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Assembly of Molybdenum/Titanium μ-Oxo Complexes via Radical Alkoxide C−O Cleavage

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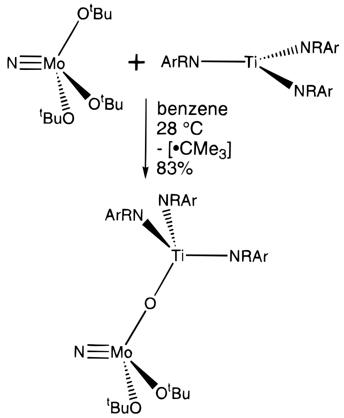
Abstract: Three-coordinate $Ti(NRAr)_3$ [$R = C(CD_3)_2(CH_3)$, $Ar = C_6H_3Me_2$] was prepared in 73% yield by sodium amalgam reduction of $ClTi(NRAr)_3$ and in 83% yield upon treatment of $TiCl_3(THF)_3$ with 3 equiv of $Li(NRAr)(OEt_2)$ in the presence of TMEDA. $Ti(^tBuNPh)_3$ was prepared similarly in 75% yield by treatment of $TiCl_3(THF)_3$ with 3 equiv of $Li(^tBuNPh)(OEt_2)$ in the presence of TMEDA. Reaction of $Ti(NRAr)_3$ with $NMo(O^tBu)_3$ in hydrocarbon solvents at −35 °C generates a thermally unstable intermediate formulated as $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$, which readily loses a *tert*-butyl radical and isomerizes at 25 °C. Kinetics of the latter process were obtained over the temperature range 20−60 °C; the process exhibits clean first-order behavior. The following activation parameters were obtained: $\Delta H^{\ddagger} = 21.4 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.7 \pm 0.6$ cal mol^{-1} K^{-1}. The oxo-bridged product $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ was isolated in 83% yield from this reaction. Full characterization of the latter diamagnetic complex included an X-ray crystal structure and an ^{15}N NMR study. $Ti(NRAr)_3$ (1 equiv) reacts further with $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ to generate a species formulated as a second paramagnetic nitrido-bridged intermediate, $(^tBuO)_2Mo\{[\mu\text{-}O]Ti(NRAr)_3\}\{[\mu\text{-}N]Ti(NRAr)_3\}$, which at 25 °C loses a *tert*-butyl radical and isomerizes to give the final product, $(^tBuO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$, isolated as an orange powder in 91% yield. Characterization of the latter diamagnetic complex included an ^{15}N NMR study. Attempts to displace a third *tert*-butyl radical by treatment of $(^tBuO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ with $Ti(NRAr)_3$ led to no reaction. Treatment of $(^tBuO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ with neat methyl iodide led to the isolation of $(MeO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ in 51% yield; ^{13}C and nitrido-^{15}N derivatives of this species were prepared for spectroscopic characterization. $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ was prepared in 59% yield upon treatment of $MoO_2(O^tBu)_2$ with 2 equiv of $Ti(^tBuNPh)_3$ in benzene at 65 °C. Full characterization of $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ included a single-crystal X-ray diffraction study. Previously reported $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ was oxidized with ferrocenium triflate to give $TfOTi(NRAr)_3$ and $OV(O^iPr)_3$. $TfOTi(NRAr)_3$ was prepared independently in 80% yield by treatment of $Ti(NRAr)_3$ with ferrocenium triflate. $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ is stable in the presence of methyl iodide. $ITi(NRAr)_3$ was prepared independently by treatment of $Ti(NRAr)_3$ with the stoichiometric amount of iodine. Paramagnetic $(^tBuO)_3V[\mu\text{-}O]Ti(NRAr)_3$ was prepared as orange-brown needles in 94% yield and was found to be thermally stable. The relatively robust μ-nitrido compound $(Me_2N)_3Mo[\mu\text{-}N]Ti(^tBuNPh)_3$, which was prepared in 77% isolated yield, showed no decomposition when heated in benzene at 70 °C for 13 h.

Introduction

This paper describes a new chemical reaction in which an alkyl radical on the periphery of an $NMoO_3$ or MoO_4 tetrahedron is replaced by a titanium-based radical. Specific to the present work are [$^{\bullet}CMe_3$] as the departing alkyl radical and, as the incoming metalloradical, the previously reported three-coordinate titanium(III) complex $Ti(NRAr)_3$ [Figure 1, $R = C(CD_3)_2CH_3$, $Ar = 3,5\text{-}C_6H_3Me_2$][1] and the new such complex $Ti(^tBuNPh)_3$. Equation 1 depicts an exemplary variant of the reaction highlighted in the present work, that of Chisholm's terminal nitrido complex $NMo(O^tBu)_3$[2] with $Ti(NRAr)_3$ to give the bridging-oxo complex $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ in near-quantitative yield (see sections II−V). This paper builds substantially on a recent communication[1] wherein we described the synthesis and structural characterization of $Ti(NRAr)_3$ and showed that it adds to $OV(O^iPr)_3$ to give the thermally stable "titanoxide" complex $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ in an example of incomplete oxo transfer (eq 2).[3−13]



(1)

Our interest in the reaction type exemplified by eq 1 is its potential utility with respect to the construction of low-

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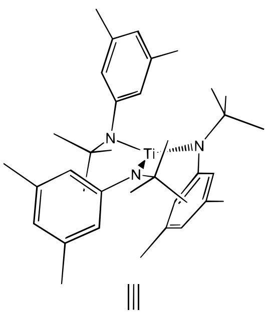
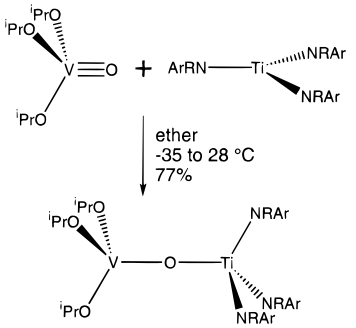


Ti(NRAr)$_3$

Figure 1. Line drawing of Ti(NRAr)$_3$ based on the previously reported X-ray structure.



(2)

coordinate transition metal complexes.[14−16] Such species have been shown to mediate new transformations of small molecules including nitrous oxide,[17,18] dinitrogen,[19,20] nitric oxide,[21−24] carbon monoxide,[25,26] white phosphorus,[27] and so on, but synthetic approaches delivering such species are largely limited at present to salt-elimination (metathesis)[28−30] or protolytic[31,32] reactions. The new μ-oxo molybdenum/titanium species described here can be thought of as molybdenum complexes supported by ancillary [μ-O]Ti(NRAr)$_3$ (“titanoxide”) ligation, and the new radical substitution reaction exemplified by eq 1 represents an efficient means for installing this ligand type.

A further impetus for studying the chemistry of molybdenum/titanium μ-oxo complexes derives from the fact that several industrial processes employ titania-supported molybdenum compounds as catalysts.[33−45] Molybdenum complexes supported by [μ-O]Ti(NRAr)$_3$ ligation could conceivably serve as soluble models for such catalysts. Such an approach has already been employed to great advantage in modeling the chemistry of silica-supported metal complexes.[46−54]

Results and Discussion

I. Synthesis of Ti(NRAr)$_3$ and Ti(^{t}BuNPh)$_3$. Green, three-coordinate Ti(NRAr)$_3$ can be prepared in 73% isolated yield by sodium amalgam reduction of ClTi(NRAr)$_3$, as previously reported,[1] or in 83% yield as reported here by direct treatment of TiCl$_3$(THF)$_3$ with the lithium etherate Li(NRAr)(OEt$_2$)[55] in the presence of Me$_2$NCH$_2$CH$_2$NMe$_2$ (TMEDA); see Experimental Section for details. The latter procedure is preferred because it involves, overall, one fewer step. Our rationale for carrying the reaction out in the presence of TMEDA is the stabilization of a presumed intermediate “ate” complex, (TMEDA)Li(μ-Cl)$_2$Ti(NRAr)$_2$, analogous to the known (Cy$_2$N)$_2$Ti(μ-Cl)$_2$Li(TMEDA).[56] The synthesis of Li(NRAr)(OEt$_2$) has been described in detail,[55] and its solid-state structure (dimeric) is known.[57] The compound Ti(^{t}BuNPh)$_3$ was prepared in 75% isolated yield by treatment of TiCl$_3$(THF)$_3$[58] with the lithium etherate Li(^{t}BuNPh)(OEt$_2$), again in the presence of TMEDA. The latter etherate is obtained in high yield as a colorless

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crystalline solid using essentially the same procedure as that used for Li(NRAr)(OEt_2),[55] substituting *N-tert*-butylaniline[59−61] for HNRAr.

Ti($NRAr)_3$ and Ti($^tBuNPh)_3$ are soluble and stable for extended periods in common solvents including pentane, benzene, ether, and tetrahydrofuran (THF), provided that oxygen and water are rigorously excluded. Ti($NRAr)_3$, because of the deuterium enrichment in its *tert*-butyl groups, is preferred in instances where it is desirable to assay paramagnetic reaction mixtures by deuterium NMR. Deuterium NMR signals are substantially narrower than corresponding proton NMR signals for paramagnetic systems.[62−68] On the other hand, in instances where syntheses have been worked out for Ti($NRAr)_3$, they can often be transferred to the less-expensive, nonisotopically-enriched Ti($^tBuNPh)_3$. A further distinction between the two systems is that complexes containing the NRAr ligand frequently exhibit greater lipophilicity and diminished crystallinity relative to corresponding compounds utilizing the ^{t}BuNPh ligand. Ti($NRAr)_3$ and Ti($^tBuNPh)_3$ exhibit effective magnetic moments consistent with the presence of one unpaired electron, as ascertained in solution by the method of Evans.[69,70] The solid state structure of Ti($NRAr)_3$ was determined by single-crystal X-ray diffraction and has been described,[1] and although we refrain from describing it in detail here, it should be borne in mind that the compound indeed represents a bona-fide example of a monomeric three-coordinate complex of titanium(III).[30,32,71−74]

II. Characterization of Thermally Unstable ($^tBuO)_3$Mo-[μ-N]Ti($NRAr)_3$. A thermally-unstable, paramagnetic, olive green complex forms within several seconds upon addition of solvent to a solid mixture of Ti($NRAr)_3$ and NMo($O^tBu)_3$ as indicated in Scheme 1. We assign to this olive green complex the formula ($^tBuO)_3$Mo[μ-N]Ti($NRAr)_3$, in which a nitrido nitrogen atom bridges the titanium and molybdenum centers.[75−77] That this species is paramagnetic is indicated by its shifted and broadened ^{1}H NMR signals. The formal oxidation state assignment we prefer for the complex is molybdenum(V)−titanium(IV) as opposed to the alternative molybdenum(VI)−titanium(III), based on EPR data (Figure 2) obtained at 103 K. Simulation (Figure 2) of the 103 K EPR spectrum of ($^tBuO)_3$Mo-[μ-N]Ti($NRAr)_3$ required inclusion of substantial molybdenum hyperfine coupling ($a_1 = 30$, $a_2 = 40$, $a_3 = 16$ G).

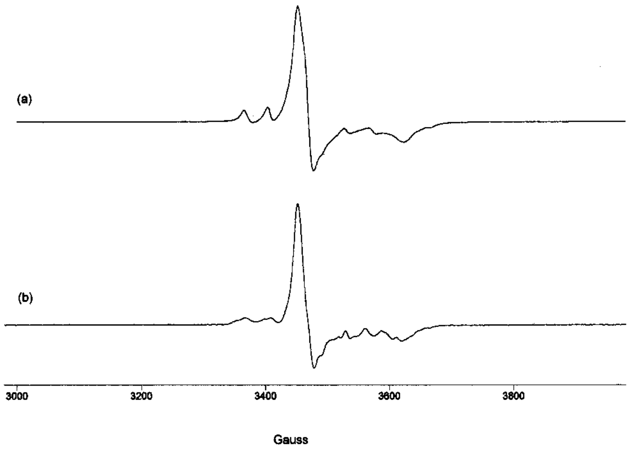
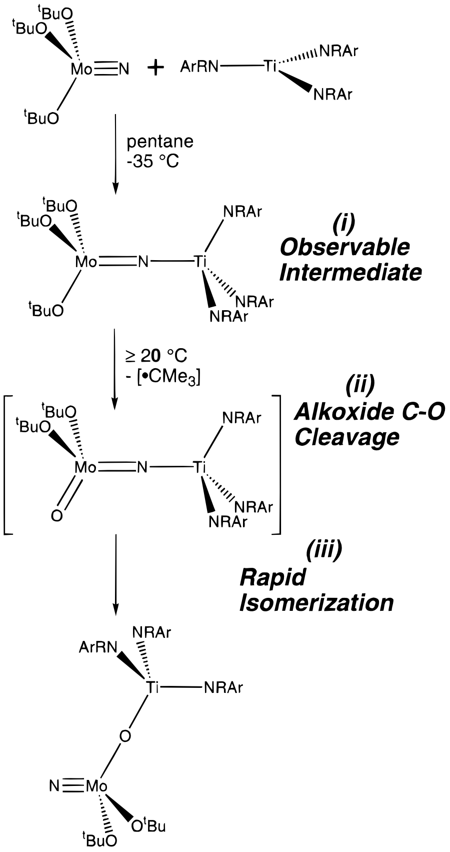


Figure 2. EPR spectrum (frozen toluene, 103 K) of ($^tBuO)_3$Mo[μ-N]-Ti($NRAr)_3$ (a) simulated with $g_1 = 1.954$, $g_2 = 1.944$, $g_3 = 1.861$, $a_1 = 30$, $a_2 = 40$, $a_3 = 16$ G, (b) observed.

Scheme 1



The assignment molybdenum(V)−titanium(IV) for ($^tBuO)_3$Mo-[μ-N]Ti($NRAr)_3$ is also consistent with our observation that the ^{1}H NMR signal corresponding to the *tert*-butoxide moieties, which are proximal to molybdenum, are severely broadened and shifted in comparison with those signals assigned to the NRAr residues, which are proximal to titanium.[62] We prepared (d_6-$^tBuO)_3$Mo[μ-N]Ti($NRAr)_3$ similarly, from Ti($NRAr)_3$ and NMo-(O^tBu-$d_6)_3$, in order to confirm by ^{2}H NMR the chemical shift assignment ($\delta = 5.6$ ppm) for the *tert*-butoxide residues. The magnitude of this shift should be compared with the ^{2}H NMR signal for the NRAr residue in this binuclear complex ($\delta = 2.2$ ppm). ($^tBuO)_3$Mo[μ-N]Ti($NRAr)_3$ possesses 3-fold symmetry according to both ^{1}H and ^{2}H NMR, consistent with the proposition of a roughly linear nitrido bridge. Of course, the NMR data alone are not sufficient to rule out an unsymmetrical, fluxional[78−80] structure for the complex, perhaps with a bridging

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tert-butoxide ligand; such a structure, however, appears sterically prohibited. Our formulation of the olive green complex as $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ is a logical one on the basis of its thermal transformation, as described in some detail below. In addition, the symmetrical N-atom bridged structure is suggested by the symmetrical O-atom bridged structure of $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ (eq 2), which has been verified in a preliminary fashion by single-crystal X-ray diffraction.[1] Attempts to obtain single crystals of $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ suitable for X-ray diffraction have been unsuccessful thus far.

We carried out two experiments to probe chemically the nature of the thermally unstable, nitrido-bridged complex, $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$. The first of these involved treatment of the complex, generated as described above, with methyl iodide. Control experiments show that $Ti(NRAr)_3$ reacts rapidly and essentially quantitatively, even at −35 °C, with CH_3I to give a mixture of two diamagnetic compounds, $ITi(NRAr)_3$ and $MeTi(NRAr)_3$ (*vide infra*). Treatment of $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ [pentane, −35 °C, devoid of starting $Ti(NRAr)_3$ according to ^{2}H NMR] with excess methyl iodide did *not* lead to significant production of $MeTi(NRAr)_3$ (according to ^{1}H NMR analysis of the crude reaction mixture), suggesting that the formation of $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ is not reversible; however $ITi(NRAr)_3$ was formed to a limited extent along with an as yet unidentified titanium species. The majority of the $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ so treated went on to $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$, as it does in the absence of methyl iodide (*vide infra*). The second experiment was an attempt to oxidize the binuclear intermediate, by adding a stoichiometric amount of iodine to a −35 °C solution containing it. This led merely to smooth production of $ITi(NRAr)_3$ and to regeneration of $NMo(O^tBu)_3$. $ITi(NRAr)_3$ was prepared independently for spectroscopic comparison, in essentially quantitative yield, by treatment of ethereal $Ti(NRAr)_3$ with the stoichiometric amount of iodine; $MeTi(NRAr)_3$ was prepared independently for spectroscopic comparison by treatment of ethereal $ITi(NRAr)_3$ with the stoichiometric amount of $LiCH_3$ (see Experimental Section for details).

III. Thermal Decomposition Kinetics for $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$. In solution or in the solid state the paramagnetic, olive green intermediate $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ persists for months at −35 °C, but transforms readily to diamagnetic, orange $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ at temperatures of ≥20 °C (Scheme 1). The latter transformation necessarily proceeds with formal ejection of a *tert*-butyl radical. The organic byproducts are those expected[81−83] for disproportionation and combination of the *tert*-butyl radical (isobutylene, isobutane, and hexamethylethane; these were collected, identified, and quantified by ^{1}H NMR at 500 MHz; see Experimental Section for details). A C−S bond cleavage process that may be related was reported recently.[84] Alkoxide C−O bond cleavage processes have been summarized.[85]

The reaction exhibits clean first-order kinetic behavior over the temperature range 20−60 °C as measured by UV−vis spectroscopy in benzene solution. This technique proved especially suitable given that olive green $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ exhibits an electronic transition at 746 nm, a wavelength at which the product, $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$, does not absorb. Observed rate constants (s^{-1}) and the temperatures at which they were obtained are as follows: 20 °C, 8.81×10^{-5}; 25 °C (three runs), $(1.72 \pm 0.06) \times 10^{-4}$; 30 °C, 3.29×10^{-4}; 35 °C, 6.16×10^{-4}; 40 °C (three runs), $(1.15 \pm 0.03) \times 10^{-3}$; 45 °C, 1.99×10^{-3}; 50 °C (three runs), $(3.62 \pm 0.15) \times 10^{-3}$; 55 °C, 5.97×10^{-3}; 60 °C, 9.85×10^{-3}. An excellent fit to the exponential form of the Eyring equation (Figure 3) was obtained for the observed temperature dependence of the first-order rate constant. From the exponential fit we extract an activation enthalpy $\Delta H^\ddagger = 21.4 \pm 0.2$ kcal mol^{-1} and an activation entropy $\Delta S^\ddagger = -3.7 \pm 0.6$ cal mol^{-1} K^{-1}. We propose that these parameters correspond to rate-determining ejection of the *tert*-butyl radical from the observable nitrido-bridged intermediate $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$, followed by rapid isomerization to the oxo-bridged product, $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ (Scheme 1). Within the confines of this scenario, the activation parameters indicate a substantial degree of C−O bond cleavage in a moderately constrained transition state. An alternative scenario, namely, rate-determining isomerization followed by rapid ejection of the *tert*-butyl radical, might have been expected to yield a more negative value of $\Delta S^\ddagger$ in view of the steric problem posed by bridging two hindered metal centers with a *tert*-butoxide moiety.[86]

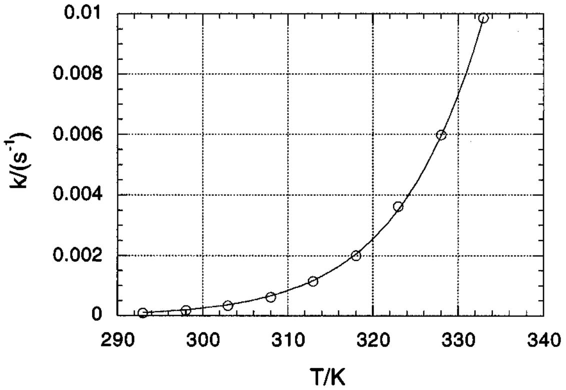

Figure 3. Exponential least-squares fit of first-order rate constants (k) versus temperature (K) to the Eyring equation $k = (k_BT/h)\exp(\Delta S^\ddagger/R)\exp(-\Delta H^\ddagger/RT)$ for the thermal conversion of $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$ to $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ with *tert*-butyl radical loss (see Scheme 1). Activation parameters obtained from the fit are $\Delta H^\ddagger = 21.4 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -3.7 \pm 0.6$ cal mol^{-1} K^{-1}.

IV. Synthesis and Characterization of $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$. The preceding sections have dealt with the formation and decay of the observable intermediate formulated as $(^tBuO)_3Mo[\mu\text{-}N]Ti(NRAr)_3$. This paragraph covers synthetic aspects pertaining to the product resulting from the above processes, namely, $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$. This heterobinuclear μ-oxo complex was isolated in 83% yield, on a scale slightly greater than 1 g, as an analytically pure orange powder subsequent to mixing $Ti(NRAr)_3$ and $NMo(O^tBu)_3$ in benzene. The highly lipophilic mono-“titanoxide” molybdenum complex is difficult to recrystallize in good yield from ether or pentane, because of its high solubility in these orthodox solvents. Because $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ is produced in essentially quantitative yield [according to ^{1}H and ^{2}H NMR monitoring of many reactions between $Ti(NRAr)_3$ and $NMo(O^tBu)_3$], its high solubility does not constitute an obstacle to obtaining it in pure form. Note that ^{1}H and ^{13}C NMR spectra of diamagnetic $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ are not sufficient

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to distinguish the complex from its nitrido-bridged isomer, (^{t}BuO)$_2$(O)Mo[μ-N]Ti(NRAr)$_3$. Our assignment of the complex as a bridging oxo complex rather than a bridging nitrido complex is based on a combination of ^{15}N NMR spectroscopic, chemical, and X-ray crystallographic (*vide infra*) data. ^{15}N-Enriched (^{t}BuO)$_2$(^{15}N)Mo[μ-O]Ti(NRAr)$_3$ (ca. 42% ^{15}N) was prepared from ^{15}NMo(O^{t}Bu)$_3$[20] and Ti(NRAr)$_3$ in a manner identical to that used for the unlabeled material. The ^{15}N NMR spectrum of (^{t}BuO)$_2$(^{15}N)Mo[μ-O]Ti(NRAr)$_3$ consists of a single signal located at $\delta = 827$ ppm (with $\delta = 0$ ppm for liquid ^{15}NH$_3$ and $\delta = 380.2$ ppm for neat nitromethane. This large downfield shift is characteristic of high-valent terminal nitrido complexes and should be compared with the signal for ^{15}NMo(O^{t}Bu)$_3$, found at $\delta = 811$ ppm,[20] and also to that for the complex NMo(NRAr)$_3$, located at $\delta = 840$ ppm.[19] Four-coordinate chromium nitrido complexes likewise exhibit dramatic downfield shifts for their nitrido nitrogen atoms, c.f. NCr(N^{i}Pr$_2$)$_3$, $\delta = 979$ ppm, and NCr(NRAr$_F$)$_3$ [Ar$_F$ = 2,5-C$_6$H$_3$FMe], $\delta = 1020$ ppm.[21] The NMR data clearly favor our formulation of the complex as having a bridging oxygen atom and a terminal nitrogen atom. This interpretation is substantiated by the X-ray crystallography (*vide infra*). Unfortunately, attempts to definitively assign ν(MoN) in the infrared spectrum of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ were not successful due to the relatively low degree of ^{15}N enrichment in the labeled complex and also due to the large number of ligand-associated bands in the relevant region of the spectrum. The proposed facile isomerization of (^{t}BuO)$_2$(O)Mo[μ-N]Ti(NRAr)$_3$ to the oxo-bridged product makes good chemical sense in view of the oxophilicity of titanium and in view of the considerable strength of the MoN triple bond.

We recently demonstrated N-atom transfer from Chisholm's NMo(O^{t}Bu)$_3$[2] to Mo(NRAr)$_3$ to give NMo(NRAr)$_3$ and 0.5 equiv of Mo$_2$(O^{t}Bu)$_6$ (when carried out in the absence of dinitrogen).[20] The latter finding indicates that Mo(NRAr)$_3$ might serve as a chemical probe for the presence of an abstractable nitrogen atom. Accordingly, the complex (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ was treated with 1 equiv of Mo(NRAr)$_3$ in benzene under static vacuum for 5 d. At the end of this period of time, all volatile material was removed and the residue was assayed by ^{1}H NMR. The ^{1}H NMR spectroscopy showed that the Mo(NRAr)$_3$ had been (essentially quantitatively) converted to NMo(NRAr)$_3$. Other peaks present in the spectrum were not assigned, and no attempt was made to isolate and separate the Ti-containing product(s). However, one can conclude from this experiment that (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ does indeed possess an abstractable nitrogen atom, a fact which provides further support for our assertion that the complex contains μ-oxo and terminal nitrido functionalities.

V. Structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$. A PLUTO representation of the molecular structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is given in Figure 4, while selected bond distances and angles are listed in Table 1. See the Experimental Section for details of the data collection and structure solution and refinement. Aside from an essentially linear [179.4(4)°] Mo−O−Ti angle, the coordination geometry at molybdenum is strikingly reminiscent of that for NMo(O^{t}Bu)$_3$. All angles at molybdenum are within 3° of the tetrahedral angle, with the N−Mo−O angles slightly compressed and the O−Mo−O angles slightly enlarged. A further similarity between NMo(O^{t}Bu)$_3$ and (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is the *syn* orientation of the *tert*-butoxide ligands with respect to the nitrido functionality. This orientation simultaneously minimizes steric interactions and maximizes O→Mo π-bonding (by placing an oxygen lone pair rich in p character perpendicular to the nitrido bond axis). The Mo−O−C angles for (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ [137.5(7) and 139.0(7)°] are larger by only 2−3° than those for NMo(O^{t}Bu)$_3$. Considered by itself, the OTi(NRAr)$_3$ moiety in (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is very nearly C_3-symmetric and superimposable upon the structure, previously reported,[87] of ClTi(NRAr)$_3$. The O−Ti−N−R dihedral angles of 34.1(9), 33.3(9), and 32(1)° require a description of the fragment as C_3 rather than C_{3v}.

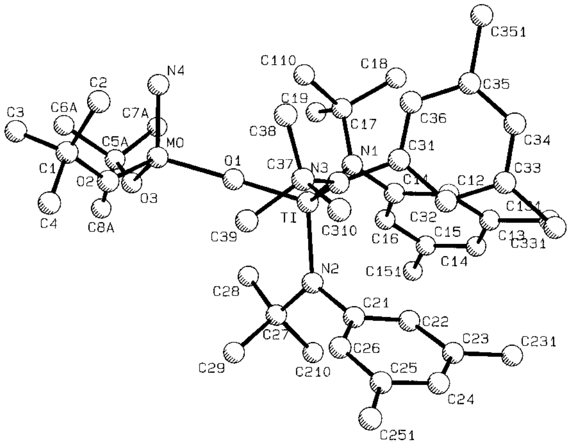

Figure 4. PLUTO drawing of the molecular structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ as determined by single-crystal X-ray diffraction. See text for selected bond lengths and angles.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$

Bond Distances			
Mo−O(1)	1.876(8)	Mo−N(4)	1.688(9)
Mo−O(2)	1.867(6)	Ti−N(1)	1.919(7)
Mo−O(3)	1.848(8)	Ti−N(2)	1.932(9)
Ti−O(1)	1.841(8)	Ti−N(3)	1.925(9)

Bond Angles			
O(1)−Mo−O(2)	112.0(3)	Mo−O(1)−Ti	179.4(4)
O(1)−Mo−O(3)	111.2(3)	Mo−O(2)−C(1)	137.5(7)
O(1)−Mo−N(4)	106.6(4)	Mo−O(3)−C(5A)	139.0(7)
O(2)−Mo−O(3)	110.8(3)	O(1)−Ti−N(1)	109.9(4)
O(2)−Mo−N(4)	108.2(4)	O(1)−Ti−N(2)	109.3(4)
O(3)−Mo−N(4)	107.9(5)	O(1)−Ti−N(3)	110.5(4)

Because (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ contains two types of Mo−O bonds, knowledge of its structure permits a direct comparison between these two types. The Mo−O^{t}Bu distances are 1.848(8) and 1.867(6) Å, both only slightly shorter than the Mo−μ-O distance of 1.876(8) Å. This slight difference can be understood if one makes the (reasonable) assumption that O^{t}Bu is a stronger π-donor than OTi(NRAr)$_3$.

A feature of some interest in the structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is the MoN triple bond length of 1.688(9) Å. This bond length is the same to within 3σ as those reported for the two polymorphs of NMo(O^{t}Bu)$_3$ [1.661(4) and 1.673(5) Å].[2] This distance alone is not sufficient to clearly distinguish (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ from its nitrido-bridged isomer, since MoO bond lengths in terminal molybdenum monoxo complexes are essentially the same (to within 3σ) as terminal MoN bond lengths. Least-squares refinements assuming the isomeric formulation (^{t}BuO)$_2$(O)Mo[μ-N]Ti(NRAr)$_3$ consistently resulted in larger thermal parameters for the two atoms in question, however, strongly supporting our assignment of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ as a terminal nitrido complex. (See the preceding section for spectroscopic substantiation of this structural assignment.) A further feature of interest in the structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is that the molecule

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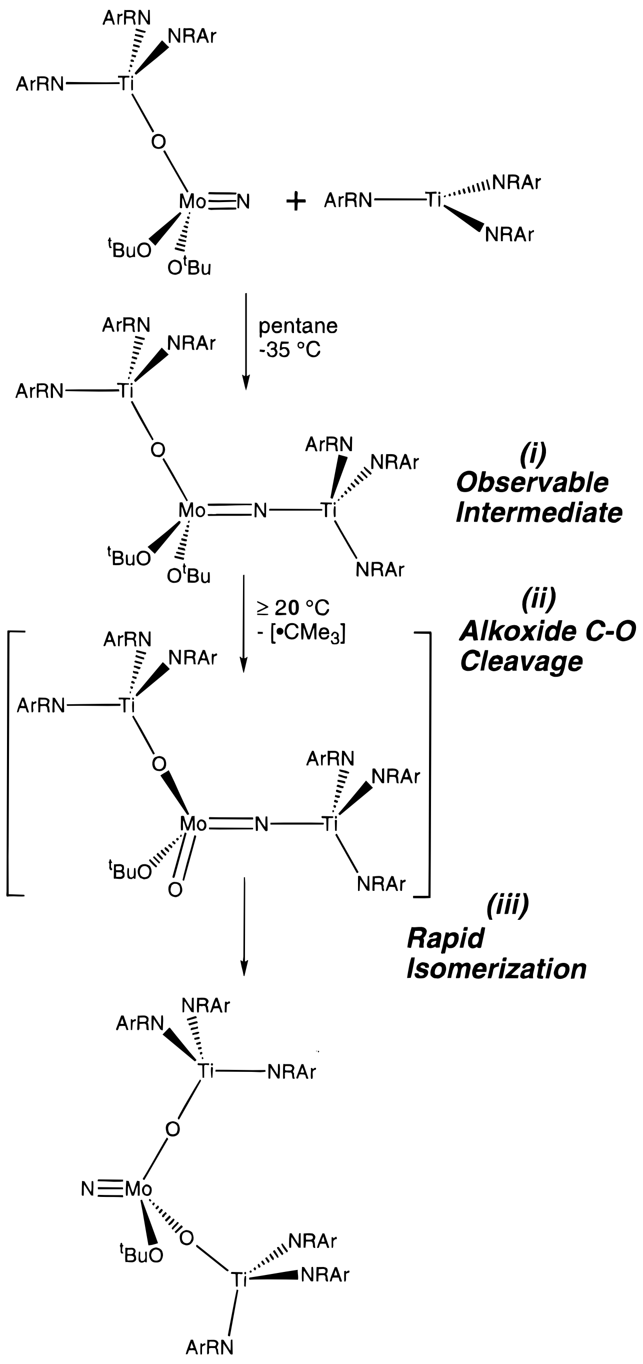
[87] Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.

Scheme 2

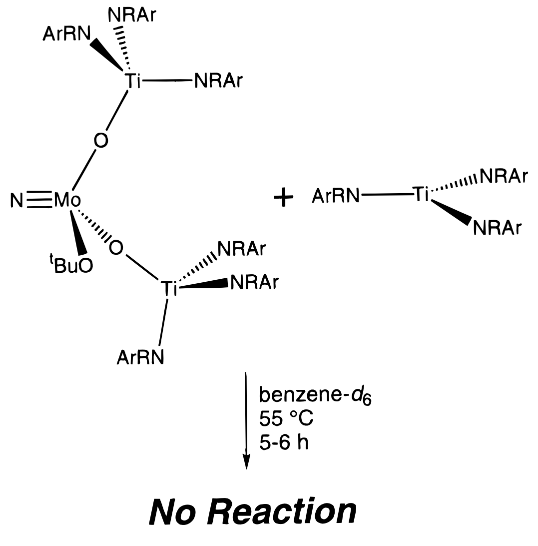


is a monomer in the solid state. NMo(O^{t}Bu)$_3$, on the other hand, is a linear polymer in the solid state by virtue of dative MoN$\cdots$Mo interactions.[2] The voluminous nature of the OTi(NRAr)$_3$ "substituent" appears to preclude analogous dative interactions in the present case; the closest intermolecular N$\cdots$Mo distance observed in the crystal packing diagram of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ is 6.349 Å.

VI. Generation of Thermally Unstable (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$}. Having in hand the mono(titanoxide) complex (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$, it was natural to ask if the process of titanium radical addition and *tert*-butyl radical elimination (Scheme 1) could be repeated. Thus we examined the reaction of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ with Ti(NRAr)$_3$ at lower temperatures (e.g., -35 °C) where we found it possible to observe, once again, a thermally unstable olive green intermediate (Scheme 2). A logical formulation for this intermediate is (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$}, with the terminal nitrido nitrogen atom again serving as a point of Ti(NRAr)$_3$ binding. This complex can be understood to form via inner sphere reduction of molybdenum(VI) to molybdenum(V) by titanium(III). Consistent with this assignment, proton NMR scrutiny revealed two distinct ArCH_3 resonances present in a 1:1 ratio; the resonances diminish simultaneously as the intermediate is allowed to decay thermally. Nominally first-order kinetic data corresponding to loss of (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$} obtained by UV$-$vis spectroscopy ($\lambda_{\max} = 805$ nm) carried out at 25 °C were difficult to interpret due to the presence of significant quantities of Ti(NRAr)$_3$, which was identified in such mixtures by EPR and by UV$-$vis spectroscopies.

VII. Synthesis and Characterization of (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. Carried out on a preparative scale, the reaction of NMo(O^{t}Bu)$_3$ with 2 Ti(NRAr)$_3$ yields the final product, (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$, in 91% isolated yield (ca. 1 g scale) as an orange powder (Schemes 1 and 2). For (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$, ^{1}H and ^{13}C NMR data effectively rule out an alternative formulation with a bridging nitrido nitrogen and a terminal oxo, because only a single set of resonances is observed for the two Ti(NRAr)$_3$ fragments. Nevertheless, we prepared an ^{15}N-enriched sample, (^{t}BuO)(^{15}N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$, for ^{15}N NMR substantiation of the presence of a terminal nitrido nitrogen. The ^{15}N NMR signal appears at $\delta = 845$ ppm for the latter complex, a greater downfield shift than observed for the other nitrido complexes discussed above. We expect the molybdenum center to become increasingly electron poor on going from NMo(O^{t}Bu)$_3$ to (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$, and finally to (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$, on the basis of the π-bonding characteristics of OCMe$_3$ (relatively strong donor) versus OTi(NRAr)$_3$ (relatively weak donor). Sequential replacement of *tert*-butoxide with titanoxide should thus render the molybdenum center increasingly more electrophilic, correlating with a greater downfield ^{15}N NMR signal for the terminal nitrido nitrogen.

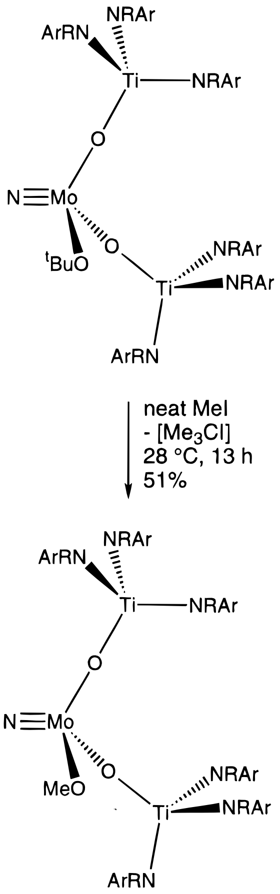
VIII. Attempted Synthesis of NMo{[μ-O]Ti(NRAr)$_3$}$_3$. Although NMo(O^{t}Bu)$_3$ possesses three potentially-replaceable *tert*-butyl groups, it appears as though a limit is reached on replacing two of them with Ti(NRAr)$_3$ radicals. No reaction was observed when (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ was treated (in benzene solution) with 1 equiv of Ti(NRAr)$_3$, even upon mild heating (eq 3). This result is unexpected on electronic grounds because the molybdenum center should be more electron-poor (as discussed above) and hence more readily reduced in (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ than in those



(3)

substrates which *do* react readily, namely, $(^tBuO)_2(N)Mo[\mu\text{-}O]\text{-}Ti(NRAr)_3$ and $NMo(O^tBu)_3$. A steric argument for the failure of $Ti(NRAr)_3$ to add to the bis(titanoxide) complex is more appealing and is consistent with steric information garnered from X-ray crystallographic characterization of the complex $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ (*vide infra*). Apparently, three $Ti(NRAr)_3$ groups cannot be accommodated on the periphery of the $NMoO_3$ tetrahedron, at least with *tert*-butyl as the fourth peripheral moiety. This result also argues for a CE rather than an EC mechanism for the observed examples of incomplete nitrido transfer noted in this work.

IX. Synthesis and Characterization of $(MeO)(N)Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$. Having in hand $(^tBuO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ as an example of a bis(titanoxide) complex, we sought reactions that would perturb the *tert*-butoxide or nitrido functionalities without disturbing the $Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ core. One such reaction is that which occurs upon dissolution of $(^tBuO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ in neat methyl iodide (eq 4). The intent was to deliver Me^+ to the terminal nitrido function with this regimen. Such alkylations have been successful for a select few terminal nitrido complexes, according to the literature.[88] (Protonation reactions of terminal nitrido ligands are also known,[89,90] although the "lone-pair" of terminal molybdenum(VI) nitrido ligands is decidedly nonbasic.[2]) In the present case, the reaction with methyl iodide proceeds slowly at 28 °C. Although the reaction is not quantitative, $(MeO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ could be isolated as a spectroscopically pure orange powder in 51% yield. That the isolated orange product contained a methyl group on a rather electronegative substituent was indicated by a sharp singlet located at $\delta = 4.68$ ppm, integrating to 3H, in its proton NMR spectrum. An alternative methylimido−oxo formulation, $(MeN)(O)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$, could not be ruled out on the basis of the proton NMR spectrum alone. To establish the atomic connectivity the isotopically labeled derivatives $(MeO)(^{15}N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ and $(H_3{}^{13}CO)(^{15}N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ were prepared. In the case of the former complex, no ^{15}N coupling to the 4.68 ppm proton NMR signal was observed, as would be expected for the alternative methylimido−oxo formulation. Even more convincing in favor of the proposed nitrido−methoxide formulation is lack of any one-bond $^{15}N{-}^{13}C$ coupling for the latter isotopomer, the methoxide ^{13}C NMR signal for which was found at $\delta = 56.45$ ppm. The overall geometry of $(MeO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$ was ascertained, via a preliminary X-ray diffraction study, to be grossly similar to that of $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ (*vide infra*).



(4)

It is of interest to consider possible mechanisms of formation of $(MeO)(N)Mo\{[\mu\text{-}O]Ti(NRAr)_3\}_2$. One possibility is that methyl iodide initially acts to methylate the nitrido nitrogen atom, creating a cationic methylimido complex.[90] Such a species could then react with iodide ion to lose $ICMe_3$ and subsequently isomerize to the observed product. An alternative scenario would involve initial attack on a *tert*-butoxide oxygen by methyl iodide and loss of $ICMe_3$ with no direct involvement of the terminal nitrido nitrogen atom. The available data do not allow us to discriminate between these two alternative paths. Neither of the pathways considered for the Me-for-^{t}Bu swap appears to involve radical chemistry, yet when juxtaposed with the radical chemistry tendered in Scheme 1 the implication emerges that *tert*-butoxide ligands may be subject to various modes of degradation.[85]

X. Synthesis of $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$. Our first substrate for assembly of μ-oxo complexes via radical substitution was Chisholm's $NMo(O^tBu)_3$,[2] a particularly easy compound to handle due to its high crystallinity and favorable solubility properties. Chisholm's group has discovered a plethora of attractive molybdenum *tert*-butoxide complexes, of which $O_2Mo(O^tBu)_2$ seemed particularly well configured as a substrate for radical substitution reactions of the type elucidated here.[91,92] (Related molybdenum dioxobis(siloxide) complexes have also been prepared.[93,94]) $O_2Mo(O^tBu)_2$ presents two *tert*-butyl leaving groups on the external surface of its MoO_4 tetrahedral core, displacement of which by two incoming titanium(III) radicals would produce a molybdenum center ligated only by two terminal oxo ligands and two μ-oxo bridge atoms. Thus $O_2Mo(O^tBu)_2$ provided an ideal opportunity to extend our radical substitution reaction to a new substrate and also offered potential access to a desirable dioxo species. Initially it appeared as though synthetic access to $O_2Mo(O^tBu)_2$ would be somewhat tedious, since the compound is prepared by direct oxygenation of $Mo_2(O^tBu)_6$, which in turn was originally prepared by alcoholysis of $Mo_2(NMe_2)_6$. The latter compound was obtained by sublimation following treatment of $MoCl_3$, prepared by solid state methods, with 3 equiv of $LiNMe_2$.[95] More recently it has been found that treatment of either $MoCl_3(THF)_3$[20] or $[MoCl_3(DME)]_2$ [DME = 1,2-dimethoxyethane][96] with the requisite amount of lithium *tert*-butoxide leads to $Mo_2(O^tBu)_6$ in a more direct fashion. Ready

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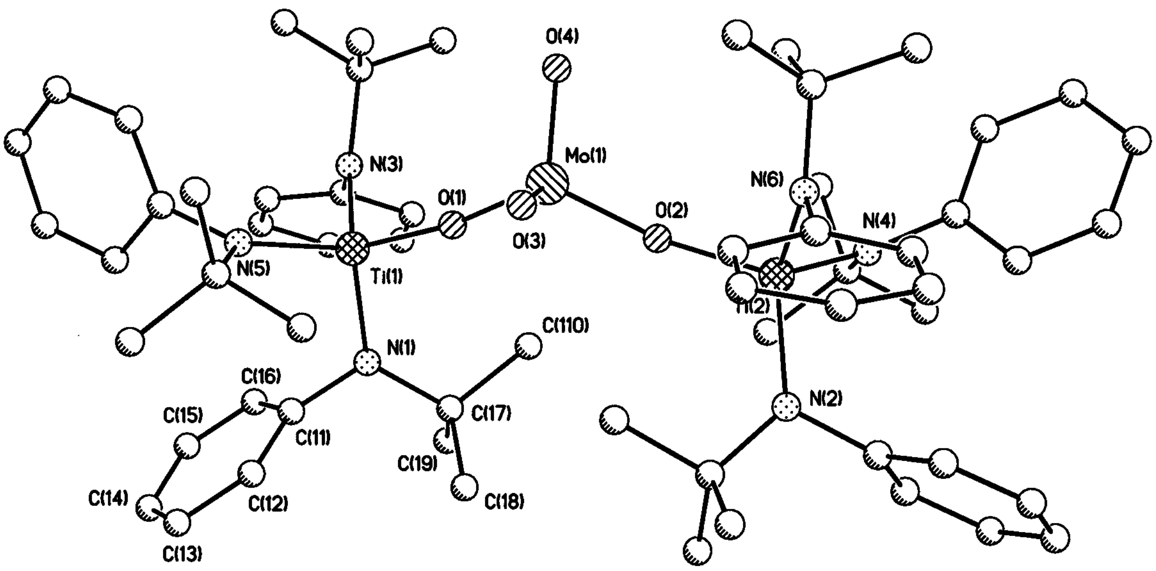
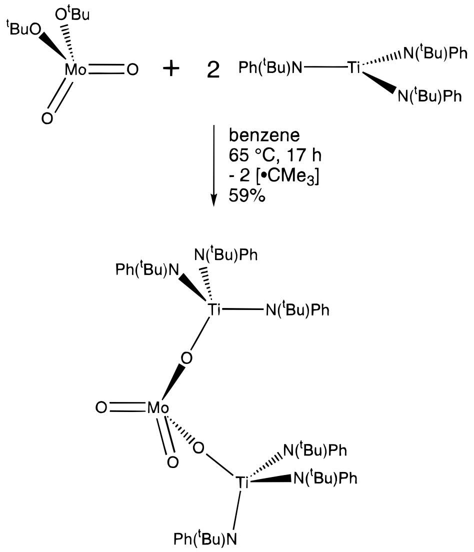


Figure 5. PLUTO drawing of the molecular structure of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ as determined by single-crystal X-ray diffraction. See Table 2 for selected bond lengths and angles.

access to O$_2$Mo(O^{t}Bu)$_2$ is therefore also a reality, since this compound, a yellow oil, can be generated *in situ* and utilized directly.

Treatment of *in situ* generated O$_2$Mo(O^{t}Bu)$_2$ with 2 equiv of Ti(^{t}BuNPh)$_3$, added via pipet as a green benzene solution, led to a murky brown reaction mixture. Subsequent heating of the reaction mixture (65 °C, 17 h) in a closed vessel produced a color change to red-orange. A bright orange powder was isolated from this mixture in 59% yield. ^{1}H and ^{13}C NMR data were consistent with formulation of the new diamagnetic orange compound as O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (eq 5). This assignment was further substantiated by combustion analysis and by a single-crystal X-ray diffraction study (see following paragraph). Although we have not yet seriously attempted to identify intermediate complexes *en route* to formation of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$, we have observed that the murky brown mixture produced upon initial addition of Ti(^{t}BuNPh)$_3$ to O$_2$Mo(O^{t}Bu)$_2$ exhibits a veritable "forest" of broad resonances over a wide chemical shift range, likely indicative of paramagnetic oxo-bridged intermediates.



(5)

Table 2. Selected Bond Distances (Å) and Angles (deg) for O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$

Bond Distances			
Mo(1)−O(4)	1.683(10)	Ti(2)−O(2)	1.897(8)
Mo(1)−O(1)	1.821(8)	Ti(1)−N(1)	1.920(11)
Mo(1)−O(3)	1.703(10)	Ti(1)−N(5)	1.901(11)
Mo(1)−O(2)	1.836(8)	Ti(1)−N(3)	1.906(11)
Ti(1)−O(1)	1.899(8)		
Bond Angles			
O(4)−Mo−O(3)	107.5(6)	O(4)−Mo−O(1)	108.9(4)
O(3)−Mo−O(1)	108.4(4)	O(4)−Mo−O(2)	109.6(5)
O(3)−Mo−O(2)	108.9(4)	Mo−O(2)−Ti(2)	145.0(5)
O(1)−Mo−O(2)	113.3(4)	Mo−O(1)−Ti(1)	171.8(5)
C(31)−N(3)−Ti(1)	121.5(8)	C(51)−N(5)−Ti(1)	121.8(8)
C(11)−N(1)−Ti(1)	119.1(8)		

XI. Structure of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$. Crystals of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ suitable for a single-crystal X-ray diffraction study were obtained by vapor diffusion of hexane into THF at 28 °C. A PLUTO diagram of the molecule is displayed in Figure 5, while selected bond distances and angles are listed in Table 2. A striking feature of the molecular structure is the encapsulation of an MoO$_4$ moiety within a shell comprised of two voluminous Ti(^{t}BuNPh)$_3$ fragments. This feature was anticipated on inspection of molecular models and inferred from the failure of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ to react with a further equivalent of Ti(^{t}BuNPh)$_3$ (eq 6).

As one might expect, the bridging MoO$_4$ moiety displays differing bond lengths for its bridging and terminal oxo ligands: the two molybdenum−μ-oxo bond distances of 1.836(8) and 1.821(8) Å are significantly longer than the two molybdenum-terminal oxo distances of 1.683(10) and 1.703(10) Å. These values are typical for compounds in which an MoO$_4$ moiety spans two transition metal or metalloid centers. For example, the compound O$_2$Mo{[μ-O]Mo(CH$_2$^{t}Bu)$_3$(N^{t}Bu)}$_2$ exhibits molybdenum−μ-oxo bond distances of 1.825(3) and 1.806(3) Å and molybdenum−terminal oxo distances of 1.704(4) and 1.690(4) Å.[97] Another such example is the recently reported O$_2$Mo([μ-O]SiPh$_3$)$_2$ whose molybdenum−μ-oxo bond distance is 1.815(5) Å and whose terminal Mo−O distance is 1.692(7) Å.[94] These molybdenum−oxo distances should be compared with the unique Mo−O distance of ca. 1.76 Å in

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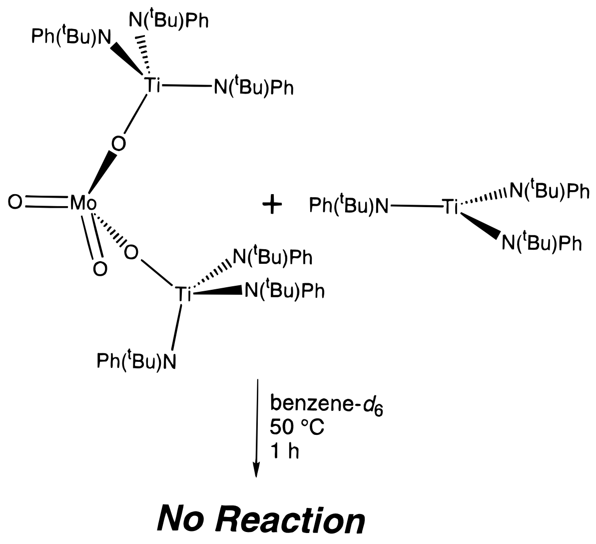

(6)

“free” MoO_4^{2-} (as the potassium salt).[98] In all of these cases, the embedded MoO_4 moiety adopts a geometry that closely approximates a regular tetrahedron. The only structurally characterized compound other than $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ in which an MoO_4 moiety spans two titanium centers is a cyclic compound, $[Cp_2Ti(MoO_4)]_2$,[99] according to a search of the Cambridge Structural Database.

A further aspect of interest is the length [1.899(8) and 1.897(8) Å] of the Ti−O bonds in $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$. Standard Ti−O bond distances in four-coordinate titanium alkoxide or siloxide complexes fall close to 1.75 Å, whereas corresponding aryloxide derivatives typically evince Ti−O bond lengths near 1.80 Å. Relatively labile η^1-triflate ligands display longer Ti−O bonds, close to 2.10 Å. These comparisons suggest that in the competition for μ-oxo electron density molybdenum wins out over titanium in $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$. For this reason the compound might best be thought of as containing a central MoO_4^{2-} ion sandwiched between two $[Ti(NRAr)_3]^+$ fragments. The electronic asymmetry of the μ-oxo bridge would be expected to be a sensitive function of the nature of the ligands on the metals it spans. Note that the Ti−O bond length in $(^tBuO)_2(N)Mo[\mu\text{-}O]Ti(NRAr)_3$ (*vide supra*) is 1.841(8) Å, which is relatively short and consistent with a more electron-rich molybdenum center in this complex.

XII. Preliminary Attempts To Reduce $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$. In the interest of generating a three-coordinate molybdenum species supported by $[\mu\text{-}O]Ti(^tBuNPh)_3$ ligation, we have added reducing agents to $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ with the ultimate objective of removing an oxygen atom. Successful oxygen atom abstraction from $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ would give $OMo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$, a complex reminiscent of $(^tBuN)W(OSi^tBu_3)_2$, which was prepared by Wolczanski and co-workers.[100] Thus far the list of compounds that fail to react with $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ includes ethylene, triethylphosphine, $Ti(^tBuNPh)_3$, $Mo(NRAr)_3$,[17,19,20,27] $(THF)V(Mes)_3$,[21,101−107] and diphenylsilane (see Experimental Section for conditions). With regard to the majority of the foregoing reagents, the inertness of $O_2Mo\{[\mu\text{-}O]Ti(^tBuNPh)_3\}_2$ can be attributed to steric protection of the dioxomolybdenum functionality (Figure 5).

XIII. Some Reactions of $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$. As noted above, the fact that $Ti(NRAr)_3$ reacts rapidly with methyl iodide giving $ITi(NRAr)_3$ and $MeTi(NRAr)_3$ can be used as a probe to address reversibility of bridge formation. We reported previously that the crystallographically-characterized vanadium titanoxide complex $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ (a thermally stable analog of the new paramagnetic nitrido-bridged complexes described above) was not observed to react with methyl iodide (18 h, ether, 27 °C). This observation constitutes convincing evidence that the formation of $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ is essentially irreversible. Intrigued by the possibility that a cationic vanadium titanoxide complex might be accessible, we treated $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$, dissolved in tetrahydrofuran, with an equivalent of ferrocenium triflate.[108] The result was quantitative cleavage of the μ-oxo bridge, as evidenced by smooth production of diamagnetic $TfOTi(NRAr)_3$ and $OV(O^iPr)_3$, identified by their characteristic ^1H NMR lines. $TfOTi(NRAr)_3$ was prepared independently (80% isolated yield) by treatment of $Ti(NRAr)_3$ with the stoichiometric amount of ferrocenium triflate.[108]

Although we felt that the thermal stability of paramagnetic $(^iPrO)_3V[\mu\text{-}O]Ti(NRAr)_3$ was a simple manifestation of the decreased reducing power of vanadium(IV) [as compared to molybdenum(V)], one could argue that the stability is due to the presence of peripheral isopropyl as opposed to *tert*-butyl residues. $V(O^tBu)_4$ is a thermally robust complex[109,110] whose existence and properties demonstrate that the *tert*-butyl radical is not readily ejected from a d^1 VO_4 tetrahedron. Nevertheless, we opted to prepare $(^tBuO)_3V[\mu\text{-}O]Ti(NRAr)_3$ to address any suspicions concerning the ability of the Ti center to somehow facilitate loss of the peripheral *tert*-butyl radical. The complex was readily obtained as orange-brown needles (94% yield) upon treatment of ethereal $Ti(NRAr)_3$ with $OV(O^tBu)_3$.[111−113] The thermally robust nature (see Experimental Section) of paramagnetic $(^tBuO)_3V[\mu\text{-}O]Ti(NRAr)_3$ [$\mu_{eff} = 2.4\ \mu_B$] is a clear sign that a difference in reducing power (Mo > V) is largely responsible for the disparity in the chemistry of d^1 $NMoO_3$ versus d^1 VO_4 tetrahedra bearing peripheral *tert*-butyl leaving groups.

XIV. Synthesis and Characterization of $(Me_2N)_3Mo[\mu\text{-}N]Ti(^tBuNPh)_3$. Postulated as key intermediates in the formation of bridging oxo species in the context of Schemes 1 and 2 are putative titanium(IV)/molybdenum(V) nitrido-bridged species. As these turned out to be unstable thermally with respect to *tert*-butyl radical elimination, it was of interest to see if a related species *not* subject to organic radical elimination could be prepared and studied. The recently-prepared molybdenum nitrido complex $NMo(NMe_2)_3$ proved a suitable substrate for this inquiry.[114] Accordingly, treatment of $NMo(NMe_2)_3$ with $Ti(^tBuNPh)_3$ provided forest green $(Me_2N)_3Mo[\mu\text{-}N]Ti(^tBuNPh)_3$ in 77% yield according to eq 7, on a scale of 0.5 mmol.

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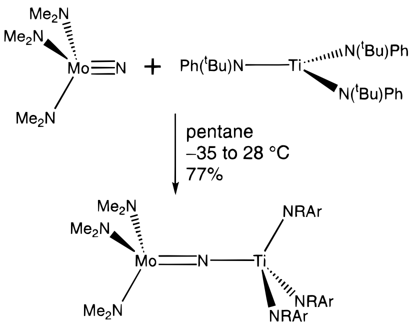

(7)

The compound proved thermally robust in that heating a benzene solution to 70 °C for 13 h resulted in no observable decomposition. Proton NMR data are consistent with a C_3-symmetric structure on the time scale of measurement. While proton NMR data are not sufficient to formulate this μ-nitrido compound as titanium(IV)/molybdenum(V) (see Experimental Section), EPR data obtained in toluene at 215 and 98 K are indicative of a d^1 molybdenum(V) system: $g_1 = 1.973$, $g_2 = 1.965$, $g_3 = 1.931$; $a_1 = 35$, $a_2 = 29$, $a_3 = 54$ G; the EPR spectrum of $(Me_2N)_3Mo[\mu\text{-}N]Ti(^tBuNPh)_3$ was adequately simulated without invoking any titanium hyperfine coupling. Presumably, loss of a methyl radical to generate putative imido $(Me_2N)_2(MeN)Mo[\mu\text{-}N]Ti(^tBuNPh)_3$ is unfavorable largely due to the relatively energetic nature of [$\cdot CH_3$] as compared with [$\cdot CMe_3$]. The ready preparation of $(Me_2N)_3Mo[\mu\text{-}N]Ti(^tBuNPh)_3$ shows that the alkoxymolybdenum function is not a requirement for adduct formation and provides strong circumstantial evidence for the sequence of events outlined in Schemes 1 and 2.

Concluding Remarks

This work illustrates a new chemical reaction involving radical substitution on the periphery of a d^0 $NMoO_3$ or MoO_4 tetrahedron. Basic features of the reaction are proposed to be (i) metalloradical attack on an exposed terminal atom, (ii) electron transfer across the bridge according to the scheme first described by Taube,[115] and (iii) departure of a peripheral substuent to regenerate an exposed terminal atom and a d^0 system. Although the temporal sequence of the latter events has not been established in a completely unequivocal fashion, the proposition is plausible and consistent with all available data. The reaction has synthetic utility. We have used this new reaction to prepare molybdenum complexes bearing one or two voluminous "titanoxide" ligands. These experiments exemplify the clean radical breakdown of a bound alkoxide ligand at a molybdenum(V) center.[116]

Experimental Section

General Considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using standard Schlenk techniques under an argon atmosphere. Anhydrous ether and toluene were purchased from Mallinckrodt; *n*-pentane and *n*-hexane were purchased from EM Science. Ether was distilled under a nitrogen atmosphere from purple sodium benzophenone ketyl. Aliphatic hydrocarbon solvents were distilled under a nitrogen atmosphere from very dark blue to purple sodium benzophenone ketyl solubilized with a small quantity of tetraglyme. Toluene was refluxed over molten sodium for at least 2 d, prior to its distillation under a nitrogen atmosphere. Distilled solvents were transferred under vacuum into Teflon-stopcocked glass vessels and stored, prior to use, in a Vacuum Atmospheres drybox. Benzene-d_6 was degassed and dried over blue sodium benzophenone ketyl and transferred under vacuum into a storage vessel. Chloroform-*d* and toluene-d_8 were degassed and dried over 4 Å sieves. Then 4 Å sieves and alumina were activated *in vacuo* overnight at a temperature above 180 °C. Ferrocenium triflate[108] and $Li(NRAr)(OEt_2)$[55] were prepared according to published procedures. Other chemicals were used as received. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Varian XL-500, Varian XL-300, or Varian Unity-300 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported with reference to solvent resonances (residual $C_6D_5\mathit{H}$ in C_6D_6, 7.15 ppm; C_6D_6, 128.0 ppm; $C\mathit{H}Cl_3$ in $CDCl_3$, 7.24 ppm; $\mathit{C}DCl_3$, 77.0 ppm). ^2H NMR chemical shifts are reported with respect to external C_6D_6 (7.15 ppm). ^{19}F NMR chemical shifts are reported with reference to external $CFCl_3$ (0 ppm). Solution magnetic susceptibilities were determined by ^1H NMR at 300 MHz using the method of Evans.[69,70] Routine coupling constants are not reported. EPR spectra were recorded on a Bruker ESP 300 spectrometer in sealed quartz tubes in toluene at either ambient temperature or low temperature by using a liquid nitrogen cooled nitrogen stream. Spectra were simulated using the program EPR-NMR (Computer Program EPR-NMR, Department of Chemistry, University of Saskatchewan, Canada, 1993). Combustion analyses (C, H, and N) were performed by Oneida Research Services, Whitesboro, NY. Melting points were obtained in sealed glass capillaries and are uncorrected.

Synthesis of $Ti(NRAr)_3$. $ClTi(NRAr)_3$ (600 mg, 953 μmol) was stirred with Na/Hg (0.10 g, 4.35 mmol Na; 15 g of Hg) in benzene (35 mL) for 60 h at 28 °C. The dark green reaction mixture was filtered through a bed of Celite. Removal of all volatile material from the filtrate left crude $Ti(NRAr)_3$ as a dark green solid. Pure $Ti(NRAr)_3$ (411 mg, 691 μmol, 73%), a forest-green crystalline solid, was obtained by recrystallization (pentane, −35 °C, three crops). Mp: 135−137 °C. ^2H NMR (frequency, C_6H_6, 25 °C): $\delta = 4.64$ ($\Delta\nu_{1/2} = 46$ Hz). μ_{eff} (300 MHz, C_6D_6, 25 °C): 2.2 μ_B. EIMS *m*/*z*(%): 594.7 (9) [M^+]. UV−vis (benzene, 25 °C): $\lambda = 638$ nm ($\epsilon = 140$ M^{-1} cm^{-1}), $\lambda = 790$ nm ($\epsilon = 170$ M^{-1} cm^{-1}). EPR (toluene, 107 K): $g_1 = 1.995$, $g_2 = 1.964$, $g_3 = 1.949$. Anal. Calcd for $C_{36}H_{36}D_{18}IN_3Ti$: C, 72.69; H, 9.15; N, 7.06. Found: C, 72.51; H, 8.98; N, 6.80.

Alternative Synthesis of $Ti(NRAr)_3$. Ether (25 mL) was added to a 50 mL 24/40 round-bottomed flask charged with a stir bar. TMEDA (340 mg, 2.93 mmol, run through activated alumina prior to use) and blue $TiCl_3(THF)_3$ (704 mg, 1.90 mmol) were then added to the ether sequentially while stirring. The resulting heterogeneous mixture was blue. The flask was then placed in the glovebox cold well (externally cooled with liquid N_2) to form a nearly frozen mixture. The reaction flask was then removed from the cold well and allowed to thaw. Two equivalents of $Li(NRAr)(OEt_2)$ (1.000 g, 3.80 mmol) were added all at once to the just-thawed mixture. On warming, the reaction mixture turned light green in color. Stirring was continued for about 10 min until it appeared that most of the blue particulate $TiCl_3(THF)_3$ had dissolved, at which point the solution suddenly gained a reddish-brown hue. The third equivalent of $Li(NRAr)(OEt_2)$ (500 mg, 1.9 mmol) was added without delay upon observation of the color change. The mixture was stirred for 45 min at ca. 28 °C and took on the rich forest-green color characteristic of ethereal $Ti(NRAr)_3$. A white precipitate was visible (assumed to be LiCl). All volatile material was removed in vacuo from the mixture. The residue was triturated with hexane (2 × 5 mL) to ensure removal of TMEDA, and then it was extracted with pentane (15 mL). The resulting mixture was filtered to remove insoluble material (e.g., LiCl). Volatile material was removed in vacuo from the green filtrate to provide 1.1 g of fine green powder, with no visible traces of orange impuritites, in 95% crude yield. ^2H NMR analysis of the crude powder showed the crude product to be 93% pure, with some trace HNRAr as the major identifiable impurity. Recrystallization of the crude material from pentane at −35 °C yielded 913 mg of large green crystals (83% yield) comprising pure $Ti(NRAr)_3$.

Synthesis of $Ti(^tBuNPh)_3$. In a 250 mL flat bottom flask with a long stir bar, $TiCl_3(THF)_3$ (3.23 g, 8.72 mmol) was added to a stirring solution of TMEDA (1.6 g, 13.8 mmol, run through activated alumina

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[116] Related radical C−N bond cleavage reactions occurring at a molybdenum(V) center will be reported in due course: Johnson, A. R.; Odom, A. L.; Cummins, C. C.

prior to use) in Et$_2$O (170 mL). The heterogeneous blue mixture was frozen in a liquid nitrogen cold well. Upon partial thawing, the first 2 equiv of powdery white Li(^{t}BuNPh)(OEt$_2$) (4.00 g, 17.4 mmol) were added at once. The solution, which gradually turned light green, was stirred vigorously for 14 min at which time the third equivalent of Li(^{t}BuNPh)(OEt$_2$) (2 g, 8.72 mmol) was added. The reaction mixture was stirred for 70 min, at which time the deep green solution was filtered through Celite and all volatile matter was removed from the filtrate *in vacuo*. (Prolonged stirring results in decomposition of green Ti(^{t}BuNPh)$_3$ to a mixture of two yellow, diamagnetic, as yet uncharacterized products.) The green residue was triturated thoroughly with hexane (2 × 30 mL) to ensure complete removal of TMEDA, leaving a green solid. This solid was redissolved in pentane (100 mL), filtered through Celite to remove any remaining salts, and stored at −35 °C. Large, deep green crystals formed within hours. A first crop of 2.79 g was collected after 4 h simply by decanting the supernatant. The supernatant was concentrated to 30 mL and stored at −35 °C for a second crop of 440 mg, giving an overall yield of 75% based on TiCl$_3$(THF)$_3$. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) of the green crystals showed two broad resonances, $\delta = 4.8$ ($\Delta\nu_{1/2} = 540$ Hz), $\delta = 9.15$ ($\Delta\nu_{1/2} = 210$ Hz) and only trace diamagnetic resonances. It should be noted that a light beige impurity can coprecipitate with the second crop of Ti(^{t}BuNPh)$_3$. Recrystallization from pentane removes this impurity. Anal. Calcd for C$_{30}$H$_{42}$N$_3$Ti: C, 73.15; H, 8.53; N, 8.59. Found: C, 73.55; H, 8.39; N, 8.66.

Generation and Observation of (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$. This thermally unstable green intermediate may be generated by addition of pentane (precooled to −35 °C) to a stoichiometric mixture of solid Ti(NRAr)$_3$ and NMo(O^{t}Bu)$_3$. Formation of green (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ is complete within seconds, and pentane solutions of the complex could be stored for months at −35 °C with very little decomposition according to ^{1}H and ^{2}H NMR analysis and on retention of the green color. (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ is considerably more soluble in pentane than is NMo(O^{t}Bu)$_3$, such that any residual white fibers of NMo(O^{t}Bu)$_3$ are easily removed by filtration. All manipulations involving (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ were carried out using prechilled glassware to insure minimal decomposition of this thermally-sensitive complex. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta = 6.66$ (s, 3H, *para* C$_6$*H*$_3$Me$_2$), 6.15 (s broad, 6H, *ortho* C$_6$*H*$_3$Me$_2$), 5.45 (s broad, 18H, OC(*Me*$_3$)$_3$, 2.20 (s, 18H, *meta* C$_6$H$_3$*Me*$_2$). A resonance corresponding to the NC(CD$_3$)$_2$(C*H*$_3$) protons was not observed. ^{2}H NMR (46 MHz, pentane, 25 °C): $\delta = 2.25$ [s, $\Delta\nu_{1/2} = 14$ Hz, C(C*D*$_3$)$_2$(CH$_3$)]. UV−vis (benzene, 25 °C): $\lambda = 746$ nm ($\epsilon = 1060$ M^{-1} cm^{-1}). EPR (toluene, 103K): $g_1 = 1.954$, $g_2 = 1.944$, $g_3 = 1.861$; $a_1 = 30$, $a_2 = 40$, $a_3 = 16$ G.

Generation and Observation of (d_6-^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$. A sample of Ti(NRAr)$_3$ (30 mg, 0.050 mmol) in 0.5 mL of benzene was chilled and added to a solution of NMo(O^{t}Bu-d_6)$_3$ [17.4 mg, 0.050 mmol] in 0.5 mL of chilled benzene in an NMR tube. The tube was shaken quickly, placed in an ice bath, and then monitored by ^{2}H NMR at 25 °C. The initial spectrum exhibited two peaks, at $\delta = 5.6$ and $\delta = 2.2$ ppm, assigned respectively to the MoO^{t}Bu-d_6 and TiN^{t}Bu-d_6 groups of (d_6-^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$. These resonances decay concomitant with the appearance of new signals at $\delta = 1.8$ and $\delta = 1.6$ ppm corresponding to the final product, (d_6-^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$. Poorly resolved resonances attributable to the expected, partially deuterated, organic products isobutylene, isobutane, and hexamethylethane were observed at $\delta = 4.5$ and $\delta = 1.0$.

Generation of (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ and Treatment with CH$_3$I. Solid green Ti(NRAr)$_3$ (81.7 mg, 0.137 mmol) was added to a chilled hexane solution (4 mL at −35 °C) of NMo(O^{t}Bu)$_3$ (45.2 mg, 0.137 mmol) in hexane (4 mL) containing an internal integration standard of hexamethylbenzene. The resulting olive green solution was stirred vigorously and allowed to stand at −35 °C for 30 min, generating (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$. Then 1.5 equiv of CH$_3$I in 2 mL of benzene was then added to the solution with stirring. Stirring was continued for 12 h at 25 °C. The volatiles were removed in vacuo. A subsequent ^{1}H NMR spectrum in C$_6$D$_6$ indicated three products, (i) ITi(NRAr)$_3$, (ii) a product whose ^{1}H NMR is consistent with an as yet unidentified XTi(NRAr)$_3$ compound, and (iii) (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$, in a 1:1:2 ratio. MeTi(NRAr)$_3$ was not observed. A similar result was obtained using ether as the solvent. Excess CH$_3$I does not react with hydrocarbon solutions of olive green (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ at −35 °C over a 1 week period. Note that slow addition of Ti(NRAr)$_3$ to a C$_6$D$_6$ solution of CH$_3$I at 25 °C affords a ca. 1:1 mixture of ITi(NRAr)$_3$ and MeTi(NRAr)$_3$.

Generation of (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ and Treatment with I$_2$. Treatment of olive green (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ (0.134 mmol, generated in situ) in ether (4 mL) with 0.5 equiv of I$_2$ at −35 °C elicited an instant color change from olive green to bright orange. After 1 h at 30 °C all volatile material was removed from the reaction mixture in vacuo. A ^{1}H NMR spectrum of the crude residue, dissolved in C$_6$D$_6$, revealed the presence of a mixture (ca. 1:1) of ITi(NRAr)$_3$ (*vide infra*) and NMo(O^{t}Bu)$_3$.

Synthesis of CH$_3$Ti(NRAr)$_3$. A solution of 312 μL of LiCH$_3$ (1.4 M in diethyl ether, 0.437 mmol) was added to a stirring suspension of ITi(NRAr)$_3$ in 8 mL of diethyl ether which had been prechilled at −35 °C. The reaction mixture turned to a homogeneous yellow solution within 5 min as it gradually warmed to 23 °C. After 10 min the solution was filtered, removing a trace of blackish residue. The volatiles were removed in vacuo, and the resulting yellow/orange residue was extracted with pentane and the extract was filtered through Celite (removing some grayish powder) into a 20 mL scintillation vial. The solution volume was reduced to 5 mL, at which point a yellow solid began to precipitate. Storing the vial at −35 °C for 15 h produced a yellow, microcrystalline material which was collected on a small sintered frit. The dry material weighed 195 mg (80.5%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta = 6.89$ (s, 6H, *ortho* C$_6$*H*$_3$Me$_2$), $\delta = 6.77$ (s, 3H, *para* C$_6$*H*$_3$Me$_2$), $\delta = 2.27$ (s, 18H, *meta* C$_6$H$_3$*Me*$_2$), $\delta = 1.30$ (s, 9H, C(CD$_3$)$_2$C*H*$_3$), $\delta = 0.60$ (s, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): $\delta = 147.33$ (aryl *ipso*), $\delta = 136.82$ (aryl *meta*), $\delta = 130.52$ (aryl *ortho*), $\delta = 127.4$ (aryl *para*), $\delta = 60.7$ (N*C*(CD$_3$)$_2$(CH$_3$)), $\delta = 57.30$ (*C*H$_3$), $\delta = 30.60$ (NC(*C*D$_3$)$_2$(CH$_3$)), $\delta = 21.50$ (NAr(*C*H$_3$)$_2$). Anal. Calcd for C$_{37}$H$_{39}$D$_{18}$N$_3$Ti: C, 72.87; H, 9.42; N, 6.89. Found: C, 73.03; H, 9.80; N, 6.75.

Kinetic Measurements for Conversion of (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ to (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ in Benzene. A stock solution of the green intermediate (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ was generated as described above using chilled benzene solvent; the frozen solution was stored at −35 °C. For example, Ti(NRAr)$_3$ (59.6 mg, 0.100 mmol) in 10 mL of chilled benzene was added to a stirring solution of NMo(O^{t}Bu)$_3$ (33.0 mg, 0.100 mmol) in 10 mL of chilled benzene. An additional 40 mL of chilled benzene was then added to the solution to give an overall concentration of 1.7×10^{-3} M. Aliquots from this stock solution were used for kinetic measurements. Data were collected on an Hewlett Packard HP 8453 diode array spectrophotometer. The reaction temperature was controlled using an HP 89090A Peltier temperature control accessory. The decay of olive green (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ was monitored at $\lambda_{\max} = 746$ nm. The orange product (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ does not absorb in this region. Samples were stirred at 250 rpm by an internal Teflon-coated magnetic stir bar and allowed to equilibrate at the desired temperature for 120 s prior to data acquisition. In a typical run, between 700 and 1000 data points were processed and used to determine rates. Between 20 and 60 °C, a plot of $\ln(A - A_\infty)$ vs time typically gave clean first-order behavior through 4 half-lives. Rate constants used as data points in Eyring plots were determined using a Kaleidograph least-squares curve-fitting program to the equation $A = A_\infty + A_0[\exp(-kt)]$.

Synthesis of (Me$_2$N)$_3$Mo[μ-N]Ti(^{t}BuNPh)$_3$. Solid Ti(^{t}BuNPh)$_3$ (250.5 mg, 0.509 mmol) was added to a stirring suspension of NMo(NMe$_2$)$_3$ (123.3 mg, 0.509 mmol) in pentane (10 mL) which had been prechilled at −35 °C. The slurry was stirred vigorously, turning to a homogeneous forest green within minutes. Stirring was continued for 1 h. Concentration to 3 mL and storage of the solution at −35 °C afforded green crystals which were collected on a frit and washed with 2 × 2 mL of cold hexamethyldisiloxane. Subsequent to drying in vacuo, 288 mg of green, crystalline material was isolated. A UV−vis spectrum of this material in benzene shows an absorbance at 760 nm ($\epsilon = 2500$ M^{-1} cm^{-1}). No appreciable decay occurs upon heating at 70 °C for 13 h. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta = 7.3$ ($\delta\nu_{1/2} = 23$ Hz, 6H, *meta* C$_6$*H*$_5$), $\delta = 6.78$ ($\delta\nu_{1/2} = 34$ Hz, 3H, *para* C$_6$*H*$_5$), $\delta = 6.4$ ($\delta\nu_{1/2} = 98$ Hz, 6H, *ortho* C$_6$*H*$_5$), $\delta = 3.45$ ($\delta\nu_{1/2} = 190$ Hz, 18H, N(C*H*$_3$)$_2$). EPR (toluene, 98 K): $g_1 = 1.973$, $g_2 = 1.965$, $g_3 = 1.931$; $a_1 = 35$, $a_2 = 29$, $a_3 = 54$ G. Attempts to obtain structural data on this species by an X-ray diffraction study have not been successful. Anal. Calcd for $C_{36}H_{60}N_7TiMo$: C, 58.85; H, 8.23; N, 13.34. Found: C, 58.45; H, 8.53; N, 13.19.

Synthesis of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$. NMo(O^{t}Bu)$_3$ (0.4791 g, 1.456 mmol) was dissolved in benzene (10 mL). An emerald green solution of Ti(NRAr)$_3$ (0.8654 g, 1.456 mmol) in benzene (5 mL) was then added quickly to the stirring solution of NMo(O^{t}Bu)$_3$. The reaction mixture rapidly turned to a homogeneous deep olive green. It was stirred at ca. 28 °C for 8 h, and its color gradually changed to a bright orange. The reaction mixture was then filtered through Celite and dried to a solid in vacuo. Triturating once with pentane (10 mL) to remove trace benzene and pumping to dryness afforded 1.14 g of an orange powder containing, according to ^{1}H NMR analysis, a small amount of residual NMo(O^{t}Bu)$_3$. The orange powder was redissolved in pentane (8 mL), cooled to -35 °C for 2 h, and filtered to remove residual white NMo(O^{t}Bu)$_3$. After this step was repeated, the orange filtrate was taken to dryness in vacuo to afford analytically pure (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ (1.05 g, 1.21 mmol, 83.3%) as a solid orange powder. Orange crystalline samples of this material (which is very soluble in aliphatic hydrocarbon solvents) may be obtained in about 40% yield by recrystallization from pentane. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.74$ (s, 3H, *para* C$_6$*H*$_3$Me$_2$), $\delta = 6.10$ (s, 6H, *ortho* C$_6$*H*$_3$Me$_2$), $\delta = 2.21$ (s, 18H, *meta* C$_6$H$_3$*Me*$_2$), $\delta = 1.67$ (s, 18H, OC(C*H*$_3$)$_3$), $\delta = 1.42$ (s, 9H, C(CD$_3$)$_2$C*H*$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25°C): $\delta = 153.29$ (aryl *ipso*), $\delta = 136.84$ (aryl *meta*), $\delta = 128.58$ (aryl *ortho*), $\delta = 126.71$ (aryl *para*), $\delta = 82.43$ (O*C*(CH$_3$)$_3$), $\delta = 60.80$ (N*C*(CD$_3$)$_2$(CH$_3$)), $\delta = 31.71$ (OC(*C*H$_3$)$_3$), $\delta = 31.61$ (NC(*C*D$_3$)$_2$(CH$_3$)), $\delta = 22.09$ (NAr(*C*H$_3$)$_2$). Anal. Calcd for $C_{44}H_{54}D_{18}MoTiN_4O_3$: C, 60.96; H, 8.37; N, 6.46. Found: C, 61.00; H, 8.26; N, 6.40.

X-ray Structure of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$. A yellow irregular crystal of approximate dimensions 0.20 × 0.10 × 0.30 mm was obtained by slow evaporation of an Et$_2$O/O(SiMe$_3$)$_2$ solution. The crystal was mounted on a glass fiber. Data were collected at -100 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation. A total of 9255 reflections were collected to a 2θ value of 44.9°, of which 8837 were unique ($R_{\text{int}} = 0.093$); equivalent reflections were merged. The linear absorption coefficient for Mo Kα is 4.6 cm^{-1}. An empirical absorption correction, using the program DIFABS2, was applied, resulting in transmission factors ranging from 0.78 to 1.11. The data were corrected for Lorentz and Polarization effects. The structure was solved by a combination of the Patterson method and direct methods. With the exception of a disordered *tert*-butoxide *tert*-butyl group (atoms C5A−C8A) and three NRAr carbon atoms (C310, C351, and C331), non-hydrogen atoms were refined anisotropically. The final cycle of least-squares refinement was based on 3910 observed reflections [$I > 3.00\sigma(I)$] and 437 variable parameters and converged with $R = 0.070$ and $R_w = 0.070$. A final difference Fourier map showed no chemically significant features. Crystal data are $a = 15.15(1)$ Å, $b = 15.74(2)$ Å, $c = 10.78(1)$ Å, $a = 107.12(8)°$, $b = 92.56(8)°$, $g = 100.78(8)°$, $V = 2401(4)$ Å^3, space group PO(1,–), Z = 2, mol wt. = 848.92 for $C_{44}H_{54}D_{18}MoTiN_4O_3$, and ρ(calcd) = 1.174 g/cm^3.

Synthesis of (^{t}BuO)$_2$(^{15}N)Mo[μ-O]Ti(NRAr)$_3$. This was prepared as described above for (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$, using 57 mg of NMo(O^{t}Bu)$_3$ (approximately 42%-^{15}N) and 102.6 mg of Ti(NRAr)$_3$ and ca. 0.7 mL of C_6D_6 solvent. ^{15}N NMR (50.65 MHz, C_6D_6, 25°C): $\delta = 827$ ppm relative to liquid ammonia (0 ppm). ^{15}NH$_2$Ph used as reference at 55 ppm (relative to liquid ammonia at 0 ppm).

Reaction of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ with Mo(NRAr)$_3$. Solid samples of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ (137.8 mg, 0.159 mmol) and Mo(NRAr)$_3$ (102 mg, 0.159 mmol) were placed in a Schlenk vessel equipped with stir bar under an atmosphere of dinitrogen. The flask was then evacuated, and 10 mL of degassed benzene was condensed into the vessel. The reaction mixture was stirred vigorously for 5 days at 22 °C, at which point the solution appeared homogeneous and was deep yellow-brown in color. All volatile material was then removed from the reaction mixture in vacuo. A ^{1}H NMR spectrum (C_6D_6) of the nonvolatile residue indicated a quantitative conversion of Mo(NRAr)$_3$ to the well-characterized terminal nitrido complex Mo-(NRAr)$_3$. A number of resonances in the spectrum of the residue could not be assigned; these could be attributed to decomposition products arising from the plausible intermediate "(^{t}BuO)$_2$Mo[μ-O]Ti(NRAr)$_3$". Similar experiments carried out in C_6D_6 indicated the production of small amounts of isobutylene.

Generation and Observation of (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$}. The procedure for generation of the green intermediate (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$} is analogous to that described above for (^{t}BuO)$_3$Mo[μ-N]Ti(NRAr)$_3$ and is achieved by stoichiometric addition of a pure sample of Ti(NRAr)$_3$ to a pure sample of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ at -35 °C in pentane. ^{2}H NMR (46 MHz, pentane, 25 °C): $\delta = 2.3$ (s, C(C*D*$_3$)$_2$(CH$_3$), $\Delta\nu_{1/2} = 20$ Hz). Solutions prepared in this way retain their green color for months when stored at -35 °C. A sample procedure follows: an orange solution of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ (23.6 mg, 0.0272 mmol) in 0.5 mL of C_6D_6 was added to an NMR tube. The solution was then frozen, and a stoichiometric amount of Ti(NRAr)$_3$ (16.2 mg, 0.0272 mmol) in C_6D_6 (0.5 mL) was added to the tube. The contents were allowed to thaw, the tube was agitated rapidly, and ^{1}H NMR data were collected. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.64$ (s, 3H, *para* C$_6$*H*$_3$Me$_2$), $\delta = 2.289$ (s, 18H, *meta* C$_6$H$_3$*Me*$_2$), $\delta = 2.208$ (s, 18H, *meta* C$_6$H$_3$*Me*$_2$). Resonances corresponding to the *tert*-butoxide ligands and the *ortho* protons of the NRAr aryl groups were not well resolved for this paramagnetic complex, though a very broad feature centered at $\delta = 6.25$ is likely a combination of these resonances. Furthermore, no resonances corresponding to the NRAr *tert*-butyl groups NC(CD$_3$)$_2$(C*H*$_3$) were observed. The assigned inequivalence of the two Ti(NRAr)$_3$ moieties in (^{t}BuO)$_2$Mo{[μ-O]Ti(NRAr)$_3$}{[μ-N]Ti(NRAr)$_3$} is based on the observation of two well-resolved signals assigned to the aryl methyl groups, which decay away at the same rate at 25 °C as the complex converts to the final product, (^{t}BuO)(N)Mo-{[μ-O]Ti(NRAr)$_3$}$_2$ (vide infra). Interpretation of UV−vis (benzene, 25 °C) spectra was complicated by the evident presence of Ti(NRAr)$_3$ in samples so interrogated.

Synthesis of (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. Ti(NRAr)$_3$ (807.9 mg, 1.358 mmol) as a solution in benzene (8 mL) was added quickly to a solution of white NMo(O^{t}Bu)$_3$ (223.5 mg, 0.679 mmol). The reaction mixture stirred at 28 °C for 12 h, during which time the solution's initial deep olive green color gradually turned orange. The reaction mixture was filtered through Celite to remove a small amount of unidentified black material. All volatile material was removed from the orange filtrate in vacuo. The crude solid was triturated once with pentane (5 mL) to afford (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ as an orange powder (953 mg, 91%). While the crude material is >95% pure according to ^{1}H, ^{2}H, and ^{13}C NMR analysis, it may be recrystallized (albeit in low yield) from diethyl ether or pentane. An alternative preparation of (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ is the stoichiometric addition of Ti(NRAr)$_3$ to a solution of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ in ether followed by a workup identical to the one described above. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.759$ (s, 3H, *para* C$_6$*H*$_3$Me$_2$), 6.250 (s, 6H, *ortho* C$_6$*H*$_3$Me$_2$), 2.248 (s, 18H, *meta* C$_6$H$_3$*Me*$_2$), 1.876 (s, 18H, OC(C*H*$_3$)$_3$), 1.548 (s, 9H, C(CD$_3$)$_2$C*H*$_3$). Anal. Calcd for $C_{76}H_{81}D_{36}MoTi_2N_7O_3$: C, 64.98; H, 8.40; N, 6.98. Found: C, 63.95; H, 8.33; N, 6.61.

Synthesis of (^{t}BuO)(^{15}N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. This was prepared by addition of a second equivalent of Ti(NRAr)$_3$ (102.6 mg) to the previously prepared solution of (^{t}BuO)$_2$(^{15}N)Mo[μ-O]Ti(NRAr)$_3$ in C_6D_6 and then allowing the solution to stand in an NMR tube for 6 h at 25 °C. ^{15}N NMR (50.65 MHz, C_6D_6, 25°C): $\delta = 845$ ppm. ^{15}NH$_2$Ph used as reference at 55 ppm (relative to liquid ammonia at 0 ppm).

Synthesis of (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. (^{t}BuO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ (870 mg , 0.619 mmol) was dissolved in 10 mL of neat MeI and stirred at 25 °C. Disappearance of the starting material was conveniently monitored by ^{1}H NMR and was complete after 13 h. The solution color had turned to a deep red-brown. The volatiles were removed in vacuo, and the resulting residue was taken up in 15 mL of pentane. Vacuum filtration removed a fine light brown powder (see below). The burgundy filtrate was pumped to dryness, and the resulting powder (825 mg) was transferred to a fine frit. Washing the solid with cold O(SiMe$_3$)$_2$ removed a burgundy filtrate and left behind a bright orange powder. Washing was repeated until the filtrate no longer had a burgundy tint (4 × 2 mL). The resulting orange powder was then stirred vigorously in 1:1 pentane/TMS$_2$O (8 mL) and allowed to settle at -35 °C overnight. A bright orange powder was isolated by filtration (430 mg, 51%), which was spectrosopically pure. The washings and filtrate still contained a significant amount of (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ but further isolation proved difficult. Pure samples of (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ may be crystallized by slow evaporation from Et$_2$O to form orange parallelepipeds. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 6.74 (s, 6H, *para* C_6H_3Me_2), δ = 5.9 (s, 12H, *ortho* C_6H_3Me_2), δ = 4.68 (s, 3H, $\text{O}\text{C}H_3$) δ = 2.20 (s, 36H, *meta* C_6H_3Me_2), δ = 1.25 (s, 18H, $\text{C(CD}_3)_2\text{C}H_3$). ^{1}H NMR (300 MHz, C$_6D_6$, 25 °C): δ = 6.76 (s, 6H, *para* C_6H_3Me_2), δ = 6.2 (s, 12H, *ortho* C_6H_3Me_2), δ = 4.61 (s, 3H, $\text{OC}H_3$) δ = 2.24 (s, 36H, *meta* C_6H_3Me_2), δ = 1.53 (s, 18H, $\text{C(CD}_3)_2\text{C}H_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ = 152.75 (aryl *ipso*), δ = 136.16 (aryl *meta*), δ = 127.58 (aryl *ortho*), δ = 125.89 (aryl *para*), δ = 60.36 ($\text{N}C\text{(CD}_3)_2\text{(CH}_3))$), δ = 56.51 ($\text{O}C\text{H}_3$), δ = 31.00 ($\text{NC(}CD_3)_2\text{(CH}_3))$), δ = 21.71 ($\text{NAr(}CH_3)_2$). Anal. Calcd for C$_{73}H_{75}D_{36}$MoTi$_2N_7O_3$: C, 64.34; H, 8.17; N, 7.20. Found: C, 63.11; H, 8.34; N, 6.95.

Note: ^{1}H NMR analysis of the fine light brown powder initially filtered away indicated the presence of the anilinium salt [H(Me)NRAr][I]. This salt was prepared independently through treatment of HNRAr with neat MeI. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 10.95 (s (br), 1H, *H*N), δ = 7.37 (s, 1H, *para* C_6H_3Me_2), δ = 7.05 (s, 2H, *ortho* C_6H_3Me_2), δ = 3.102 (d, 3H, $\text{NC}H_3$), δ = 2.31 (s, 6H, *meta* C_6H_3Me_2), δ = 1.51 (s, 3H, $\text{C(CD}_3)_2CH_3$).

Spectroscopic Study of (MeO)(^{15}N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$ and (H$_3$^{13}CO)(^{15}N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. Mo(^{15}N)(O^{t}Bu)[OTi(NRAr)$_3$]$_2$ (75 mg, 0.53 mmol) was stirred in MeI (2 mL) for 13 h and worked up as described above for (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) indicated no splitting of the resonance at δ = 4.61 ppm, consistent with an O-bound methyl group rather than an N-bound methyl group. As it was difficult to definitively assign the methyl resonance in the ^{13}C NMR spectrum, a sample was prepared using ^{13}CH$_3$I. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C) revealed an enhanced methyl resonance exhibiting no ^{15}N coupling at δ = 56.45. The gated-decoupled spectrum showed a quartet for this resonance (J_{CH} = 140 Hz), consistent with the ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) spectrum of this sample which showed a doublet at δ = 4.69p (J_{CH} = 135 Hz). These data strongly support our assignment of an O-bound methyl group.

Attempted X-ray Structure of (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. Further confirmation of the proposed O−CH$_3$ connectivity was sought by an X-ray diffraction study of an orange crystal of (MeO)(N)Mo{[μ-O]Ti(NRAr)$_3$}$_2$. Though the presence of the two titanoxo moieties was confirmed, a disorder problem prevented the assignment of the methyl linkage (i.e., CH$_3$−O−Mo versus CH$_3$−N═Mo).

Synthesis of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$. MoO$_2$(O^{t}Bu)$_2$ was prepared by the (slightly modified) method[91,92] of Chisholm and coworkers: Mo(O^{t}Bu)$_6$ (471 mg, 0.747 mmol) was dissolved in Et$_2$O (10 mL) under N$_2$ in a Schlenk vessel fitted with a septum. Dry oxygen (40 mL, 1 atm, 1.63 mmol) was added via syringe, and the orange reaction mixture was stirred at 25 °C. After 15 min, another 10 mL of O$_2$ was added to ensure complete consumption of Mo$_2$(O^{t}Bu)$_6$, as suggested by the production of a yellow solution lacking any orange tint. Volatile material was removed *in vacuo*, and the yellow oil was triturated once with toluene in order to remove any residual ^{t}BuOH. The yellow oil thereby obtained was used without further purification in preparing O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ as follows.

A green solution of Ti(^{t}BuNPh)$_3$ (706 mg, 1.43 mmol) in benzene (15 mL) was added via pipet to a stirring solution of freshly prepared, yellow MoO$_2$(O^{t}Bu)$_2$ (197 mg, 0.717 mmol) in benzene (1.3 mL). The murky reaction mixture adopted a brown color after the addition was complete. The solution was transferred to a 100 mL glass vessel with a Teflon needle plug and was stirred at 65 °C for 17 h, by which time the solution had turned reddish-orange in color. Volatile material was removed *in vacuo*, and the residue was triturated with pentane (1 × 5 mL) affording a reddish-orange solid. This solid was transferred to a sintered glass frit and washed with cold pentane (3 × 5 mL) until a fine, bright orange powder (440 mg) remained on the frit. This powder, when pure, has very low solubility in pentane. A second crop of 40 mg was attained by slow cooling of the combined washings at −35 °C, affording 480 mg (58.5%) of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ overall. This powder was spectroscopically pure. The product can be recrystallized efficiently by vapor diffusion of hexane into a THF solution to form red-orange crystals. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.05 (m, 18H, *para,meta* C_6H_5), δ = 6.26 (d, 12H, *ortho* C_6H_5), δ = 1.15 (s, 54H, $\text{C(}CH_3)_3$. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.12 (m, 18H, *meta* C_6H_5), δ = 7.03 (t, 6H, *para* C_6H_5), δ = 6.49 (d, 12H, *ortho* C_6H_5), δ = 1.43 (s, 54H, $\text{C(}CH_3)_3$. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ = 152.01 (aryl *ipso*), δ = 127.63 (aryl *meta*), δ = 129.31 (aryl *ortho*), δ = 125.23 (aryl *para*), δ = 62.20 ($\text{N}C\text{(CH}_3)_3$), δ = 30.97 ($\text{NC(}CH_3)_3$). Anal. Calcd for C$_{60}$H$_{84}$MoTi$_2$N$_6$O$_4$: C, 62.90; H, 7.39; N, 7.34. Found: C, 63.00; H, 7.32; N, 7.15.

X-ray Structure of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$. Crystal structure data for C$_{60}$H$_{84}$MoN$_6$O$_4$Ti$_2$: orange plate, 0.65 × 0.35 × 0.05 mm, monoclinic, a = 18.0093(13) Å, b = 18.6394(14) Å, c = 18.9783(14) Å, β = 112.5350(10)°, V = 5884.3(8) Å^3, Z = 4, space group $P2_1/n$, u = 0.524 mm^{-1}, ρ_{calc} = 1.293 g/cm^3, $F(000)$ = 2416. Data collection on a Siemens Platform goniometer with a CCD detector at 193(2) K using Mo Kα radiation [λ = 0.710 73 Å] ($-20 \leq h \leq 18$, $-16 \leq k \leq 20$, $-14 \leq l \leq 21$). Total data 8680 (3545 unique, R_{int} = 0.0605). Data were corrected for Lorentz polarization and absorption (T_{max}, T_{min}, 1.0000 and 0.9334 respectively). Structure solved by direct methods (SHELXTL V5.0, Sheldrick, G. M. and Siemens Industrial Automaion, Inc. 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F^2 converged with final residuals: R_1 = 0.0827, wR$_2$ = 0.1497, and GOF = 1.235 based upon $I > 2\sigma(I)$. Residual electron density, +0.326 and −0.324 e Å^{-3}.

Attempted Reaction of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with Ti(^{t}BuNPh)$_3$. Ti(^{t}BuNPh)$_3$ (21.3 mg, 0.0432 mmol) in C$_6$D$_6$ (0.5 mL) was added to O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (49.5 mg, 0.0432 mmol) in C$_6$D$_6$ (0.5 mL). None of the starting O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ was consumed, even with gentle heating at 50 °C for 1 h, as indicated by ^{1}H NMR. This was confirmed by intergration against an internal standard (hexamethylbenzene).

Attempted Deoxygenation of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with PEt$_3$. O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (70 mg, 0.0611 mmol) was dissolved in 5 mL of a 1:1 solution of benzene/PEt$_3$ (by volume). There was no indication of deoxygenation after 1 week at 70 °C as ascertained by removal of volatile material *in vacuo* and subsequent ^{1}H NMR analysis of the residue. Similar results were obtained using P(OEt)$_3$ in place of PEt$_3$ in an otherwise identical experiment.

Attempted Deoxygenation of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with Mo(NRAr)$_3$. One equivalent of Mo(NRAr)$_3$ (15.4 mg, 0.0239 mmol) in C$_6$D$_6$ (0.5 mL) was added to O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (27.4 mg, 0.0239 mmol) in C$_6$D$_6$ (0.5 mL). The reaction was monitored by ^{2}H NMR. No diminishment of intensity of the Mo(NRAr)$_3$ 64 ppm signal was noted after 1 h at 55 °C.

Attempted Deoxygenation of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with (THF)V(Mes)$_3$. One equivalent of V(Mes)$_3$(THF) (12 mg, 0.025 mmol) was added as a blue solid to O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (28.6 mg, 0.025 mmol) in toluene (2 mL). After 9 h at 70 °C, it appeared that some of the starting O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ had been consumed (^{1}H NMR). However, no OV(Mes)$_3$ was observed and isolation of a Mo/Ti product was not attempted.

Attempted Reaction of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with Ethylene. O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (40 mg, 0.035 mmol) in C$_6$D$_6$ (2.5 mL) was stirred under an atmosphere of ethylene at 70 °C for 1 week. No reaction was observed as ascertained by removal of volatile material *in vacuo* and subsequent ^{1}H NMR analysis of the residue.

Attempted Reaction of O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ with Ph$_2$SiH$_2$. One equivalent of Ph$_2$SiH$_2$ (15 mg, 0.0169 mmol) in C$_6$D$_6$ (0.5 mL) was added to O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (19.3 mg, 0.0169 mmol) in C$_6$D$_6$ (0.5 mL). There was no reaction after 3 days at 70 °C, as indicated by ^{1}H NMR.

Synthesis of (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$. A −35 °C solution of Ti(NRAr)$_3$ (399.6 mg, 672 μmol) in ether (10 mL) was added dropwise via pipet to a thawing solution of OV(O^{i}Pr)$_3$ (164.0 mg, 672 μmol) in ether (5 mL). The reaction mixture warmed to 30 °C and was stirred for 3 h. Removal of all volatile material in vacuo left a yellow-green solid. Three recrystallizations (ether, −35 °C) yielded pure (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$ (434.7 mg, 518 μmol, 77%). Mp: 154−156 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 6.76 (s, 3H, *para* ArH, $\Delta\nu_{1/2}$ = 10 Hz), 6.11 (bs, $\Delta\nu_{1/2}$ = 77 Hz, 6H, *ortho* ArH), 4.15 (s, $\Delta\nu_{1/2}$ = 203 Hz, 27H, $\text{OCH(C}H_3)_2$), 2.23 (s, $\Delta\nu_{1/2}$ = 12 Hz, 18H, meta ArCH$_3$), ~2.2 (vbs, 9H, NCCH$_3$), no signal corresponding to $\text{OC}H\text{(CH}_3)_2$ was located. ^{2}H NMR (300 MHz, ether, 25 °C): δ = 2.29 ($\Delta\nu_{1/2}$ = 10

Hz, $NCCD_3$). μ_{eff} (300 MHz, C_6D_6, 25 °C): 2.4 μ_B. Anal. Calcd for $C_{48}H_{63}D_{18}N_3O_4TiV$: C, 64.42; H, 9.01; N, 5.01. Found: C, 64.76; H, 9.22; N, 4.84.

Reaction of (^{i}PrO)$_3$V[*μ*-O]Ti(NRAr)$_3$ with [FeCp$_2$][OTf]. To a cold (−35 °C) solution of (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$ (21.4 mg) in THF (2 mL) was added [FeCp$_2$][OTf] (9.4 mg, 1.1 equiv). As blue [FeCp$_2$][OTf] was consumed, the color of the reaction mixture changed from yellow-green to orange-brown and finally to bright orange. After the solution was stirred for 1 h at 29 °C, examination of the reaction mixture by ^{2}H NMR showed a single peak at 1.48 ppm ($\Delta\nu_{1/2} = 8.43$ Hz) suggesting formation of a diamagnetic entity. All volatile material was removed from the reaction mixture after stirring 2.5 h. The bright orange solid was dissolved in C_6D_6 for examination by ^{1}H NMR; TfOTi(NRAr)$_3$ was thereby identified as the sole NRAr-containing product [see the independent synthesis and characterization of TfOTi(NRAr)$_3$ given below], while ferrocene was identified by a singlet at 4.00 ppm. The only isopropoxide resonances observed were those belonging to OV(O^{i}Pr)$_3$.

Treatment of (^{i}PrO)$_3$V[*μ*-O]Ti(NRAr)$_3$ with CH$_3$I. To a stirring solution of (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$ (20 mg) in ether (5 mL) was added methyl iodide (5 μL, ~3 equiv) via syringe. The reaction mixture stirred for 18 h at 27 °C; no color change was observed. Examination by ^{2}H NMR of an aliquot taken at this time showed only unreacted (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$. All volatile material was then removed from the reaction mixture in vacuo. Examination by ^{1}H NMR of the yellow-green solid thereby obtained confirmed the presence of only unreacted (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$. Since Ti(NRAr)$_3$ reacts rapidly with methyl iodide to give ITi(NRAr)$_3$ and MeTi(NRAr)$_3$, we conclude that (^{i}PrO)$_3$V[μ-O]Ti(NRAr)$_3$ does not dissociate in solution to Ti(NRAr)$_3$ and OV(O^{i}Pr)$_3$.

Synthesis of (^{t}BuO)$_3$V[*μ*-O]Ti(NRAr)$_3$. A −35 °C solution of Ti(NRAr)$_3$ (500 mg, 841 μmol) in ether (20 mL) was added dropwise via pipet to a thawing solution of OV(O^{t}Bu)$_3$ (241 mg, 841 μmol) in ether (5 mL). The resulting orange-brown reaction mixture warmed to 30 °C and was agitated for 30 min. Removal of all volatile material in vacuo left an orange-brown solid (710 mg, 806 μmol, 96%). Recrystallization (ether, −35 °C) provided dark orange-brown needles (700 mg, 794 μmol, 94%, two crops). Mp: 176−177 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.76$ (s, 3H, *para* ArH), 6.14 (bs, $\Delta\nu_{1/2} = 87$ Hz, 6H, *ortho* ArH), 3.26 (bs, $\Delta\nu_{1/2} = 235$ Hz, 27H, $OC(CH_3)_3$), 2.24 (s, $\Delta\nu_{1/2} = 8$ Hz, 18H, meta $ArCH_3$), ~2.5 (vbs, 9H, $NCCH_3$). ^{2}H NMR (46 MHz, pentane, 25 °C): $\delta = 2.40$ ($\Delta\nu_{1/2} = 11$ Hz, $NCCD_3$). μ_{eff} (300 MHz, C_6D_6, 25 °C): 2.4 μ_B. Anal. Calcd for $C_{48}H_{63}D_{18}N_3O_4TiV$: C, 65.43; H, 9.27; N, 4.77. Found: C, 65.94; H, 9.60; N, 4.65.

Synthesis of ITi(NRAr)$_3$. A solution of iodine (22.5 mg, 87.5 μmol) in ether (2 mL) was added to an agitated, dark green solution of Ti(NRAr)$_3$ (104 mg, 175 μmol) in ether (5 mL). The color of the reaction mixture rapidly turned bright orange. After 5 min all volatile material was removed in vacuo leaving 126 mg (175 μmol, ca. 100%) of bright orange solid ITi(NRAr)$_3$ (>95% pure according to ^{1}H NMR). Further purification can readily be accomplished by recrystallization (ether, −35 °C). Mp: 217−218 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.91$ (s, 6H, *ortho* ArH), 6.81 (s, 3H, *para* ArH), 2.25 (s, 18H, *meta* $ArCH_3$), 1.36 (s, 9H, $NCCH_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.88$ (s, 3H, *para* ArH), 6.65 (s, 6H, *ortho* ArH), 2.28 (s, 18H, *meta* $ArCH_3$), 1.19 (s, 9H, $NCCH_3$). ^{2}H NMR (46 MHz, C_6H_6, 25 °C): $\delta = 1.3$ ($\Delta\nu_{1/2} = 7$ Hz). ^{13}C NMR (75.43 MHz, $CDCl_3$, 25 °C): $\delta = 143.68$ (s, *ipso* NC), 136.81 (q, $^2J_{CH} = 5.9$ Hz, *meta* CCH_3), 130.53 (d, $^1J_{CH} = 157.5$ Hz, *ortho* Ar), 128.68 (d, $^1J_{CH} = 153.7$ Hz, *para* Ar), 63.85 (s, $NC(CD_3)_2CH_3$), 30.53 (q, $^1J_{CH} = 125.6$ Hz, $NC(CD_3)_2CH_3$), 29.79 (m, $NC(CD_3)_2CH_3$), 21.47 (q, $^1J_{CH} = 126.3$ Hz, *meta* $ArCH_3$). Anal. Calcd for $C_{36}H_{36}D_{18}IN_3Ti$: C, 59.91; H, 7.54; N, 5.82. Found: C, 60.35; H, 7.81; N, 5.71.

Synthesis of TfOTi(NRAr)$_3$. Solid ferrocenium triflate (309 mg, 922 μmol, 1.1 equiv) was added to a cold (−35 °C) solution of Ti(NRAr)$_3$ (498 mg, 837 μmol) in THF (7 mL). The resulting red solution was warmed to 25 °C and was stirred for 4 h. The reaction mixture was then filtered, and all volatile material was removed in vacuo. ^{1}H NMR examination of the crude red solid showed only ferrocene and TfOTi(NRAr)$_3$. The crude solid was dissolved in 9:1 (v/v) pentane/ether (50 mL), the solution was filtered, and the filtrate was cooled to −35 °C overnight. Bright red crystals of TfOTi(NRAr)$_3$ (pure by ^{1}H NMR) were thereby obtained (500 mg, 672 μmol, 80%). Mp: 205−206 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.84$ (s, 3H, *para* ArH), 6.39 (s, 6H, *ortho* ArH), 2.27 (s, 18H, *meta* $ArCH_3$), 1.11 (s, 9H, $NCCH_3$). ^{2}H NMR (46 MHz, THF, 25 °C): $\delta = 1.32$ ($\Delta\nu_{1/2} = 7.62$ Hz). ^{19}F NMR (frequency, $CDCl_3$, 25 °C): $\delta = -76.21$ ($\Delta\nu_{1/2} = 7.62$ Hz). ^{13}C NMR (75.43 MHz, $CDCl_3$, 25 °C): $\delta = 147.86$ (s, *ipso* NC), 137.27 (q, *meta* CCH_3), 128.31 (d, *ortho* CH), 127.38 (d, *para* CH), 118.86 (m, tentative asst CF_3), 63.98 (s, $NC(CD_3)_2CH_3$), 29.91 (q, $NC(CD_3)_2CH_3$), 29.40 (m, $NC(CD_3)_2CH_3$), 21.60 (q, *meta* CCH_3). Anal. Calcd for $C_{37}H_{36}D_{18}F_3N_3O_3STi$: C, 59.74; H, 7.32; N, 5.65. Found: C, 59.83; H, 7.35; N, 5.51.

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Supporting Information Available: Fractional coordinates and thermal parameters for the X-ray structures of (^{t}BuO)$_2$(N)Mo[μ-O]Ti(NRAr)$_3$ and O$_2$Mo{[μ-O]Ti(^{t}BuNPh)$_3$}$_2$ (5 pages). See any current masthead page for ordering and Internet access instructions.

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