

Reaction of (Bisimido)niobium(V) Complexes with Organic Azides: [3 + 2] Cycloaddition and Reversible Cleavage of β -Diketiminato Ligands Involving Nitrene Transfer

Andreas H. Obenhuber, Thomas L. Gianetti, Xavier Berrebi, Robert G. Bergman,* and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: We describe the unusual reactivity of a highly labile diethyl ether adduct of an asymmetric niobium(V) bis(imido) $2.OEt_2$ containing the monoazabutadiene (MAD) ligand. This species undergoes clean nitrene transfer on treatment with *tert*-butyl- or diisopropylphenyl azide resulting in the unprecedented reformation of nacnac ligands bound to the metal center. Corresponding reactions with trimethylsilyl- or *tert*-butyl azide allowed the isolation of two rare intermediates prior to N_2 loss; mechanistic studies support the involvement of two different niobium species.

The β -diketiminato (or 'nacnac') moiety has found widespread application as a supporting ligand for catalytic transformations,¹ complexes containing metal–ligand multiple bonds,² reactive organometallic species with low coordination numbers and oxidation states across the periodic table.³ However, limitations in its conventional role as a spectator ligand in early transition (and recently also in main group) metal compounds have been reported resulting from overall irreversible nitrene group transfer from a nacnac ligand to the metal center.⁴ Reversing such intramolecular ligand degradation would allow access to masked low valent metal centers and make them available for further reactivity. Additionally, intermolecular synthetic routes to metal-imido complexes routinely comprise the use of organic azides (RN_3) which upon loss of N_2 act as valuable nitrene-transfer agents.⁵ Despite this long-standing synthetic application, few unfragmented organoazido metal intermediates have been isolated and fully characterized,⁶ and mechanistic information on how this nitrene transfer occurs remains scarce.

As part of our continuing interest in the chemistry of group 5 mono-^{1c,2a,b,3d,e} and bis-(imido)⁷ complexes, we recently reported the synthesis of $(MAD)Nb(N^tBu)(NAr)(L)$ ($L = Py, THF$),^{2b} in which both the pyridine and THF ligands were tightly bound to the metal center, thus hampering their displacement under mild conditions. We speculated that a more labile Et_2O adduct might pave the way to a π -loaded niobium center displaying imido reactivity.

Complex $2.OEt_2$ was therefore synthesized as shown in Scheme 1 and was found to be structurally analogous to its congeners (see Supporting Information (SI)). Adding $TMSN_3$ to a benzene solution of $2.OEt_2$ at room temperature resulted in an immediate color change from orange to deep red. No further reaction was observed after several hours, and an

intractable mixture of products was formed upon either slight heating (40 °C) or photolysis. The resulting complex $(MAD)Nb(N^tBu)(NAr)(N_3TMS)$ (**3**) (Scheme 1) was isolated as red crystals from HMDSO (−40 °C) in 68% yield. The IR spectrum revealed one strong stretch at 2201 cm^{-1} in the solid state and three in solution ($\nu = 2199, 2138, \text{ and } 2093\text{ }cm^{-1}$) consistent with absorbances due to $N=N$ functionalities. Solution NMR spectroscopy suggested a low-symmetry complex in which the monoazabutadiene and the two imido ligands were conserved.

Crystals suitable for X-ray diffraction (XRD) were obtained from hexanes cooled to −40 °C, clarifying coordination of the linear azide to the metal center *via* the γ -nitrogen (Figure 1, left). Complex **3** possesses a distorted trigonal-bipyramidal geometry, similar to that of the previously described bis-imido MAD niobium complexes (see SI). The $TMSN_3$ ligand is located in the apical position with a Nb–N azide bond length (Nb–N4: 2.271(3) Å) comparable to the Nb–N_{py} bond length of the MAD pyridine adduct (Nb–N_{pyridine}: 2.271(3) Å).^{2b} The two short N–N bonds (N4–N5: 1.131(4) Å and N5–N6: 1.208(4) Å) further indicate the presence of an electronically unperturbed azide ligand. This contrasts with known terminal azide complexes of group 5 metals, which have been found to possess formally reduced diazenylimido entities.^{6b,c}

Interestingly, treating $2.OEt_2$ with tBuN_3 at room temperature for 15 min resulted in a different color change (from orange to dark brown), and dark red crystals of **4** were obtained in 65% yield by directly cooling the reaction solution to −40 °C overnight (Scheme 1). 1D and 2D NMR spectra measured at −22 °C revealed the presence of one compound with two different N^tBu moieties (1.39 and 1.26 ppm in the 1H NMR spectrum), in which the MAD ligand remained unchanged. The restricted rotation about both N–Ar bonds (4 different methine and 8 methyl groups in 1H NMR spectrum) provided an indirect hint that the arylimido moiety was incorporated into a cyclic structure. XRD revealed the formation of a rare example of an early transition metal tetraazametallacyclopentene complex, formed by [3 + 2] cycloaddition to one imido group (see Figure 1, right).^{6e,8} Complex **4** possesses two Nb–N bond distances consistent with the description of the corresponding ligands as amido groups (Nb–N2: 2.106(4) and Nb–N4: 2.069(4) Å), along with two N–N single (N4–N5:

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Scheme 1

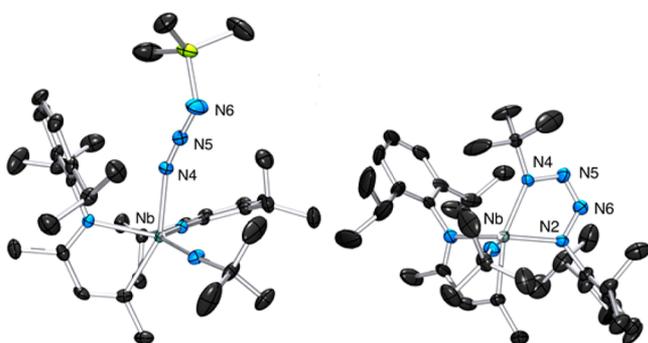
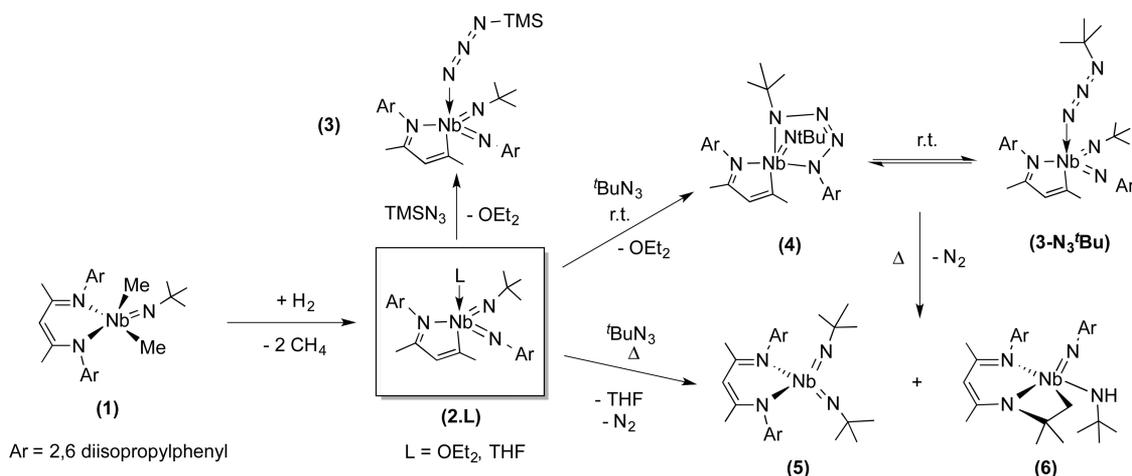


Figure 1. ORTEP diagrams of complexes **3** (left) and **4** (right). H atoms have been removed for clarity. Selected bond distances are presented in Table S.3.

1.393(6) Å and N6–N2: 1.388(6) Å) and one N=N double bond (N5–N6: 1.273(6) Å).

An equilibrium reversing the [3 + 2] cycloaddition in **4**, liberating the aryl-imido moiety, was observed *via* a variable temperature ¹H NMR study in toluene (Scheme 1). Starting with **4** at –30 °C and incrementally raising the temperature to +35 °C, we observed a continuous, yet reversible, increase in the concentration of a second compound **3-N₃^tBu**. Comparing the ¹H NMR profile of **3-N₃^tBu** to that of (MAD)Nb(N^tBu)(NAr)(N₃TMS) **3**, along with similar solution IR fingerprints (see SI), prompted us to assign **3-N₃^tBu** as a γ -coordinated ^tBuN₃ species. Further evidence for the proposed equilibrium between **4** and **3-N₃^tBu** was provided through a ¹H,¹H EXSY experiment and DFT calculation (see SI). A van't Hoff plot ($K_{eq} = [4]/[3-N_3^tBu]$) allowed the determination of thermodynamic parameters $\Delta H^\circ = -10.2 \pm 0.4$ kcal/mol and $\Delta S^\circ = -32.5 \pm 1.5$ cal/mol·K; see SI). The large negative reaction entropy might be explained by the loss of rotational degrees of freedom around the N–Ar bond in the tetrazene complex **4**. Interestingly, variable temperature experiments with **3** provided no evidence for a related equilibrium process. DFT calculations reveal that a putative tetrazine complex with TMSN₃ is significantly less thermodynamically stable than the γ -adduct and also requires a more energetically demanding transition state (see SI).

Surprisingly, unlike the intractable mixture obtained with **3**, when the mixture (**4**)/(**3-N₃^tBu**) was warmed to a temperature higher than +35 °C, the fast, clean, and irreversible formation of

two new compounds, **5** and **6**, in a ratio of 85:15 (based on ¹H NMR spectroscopy), was observed (Scheme 1). The same product mixture was obtained by directly treating **2.L** (L = THF or Et₂O); however, their respective ratios were dependent on both the azide concentration and temperature. Complex **5** was formed as the major product when an excess of ^tBuN₃ and moderate heating ($T = 60$ °C) were employed. Crystallization from HMDSO at –40 °C allowed isolation of the major species, **5**, in 42% yield. NMR spectroscopy and an XRD study clearly confirmed the formation of (BDI)Nb(N^tBu)₂ (**5**) (Figure 2, left). Complex **5** is an example of a rare four-

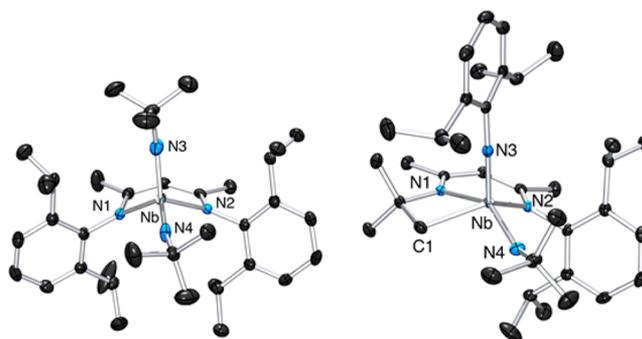
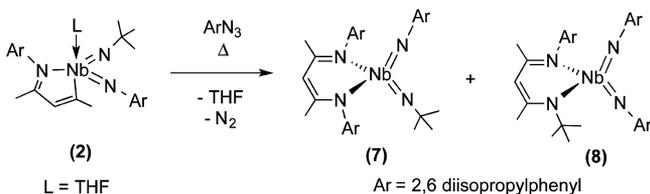


Figure 2. ORTEP diagram of complexes **5** (left) and **6** (right). H atoms have been removed for clarity. Selected bond distances are presented in Table S.4.

coordinate bis-imido niobium complex, exhibiting a pseudotetrahedral geometry in which both imides are structurally equivalent (Nb–N_{av}: 1.81 Å; see SI).⁹ Interestingly, a change in selectivity resulting in the exclusive formation of **6** was achieved when a more dilute solution of ^tBuN₃ (0.1 M) was slowly added to the THF adduct **2** at 70 °C. The identity of **6** was unequivocally assigned based on NMR analysis and X-ray crystallography (72% yield). Thus both metal-bonded imido groups are able to participate in the reformation of differently substituted nacnac species. The anticipated highly reactive nature of a four-coordinate bis-imido complex is reflected in the cyclometalation of the *tert*-butyl imino group of the newly formed nacnac ligand (Figure 2, right), in which C–H bond activation is found to occur exclusively across the presumably more basic Nb=N^tBu bond.

Treating **2**.THF with a slight excess of ArN₃ (1.6 equiv, Ar = 2,6-diisopropylbenzene) at 55 °C in benzene led to similar but slower (24 h) reactivity, compared with that of the alkyl azide. Two new niobium compounds **7** and **8** were formed selectively in a 1/1 ratio (Scheme 2). Complex **7** was crystallized from

Scheme 2

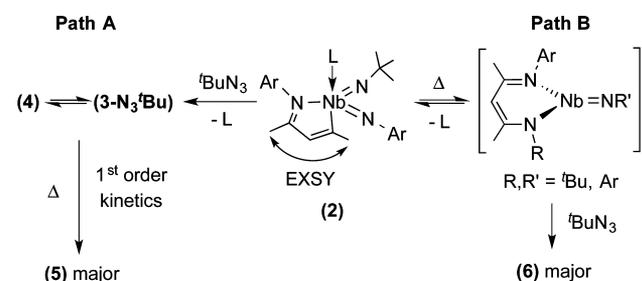


pentane at -40 °C (32% yield), and **8** was recrystallized from a THF/hexanes mixture at -40 °C (30% yield). Both were analyzed by NMR spectroscopy and X-ray diffraction (see SI).¹⁰ The crystal structures of **7** and **8** provide two further examples of four-coordinate, tetrahedral bis-imido niobium complexes in which the resulting Nb–N imido bond distances are comparable to those previously reported for BDI niobium imido complexes (see SI; Nb–N_{av}: 1.82 Å).^{2a,b} We expect this reaction, demonstrated for ArN₃ and ^tBuN₃, to be generalizable to other organic 1,3-dipolar compounds.

Intrigued by the different reaction conditions changing the selectivity of **5/6**, we undertook a preliminary mechanistic study of this unexpected nitrene-transfer reaction. We were able to gain further insight by monitoring the disappearance of the azide complexes **4** and **3-N₃^tBu** by means of ¹H NMR spectroscopy at 55 °C. Under these conditions, in which the regioisomer **5** is favored, the disappearance of (**4**)/(**3-N₃^tBu**) follows exponential decay, and no dependence of the calculated rate constant on the initial concentration was observed, suggesting a first order formation of **5** and **6**, consistent with an intramolecular transformation. However, starting from **2**.THF, with a substoichiometric amount of azide and at a higher temperature (70 °C), we observed the selective formation of **6**, suggesting a different reaction pathway. A ¹H,¹H EXSY experiment performed on a C₇D₈ solution of **2**.THF at 100 °C (see SI) revealed the chemical exchange of the MAD backbone methyl groups together with broadening and coalescence of the associated THF signals. Such a chemical exchange suggests that a slow and reversible reformation of nacnac ligands occurs even in the absence of azide. DFT calculations predict an activation barrier that is rather high, yet accessible at elevated temperature (see SI).

Thus, we believe that two different pathways (Scheme 3, Path A and B), involving distinct d² niobium intermediates, are involved in the reformation of nacnac ligands and azide

Scheme 3



activation. We further suggest, as the origin of the observed selectivity, the involvement of either (a) five-coordinate niobium(V) bis(imides), supported *via* first order kinetics (*vide infra*), favoring **5** (Scheme 3, Path A), or (b) a 3-fold coordinated d² niobium(III) mono(imide), supported *via* ¹H,¹H EXSY NMR and DFT calculations, favoring **6** (Scheme 3, Path B). Finally, each path is highly dependent on azide concentration: excess azide promotes the formation of (**4**)/(**3-N₃^tBu**) and favors pathway A, while a substoichiometric amount of azide promotes pathway B.

Further studies providing more details of this unusual azide activation mechanism/nacnac reformation will be addressed in a full account.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, analytical data, NMR spectra, crystals data, Cif files for complexes **2**.OEt₂, **3**, **4**, **5**, **6**, **7**, and **8**; and DFT calculations method and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

arnold@berkeley.edu

Notes

The authors declare no competing financial interest.

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(9) We additionally reported the preparation of the Lewis base adduct (BDI)Nb(py)(N^tBu)₂ using a different synthetic route. Notably, attempts to generate the 4-fold coordinated bis(imido) complex through abstracting pyridine with B(C₆F₅)₃ in benzene resulted in the fast formation of a tautomeric form BDI[#]Nb(N^tBu)-(NH^tBu) (BDI[#] = H₂C=C(NAr)CH=C(NAr)Me) through C–H activation of the ligand backbone.^{2a} Similar transformations in related BDI systems were previously observed: (a) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (b) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003. (c) Meltzer, A.; Inoue, S.; Praesang, C.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038.

(10) 1D and 2D NMR, along with IR and MS, analysis revealed a 2:1 cocrystallization of **8** together with diisopropylaryl diazene ArN=NAr (see SI). A control experiment confirmed the necessity of niobium compounds to participate in the diazene formation. This transformation is currently under further investigation.