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Methylene-Linked Anilide—Bis(aryloxide) Ligands: Lithium, Sodium, Potassium, Chromium(III), and Vanadium(III) Ligation

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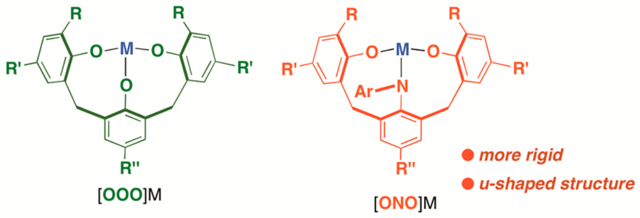
Supporting Information

ABSTRACT: The anilide−bis(aryloxide) proligands H_3[**ONO**^{R}] (where H_3[**ONO**^{R}] = 2,6-(3-R^1-5-R^2-2-hydroxybenzyl)-4-*tert*-butyl-*N*-tolyl-aniline; H_3[**ONO**^{tBu}], R^1 = ^{t}Bu, R^2 = Me; H_3[**ONO**^{Me}], R^1 = Me, R^2 = ^{t}Bu; H_3[**ONO**^{Me2}], R^1 = R^2 = Me) were synthesized from 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester in three steps in multigram scale. The ligand precursor H_3[**ONO**^{tBu}] was readily doubly and triply deprotonated with alkali metal reagents to generate the related derivatives M_2[H(**ONO**^{tBu})] and M_3[**ONO**^{tBu}] (M = Li, Na, K). The extent of ligand deprotonation is observed to depend on the choice of deprotonating reagents and solvents. Transmetalation reaction of the trilithium derivative Li_3[**ONO**^{tBu}] with $MCl_3(THF)_3$ (M = Cr, V; THF = tetrahydrofuran) afforded [(**ONO**^{tBu})CrCl(THF){Li(THF)}] (**5**) and [(**ONO**^{tBu})V(THF)] (**6**). The vanadium complex **6** reacted readily with 2-butyne, styrene oxide, and mesityl azide, yielding [(**ONO**^{tBu})V(η^2-MeCCMe)] (**7**), [(**ONO**^{tBu})V(O)] (**8**), and [(**ONO**^{tBu})-V(NMes)] (**9**), respectively. The solid-state structures of H_3[**ONO**^{tBu}] and metal complexes were determined by X-ray crystallography. The [**ONO**^{tBu}] ligand adopts a u-shaped structure in solution and solid state.



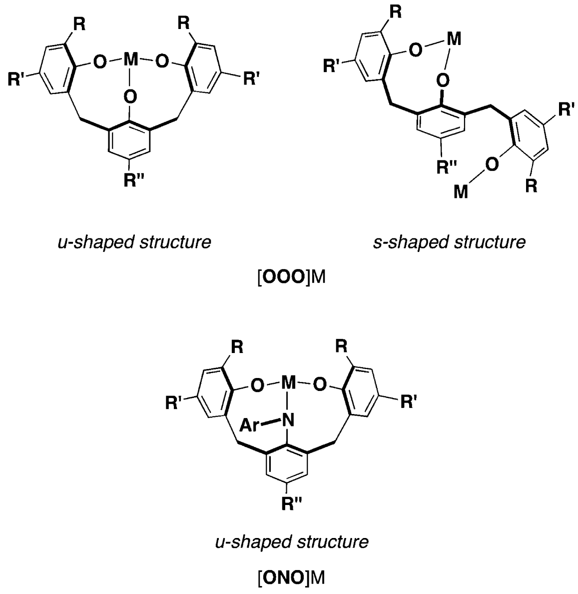
■ INTRODUCTION

Multidentate ligands constitute an invaluable class of supporting ligands in inorganic chemistry and continue to be utilized to prepare new classes of metal complexes and catalyst auxiliaries.[1,2] Such ligands are usually associated with high thermodynamic and kinetic stability of resulting complexes. Chelating donor arrays also impose restrictions on metal coordination geometry, which can have important chemical consequences.

Aryloxides are prevalent in multidentate ligands and are frequently used as components of mixed donor units.[3−6] This versatility stems from the ease of introducing substituents onto the aryloxide ring, allowing its integration into multidentate ligand frameworks of diverse topologies. Examples include calixarene derivatives of various metals,[7] and Floriani and co-workers described novel reactivities of calix[4]arene complexes of group 4−6 metals in particular.[8] Sulfur-bridged bis(aryloxides) are widely used as supporting ligands; titanium complexes are precursors for olefin polymerization catalysts upon activation with methylaluminoxane,[9] and copper complexes catalyze aerial oxidation of primary and secondary alcohols.[10]

We have reported coordination chemistry of trianionic tridentate triaryloxide ligands [OOO]$^{3-}$, which are composed of three aryloxide groups linearly connected at *ortho* positions through methylene linkers (Scheme 1).[11,12] The [OOO] ligand can assume a u-shaped structure reminiscent of the cone conformation of calix[4]arene and support metal complexes capable of activating small molecules such as dinitrogen and carbon monoxide.[12] However, [OOO] complexes may exist in several isomeric forms due to the flexibility of methylene linkers, and the products were often obtained as mixtures of isomers that were difficult to purify, precluding any substantial characterization.

Scheme 1. Ligands [OOO]$^{3-}$ and [ONO]$^{3-}$



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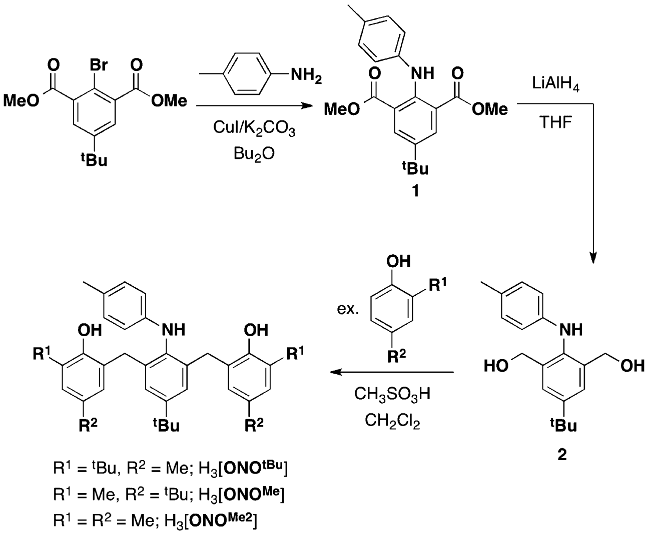
Since flexible ligand framework is a major obstacle to investigating the reactivity of [**OOO**] complexes, we sought to develop a more rigid aryloxide-based trianionic tridentate ligand with the aim of preserving the important characteristics of the [**OOO**] ligand. As part of this effort, we conceived and synthesized a new preorganized anilide−bis(aryloxide) ligand $[\mathbf{ONO}]^{3-}$, in which one anilide and two aryloxide groups are likewise linked by methylene units. Aryloxides and anilides are monoanionic, strong π-donor ligands, and an anilide has two substituents on the donor atom in contrast to less-hindered aryloxides. The [**ONO**] ligand set is therefore likely to provide a similar electronic environment to $[\mathbf{OOO}]^{3-}$. This ligand design further exploits the conformational pattern of 1,2,3-trisubstituted benzenes, where the substituents have a tendency to be situated alternately below and above the benzene ring. Sterically demanding groups are attached to substituents at 1,2,3-positions, thereby forcing the [**ONO**] ligand to adopt a u-shaped structure and limiting the degree of conformational freedom.

Here we describe the synthesis and characterization of aniline−bis(phenol) $H_3[\mathbf{ONO}]$ and their conversion to alkali metal derivatives. These later complexes are useful reagents for the preparation of transition metal complexes. In addition, the coordination chemistry of this ligand system with chromium(III) and vanadium(III) is included.

■ RESULTS

Ligand Synthesis. The tridentate ligand precursors consisting of an aniline flanked by two phenol arms having different substituents were synthesized as white powders in three steps from known starting materials (Scheme 2). Copper-catalyzed amination of 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester with *p*-toluidine provided a diarylamine **1**,[13] which could be converted to a bis(hydroxymethyl)aniline **2** upon reduction with $LiAlH_4$. Condensation of **2** with 2,4-disubtituted phenol in the presence of methanesulfonic acid delivered aniline−diphenols in 58% yield for $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$, 61% for $H_3[\mathbf{ONO}^{\mathrm{Me}}]$, and 17% for $H_3[\mathbf{ONO}^{\mathrm{Me2}}]$. This methodology was previously employed to prepare related methylene-linked triaryloxide derivatives.[5a,14] Compared to $H_3[\mathbf{ONO}^{\mathrm{Me2}}]$, incorporation of *tert*-butyl groups on the phenol rings in $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$ and $H_3[\mathbf{ONO}^{\mathrm{Me}}]$ was beneficial, as it increased the solubility of the ligand. The choice of anilide−bis(aryloxide) ligands allows for a range of solubility and crystallinity of the final product. All protio ligands were characterized by spectroscopic and elemental analyses. The protons of the methylene linkers appear as a singlet at ~3.7 ppm in the ^{1}H NMR spectra. Upon coordination, these methylene protons become inequivalent, yielding pairs of doublets. This provides a convenient handle for determining that coordination has taken place.

Scheme 2. Synthesis of $H_3[\mathbf{ONO}^{\mathrm{R}}]$



For $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$, colorless crystals suitable for X-ray diffraction analysis were obtained by crystallization from a saturated solution in toluene. The solid-state molecular structure of $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$ is shown in Figure 1. As expected, the two phenol groups are positioned above and the tolyl substituent below the central arene ring to reduce steric congestion. This is in contrast to the s-shaped conformation reported for $H_3[\mathbf{OOO}]$ (Scheme 1).[5a] One of the phenolic protons is pointed toward the aniline nitrogen atom to form a hydrogen bond,[15,16] while the other is pointed away from it.

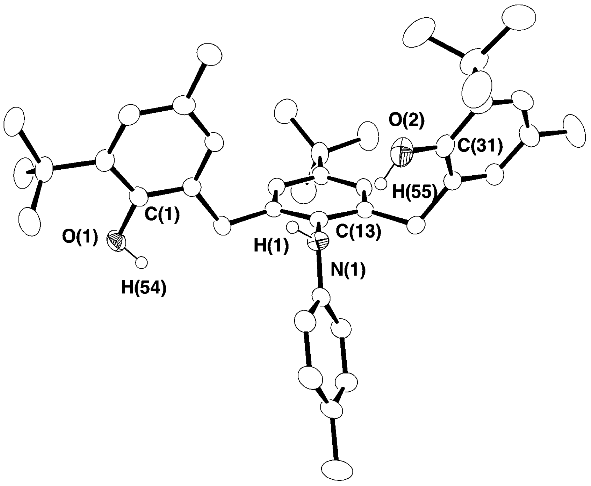
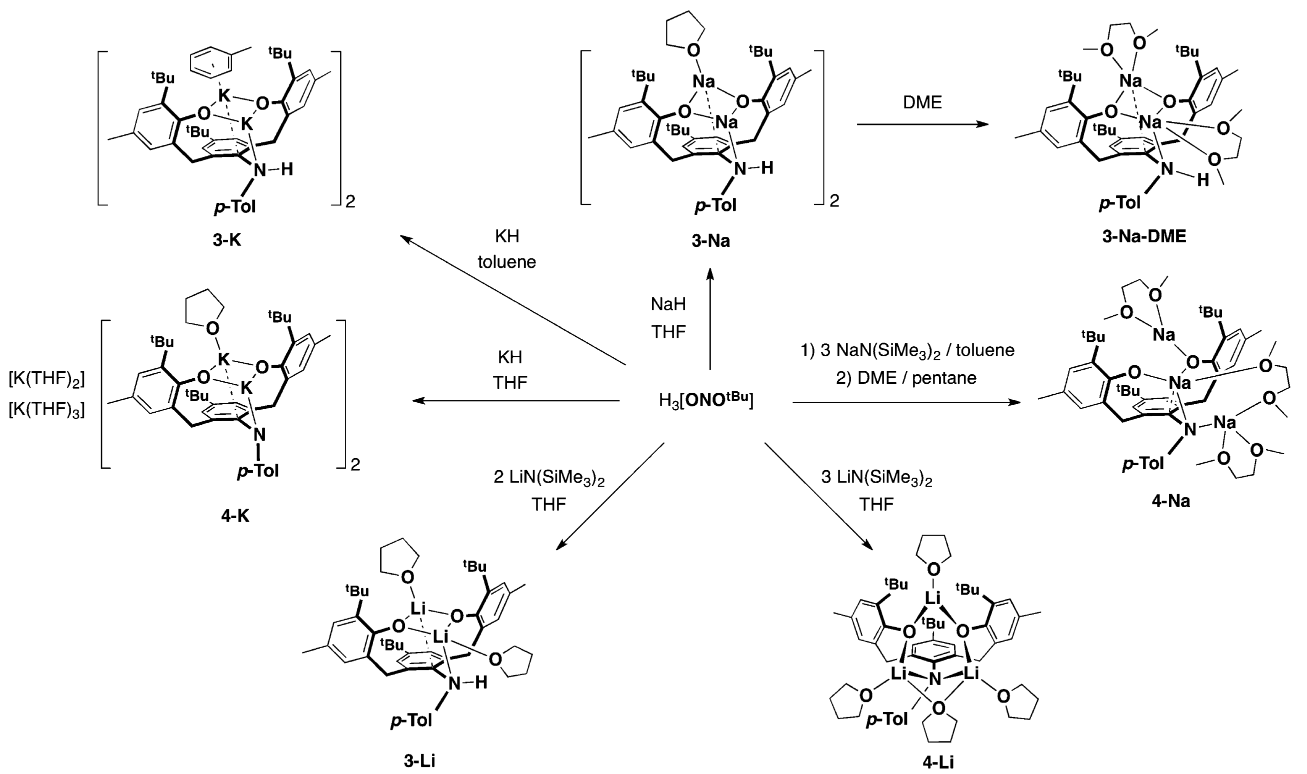


Figure 1. Structure of $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$ with ellipsoids at the 50% probability level. C-bound H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): O(2)−H(55) 0.97(3), N(1)···H(55) 2.22(3), N(1)−O(2) 3.170(3); O(1)−H(55)···N(1) 166(3).

Synthesis of Alkali Metal Derivatives. We sought to prepare alkali metal derivatives of $[\mathbf{ONO}^{t\mathrm{Bu}}]$ for use in subsequent salt metathesis reaction with metal halides. The choice of deprotonating reagents and solvents turned out to be critical to the extent of ligand deprotonation (Scheme 3), although the reaction was nearly quantitative in all cases. Owing to their favorable acidity, the phenol groups were preferentially deprotonated. For example, treatment of $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$ with an excess of KH in toluene resulted in formation of a dipotassium salt $[\{H(\mathbf{ONO}^{t\mathrm{Bu}})\}K_2(\mathrm{toluene})]$ (**3-K**), where the diarylamine proton remained intact. However, upon carrying out the reaction in THF, deprotonation proceeded completely to generate $[(\mathbf{ONO}^{t\mathrm{Bu}})K_3(\mathrm{THF})_{3.5}]$ (**4-K**). The analogous reaction using NaH in THF afforded only a disodium salt $[\{H(\mathbf{ONO}^{t\mathrm{Bu}})\}Na_2(\mathrm{THF})]$ (**3-Na**), regardless of the reagent stoichiometry. When $H_3[\mathbf{ONO}^{t\mathrm{Bu}}]$ was treated with 3 equiv of $NaN(SiMe_3)_2$ in toluene, a trisodium compound $[(\mathbf{ONO}^{t\mathrm{Bu}})Na_3(\mathrm{DME})_3]$ (**4-Na**) was obtained after recrystallization from 1,2-dimethoxyethane (DME)/pentane. Similarly, lithium derivatives $[\{H(\mathbf{ONO}^{t\mathrm{Bu}})\}Li_2(\mathrm{THF})_2]$ (**3-Li**) and $[(\mathbf{ONO}^{t\mathrm{Bu}})$-

Scheme 3. Synthesis of Alkali Metal Derivatives



$Li_3(THF)_4$] (**4-Li**) were prepared by reactions using $LiN(SiMe_3)_2$ in stoichiometric amounts in THF.

Characterization of [{H(ONO^{tBu})}M$_2$] (M = Li, Na, K). Alkali metal clusters with aryloxide ligands are known to display considerable structural diversity,[16−22] mainly by virtue of a high propensity of anionic oxygen donor ligands to bridge electropositive metal centers. The structures of these clusters significantly change through subtle variations in substituents of the ligand or solvents. Therefore, structures of alkali metal complexes newly prepared herein were crystallographically characterized.

Cooling of concentrated toluene solutions of **3-K** and **3-Na** provided colorless crystals of solvent adducts. Because their molecular structures are very much alike, only the structure of **3-Na** is presented in Figure 2.[23] The compound **3-Na** is dimeric with pseudo C_2 symmetry, in which two [H(**ONO**^{tBu})Na$_2$] units are joined by short Na···arene(aryloxide) contacts. Each [H(**ONO**^{tBu})Na$_2$] unit possesses a four-membered Na_2O_2 ring. One of two metals in the Na_2O_2 ring core is bound by two aryloxide oxygens of the [H(**ONO**^{tBu})] ligand, the π system of the central aniline arene ring, and one THF molecule. There is an additional contact to an *ipso* carbon of one aryloxide arene ring, as is typically the case in alkali metal aryloxide complexes.[18,22] The other metal center is κ^3-O$_2$N coordinated by the [H(**ONO**^{tBu})] ligand, and its coordination sphere is completed by a π-interaction with one aryloxide arene ring of the second molecule. The amine proton points toward one of the aryloxide oxygens with a hydrogen bond interaction.[24]

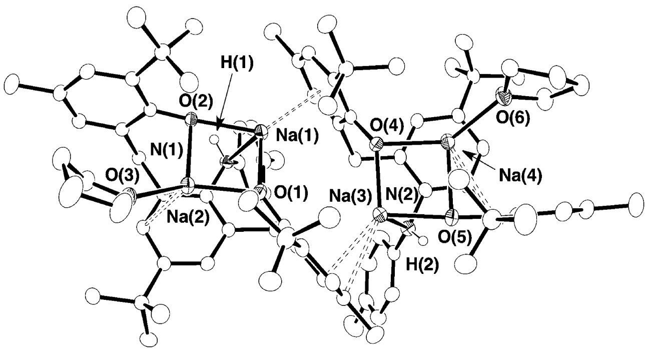


Figure 2. Structure of [{H(**ONO**^{tBu})}Na$_2$(THF)] (**3-Na**) with ellipsoids at the 50% probability level. C-bound H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Na(1)−N(1) 2.7332(15), Na(1)−O(1) 2.2289(12), Na(1)−O(2) 2.2509(12), Na(2)−O(1) 2.2723(12), Na(2)−O(2) 2.4130(13), Na(2)−O(3) 2.3509(13), Na(3)−N(2) 2.6487(15), Na(3)−O(4) 2.2886(14), Na(3)−O(5) 2.2550(12), Na(4)−O(4) 2.2354(12), Na(4)−O(5) 2.4154(13), Na(4)−O(6) 2.3539(13), N(1)−H(1) 0.87(2), H(1)···O(2) 2.15(2), N(2)−H(2) 0.877(18), H(2)···O(5) 2.225(17); N(1)−Na(1)−O(2) 67.24(4), N(1)−Na(1)−O(1) 95.61(5), O(1)−Na(1)−O(2) 94.91(5), O(1)−Na(2)−O(2) 89.52(4), Na(1)−O(1)−Na(2) 89.70(4), Na(1)−O(2)−Na(2) 85.72(4), O(5)−Na(3)−N(2) 70.15(4), O(4)−Na(3)−N(2) 99.68(5), O(5)−Na(3)−O(4) 96.19(5), O(4)−Na(4)−O(5) 93.21(5), Na(4)−O(4)−Na(3) 86.93(5), Na(3)−O(5)−Na(4) 83.50(4).

Recrystallization of **3-Na** gave colorless crystals formulated as [{H(**ONO**^{tBu})}Na$_2$(DME)$_2$] (**3-Na-DME**). An X-ray diffraction study reveals that the DME adduct is a monomer illustrated in Scheme 3.[23] The monomeric structure of the DME adduct can be ascribed to the chelating nature of the coordinating solvent, which is more strongly bound than the π-interaction between the sodium metal and the arene ring.

The doubly deprotonated materials **3-Na**, **3-Na-DME**, and **3-K** were additionally characterized by spectroscopic and combustion analyses. The ^{1}H NMR spectra of these doubly deprotonated species in C_6D_6 at room temperature contain a

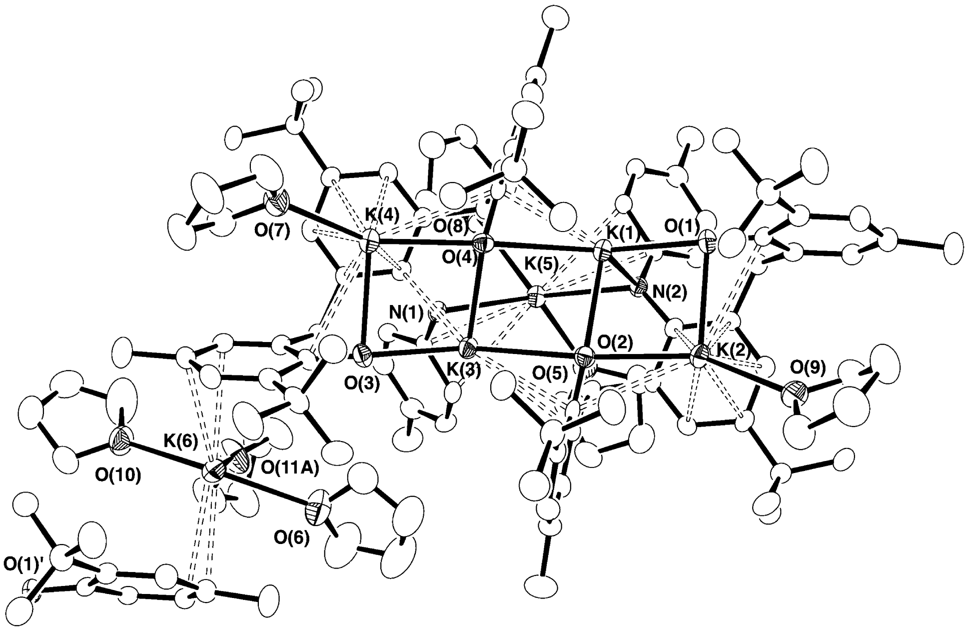


Figure 3. Structure of [{(**ONO**^{tBu})K$_2$}$_2${K(THF)$_2$}{K(THF)$_3$}] (**4-K**) with ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): K(1)−O(1) 2.555(3), K(1)−O(2) 2.639(3), K(1)−N(1) 2.828(3), K(1)−O(4) 2.921(3), K(2)−O(1) 2.679(3), K(2)−O(2) 2.691(3), K(3)−O(3) 2.554(3), K(3)−O(4) 2.614(3), K(3)−N(2) 2.784(3), K(3)−O(2) 2.866(3), K(4)−O(4) 2.660(3), K(4)−O(3) 2.711(3), K(5)−N(2) 2.959(3), K(5)−N(1) 3.016(3); O(1)−K(1)−O(2) 97.95(9), O(2)−K(1)−O(4) 79.68(8), O(1)−K(2)−O(2) 93.73(8), O(3)−K(3)−O(4) 97.12(9), O(4)−K(3)−O(2) 81.11(8), O(4)−K(4)−O(3) 92.33(8), K(1)−O(1)−K(2) 84.09(8), K(1)−O(2)−K(2) 82.25(8), K(1)−O(2)−K(3) 91.02(8), K(3)−O(3)−K(4) 84.29(8), K(3)−O(4)−K(4) 84.16(8), K(3)−O(4)−K(1) 90.31(8).

pair of mutually coupled doublets for the methylene protons and a set of resonances for two equivalent aryloxide groups. This pattern is a good indicator that the [H(**ONO**^{tBu})] ligand adopts a u-shaped conformation with average C_s symmetry in solution. The NMR data for these compounds are similar, and they are more symmetrical than their solid-state structures would suggest. This discrepancy can be attributed to rapid fluxional process on the NMR time scale, involving formation of monomeric species [{H(**ONO**^{tBu})}M$_2$] via solvation and rapid dissociation/inversion of the aniline nitrogen. The presence of the NH proton is suggested by a resonance at 8.31 ppm for **3-Na**, 8.31 ppm for **3-Na-DME**, and 9.63 ppm for **3-K**, which is shifted significantly downfield form H$_3$[**ONO**^{tBu}] (5.66 ppm). The IR spectra of **3-Na**, **3-Na-DME**, and **3-K** exhibit an NH stretching band at 3316, 3365, and 3181 cm^{-1}, respectively.

Attempts to grow crystals of the dilithio derivative **3-Li** were unsuccessful. The ^{1}H NMR spectrum of **3-Li** in C$_6$D$_6$ indicates the incorporation of two THF molecules and shows a NH resonance at 7.84 ppm. The resonances associated with the [H(**ONO**)^{tBu}] ligand are nearly identical to those observed in the sodium and potassium analogues. The ^{7}Li NMR spectrum shows two resonances at δ 0.15 and −2.36 in a 1:1 ratio, suggesting that one of lithium cations is located above the aryl group in the shielding region of the diamagnetic ring current. This upfield resonance is comparable to that reported for the related [**OOO**] ligand system.[25] These spectral features imply that the structure of **3-Li** in solution is similar to those found in the disodium and dipotassium derivatives (Scheme 3).

Characterization of [(ONO^{tBu})M$_3$] (M = Li, Na, K). Diffraction-quality crystals of the tripotassium derivative **4-K** were grown from a THF solution at −30 °C, and the structure of the dimeric complex with pseudo C_2 symmetry is shown in Figure 3. It consists of two [(**ONO**^{tBu})K$_2$] fragments bridged by two aryloxide oxygen atoms. The overall structure further involves two potassium atoms [K(5) and K(6)] per dimeric fragment. The K(5) atom, which is solvated by two THF molecules, is η^3-C$_2$N-bound by two tolyl substituents of the anilide groups. The other metal K(6) sits in a pocket created by two aryloxide arene rings from separate dimeric fragments and three THF molecules, and this structure is repeated in one dimension throughout the lattice.

An interesting feature evident in the dimeric structure of **4-K** is a ladderlike core composed of three K$_2$O$_2$ rings. This type of aggregation is a common structural feature in alkali metal aryloxide chemistry.[16,18,19,20a,b] The two potassium ions K(2) and K(4) at the outer rungs of the K$_4$O$_4$ ladder core are κ^2-O$_2$-coordinated by the [**ONO**^{tBu}] ligand and are located inside the u-shaped ligand cavity, facilitating π-interaction with the central anilide arene ring and close contacts to two *ipso*-carbon atoms of the aryloxide groups. The coordination sphere at each outer-rung potassium is completed by a THF molecule. The other two potassium metals K(1) and K(3) at the inner rungs have a κ^3-O$_2$N-bound [**ONO**^{tBu}] ligand. Additional close contacts are found for the inner-rung potassium with one *ipso*-carbon atom of the anilide group and two carbon atoms of the adjacent aryloxide arene ring. Aniline deprotonation causes a shortening of the K−N distances in **4-K** with respect to **3-K**.[26,27]

Although the trisodium derivative was difficult to crystallize as a THF adduct, **4-Na** crystallized well from a saturated pentane solution containing a small amount of DME. The crystal structure of **4-Na**, which is illustrated in Scheme 3, considerably differs from that of **4-K**.[23] Like the disodium derivative **3-Na-DME**, the chelate nature of DME would enable isolation of monomeric **4-Na**.

The trilithium analogue **4-Li** was crystallized from pentane or THF to give the THF adduct formulated as [(**ONO**^{tBu})-Li$_3$(THF)$_4$] as deduced from NMR data in solution. A number of X-ray diffraction studies on single crystals of the THF adducts were unable to provide high-quality structural data but nevertheless unequivocally show connectivity illustrated in Scheme 3. The three lithium cations are bound within the u-shaped ligand platform. Each of donor groups in [**ONO**$^{t\mathrm{Bu}}$] bridge adjacent lithium cations, forming a puckered six-membered [Li_3O_2N] ring core. This structural feature of **4-Li** is closely related to those found in [(**OOO**)$Li_3(THF)_4$],[5a] and six-membered-ring motifs analogous to that found in **4-Li** are commonplace in alkali metal aryloxide/amide chemistry.[17a−c,28] The structure of the trilithium derivative is remarkably different from those found in **4-K** and **4-Na**. This difference is most likely a reflection of the decreased size of lithium relative to sodium and potassium.

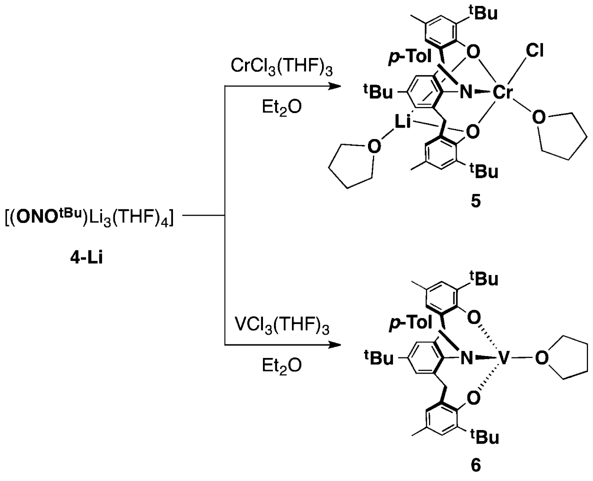
Elemental combustion analysis data of the triply deprotonated materials **4-Li**, **4-Na**, and **4-K** were in agreement with their proposed formulations. After removal of bound THF on potassium ion under vacuum, **4-K** has negligible solubility in common organic solvents (even in THF) due to its extended solid-state structure, and thus no meaningful NMR spectroscopic data could be obtained for this compound. The lithium and sodium derivatives are soluble in benzene. In solution (C_6D_6), **4-Li** displays C_s symmetry, with the ligand methylene protons appearing as a pair of doublets at δ 3.53 and 4.15 (J = 14.5 Hz) and two aryloxide groups being equivalent in the ^{1}H NMR spectrum. The disappearance of the NH resonance confirms the complete deprotonation of the ligand. The ^{7}Li NMR spectrum in C_6D_6 at room temperature contains two resonances at δ 0.83 and −1.79 in a 2:1 ratio consistent with the solid-state structure being maintained in solution on the NMR time scale. In contrast, the ^{1}H NMR spectrum of **4-Na** in toluene-d_8 at 373 K displays broad resonances for the [**ONO**$^{t\mathrm{Bu}}$] ligand. Turning to the aliphatic region, the methylene protons are observed as a broad singlet at δ 3.73, suggesting that the compound exhibits some fluxional behavior in solution. The resonances remained virtually unchanged upon increasing and decreasing measurement temperatures. The largely ionic nature of the sodium-ligand interaction may render structural reorganization facile.

Synthesis and Characterization of Cr(III) and V(III) Complexes. To probe the coordination ability of [**ONO**$^{t\mathrm{Bu}}$]$^{3-}$, we carried out transmetalation reactions of this ligand with chromium and vanadium precursors. Although initial reactions with sodium or potassium salts (**4-Na**, **4-K**) were performed, we discovered that much cleaner reactions and higher yields were obtained when the trilithio derivative **4-Li** was used as a ligand transfer reagent (Scheme 4). This difference might be ascribed to the rigid structure of **4-Li**, and the ligand framework in **4-Li** is preorganized into a geometry more akin to that required to bind a transition-metal center.

Addition of an Et_2O solution of the trilithio derivative **4-Li** into $CrCl_3(THF)_3$ in Et_2O at −35 °C resulted in an immediate color change from purple to dark brown. An “ate” complex [(**ONO**$^{t\mathrm{Bu}}$)CrCl(THF){Li(THF)}] (**5**) was isolated as a moss-green powder in 77% yield after workup. The compound **5** displays a solution magnetic moment of 3.6 μ_B, as measured by the Evans method[29] at room temperature, indicative of a high-spin d^3 system. The ^{1}H NMR spectrum consists of a series of very broad, paramagnetically shifted resonances at 0.9−19 ppm, from which no structural information could be ascertained.

The crystal structure reveals that **5** is a five-coordinate chromium(III) complex with a u-shaped [**ONO**$^{t\mathrm{Bu}}$], a chloride ligand, and a THF molecule (Figure 4). The geometry at chromium is best described as distorted square pyramidal (τ = 0.08).[30] The anilide group occupies the apical site, and the chromium metal is located 0.3193(10) Å above the basal square plane. The Cr−O(aryloxide) and Cr−N distances are compared with those of known chromium(III) aryloxide and amide complexes.[21c,31,32] The two aryloxide groups further bridge a lithium metal solvated by one THF molecule, forming a LiO_2Cr core. The coordination sphere at lithium is completed by π interactions with the central anilide arene ring. A dramatic color change from green to brown was observed upon dissolving **5** in chelating solvents such as DME, presumably as a result of solvating the lithium cation and thereby generating an ion-separated pair or a LiCl-free species. However, all attempts to isolate these types of chromium complexes were unsuccessful.

Scheme 4. Synthesis of Chromium(III) and Vanadium(III) Complexes



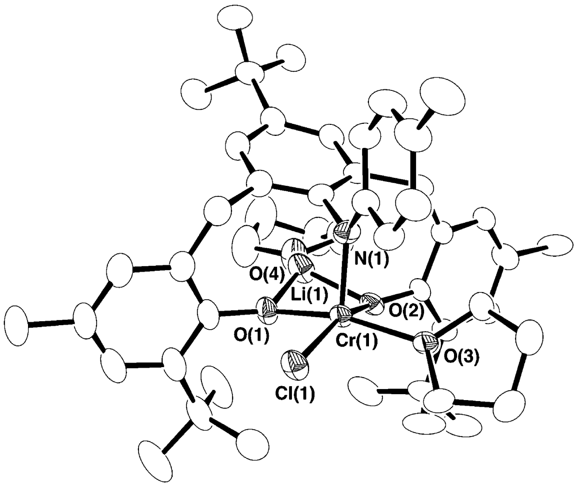


Figure 4. Structure of [(**ONO**$^{t\mathrm{Bu}}$)CrCl(THF){Li(THF)}] (**5**) with ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−N(1) 1.921(2), Cr(1)−O(1) 1.942(2), Cr(1)−O(2) 1.9563(19), Cr(1)−O(3) 2.0549(19), Cr(1)−Cl(1) 2.2784(8); N(1)−Cr(1)−O(1) 98.88(10), N(1)−Cr(1)−O(2) 97.09(9), O(1)−Cr(1)−O(2) 81.03(8), N(1)−Cr(1)−O(3) 96.27(9), O(1)−Cr(1)−O(3) 163.83(9), O(2)−Cr(1)−O(3) 91.53(8), N(1)−Cr(1)−Cl(1) 103.23(7), O(1)−Cr(1)−Cl(1) 92.24(6), O(2)−Cr(1)−Cl(1) 159.37(6), O(3)−Cr(1)−Cl(1) 89.78(6).

A vanadium complex [(**ONO**$^{t\mathrm{Bu}}$)V(THF)] (**6**) was synthesized through the transmetalation of **4-Li** with $\mathrm{VCl_3(THF)_3}$ in $\mathrm{Et_2O}$ at −35 °C and was isolated as a forest green powder in 81% yield. The result of X-ray diffraction study confirms the monomeric four-coordinate molecular structure of **6** (Figure 5).

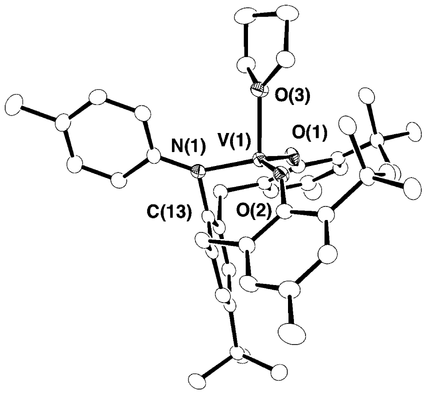


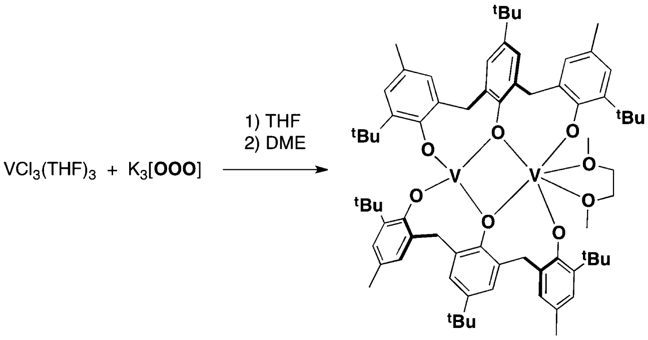
Figure 5. Structure of [(**ONO**$^{t\mathrm{Bu}}$)V(THF)] (**6**) with ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V(1)−O(1) 1.8545(12), V(1)−O(2) 1.8655(12), V(1)−N(1) 1.8703(14), V(1)−O(3) 2.0457(12), V(1)−C(13) 2.3772(15), O(1)−V(1)−O(2) 127.31(5), O(1)−V(1)−N(1) 113.77(6), O(2)−V(1)−N(1) 114.59(6), O(1)−V(1)−O(3) 92.36(5), O(2)−V(1)−O(3) 97.42(5), N(1)−V(1)−O(3) 101.54(5).

It possesses what is nearer to a trigonal monopyramidal geometry than a tetrahedral geometry, with a THF molecule occupying the apical site.[30] The vanadium atom is displaced from the $\mathrm{O_2N}$ basal plane by just 0.2242(7) Å. The V−O(aryloxide) distances are unexceptional.[33] The V−N distance of 1.8703(14) Å is shorter than those of known vanadium(III) amides $[\mathrm{V\{N(3,5\text{-}Me_2\text{-}C_6H_3)Ad\}_3}]$ (1.900(3)−1.945(3) Å)[34] and $[\mathrm{\{(Me_3Si)_2N\}_2VSSi(SiMe_3)_3}]$ (1.926(4) Å),[35] and the V−N−C(13) angle of 91.0(1) ° is narrow. This distorted bonding mode of the u-shaped [**ONO**$^{t\mathrm{Bu}}$] ligand permits the central anilide arene ring to approach the metal center [V···C(13) = 2.3772(15) Å]. Close contact to anilide *ipso*-carbons to electrophilic metal centers is precedented.[36] The ^{1}H NMR spectrum exhibits broad resonances ranging from 0 to 18 ppm, and the room-temperature solution magnetic susceptibility (μ_{eff} = 2.5 μ_{B}) is close to the spin-only value of vanadium(III) d^2 complex.

We attempted to prepared chromium and vanadium complexes of [**ONO**$^{\mathrm{Me}}$] or [**ONO**$^{\mathrm{Me2}}$] ligands in a similar manner. For example, the reaction of $\mathrm{VCl_3(THF)_3}$ with $\mathrm{Li_3}$[**ONO**$^{\mathrm{Me}}$] generated a vanadium complex analogous to **6**; however, unidentified paramagnetic products were also observed, and they could not be isolated. This is possibly attributable to the loss of the favorable steric congestion *ortho* to the hydroxyl groups, which might allow the phenoxide groups to bridge adjacent metals.

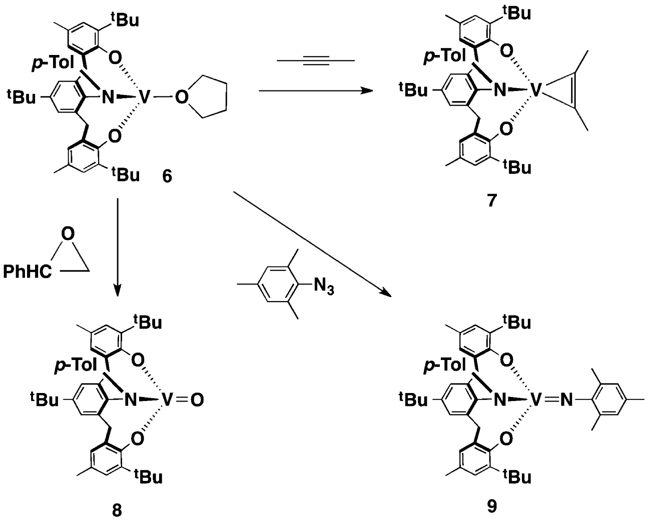
A comparison of the [**ONO**$^{t\mathrm{Bu}}$] complex **6** with the [**OOO**] derivative deserves mention. Treatment of $\mathrm{VCl_3(THF)_3}$ with $\mathrm{K_3}$[**OOO**] followed by recrystallization from DME afforded [(**OOO**)$_2$V$_2$(DME)]. The preliminary result of X-ray diffraction study shows that [(**OOO**)$_2$V$_2$(DME)] is dinuclear, in which the two [**OOO**] ligands span both metals (Scheme 5). One [**OOO**] ligand adopts an s-shaped conformation, while the other adopts a u-shaped conformation. This coordination mode of the [**OOO**] ligand resembles those found in [(**OOO**)$_2$Ti$_2$X$_2$] (X = O^{i}Pr, Cl)[5c,25] and [(**OOO**)$_2$V$_2$(O)$_2$].[5d] This might reflect a greater flexibility of the [**OOO**] ligand compared to the [**ONO**] ligand.

Scheme 5. Synthesis of [(OOO)$_2$V$_2$(DME)]



Reactivity of the V(III) Complex. We report here a brief account of selected reactions of the vanadium(III) complex **6** to prove the ability of the [**ONO**] ligand to support reactive metal centers. We focused particularly on the reactivity of **6** because of the ease with which the THF ligand is displaced under mild condition (Scheme 6). The complex **6**, combined with the lability of the THF ligand, can act as a two-electron reductant. Addition of excess 2-butyne to a solution of **6** in toluene/hexane immediately caused the solution to turn dark brown. The product is identified as diamagnetic [(**ONO**$^{t\mathrm{Bu}}$)V(η^2-MeCCMe)] (**7**), which formed cleanly and quantitatively as judged by NMR spectroscopy. The ^{1}H NMR spectrum of **7** displays a C_s symmetric pattern of [**ONO**$^{t\mathrm{Bu}}$] resonances, consistent with the u-shaped ligand structure being retained in solution. The alkyne methyl groups appear as a singlet at room temperature, thus indicating that the rate of rotation around the alkyne-metal bond is fast on the NMR time scale at room temperature. An X-ray diffraction study further confirmed the formulation of **7** (Figure 6). The short V−C(alkyne) distances of 1.987(3) and 1.998(3) Å, in conjuction with the elongated alkyne C(1)−C(2) distance [1.290(5) Å] and the bent C−C−C(Me) angles [143.2(3), 144.4(3)°], are indicative of significant back-bonding from the metal. Therefore, the

Scheme 6. Reactions of [(ONO$^{t\mathrm{Bu}}$)V(THF)] (6)



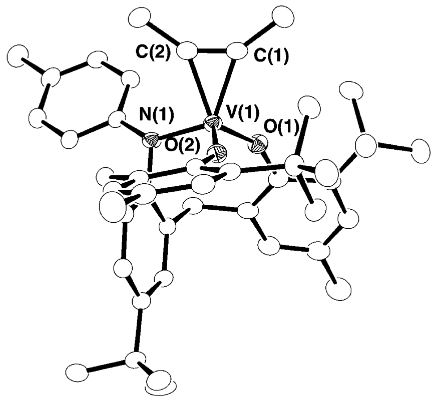


Figure 6. Structure of [(**ONO**^{tBu})V(μ^2-MeCCMe)] (**7**) with ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V(1)−C(1) 1.987(3), V(1)−C(2) 1.998(3), C(1)−C(2) 1.290(4), V(1)−O(2) 1.8004(19), V(1)−O(1) 1.829(2), V(1)−N(1) 1.859(2), O(2)−V(1)−O(1) 117.67(9), O(2)−V(1)−N(1) 110.11(9), O(1)−V(1)−N(1) 101.24(10), C(1)−V(1)−C(2) 37.76(11), C(2)−C(1)−C(3) 143.2(3), C(1)−C(2)−C(4) 144.4(3).

geometry of coordinated alkyne in **7** can be viewed as a formal vanadium(V) metallacyclopropene.[37] This description is further evidenced by the downfield shift of the ^{13}C NMR resonance of the alkyne moiety (205.3 ppm).[38] These geometrical parameters are comparable to those of structurally characterized vanadium alkyne complexes.[39] Unlike the THF adduct **6**, no arene interaction is observed in the structure of **7**.

Treatment of **6** with styrene oxide and mesityl azide produced [(**ONO**^{tBu})V(O)] (**8**) and [(**ONO**^{tBu})V(NMes)] (**9**), respectively, along with oxidation of V(III) to V(V). The formation of **8** and **9** was quantitative by ^{1}H NMR spectroscopy, but the lower isolated yield of **9** was obtained on the preparative scale owing to its high solubility in organic solvents. The solid-state structures confirm **8** and **9** as a four-coordinate monomer with an approximately tetrahedral geometry at the metal (Figure 7). Vanadium(V) complexes of the types $X_3V{=}O$[40,41] and $X_3V{=}NR$[42] (X = halide, amide, alkoxide) are well-known. The V−oxo and V−imide distances are within the expected ranges for such linkages,[7f,40,42,43] and the imide group displays a nearly linear V−N−C bond angle of 170.55(17)°. As with **7**, there are no arene interactions in **8** and **9**. NMR spectroscopic data of **8** and **9** show a set of resonances typical of a C_s symmetric [(**ONO**^{tBu})V] fragment and are in agreement with the solid-state structures. A signal in the ^{51}V NMR spectrum is observed at −450 ppm for **8** and −370 ppm for **9**, upfield shifted from that of the alkyne adduct **7** at 344 ppm.[43] This upfield shift is ascribed to pπ−dπ donation from oxo and imide functionalities. The presence of the terminal V=O bond in **8** is also revealed by a strong band at 986 cm^{-1}.

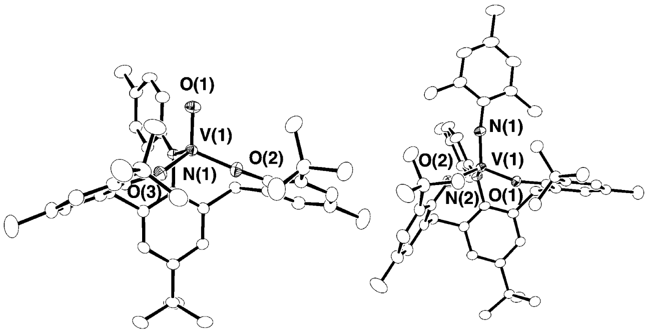


Figure 7. Structures of [(**ONO**^{tBu})V(O)] (**8**) and [(**ONO**^{tBu})V(NMes)] (**9**) with ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **8**: V(1)−O(1) 1.5967(14), V(1)−O(3) 1.7879(14), V(1)−O(2) 1.7925(14), V(1)−N(1) 1.8187(16), O(3)−V(1)−O(2) 111.28(7), O(3)−V(1)−N(1) 108.34(7), O(2)−V(1)−N(1) 109.94(7). For **9**: V(1)−N(1) 1.6634(18), V(1)−O(1) 1.8071(15), V(1)−O(2) 1.8290(16), V(1)−N(2) 1.8383(18), O(1)−V(1)−O(2) 115.82(7), O(1)−V(1)−N(2) 107.52(7), O(2)−V(1)−N(2) 108.62(7), C(30)−N(1)−V(1) 170.55(17).

■ CONCLUSIONS

The synthesis of the protio ligands H_3[**ONO**] was accomplished via three steps from known starting materials. The synthetic route employed here is appealing since the intermediate aniline and the resulting aniline−bis(phenol) can be produced in multigram quantities in relatively high yield except for H_3[**ONO**^{Me2}]. The anilide−bis(aryloxide) [**ONO**]$^{3-}$ appears to be a versatile ligand and prefers a u-shaped coordination as evidenced by the structures of derivatives of alkali metals, vanadium, and chromium. The reaction chemistry of the metal complexes described here is the subject of ongoing work. We are also attempting the synthesis of [**ONO**] complexes of other transition metals.

■ EXPERIMENTAL SECTION

General Considerations. All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk techniques and in an MBraun glovebox unless otherwise stated. Anhydrous hexane, pentane, and toluene were purchased from Kanto Chemical Co. and dried by passage through two columns of activated alumina and a Q-5 column, while stabilizer-free Et_2O and THF were purchased from Kishida Chemical Co. and dried by passage through two columns of activated alumina. $CDCl_3$ was dried over CaH_2 and then vacuum-transferred prior to use. Benzene-d_6 was dried and degassed over a potassium mirror, vacuum-transferred, and then stored in a glovebox. NMR spectra were recorded on a Bruker DRX500 as well as a JEOL ECX-500 spectrometer. ^{1}H NMR are reported with reference to solvent resonances of $CDCl_3$, C_6D_6, or toluene-d_8 residual protons δ = 7.26, 7.16, or 2.08 (CD_3) ppm, respectively. ^{13}C NMR spectra are referenced to deuterated solvent peaks δ = 77.23 ($CDCl_3$) or 128.13 (C_6D_6) ppm, respectively. ^{7}Li chemical shifts are referenced to LiCl in THF-d_8 (0.0 ppm). ^{51}V NMR chemical shifts are referenced to neat $VOCl_3$ (0.0 ppm). Elemental analyses (C, H, and N) were measured using an Elementar vario MICRO cube apparatus. Solid-state magnetic susceptibility values were obtained by using a Sherwood Scientific MSB-AUTO balance. Solution-state magnetic susceptibility was measured by the Evans method[29] on a Bruker DRX500 instrument in benzene-d_6 at 297 K.

*Synthesis of 4-tert-Butyl-1-(p-tolylamino)-2,6-bis(methoxycarbonyl)benzene (**1**).* To a 2 L two-neck round-bottom flask equipped with a reflux condenser and a magnetic stir bar were added 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester (111.0 g, 0.337 mol), *p*-toluidine (74.2 g, 0.692 mol), and Bu_2O (0.6 L), which was subsequently heated at 50 °C until it became a solution. Under an argon atmosphere, CuI (12.8 g, 0.0672 mol) and K_2CO_3 (93.2 g, 0.674 mol) were added to the solution and then heated at 90 °C for 3 d. The reaction mixture was filtered through Celite, and the volatiles were removed by vacuum distillation. The crude compound was collected by Kugelrohr distillation (120−170 °C/vac.), and then recrystallized from pentane at 5 °C to give **1** as pale yellow crystals. The pale yellow crystals were dried under vacuum. Yield: 100.2 g (83.6%). ^{1}H NMR ($CDCl_3$, 500.1 MHz, δ/ppm): 1.33 (s, 9H, tBu), 2.27 (s, 3H, (Me, *p*-Tol)), 3.59 (s, 6H, MeO), 6.89 (d, *J* = 8.15 Hz, 2H, *p*-Tol), 7.04 (d, *J*

= 8.15 Hz, 2H, *p*-Tol), 7.94 (s, 2H, ArH), 9.50 (s, 1H, NH). ^{13}C NMR (CDCl$_3$, 125.8 MHz, δ/ppm): 20.9 (Me, *p*-Tol), 31.4 (C*Me*$_3$), 34.3 (CMe$_3$), 52.1 (MeO), 118.9 (Ar), 119.3 (CH, Ar), 130.0 (CH, Ar), 132.3, 132.9 (CH, Ar), 140.9, 141.5, 144.0 (Ar), 168.9 (C=O). Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 71.43; H, 7.47; N, 3.81%. UV–vis (hexane; λ_{max}/nm (ε/M^{-1} cm^{-1})): 287 (13 100), 320 (10 700), 375 (7100). IR (KBr; ν/cm^{-1}): 3310 (NH), 1719 (C=O).

*Synthesis of 4-tert-Butyl-2,6-bis(hydroxymethyl)-N-(p-tolyl)-aniline (**2**).* To a 1 L two-neck round-bottom flask equipped with a dropping funnel and a magnetic stir bar, **1** (42.6 g, 120 mmol) in THF (150 mL) was added and cooled to −78 °C. A suspension of LiAlH$_4$ (10.2 g, 269 mmol) in THF (125 mL) was added via dropping funnel to the solution at −78 °C, and then the mixture was allowed to warm to room temperature. After stirring for 6 h, a saturated Na$_2$SO$_4$ water solution was very slowly added to the resulting suspension until gas evolution ceased. Anhydrous Mg$_2$SO$_4$ was added to dry the suspension, and then the solids were filtered off. The filtrate was evaporated, and the resulting solid was dried under vacuum to give a colorless powder. Yield: 31.4 g (87.5%). Recrystallization from MeOH at 5 °C afforded an analytically pure sample of **2** as colorless crystals. ^{1}H NMR (CDCl$_3$, 500.1 MHz, δ/ppm): 1.35 (s, 9H), 2.25 (s, 3H), 4.57 (s, 4H), 5.72 (br, 2H), 5.80 (br, 1H), 6.56 (d, *J* = 8.30 Hz, 2H), 6.98 (d, *J* = 8.30 Hz, 2H), 7.35 (s, 2H). ^{13}C NMR (CDCl$_3$, 125.8 MHz, δ/ppm): 20.7 (Me), 31.6 (C*Me*$_3$), 34.8 (CMe$_3$), 63.8 (CH$_2$), 115.2 (CH, Ar), 126.1 (CH, Ar), 129.2 (Ar), 130.1 (CH, Ar), 136.8, 136.9, 143.9, 148.8 (Ar). Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.38; H, 8.24; N, 4.71%. IR (KBr; ν/cm^{-1}): 3395, 3326 (NH, OH).

*Synthesis of 2,6-Bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-tert-butyl-N-(p-tolyl)aniline (H$_3$[**ONO**^{tBu}]).* 4-*tert*-Butyl-2,6-bis-(hydroxymethyl)-*N*-(*p*-tolyl)aniline **2** (15.0 g, 50.0 mmol) and 2-*tert*-butyl-*p*-cresol (75.0 g, 456 mmol) were dissolved in CH$_2$Cl$_2$ (500 mL) in a 1 L round flask. Methanesulfonic acid (3 mL) was added dropwise to the CH$_2$Cl$_2$ solution, which was then stirred at room temperature for 7 d. The CH$_2$Cl$_2$ solution was washed with saturated aqueous NaHCO$_3$, and then the organic layer was dried over MgSO$_4$, filtered, and concentrated. Excess *p*-cresol was removed by vacuum distillation, and the residue was immersed in pentane and sonicated to afford H$_3$[**ONO**^{tBu}] as a colorless powder. The powder was washed with pentane and dried under vacuum. Yield: 17.1 g (57.5%). An analytically pure sample of H$_3$[**ONO**^{tBu}] was afforded by recrystallization from Et$_2$O and dried at 150 °C under vacuum. ^{1}H NMR (CDCl$_3$, 500.2 MHz, δ/ppm): 1.34 (s, 9H, ^{t}Bu), 1.41 (s, 18H, ^{t}Bu), 2.27 (s, 6H, Me), 2.33 (s, 3H, Me), 3.79 (s, 4H, CH$_2$), 5.66 (brs, 1H, NH), 6.43 (s, 2H, OH), 6.64 (d, *J* = 8.30 Hz, 2H, *p*-Tol), 6.83 (s, 2H, ArO), 6.99 (s, 2H, ArO), 7.08 (d, *J* = 8.30 Hz, 2H, *p*-Tol), 7.31 (s, 2H, ArN). ^{13}C NMR (CDCl$_3$, 125.8 MHz, δ/ppm): 20.8 (Me, *p*-Tol), 21.1 (Me, ArO), 30.1 (C*Me*$_3$, ArO), 31.6 (C*Me*$_3$, ArN), 33.9 (2C, (CH$_2$), (CMe$_3$, ArO)), 34.74 (CMe$_3$, ArN), 116.0 (CH, *p*-Tol), 126.4, (CH, ArO), 126.6 (CH, ArN), 126.8, 128.5 (CH, ArO), 129.1, 130.2 (CH, *p*-Tol), 130.6, 135.3, 136.6, 137.3, 143.8, 150.3, 150.9 (Ar). Anal. Calcd for $C_{41}H_{53}NO_2$: C, 83.20; H, 9.03; N, 2.37. Found: C, 83.44; H, 9.23; N, 2.31%. IR (KBr; ν/cm^{-1}): 3578, 3333 (NH, OH).

*Synthesis of 2,6-Bis(5-tert-butyl-3-methyl-2-hydroxybenzyl)-4-tert-butyl-N-(p-tolyl)aniline (H$_3$[**ONO**^{Me}]).* Following the procedure for H$_3$[**ONO**^{tBu}], 4-*tert*-butyl-2,6-bis(hydroxymethyl)-*N*-(*p*-tolyl)-aniline **2** (5.00 g, 16.7 mmol) and 4-*tert*-butyl-*o*-cresol (40.0 g, 244 mol) were reacted in CH$_2$Cl$_2$ (80 mL) in the presence of methanesulfonic acid (ca. 4 mL) at 40 °C for 2 d, giving H$_3$[**ONO**^{Me}] as a colorless powder. Yield: 6.05 g (61.2%). ^{1}H NMR (CDCl$_3$, 500.2 MHz, δ/ppm): 1.29 (s, 18H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 2.17 (s, 6H, Me), 2.31 (s, 3H, Me), 3.79 (s, 4H, CH$_2$), 6.60 (br, 1H, NH), 6.71 (d, *J* = 7.43 Hz, 2H, *p*-Tol), 6.90 (br, 2H, OH), 6.95 (s, 2H, ArO), 7.05 (d, *J* = 7.43 Hz, 2H, *p*-Tol), 7.08 (s, 2H, ArO), 7.34 (s, 2H, ArN). ^{13}C NMR (CDCl$_3$, 125.8 MHz, δ/ppm): 16.7 (Me, ArO-*o*), 20.8 (Me, *p*-Tol), 31.4 (C*Me*$_3$, ArN), 31.7 (C*Me*$_3$, ArO), 33.8 (CH$_2$), 34.0 (CMe$_3$, ArO), 34.5 (CMe$_3$, ArN), 116.3 (CH), 123.6, 124.9 (CH), 126.0, 126.2 (CH), 126.3 (CH), 130.0 (CH), 130.6, 134.7, 137.5, 142.9, 144.0, 149.6, 149.9. Anal. Calcd for $C_{41}H_{53}NO_2$: C, 83.20; H, 9.03; N, 2.37. Found: C, 83.58; H, 9.27; N, 2.30%. IR (KBr; ν/cm^{-1}): 3328, 3253.

*Synthesis of 2,6-Bis(3,5-dimethyl-2-hydroxybenzyl)-4-tert-butyl-N-(p-tolyl)aniline (H$_3$[**ONO**^{Me2}]).* Following the procedure for H$_3$[**ONO**^{tBu}], 4-*tert*-butyl-2,6-bis(hydroxymethyl)-*N*-(*p*-tolyl)aniline **2** (1.82 g, 6.08 mmol) and 2,4-dimethylphenol (4.67 g, 38.2 mmol) were reacted in CH$_2$Cl$_2$ (100 mL) in the presence of methanesulfonic acid (ca. 1 mL), giving H$_3$[**ONO**^{Me2}] as a colorless powder. Yield: 0.510 g, (16.5%). ^{1}H NMR (CDCl$_3$, 500.2 MHz, δ/ppm): 1.32 (s, 18H, ^{t}Bu), 2.14 (s, 6H, Me), 2.22 (s, 6H, Me), 2.29 (s, 3H, Me), 3.75 (s, 4H, CH$_2$), 6.66 (d, *J* = 8.20 Hz, 2H, *p*-Tol), 6.76 (s, 2H, ArO), 6.83 (s, 2H, ArO), 7.03 (d, *J* = 8.20 Hz, 2H, *p*-Tol), 7.30 (s, 2H, ArN) (signals for NH and OH protons were not found). ^{13}C NMR (CDCl$_3$, 125.8 MHz, δ/ppm): 16.3 (Me, ArO-*o*), 20.6 (Me, ArO-*p*), 20.8 (Me, *p*-Tol), 31.6 (C*Me*$_3$), 33.8 (CH$_2$), 34.7 (CMe$_3$), 116.4 (CH), 124.2, 126.3, 126.6 (CH), 128.5 (CH), 129.5, 130.03 (CH), 130.06 (CH), 130.8, 134.9, 137.3, 144.0, 149.8, 150.1. Anal. Calcd for $C_{35}H_{41}NO_2$: C, 82.80; H, 8.14; N, 2.76. Found: C, 82.79; H, 8.43; N, 2.69%. IR (KBr; ν/cm^{-1}): 3379, 3284.

*Synthesis of [{H(**ONO**^{tBu})}Li$_2$] (**3-Li**). (a). Reaction with LiN-(SiMe$_3$)$_2$.* To a solution of H$_3$[**ONO**^{tBu}] (296 mg, 0.500 mmol) in THF (5 mL) was added a solution of LiN(SiMe$_3$)$_2$ (167 mg, 1.00 mmol) in THF (5 mL), which was then stirred for 4 h at room temperature. Volatiles were evaporated under reduced pressure, and the colorless residue was washed with pentane and dried under vacuum to give **3-Li** as a colorless powder, which was formulated as [{H(**ONO**^{tBu})}Li$_2$(THF)$_2$]. Yield: 316 mg (79.2%).

(b). Reaction with LiO^{t}Bu. To a solution of H$_3$[**ONO**^{tBu}] (592 mg, 1.00 mmol) in THF (10 mL) was added a solution of LiO^{t}Bu (240 mg, 3.00 mmol) in THF (10 mL), which was then stirred for 3 h at room temperature. Volatiles were evaporated under reduced pressure, and the colorless residue was washed with pentane and dried under vacuum to give **3-Li** as a colorless powder, which was formulated as [{H(**ONO**^{tBu})}Li$_2$(THF)$_2$]. Yield: 692 mg (92.5%). ^{1}H NMR (C$_6$D$_6$, 500.2 MHz, δ/ppm): 1.09 (m, 8H, THF), 1.11 (s, 9H, ^{t}Bu), 1.63 (s, 18H, ^{t}Bu), 2.13 (s, 3H, Me), 2.39 (s, 6H, Me), 3.16 (br, 8H, THF), 3.62 (d, *J* = 14.5 Hz, 2H, CH$_2$), 4.44 (d, *J* = 14.5 Hz, 2H, CH$_2$), 6.69 (d, *J* = 8.3 Hz, 2H, *p*-Tol), 6.92 (d, *J* = 8.3 Hz, 2H, *p*-Tol), 7.09 (d, *J* = 2.3 Hz, 2H, ArO), 7.25 (d, *J* = 2.3 Hz, 2H, ArO), 7.42 (s, 2H, ArN), 7.84 (s, 1H, NH). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz, δ/ppm): 20.3 (Me, *p*-Tol), 21.0 (Me, ArO), 24.8 (THF), 30.7 (C*Me*$_3$, ArO), 31.2 (C*Me*$_3$, ArN), 34.1 (CMe$_3$, ArN), 34.9 (CMe$_3$, ArO), 37.5 (CH$_2$), 67.8 (THF), 116.0 (CH), 121.0, 124.1 (CH), 126.3 (CH), 129.0, 129.7 (CH), 129.9 (CH), 130.5, 136.9, 137.2, 137.7, 144.5, 147.6, 162.8. ^{7}Li NMR (C$_6$D$_6$, 194.4 MHz, δ/ppm): 0.15, −2.36. Anal. Calcd for $C_{49}H_{67}Li_2NO_4$: C, 78.69; H, 9.03; N, 1.87. Found: C, 79.04; H, 9.15; N, 1.89%. IR (KBr; ν/cm^{-1}): 3386 (NH).

*Synthesis of [{H(**ONO**^{tBu})}Na$_2$] (**3-Na**).* Sodium hydride (72.0 mg, 3.00 mmol) was added in portions to a solution of [**ONO**^{tBu}]H$_3$ (592 mg, 1.00 mmol) in THF (40 mL) with stirring. After stirring overnight, THF was evaporated, and the residue was extracted with toluene and filtered through a membrane filter. The filtrate was evaporated under vacuum to give **3-Na** as a colorless powder. Yield: 590 mg (83.3%). An analytically pure sample of **3-Na** formulated as [{H(**ONO**^{tBu})}Na$_2$(THF)]$_2$ was obtained by recrystallization from toluene and dried under vacuum. Single crystals that contain 3 equiv of cocrystallized solvent molecules, suitable for X-ray diffraction study, were grown from a toluene solution at −30 °C. ^{1}H NMR (C$_6$D$_6$, 500.2 MHz, δ/ppm): 0.97 (s, 9H, ^{t}Bu), 1.19 (m, 8H, THF), 1.53 (s, 18H, ^{t}Bu), 2.18 (s, 3H, Me), 2.41 (s, 6H, Me), 2.98 (br, 8H, THF), 3.49 (d, *J* = 14.6 Hz, 2H, CH$_2$), 4.35 (d, *J* = 14.6 Hz, 2H, CH$_2$), 6.75 (d, *J* = 8.3 Hz, 2H, *p*-Tol), 7.03 (d, *J* = 8.3 Hz, 2H, *p*-Tol), 7.10 (s, 2H, ArO), 7.18 (s, 2H, ArO), 7.23 (s, 2H, ArN), 8.31 (s, 1H, NH). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz, δ/ppm): 20.8 (Me, *p*-Tol), 21.4 (Me, ArO), 25.4 (THF), 30.8 (C*Me*$_3$, ArO), 31.3 (C*Me*$_3$, ArN), 34.4 (CMe$_3$, ArN), 35.2 (CMe$_3$, ArO), 37.3 (CH$_2$), 68.0 (THF), 116.7 (CH), 118.6, 122.9 (CH), 126.9 (CH), 129.2, 130.1 (CH), 130.6 (CH), 131.3, 137.4, 139.3 (br), 139.6 (br), 145.5, 148.2, 165.4. Anal. Calcd for $C_{45}H_{59}NNa_2O_3$: C, 76.35; H, 8.40; N, 1.98. Found: C, 75.93; H, 8.88; N, 1.87%. IR (KBr; ν/cm^{-1}): 3316 (NH).

Formation of $[\{H(ONO^{tBu})\}\{Na(DME)\}_2]$ *(3-Na-DME).* Addition of DME (1 mL) to a solution of **3-Na** in toluene (2 mL) followed by stirring for 10 min and removal of volatiles gave **3-Na-DME** as a colorless powder in a quantitative yield. ^{1}H NMR (C_6D_6, 500.2 MHz, δ/ppm): 1.07 (s, 9H, ^{t}Bu), 1.61 (s, 18H, ^{t}Bu), 2.17 (s, 3H, Me), 2.42 (s, 6H, Me), 2.81 (s, 12H, DME), 2.87 (s, 8H, DME), 3.49 (d, J = 14.6 Hz, 2H, CH_2), 4.35 (d, J = 14.6 Hz, 2H, CH_2), 6.75 (d, J = 8.3 Hz, 2H, p-Tol), 7.03 (d, J = 8.3 Hz, 2H, p-Tol), 7.10 (s, 2H, ArO), 7.18 (s, 2H, ArO), 7.23 (s, 2H, ArN), 8.31 (s, 1H, NH). ^{13}C NMR (C_6D_6, 125.8 MHz, δ/ppm): 20.7 (Me, p-Tol), 21.4 (Me, ArO), 30.6 (CMe_3, ArO), 31.4 (CMe_3, ArN), 34.5 (CMe_3, ArN), 35.3 (CMe_3, ArO), 37.3 (CH_2), 59.2 (Me−DME), 71.1 (CH_2−DME), 116.2 (CH), 118.3, 123.4 (CH), 126.8 (CH), 128.6, 130.1 (CH), 130.5 (CH), 131.6, 136.9, 138.8, 139.6, 146.2, 148.2, 166.1. Anal. Calcd for $C_{49}H_{71}NNa_2O_6$: C, 72.12; H, 8.77; N, 1.72. Found: C, 71.99; H, 8.85; N, 1.90%. IR (KBr; ν/cm^{-1}): 3365 (NH).

Synthesis of $[H(ONO^{tBu})K_2]$ *(3-K). (a). Reaction with KH.* Potassium hydride (88.0 mg, 2.19 mmol) was added in portions to a colorless solution of $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (592 mg, 1.00 mmol) in toluene (15 mL) with stirring at room temperature. The solution immediately turned pale yellow with effervescence. After stirring for 3 h, the solvent was evaporated, and the residue was extracted with toluene and filtered through a membrane filter. The filtrate was evaporated under vacuum to give **3-K** as a colorless powder, which was formulated as $[(\mathbf{ONO}^{\mathbf{tBu}})K_2H(\text{toluene})]_2$. Yield: 636 mg (79.7%). X-ray quality crystals of **3-K** containing 1 equiv of cocrystallized solvent molecule were grown from a toluene solution at −30 °C. Anal. Calcd for $C_{48}H_{59}K_2NO_2$: C, 75.84; H, 7.82; N, 1.84. Found: C, 75.48; H, 8.06; N, 2.30%.

(b). Reaction with KO^{t}Bu. To a solution of $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (296 mg, 0.500 mmol) in THF (4 mL) was added a solution of KO^{t}Bu (112 mg, 1.00 mmol) in THF (10 mL). The mixture was then stirred at room temperature for 3 h. Volatiles were evaporated under reduced pressure, and the colorless residue was washed with pentane and dried under vacuum to give **3-K** as a colorless powder. Yield: 306 mg (82.7%). ^{1}H NMR (C_6D_6, 500.2 MHz, δ/ppm): 0.90 (s, 9H, ^{t}Bu), 1.41 (m, 8H, THF), 1.47 (s, 18H, ^{t}Bu), 2.21 (s, 3H, Me), 2.47 (s, 6H, Me), 3.29 (d, J = 14.3 Hz, 2H, CH_2), 3.44 (br, 4H, THF), 4.28 (d, J = 14.3 Hz, 2H, CH_2), 6.82 (d, J = 8.3 Hz, 2H, p-Tol), 7.13 (d, J = 8.3 Hz, 2H, p-Tol), 7.15 (s, 2H, ArN), 7.17 (s, 2H, ArO), 7.18 (s, 2H, ArO), 9.63 (s, 1H, NH). ^{13}C NMR (C_6D_6, 125.8 MHz, δ/ppm): 20.9 (Me, p-Tol), 21.2 (Me, ArO), 25.8 (THF), 30.2 (CMe_3, ArO), 31.3 (CMe_3, ArN), 34.2 (CMe_3, ArN), 35.1 (CMe_3, ArO), 36.5 (CH_2), 67.8 (THF), 116.0 (CH), 117.9, 123.7 (CH), 127.0 (CH), 130.1 (CH), 131.6 (CH), 131.9, 136.4, 140.0, 146.3, 148.0, 165.8. Signals for two sets of aromatic carbons were not observed. Anal. Calcd for $C_{45}H_{59}K_2NO_3$: C, 73.02; H, 8.03; N, 1.89. Found: C, 73.41; H, 7.84; N, 1.91%. IR (KBr; ν/cm^{-1}): 3181 (w).

Synthesis of $[(ONO^{tBu})Li_3]$ *(4-Li).* To a solution of $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (5.92 g, 10.0 mmol) in THF (30 mL) was slowly added a solution of $LiN(SiMe_3)_2$ (5.02 g, 30.0 mmol) in THF (30 mL) at room temperature. The mixture was stirred for 3 h, and then the solvent was evaporated under reduced pressure. The resulting colorless solid was washed with THF (3 × 10 mL) and dried under vacuum to give a colorless powder, which was formulated as $[(\mathbf{ONO}^{\mathbf{tBu}})Li_3(THF)_6]$ according to ^{1}H NMR spectroscopy. Yield: 7.65 g (73.4%). A second crop of crystals (0.97 g) were obtained from the THF mother liquor stored at −35 °C. The total yield was 8.62 g (82.7%).

After the isolated compound $[(\mathbf{ONO}^{\mathbf{tBu}})Li_3(THF)_6]$ was suspended in pentane and stirred overnight, all volatiles were removed under reduced pressure at room temperature, quantitatively yielding an analytically pure white powder formulated as $[(\mathbf{ONO}^{\mathbf{tBu}})Li_3(THF)_4]$ (**4-Li-THF**). ^{1}H NMR (C_6D_6, 500.1 MHz, 333 K, δ/ppm): 1.14 (s, 9H, ^{t}Bu), 1.29 (m, 16H, THF), 1.54 (s, 18H, ^{t}Bu), 2.31 (s, 3H, Me), 2.33 (s, 6H, Me), 3.49 (br, 16H, THF), 3.53 (d, J = 14.5 Hz, 2H, CH_2), 4.15 (d, J = 14.5 Hz, 2H, CH_2), 6.49 (br, 2H, p-Tol), 7.00 (d, J = 8.3 Hz, 2H, p-Tol), 7.09 (d, J = 1.9 Hz, 2H, ArO), 7.15 (d, J = 1.9 Hz, ArN), 7.44 (s, 2H, ArN). ^{13}C NMR (C_6D_6, 125.8 MHz, 333 K, δ/ppm): 20.8 (Me, p-Tol), 21.3 (Me, ArO), 25.4 (THF), 31.2 (CMe_3, ArO), 31.8 (CMe_3, ArN), 34.3 (CMe_3, ArN), 35.3 (CMe_3, ArO), 37.0 (CH_2), 69.0 (THF), 114.8 (br, $\nu_{1/2}$ = 128 Hz, CH), 119.2, 121.7, 125.4 (CH), 126.3 (CH), 130.0 (CH), 130.3 (br, $\nu_{1/2}$ = 128 Hz, CH), 133.5, 137.3, 140.2, 144.8, 148.1, 159.3, 163.4. ^{7}Li NMR (C_6D_6, 194.4 MHz, δ/ppm): 0.83, −1.79. Anal. Calcd for $C_{57}H_{82}Li_3NO_6$: C, 76.23; H, 9.20; N, 1.56. Found: C, 76.42; H, 8.70; N, 1.82%.

Synthesis of $[(ONO^{tBu})Na_3]$ *(4-Na).* A solution of $NaN(SiMe_3)_2$ (177 mg, 0.965 mmol) in toluene (5 mL) was slowly added to $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (190 mg, 0.321 mmol) in toluene (10 mL), during which time the color of the solution changed from colorless to yellow. The mixture was stirred for another 6 h and was then evaporated to dryness under reduced pressure. The resulting pale yellow powder was redissolved in pentane (5 mL), and addition of DME (1 mL) led to formation of a suspension. The resulting powder was washed with pentane and then dried under vacuum to give **4-Na** as a colorless powder, which was formulated as $[(\mathbf{ONO}^{\mathbf{tBu}})Na_3(DME)_3]$. Yield: 198 mg (66.5%). ^{1}H NMR (toluene-d_8, 500.1 MHz, 373 K, δ/ppm): 1.14 (brs, 9H, ^{t}Bu), 1.35 (brs, 18H, ^{t}Bu), 1.99 (brs, 3H, Me), 2.15 (brs, 6H, Me), 2.98 (s, 18H, DME), 3.10 (s, 12H, DME), 3.73 (br, 4H, CH_2), 6.01 (br, 2H, Ar), 6.62 (br, 2H, Ar), 6.85 (br, 4H, Ar), 7.16 (br, 2H, Ar). Anal. Calcd for $C_{53}H_{80}NNa_3O_8$: C, 68.58; H, 8.69; N, 1.51. Found: C, 68.73; H, 8.82; N, 1.59%.

Synthesis of $[(ONO^{tBu})K_3]$ *(4-K). (a). Reaction with* $KN(SiMe_3)_2$*.* To a solution of $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (296 mg, 0.500 mmol) in THF (4 mL) was slowly added a solution of $KN(SiMe_3)_2$ (299 mg, 1.50 mmol) in THF (6 mL). The mixture was stirred overnight, giving a pale yellow suspension. The resulting suspension was centrifuged to remove the THF supernatant. The precipitate was washed with THF and dried under vacuum to provide **4-K** as a pale yellow powder, which contained no coordinated THF molecule. Yield: 334 mg (94.5%). Anal. Calcd for $C_{41}H_{50}K_3NO_2$: C, 69.74; H, 7.14; N, 1.98. Found: C, 69.95; H, 7.48; N, 2.28%.

(b). Reaction with KH. A suspension of potassium hydride (60.0 mg, 1.50 mmol) in THF was added slowly to a colorless solution of $H_3[\mathbf{ONO}^{\mathbf{tBu}}]$ (296 mg, 0.500 mmol) in THF (10 mL) with stirring at room temperature. The solution immediately turned pale yellow with effervescence and stirred overnight. The resulting suspension was centrifuged to remove the THF supernatant. The resulting powder was washed with THF and dried under vacuum to give **4-K** as a pale yellow powder. Yield: 331 mg (94.0%). After centrifugation of the reaction mixture, standing the supernatant at −35 °C produced single crystals of **4-K** formulated as $[\{(\mathbf{ONO}^{\mathbf{tBu}})K_2(THF)\}_2\{K(THF)_2\}\{K(THF)_3\}]_\infty$.

Synthesis of $[(ONO^{tBu})CrCl(THF)\{Li(THF)\}]$ *(**5**).* A suspension of $CrCl_3(THF)_3$ (375 mg, 1.00 mmol) in Et_2O (10 mL) was cooled to −35 °C. To the vigorously stirred $CrCl_3(THF)_3$ suspension was added a precooled Et_2O (30 mL) solution of $[(\mathbf{ONO}^{\mathbf{tBu}})Li_3(THF)_6]$ (1.04 g, 1.00 mmol) dropwise by Pasteur pipet. Then the mixture was allowed to warm to room temperature, and the purple suspension immediately turned dark brown. After the mixture was stirred for an additional 12 h, the volatiles were evaporated. The resulting residue was dissolved in toluene/hexane and centrifuged to remove an insoluble solid. After the supernatant was evaporated under reduced pressure, the resulting solid was washed with pentane and dried under vacuum to afford **5** as a moss-green powder. Yield: 634 mg (76.6%). An analytically pure sample of **5** was obtained by recrystallization from toluene/pentane at room temperature and dried under vacuum. X-ray quality crystals of **5** containing 2 equiv of cocrystallized solvent were grown from a toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500.1 MHz, δ/ppm): 0.94, 3.79, 13.6, 18.7. Anal. Calcd for $C_{49}H_{66}ClCrLiNO_4$: C, 71.13; H, 8.04; N, 1.69. Found: C, 71.42; H, 7.99; N, 1.66%. UV−vis (THF; λ_{max}/nm (ε/M^{-1} cm^{-1})): 555 (370), 691 (360). μ_{eff} (Evans method, benzene-d_6): 3.6 μ_B. μ_{eff} (solid state, 300 K): 3.89 μ_B.

Synthesis of $[(ONO^{tBu})V(THF)]$ *(6).* A suspension of $VCl_3(THF)_3$ (6.30 g, 16.9 mmol) in Et_2O (50 mL) was stirred and cooled to −30 °C, after which a precooled Et_2O (80 mL) solution of $[(ONO)Li_3(THF)_{8.5}]$ (20.7 g, 16.9 mmol) was added dropwise by Pasteur pipet to give a dark brownish suspension. The mixture was allowed to warm to room temperature, forming a forest-green suspension. After the volatiles were evaporated, the residue was dissolved in toluene/hexane, and the mixture was centrifuged to remove the insoluble solid.

The supernatant was evaporated under reduced pressure, and the resulting dark green powder was washed with pentane (2 × 10 mL) and dried under vacuum to give **6** as a forest-green powder. Yield: 10.2 g (85.0%). An analytically pure sample of **3** was obtained by recrystallization from THF and dried under vacuum. X-ray quality crystals of **3** containing 2 equiv of cocrystallized solvent were grown from a toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500.1 MHz, δ/ppm): 0.02, 1.26, 1.65, 2.06, 5.38, 6.14, 14.2, 18.4. Anal. Calcd for $C_{45}H_{58}NO_3V$: C, 75.92; H, 8.21; N, 1.97. Found: C, 75.72; H, 8.33; N, 2.11%. UV−vis (THF; λ_{max}/nm (ε/M^{-1} cm^{-1})): 586 (370), 661 (290). μ_{eff} (Evans method, benzene-d_6, 297 K): 2.5 μ_B. μ_{eff} (solid state, 300 K): 2.67 μ_B.

Reactoin of 6 with 2-Butyne. To a forest-green solution of **6** (153 mg, 0.215 mmol) in toluene (6 mL) was added excess 2-butyne (0.1 mL), which was precooled to −35 °C. The solution immediately turned dark brown and was stirred overnight. Removal of all volatiles in vacuo left a dark brown solid. The residue was washed with pentane and dried in vacuo, yielding [(**ONO**^{tBu})V(μ^2-MeCCMe)] (**7**) as a dark brown powder. Yield 97.4 mg (65.3%). X-ray quality crystals of **7** containing 2.5 solvent molecules were grown from a toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500.1 MHz, δ/ppm): 1.00 (s, 9H, ^{t}Bu), 1.54 (s, 18H, ^{t}Bu), 2.12 (s, 3H, *p*-Tol), 2.24 (s, 6H, ArO), 2.67 (s, 6H, MeC═C), 3.47 (d, *J* = 13.6 Hz, 2H), 4.25 (d, *J* = 13.6 Hz, 2H), 6.93 (s, 4H, *p*-Tol), 6.97 (br, 2H, ArO), 7.08 (br, 2H, ArO), 7.36 (s, 2H, ArN); ^{13}C NMR (C_6D_6, 125.8 MHz, δ/ppm): 19.4 (MeC═C), 21.1 (Me, *p*-Tol), 21.3 (Me, ArO), 31.3 (2C, C*Me*$_3$, ArN or ArO), 34.7 (CMe$_3$, ArN), 35.5 (CMe$_3$, ArO), 35.8 (CH$_2$), 122.7 (CH), 125.6 (CH), 126.2 (CH), 129.2 (CH), 129.5 (CH), 130.0, 130.3, 134.1, 135.8, 137.7, 141.0, 153.0, 156.5, 163.3, 205.3; ^{51}V NMR (C_6D_6, 131.6 MHz, δ/ppm) 344.0. Anal. Calcd for $C_{45}H_{56}NO_2V$: C, 77.89; H, 8.13; N, 2.02. Found: C, 77.66; H, 7.87; N, 2.33%. UV−vis (toluene; λ_{max}/nm (ε/M^{-1} cm^{-1})): 367 (9200).

Reactoin of 6 with Styrene Oxide. Addition of **6** (358 mg, 0.503 mmol) in hexane (5 mL) into a hexane (5 mL) solution of styrene oxide (120 mg, 1.00 mmol) gave a dark red suspension. After it was stirred overnight, the resulting suspension was centrifuged to remove a supernatant. The residual dark red powder was dried in vacuo to give [(**ONO**^{tBu})V(O)] (**8**) as a dark red powder. Yield 262 mg (79.4%). X-ray quality crystals of **8** containing 2.5 solvent molecules were grown from a toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500.1 MHz, δ/ppm): 0.90 (s, 9H), 1.61 (s, 18H), 2.04 (s, 3H), 2.25 (s, 3H), 3.40 (d, *J* = 14.3 Hz, 2H), 3.91 (d, *J* = 14.3 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 2H), 6.84 (br, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 7.16 (br, 2H), 7.35 (s, 2H); ^{13}C NMR (C_6D_6, 125.8 MHz, δ/ppm): 20.9 (Me, *p*-Tol), 21.3 (Me, ArO), 31.1 (C*Me*$_3$, ArN), 31.4 (C*Me*$_3$, ArO), 34.8 (CMe$_3$, ArN), 35.7 (CMe$_3$, ArO), 35.9 (CH$_2$), 117.2, 126.3 (CH), 126.5, 127.2 (CH), 130.1 (CH), 130.2 (CH), 130.5 (CH), 137.7, 138.1, 139.2, 153.2, 155.4, 163.7; ^{51}V NMR (C_6D_6, 131.5 MHz, δ/ppm) −449.5. Anal. Calcd for $C_{41}H_{50}NO_3V$: C, 75.09; H, 7.69; N, 2.14. Found: C, 75.59; H, 7.48; N, 2.03%. IR (KBr; ν/cm^{-1}): 986 (V═O). UV−vis (toluene; λ_{max}/nm (ε/M^{-1} cm^{-1})): 456 (13 400).

Reactoin of 6 with Mesityl Azide. To a solution of $MesN_3$ (31.9 mg, 0.198 mmol) in toluene (6 mL) was added a solution of **6** (142.3 mg, 0.200 mmol) in toluene (2 mL). The solution changed color from forest-green to reddish-brown, and was stirred for 2 d. Volatiles were removed under vacuum to give a dark red solid. Recrystallization from pentane (2 mL) at −35 °C afforded [(**ONO**^{tBu})V(NMes)] (**9**) as a dark red powder. The powder was washed with cold pentane (2 mL × 2) and dried under vacuum. Yield 92.7 mg (60.0%). X-ray quality crystals of **9** containing one molecule of $MesN_3$ were grown from a toluene solution at −35 °C. ^{1}H NMR (C_6D_6, 500.1 MHz, δ/ppm): 0.96 (s, 9H), 1.60 (s, 18H), 1.99 (s, 6H), 2.28 (s, 6H), 2.52 (s, 6H), 3.56 (d, *J* = 14.1 Hz, 2H), 4.27 (d, *J* = 14.1 Hz, 2H), 6.51 (s, 2H, Mes), 6.79 (d, *J* = 7.6 Hz, 2H, *p*-Tol), 6.90 (br, 2H, OAr), 7.19 (br, 2H, OAr), 7.32 (br, 2H, *p*-Tol) 7.36 (s, 2H, NAr); ^{13}C NMR (C_6D_6, 125.8 MHz, δ/ppm): 19.1 (*o*-Me−Mes), 20.7(Me, *p*-Tol), 21.29 (*p*-Me−Mes), 21.32 (Me, ArO), 31.2 (C*Me*$_3$, ArN), 32.6 (C*Me*$_3$, ArO), 34.8 (CMe$_3$, ArN), 35.7 (CMe$_3$, ArO), 36.1 (CH$_2$), 117.9, 126.0 (CH, ArN), 127.1 (CH, ArO), 128.1 (CH, Mes), 128.6 (CH, ArO), 129.2, 130.1 (CH, *p*-Tol), 130.2 (CH, *p*-Tol), 133.9, 135.1, 137.1, 137.3, 138.3, 138.9, 154.6, 155.6, 162.5, 163.3. ^{51}V NMR (C_6D_6, 103.1 MHz, δ/ppm) −369.5. Anal. Calcd for $C_{50}H_{61}N_2O_2V$: C, 77.69; H, 7.95; N, 3.62. Found: C, 77.88; H, 7.82; N, 3.91%. UV−vis (toluene; λ_{max}/nm (ε/M^{-1} cm^{-1})): 448 (16 200), 313 (15 700).

X-ray Crystallography. Single crystals were immersed in immersion oil on micromount and transferred to a Rigaku VariMax with Saturn system or XtaLABmini system equipped with a Rigaku GNNP low-temperature device. Data were collected under a cold nitrogen stream at 123 K using graphite-monochromated Mo Kα radiation (λ = 0.710 75 Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) program. Empirical absorption collections were applied. All structures were solved by direct methods (SIR2004) and refined by full-matrix least-squares methods on F^2 for all data using SHELXL. All of OH and NH hydrogen atoms were found in the Fourier map and refined with isotropic thermal parameters. The other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Crystallographic data for each compound can be found in the Supporting Information.

For **3-Na**, one of *tert*-butyl groups was disordered. For **3-Na-DME**, two DME molecules were disordered. For **3-K**, three toluene molecules were disordered. For **4-Na**, one site occupied by pentane was identified in the unit cell. The solvent molecule was significantly disordered and was treated by SQUEEZE as a diffuse contribution. In the resulting void space, a contribution of 92 e^- per unit cell was found and taken to represent one-half of pentane molecule in the asymmetric unit. For **4-K-THF**, two THF molecules were disordered. For **5**, one of *tert*-butyl groups, one of methyl groups, the Li-bound THF molecule, a solvent toluene molecule were disordered.

Crystal Data for H_3[ONO^{tBu}]. $C_{41}H_{53}NO_2\cdot(C_7H_8)_{0.5}$, M = 637.91, triclinic, space group $P\bar{1}$ (#2), a = 10.6017(11) Å, b = 13.5051(9) Å, c = 14.6823(4) Å, α = 67.708(12)°, β = 81.070(14)°, γ = 87.903(18)°, V = 1920.9(2) Å^3, Z = 2; 20 447 reflections measured, 8782 independent reflections (R_{int} = 0.0612). The final R_1 value was 0.0710 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1848 (all data). The goodness-of-fit on F^2 was 1.031.

*Crystal Data for **3-Na**.* $C_{90}H_{118}N_2Na_4O_6\cdot(C_7H_8)_3$, M = 1692.23, triclinic, space group $P\bar{1}$ (#2), a = 16.015(4) Å, b = 17.626(5) Å, c = 18.858(4) Å, α = 77.160(8)°, β = 70.705(6)°, γ = 86.825(7)°, V = 4898(2) Å^3, Z = 2; 52 336 reflections measured, 22 394 independent reflections (R_{int} = 0.0327). The final R_1 value was 0.0486 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1285 (all data). The goodness-of-fit on F^2 was 1.053.

*Crystal Data for **3-Na-DME**.* $C_{49}H_{71}NNa_2O_6$, M = 816.05, orthorhombic, space group $Pbca$ (#61), a = 15.4706(17) Å, b = 18.030(2) Å, c = 34.053(4) Å, V = 9498.5(18) Å^3, Z = 8; 75 105 reflections measured, 10 861 independent reflections (R_{int} = 0.0613). The final R_1 value was 0.0822 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2062 (all data). The goodness-of-fit on F^2 was 1.172.

*Crystal Data for **3-K**.* $C_{96}H_{118}K_4N_2O_4\cdot(C_7H_8)$, M = 1612.46, triclinic, space group $P2_1/n$ (#14), a = 14.8790(6) Å, b = 19.6314(8) Å, c = 32.3606(14) Å, β = 96.914(2)°, V = 9383.7(7) Å^3, Z = 4; 96 318 reflections measured, 21 514 independent reflections (R_{int} = 0.0684). The final R_1 value was 0.0498 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1343 (all data). The goodness-of-fit on F^2 was 1.077.

*Crystal Data for **4-Na**.* $C_{53}H_{80}NNa_3O_8\cdot(C_5H_{12})_{0.5}$, M = 964.22, monoclinic, space group $P2_1/c$ (#14), a = 12.042(2) Å, b = 16.809(3) Å, c = 29.107(6) Å, β = 97.968(3)°, V = 5835(2) Å^3, Z = 4; 47 476 reflections measured, 13 004 independent reflections (R_{int} = 0.1242). The final R_1 value was 0.0948 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2761 (all data). The goodness-of-fit on F^2 was 0.983.

*Crystal Data for **4-K**.* $C_{110}H_{156}K_6N_2O_{11}$, M = 1916.97, triclinic, space group $P\bar{1}$ (#2), a = 14.396(6) Å, b = 17.804(7) Å, c = 23.302(8) Å, α = 101.930(3)°, β = 93.093(3)°, γ = 113.386(2)°, V = 5302(4) Å^3, Z = 2; 56 913 reflections measured, 24 261 independent reflections (R_{int} = 0.0808). The final R_1 value was 0.0651 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1866 (all data). The goodness-of-fit on F^2 was 1.231.

*Crystal Data for **5**.* $C_{49}H_{66}ClCrLiNO_4\cdot(C_7H_8)_{1.5}$, M = 965.62, monoclinic, space group $C2/c$ (#15), a = 36.094(7) Å, b = 13.370(2)

Å, c = 26.077(5) Å, β = 121.573(2)°, V = 10 721(3) Å^3, Z = 8; 53 483 reflections measured, 12 250 independent reflections (R_{int} = 0.0489). The final R_1 value was 0.0725 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2256 (all data). The goodness-of-fit on F^2 was 1.054.

*Crystal Data for **6**.* $\mathrm{C_{45}H_{58}NO_3V{\cdot}(C_7H_8)_{1.5}}$, M = 850.07, monoclinic, space group $P2_1/n$ (#14), a = 15.9632(16) Å, b = 13.6482(13) Å, c = 22.591(2) Å, β = 104.0735(12)°, V = 4774.1(8) Å^3, Z = 4; 58 357 reflections measured, 10 940 independent reflections (R_{int} = 0.0373). The final R_1 value was 0.0519 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1350 (all data). The goodness-of-fit on F^2 was 1.099.

*Crystal Data for **7**.* $\mathrm{C_{45}H_{56}NO_2V{\cdot}2.5(C_7H_8)}$, M = 924.18, triclinic, space group $P\bar{1}$ (#2), a = 10.8758(15) Å, b = 15.063(3) Å, c = 17.402(3) Å, α = 108.080(5)°, β = 97.627(6)°, γ = 96.668(4)°, V = 2648.4(8) Å^3, Z = 2; 28 355 reflections measured, 12 087 independent reflections (R_{int} = 0.0720). The final R_1 value was 0.0718 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2119 (all data). The goodness-of-fit on F^2 was 1.061.

*Crystal Data for **8**.* $\mathrm{C_{41}H_{50}NO_3V{\cdot}(C_7H_8)}$, M = 747.89, triclinic, space group $P\bar{1}$ (#2), a = 13.238(2) Å, b = 13.7138(19) Å, c = 14.4689(15) Å, α = 60.738(11)°, β = 65.948(12)°, γ = 71.376(13)°, V = 2068.6(5) Å^3, Z = 2; 25 736 reflections measured, 9437 independent reflections (R_{int} = 0.0432). The final R_1 value was 0.0522 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1465 (all data). The goodness-of-fit on F^2 was 1.068.

*Crystal Data for **9**.* $\mathrm{C_{50}H_{61}N_2O_2V{\cdot}C_9H_{11}N_3}$, M = 934.16, triclinic, space group $P\bar{1}$ (#2), a = 11.032(3) Å, b = 14.833(5) Å, c = 16.368(5) Å, α = 85.840(7)°, β = 83.155(8)°, γ = 79.888(7)°, V = 2614.4(14) Å^3, Z = 2; 27 757 reflections measured, 11 852 independent reflections (R_{int} = 0.0364). The final R_1 value was 0.0555 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1627 all data). The goodness-of-fit on F^2 was 1.070.

ASSOCIATED CONTENT

Supporting Information

Molecular structures of **3-K**, **3-Na-DME**, and **4-Na**, and crystallographic details (as CIF files). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-990684 (for $\mathrm{H_3}$[**ONO**$^{t\mathrm{Bu}}$]), CCDC-990685 (for **3-K**), CCDC-990686 (for **3-Na**), CCDC-990687 (for **3-Na-DME**), CCDC-990688 (for **4-K**), CCDC-990689 (for **4-Na**), CCDC-990690 (for **5**), CCDC-990691 (for **6**), CCDC-1002287 (for **7**), CCDC-1002288 (for **8**), and CCDC-1002289 (for **9**), contain the supplemental crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request.cif.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Gade, L. H. *Chem. Commun.* **2000**, 173−181. (c) Kameo, H.; Nakazawa, H. *Chem.—Asian J.* **2013**, *8*, 1720−1734. (d) Annibale, V. T.; Song, D. *RSC Adv.* **2013**, 3, 11432−11449. (e) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9−16. (f) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680−699. (g) Benito-Garagorri, D.; Kirchner, K. *Acc. Res. Chem.* **2008**, *41*, 201−213. (h) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781. (i) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759−1792. (j) Chomitz, W. A.; Arnold, J. *Chem.—Eur. J.* **2009**, *15*, 2020−2030.

(2) (a) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445−1447. (b) Lee, Y.; Mankad, N. P.; Peters, J. C. *Nat. Chem.* **2010**, *2*, 558−565. (c) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76−78.

(3) (a) Wichmann, O.; Sillanpää, R.; Lehtonen, A. *Coord. Chem. Rev.* **2012**, *256*, 371−392. (b) Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2004**, *689*, 4228−4243.

(4) (a) Fokken, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4240−4242. (b) Chisholm, M. H.; Huang, J.-H.; Huffman, J. C.; Streib, W. E.; Tiedtke, D. *Polyhedron* **1997**, *16*, 2941−2949. (c) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66−67. (d) Kayal, A.; Ducruet, A. F.; Lee, S. C. *Inorg. Chem.* **2000**, *39*, 3696−3704.

(5) (a) Gordon, B. W. F.; Scott, M. J. *Inorg. Chim. Acta* **2000**, *297*, 206−216. (b) Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2001**, *40*, 1029−1036. (c) Appiah, W. O.; DeGreeff, A. D.; Razidlo, G. L.; Spessard, S. J.; Pink, M.; Young, V. G., Jr.; Hofmeister, G. E. *Inorg. Chem.* **2002**, *41*, 3656−3667. (d) Redshaw, C.; Warford, L.; Dale, S. H.; Elsegood, M. R. J. *Chem. Commun.* **2004**, 1954−1955.

(6) (a) Arnold, P. L.; Natrajan, L. S.; Hall, J. J.; Bird, S. J.; Wilson, C. *J. Organomet. Chem.* **2002**, *647*, 205−215. (b) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321−1326. (c) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A. *Organometallics* **2000**, *19*, 2498−2503.

(7) (a) Roundhill, D. M. *Prog. Inorg. Chem.* **1995**, *43*, 533−592. (b) Wieser, C.; Dieleman, C. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93−161. (c) Hoppe, E.; Limberg, C.; Ziemer, B. *Inorg. Chem.* **2006**, *45*, 8308−8317. (d) Hoppe, E.; Limberg, C.; Ziemer, B.; Mügge, C. *J. Mol. Catal. A: Chem.* **2006**, *251*, 34−40. (e) Hoppe, E.; Limberg, C. *Chem.—Eur. J.* **2007**, *13*, 7006−7016. (f) Limberg, C. *Eur. J. Inorg. Chem.* **2007**, 3303−3314.

(8) (a) Guillemot, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **2001**, *20*, 2446−2448. (b) Floriani, C. *Chem.—Eur. J.* **1999**, *5*, 19−23. (c) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 8296−8305. (d) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823−824. (e) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437−438. (f) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270*, 298−311. (g) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2825−2827.

(9) (a) Okuda, J.; Masoud, E. *Macromol. Chem. Phys.* **1998**, *199*, 543−545. (b) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069−5072. (c) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008−3021.

(10) (a) Chaudhuri, P.; Hess, M.; Müller, J.; Hildenbrand, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 9599−9610. (b) Chaudhuri, P.; Hess, M.; Weyhermüller, T.; Wieghardt, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1095−1098.

(11) (a) Matsuo, T.; Kawaguchi, H.; Sakai, M. *J. Chem. Soc., Dalton Trans.* **2002**, 2536−2540. (b) Matsuo, T.; Kawaguchi, H. *Inorg. Chem.* **2002**, *41*, 6090−6098. (c) Matsuo, T.; Kawaguchi, H. *Inorg. Chem.* **2007**, *46*, 8426−8434. (d) Kawaguchi, H.; Matsuo, T. *J. Am. Chem. Soc.* **2003**, *125*, 14254−14255. (e) Watanabe, T.; Kurogi, T.; Ishida, Y.; Kawaguchi, H. *Dalton Trans.* **2011**, *40*, 7701−7703. (f) Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2005**, *690*, 5333−5345. (g) Matsuo,

T.; Kawaguchi, H. *Organometallics* **2003**, *22*, 5379−5381. (h) Kurogi, T.; Ishida, Y.; Hatanaka, T.; Kawaguchi, H. *Chem. Commun.* **2012**, *48*, 6809−6811.

(12) (a) Kawaguchi, H.; Matsuo, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2792−2794. (b) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2005**, *127*, 17198−17199. (c) Watanabe, T.; Ishida, Y.; Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2009**, *131*, 3474−3475.

(13) Field, J. E.; Hill, T. J.; Venkataraman, D. *J. Org. Chem.* **2003**, *68*, 6071−6078.

(14) Sone, T.; Ohba, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1111−1116.

(15) (a) Loehlin, J. H.; Etter, M. C.; Gendreau, C.; Cervasio, E. *Chem. Mater.* **1994**, *6*, 1218−1221. (b) Kober, E.; Nerkowski, T.; Janas, Z.; Jerzykiewicz, L. B. *Dalton Trans.* **2012**, *41*, 5188−5192. (c) Reckling, A. M.; Martin, D.; Dawe, L. N.; Decken, A.; Kozak, C. M. *J. Organomet. Chem.* **2011**, *696*, 787−794.

(16) Judmaier, M. E.; Wallner, A.; Stipicic, G. N.; Kirchner, K.; Baumgartner, J.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2009**, *48*, 10211−10221.

(17) (a) van der Schaaf, P. A.; Hogerheide, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1703−1705. (b) Vilardo, J. S.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1998**, *17*, 769−771. (c) Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Vick, S. C.; Rodriguez, M. A. *Inorg. Chem.* **2000**, *39*, 5133−5146.

(18) (a) Cousins, D. M.; Davidson, M. G.; García-Vivó, D.; Mahon, M. F. *Dalton Trans.* **2010**, *39*, 8203−8209. (b) Huang, C.-A.; Chen, C.-T. *Dalton Trans.* **2007**, 5561−5566. (c) Carmichael, C. D.; Fryzuk, M. D. *Dalton Trans.* **2008**, 800−806. (d) Hsu, Y.-L.; Liang, L.-C. *Organometallics* **2010**, *29*, 6201−6208. (e) Hsueh, M.-L.; Ko, B.-T.; Athar, T.; Lin, C.-C.; Wu, T.-M.; Hsu, S.-F. *Organometallics* **2006**, *25*, 4144−4149. (f) Huang, Y.; Tsai, Y.-H.; Hung, W.-C.; Lin, C.-S.; Wang, W.; Huang, J.-H.; Dutta, S.; Lin, C.-C. *Inorg. Chem.* **2010**, *49*, 9416−9425.

(19) (a) Dean, R. K.; Granville, S. L.; Dawe, L. N.; Decken, A.; Hattenhauer, K. M.; Kozak, C. M. *Dalton Trans.* **2010**, *39*, 548−559. (b) Dean, R. K.; Reckling, A. M.; Chen, H.; Dawe, L. N.; Schneidera, C. M.; Kozak, C. M. *Dalton Trans.* **2013**, *42*, 3504−3520.

(20) (a) Clegg, W.; Davidson, M. G.; Graham, D. V.; Griffen, G.; Jones, M. D.; Kennedy, A. R.; O'Hara, C. T.; Russo, L.; Thomson, C. M. *Dalton Trans.* **2008**, 1295−1301. (b) Zhang, J.; Wang, C.; Lu, M.; Yao, Y.-M.; Zhang, Y.; Shen, Q. *Polyhedron* **2011**, *30*, 1876−1883. (c) Cole, M. L.; Junk, P. C.; Proctor, K. M.; Scott, J. L.; Strauss, C. R. *Dalton Trans.* **2006**, 3338−3349. (d) Cragg-Hine, I.; Davidson, M. G.; Kocian, O.; Kottke, T.; Mair, F. S.; Snaith, R.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1993**, 1355−1357. (e) Dubberly, S. R.; Blake, A. J.; Mountford, P. *Chem. Commun.* **1997**, 1603−1604.

(21) (a) Boyle, T. J.; Andrews, N. L.; Rodriguez, M. A.; Campana, C.; Yiu, T. *Inorg. Chem.* **2003**, *42*, 5357−5366. (b) Arnold, P. L.; Hall, J. J.; Natrajan, L. S.; Blake, A. J.; Wilson, C. *Dalton Trans.* **2003**, 1053−1055. (c) Cox, A. R. F.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Yeldon, D. *Dalton Trans.* **2006**, 5014−5023. (d) Binda, P. I.; Delbridge, E. E.; Dugah, D. T.; Skelton, B. W.; White, A. H. *Z. Anorg. Allg. Chem.* **2008**, *634*, 325−334.

(22) (a) Zhang, Z.; Xu, X.; Sun, S.; Yao, Y.; Zhang, Y.; Shen, Q. *Chem. Commun.* **2009**, 7414−7416. (b) Calvo, B.; Davidson, M. G.; García-Vivó, D. *Inorg. Chem.* **2011**, *50*, 3589−3595. (c) Schofield, A. D.; Barros, M. L.; Cushion, M. G.; Schwarz, A. D.; Mountford, P. *Dalton Trans.* **2009**, 85−96. (d) Cornish, A. D.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. *C. R. Chim.* **2010**, *13*, 593−602. (e) Zuniga, M. F.; Deacon, G. B.; Ruhlandt-Senge, K. *Inorg. Chem.* **2008**, *47*, 4669−4681.

(23) See the Supporting Information for the structures of **3-K**, **3-Na-DME**, and **4-Na**.

(24) (a) Pirard, B.; Baudoux, G.; Durant, F. *Acta Crystallogr.* **1995**, *B51*, 103−107. (b) Habbadi, N.; Dartiguenave, M.; Lamandé, L.; Sanchez, M.; Simard, M.; Beauchamp, A. L.; Souiri, A. *New. J. Chem.* **1998**, 983−987. (c) Davidson, M. G.; Doherty, C. L.; Johnson, A. L.; Mahon, M. F. *Chem. Commun.* **2003**, 1832−1833.

(25) Matsuo, T.; Kawaguchi, H. *Chem. Lett.* **2004**, *33*, 640−645.

(26) Clegg, W.; Doherty, S.; Izod, K.; Kagerer, H.; O'Shaughnessy, P.; Sheffield, J. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1825−1829.

(27) (a) Jin, G.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Rose, R. P.; Stasch, A. *New J. Chem.* **2009**, *33*, 64−75. (b) Arnold, P. L.; Liddle, S. T. *C. R. Chim.* **2008**, *11*, 603−611.

(28) (a) Armstrong, D. R.; Henderson, K. W.; Kennedy, A. R.; Kerr, W. J.; Mair, F. S.; Moir, J. H.; Moran, P. H.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1999**, 4063−4068. (b) Hellmann, K. W.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Inorg. Chem.* **1994**, *33*, 5974−5977. (c) Dubberley, S. R.; Mountford, P.; Adams, N. *Acta Crystallogr.* **2002**, *E58*, m342−m343. (d) Matthes, C.; Noltemeyer, M.; Klingebiel, U.; Schmatz, S. *Organometallics* **2007**, *26*, 838−845.

(29) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. (b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.

(30) (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356. (b) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955−964.

(31) (a) Ballem, K. H. D.; Shetty, V.; Etkin, N.; Patrick, B. O.; Smith, K. M. *Dalton Trans.* **2004**, 3431−3433. (b) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J.; Young, V. G., Jr. *J. Chem. Soc., Dalton Trans.* **1999**, 147−154. (c) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J. *Organometallics* **1997**, *16*, 5116−5119. (d) Ruppa, K. B. P.; Feghali, K.; Kovacs, I.; Aparna, K.; Gambarotta, S.; Yap, G. P. A.; Bensimon, C. *J. Chem. Soc., Dalton Trans.* **1998**, 1595−1605. (e) Schneider, S.; Filippou, A. C. *Inorg. Chem.* **2001**, *40*, 4674−4677.

(32) (a) O'Reilly, M.; Falkowski, J. M.; Ramachandran, V.; Pati, M.; Abboud, K. A.; Dalal, N. S.; Gray, T. G.; Veige, A. S. *Inorg. Chem.* **2009**, *48*, 10901−10903. (b) Hesschenbrouck, J.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Chem. Soc., Dalton Trans.* **2000**, 191−198. (c) Redshaw, C.; Homden, D.; Hughes, D. L.; Wright, J. A.; Elsegood, M. R. J. *Dalton Trans.* **2009**, 1231−1242. (d) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 827−829. (e) Sun, M.; Xu, T.; Gao, W.; Liu, Y.; Wu, Q.; Mu, Y.; Ye, L. *Dalton Trans.* **2011**, *40*, 10184−10194.

(33) (a) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1998**, *17*, 2328−2336. (b) Castellano, B.; Solari, E.; Floriani, C.; Scopelliti, R.; Re, N. *Inorg. Chem.* **1999**, *38*, 3406−3413. (c) Henderson, R. A.; Hughes, D. L.; Janas, Z.; Richards, R. L.; Sobota, P.; Szafert, S. *J. Organomet. Chem.* **1998**, *554*, 195−201. (d) Janas, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sobota, P. *Chem. Commun.* **1999**, 1015−1016. (e) Wilisch, W. C. A.; Scott, M. J.; Armstrong, W. H. *Inorg. Chem.* **1988**, *27*, 4333−4335.

(34) Ruppa, K. B. P.; Desmangles, N.; Gambarotta, S.; Yap, G.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 1194−1197.

(35) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770−5780.

(36) (a) Wanandi, P. W.; Davis, W. M.; Cummins, C. C.; Russell, M. A.; Wilcox, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 2110−2111. (b) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825−3835. (c) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836−5837. (d) Tran, B. L.; Singhal, M.; Park, H.; Lam, O. P.; Pink, M.; Krzystek, J.; Ozarowski, A.; Telser, J.; Meyer, K.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 9871−9875.

(37) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

(38) Early transition metal metallacyclopropene systems have revealed highly deshielded α-carbon resonances: (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288−3290. (b) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860−3868. (c) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387−393. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (e) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1991**, *10*, 118−127.

(39) (a) Petersen, J. L.; Griffith, L. *Inorg. Chem.* **1980**, *19*, 1852−1858. (b) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925−1936. (c) Liu, G.; Lu, X.; Gagliardo, M.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 2316−2320. (d) Liu, G.; Liang, X.; Meetsma, A.; Hessen, B. *Dalton Trans.* **2010**, *39*, 7891−7893. (e) Protasiewicz, J. D.; Lippard, S. J. *J.*

Am. Chem. Soc. **1991**, *113*, 6564−6570. (f) Gailus, H.; Maelger, H.; Rehder, D. *J. Organomet. Chem.* **1994**, *465*, 181−185.

(40) (a) Redshaw, C.; Rowan, M. A.; Warford, L.; Homden, D. M.; Arbaoui, A.; Elsegood, M. R. J.; Dale, S. H.; Yamato, T.; Casas, C. P.; Matsui, S.; Matsuura, S. *Chem.—Eur. J.* **2007**, *13*, 1090−1107. (b) Spandl, J.; Brüdgam, I.; Hartl, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2125−2132. (c) Hillerns, F.; Olbrich, F.; Behrens, U.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 447−448.

(41) (a) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 533−542. (b) Seidel, W.; Kreisel, G. *Z. Chem.* **1982**, *22*, 113.

(42) (a) Nishina, M.; Moriuchi, T.; Hirao, T. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 606−612. (b) Song, J.-I.; Gambarotta, S. *Chem.—Eur. J.* **1996**, *2*, 1258−1263. (c) Lutz, M.; Hagen, H.; Schreurs, A. M. M.; Spek, A. L.; van Koten, G. *Acta Crystallogr.* **1999**, *C55*, 1636−1639. (d) Zhang, W.; Nomura, K. *Inorg. Chem.* **2008**, *47*, 6482−6492. (e) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408−7416.

(43) (a) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770−5780. (b) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689−1694.