Amine−Phenolate Ligands in Niobium Chemistry: π-Interactions Probed by an Ancillary Alkyne Ligand

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A series of alkyne niobium complexes based on tetrapodal amine bis(phenolato) ligands NbCl[ONNO]$_R$(MeCCMe) ([ONNO]$_R$ = N(CH$_2$CH$_2$NMe$_2$)$_2$(CH$_2$C$_6$H$_2$-3,5-R$_2$-2-O), R = H, Me) (**4**), and tripodal amine phenolato ligands NbCl$_2$[ONN]$_{Me}$(MeCCMe) ([ONN]$_{Me}$ = NMe(CH$_2$CH$_2$NMe$_2$)(CH$_2$C$_6$H$_2$-3,5-Me$_2$-2-O)) (**5**) and NbCl$_2$[ONOO]$_R$(MeCCMe) ([ONOO]$_R$ = N(CH$_2$CH$_2$OMe)$_2$(CH$_2$C$_6$H$_2$-3,5-R$_2$-2-O)) (R = *t*Bu, Me) (**6**), have been synthesized and characterized by spectroscopic and X-ray studies. For complexes **4** and **5**, two isomers differing by the alkyne position have been obtained, separated, and fully characterized. The alkyne ligand is either trans to the sidearm NMe$_2$ group or to the tripodal nitrogen atom. The methyl derivatives of **4** and **5**, NbMe[ONNO]$_H$(MeCCMe) (**7**) and NbMe(Cl)[ONN]$_{Me}$(MeCCMe) (**8**), respectively, have been synthesized. Throughout the series, structural and ^{13}C NMR data testify to the competition between alkyne and phenolato orbitals for available d orbitals on the niobium, a rarely observed picture for group 5 metal complexes.

Introduction

The design of non-Cp-type ligands has been explored to control the stability and activity of early transition metal catalysts, particularly in the field of olefin polymerization. Amine mono(phenolate) [ONX][1] or bis(phenolate) ligands [ONXO][2] whose steric and electronic properties can easily be tuned are one of these new generation ligands. Such ability has particularly been studied in the polymerization of 1-hexene showing that the presence of a sidearm donor is important to obtain a highly active zirconium catalyst.[3] Phenoxy-type ligands have been successful in early transition metal complexes due to the oxophilic behavior of these metals.[4] Vanadium[5] and tantalum[6] complexes of amine mono- or bis(phenolate) ligands have been described, but to the best of our knowledge, the coordination of such ligands to a niobium center was surprisingly unknown before this work. Most probably this can be attributed to the general behavior of less stable and more labile niobium derivatives.

In this Article, we describe the synthesis and characterization of new amine mono- or bis(phenolate) alkyne niobium complexes. Our study focuses on a dianionic [ONNO] ligand bearing a sidearm nitrogen donor (**1**), and monoanionic [ONN] (**2**) and [ONOO] (**3**) ligands with amino and methoxy sidearms, respectively (Chart 1). Simple methyl complexes have also been obtained. The electron reservoir properties of the alkyne ligands will be highlighted thanks to NMR and structural studies.

Results

Synthesis and Characterization of NbCl[ONNO]$_R$(MeCCMe)(4a,b). Reacting NbCl$_3$(DME)(MeCCMe)[7] with [ONNO]$_R$H$_2$ (**1a**,**b**) in tetrahydrofuran in the presence of triethylamine affords after workup the desired niobium complex NbCl[ONNO]$_R$(MeCCMe) (**4a**,**b**) as a yellow powder in 73−75% yield (Scheme 1).

The room-temperature ^{1}H NMR spectrum of **4a**,**b** reveals the presence of two isomers in each case. In both of them, the phenolate rings are equivalents assuming C_s symmetry for the octahedral complex with the two phenoxy groups in trans configuration. The Ar−C*H*$_2$−N methylene protons are diastereotopic exhibiting an AB system, and due to the plane of symmetry they are pairwise equivalent. From these spectroscopic data, we suggest that the two isomers possess the alkyne ligand

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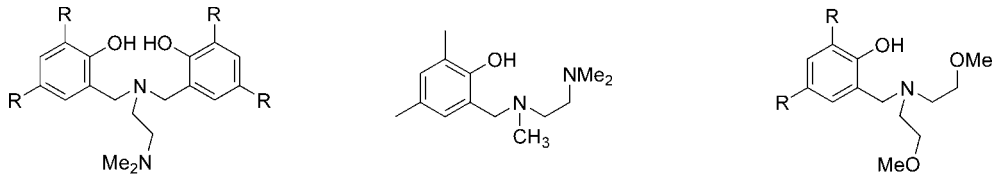
Chart 1



1a R: Me $[ONNO]_{Me}H_2$

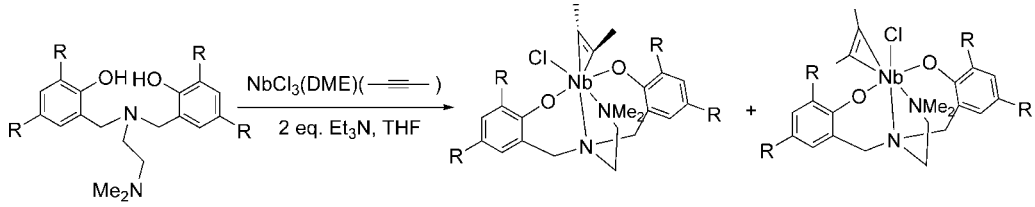
1b R: H $[ONNO]_{H}H_2$

2 $[ONN]_{Me}H$

3a R: *t*Bu $[ONOO]_{tBu}H$

3b R: Me $[ONOO]_{Me}H$

Scheme 1. Synthesis of NbCl[ONNO]$_R$(MeCCMe) (4)



R: Me **1a** **4a$_1$** **4a$_2$**

R: H **1b** **4b$_1$** **4b$_2$**

either trans to the tripodal nitrogen (**4a$_1$** or **4b$_1$**) or trans to the sidearm NMe_2 group (**4a$_2$** or **4b$_2$**) (Scheme 1). For each isomer, only one broad singlet is observed for the methyl groups of the alkyne ligand, indicating easy rotation about the Nb−alkyne bond. Addition of pyridine to **4b** does not affect the ^{1}H NMR spectrum after 5 h at room temperature or 1 h at 50 °C, indicating that the sidearm NMe_2 group is strongly coordinated to the metal. Moreover, no interconversion between the two isomers is observed by variable-temperature studies in the range of 193−353 K and by EXSY experiments at 298 and 353 K. Thus, it is remarkable that for both **4a**,**b** the relative amount of the two isomers only depends on the exact synthetic experimental conditions, and that they do not readily interconvert in solution. NMR spectra at low temperature (193 K) were carried out for complexes **4**. In the slow exchange limit, the phenolate rings and the ArCH_2N methyl diastereotopic pairs for a given isomer are no longer equivalent, indicating that C_1 symmetry is adopted at low temperature. All complexes **4** lose their C_s symmetry, indicating some degree of flexibility of the dianionic $[ONNO]_R$ ligand. At 193 K, the alkyne methyl groups appear as two singlets for each isomer, implying slow rotation on the NMR time scale. In the ^{13}C NMR spectra, the chemical shifts of the coordinated alkyne carbons are in the region δ 181−177. The ^{13}C chemical shifts of the metal-bound alkyne carbons have been correlated to the electron donation ability of the alkyne.[8,9a] Typically, $\delta > 200$ is characteristic of "four-electron" (4e)-donor alkynes, $185 > \delta > 165$ describes formally (3e)-donor alkynes, whereas conventional (2e)-donor alkynes are characterized by $\delta \approx 120$. It must be emphasized that the formal (3e)-donor description strictly applies to bis(alkyne) complexes where there is no metal orbital of appropriate symmetry to interact with the symmetric linear combination of alkynes $\pi_\perp$ orbitals.[9] Nonetheless, the chemical shifts for all isomers of **4a**,**b** indicate competition between alkyne and phenoxy π-type orbitals for an available Nb d orbital, the phenoxy being a good π-donor. Counting the alkyne as a (4e)-donor (both π systems are involved) and including donation from the tripodal nitrogen make complexes **4** formally 16e species. Adding one phenolate π interaction would make them 18e species (see below).

Crystals of **4a** were obtained from a toluene/pentane mixture of **4** at −25 °C. An ORTEP drawing of complex **4a** is shown in Figure 1. Selective crystallization is observed because only the isomer with the alkyne ligand trans to the tripodal nitrogen atom crystallizes (**4a$_1$**). The complex adopts a distorted octahedral geometry with the alkyne occupying a single coordination site. The equatorial plane containing the NMe_2 sidearm, the chloro ligand, and the phenolate groups fold down toward the tripodal nitrogen (∼80°), and the alkyne and the trans tripodal nitrogen are not strictly aligned (176°). The Nb(1)−O lengths (1.929(4) and 1.925(4) Å) and the Nb(1)−Cl(1) (2.5057(16) Å) distances are in a classical range for such a bond. The tripodal N(1)−Nb(1) bond distance (2.440(5) Å) is significantly longer than the sidearm N(2)−Nb(1) length (2.365(6) Å) probably due to a strong trans influence of the alkyne ligand. The Nb(1)−O−C(Ph) angle of ca. 144° is in the classical range for phenolate d^0 or d^2 Nb complexes, although this suggests π donation from the aryloxy oxygen to the metal is mainly significant for the oxygen

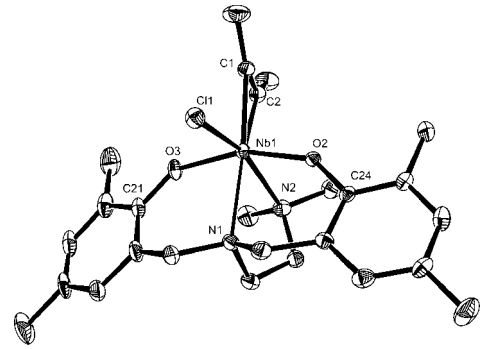


Figure 1. Molecular structure of complex **4a$_1$**. Selected bond lengths (Å) and angles (deg): Nb(1)−O(2) 1.929(4), Nb(1)−O(3) 1.925(4), Nb(1)−Cl(1) 2.5057(16), Nb(1)−N(1) 2.440(5), Nb(1)−N(2) 2.365(6), Nb(1)−C(1) 2.092(7), Nb(1)−C(2) 2.123(7), C(1)−C(2) 1.274(10), Nb(1)−O(2)−C(24) 144.7(4), Nb(1)−O(3)−C(21) 144.3(5).

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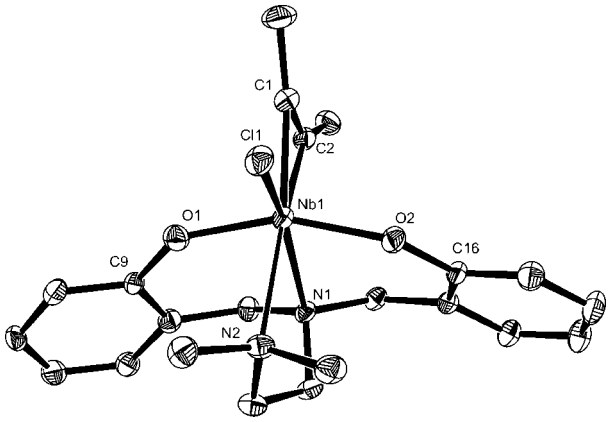

Figure 2. Molecular structure of complex **4b$_2$**. Selected bond lengths (Å) and angles (deg): Nb(1)−O(1) 1.943(4), Nb(1)−O(2) 1.922(4), Nb(1)−Cl(1) 2.4654(14), Nb(1)−N(1) 2.373(4), Nb(1)−N(2) 2.467(4), Nb(1)−C(1) 2.098(5), Nb(1)−C(2) 2.140(5), C(1)−C(2) 1.282(8), Nb(1)−O(1)−C(5) 143.2(4), Nb(1)−O(3)−C(13) 144.9(3).

p orbital lying in the O_2ClN plane (see Discussion).[3,4c−e,5a−c,6,10] The alkyne ligand approximately lies in the pseudo mirror plane of the molecule, which bisects the O−Nb−O angle and contains the tripodal nitrogen atom and the sidearm NMe_2 group (the torsion angle Cl(1)−Nb(1)−C(2)−C(1) is 14°). This perpendicular alkyne conformation with respect to the π-donor aryloxy groups can be rationalized on simple orbital grounds (see below). The Nb(1)−C(1) and Nb(1)−C(2) bond distances (2.092(7) and 2.123(7) Å, respectively) are relatively long for a (4e)-donor alkyne in niobium complexes (typical range [2.00−2.08] Å).[11−15] The C(1)−C(2) bond length (1.274(10) Å) is between that of double and triple C−C bonds. Again, this characterizes competition between π-donors for available orbital space on the metal.

An X-ray diffraction study was also carried out on complex **4b**. Two independent molecules are observed in the cell with very similar structural parameters, but only one of them is shown in Figure 2 and described herein. In contrast to the case of **4a**, selective crystallization surprisingly affords isomer **4b$_2$** in which the alkyne ligand is trans to the sidearm NMe_2 group (and consequently the chloro ligand is now trans to the tripodal nitrogen). The crystal structures of complexes **4a**,**b** confirm the two possible types of isomers suggested by the spectroscopic data. Beyond this difference, the coordination spheres in **4a$_1$** and **4b$_2$** are fully comparable. In **4b$_2$**, the Nb(1)−N(2) (sidearm nitrogen atom) bond length (2.467(4) Å) is longer than the Nb(1)−N(1) (tripodal nitrogen atom) (2.373(4) Å) due to the alkyne trans influence, an alternative situation as compared to **4a$_1$**. The bond lengths of Nb(1)−C(1)/Nb(1)−C(2) (2.098(5) and 2.140(5) Å, respectively) and C(1)−C(2) (1.282(8) Å) are in the same range as the values observed for **4a$_1$**, indicating similar electronic and orbital interactions as discussed below.

Synthesis and Characterization of $NbCl_2[ONN]_{Me}$(MeCCMe) (5) and $NbCl_2[ONOO]_R$(MeCCMe) (6). The complex $NbCl_2[ONN]_{Me}$(MeCCMe) (**5**) is obtained as an orange powder in 69% yield following addition of a mixture of triethylamine and aminophenol $[ONN]_{Me}H$ **2** in THF to a solution of $NbCl_3$(DME)(MeCCMe) (Scheme 2). Complex **5** is fully characterized by elemental analysis, ^{1}H and ^{13}C NMR, as well as by determination of an X-ray crystal structure.

As for the dianionic $[ONNO]_R$ complexes **4a**, two noninterconverting isomers are observed by ^{1}H NMR spectroscopy, probably one with the alkyne trans to the tripodal nitrogen atom (**5$_1$**) and another one with the alkyne ligand trans to the sidearm NMe_2 (**5$_2$**). Depending on crystallization conditions, complete isomer separation can be achieved, whereas this has never been realized for the other complexes in this study. The ^{13}C NMR spectrum displays a signal in the region of δ 207 for the coordinated carbons of the alkyne, a value characteristic of a (4e)-donor alkyne.

An X-ray diffraction study of complex **5** was carried out (Figure 3). A single isomer of the six coordinated **5$_1$** is observed with the alkyne trans to the tripodal nitrogen atom N(1) and cis to the two chloro ligands. The alkyne is roughly aligned with the Nb(1)−Cl(1) bond, and perpendicular to O(1)−Nb(1)−Cl(2). Nb(1)−Cl(1) is significantly longer (>0.06 Å) than Nb(1)−Cl(2). Both structural features again translate competing π effects on niobium. The $Nb-O_{phenoxy}$ bond is the shortest in this study. Attempts at discussing net Nb−O bond order here and for the other complexes in this study are hampered by the presence of several competing π-type ligands (Cl, phenoxy-O, alkyne) whose number and relative stereochemistry are varied. It is noteworthy that the niobium−alkyne carbon bonds in **5$_1$** are shorter than those in **4a$_1$**, whereas the coordinated alkyne CC bonds are (slightly) longer in **5$_1$** than in **4a$_1$**. These data are in agreement with the ^{13}C NMR data, indicating that the alkyne behaves as a "genuine" (4e)-donor.

The synthesis of a complex bearing a methoxy sidearm instead of an amino group was also investigated. In addition, a second dangling methoxy sidearm has been added. This potential extra ligand may reversibly coordinate to a cationic metal center once an X ligand (i.e., Cl) is removed. Yellow $NbCl_2[ONOO]_{tBu}$(MeCCMe) (**6a**) is obtained by addition of a triethylamine and $[ONOO]_{tBu}$ mixture in THF to a solution of $NbCl_3$(DME)(MeCCMe) (Scheme 3). As ascertained by ^{1}H NMR, a single isomer is present: in this case, this is probably due to the strong field alkyne ligand preferring the trans weaker methoxy sidearm (see X-ray structure below). The coordinated alkyne carbons are detected (^{13}C NMR) at δ 209, indicating (4e) behavior. The complex $NbCl_2[ONOO]_{tBu}$(MeCCMe) (**6b**) obtained from the less hindered $[ONOO]_{Me}$ ligand bearing Me groups in place of *t*Bu groups has also been synthesized in the form of a single isomer according to its ^{1}H NMR spectrum. In contrast to **6a**, **6b** readily reacts at room temperature in solution with adventitious proton sources to give the zwitterionic $NbCl_4[ONOO]_{Me}[ON(H)OO]_{Me}$ (**6H**), which has been identified by its X-ray crystal structure (see Supporting Information).

Crystals of **6a** suitable for an X-ray structure determination were obtained from a pentane solution at room temperature. Two independent molecules with very similar structural parameters are observed in the asymmetric unit, and only one of

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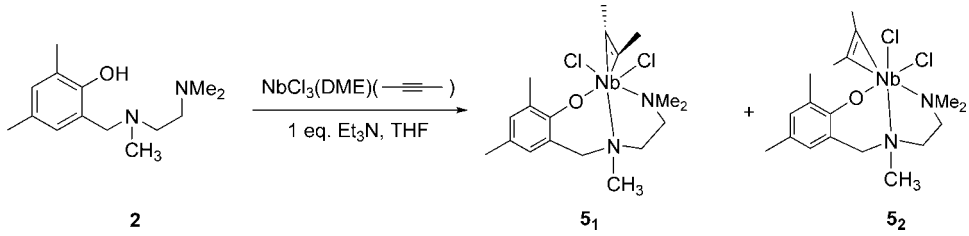
Scheme 2. Synthesis of $NbCl_2[ONN]_{Me}(MeCCMe)$ (5)



2 **5_1** **5_2**

them is shown in Figure 4. The alkyne ligand is trans to the methoxy sidearm. The niobium is bound to two cis chloro ligands, and the cis alkyne bisects the $Cl-Nb-O_{phenoxy}$ and $Cl-Nb-N_{tripodal}$ angles. In contrast to the other structures presented in this work, the alkyne is not perpendicular to the niobium−π-donor bond. Shorter $Nb(2)-C_{alkyne}$ bond lengths (2.059(5) and 2.081(5) Å) and a longer $C_{alkyne}-C_{alkyne}$ bond distance (1.302(6) Å) as compared to complex **5** ($Nb-C_{alkyne}$: 2.109(5) and 2.085(4) Å and $C_{alkyne}-C_{alkyne}$ 1.281(7) Å), which also contains two cis choro ligands and a tripodal nitrogen, indicate that the (4e) character is stronger in **6** than in **5**. Recall that the barrier to alkyne rotation is relatively low because single alkyne signals are observed at room temperature.

One goal of this work was to synthesize alkyl complexes on the basis of these new ligands. Treatment of **4b** or **5** with methyllithium or methylgrignard reagent, respectively, yielded $NbMe[ONNO]_H(MeCCMe)$ (**7**) and $NbMeCl[ONN]_{Me}$ (MeCCMe) (**8**) complexes, which were characterized by ^1H and ^{13}C NMR. As expected, two isomers are present in each case. In the ^1H and ^{13}C NMR spectra, the methyl signals are observed around δ 1.6 and 40−45, respectively, for both complexes. The substitution of a π-donor chloro ligand by a σ-donor methyl group affects the alkyne behavior. The methyl niobium complexes display a low field alkyne signal (δ 191 and 213 for **7** and **8**, respectively) as compared to the chloro analogue (δ 181 and 208 for **4b** and **5**, respectively), indicating slightly increased donation to the metal. Despite repeated attempts to synthesize so-called α-CC agostic complexes,[12] no reaction was observed between either **4b** or **5** and cyclopropyl magnesium or lithium salts.

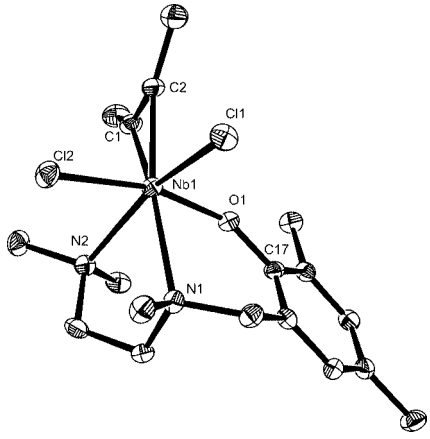
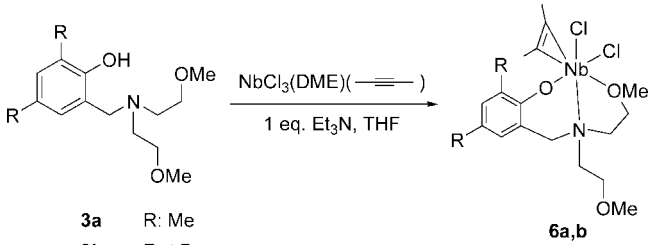


Figure 3. Molecular structure of complex $\mathbf{5_1}$. Selected bond lengths (Å) and angles (deg): Nb(1)−O(1) 1.890(3), Nb(1)−Cl(1) 2.4779(14), Nb(1)−Cl(2) 2.4112(12), Nb(1)−N(1) 2.496(4), Nb(1)−N(2) 2.360(4), Nb(1)−C(1) 2.109(5), Nb(1)−C(2) 2.085(4), C(1)−C(2) 1.281(7), Nb(1)−O(1)−C(17) 149.1(3).

Scheme 3. Synthesis of $NbCl_2[ONOO]_R(MeCCMe)$ (6)



3a R: Me
3b R: *t*-Bu

6a,b

Discussion

Alkyne ligands possess tunable π-donation ability and behave as electron buffers.[8] This flexibility is due to the presence of a set of two orthogonal π systems ($\pi_{||}/\pi_{||}^*$ or $\pi_{\perp}/\pi_{\perp}^*$). Alkynes behave as formal (2e)-donors when only the $\pi_{||}/\pi_{||}^*$ system is involved in the coordination. Adding interaction of the filled $\pi_{\perp}$ orbital with the symmetry appropriate vacant metal orbital will implement formal electron donation up to 4e. Beyond this formal electron count, the alkyne nicely responds to electron demand on the metal. In this context, ^{13}C NMR spectroscopy has been shown to be a very sensitive probe of the true electron flow between the metal and the alkyne. $M-C_{alkyne}$ and coordinated CC bond of the alkyne also respond to the variation of electron density with shorter M−C bonds and longer CC bonds as the donation of the alkyne increases. This overall picture is well documented for group 6 metal alkyne complexes,[9a] but less so for group 5 complexes. We briefly discuss these effects for the new complexes described in the Results section.

Aryloxo ligands can formally be considered as up to 6e donors, with one σ and two π-type interactions. Depending on molecular symmetry and taking into account the electronegativity of O, one of these two π-type orbitals will interact more

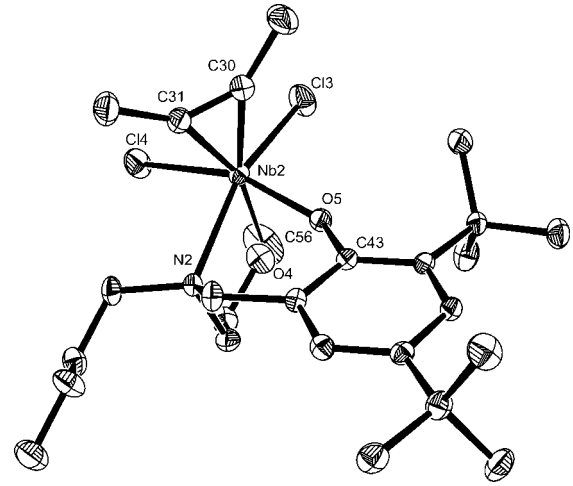
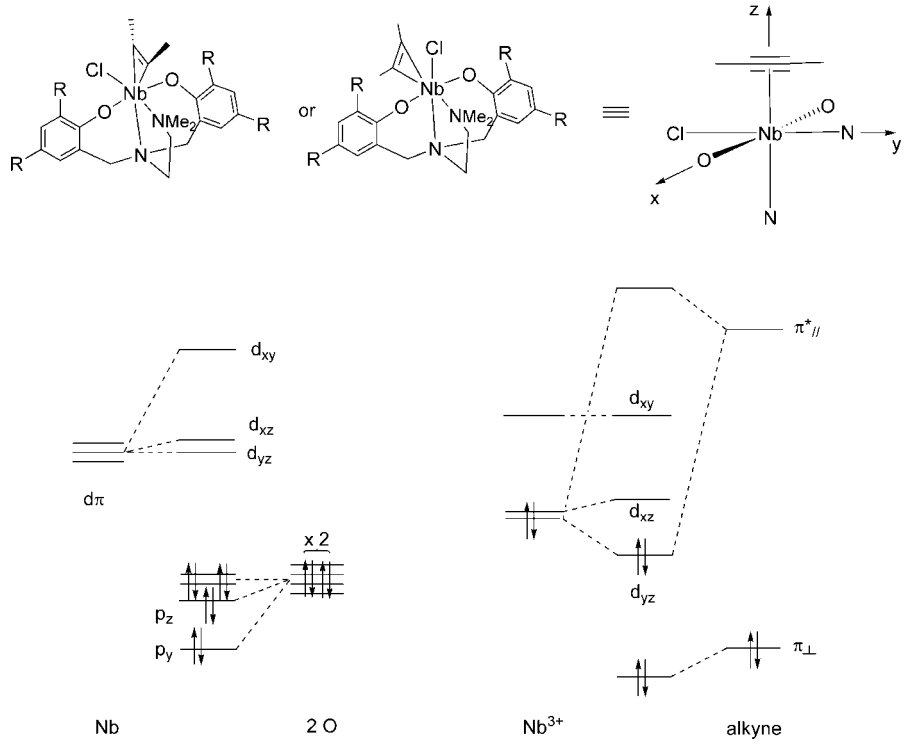


Figure 4. Molecular structure of complex **6a**. Selected bond lengths (Å) and angles (deg): Nb(2)−O(5) 1.915(3), Nb(2)−O(4) 2.380(3), Nb(2)−Cl(3) 2.4176(11), Nb(2)−Cl(4) 2.4436(13), Nb(2)−N(2) 2.388(3), Nb(2)−C(30) 2.059(5), Nb(2)−C(31) 2.081(5), C(30)−C(31) 1.302(6), Nb(2)−O(5)−C(43) 144.4(2).

Scheme 4. Qualitative π-type Orbital Splitting in Phenoxo Complexes of Niobium: (Left) Fragment Analysis without the Alkyne Ligand, and (Right) with the Alkyne Ligand



strongly. A qualitative orbital diagram depicted in Scheme 4 summarizes potential interactions, indicating that there is an orbital preference for the alkyne to sit perpendicular to either one or two π-donors. By doing so, the alkyne satisfies its need for one filled and one vacant dπ orbital on Nb. With Nb−O−C(aryl)bond angles much below 180° as is the case for **4** and **5** (ca. 144°), the involvement of the oxygen p_z can be minimized, and d_{xz} is then almost a bystander. The number of π-donors is relatively unimportant because this qualitative picture applies both for the dialkoxo **4a** and **4b** and for the monoalkoxo **5**. When two trans alkoxo π-donors are present, they additionally compete with each other. Even if their role can be qualitively neglected as significant π-donors, we have seen above that the chloro ligands also responded to this competition.

Remarkably, the two possible coordination sites have been characterized in **4a$_1$** and **4b$_2$**. A high barrier prevents interconvertion between these isomers, and as already mentionned the isomer ratios vary from one synthesis to the other. In each case, competition between alkoxo and alkyne orbitals for orbital space on the metal is testified by variations of key structural and NMR parameters. For the dialkoxo, the upfield shift of the alkyne carbon resonances in the ^{13}C NMR spectrum is accompanied by longer Nb−C_{alkyne} bonds and shorter alkyne CC bonds.[13] Interestingly, the competition is such that the alkyne chemical shift approaches that commonly observed for so-called (3e)-donor alkynes in bis(alkyne) complexes. Similarly in **5**, the Nb−Cl bond is longer to the chloro cis to the π-donor alkoxo, and fully similar to that observed in **4a**, **4b** where Cl is necessarily cis. Competition between the trans alkoxo ligands in **4a**, **4b** can also be seen from the longer Nb−O bonds (ca. 1.93 Å) as compared to the shorter one in **5** (ca. 1.89 Å). Given the number of possible competing effects and their effect on the structural parameters (and most prominently metal−ligand bond lengths), a detailed discussion based on tentative Nb−O bond orders does not seem as appealing as might be thought. Using space-filling models to examine the structures, it can be noted that there are short contacts between one alkyne Me and either of the Me groups of the NMe_2 sidearm (**4a$_1$**, **5**), or the H atoms from the benzylic CH_2 (**4b$_2$**), so the orbital preference seems sufficient to overcome small potential steric interactions. Recall, however, that barriers to alkyne rotation remain low in all cases studied here because single ^{1}H or ^{13}C NMR alkyne signals are observed at room temperature.

The case of complex **6** remains puzzling in the sense that the alkyne ligand does not occupy the supposedly preferred conformation perpendicular to the alkoxo π-donor. The absence of competition between the alkyne and the alkoxo orbitals for Nb orbitals is nicely indicated by shorter Nb−C_{alkyne} bonds, longer alkyne CC bonds, and deshielded alkyne carbons, all of which point to a "true" (4e)-alkyne behavior. Considering space-filling models of the X-ray structure of **6**, we have been unable to find any intramolecular interaction that would have hampered alkyne alignment with the cis Nb−O bond. Once again, orbital preferences remain modest in these pseudooctahedral systems, and any small unidentified effect, most probably from electronic origin, would be significant enough to overcome this preference.

Summary

This work represents the first syntheses and characterizations of niobium alkyne complexes based on popular amine phenolate ligands. The alkyne responds to the π-interactions imposed by the coordination of the phenoxo ligands. In one case, both possible alkyne coordination isomers have been characterized by X-ray diffraction. Methyl derivatives have been obtained, and this suggests that chemistry related to alkene polymerization is at hand within this new series.

Experimental Section

All experiments requiring a dry atmosphere were performed using a conventional vacuum line and Schlenk tube techniques. THF and

toluene were dried and distilled by refluxing over sodium under argon. Triethylamine was refluxed and dried over NaOH under an atmosphere of argon, collected, and stored over molecular sieves. Starting materials for ligand precursor synthesis were purchased from Aldrich Inc. and used as received. The ligands $[ONNO]_{Me}H_2$,[4a] $[ONNO]_HH_2$,[14] $[ONOO]_{Me}H$,[15] $[ONOO]_{tBu}H$,[1] and the complex $NbCl_3(DME)(MeCCMe)$[7] were synthesized according to published procedures. NMR solvents were stored over molecular sieves under argon. NMR data were recorded using ARX-250, DPX-300, or AV-500 MHz Bruker spectrometers. Elemental analyses were performed in the Analytical Service of our laboratory.

Synthesis of $[ONN]_{Me}H$. A methanol solution (10 mL) of 2,4-dimethylphenol (2 mL, 16.55 mmol), *N*,*N*,*N*′-trimethylethylenediamine (2.1 mL, 16.55 mmol), and formaldehyde (5.6 mL of a 36% aqueous solution, 66.20 mmol) was refluxed overnight. After volatile materials were removed, an aqueous solution of HCl (7 mL of a 37% solution) was added to the reaction mixture. The aqueous layer was washed with petroleum ether (3 × 50 mL). The aqueous layer was neutralized with KOH solution and extracted with ether (3 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$. After evaporation, the desired product was yielded as a colorless oil (2.6 g, 67%). Anal. Calcd for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.23; N, 11.85. Found: C, 70.97; H, 10.10; N, 11.78. ^{1}H NMR (250.13 MHz, 298 K, C_6D_6): 7.01 (s, 1H, H_{aryl}), 6.76 (s, 1H, H_{aryl}), 3.44 (s, 2H, ArCH_2), 2.58 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.33−2.23 (m, 4H, NCH_2CH_2N), 2.13 (s, 6H, N(CH_3)$_2$), 2.09 (s, 3H, CH_3). ^{13}C NMR (62.89 MHz, 298 K, C_6D_6): δ 154.3 (C_{aryl}), 130.8 (C_{aryl}H), 127.3 (C_{aryl}H), 126.6 (C_{aryl}), 124.8 (C_{aryl}), 121.9 (C_{aryl}), 59.7 (CH_2), 56.5 (CH_2), 54.2 (CH_2), 44.9 (NCH_3), 41.6 (NCH_3), 20.5 (CH_3), 16.2 (CH_3).

Synthesis of $NbCl[ONNO]_R(MeCCMe)$ (4). All compounds were prepared according to the same general procedure described here in detail for **4a**. A solution of $[ONNO]_{Me}H_2$ (517 mg, 1.45 mmol) and triethylamine (0.47 mL, 3.34 mmol) in THF (20 mL) was added to a solution of $NbCl_3(DME)(MeCCMe)$ (500 mg, 1.45 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 3 h. After the volatiles were removed, the residue was dissolved in toluene and filtered through a pad of celite, affording a yellow solution. The solvent was removed under vacuum, and $NbCl[ONNO]_{Me}(MeCCMe)$ **4a** was obtained.

$NbCl[ONNO]_{Me}(MeCCMe)$ (4a). Yellow powder (585 mg, 1.09 mmol, 75% yield). Crystals were obtained from a toluene/pentane mixture at −25 °C. Anal. Calcd for $C_{26}H_{36}ClN_2NbO_2$: C, 58.16; H, 6.76; N, 5.22. Found: C, 58.04; H, 6.53; N, 5.44. ^{1}H NMR (250.13 MHz, 298 K, C_6D_6): Isomer 1, δ 6.87 (s, 2H, H_{aryl}), 6.66 (s, 2H, H_{aryl}), 5.75 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 3.33 (br.s, 6H, CH_{3alk}), 2.85 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 2.35 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.26 (m, 2H, N−CH_2), 2.26 (s, 6H, CH_3), 1.82 (m, 2H, N−CH_2). Isomer 2, δ 6.81 (s, 2H, H_{aryl}), 6.71 (s, 2H, H_{aryl}), 5.03 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 3.24 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 2.65 (br. s, 6H, CH_{3alk}), 2.26 (m, 2H, N−CH_2), 2.24 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 1.82 (m, 2H, N−CH_2). ^{1}H NMR (500.33 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 6.86 (s, 1H, H_{aryl}), 6.83 (s, 1H, H_{aryl}), 6.79 (s, 1H, H_{aryl}), 6.75 (s, 1H, H_{aryl}), 5.23 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 5.08 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 3.23 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 3.19 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 2.93 (m, 1H, NCH_2), 2.74 (s, 3H, CH_{3alk}), 2.72 (s, 3H, NCH_3), 2.62 (s, 3H, CH_{3alk}), 2.49 (m, 1H, NCH_2), 2.42 (m, 1H, NCH_2), 2.37 (s, 3H, NCH_3), 2.19 (s, 6H, CH_3), 1.98 (m, 1H, NCH_2), 1.89 (s, 3H, CH_3), 1.85 (s, 3H, CH_3). Isomer 2, δ 6.87 (s, 1H, H_{aryl}), 6.83 (s, 1H, H_{aryl}), 6.80 (s, 1H, H_{aryl}), 6.71 (s, 1H, H_{aryl}), 5.09 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 4.97 (d, $^2J_{HH}$ = 13.1 Hz, 1H, ArCH_2), 3.77 (d, $^2J_{HH}$ = 13.5 Hz, 1H, ArCH_2), 3.71 (d, $^2J_{HH}$ = 13.1 Hz, 1H, ArCH_2), 3.09 (m, 1H, NCH_2), 2.73 (s, 3H, CH_{3alk}), 2.69 (s, 3H, CH_{3alk}), 2.43 (m, 1H, NCH_2), 2.44 (s, 3H, NCH_3), 2.41 (s, 3H, CH_3), 2.30 (m, 1H, NCH_2), 2.20 (s, 3H, CH_3), 2.09 (s, 3H, NCH_3), 2.11 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.85 (m, 1H, NCH_2). ^{13}C NMR (125.80 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 185.3 (MeC≡), 176.4 (MeC≡), 155.0 (C_{aryl}), 153.9 (C_{aryl}), 131.5 (C_{aryl}H), 130.9 (C_{aryl}H), 130.0 (C_{aryl}), 129.8 (C_{aryl}), 128.6 (C_{aryl}H), 128.2 (C_{aryl}H), 125.9 (C_{aryl}), 125.7 (C_{aryl}), 125.4 (C_{aryl}), 124.3 (C_{aryl}), 63.3 (ArCH_2), 62.4 (ArCH_2), 61.9 (NCH_2), 53.2 (NCH_3), 51.2 (NCH_2), 47.3 (NCH_3), 20.7 (CH_3), 20.6 (CH_3), 18.0 (CH_3C≡), 16.2 (CH_3C≡), 16.0 (CH_3), 15.8 (CH_3). Isomer 2, δ 178.9 (MeC≡), 177.2 (MeC≡), 155.6 (C_{aryl}), 153.9 (C_{aryl}), 131.7 (C_{aryl}), 131.2 (C_{aryl}), 128.9 (C_{aryl}), 128.2 (C_{aryl}), 128.0 (C_{aryl}), 124.7 (C_{aryl}), 124.8 (C_{aryl}), 123.6 (C_{aryl}), 122.9 (C_{aryl}), 121.5 (C_{aryl}), 66.3 (ArCH_2), 65.5 (ArCH_2), 59.2 (NCH_2), 54.4 (NCH_2), 49.2 (NCH_3), 45.5 (NCH_3), 17.7 (CH_3), 17.2 (CH_3), 17.1 (CH_3), 16.8 (CH_3), 16.2 (CH_3C≡), 15.7 (CH_3), 15.8 (CH_3C≡).

$NbCl[ONNO]_H(MeCCMe)$ (4b). Yellow powder (520 mg, 1.08 mmol, 75% yield). Crystals were obtained from a toluene/pentane mixture at −25 °C. Anal. Calcd for $C_{22}H_{28}ClN_2NbO_2$: C, 54.95; H, 5.87; N, 5.83. Found: C, 54.51; H, 5.60; N, 5.65. ^{1}H NMR (250.13 MHz, 298 K, C_6D_6): Isomer 1, δ 6.98−6.65 (m, 6H, H_{aryl}), 6.47 (d, $^2J_{HH}$ = 8.0 Hz, 2H, H_{aryl}), 5.55 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2N), 3.17 (br. s, 3H, CH_{3alk}), 2.61 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2N), 2.19 (s, 6H, N(CH_3)$_2$), 2.17 (m, 2H, N−CH_2), 1.70 (m, 2H, N−CH_2). Isomer 2, δ 6.98−6.65 (m, 6H, H_{aryl}), 6.51 (d, $^2J_{HH}$ = 8.2 Hz, 2H, H_{aryl}), 4.85 (d, $^2J_{HH}$ = 13.6 Hz, 2H, ArCH_2N), 3.04 (d, $^2J_{HH}$ = 13.6 Hz, 2H, ArCH_2N), 2.57 (br.s, 3H, CH_{3alk}), 2.27 (s, 6H, N(CH_3)$_2$), 2.17 (m, 2H, N−CH_2), 1.70 (m, 2H, N−CH_2). ^{1}H NMR (500.33 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 7.25−7.12 (m, 4H, H_{aryl}), 6.90−6.82 (m, 2H, H_{aryl}), 6.47 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H_{aryl}), 5.35 (d, $^2J_{HH}$ = 13.7 Hz, 1H, ArCH_2N), 5.18 (d, $^2J_{HH}$ = 13.9 Hz, 1H, ArCH_2N), 3.37 (d, $^2J_{HH}$ = 13.9 Hz, 1H, ArCH_2N), 3.33 (d, $^2J_{HH}$ = 13.7 Hz, 1H, ArCH_2N), 2.98 (m, 1H, NCH_2), 2.75 (s, 3H, CH_{3alk}), 2.62 (s, 3H, CH_{3alk}), 2.53 (m, 1H, NCH_2), 2.50 (s, 3H, NCH_3), 2.46 (m, 1H, NCH_2), 2.32 (s, 3H, NCH_3), 2.02 (m, 1H, NCH_2). Isomer 2, δ 7.25−7.12 (m, 4H, H_{aryl}), 6.90−6.82 (m, 2H, H_{aryl}), 6.50 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 3.1 Hz, 2H, H_{aryl}), 5.18 (d, $^2J_{HH}$ = 13.9 Hz, 1H, ArCH_2N), 5.07 (d, $^2J_{HH}$ = 13.6 Hz, 1H, ArCH_2), 3.91 (d, $^2J_{HH}$ = 13.9 Hz, 1H, ArCH_2), 3.84 (d, $^2J_{HH}$ = 13.6 Hz, 1H, ArCH_2), 3.10 (m, 1H, NCH_2), 2.83 (s, 3H, CH_{3alk}), 2.69 (s, 3H, CH_{3alk}), 2.42 (m, 1H, NCH_2), 2.43 (s, 3H, NCH_3), 2.28 (m, 1H, NCH_2), 2.12 (s, 3H, NCH_3), 1.92 (m, 1H, NCH_2). ^{13}C{^{1}H} NMR (125.80 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 185.8 (MeC≡), 176.9 (MeC≡), 158.7 (C_{aryl}), 157.4 (C_{aryl}), 130.7 (C_{aryl}), 130.1 (C_{aryl}), 130.0 (C_{aryl}), 129.2 (C_{aryl}), 126.8 (C_{aryl}), 126.2 (C_{aryl}), 121.4 (C_{aryl}), 121.2 (C_{aryl}), 117.7 (C_{aryl}), 116.6 (C_{aryl}), 63.2 (ArCH_2), 62.4 (ArCH_2), 61.8 (NCH_2), 53.1 (NCH_3), 51.6 (NCH_2), 48.4 (NCH_3), 18.2 (CH_3C≡), 16.2 (CH_3C≡). Isomer 2, δ 181.0 (MeC≡), 180.1 (MeC≡), 159.5 (C_{aryl}), 157.8 (C_{aryl}), 130.6 (C_{aryl}), 130.4 (C_{aryl}), 130.0 (C_{aryl}), 129.9 (C_{aryl}), 124.3 (C_{aryl}), 123.8 (C_{aryl}), 120.2 (C_{aryl}), 119.9 (C_{aryl}), 117.1 (C_{aryl}), 116.0 (C_{aryl}), 66.2 (ArCH_2), 65.5 (ArCH_2), 59.1 (NCH_2), 54.5 (NCH_2), 49.8 (NCH_3), 46.2 (NCH_3), 17.8 (CH_3C≡), 15.7 (CH_3C≡). DCI/NH_3-MS: *m*/*z*: 481.3 − complex + H^+.

Synthesis of $NbCl_2[ONX]_R(MeCCMe)$ (5, 6a,b): General Procedure. A solution of [ONX]H (1.30 mmol) and triethylamine (0.27 mL, 1.95 mmol) in THF (20 mL) was added to a solution of $NbCl_3(DME)(MeCCMe)$ (620 mg, 1.30 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 3 h. After the volatiles were removed, the residue was dissolved in toluene and filtered through a pad of celite. The solvent was removed under vacuum, and the desired complex was obtained.

$NbCl_2[ONN]_{Me}(MeCCMe)$ (5). Orange powder (406 mg, 0.94 mmol, 72% yield). Crystals were obtained in a toluene solution at −25 °C. Anal. Calcd for $C_{18}H_{29}Cl_2N_2NbO$: C, 47.70; H, 6.45; N, 6.18. Found: C, 47.76; H, 6.54, N, 6.00. ^{1}H NMR (300.13 MHz, 298 K, C_6D_6): Isomer 1, δ 6.67 (s, 1H, H_{aryl}), 6.40 (s, 1H, H_{aryl}), 5.57 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2), 3.06−2.56 (m, 2H, NCH_2), 2.93 (s, 6H, CH_{3alk}), 2.89 (s, 3H, CH_3), 2.74 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2), 2.69 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.04 (s, 3H,

CH_3), 1.84 (s, 3H, CH_3), 1.54−1.36 (m, 2H, NCH_2). Isomer 2, δ 6.69 (s, 1H, H_{aryl}), 6.38 (s, 1H, H_{aryl}), 4.15 (d, $^2J_{HH}$ = 14.5 Hz, 1H, ArCH_2), 3.10−2.88 (m, 2H, NCH_2), 2.95 (m, 1H, ArCH_2), 2.90 (s, 3H, CH_3), 2.78 (s, 6H, CH_{3alk}), 2.73 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.54−1.36 (m, 2H, NCH_2). ^{1}H NMR (500.33 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 6.84 (s, 1H, H_{aryl}), 6.72 (s, 1H, H_{aryl}), 4.35 (d, $^2J_{HH}$ = 15.2 Hz, 1H, ArCH_2), 3.64 (d, $^2J_{HH}$ = 15.2 Hz, 1H, ArCH_2), 3.30 (m, 1H, NCH_2), 3.21 (m, 1H, NCH_2), 3.06 (s, 3H, NCH_3), 2.76 (s, 3H, NCH_3), 2.72 (br. s, 3H, CH_{3alk}), 2.60 (br.s, 3H, CH_{3alk}), 2.35 (s, 3H, NCH_3), 2.32 (m, 1H, NCH_2), 2.30 (m, 1H, NCH_2), 2.17 (s, 3H, CH_3), 1.96 (s, 3H, CH_3). Isomer 2, δ 6.83 (s, 1H, H_{aryl}), 6.73 (s, 1H, H_{aryl}), 5.20 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2), 3.44 (m, 1H, NCH_2), 3.19 (d, $^2J_{HH}$ = 14.0 Hz, 1H, ArCH_2), 3.04 (s, 3H, NCH_3), 2.94 (m, 1H, NCH_2), 2.86 (s, 3H, CH_{3alk}), 2.80 (s, 3H, NCH_3), 2.74 (s, 3H, CH_{3alk}), 2.55 (s, 3H, NCH_3), 2.38 (m, 1H, NCH_2), 2.27 (m, 1H, NCH_2), 2.16 (s, 3H, CH_3), 1.82 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125.80 MHz, 193 K, CD_2Cl_2): Isomer 1, δ 212.1 (Me*C*≡), 206.5 (Me*C*≡), 154.2 (C_{aryl}), 130.7 (C_{aryl}), 130.0 (C_{aryl}), 126.9 (C_{aryl}), 124.7 (C_{aryl}), 120.2 (C_{aryl}), 64.8 (Ar*C*H_2), 56.7 (N*C*H_2), 55.4 (N*C*H_2), 52.2 (N*C*H_3), 50.7 (N*C*H_3), 46.1 (N*C*H_3), 20.6 (*C*H_3C═), 20.6 (*C*H_3), 18.7 (*C*H_3C═), 16.0 (*C*H_3). Isomer 2, δ 210.8 (Me*C*≡), 199.7 (Me*C*≡), 153.7 (C_{aryl}), 131.9 (C_{aryl}), 131.0 (C_{aryl}), 128.5 (C_{aryl}), 126.1 (C_{aryl}), 125.5 (C_{aryl}), 62.6 (Ar*C*H_2), 60.8 (N*C*H_2), 54.2 (N*C*H_3), 52.0 (N*C*H_2), 49.0 (N*C*H_3), 47.5 (N*C*H_3), 19.6 (*C*H_3C═), 18.3 (*C*H_3C═), 17.1 (*C*H_3), 16.0 (*C*H_3).

$NbCl_2[ONOO]_{tBu}$(MeCCMe) (6a). 6a was readily protonated, and no elemental analysis or yield was obtained. Yellow powder. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 7.43 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H_{aryl}), 7.00 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H_{aryl}), 5.37 (d, 1H, $^2J_{HH}$ = 13.9 Hz, ArCH_2N), 4.21, 3.89, 2.99, 2.44 (m, 4H, NCH_2CH_2O), 4.19, 3.72, 3.39, 3.17 (m, 4H, NCH_2CH_2O), 3.82 (s, 3H, OCH_3), 3.58 (d, 1H, $^2J_{HH}$ = 13.9 Hz, ArCH_2N), 3.01 (s, 3H, OCH_3), 2.82 (s, 6H, 'C−CH_3), 1.63 (s, 3H, *t*BuCH_3), 1.37 (s, 3H, *t*BuCH_3). ^{13}C NMR (75 MHz, 298 K, C_6D_6): 209.8 (Me*C*≡), 156.4 (C_{aryl}), 143.1 (C_{aryl}), 137.3 (C_{aryl}), 128.1 (C_{aryl}), 124.2 (*C*H$_{aryl}$), 121.6 (*C*H$_{aryl}$), 70.7, 67.5, 61.1, 57.7, 51.2 (N*C*H$_2$, *C*H$_2$O), 61.6 (O*C*H$_3$), 58.5 (OCH$_3$), 35.0 (*C*CH$_3$), 30.0 (*C*CH$_3$), 31.7 (C*C*H$_3$), 29.6 (C*C*H$_3$), 19.1 (*C*H$_3$C≡).

$NbCl_2[ONOO]_{Me}(CH_3C'CCH_3)$ (6b). 6b was even more readily protonated than **6a**, and no elemental analysis or yield was obtained. Similarly, overlapping of the ^{13}C NMR signals of **6a** and **6H** (see text) prevented definitive assignments, except for the alkyne carbons. Yellow powder. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 6.72 (s, 1H, H$_{aryl}$), 6.49 (s, 1H, H$_{aryl}$), 5.24 (d, $^2J_{HH}$ = 13.7 Hz, 1H, ArCH_2N), 4.00−1.72 (m, 9H, NCH_2, ArCH_2N), 3.75 (s, 3H, OCH_3), 3.09 (s, 3H, OCH_3), 2.90 (s, 6H, CH_{3alk}), 2.34 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ 215 (Me*C*≡).

Synthesis of $NbMe[ONNO]_H$(MeCCMe) (7). A solution of methyl lithium in diethyl ether (0.13 mL, 0.21 mmol) was added to a solution of $NbCl[ONNO]_H$(MeCCMe) (**4b**) (100 mg, 0.21 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 3 h. After the volatile materials were removed, the residue was dissolved in toluene and filtered through a pad of celite. The solvent was removed under vacuum, and the desired complex **7** was obtained as a brown powder (60 mg, 0.13 mmol, 62% yield). Anal. Calcd for $C_{23}H_{31}N_2NbO_2$: C, 60.00; H, 6.79; N, 6.08. Found: C, 60.51; H, 7.08, N, 5.60. ^{1}H NMR (500.33 MHz, 323 K, C_7D_8): δ Isomer 1, δ 6.86−7.00 (m, 4H, H_{aryl}), 6.68 (pt d, J_{HH} = 7.4 Hz, J_{HH} = 1.1 Hz, 2H, H_{aryl}), 6.39 (dd, J_{HH} = 8.1 Hz, J_{HH} = 1.0 Hz, 2H, H_{aryl}), 4.92 (d, $^2J_{HH}$ = 13.6 Hz, 2H, ArCH_2), 2.87 (d, $^2J_{HH}$ = 13.6 Hz, 2H, ArCH_2), 2.68 (br. s, 6H, CH_{3alk}), 2.32 (m, 2H, NCH_2), 2.22 (s, 6H, NCH_3), 1.71 (m, 2H, NCH_2), 1.54 (s, 3H, CH_3). Isomer 2, δ 6.86−7.00 (m, 4H, H_{aryl}), 6.66 (pt d, J_{HH} = 7.4 Hz, J_{HH} = 1.2 Hz, 2H, H_{aryl}), 6.37 (dd, J_{HH} = 8.1 Hz, J_{HH} = 1.0 Hz, 2H, H_{aryl}), 4.90 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 3.13 (d, $^2J_{HH}$ = 13.5 Hz, 2H, ArCH_2), 2.32 (m, 2H, NCH_2), 2.80 (br. s, 6H, CH_{3alk}), 2.15 (s, 6H, NCH_3), 1.82 (m, 2H, NCH_2), 1.66 (s, 3H, CH_3). ^{13}C NMR (125.80 MHz, 324.5 K, C_7D_8): Isomer 1, δ 189.4 (Me*C*≡), 159.9 (C_{aryl}), 129.6 (C_{aryl}), 129.4 (C_{aryl}), 125.8 (C_{aryl}), 119.5 (*C*H$_{aryl}$), 117.97 (*C*H$_{aryl}$), 63.6 (Ar*C*H$_2$), 60.1 (N*C*H$_2$), 53.2 (N*C*H$_3$), 48.4 (NMe$_2$), 44.3 (br, Nb*C*H$_3$), 15.8 (br, *C*H$_3$C′). Isomer 2, δ 192.5 (Me*C*≡), 160.7 (C_{aryl}), 129.9 (*C*H$_{aryl}$), 129.6 (*C*H$_{aryl}$), 123.8 (C_{aryl}), 118.2 (*C*H$_{aryl}$), 117.3 (*C*H$_{aryl}$), 65.2 (Ar*C*H$_2$), 60.8 (N*C*H$_2$), 52.3 (N*C*H$_3$), 47.3 (NMe$_2$), 45.0 (Nb*C*H$_3$), 16.8 (*C*H$_3$C≡).

Synthesis of $NbMeCl[ONN]_{Me}$(MeCCMe) (8). A solution of methylmagnesium chloride in tretrahydrofuran (0.24 mL, 0.73 mmol) was added to a solution of $NbCl[ONN]_{Me}$(MeCCMe) (**5**) (300 mg, 0.66 mmol) in THF (10 mL) at −20 °C. After 6 h at −20 °C, the volatile materials were removed. The residue obtained was dissolved in toluene and filtered through a pad of celite. After evaporation, complex **8** was obtained as a brown powder (150 mg, 0.35 mmol, 53% yield). Anal. Calcd for $C_{19}H_{32}ClN_2NbO$: C, 52.72; H, 7.45; N, 6.47. Found: C, 53.19; H, 7.85, N, 6.11. ^{1}H NMR (300.13 MHz, 298 K, C_6D_6): Two isomers, δ 6.72, 6.66, 6.47, 6.42 (s, H_{aryl}), 4.62 (d, $^2J_{HH}$ = 14.6 Hz, 1H, ArCH_2), 3.92 (d, $^2J_{HH}$ = 14.6 Hz, 1H, ArCH_2), 3.11−3.05, 2.89−2.81, 2.53−2.44, 1.53−1.38 (m, 8H, NCH_2), 3.00 (d, $^2J_{HH}$ = 14.6 Hz, 1H, ArCH_2), 2.91 (d, $^2J_{HH}$ = 13.7 Hz, 1H, ArCH_2), 2.85 (s, 6H, CH_{3alk}), 2.81 (s, 3H, NCH_3), 2.76 (s, 3H, NCH_3), 2.72 (s, 6H, CH_{3alk}), 2.65 (s, 3H, NCH_3), 2.55 (s, 3H, NCH_3), 2.13 (s, 3H, ArCH_3), 2.12 (s, 3H, ArCH_3), 2.03 (s, 3H, NCH_3), 1.99 (s, 3H, ArCH_3), 1.81 (s, 3H, ArCH_3), 1.86 (s, 3H, NCH_3), 1.64 (s, 3H, NbCH_3), 1.55 (s, 3H, NbCH_3). ^{13}C NMR (75 MHz, 298 K, C_6D_6): Two isomers: δ 214.4, 211.9 (Me*C*≡), 155.4, 154.8, 127.8, 127.2 (*C*H$_{aryl}$), 137.5, 130.8, 130.6, 129.1, 126.1, 124.2, 123.6, 120.5 (C_{aryl}), 64.1, 62.7, 58.2, 58.0, 53.5, 53.2 (N*C*H$_2$), 51.7, 50.1, 49.8, 49.0, 45.7, 45.5 (N*C*H$_3$), 42.1, 39.8 (br. s, Nb*C*H$_3$), 20.3, 20.2, 15.6, 15.5 (Ar*C*H$_3$), 18.5, 18.1 (*C*H$_3$C≡).

Supporting Information Available: Tables of crystallographic data and CIF files for all complexes including **6H**. This material is available free of charge via the Internet at http://pubs.acs.org.

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