more acute than those for the mutually *trans* isocyanides, which Royo attributes to weakening of the *trans*-to-chloride C–N bond relative to the other two isocyanides. Compound **6** exhibits a similar contraction of the Nb(1)–C(2)–N(2) bond angle (169.6(2)°) compared to that in the mutually *trans* isocyanides (Nb(1)–C(1)–N(1) 178.2(2)°, Nb(1)–C(3)–N(3) 177.5(2)°), although not to the degree observed by Royo. In contrast to the Royo complex, the isocyanide C–N bond distances for **6** (C(1)–N(1) 1.173(3) Å, C(2)–N(2) 1.165(3) Å, C(3)–N(3) 1.163(3) Å) do not vary significantly relative to the position of the isocyanide carbon about the metal center.

An IR spectrum of **6** revealed only two isocyanide N–C stretching frequencies ($\nu_{\text{CN}} = 2011, 1986 \text{ cm}^{-1}$) despite the averaged C_s symmetry observed in solution by NMR spectroscopy and the pseudo- C_s symmetry observed in the solid state. Several factors could lead to this apparent discrepancy, such as insufficient resolution of the instrument, low intensity of one of the signals, or coincidence of two of the IR-active modes. In the related work by Royo and co-workers only two isocyanide stretches were observed for $\text{Cp}^*\text{NbCl}_2(\text{CNXyl})_3$ despite the three predicted by group theory for complexes of this symmetry (C_s) with three meridionally arranged $\text{C}\equiv\text{X}$ ligands (X = O, NR).

Synthesis of stable Nb(III) dicarbonyl complexes—Carbon monoxide also reacted readily with **3** at -72°C , yielding the dark-red pyridine-coordinated dicarbonyl complex (BDI)Nb(N^tBu)(CO)₂(py) (**7**, Scheme 5). The room temperature ¹H NMR spectrum of the product is broadened due to reversible pyridine dissociation in solution ($\Delta G^\ddagger = 15.1(2) \text{ kcal/mol}$). This observation is supported by the change from an average C_1 symmetric complex observed at 253 K to a complex with average C_{2v} symmetry at 343 K; the high temperature spectrum begins to approximate that of **9** and free pyridine. The pyridine ligand readily exchanges with added pyridine-*d*₅ at room temperature to yield **7-*D*₅** and free C₅H₅N, and the CO groups are also exchanged by allowing a solution of **7** to stand under an atmosphere of ¹³CO. Isotope enrichment was needed for identification of the broad CO carbon resonances in the ¹³C{¹H} NMR spectrum (250.2 and 243.6 ppm). The natural abundance CO stretching frequencies for **7** ($\nu_{\text{CO}} = 1954, 1863$) are lower in magnitude by *ca.* 30 cm^{-1} than those for **9** ($\nu_{\text{CO}} = 1988, 1893$), consistent with **7** possessing a more electron-rich metal center.

An X-ray crystal structure of the product (Figure 6) supported the proposed C_1 symmetry observed in solution. The complex is pseudo-octahedral with the imido group located centrally above one of the flanking aryl rings. The Nb=N^tBu bond length (1.806(2) Å) is one of the longest known (alkylimido)niobium bond distances, being on the order of niobium arylimido bonding interactions which are lengthened due to resonance stabilization from the imido nitrogen into the aryl ring. The long metal-imido bond length for **7** may be attributed to the presence of metal-centered π -electrons that occupy orbitals of the same symmetry as

those containing the nitrogen-based p_π electrons. This metal-based approach to π -loading therefore draws an analogy to other π -loaded Nb(V) systems. The longest known Nb=NR (R = alkyl) bond distance in the literature is that of the niobocene imido cation [(Me₃SiC₅H₄)₂Nb(N^tBu)(CN^tBu)][BPh₄] which, despite the cationic charge at the metal center, has a long Nb=N^tBu distance (1.796(2) Å) due to the ligation of three 1 σ ,2 π ligands.⁴¹ Similarly, our recently reported *bis*(imido) niobium complexes bearing the BDI ligand (BDI)Nb(N^tBu)₂(L^{py}) (**8**, L^{py} = pyridine, 4-(dimethylamino)pyridine, Figure 7) exhibit long Nb=N^tBu bond lengths (1.795(3)–1.809(2) Å) consistent with the π -loading effect resulting from the introduction of multiple imido groups.³⁸

The crystal structure of **7** also reveals that the two carbonyl ligands are located *cis* to one another, with the more proximal (to the metal) carbonyl ligand (Nb(1)-C(1) 2.095(3) Å) found *trans* to the pyridine and the more distal carbonyl (Nb(1)-C(2) 2.103(3) Å) *trans* to one of the BDI nitrogens. The difference between the two Nb–C bond lengths is only marginally statistically significant. This trend is reflected in the similarity between the two C–O bond lengths, which are found to be identical within experimental error. The implication from this similarity is that the BDI ligand is not π -bonding significantly with the metal center, since the pyridine ligand should be a weak π -donor.

Next, we were interested in finding an efficient route to the pyridine-free complex **9** for the purposes of exploring Nb(III)-based reaction chemistry. The direct synthesis of **9** from the reaction of **4** with CO gave only modest yields (*ca.* 40%) of the dicarbonyl.³³ From related chemistry with the *bis*(imido) compounds **8**, it was found that the highly electrophilic borane reagent B(C₆F₅)₃ can be used to extract pyridine to form a separable py•B(C₆F₅)₃ complex.³⁸ With the dicarbonyl **7**, B(C₆F₅)₃ does preferentially bind pyridine in benzene solution (Scheme 6), but separation of py•B(C₆F₅)₃ from **9** is tedious and the reaction requires large amounts of the borane reagent. Another impractical but interesting method for forming **9** was found on reacting **7** with [Cp₂Fe][B(3,5-(CF₃)₂-C₆H₃)₄] in benzene (Scheme 6). Upon mixing of the reagents, the color of the solution lightened from dark red to orange-green over *ca.* 30 min as the sparingly soluble ferrocenium reagent was consumed with commensurate precipitation of a black solid. ¹H NMR analysis of the reaction mixture indicated that **9** had formed cleanly, along with one equivalent of ferrocene. Neither the mechanism of this reaction nor the identity of the insoluble solid are known at this time. Attempts at performing this reaction with other ferrocenium salts ([Cp₂Fe][OTf], [Cp₂Fe][PF₆]) failed to give clean reactions, and reaction of the ferrocenium borate salt with the pyridine-coordinated dichloride **1** also failed to give the product of pyridine abstraction.

Our preferred method for forming **9** involved initial formation of the ketimine complex (BDI)Nb(N^tBu)(η^2 -^tBuNCMe₂). We have shown previously that displacement of a coordinated ketimine ligand by CO to yield the dicarbonyl complex proceeded cleanly under mild conditions.³³ Accordingly, starting from **1**, methylation, isocyanide insertion, and ketimine displacement with CO could be performed in one pot to give the dicarbonyl **9** in 70% yield based on the dichloride (Scheme 7). The product crystallized as large yellow-green dichroic blocks from hexane and exhibited analytical data identical to those obtained by direct carbonylation of **4**.

The room temperature NMR spectra of **9** are surprising in that they indicate average molecular C_{2v} symmetry in solution; low-temperature NMR experiments indicate a lowering of symmetry, but the peaks were still broad at the temperature limit of the instrument (193 K). The crystallographically-determined molecular geometry of **9** is square pyramidal with an apical carbonyl ligand (Figure 8). The asymmetric unit of the unit cell contains two independent molecules of **9** with essentially identical metric parameters, indicating that the low symmetry of the solid state geometry is not due to crystal packing forces. The

crystallographic data suggest that the high symmetry observed in solution is the result of rapid intramolecular rearrangement processes. Bridging CO ligands could also account for the high observed symmetry, but the solution-state IR spectrum of **9** ($\nu_{\text{CO}} = 1988, 1893$) suggests that both CO ligands are terminally bound to the metal on the IR time-scale.

The X-ray crystal structure of **9** reveals long Nb=N^tBu bond distances (Nb(1)-N(1) 1.792(3), Nb(2)-N(4) 1.794(4)), which are shorter than those for the pyridine coordinated dicarbonyl but longer than most other (alkylimido)niobium complexes. The structures are distorted slightly from that of an idealized square pyramidal geometry ($\tau_{\text{Nb}(1)} = 0.16$, $\tau_{\text{Nb}(2)} = 0.11$), and, without a *trans* ligand, the apical CO ligands lie closer to the metal center (Nb(1)-C(1) 2.057(5) Å, Nb(2)-C(36) 2.063(6) Å) than the corresponding CO ligand of **7**.

In all three compounds **6**, **7**, and **9**, the Nb-N_{BDI} bond lengths change only slightly with their relative orientation to the imido group and this asymmetry does not lead to bond alternation within the BDI NCCCN ligand backbone as has been observed for related d^0 compounds.³⁸ A similar effect was observed for the *bis*(imido) compounds **8**, indicating that the metal-based π -symmetry orbitals involved in bonding with the BDI π -system are occupied in the d^2 compounds **6**, **7**, and **9**, just as they would be for π -loaded *bis*(imido) compounds. The difference in Nb-N_{BDI} bond distances is a result of σ -based *trans*-influences of the imido ligand compared to the CO or isocyanide ligands.

Formation of Nb=Y (Y = NMes, O, C(Me)OLi) bonds by reactions with Nb(III) compounds

Oxidation of (BDI)Nb(N^tBu)(py) with MesN₃—While **3** could only be generated *in situ*, we were interested in the possibility of utilizing the Nb(III) complex as a precursor for the selective introduction of a second imido group. Addition of mesityl azide to a stirred slurry of **3** at -72 °C resulted in an immediate color change from blue to dark orange, producing the *bis*(imido) complex (BDI)Nb(N^tBu)(NMes)(py) (**10**, Scheme 8, Mes = 2,4,6-Me₃-C₆H₂), which was isolated in 46% yield after crystallization from pentane. Notably, the solution effervesced rapidly upon azide addition, and the color of the solution did not change appreciably after gas evolution ceased. These observations indicate that formation of the **10** was rapid at low temperature. By contrast, ^tBuN₃ failed to react competitively with ligand degradation.

The crystal structure of **10** (Figure 9) indicates features similar to those of the *bis*(^tBu-imido) complexes discussed previously (compounds **8**, Figure 7), with the exception that the geometry at the metal center can now more accurately be described as pseudo-trigonal bipyramidal ($\tau = 0.58$). The shift in geometry from compounds **8** likely reflects a relaxation of steric constraints on changing to the planar arylimido group, since a trigonal bipyramidal geometry with two equatorial imido groups has been predicted to be the most stable conformation for MT₂Ln₃ complexes (M = transition metal, T = potentially triply-bonded ligand, Lⁿ = σ -bonding ligand).⁴² This preferred geometry for *bis*(imido) complexes can be compared to the well-known stability of the bent metallocene systems, in that a trigonal bipyramidal L₃M(NR)₂ structure with equatorial imido groups would be isolobal to a bent metallocene system with three ligands lying in the plane bisecting the Ct-M-Ct angle (Ct = cyclopentadienyl ring centroid). The frontier orbitals for such *bis*(imido) complexes have been found by computational studies to match those of the bent metallocene fragment,⁴³ with the three unoccupied frontier orbitals (two with a_1 symmetry, one with b_2 symmetry) lying in the plane bisecting the N_{imido}-M-N_{imido} angle. An important finding from these calculations is that the frontier orbitals of bent *bis*(imido) complexes lack any unoccupied, out-of-plane orbitals to participate in π -bonding with the ligands bound to the metallocene-like wedge (in direct analogy with the metallocene systems), thus explaining why the bonding within the BDI NCCCN plane is relatively unperturbed despite the substantially different *trans*-influences of the ligands *trans* to the BDI nitrogens. The π -electrons from the

metallacycle are localized within the NCCCN portion of the molecule, whereas vacant π -symmetry metal-based orbitals are available for bonding in complexes such as **1** and **4**. The preference of MT_2L_3 complexes for a trigonal bipyramidal geometry with equatorial imido groups (T ligands) is further supported by the molecular geometry of complexes **2•s** ($s = \text{py}$, thf), which only appear to deviate from an idealized trigonal bipyramidal structure as a result of the constrained geometry of the five-membered niobacycle.

Oxidation of $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CO})_2$ with Ph_2SO —With an interest in forming a terminal $\text{Nb}=\text{O}$ bond, we sought oxidation of **9** with Ph_2SO . The reaction of **9** with 1.0 equiv of Ph_2SO in benzene initially formed a dark green solution from the light green color of the starting material. This initial reaction was followed by a continual effervescence over 1 h at room temperature as the color turned yellow; near the end of the reaction, a crystalline material precipitated from solution. Monitoring the reaction by ^1H NMR spectroscopy indicated that two products formed initially, which were cleanly converted into a single product with averaged C_s symmetry at the end of the reaction; the relationship between this final species and that of the material that precipitated from solution is currently unknown. The precipitated material was found to be highly insoluble in common solvents, and elemental analysis indicated that the product did not contain sulfur.

An X-ray crystal structure of the product revealed it to be the *bis*(μ -oxo)-bridged dimer $[(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})]_2(\mu^2\text{-O})_2$ (**11**, Scheme 9, Figure 10), presumably resulting from reductive $\text{S}=\text{O}$ bond cleavage to give a terminal $\text{Nb}=\text{O}$, which dimerized in solution to yield insoluble **11**. Attempts at monitoring the course of the reaction by *in situ* solution IR spectroscopy of the reaction mixture failed to give evidence for a measurable concentration of the terminal oxo in solution, indicating that the two products observed by ^1H NMR may be two diastereomers of Ph_2SO coordination. The mechanism of dialkylsulfoxide reduction by various molybdenum and tungsten complexes in d^2 oxidation states has been studied extensively in the context of modeling the active site of dimethylsulfoxide reductase. Mechanistic studies on these systems have indicated that the *O*-bound species is the only intermediate on the reaction pathway.⁴⁴

In the X-ray crystal structure of **11** the molecule sits on a crystallographic inversion center which defines the Nb_2O_2 diamond-shaped core. The $\text{Nb}-\text{O}$ bond distances are symmetrically distributed ($\text{Nb}(1)-\text{O}(1)$ 1.967(2) Å, $\text{Nb}(1)-\text{O}(1)^*$ 1.961(2) Å) and of normal magnitudes for Nb oxo-bridged dimers. The $\text{Nb}-\text{O}$ distances match those for terminal $\text{Nb}-\text{OR}$ bond lengths,⁴⁵ indicating that the oxo bridge is acting as a normal alkoxide donor to each metal center. The $\text{O}-\text{O}$ distance (2.521 Å) places the oxygen atoms well outside the covalent radii of one another ($r_c(\text{O}) = 0.66(2)$ Å), but the $\text{Nb}-\text{Nb}$ distance (3.0128(6) Å) is inside the sum of the covalent radii of the metals ($r_c(\text{Nb}) = 1.64(6)$ Å).⁴⁶ Still, the regularity in the bonding between the metal center and the N/O ligands as well as the regularity of the bond lengths within the ligand backbone indicate that the complex is best described as formally carrying two d^0 metal centers, indicating that the close proximity of the metals is a result of the geometric constraints of the oxide bridges ($\text{Nb}(1)-\text{O}(1)-\text{Nb}(1)^*$ 100.16(10)°), not a $\text{Nb}-\text{Nb}$ bonding interaction.

Reaction of $(\text{BDI})\text{Nb}(\text{N}^t\text{Bu})(\text{CO})_2(\text{py})$ with MeLi —Treatment of the Nb(III) carbonyl complexes with trimethylsilyldiazomethane, a carbon-based oxidant conceptually related to the [RN] and [O] transfer reagents used for the synthesis of complexes **10** and **11**, failed to give tractable mixtures of products. We were thus interested in forming a Group 5 carbene in which the reducing capability of the metal would still lead to significant Nb-C double-bond character. Group 6 and later transition metal carbonyls are well-known to undergo addition of nucleophiles at the electrophilic, metal-bound carbonyl carbon. The initial addition forms an acylate, analogous to an organic enolate, which can be quenched at the

oxygen with electrophiles (*e.g.* Me⁺, Me₃Si⁺, etc.) to yield neutral Fischer carbenes.⁴⁷ Considering that the seminal work on transition metal carbenes employed Group 6 metals, it is surprising that only a handful of structurally authenticated Group 5 Fischer-type carbenes are known.^{48–52}

The pyridine adduct of the dicarbonyl species readily adds MeLi to form the dimeric acylate complex [(BDI)Nb(N^tBu)(C(Me)OLi)(CO)]₂ (**12**, Scheme 10) in good yields. The reaction occurred immediately in Et₂O and was accompanied by a color change from dark red to red-orange, followed by precipitation of the product as a red solid after a few minutes at room temperature. The isolated product exhibits a single IR stretch in the range from 2200 to 1600 cm⁻¹, corresponding to the terminal carbonyl group ($\nu_{\text{CO}} = 1951 \text{ cm}^{-1}$), but the limited solubility of **12** in non-coordinating solvents (pentane, Et₂O, C₆H₆, toluene, chlorobenzene, CH₂Cl₂) and its observed reactivity with donor solvents (THF, py) hampered characterization of the product in solution. Nonetheless, a ¹H NMR spectrum of **12** obtained in chlorobenzene (10% C₆D₆) indicated the presence of two isomers in solution. On addition of either THF or pyridine, the sets of resonances for the two isomers collapsed into those characteristic of a single product. The products resulting from the addition of donor solvents were thermally unstable in solution, decomposing into multiple products over *ca.* 30 min at room temperature.

The solid-state structure of **12** was determined by X-ray crystallography on a crystalline sample obtained from cooling a concentrated CH₂Cl₂ solution. The data obtained from this measurement demonstrated the dimeric molecular structure of **12**, resulting from a Li₂O₂ diamond-shaped core situated on a crystallographic inversion center (Figure 11). Interestingly, the Li atoms are also coordinated to the imido nitrogen, forming a highly distorted, but planar, 5-membered niobacycle. The N(1)-Li(1) interaction causes a lengthening of the Nb(1)-N(1) distance from 1.793 Å (avg.) for **9** to 1.830(3) Å for **12**, a range similar to that of an aryl-substituted imido ligand, which is consistent with a weakening of one of N(*p*_π)-Nb(*d*_π) bonding interactions and an increased coordination number at the nitrogen. The Li(1)-N(1)* (2.092(9) Å) and Li(1)-O(1)* (1.871(9) Å) distances are within the ranges of known Li-O/N interactions, but the Li(1)-O(1) distance (1.790(9) Å) is short, falling within the shortest 5% of structurally characterized Li-O bonds. The geometry of the metal centers is square pyramidal ($\tau = 0.29$), with the lithiooxazaniobacycle bridging between apical (acylate) and basal (imido) coordination sites. The Nb(1)-C(3) bond (2.143(5) Å) is longer than for the Nb-C_{basal} bond lengths of **9**, despite the presumably weaker π -accepting acylate ligand compared to the terminal carbonyl of **9**. Also, despite the expected *trans* effect of the imido group on the *trans* Nb-N_{BDI} bond length, the Li coordination to the nitrogen appears to attenuate this effect, as the Nb-N bond *trans* to the imido is only 0.023 Å further from the metal than the BDI nitrogen *trans* to the carbonyl.

The bonding within the acyl group indicates significant multiple bond character between the metal and the acyl carbon. The Nb(1)-C(1) bond (2.059(4) Å) is shortened considerably from the Nb-C σ -bonds of the dimethyl complex (2.1776(17), 2.1874(17) Å), and the long C(1)-O(1) bond distance (1.307(5) Å) is consistent with enolate-type bonding within the acylate group (Figure 12). In accord with the greater electron density at the niobium-bound carbon than for related *d*⁰ acyls, compound **12** does not add trialkylphosphines to form phosphine trapped acyls. In the one literature account of a structurally-authenticated, Fischer-type carbene complex of Nb, the cyclic dithiocarbene complex Cp₂Nb[=C{SC(CF₃)₂}]₂[C(CF₃)=CH(CF₃)],⁵¹ a similar Nb-C bond length (2.06(4) Å) is observed. While several formalisms could be invoked to describe the Nb-C_{acylate} interaction, we find it instructive to consider that the energy of the carbonyl π^* orbital *not* involved in MeLi addition should remain relatively unchanged following MeLi addition,

indicating that a back-bonding/Nb(III) model provides a better rational for the short Nb–C distance than either a ligand radical/Nb(IV) or alkylidene/Nb(V) model. Furthermore, the interaction of the acylate oxygen with *two* lithium cations should serve to remove considerable electron density from the acylate C–O π -system, similar to the effects of electrophile addition during a traditional Fischer carbene synthesis.

Stoichiometric reduction of unsaturated organic substrates with (BDI)Nb(N^tBu)(CO)₂

Reduction of 4,4'-dichlorobenzophenone—An initial investigation into C–C bond forming reactions promoted by the Nb(III) dicarbonyl complex led to the observation of a pinacol coupling product on reaction with a ketone. Addition of 4,4'-dichlorobenzophenone to **9** resulted in a rapid reaction, concurrent with CO release and a color change from green to yellow, to give the pinacol coupling product (BDI)Nb(N^tBu)(O₂C₂Ar^{Cl}₄) (**13**, Scheme 11, Ar^{Cl} = 4-chlorophenyl) in quantitative yield. The product exhibits average C_s symmetry in solution by ¹H NMR spectroscopy, along with a downfield shifted ^tBu group. These data are consistent with a square pyramidal complex that places the imido group in the apical position. A new ¹³C{¹H} NMR resonance was observed at 107.5 ppm, consistent with an aliphatic alkoxide carbon bound by electron withdrawing groups.

Introducing 1.0 equiv of the ketone to a solution of **9** resulted in a 1: 1 mixture of **9** and **13**, indicating either that ketone coordination to form a 1: 1 adduct is reversible or that incorporation of the second equivalent of ketone is much faster than ketone coordination to **9**. The reaction can be considered to occur *via* one of two likely mechanistic pathways. The first involves initial metallaoxirane formation (formally a 2e[−] oxidative process) followed by coordination and insertion of a second equivalent of ketone into the initially formed Nb–C bond (Scheme 12, Mechanism A). This reaction is reminiscent of Pedersen's Nb(III)-mediated aminoalcohol synthesis,⁵³ wherein an isolated Nb–aldimine complex readily reacts with aldehydes and ketones to form 2-aminoalcohols in high yields.

Pinacol coupling could also occur by a radical mechanism in which a 1e[−] reduction of the ketone would produce an initial metal-bound ketyl radical (Scheme 12, Mechanism B).⁵⁴ Several reports of the isolation of stable, metal-bound ketyl complexes have appeared in the literature.^{55–59} Of particular relevance here is the work of Wolczanski and coworkers who found that 1e[−] reduction of di-*tert*-butyl ketone by the Ti^{III} *tris*(siloxide) complex Ti(OSi^tBu₃)₃ led to a ketyl-Ti^{IV} species capable of thermal dissociation of the *neutral* ketone to regenerate Ti(OSi^tBu₃)₃.⁶⁰ The possibility of reversible ketone binding to **9** could account for the observed 1: 1 mixture of **9** and **13** when only 1.0 equiv of ketone was added to **9**. In the presence of a second equivalent of ketone, the Nb(IV)-ketyl complex could then proceed through a number of possible intra- or intermolecular reactions to arrive at the Nb(V)-pinacolate product; one example is given in Scheme 12 for illustrative purposes. Further work in this area will be directed toward elucidating the mechanism of formation of the pinacol coupling product, including investigations into the effects different ketone substituents have on the observed reactivity and on the detectability of transient radical-containing species.

Reaction of (BDI)Nb(N^tBu)(CO)₂ with PhC≡CMe—Addition of the internal alkyne PhC≡CMe to solutions of **9** in benzene immediately caused the solution to turn yellow, which was accompanied by effervescence throughout the color change. The product was identified as the metallacyclopropene/alkyne complex (BDI)Nb(N^tBu)(η^2 -MeCCPh)(CO) (**14**, Scheme 13), which formed cleanly and quantitatively as judged by NMR spectroscopy but was unstable in solution, decomposing into multiple unidentified species after several hours at room temperature.

CO coordination to the metal center in **14** appears to be weak, as degassing a solution of **14** in benzene caused the color to change from yellow to orange; reintroducing CO reverses the color change. Isotopically labeled ^{13}CO can be introduced in this manner, allowing for the observation of a ^{13}CO signal at 212 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. This relatively high-field value for a coordinated CO ($\delta_{\text{CO}}(\mathbf{9}) = 255.6$ ppm; δ (free CO) = 192 ppm) empirically matches the trend observed by IR spectroscopy in which **14** displays only a modest weakening of the C=O bond relative to free CO with respect to the dicarbonyl complex **9** ($\nu_{\text{CO}}(\text{CO}) = 2143$ cm^{-1} ; $\nu_{\text{CO}}(\mathbf{14}) = 2039$ cm^{-1} ; $\nu_{\text{CO}}(\mathbf{9}) = 1988, 1893$). Ambiguity in assigning a formal oxidation state to transition metal alkyne complexes is common in the literature, but the metallacyclopropene character of the complex does appear to increase for more electropositive metal centers. Related $\text{TpNbX}_2(\text{alkyne})$ complexes ($\text{Tp} = \text{tris-pyrazolylborate}$) are known to exhibit behavior consistent with both Nb(III) and Nb(V) character.⁶¹ In agreement with this literature, the reaction of **14** with HCl in MeOH points to both Nb(V)-metallacyclopropene and Nb(III)-alkyne character. Following the treatment of **14** with 1.0 M HCl in MeOH, a GC/MS analysis of the organic products confirmed the formation of β -methylstyrene in a 2:1 ratio with 1-phenyl-1-propyne, the starting alkyne (Scheme 14). The mechanisms leading to both of these products likely involve initial protonation at the metal center.⁶² The styrene product would form *via* subsequent proton transfer to one of the metallacyclopropene carbons followed by a second protonolysis of the Nb-alkenyl bond, while the alkyne would be liberated by the oxidative process of H^+ addition to the metal. Niobium chemistry related to the latter reaction has been reported by Cummins and coworkers, who used an alkyne to “protect” Nb(III) chloride during a ligand metallation step.⁶³ Oxidation of the resulting complex with I_2 furnished the “deprotected” Nb(V) diiodide along with the starting alkyne.

Summary and Conclusions

Our initial attempts at forming low-valent (BDI)Nb compounds supported by the imido ligand resulted in reductive cleavage of one of the ligand N–C_{imine} bonds. This reaction appears to constitute a general route for the introduction of imido groups onto early transition metals. In the current study, this cleavage led to the rare *bis*(imido) moiety, which has been largely unexplored for the Group 5 metals despite its widespread use within Group 6 chemistry. This disparity likely stems from the lack of available starting materials, as the concentration of four valencies at two coordination sites creates difficulties in forming stable complexes.

On attempting to form a Nb(III) complex supported by phosphines, chemical reduction of **1** in the presence of dmpe led to the Nb(IV) complex, **5**. Attempts at forming related Nb(IV) complexes with monodentate phosphines were unsuccessful, suggesting that the higher coordination number and/or electron density provided by the chelating diphosphine were essential to the stability of the isolated Nb(IV) species.

During the course of the reaction leading to **2•py**, a blue solution was observed at low temperatures, which was assigned as the Nb(III) complex **3** based on chemical derivatization. This species was trapped with strong π -acids, leading to the *tris*(isocyanide) **6** and pyridine-coordinated dicarbonyl complex **7**. These compounds were found to be indefinitely stable when stored under an inert atmosphere at room temperature, indicating that the propensity of the formally d^2 metal center to undergo reductive cleavage of the ligand N–C_{imine} bond had been effectively quelled.

Oxidation of **3** with an aryl azide resulted in the formation of the Nb(V) *bis*(imido) complex **10**, which is structurally analogous to the *bis*(imido) complexes described previously.³⁸ This intermolecular redox reaction represents a third route to *bis*(imido) niobium complexes

supported by the BDI ligand,³⁸ indicating that the dearth of precedent for such complexes does not reflect the instability of the ligand *bis(imido)* motif.

The formation of thermally stable Nb(III) complexes led to a range of intermolecular reactivity unavailable with **3** due to its thermal instability. The addition of Ph₂SO to the penta-coordinate dicarbonyl complex **9** gave a clean reaction to form the *bis*(μ -oxo) bridged dimer **11**, which presumably results from dimerization of an initial terminal Nb=O functionality. The dicarbonyl complex **7** readily adds MeLi to generate the niobium acylate complex **12**. This species contains a short Nb=C bond, consistent in magnitude to related alkylidene and carbene complexes. Initial attempts at methylating the acylate using common Me⁺ sources have been unsuccessful, but the anionic moiety may prove to be an interesting starting point for forming heterobimetallic dinuclear clusters.

In an initial application of the reducing capability of **9** toward C–C bond formation, the reaction of **9** with 4,4'-dichlorobenzophenone was found to result in the reductive coupling of two equivalents of the ketone to yield the pinacol coupling product. The mechanism leading to this product could proceed through a number of pathways, as literature precedent on related reactions indicates that either 2e[−] or 1e[−] processes may be operative. Further investigations into this and related reactions between the dicarbonyl and ketones may provide insight into the mechanism of a C–H bond activation reaction described previously, which was proposed to result from an intermediate 1:1 acetone adduct of Nb(III).³³

Finally, the reaction of PhC≡CMe with **9** led to the clean formation of a metallacyclopentene complex, **14**. This species possesses a weakly coordinated CO ligand and was found to react with H⁺ to form both β -methylstyrene and 1-phenyl-1-propyne, which indicates significant contribution from both the Nb(III) and Nb(V) resonance structures to the overall electronic structure of the complex.

Experimental

General Considerations

Unless otherwise noted, all reactions were performed using standard Schlenk line techniques or in an MBraun inert atmosphere box under an atmosphere of nitrogen (<1 ppm O₂/H₂O). Glassware, cannulae, and Celite were stored in an oven at ca. 425 K. Pentane, hexane, Et₂O, THF, toluene, and benzene were purified by passage through a column of activated alumina and degassed prior to use.⁶⁴ Pyridine was distilled from CaH₂. Deuterated solvents were vacuum-transferred from either sodium/benzophenone (C₆D₆, THF-*d*₈) or CaH₂ (pyridine-*d*₅) and degassed with three freeze-pump-thaw cycles. NMR spectra were recorded on Bruker AV-300, AVQ-400, AVB-400, DRX-500, AV-500, and AV-600 spectrometers. ¹H and ¹³C{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) or ¹H-¹³C (HSQC and HMB) experiments. Infrared (IR) samples were either prepared as Nujol mulls and taken between KBr disks or prepared in solution and taken between NaCl plates. MesN₃,⁶⁵ dmpe,⁶⁶ and KC₈⁶⁷ were prepared using standard literature procedures. PhC≡CMe was purified by passage through a plug of activated alumina prior to use. All other reagents were acquired from commercial sources and used as received. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. The X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley on Bruker SMART 1000, SMART APEX, or MicroSTAR-H X8 APEXII diffractometers.

EPR Spectra Measurements

Solution EPR spectra were collected at 9.251 GHz (X-band) and 34.326 GHz (Q-band) frequencies at room temperature in benzene. X-band EPR spectra were collected using a Varian E-109 spectrometer equipped with an E-102 microwave bridge. Q-band EPR spectra were collected using a Bruker EPR spectrometer (EMX 10/12 with ER5106QT Flexline resonator). Both X- and Q-band measurements were taken with 100 kHz magnetic field modulation. The microwave frequency was calibrated using a standard sample of TEMPO (Aldrich, 30 μ M, 50 v/v% glycerol solution).

Representative procedure for X-ray crystallography

A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kapton[®] loop. The loop was transferred to a diffractometer equipped with a CCD area detector,⁶⁸ centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.⁶⁹ Cell dimensions reported were calculated from all reflections with $I > 10 \sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.⁷⁰ An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁷¹ Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined on F^2 using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically. ORTEP diagrams were created using the ORTEP-3 software package.⁷² For all structures, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. See reference ³³ for complete crystallographic data on compound **9**.

(mad)Nb(NAr)(N^tBu)(py) (2•py)

A flask containing a suspension of **1** (335 mg, 0.46 mmol) in Et₂O (20 mL) was cooled to -72°C , and to it was added a suspension of K₂C₈ (124 mg, 0.92 mmol) in Et₂O (10 mL). The solution rapidly darkened to a deep blue color. Stirring was continued at -72°C until all of the starting materials were consumed (*ca.* 10 min). The flask was then allowed to warm to room temperature, during which time the color of the solution turned progressively green, then yellow. Stirring was continued for 12 h; the volatile material was then removed *in vacuo* and the residue was extracted with pentane (3 $\times$ 15 mL). The filtrate was concentrated and stored at -35°C until crystalline material formed. The product was collected by filtration and the residual solvent was removed under vacuum. Yield: 70 mg, 23%. ¹H NMR (500 MHz, C₆D₆, 298 K): δ 8.36 (dd, 2H, py), 7.27 (d, 2H, Nb=NAr_m), 7.01 (t, 1H, Nb=NAr_p), 6.87 (dd, 1H, C=NAr), 6.81 (t, 1H, C=NAr), 6.80 (d, 1H, HC(C(Me)NAr)(CMe)), ⁴J_{HH} = 1 Hz), 6.58 (dd, 1H, C=NAr), 6.50 (tt, 1H, py), 6.11 (m, 2H, py), 4.76 (sept, 2H, HCMe₂ of Nb=NAr), 3.62 (sept, 1H, HCMe₂ of C=NAr), 2.95 (sept, 1H, HCMe₂ of C=NAr), 2.91 (d, 3H, HC(C(Me)NAr)(CMe)), ⁴J_{HH} = 1.0 Hz), 1.64 (s, 3H, HC(C(Me)NAr)(CMe)), 1.52 (s, 9H, ^tBu), 1.50 (d, 6H, HCMe₂ of Nb=NAr), 1.33 (d, 3H, HCMe₂ of C=NAr), 1.23 (d, 6H, HCMe₂ of Nb=NAr), 1.05 (d, 3H, HCMe₂ of C=NAr), 1.00 (d, 3H, HCMe₂ of C=NAr), 0.80 (d, 3H, HCMe₂ of C=NAr). ¹³C{¹H} NMR (125 MHz, C₆D₆): δ 185.93 ((HC(C(Me)NAr)(CMe)), 154.04 ((HC(C(Me)NAr)(CMe)), 153.42 (py), 145.37 (Ar), 142.75 (2 $\times$ Nb=NAr), 141.78 (Ar), 141.21 (Ar), 137.73 (py), 131.75 ((HC(C(Me)NAr)(CMe)), 126.32 (Ar), 124.20 (Ar), 123.68 (Ar), 123.53 (py), 122.84 (Nb=NAr), 120.92 (Ar), 64.77 (^tBu, C_o), 34.54 (HC(C(Me)NAr)(CMe)), 34.32 (^tBu, C_β), 28.99 (CHMe₂ of C=NAr), 28.21 (CHMe₂ of C=NAr), 27.58 (CHMe₂ of Nb=NAr), 25.13 (CHMe₂ of C=NAr), 25.05 (CHMe₂ of C=NAr), 25.03 (CHMe₂ of Nb=NAr), 24.79 (CHMe₂

of Nb=NAr), 24.51 (CHMe₂ of C=NAr), 23.56 (CHMe₂ of C=NAr), 23.16 (HC(C(Me)NAr)(CMe)). Anal. Calcd for C₃₈H₅₅N₄Nb: C, 69.07; H, 8.39; N, 8.48. Found: C, 68.81, H 8.56; N, 8.54.

(mad)Nb(NAr)(N^tBu)(thf) (2•thf)

A solution of **4** (300 mg, 0.49 mmol) in 10 mL THF was added to a 100 mL Schlenk flask. The yellow solution was degassed by three freeze-pump-thaw cycles. Then, with the solution frozen, the flask was back-filled with an atmosphere of H₂. The flask was sealed tightly and allowed to warm to room temperature with stirring as the solid melted. The color rapidly changed from pale yellow to orange upon thawing. The solution was stirred overnight, then the volatile materials were removed under vacuum, and the residue was extracted with pentane (2 × 15 mL) and filtered. The filtrate was concentrated to ca. 5 mL and stored at -35 °C until a bright yellow crystalline solid formed. The crystalline material collected by filtration and the residual solvent was removed under vacuum. Yield: 77 mg, 24%. ¹H NMR (500 MHz, C₆D₆, 298K): δ 7.28 (d, 2H, Nb=NAr_m), 7.06-7.01 (m, 3H, Nb=NAr_p and C=NAr_m), 6.97 (dd, 1H, C=NAr_p), 6.64 (d, 1H, HC(C(Me)NAr)(CMe), ⁴J_{HH} = 1.0 Hz), 4.85 (sept, 2H, HCMe₂ of Nb=NAr), 3.64 (sept, 1H, HCMe₂ of C=NAr), 3.57 (m, 2H, THF), 3.25 (m, 2H, THF), 3.10 (sept, 1H, HCMe₂ of C=NAr), 2.75 (d, ⁴J_{HH} = 1.0 Hz, 3H, HC(C(Me)NAr)(CMe)), 1.53 (d, 6H, CHMe₂ of Nb=NAr), 1.52 (s, 9H, ^tBu), 1.42 (d, 6H, CHMe₂ of Nb=NAr), 1.35 (d, 3H, CHMe₂ of C=NAr), 1.15 (d, 3H, CHMe₂ of C=NAr), 1.09 (d, 3H, CHMe₂ of C=NAr), 1.06 (d, 3H, CHMe₂ of C=NAr), 1.00 (m, 4H, THF). ¹³C NMR (125 MHz, C₆D₆, 298K): δ 185.25 (HC(C(Me)NAr)(CMe)), 153.3 ((HC(C(Me)NAr)(CMe)), 145.11 (Ar), 143.27 (2 × Nb=NAr), 142.30 (Ar), 142.11 (Ar), 130.43 ((HC(C(Me)NAr)(CMe)), 126.71 (Ar), 124.52 (Ar), 123.84 (Ar), 122.79 (Nb=NAr), 121.42 (Ar), 77.92 (THF), 64.53 (^tBu, C_α), 34.71 (^tBu, C_β), 34.16 (HC(C(Me)NAr)(CMe)), 29.36 (CHMe₂ of C=NAr), 28.16 (CHMe₂ of C=NAr), 27.60 (CHMe₂ of Nb=NAr), 25.72 (THF), 25.43 (CHMe₂ of Nb=NAr), 25.25 (CHMe₂ of C=NAr), 24.88 (CHMe₂, 4C from Nb=NAr and C=NAr), 23.84 (CHMe₂ of C=NAr), 22.62 (HC(C(Me)NAr)(CMe)). Anal. Calcd for C₃₇H₅₈N₃NbO: C, 67.97; H, 8.94; N, 6.43. Found: C, 67.72, H 9.18; N, 6.33.

(BDI)Nb(N^tBu)Cl(dmpe) **5**

Et₂O (15 mL) was added to a Schlenk flask containing **1** (300 mg, 0.41 mmol) and dmpe (123 mg, 0.82 mmol). The flask was cooled to -72 °C, then a cold (-72 °C) slurry of K₂CO₃ in Et₂O (5 mL) was added by cannula transfer. The color quickly turned dark yellow-brown. The flask was sealed and the solution was stirred overnight at room temperature, after which time the color turned yellow-green. The volatile materials were removed under vacuum, and the product was extracted with pentane (3 × 10 mL). The filtrate was concentrated until a microcrystalline material began to form. Filtration of this solution and storage of the filtrate at -40 °C caused crystallization of the product as yellow-green dichroic crystals. The crystals were collected by filtration and the residual solvent was removed under vacuum. Yield: 120 mg, 38 %. ¹H NMR (400 MHz, C₆D₆, 298 K): broad signals observed at δ 9.86, 8.41, 6.36, 3.56, 2.16, 1.81, 1.24, -2.10. Anal. Calcd for C₃₉H₆₆ClN₃NbP₂: C, 61.05; H, 8.67; N, 5.48. Found: C, 61.41, H 8.97; N, 5.85. μ_{eff} = 1.53 μ_B (Evans' method,⁷³ benzene, 22 °C)

(BDI)Nb(N^tBu)(CNXyl)₃ **6**

A suspension of K₂CO₃ (66.5 mg, 0.49 mmol) in Et₂O (5 mL) was cooled to -72 °C and added by cannula to a stirred slurry of **1** (180 mg, 0.25 mmol) in Et₂O (15 mL) at -72 °C. The resulting slurry was stirred for 10 min at -72 °C, then XylNC (96.8 mg, 0.74 mmol) was added as a solid in one portion. The color of the solution immediately turned dark red then slowly blue-green on warming to room temperature. The slurry was stirred overnight, then the volatile materials were removed under vacuum, leaving the dark blue-green solid. The

product was extracted with pentane (2×15 mL), filtered, and concentrated until a purple microcrystalline material began to form. Storing the flask at -40 °C for 2 d precipitated more purple material. The solid was collected by filtration and the residual solvent was removed under vacuum. Yield: 77 mg, 32 %. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 7.21 (br s, 3H), 6.91 (br s, 3H), 6.80 (m, 9H), 5.23 (s, 1H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 4.01 (br sept, 2H, CHMe_2), 3.60 (br sept, 2H, CHMe_2), 2.45 (s, 12H, Xyl), 2.29 (s, 6H, Xyl), 2.12 (br s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.91 (br s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.37 (br d, 6H, CHMe_2), 1.28 (br d, 6H, CHMe_2), 1.21 (br d, 6H, CHMe_2), 1.10 (br d, 6H, CHMe_2), 1.07 (s, 9H, ^tBu). ^1H NMR (500 MHz, $\text{THF}-d_8$, 223 K): δ 7.18 (m, 4H, Ar), 7.07 (m, 5H), 6.95 (m, 3H), 6.84 (m, 3H), 5.05 (s, 1H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 3.77 (sept, 2H, CHMe_2), 3.36 (sept, 2H, CHMe_2), 2.43 (s, 12H, Xyl), 2.18 (s, 6H, Xyl), 1.99 (s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.71 (s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.12 (m, 12H, CHMe_2), 1.00 (d, 6H, CHMe_2), 0.92 (d, 6H, CHMe_2), 0.75 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $\text{THF}-d_8$, 223 K): δ 161.9, 158.8, 152.6, 152.5, 143.9, 142.8, 133.7, 132.8, 129.9, 129.0, 128.5, 127.6, 127.4, 125.0, 124.6, 124.4, 124.1, 94.2, 66.8, 32.9, 28.7, 28.5, 27.4, 26.2, 26.0, 25.7, 25.5, 20.5, 19.2. IR (KBr, nujol, cm^{-1}): 2011 (s), 1986 (s). Anal. Calcd for $\text{C}_{60}\text{H}_{77}\text{N}_6\text{Nb}$: C, 73.90; H, 7.96; N, 8.62. Found: C, 73.51, H 8.03; N, 8.46.

(BDI)Nb(^tBu)(CO) $_2$ (py) 7

A solution of **3** was prepared as for **6**, using 500 mg of **1** (0.68 mmol) and 194 mg of K_2C_8 (1.44 mmol). CO was admitted by slowly bubbling the gas through the cold slurry for 2 min; the color of the solution immediately turned red. After warming to room temperature, the solution was stirred for 1 h, then the volatile materials were removed under vacuum. Extraction of the product with pentane (50 mL) gave a dark red solution, which was concentrated (35 mL), filtered, and stored at -40 °C for several days. The red crystalline material that formed was collected by filtration and any residual solvent was removed under vacuum. Yield: 182 mg, 37 %. ^1H NMR (600 MHz, C_6D_6 , 298 K): δ 8.90 (br d, 2H, py), 7.20 (m, 4H, Ar), 7.07 (br s, 2H, Ar), 6.80 (br m, 1H, py), 6.50 (br s, 2H, py), 5.24 (s, 1H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 3.78 (br s, 1H, CHMe_2), 3.15 (br s, 1H, CHMe_2), 2.67 (br s, 1H, CHMe_2), 2.44 (br s, 1H, CHMe_2), 1.92 (br s, 3H), 1.78 (br s, 3H), 1.73 (br s, 3H), 1.62 (br s, 3H), 1.28 (br s, 3H), 1.14 (br s, 3H), 0.96 (br s, ^tBu), 0.82 (br s, 3H), 0.74 (br s, 3H). ^1H NMR (500 MHz, $\text{C}_6\text{H}_5\text{Cl}/10\%$ C_6D_6 , 253 K): δ 9.26 (s, 1H, py), 8.60 (s, 1H, py), 5.22 (s, 1H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 3.70 (sept, 1H, CHMe_2), 3.07 (sept, 1H, CHMe_2), 2.62 (sept, 1H, CHMe_2), 2.39 (sept, 1H, CHMe_2), 1.89 (s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.72 (s, 3H, $\text{HC}(\text{C}(\text{Me})\text{NAr})_2$), 1.67 (d, 3H, CHMe_2), 1.54 (d, 3H, CHMe_2), 1.21 (d, 3H, CHMe_2), 1.07 (d, 3H, CHMe_2), 0.99 (d, 3H, CHMe_2), 0.95 (d, 3H, CHMe_2), 0.90 (s, 9H, ^tBu), 0.77 (d, 3H, CHMe_2), 0.71 (d, 3H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, $\text{C}_6\text{H}_5\text{Cl}/10\%$ C_6D_6 , 253 K): δ 250.2, 243.6, 164.5, 163.2, 153.3, 153.2, 149.8, 149.5, 143.9, 143.5, 143.0, 142.7, 141.8, 141.6, 137.2, 125.9, 125.8, 124.1, 124.0, 123.9, 123.5, 96.0, 65.5, 30.7, 29.1, 29.0, 28.6, 28.5, 26.1, 25.9, 25.7, 25.6, 25.1, 25.0, 24.8, 24.7, 24.5. Anal. Calcd for $\text{C}_{40}\text{H}_{55}\text{N}_4\text{NbO}_2$: C, 67.02; H, 7.73; N, 7.82. Found: C, 66.90, H 7.89; N, 7.90. IR (KBr, nujol, cm^{-1}): 1954 (s), 1863 (s).

(BDI)Nb(^tBu)(CO) $_2$ 9

An alternative synthesis³³ of **9** can be performed as follows, providing the product in higher overall yields. A solution of **1** (1.46 g, 2.0 mmol) in Et_2O (50 mL) was cooled to -40 °C. With vigorous stirring, a solution of MeMgBr in Et_2O (1.33 mL, 3.0 M, 4.0 mmol) was added dropwise by syringe. The solution rapidly turned bright yellow and a white precipitate formed. The flask was allowed to warm to room temperature, then the volatile materials were removed under vacuum. The yellow material was extracted with hexane (3×35 mL) and the solution was filtered into a 500 mL round-bottom flask to give a clear yellow filtrate. The yellow solution was stirred and cooled to 0 °C, then a solution of $^t\text{BuNC}$ (226.3 μL , 2.0

mmol) in Et₂O (10 mL) was added dropwise by syringe. The solution immediately turned dark red. After 15 min of stirring at room temperature, the red solution was concentrated to 50 mL, then the headspace of the flask was back-filled with CO (1 atm). The flask was sealed and the solution was stirred vigorously for 4 h after which time the headspace was refilled with CO to maintain 1 atm of pressure. Stirring for a further 8 h resulted in a dark green solution indicating completion of the reaction. The solution was concentrated until a green crystalline material began to form; storage of the sealed flask at -40 °C for 24 h caused the product to precipitate as dark yellow-green dichroic blocks. The material was collected by filtration and the residual solvent was removed under vacuum. Yield: 919 mg, 72 % (from two crops). The analytical data for **9** prepared by this method were identical to those given previously.

(BDI)Nb(N^tBu)(NMe₂)(py) **10**

A flask containing a suspension of **1** (817 mg, 1.12 mmol) in Et₂O (30 mL) was cooled to -72 °C, and to it was added a cold (-72 °C) suspension of K₂C₈ (302 mg, 2.23 mmol) in Et₂O (10 mL). The solution rapidly darkened to a deep blue color. Stirring was continued at -72 °C for 10 min, then a solution of MesN₃ in Et₂O (5 mL) at -72 °C was added by cannula, causing the solution to rapidly turn dark orange. The cold bath was removed and the solution was allowed to attain room temperature. After stirring for 12 h at room temperature, the volatile materials were removed under vacuum, and the product was extracted with pentane (3 × 10 mL), concentrated, and stored at -40 °C for 2 d. An orange microcrystalline solid was collected and the residual solvent was removed under vacuum. Yield 408 mg, 46 %. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 8.20 (br s, 1H, py), 7.16 (br s, 3H), 7.06 (br s, 3H), 6.88 (br s, 1H), 6.51 (br s, 2H), 6.15 (br s, 2H), 5.23 (s, 1H, HC(C(Me)NAr)₂), 3.82 (br sept, 2H, CHMe₂), 3.68 (br s, 1H, CHMe₂), 3.34 (br s, 1H, CHMe₂), 2.98 (s, 3H, Mes), 2.80 (s, 3H, Mes), 2.31 (s, 3H, Mes), 1.73 (br s, 3H, HC(C(Me)NAr)₂), 1.66 (br s, 3H, HC(C(Me)NAr)₂), 1.61 (d, 6H, CHMe₂), 1.28 (d, 9H, CHMe₂), 1.14 (d, 6H, CHMe₂), 0.77 (s, 9H, ^tBu), 0.60 (br s, 3H, CHMe₂). ¹H NMR (400 MHz, THF-*d*₈, 233 K): δ 8.51 (d, 1H), 7.58 (m, 2H), 7.25 (m, 2H), 7.02 (m, 4H), 6.80 (t, 1H), 6.73 (s, 2H), 6.57 (d, 1H), 5.37 (s, 1H, HC(C(Me)NAr)₂), 3.70 (m, 2H, CHMe₂), 3.29 (sept, 1H, CHMe₂), 3.22 (sept, 1H, CHMe₂), 2.61 (s, 3H, Mes), 2.40 (s, 3H, Mes), 2.23 (s, 3H, Mes), 1.78 (s, 3H, HC(C(Me)NAr)₂), 1.71 (s, 3H, HC(C(Me)NAr)₂), 1.58 (d, 3H, CHMe₂), 1.44 (d, 3H, CHMe₂), 1.30 (d, 3H, CHMe₂), 1.16 (d, 3H, CHMe₂), 1.06 (d, 3H, CHMe₂), 0.85 (d, 3H, CHMe₂), 0.77 (d, 3H, CHMe₂), 0.45 (d, 3H, CHMe₂), 0.40 (s, 9H, ^tBu). ¹³C{¹H} NMR (125.8 MHz, THF-*d*₈, 223K): δ 167.70, 167.23, 155.31, 153.95, 152.93, 152.67, 148.90, 143.62, 143.35, 142.42, 142.04, 138.10, 134.16, 129.57, 129.34, 128.85, 128.07, 126.69, 125.67, 125.08, 124.72, 124.56, 124.19, 122.76, 100.34, 65.70, 33.07, 32.53, 29.96, 29.17, 28.82, 27.80, 27.36, 26.13, 25.01, 24.87, 24.73, 24.66, 24.03, 21.52, 21.46, 20.89. Anal. Calcd for C₄₇H₆₆N₅Nb: C, 71.10; H, 8.38; N, 8.82. Found: C, 70.76, H 8.30; N, 8.83.

[(BDI)Nb(N^tBu)]₂(μ²-O)₂ **11**

A solution of Ph₂SO (15.2 mg, 0.08 mmol) in benzene (2 mL) was added to a solution of **9** (47.8 mg, 0.08 mmol) in benzene (5 mL) at room temperature. The solution quickly turned dark yellow-green and began to effervesce slowly. The homogeneous mixture was allowed to stand at room temperature for 12 h over which time the color turned bright yellow and a yellow crystalline solid deposited from solution. The solvent was decanted and the solid was washed with benzene (5 mL) and collected by filtration. Residual solvent was removed under vacuum to yield a bright yellow crystalline solid. Yield: 40 mg, 86 %. NMR data for the majority species before product precipitation: ¹H NMR (500 MHz, C₆D₆, 298 K): δ 7.30 (m, 4H, Ar), 6.92 (m, 2H, Ar), 5.22 (s, 1H, HC(C(Me)NAr)₂), 3.79 (sept, 2H, CHMe₂), 2.99 (sept, 2H, CHMe₂), 1.47 (s, 6H, HC(C(Me)NAr)₂), 1.42 (d, 6H, CHMe₂), 1.26 (s, 9H, ^tBu),

1.24 (d, 6H, CHMe₂), 1.07 (d, 6H, CHMe₂), 0.56 (d, 6H, CHMe₂). The low solubility of **11** in common organic solvents prevented further characterization by NMR spectroscopy. Anal. Calcd for C₆₆H₁₀₀N₆Nb₂O₂: C, 66.32; H, 8.43; N, 7.03. Found: C, 66.11, H 8.69; N, 7.12.

[(BDI)Nb(N^tBu)(C(Me)OLi)(CO)]₂ **12**

MeLi in Et₂O (1.7 M, 0.123 mL, 0.21 mmol) was added dropwise to a stirred solution of **7** (150 mg, 0.21 mmol) in Et₂O (5 mL) at room temperature. The solution immediately turned dark orange as a microcrystalline precipitate began to form. Pentane (1 mL) was added and the solution was allowed to stand at room temperature for 2 h, over which time more microcrystalline solid precipitated from solution. The supernatant was decanted and the residual solvent was removed from the crystalline material under vacuum to yield a dark orange powder. Yield: 94 mg, 68 %. ¹H NMR (500 MHz, C₆H₅Cl/10 % C₆D₆, 298 K, major isomer): δ 5.48 (s, 1H, HC(C(Me)NAr)₂), 3.62 (sept, 1H, CHMe₂), 3.14 (sept, 1H, CHMe₂), 2.90 (sept, 1H, CHMe₂), 2.81 (sept, 1H, CHMe₂), 1.92 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 1.42 (d, 3H, CHMe₂), 1.38 (d, 3H, CHMe₂), 1.26 (m, 18H, CHMe₂), 1.18 (d, 3H, CHMe₂), 1.13 (d, 3H, CHMe₂), 1.07 (d, 3H, CHMe₂), 0.98 (br s, ^tBu). ¹H NMR (500 MHz, C₆H₅Cl/10 % C₆D₆, 298 K, minor isomer): δ 5.47 (s, 1H, HC(C(Me)NAr)₂), 3.64 (sept, 1H, CHMe₂), 3.07 (sept, 1H, CHMe₂), 2.83 (sept, 1H, CHMe₂), 2.81 (sept, 1H, CHMe₂), 1.93 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H), 1.54 (d, 3H, CHMe₂), 1.33 (d, 3H, CHMe₂), 1.26 (m, 6H, CHMe₂), 1.24 (d, 3H, CHMe₂), 1.22 (d, 3H, CHMe₂), 1.12 (d, 3H, CHMe₂), 1.05 (d, 3H, CHMe₂), 0.93 (s, ^tBu). Anal. Calcd for C₇₂H₁₀₆Li₂N₆Nb₂O₄: C, 65.55; H, 8.10; N, 6.37. Found: C, 65.18, H 8.21; N, 6.55. IR (KBr, nujol, cm⁻¹): 1951 (s).

(BDI)Nb(N^tBu)(O₂C₂Ar^{Cl}₄) **13**

A solution of 4,4'-Cl₂-benzophenone (82.8 mg, 0.31 mmol) in toluene (3 mL) was added dropwise to a stirred solution of **2.1** (105 mg, 0.16 mmol) in toluene (5 mL) at room temperature. The solution effervesced rapidly as the color changed from dark green to bright yellow. After 20 min at room temperature, the volatile materials were removed under vacuum to give a bright yellow powder. The product was crystallized from a concentrated toluene solution stored at -35 °C for 3 d. The crystallized product was collected by filtration and the residual solvent was removed under vacuum to provide a yellow powder. Yield: 128 mg, 71 %. ¹H NMR (500 MHz, C₆D₆, 298 K): δ 7.27 (d, 4H), 7.03 (m, 4H), 6.94 (dd, 2H), 6.91 (d, 4H), 6.76 (d, 4H), 6.57 (d, 4H), 5.37 (s, 1H, HC(C(Me)NAr)₂), 4.06 (sept, 2H, CHMe₂), 2.26 (sept, 2H, CHMe₂), 1.61 (s, 6H, HC(C(Me)NAr)₂), 1.44 (s, 9H, ^tBu), 1.24 (d, 6H, CHMe₂), 1.18 (d, 6H, CHMe₂), 0.94 (d, 6H, CHMe₂), 0.82 (d, 6H, CHMe₂). ¹³C{¹H} NMR (125 MHz, THF-*d*₈, 313 K): δ 171.0, 147.7, 147.0, 146.5, 144.3, 143.2, 132.8, 132.4, 131.7, 131.2, 129.8, 129.0, 128.0, 127.7, 126.8, 125.7, 124.8, 107.5, 107.2, 71.4, 33.0, 29.3, 28.6, 26.3, 26.4, 26.0, 25.8, 24.7. Anal. Calcd for C₅₉H₆₆Cl₄N₃NbO₂: C, 65.38; H, 6.14; N, 3.88. Found: C, 66.54, H 5.95; N, 4.09 (average of two measurements; both measurements where greater than 0.4 % above the calculated value for carbon which is due to the presence of residual toluene in the sample).

(BDI)Nb(N^tBu)(η²-MeCCPh)(CO) **14**

PhC≡CMe (9.62 μL, 0.08 mmol) was added by pipette to a solution of **2.1** (49 mg, 0.08 mmol) in C₆D₆ (0.6 mL). The solution rapidly effervesced as the color turned from dark green to bright yellow. The solution was transferred to an NMR tube and quickly cooled in the probe to 253 K for analysis. For introduction of ¹³CO, the solution was added to a J. Young tube and degassed with three freeze-pump-thaw cycles. After warming the solution to room temperature following the third cycle, the tube was refilled with ¹³CO, sealed and shaken vigorously. The material was characterized without isolation due to the thermal instability of the product. The product was characterized in solution by NMR and IR spectroscopies. ¹H NMR (500 MHz, C₇D₈, 253 K): δ 7.40 (d, 2H, PhC≡CMe), 7.27 (t, 2H,

PhC≡CMe), 7.15-6.90 (m, 7H, Ar and *PhC≡CMe*), 5.20 (s, 1H, *HC(C(Me)NAr)₂*), 3.81 (sept, 1H, *CHMe₂*), 3.45 (m, 2H, *CHMe₂*), 2.75 (s, 3H, *PhC≡CMe*), 2.41 (sept, 1H, *CHMe₂*), 1.84 (s, 3H, *HC(C(Me)NAr)₂*), 1.52 (m, 9H, *CHMe₂* and *HC(C(Me)NAr)₂*), 1.23 (d, 3H, *CHMe₂*), 1.10 (d, 3H, *CHMe₂*), 1.93 (d, 3H, *CHMe₂*), 0.86 (m, 6H, *CHMe₂*), 0.80 (d, 3H, *CHMe₂*), 0.74 (s, ^tBu). ¹³C{¹H} NMR (125.7 MHz, C₇D₈, 253 K): δ 213.5 (CO, Δν_{1/2} = 54 Hz), 179.9, 179.7, 168.5, 164.2, 152.6, 152.0, 151.7, 150.3, 142.1, 142.0, 141.9, 141.7, 141.3, 131.7, 130.6, 129.1, 128.4, 126.4, 125.6, 124.9, 124.5, 124.6, 123.6, 100.2, 68.4, 31.0, 29.1, 28.9, 27.7, 27.3, 25.4, 25.2, 25.2, 24.8, 24.6, 24.4, 24.3, 24.0, 23.2, 18.2. IR (Si⁰, benzene, cm⁻¹): 2039 (s).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Molecular structure of **2•py** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and *iso*-propyl groups were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths(Å): Nb(1)-N(1) 1.803(5), Nb(1)-N(2) 1.821(5), Nb(1)-N(3) 2.340(5), Nb(1)-N(4) 2.279(6), Nb(1)-C(32) 2.213(7), C(31)-C(32) 1.327(8), C(30)-C(31) 1.447(9), N(3)-C(30) 1.267(7). Selected bond angles (°): N(1)-Nb(1)-N(2) 114.96(19), N(1)-Nb(1)-N(3) 116.3(2), N(2)-Nb(1)-N(3) 128.72(17), C(32)-Nb(1)-N(4) 154.00(19), C(1)-N(1)-Nb(1) 161.2(4), C(5)-N(2)-Nb(1) 173.4(4).

Figure 2.

Left: Proposed reaction scheme leading to **2•thf**. *Right:* Molecular structure of **2•thf** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and *iso*-propyl groups were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-N(1) 1.786(3), Nb(1)-N(2) 1.826(4), Nb(1)-N(3) 2.332(3), Nb(1)-O(1) 2.259(3), Nb(1)-C(18) 2.203(5), N(3)-C(20) 1.294(6), C(19)-C(20) 1.450(7), C(18)-C(19) 1.346(7), N(1)-C(1) 1.465(6), N(2)-C(5) 1.390(6). Selected bond angles (°): N(1)-Nb(1)-N(2) 116.91(18), N(1)-Nb(1)-C(18) 99.2(2), N(2)-Nb(1)-C(18) 91.39(19), N(1)-Nb(1)-O(1) 100.54(17), N(2)-Nb(1)-O(1) 94.06(15), C(18)-Nb(1)-O(1) 154.44(15), N(1)-Nb(1)-N(3) 115.53(15), N(2)-Nb(1)-N(3) 126.94(14), C(18)-Nb(1)-N(3) 72.90(16), O(1)-Nb(1)-N(3) 83.95(13), C(1)-N(1)-Nb(1) 168.5(4), C(5)-N(2)-Nb(1) 176.2(4).

Figure 3.

Molecular structure of **5** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and *iso*-propyl groups were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-N(1) 1.789(2), Nb(1)-N(2) 2.286(2), Nb(1)-N(3) 2.268(2), Nb(1)-P(1) 2.6839(8), Nb(1)-P(2) 2.6757(8), Nb(1)-Cl(1) 2.5802(7), N(2)-C(24) 1.332(4), C(24)-C(25) 1.404(4), C(25)-C(26) 1.396(4), N(3)-C(26) 1.338(3). Selected bond angles (°): N(1)-Nb(1)-N(3) 99.09(9), N(1)-Nb(1)-N(2) 98.81(9), N(3)-Nb(1)-N(2) 84.15(8), N(1)-Nb(1)-Cl(1) 167.68(7), N(3)-Nb(1)-Cl(1) 87.78(6), N(2)-Nb(1)-Cl(1) 92.03(6), N(1)-Nb(1)-P(2) 96.83(8), N(3)-Nb(1)-P(2) 163.81(6), N(2)-Nb(1)-P(2) 96.35(6), Cl(1)-Nb(1)-P(2) 76.04(3), N(1)-Nb(1)-P(1) 94.59(7), N(3)-Nb(1)-P(1) 100.21(6), N(2)-Nb(1)-P(1) 165.10(6), Cl(1)-Nb(1)-P(1) 74.02(3), P(2)-Nb(1)-P(1) 75.49(2), C(1)-N(1)-Nb(1) 176.5(2).

Figure 4.

Top: X-band EPR spectrum of **5**. *Bottom:* Simulated and experimental Q-band EPR spectra of **5**. Both experimental spectra were recorded at 298 K.

Figure 5.

Molecular structure of **6** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and the N(5) and N(6) aryl groups were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-C(1) 2.216(3), Nb(1)-C(2) 2.183(2), Nb(1)-C(3) 2.203(3), Nb(1)-N(4) 1.797(2), Nb(1)-N(5) 2.2707(18), Nb(1)-N(6) 2.326(2), C(1)-N(1) 1.173(3), C(2)-N(2) 1.165(3), C(3)-N(3) 1.163(3), N(5)-C(45) 1.318(3), C(45)-C(46) 1.406(4), C(46)-C(47) 1.403(4), N(6)-C(47) 1.332(3). Selected bond angles (°): N(1)-C(1)-Nb(1) 178.2(2), N(2)-C(2)-Nb(1) 169.6(2), N(3)-C(3)-Nb(1) 177.5(2), C(28)-N(4)-Nb(1) 173.21(18), C(3)-Nb(1)-C(1) 175.83(8), C(2)-Nb(1)-N(5) 171.74(8), N(4)-Nb(1)-N(6) 171.30(8).

Figure 6.

Molecular structure of **7** as determined by a single crystal X-ray diffraction study. The hydrogen atoms were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-C(1) 2.095(3), Nb(1)-C(2) 2.103(3), Nb(1)-N(1) 1.806(2), Nb(1)-N(2) 2.246(2), Nb(1)-N(3) 2.308(2), Nb(1)-N(4) 2.350(2), C(1)-O(1) 1.152(3), C(2)-O(2) 1.147(3), N(2)-C(20) 1.330(3), C(20)-C(21) 1.387(4), C(21)-C(22) 1.400(4), N(3)-C(22) 1.336(6). Selected bond angles (°): C(2)-Nb(1)-N(2) 167.96(10), N(1)-Nb(1)-N(3) 169.43(9), C(1)-Nb(1)-N(4) 173.24(10), O(1)-C(1)-Nb(1) 169.9(2), O(2)-C(2)-Nb(1) 172.6(3), C(3)-N(1)-Nb(1) 169.3(2).

Figure 7.
Diagram of (BDI)Nb(N^tBu)₂L^{py} (**8**).

Figure 8.

Molecular structure of one of the two crystallographically independent molecules in the asymmetric unit of **9** as determined by a single crystal X-ray diffraction study.³³ The hydrogen atoms were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-C(1) 2.057(5), Nb(1)-C(2) 2.122(5), Nb(1)-N(1) 1.792(3), Nb(1)-N(2) 2.191(3), Nb(1)-N(3) 2.223(3), C(1)-O(1) 1.143(5), C(2)-O(2) 1.143(5), N(2)-C(20) 1.343(5), C(20)-C(21) 1.399(6), C(21)-C(22) 1.381(6), N(3)-C(22) 1.346(5). Selected bond angles (°): N(1)-Nb(1)-C(1) 88.53(17), N(1)-Nb(1)-C(2) 81.13(16), C(1)-Nb(1)-C(2) 83.77(18), N(1)-Nb(1)-N(2) 106.08(14), C(1)-Nb(1)-N(2) 108.72(16), C(2)-Nb(1)-N(2) 165.41(15), N(1)-Nb(1)-N(3) 156.02(14), C(1)-Nb(1)-N(3) 110.10(15), C(2)-Nb(1)-N(3) 85.91(15), N(2)-Nb(1)-N(3) 82.73(13), C(3)-N(1)-Nb(1) 170.2(3), O(1)-C(1)-Nb(1) 177.3(4), O(2)-C(2)-Nb(1) 172.3(4).

Figure 9.

Molecular structure of **10** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and *iso*-propyl groups were omitted for clarity; the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-N(1) 1.791(3), Nb(1)-N(2) 1.816(3), Nb(1)-N(3) 2.209(3), Nb(1)-N(4) 2.289(3), Nb(1)-N(5) 2.316(3), N(3)-C(27) 1.326(5), C(27)-C(28) 1.402(5), C(28)-C(29) 1.392(5), N(4)-C(29) 1.331(5). Selected bond angles (°): N(1)-Nb(1)-N(2) 115.64(15), N(1)-Nb(1)-N(3) 98.22(13), N(2)-Nb(1)-N(3) 99.75(12), N(1)-Nb(1)-N(4) 129.35(13), N(2)-Nb(1)-N(4) 114.11(13), N(3)-Nb(1)-N(4) 82.19(12), N(1)-Nb(1)-N(5) 84.84(12), N(2)-Nb(1)-N(5) 92.58(13), N(3)-Nb(1)-N(5) 164.39(12), N(4)-Nb(1)-N(5) 84.06(11), C(1)-N(1)-Nb(1) 165.4(3), C(5)-N(2)-Nb(1) 174.1(3).

Figure 10.

Molecular structure of **11** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and the N(2), N(2)*, N(3), and N(3)* aryl groups were omitted for clarity (* denotes atomic position determined by crystallographic inversion center); the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-O(1) 1.967(2), Nb(1)-O(1)* 1.961(2), Nb(1)-N(1) 1.764(3), Nb(1)-N(2) 2.227(3), Nb(1)-N(3) 2.218(3), N(2)-C(21) 1.337(4), C(21)-C(22) 1.393(5), C(22)-C(23) 1.389(5), N(3)-C(23) 1.345(5). Selected bond angles (°): N(1)-Nb(1)-O(1)* 112.47(11), N(1)-Nb(1)-O(1) 112.35(11), O(1)*-Nb(1)-O(1) 79.84(10), N(1)-Nb(1)-N(3) 97.52(12), O(1)*-Nb(1)-N(3) 90.95(10), O(1)-Nb(1)-N(3) 150.06(11), N(1)-Nb(1)-N(2) 98.30(12), O(1)*-Nb(1)-N(2) 149.17(10), O(1)-Nb(1)-N(2) 90.47(10), N(3)-Nb(1)-N(2) 82.99(10), Nb(1)*-O(1)-Nb(1) 100.16(10), C(1)-N(1)-Nb(1) 179.1(3).

Figure 11.

Molecular structure of **12** as determined by a single crystal X-ray diffraction study. The hydrogen atoms and the N(2), N(2)*, N(3), and N(3)* aryl groups were omitted for clarity (* denotes atomic position determined by crystallographic inversion center); the thermal ellipsoids were set at the 50 % probability level. Selected bond lengths (Å): Nb(1)-C(1) 2.059(4), Nb(1)-C(3) 2.143(5), Nb(1)-N(1) 1.830(3), Nb(1)-N(2) 2.235(3), Nb(1)-N(3) 2.212(3), C(1)-C(2) 1.523(6), C(1)-O(1) 1.307(5), O(1)-Li(1) 1.790(9), O(1)-Li(1)* 1.871(9), N(1)-Li(1)* 2.092(9), O(2)-C(3) 1.139(5), N(2)-C(21) 1.345(5), C(21)-C(22) 1.389(6), C(22)-C(23) 1.416(6), N(3)-C(23) 1.330(5). Selected bond angles (°): N(1)-Nb(1)-C(1) 100.05(16), N(1)-Nb(1)-C(3) 83.33(16), C(1)-Nb(1)-C(3) 87.05(17), N(1)-Nb(1)-N(3) 105.11(14), C(1)-Nb(1)-N(3) 100.11(15), C(3)-Nb(1)-N(3) 167.61(14), N(1)-Nb(1)-N(2) 150.24(14), C(1)-Nb(1)-N(2) 106.42(15), C(3)-Nb(1)-N(2) 84.66(15), N(3)-Nb(1)-N(2) 83.62(12), C(1)-O(1)-Li(1) 174.2(4), C(1)-O(1)-Li(1)* 96.7(4), O(1)-Li(1)*-N(1) 115.1(4), O(1)-C(1)-Nb(1) 131.1(3), Nb(1)-N(1)-Li(1)* 95.9(3), O(2)-C(3)-Nb(1) 173.0(4), C(4)-N(1)-Nb(1) 163.1(2).

Figure 12. Possible resonance structures for compound **12**, illustrating the contribution of Nb-based backbonding into the acylate π^* -system.

Scheme 1.
12

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.

Scheme 9.

Scheme 10.

Scheme 11.

Scheme 12.

Scheme 13.

Scheme 14.

Table 1Crystallographic data for compounds **2•py**, **2•thf**, **5**, and **6**.

	2•py	2•thf	5	6
Formula	C ₃₈ H ₅₅ N ₄ Nb	C ₃₇ H ₅₈ N ₃ NbO	C ₃₉ H ₆₆ ClN ₃ NbP ₂	C ₆₀ H ₇₇ N ₆ Nb
Formula weight	660.77	653.77	767.25	975.19
Space Group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.847(17)	10.486(2)	13.149(1)	17.217(1)
<i>b</i> (Å)	17.61(4)	18.636(3)	19.025(2)	15.633(1)
<i>c</i> (Å)	21.45(4)	21.082(4)	16.896(2)	20.637(2)
<i>α</i> (°)	90	90	90	90
<i>β</i> (°)	90	90	105.557(1)	103.469(5)
<i>γ</i> (°)	90	90	90	90
<i>V</i> (Å ³)	4099(13)	4119.6(12)	4072.0(7)	5401.7(8)
<i>Z</i>	4	4	4	4
ρ_{calcd} (g/cm ³)	1.071	1.054	1.252	1.199
<i>F</i> ₀₀₀	1408	1400	1636	2080
μ (mm ⁻¹)	0.32	0.32	0.47	0.21
<i>T</i> _{min} / <i>T</i> _{max}	0.769670	0.871553	0.925258	0.7418
No. rflns measured	20155	16324	17946	40699
No. indep. rflns	6838	5052	6807	9642
<i>R</i> _{int}	0.0730	0.0580	0.0250	0.0516
No. obs. (<i>I</i> > 2.00σ(<i>I</i>))	5384	4365	5337	7815
No. variables	388	389	434	605
<i>R</i> ₁ , <i>wR</i> ₂	0.0570, 0.1246	0.0417, 0.0896	0.0363, 0.0929	0.0396, 0.1066
<i>R</i> ₁ (all data)	0.0771	0.0504	0.0528	0.0518
GoF	1.021	0.966	1.113	1.340
Res. peak/hole (e ⁻ /Å ³)	0.830/−0.468	0.320/−0.336	0.836/−0.304	0.624/−0.851
CCDC ref. #	770334	770335	770336	770337

Table 2Crystallographic data for compounds **7**, **10**, **11**, and **12**.

	7	10	11	12
Formula	C ₄₀ H ₅₅ N ₄ NbO ₂	C ₄₇ H ₆₆ N ₅ Nb	C ₆₆ H ₁₀₀ N ₆ Nb ₂ O ₂	C ₃₆ H ₅₃ Cl ₂ LiN ₃ NbO ₂
Formula weight	716.79	793.96	1195.35	730.56
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	9.159(1)	12.471(3)	21.829(1)	11.434(1)
<i>b</i> (Å)	35.775(5)	17.964(4)	14.057(1)	12.999(1)
<i>c</i> (Å)	11.628(2)	19.609(4)	22.763(1)	14.214(1)
<i>α</i> (°)	90	90	90	73.069(1)
<i>β</i> (°)	93.587(2)	96.922(3)	114.707(1)	85.136(1)
<i>γ</i> (°)	90	90	90	74.461(1)
<i>V</i> (Å ³)	3802.6(8)	4361.3(15)	6345.2(6)	1947.13(16)
<i>Z</i>	4	4	8	2
<i>ρ</i> _{calcd} (g/cm ³)	1.252	1.209	1.251	1.246
<i>F</i> ₀₀₀	1520	1696	2544	768
<i>μ</i> (mm ⁻¹)	0.35	0.31	0.41	0.48
<i>T</i> _{min} / <i>T</i> _{max}	0.8732	0.874393	0.8556	0.854988
No. rflns measured	41368	14628	65971	40569
No. indep. rflns	6958	4437	5839	7101
<i>R</i> _{int}	0.0828	0.0487	0.0838	0.0742
No. obs. (<i>I</i> > 2.00σ(<i>I</i>))	5097	3409	4552	5541
No. variables	426	478	395	419
<i>R</i> ₁ , <i>wR</i> ₂	0.0436, 0.0758	0.0356, 0.0832	0.0462, 0.1198	0.0607, 0.1573
<i>R</i> ₁ (all data)	0.0729	0.0551	0.0654	0.0827
GoF	1.147	1.114	1.481	1.260
Res. peak/hole (e ⁻ /Å ³)	0.350/−0.454	0.306/−0.226	1.348/−0.628	1.487/−0.914
CCDC ref. #	770338	770339	770340	770341