

Addition-Elimination Reactions across the M–C Bond of Metal N-Heterocyclic Carbenes

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In homogeneous catalysis the lanthanides and actinides are characterized by their facile bond activation reactions that proceed through a four-centered σ -bond metathesis mechanism rather than a conventional two-electron oxidative addition–reductive elimination pathway.¹ Indeed, the first example of methane activation was observed in the reaction between Cp^*YCH_3 ($\text{Cp}^* = \text{C}_5\text{Me}_5$) and $^{13}\text{CH}_4$ which results in the interchange of labeled $\text{Y}-^{13}\text{CH}_3$ and unlabeled $\text{Y}-^{12}\text{CH}_3$ groups.² Attractive transformations based on the σ -bond metathesis reactivity can be envisaged if turnover could be achieved, but these systems are limited by the absence of further functionality or valence electrons.³ Organo-f-block systems (i.e., alkyls, hydrides, and amido compounds) are excellent catalysts for the hydroamination, phosphination, alkoxylation, and silylation of alkenes⁴ but rely on σ -bond metathesis mechanisms solely to exchange substrate and product.

In contrast, the ready availability of controlled two-electron redox processes in the platinum group metals provides a platform for a vast array of catalyzed reactions. N-Heterocyclic carbenes (NHCs) are now used widely as ancillary ligands for supporting these metal cations;⁵ while generally innocent, alkylated compounds can be destroyed by reductive elimination processes, for example *cis*- $\text{PdMe}(\text{NHC})_2$ complexes can eliminate 2-alkyl imidazolium salts, forming palladium black.⁶

Herein, we show how NHCs can be used as reactive ligands to allow further chemistry to be accessed for redox inactive metals: The addition of reagents across the neutral metal–carbon dative bond in d^0 Group 3 and f-block metal NHC complexes, in a reversible manner, allows additional functional groups such as silanes, phosphines, stannanes and boranes to be incorporated into compounds that are active for σ -bond metathesis chemistry.

We recently described the synthesis of $d^0 \text{Ln}^{\text{III}} \text{Y}(\text{L})\text{N}''_2$ and $\text{U}^{\text{VI}} \text{UO}_2(\text{L})_2$ complexes of robust alkoxy-N-heterocyclic carbene ligands L in which the carbene backbone is saturated ($\text{N}'' = \text{N}(\text{SiMe}_3)_2$, $\text{L} = \text{OCMe}_2\text{CH}_2\{\text{C}(\text{NCH}_2\text{CH}_2\text{NR})\}$; $\text{R} = \text{Pr}$, Mes ($= 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$), Dipp ($= 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$)).⁷ This obviates the potential for “abnormal”-type reactions of the backbone C–H protons, which are relatively acidic in the unsaturated carbene.⁸ Furthermore, the tethering of the carbene to the anionic group prevents its loss, allowing the reactivity of this nucleophilic heterocycle to be incorporated into the reaction chemistry of the f-element complex.

Bright yellow $\text{Ce}(\text{L}^{\text{D}})\text{N}''_2$ and dark blue $\text{U}(\text{L}^{\text{D}})\text{N}''_2$ can be made from CeN''_3 or UN''_3 by analogous protonolysis reactions to those that made $\text{Y}(\text{L})\text{N}''_2$ by treatment with an equivalent of HL^{D} ($\text{D} = \text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3$) in toluene or hexanes respectively at room temperature. All three derivatives were isolated in good yield as hydrocarbon-soluble crystalline solids. A single crystal X-ray

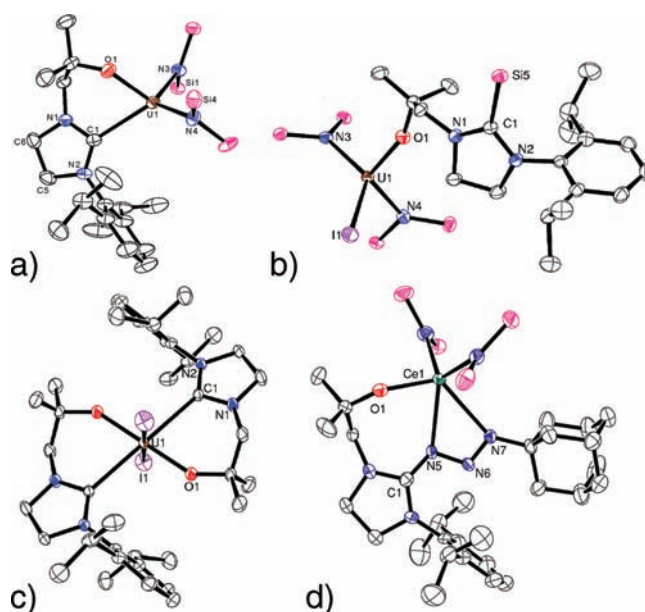
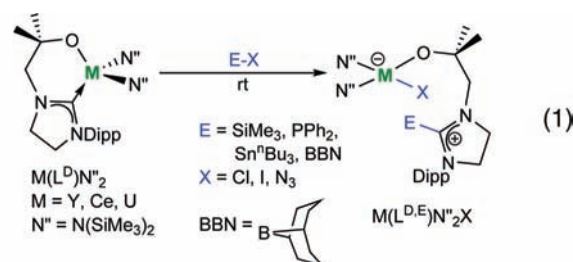


Figure 1. Thermal displacement drawings (50% probability ellipsoids) of the molecular structures of (a) $\text{U}(\text{L}^{\text{D}})\text{N}''_2$, (b) $\text{U}(\text{L}^{\text{D,Si}^i})\text{N}''_2\text{I}$, (c) $\text{U}(\text{L}^{\text{D}})_2\text{I}_2$, and (d) $\text{Ce}(\text{L}^{\text{D,AdN}_3})\text{N}''_2$.

diffraction study of the *N*-Dipp complex $\text{U}(\text{L}^{\text{D}})\text{N}''_2$, Figure 1a, confirms the molecular structure. Distances and angles are within literature ranges for low-coordinate U^{III} complexes.

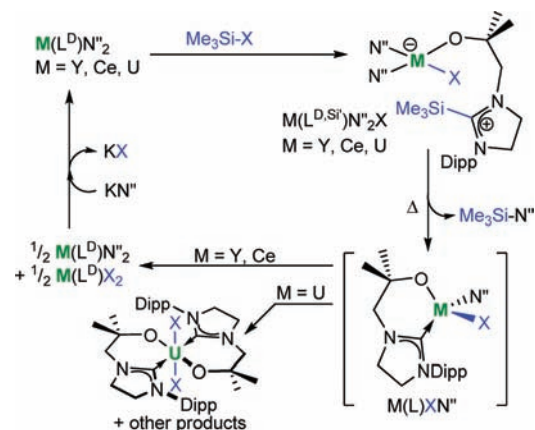


Treatment of a solution of any of the complexes $\text{M}(\text{L}^{\text{D}})\text{N}''_2$ ($\text{M} = \text{Y}$, Ce , U) with 1 equiv of Me_3SiI in benzene or toluene at room temperature immediately produces a colorless (Y), pale yellow (Ce), or dark brown (U) solution. In each case, a complex formulated as $[\text{Me}_3\text{Si}\{\text{C}(\text{NDippCH}_2\text{CH}_2\text{N})\}\text{CH}_2\text{CMe}_2\text{O}\{\text{M}\}\text{N}''_2\text{I}$, denoted $\text{M}(\text{L}^{\text{D}})\text{N}''_2\text{I}$, is isolated in good yield. This reaction can formally be seen as the addition of the silyl halide across the metal–carbene bond, forming the metal iodide *bis*(amido) alkoxide with a pendant silylated imidazolium group, eq 1. The addition reaction is equally facile for Me_3SiCl or Me_3SiN_3 and can be further generalized since the group added to the carbene carbon can also be varied. The use

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Scheme 1. Addition–Elimination Cycles of Reactivity for d^0 Metal Carbene Complexes with $\text{Me}_3\text{Si-X}$ ($\text{X} = \text{Cl, I, N}_3$), $\text{Si}^+ = \text{SiMe}_3$



of halophosphines, boranes, and stannanes allows the formation of C–P, C–B, and C–Sn containing substrates, with the metal *pseudohalide* bond providing a significant driving force for the reaction.

Once formed, all these addition complexes are stable at ambient temperature (for characterization, see Supporting Information). The complexes are less soluble than the parent amido complexes, but readily crystallize, allowing the isolation of pure materials and characterization by X-ray diffraction; the molecular structure of the trivalent uranium imidazolium iodide $\text{U}(\text{L}^{\text{D,E}})\text{N}''_2\text{I}$ is shown in Figure 1b.

Heating a benzene solution of the Y or Ce addition products $\text{M}(\text{L}^{\text{D,E}})\text{N}''_2\text{X}$ ($\text{E} = \text{SiMe}_3$) (the metal complexes that are not readily oxidizable) results in the elimination of *tris*(trimethylsilyl)amine N'''' (identified by GC) and the reformation of the metal carbene bond in $\text{M}(\text{L}^{\text{D}})\text{XN}''$, Scheme 1. This mixed ligand complex rearranges to a 50:50 mixture of the starting material $\text{M}(\text{L}^{\text{D}})\text{N}''_2$ and $\text{M}(\text{L}^{\text{D}})\text{X}_2$, which can be converted to the starting material by a salt metathesis reaction with 1 equiv of KN'' .

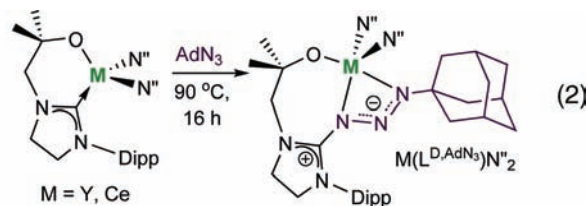
The reversibility of the addition–elimination of substrates across the metal–carbene bond is effective for the range of substrates tried so far; thus silyl, phosphinyl, boryl, and stannyl groups can be incorporated into σ -bound lanthanide or actinide ligands.

In the uranium complex, the metal carbene bond is also reformed, but the resulting halide complex undergoes a rearrangement to the thermodynamically more stable, pink U^{IV} complex $\text{U}(\text{L}^{\text{D}})_2\text{X}_2$, whose poor solubility makes the isolation and structural characterization of this complex straightforward, Figure 1c. In the solid state structure, the uranium(IV) cation is *pseudooctahedral* with two *trans*-iodide ligands and the two bidentate OC ligands also *trans*-disposed. The bond distances are within the ranges observed for similar complexes reported in the literature. The other uranium-containing byproducts could not be identified.

In the reaction to insert adamantyl azide into the metal–carbene bond of the lanthanide complexes $\text{M}(\text{L}^{\text{D}})\text{N}''_2$ ($\text{M} = \text{Y, Ce}$) the N–C bond is not cleaved, so an unusual insertion product $\text{M}(\text{L}^{\text{D,AdN}_3})\text{N}''_2$ is isolated instead, eq 2. In this, the formerly neutral azide group now binds as a $\kappa^2\text{N}^{1,3}$ triazenido anion to the metal, with a covalent bond formed between the terminal azido nitrogen and the carbene carbon: Charge compensation is achieved by the associated positive charge now on the imidazolium NCN group.

Structural characterization of the complex $\text{Ce}(\text{L}^{\text{D,AdN}_3})\text{N}''_2$ by a single crystal X-ray diffraction study, Figure 1d, confirms the connectivity. Similar insertion chemistry has been observed previ-

ously into organo-f-block complex σ -alkyl bonds, but not into a metal–ligand dative bond.⁹



No evidence of extrusion of N_2 (to form the superbasic imidazolin-iminato group used by Tamm *et al.*¹⁰) was observed upon heating a solution of $\text{Ce}(\text{L}^{\text{D,AdN}_3})\text{N}''_2$ to 80 °C for 24 h.

In recent years, the use of transition metal catalysts has opened up many new possibilities in the area of heteroatom functionalization chemistry such as borylation and phosphination reactions; work is in progress to identify opportunities for these carbene-functionalized organolanthanide systems to incorporate other functional groups or unsaturated molecules into their σ -bond metathesis chemistry, and to develop the potential for a relevant catalytic cycle.¹¹ The potential for the incorporation of the triazenido, arrested insertion intermediate in insertion chemistry and heterocycle syntheses will also be reported on in due course.

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Supporting Information Available: Full experimental details and X-ray crystallographic data (CIFs deposited with the CCDC, codes 759036–759041, and 766364). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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