

Nitrene Metathesis and Catalytic Nitrene Transfer Promoted by Niobium Bis(imido) Complexes

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Supporting Information

ABSTRACT: We report a metathesis reaction in which a nitrene fragment from an isocyanide ligand is exchanged with a nitrene fragment of an imido ligand in a series of niobium bis(imido) complexes. One of these bis(imido) complexes also promotes nitrene transfer to catalytically generate asymmetric dialkylcarbodiimides from azides and isocyanides in a process involving the Nb(V)/Nb(III) redox couple.

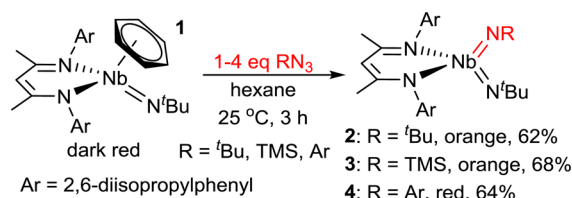
Since the initial discovery of C–H activations and cycloadditions across terminal zirconium imido π bonds in 1988,¹ a number of nitrene transfer processes involving reactions across metal–nitrogen multiple bonds, especially those in high-valent group 4 complexes, have been explored.^{2,3} Many of these systems have been shown to undergo cycloadditions with a variety of unsaturated substrates.^{2–4} This reactivity has been developed into useful catalytic nitrene transfer processes, including hydroaminations^{2,5} and carboaminations⁶ as well as imine⁷ and azide⁸ metatheses. In contrast to group 4 systems, relatively few studies have focused on reactions across imido groups in group 3⁹ and group 5 systems.^{10–12}

In our efforts to design group 5 systems that are reactive across metal–nitrogen multiple bonds, we have been investigating niobium and tantalum imido complexes supported by β -diketiminate (BDI) ligands.¹³ While we have found that the imido group behaves purely as an ancillary ligand for a variety of low- and high-valent mono(imido) derivatives, we hypothesized that the introduction of a second imido moiety could enhance the reactivity of the imido groups. This “ π -loading” effect results from interactions of multiple ligand-based p orbitals with the same metal-based d orbital, causing a net decrease in bonding character of the HOMO.^{12,13b,14} We recently reported a synthetic route to a series of four-coordinate niobium bis(imido) complexes.¹¹ Herein we report the novel stoichiometric and catalytic reactivity of these niobium bis(imido) complexes with alkyl and aryl isonitriles.

Niobium bis(imido) complexes 2–4 were prepared by reaction of the Nb(III) precursor 1 with azides RN₃ (R = 2,6-Dipp, ^tBu, TMS) (Scheme 1). Synthetic procedures for 2–4 and full characterization data for compound 3 are reported in the Supporting Information (SI).

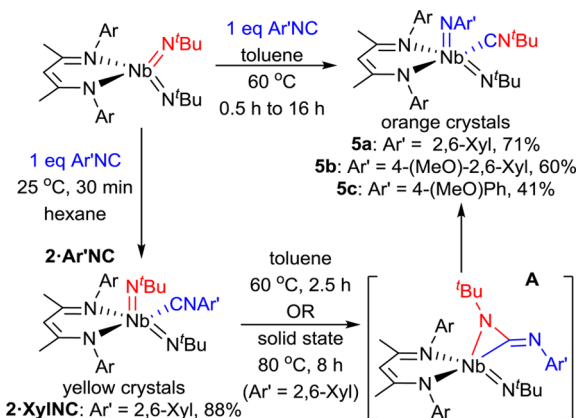
Addition of 2,6-dimethylphenyl isocyanide (XylNC) to a solution of 2 resulted in slight lightening of the color of the orange solution; ¹H NMR spectroscopic and crystallographic analysis of the yellow crystals obtained from this reaction were consistent with isocyanide adduct 2·XylINC (see the SI). Upon

Scheme 1



heating to 60 °C for 2.5 h, a yellow solution of 2·XylINC in toluene underwent a color change to give an orange solution from which bright-orange crystals were isolated. NMR spectroscopic and crystallographic data indicated clean conversion to 5a, in which the nitrene fragments from one *tert*-butylimido group and the coordinated isonitrile were exchanged to generate a complex containing a thermodynamically favored aryl(imido) ligand with coordinated ^tBuNC (Scheme 2). The X-

Scheme 2



ray crystal structure of 5a (Figure 1, left) showed a geometry intermediate between trigonal-bipyramidal and square-pyramidal ($\tau = 0.41$);¹⁵ a similar geometry was observed for 2·XylINC ($\tau = 0.47$; see the SI). Notably, clean conversion of 2·XylINC to 5a was also observed when solid 2·XylINC was heated to 80 °C for 8 h. While reactions of early transition metal imido complexes with isocyanides across imido groups have been documented in the literature, these reactions typically lead to either coupling of multiple equivalents of isocyanide after addition,^{4c,e} formation of η^2 -carbodiimide complexes,^{4a} or production of carbodiimide.^{4g,16}

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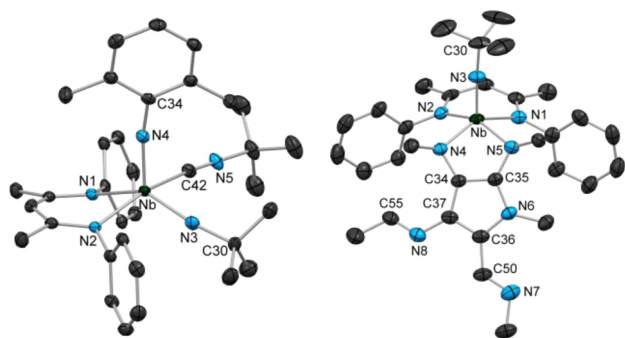


Figure 1. Molecular structures of (left) **5a** and (right) **8** determined by X-ray diffraction. H atoms and aryl ¹Pr groups have been omitted and *n*-alkyl groups have been truncated for clarity; thermal ellipsoids are displayed at the 50% probability level.

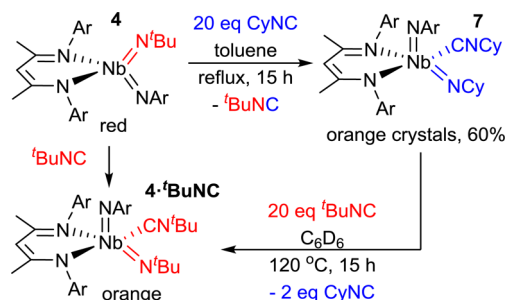
To our knowledge, the conversion of **2** to **5** is the first example in which the nitrene fragments are simply exchanged to generate a new imido group and a new isocyanide. Hence, this represents a new method for both incorporation of imido moieties into metal complexes and integration of various substituents into isonitriles.

Although it still contained a basic *tert*-butylimido group, **5a** was much less reactive toward nitrene metathesis than **2**; addition of a second equivalent of XylNC to **5a** resulted in the establishment of an equilibrium between ^tBuNC and XylNC adducts, but heating to 120 °C for 8 h was required to exchange the remaining *tert*-butylimido group, generating 1 equiv of free ^tBuNC and a new niobium compound identified as BDINb(NXyl)₂CN^tBu (**6**) by ¹H and ¹³C NMR spectroscopy.

Compound **2** reacted with 4-methoxy-substituted aryl isocyanides to give compounds **5b** and **5c**, as shown in Scheme 2. Formation of **5b** proceeded much more slowly than formation of **5a**; addition of 4-methoxy-2,6-dimethylphenyl isocyanide (MeOXylNC) to a solution of **2** again resulted in the immediate formation of the adduct **2·MeOXylNC**, but heating to 60 °C for 16 h was needed to observe 95% conversion to **5b** by ¹H NMR spectroscopy. In contrast, **2·XylNC** underwent 95% conversion to **5a** after heating to 60 °C for 2 h. This observation can be rationalized by the fact that the donating 4-methoxy substituent increases the electron density at the isocyanide carbon, making it a less electrophilic target for nucleophilic attack by an imido moiety. Conversely, the formation of **5c** proceeded significantly faster than the formation of either **5a** or **5b** (>95% conversion within 0.5 h at 60 °C), indicating that (a) the rate-determining transition state is relatively sterically encumbered compared with the starting isocyanide adduct and (b) reducing the steric profile of the isocyanide by eliminating the *o*-methyl substituents has a more pronounced effect on the reaction rate than adding a donating *p*-methoxy substituent.

While no evidence of nitrene metathesis was observed from reactions of alkyl-substituted isocyanides with **2** (see below), the mixed aryl/alkyl bis(imido) complex **4** reacted with alkyl isocyanides to generate ^tBuNC and exchange the alkyl substituent into the imido position. The reaction with cyclohexyl isocyanide (CyNC) was particularly clean, and compound **7** was isolated after heating of a solution of **4** in refluxing toluene in the presence of excess CyNC for 15 h (Scheme 3). Heating of isolated **7** to 120 °C in the presence of excess ^tBuNC resulted in conversion to **4·^tBuNC**, which was identified by ¹H NMR spectroscopy and prepared independently from coordination of ^tBuNC to **4**. Interestingly, during the course of this reaction, a significant amount of ^tBuNC was isomerized to unreactive

Scheme 3



^tBuCN, hampering the conversion of **7** to **4·^tBuNC**. This isomerization did not occur in the absence of the niobium complex, indicating that it likely was metal-catalyzed; limited examples of this metal-catalyzed process exist in the literature.¹⁷

While reactions with **3** were not explored in as much detail because of a lack of selectivity between reactions across TMS and ^tBu imido groups leading to mixtures of products, **3** did react with a large excess of ^tBuNC upon heating to 120 °C for 15 h to give **2·^tBuNC**. In this case, isomerization of ^tBuNC to ^tBuCN was also observed, halting the reaction to give **2·^tBuNC** after ~60% conversion.

DFT calculations provide support for the proposed mechanistic pathway shown in Figure 2. Coordinated isocyanide first

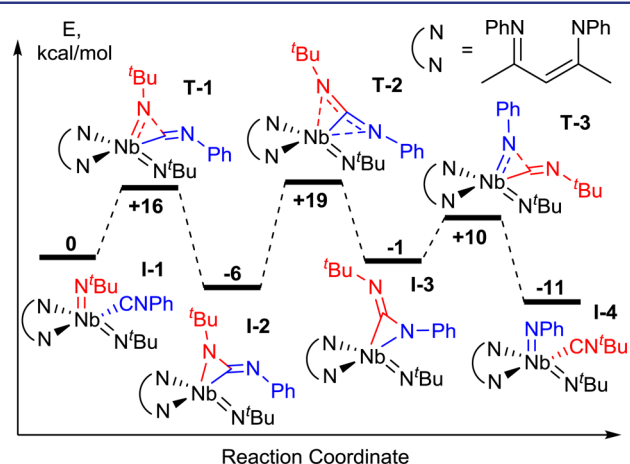


Figure 2. DFT-calculated energy profile for nitrene metathesis.

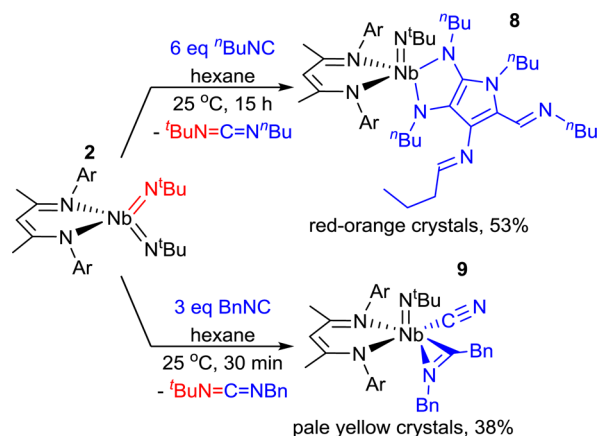
adds across an imido moiety in **I-1** to give η^2 -carbodiimide intermediate **I-2**, which has precedent in the literature.^{4a,g,16} The lowest-energy pathway found for the following step involves passage through the nearly linear η^3 -carbodiimide transition state **T-2** to give **I-3**, which then proceeds to give the thermodynamically favored product **I-4** by the reverse of the first step. While the highest-energy transition state **T-2** is 25 kcal/mol higher in energy than intermediate **I-2**, it is not unreasonable that this process could proceed readily at 60 °C. In fact, neither intermediate **I-2** nor **I-3** was observed experimentally when the reaction was followed by ¹H NMR spectroscopy, indicating that they are likely higher in energy than the calculated values relative to **I-1**. Diisopropylphenyl substituents were modeled as phenyl substituents in the calculations, so this discrepancy is not surprising, as **I-2** and **I-3** are much more prone to steric clashing with BDI aryl groups than **I-1** since the imido and isocyanide substituents of **I-1** are nearly 180° from the metal center. Calculated reaction pathways for analogues incorporating 4-

MeOPh and 2,6-Xyl isocyanide substituents are shown in Figures S10 and S11, respectively, and are consistent with the experimentally observed influence of the electron-donating ability and steric bulk of the isocyanide aryl substituent on the reaction rate (see above).

Reaction of **2** with primary alkyl isocyanides AkNC (Ak = ⁿBu, Bn) resulted in color changes to red-brown solutions. In both cases, conversion to a single major metal-containing product was observed by ¹H NMR spectroscopy within 12 h for Ak = ⁿBu or within 20 min for Ak = Bn. In contrast to reactions with aryl isocyanides, both reactions proceeded at room temperature without any generation of ^tBuNC; instead, in each case generation of 1 equiv of the organic product AkN=C=N^tBu was observed.

Remarkably, compound **2** reacted with 6 equiv of ⁿBuNC to release 1 equiv of ⁿBuN=C=N^tBu and give compound **8** as a red-orange microcrystalline material in 53% yield (Scheme 4).

Scheme 4



The reaction to give **8** involved the formation of four new C–C bonds and a C–N bond to generate a heavily substituted κ^2 -N,N-pyrrolediamido ligand. The solid-state structure (Figure 1, right) shows a distorted square-pyramidal geometry ($\tau = 0.1$) with the imido moiety in the apical position. A plausible reaction mechanism for the formation of **8** is shown in Scheme S1. While related couplings of isocyanides by reduced metal centers have been observed,¹⁸ to our knowledge this is the first example of the formation of a pyrrolediamido transition metal complex.

A related reaction occurred between **2** and 3 equiv of benzyl isocyanide (BnNC) to give **9**, which precipitated from the reaction mixture within minutes as pale-yellow needles (Scheme 4). In **9**, a benzyl group was transferred from one equivalent of isocyanide to another to give a C-bound terminal cyanide ligand and an η^2 -iminoacyl ligand.

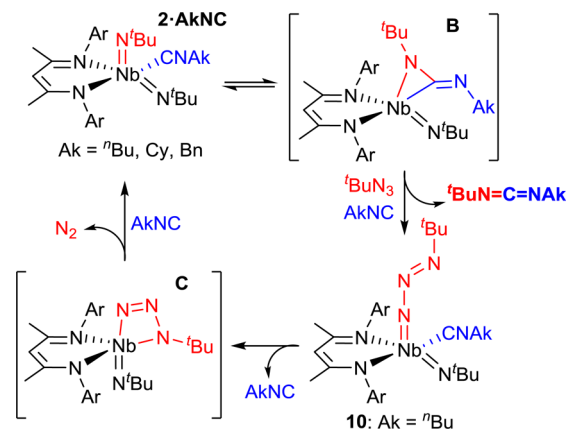
Several pieces of experimental evidence support that these reactions proceeded through Nb(III) intermediates. First, the same products **8** and **9** were observed from the reactions of Nb(III) complex **1** with either 5 equiv of ⁿBuNC or 2 equiv of BnNC. Second, addition of 1 equiv of BnNC to **2** to give **2**·BnNC followed by addition of 3 equiv of XylNC resulted in an immediate color change to green-blue, and the ¹H NMR spectrum was consistent with the formation of the reported Nb(III) complex BDINb(N^tBu)(CNXyl)₃.^{12c}

On the basis of these results, it seemed possible that the Nb(III) intermediate generated in these reactions could be trapped by an azide to regenerate the four-coordinate bis(imido)

starting material, thus rendering the formation of carbodiimide catalytic. In fact, within seconds at room temperature, addition of excess ^tBuN₃ to a solution of **2**·BnNC resulted in a color change from yellow-orange to orange, consistent with conversion to the four-coordinate bis(imido) complex **2**. Conversion to **2** and production of BnN=C=N^tBu were confirmed by ¹H NMR spectroscopy and GC–MS. Similarly, generation of **2** and the corresponding carbodiimides was observed after excess ^tBuN₃ was added to **2**·ⁿBuNC or **2**·CyNC, although the reaction with **2**·ⁿBuNC only proceeded within 12 h at room temperature and the reaction with **2**·CyNC required heating at 60 °C for 15 h to go to completion. No formation of carbodiimide was observed with ^tBuNC even at temperatures up to 120 °C. Catalytic reactions were carried out in J. Young valve NMR tubes using mixtures of C₆D₆ and ^tBuN₃ as the solvent, and the conversion to carbodiimide was followed by ¹H NMR spectroscopy; higher turnover numbers were observed when the catalytic reactions were carried out in the presence of a large excess (~200 equiv) of ^tBuN₃. Up to 17 turnovers (6% catalyst loading) were observed for Ak = Cy (20 h at 80 °C) before complete catalyst degradation, while lower turnover numbers (5–8) were observed for Ak = Bn and Ak = ⁿBu.

The catalytic reactions likely proceeded via the mechanism outlined in Scheme 5. Notably, buildup of an intermediate was

Scheme 5



observed by ¹H NMR spectroscopy under the catalytic conditions. The intermediate was especially prominent for Ak = ⁿBu; in fact, when a solution containing **2**·ⁿBuNC, 4 additional equiv of ⁿBuNC, and 20 equiv of ^tBuN₃ was left at room temperature for 16 h, complete conversion of **2**·ⁿBuNC to this new species was observed. The product of this reaction was isolated and identified by X-ray crystallography and NMR spectroscopy as the terminal (*tert*-butylazido)niobium complex **10**. This represents the first characterized example of a terminal (organoazido)niobium complex, but sparse examples of other terminal (organoazido)metal species exist in the literature.¹⁹ In one notable example,^{19c} detailed mechanistic studies showed that a related (phenylazido)tantalum complex is an intermediate species in nitrene transfer from an azide to a low-valent tantalum center and that nitrene transfer to generate an imido group and release N₂ goes through a four-center intermediate analogous to **C**. Similarly, isolated **10** slowly converts to **2**·ⁿBuNC and N₂ in solution and is also a competent catalyst for carbodiimide formation.

While a handful of mid and late transition metal catalysts for this transformation have been reported,²⁰ this represents only

the second example of catalytic carbodiimide formation mediated by an early transition metal complex.¹⁶ In the previous example, the Zr center remained in its more stable Zr(IV) oxidation state throughout the cycle, while two-electron redox changes were mediated by a redox-active ligand. In the present case, the energy difference between high-valent Nb(V) and low-valent Nb(III) is small enough that reductive elimination of η^2 -carbodiimide occurs readily in the presence of either an alkyl azide or excess isocyanide. As demonstrated here and in our previous work,^{13e,f} a niobium center with a suitable ligand environment can both give access to the unique reactivity observed for early transition metal complexes and allow cycling between Nb(III) and Nb(V) in catalytic processes.

To summarize, we have discovered a novel nitrene exchange process in which a substituent is exchanged between an alkylimido group in a Nb(V) bis(imido) complex and an aryl isocyanide. The reaction likely proceeds through cycloaddition and cycloreversion involving Nb(V) η^2 -carbodiimide intermediates and occurs at a single metal center without elimination of carbodiimide. In contrast, reaction with unhindered alkyl isocyanides resulted in extrusion of carbodiimide, a process that was rendered catalytic in the presence of excess azide. Further exploration of the scope and mechanism of the stoichiometric and catalytic nitrene transfer processes is ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11287.

Proposed mechanism for the formation of **8**, experimental procedures, analytical data, crystal data, DFT methods and results, and NMR data (PDF)

CIF files for **2**·XylNC, **3**, **5a**, **5c**, **7**, **8**, **9**, and **10** (ZIP)

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Notes

The authors declare no competing financial interest.

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