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Reductive Coupling of Azides Mediated by an Iron(II) Bis(alkoxide) Complex

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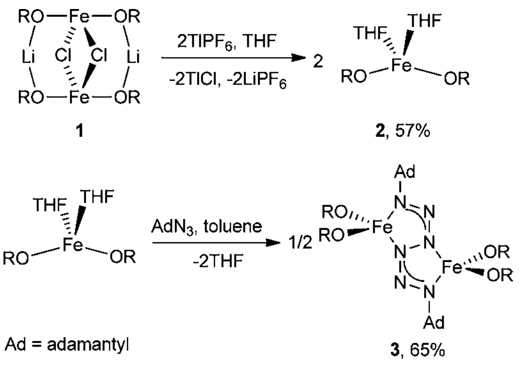
Supporting Information

ABSTRACT: The iron(III) hexazene complex $(RO)_2Fe(\mu\text{-}\kappa^2{:}\kappa^2\text{-}AdN_6Ad)Fe(OR)_2$ (**3**) was synthesized via reductive coupling of 1-azidoadamantane at the iron(II) bis(alkoxide) complex $Fe(OR)_2(THF)_2$ (**2**). The X-ray crystal structure depicts electron delocalization within the hexazene moiety. Density functional theory studies propose the formation of an iron azide dimer on the route to hexazene, in which each azide is monoreduced and the iron centers are oxidized to the 3+ oxidation state.

The reaction of an azide with a low-valent metal center typically results in dinitrogen extrusion, forming a metal imide functionality.[1−8] Transition-metal imido complexes are numerous and have been obtained for virtually all of the transition metals.[3,9] However, two azides may also undergo one-electron reductive coupling, which results in the formation of a metal-bound hexazene dianion, $[RNNNNNNR]^{2-}$. This rather unusual transformation requires strong radical character on the bound azide and has been demonstrated only for strongly reducing iron(I) and magnesium(I) NacNac-ligated systems.[10−12] Herein we demonstrate that a unique iron(II) bis(alkoxide) system reductively couples azides to form hexazene. We also shed light on a possible reaction mechanism for this transformation.

We are investigating the reactivity of low-coordinate first-row transition-metal complexes ligated by bulky alkoxide ligands in the activation of strong bonds. Alkoxide ligands are attractive candidates for the design of low-coordinate electronically unsaturated complexes: their strong ionic bonding to the early and middle first-row transition metals is reinforced by π donation.[13−15] Several three-coordinate metal complexes ligated by bulky alkoxides (or by the related siloxides and aryloxides) have been previously demonstrated to bind and activate inert substrates.[16−22] In contrast, much less work has been devoted toward the design and reactivity of two-coordinate bis(alkoxide) complexes.[23−25] To access first-row complexes featuring bis(alkoxide) ligation, we have recently introduced a new bulky alkoxide $[OC^tBu_2Ph]$ ([OR] henceforth). As expected, the reaction of 2 equiv of LiOR with MCl_2 selectively incorporates two alkoxides at each transition metal, forming unusual clusters of the general form $M_2Li_2Cl_2(OR)_4$ (M = Cr−Co) with a seesaw geometry at the transition-metal centers.[26] Next, we treated these clusters with 2 equiv of thallium(I) hexafluorophosphate to remove the incorporated lithium chloride. The addition of $TlPF_6$ to the iron(II) dimer **1** led to formation of the bis(alkoxide) complex $Fe(OR)_2(THF)_2$ (**2**), which was recrystallized from hexane in 57% yield (Scheme 1). The crystal structure of **2** (Figure 1) reveals a distorted tetrahedral geometry at the iron center, with an O−Fe−O angle of about 139°, indicative of the high steric demand of the alkoxide ligand. We postulated that **2** represents a protected form of a two-coordinate species in which weakly bound THF ligands can be replaced by an incoming substrate. Somewhat related complexes have been previously

Scheme 1. Synthesis of Iron(II) Bis(alkoxide) Complex and Its Reaction with Adamantyl Azide



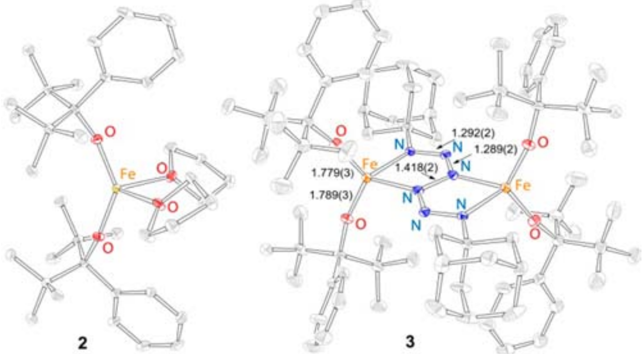


Figure 1. Crystal structures of **2** and **3**, with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Important bond lengths for **3** are indicated.

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synthesized.[23,27−30] However, their reactivity has not been explored.

The addition of 1 equiv of 1-azidoadamantane to the iron bis(alkoxide) complex **2** in toluene led to a gradual color change to dark orange over the course of a few minutes. Crystallization from hexane afforded the unusual product **3** as dark-orange crystals in 65% yield. The crystal structure reveals that complex **3** is $(RO)_2Fe(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}AdN_6Ad)Fe(OR)_2$, with two azides reductively coupled through the terminal nitrogen atoms (Figure 1). The diiron−hexazene core is essentially planar, with each iron center displaying a distorted tetrahedral geometry. The internal azide bond distances are about 1.29 Å, indicative of bond lengths between single and double bonds. This shows that electron delocalization is present in the azide moieties. The distance between the two coupled azides is lengthened by about 0.1 Å and is more akin to a N−N single bond. The Fe−O bond lengths are comparable to those in similar iron alkoxide complexes possessing iron(III).[28,31,32] The Fe−O bonds are also noticeably shorter in the hexazene complex compared to those in the bis(alkoxide) complex **2**. This suggests the presence of iron(III). The ^1H NMR spectrum of **3** failed to provide any meaningful data toward its characterization. The magnetic moment of **3** in solution (11.2 μB) is consistent with two uncoupled iron(III) centers. This complex is similar to the iron(II) hexazene complex previously synthesized by Holland and co-workers.[10] However, Holland and co-workers have obtained their hexazene complex starting from an iron(I) starting material, while ours was derived from the significantly less reducing iron(II).

To gain insight into the electronic structure of **3**, we turned to density functional theory (DFT) calculations[33−36] on a model system with methyl azide and methoxide ligands. Despite these simplifications, excellent agreement is seen for the hexazene bond lengths (Figure 2, left)[37] in the lowest-energy spin state.[38] This structure had 10 unpaired electrons ($S = 5$) with 5 singly occupied molecular orbitals on each iron center (see Figure S5 in the Supporting Information, SI), implying $^{HS}Fe^{III}$ ions and a dianionic hexazene ligand. This conclusion is similar to that for previously reported dimetallic hexazene compounds.[10,11] The azide is not reduced upon binding to the bis(alkoxide)iron(II) fragment like it was for $(NacNac)Fe^{I}$ (see Figure S6 in the SI). However, dimer formation (Figure 2, right) results in a $S = 4$ species that has two $^{HS}Fe^{III}$ ions antiferromagnetically coupled to the monoreduced, bridging azide radicals (see Figure S7 in the SI). To our knowledge, such a dimer is unprecedented even though bimetallic species with bridging azides (N_3^-) are known.[1] The structure places the terminal nitrogen atoms in close proximity for coupling (2.937 Å). Earlier work on $[(NacNac)FeN_3Ad]_2$ suggested that solvent binding was important and may disrupt this dimer formation.[10] Our computed thermodynamics for dimer formation are highly dependent on the functional chosen, but both B3LYP and BLYP suggest that dimerization is enthalpically favored.[39−41] Work is ongoing to find a reaction path between the dimer and hexazene that is complicated by spin surface crossing and may allow for isolation of the proposed dimer intermediate ($\Delta G = -15.0$ kcal/mol for this model).

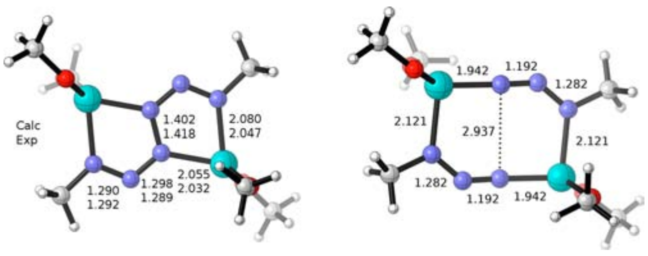

Figure 2. Comparison of computed and experimental bond lengths (Å) for the lowest-energy $S = 5$ state (left) and a putative intermediate prior to reductive coupling (right).

Nitrogen-rich compounds are known to be energetic materials.[42] Therefore, we assessed the potential of the hexazene complex **3** as a primary explosive. The complex did not detonate when subjected to impact, heat, or electrostatic discharge, confirming its stability toward explosive decomposition and its subsequent safe handling.

In summary, we have demonstrated a rare example of the reductive coupling of azide using a low-coordinate iron(II) bis(alkoxide) precursor. Remarkably, the reducing power of an iron(I) species is not required to promote this reductive coupling, which raises provocative questions about how and why azides couple instead of expelling dinitrogen. Studies on the reductive coupling of other substrates by our reactive $Fe(OR)_2$ fragment are currently being pursued.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, procedures for the synthesis of **2** and **3**, X-ray crystallographic details, IR spectra for **2** and **3**, procedure for the Evans method, and additional computational data and details, including Cartesian coordinates for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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