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A Bridging Hexazene (RNNNNNR) Ligand from Reductive Coupling of Azides

Ryan E. Cowley,[†] Jérôme Elhaïk,[†] Nathan A. Eckert,[†] William W. Brennessel,[†]
Eckhard Bill,[‡] and Patrick L. Holland*[†]

Department of Chemistry, University of Rochester, Rochester, New York 14627, and
Max-Planck-Institut für Bioorganische Chemie, D-45470 Mülheim an der Ruhr, Germany

Received February 24, 2008; E-mail: holland@chem.rochester.edu

Hexaaza-1,5-dienes^{1,2} (Figure 1a) are unusual high-energy molecules that are often shock-sensitive. Only two have been crystallographically characterized.³ They decompose thermally and photochemically,⁴ and the products can be triazene and azide,³ *N,C*-disubstituted tetrazoles,⁶ or diazo compounds.⁷ Their oligomers and polymers have also been studied.^{4a,5} Hexaza-1,5-dienes have been synthesized via two routes: *N*–*N* coupling of two aryl diazonium equivalents with a diacylhydrazine,⁶ and coupling of two in situ generated triazenyl radicals.^{2,7} No coordination chemistry of hexaazadienes has been reported. Here we describe iron complexes of the 1,6-bis(1-adamantyl)hexaaza-1,5-dienyl (“hexazene”) ligand (Figure 1b) that show surprising thermal and photolytic stability. In addition to structural and spectroscopic characterization of the complexes, we show that the hexazene ligand mediates magnetic coupling between high-spin metal centers.

We recently reported that the metastable imidoiron(III) complex $L^{\text{Me}}\text{Fe}(\text{NAd})(\text{tBupy})$ ($L^{\text{Me}} = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2]$) can be generated from addition of 1-adamantyl azide (N_3Ad) to an iron(I) source in the presence of *tert*-butylpyridine.^{8,9} However, an analogous reaction in the *absence* of coordinating ligands does not give an imidoiron complex. Thus, addition of 2.0 equiv of N_3Ad to $L^{\text{Me}}\text{FeNNFeL}^{\text{Me}}$ in pentane immediately produces an orange precipitate in 74% yield. The solid is poorly soluble in common solvents, preventing reliable solution characterization. Crystallography reveals that the product is $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$. A similar hexazene complex supported by L^{tBu} ($L^{\text{tBu}} = \text{HC}[\text{C}(\text{tBu})\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2]$) is obtained by reaction of $L^{\text{tBu}}\text{FeNNFeL}^{\text{tBu}}$ with 2.0 equiv of N_3Ad in hexanes at -78°C . The solid-state structures (L^{Me} , Figure 2; L^{tBu} , Figure S-1) show that a new *N*–*N* bond exists between two N_3Ad units, with the resulting AdN_6Ad ligand connected to two four-coordinate Fe centers.

The metrical parameters of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ and $L^{\text{tBu}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{tBu}}$ are similar to one another (Table 1), and so only the L^{Me} complex is discussed in detail here. Each iron atom has a roughly tetrahedral geometry and is bound to both halves of the AdN_6Ad unit and to a diketiminate ligand. There is a crystallographic inversion center between N3 and N3A that renders the two halves of the molecule equivalent. Each FeN_4 metallacycle is planar (maximum deviation from the least-squares N_2C_3 plane is 0.0019(9) Å) and each iron resides out of the diketiminate N_2C_3 plane (0.753(2) Å).

The bond distances within the hexazene unit give insight into the electron localization within the complex. The equivalent N1–N2 and N2–N3A distances are ca. 0.1 Å shorter than the N3–N3A single bond.¹⁰ This is characteristic of π -electron delocalization between N(1), N(2), and N(3A) and thus suggests resonance between allyl-like Lewis

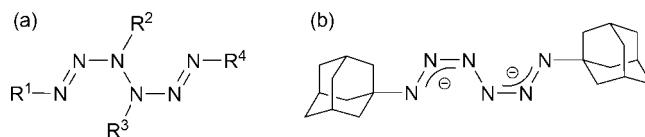


Figure 1. (a) General structure of hexaaza-1,5-dienes. (b) The “hexazene” ligand reported here.

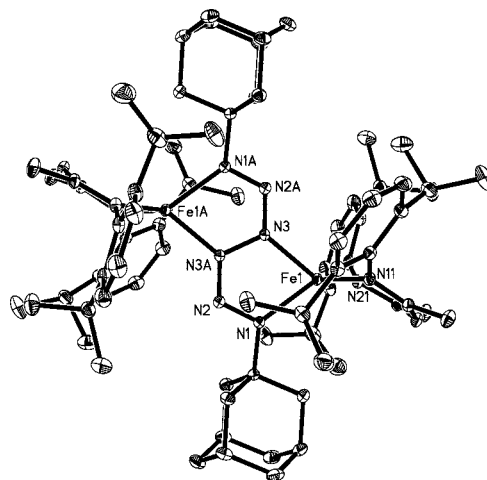


Figure 2. The solid-state structure of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$, using 50% thermal ellipsoids. Hydrogen atoms and a cocrystallized molecule of CH_2Cl_2 are omitted for clarity. The thermal ellipsoid plot of $L^{\text{tBu}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{tBu}}$ is shown in Figure S-1. Selected bond lengths for both complexes are listed in Table 1.

Table 1. Bond Lengths (Å) in $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ and $L^{\text{tBu}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{tBu}}$

| | L^{Me} complex | L^{tBu} complex |
|-------------|-------------------------|--------------------------|
| Fe(1)–N(11) | 2.016(1) | 2.018(2) |
| Fe(1)–N(21) | 2.021(1) | 2.043(2) |
| Fe(1)–N(1) | 2.059(1) | 2.061(2) |
| Fe(1)–N(3) | 2.003(1) | 2.013(2) |
| N(1)–N(2) | 1.305(2) | 1.307(2) |
| N(2)–N(3A) | 1.305(2) | 1.318(2) |
| N(3)–N(3A) | 1.411(2) | 1.408(3) |

structures (Figure 3). The presence of two negatively charged allyl-like fragments indicates that AdN_6Ad is dianionic, which in turn implies a +2 oxidation state at each iron atom. To confirm this hypothesis, we collected the zero-field Mössbauer spectrum of a solid sample of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ at 80 K. The spectrum (Figure 4) shows a single quadrupole doublet with $\delta = 0.75$ mm/s and $\Delta E_Q = 3.12$ mm/s. The iron sites of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{-}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ are equivalent as in the X-ray crystal structure. These values are consistent with high-spin iron(II), as found in other ferrous β -diketimate complexes,¹¹ in four-coordinated complexes supported

[†] University of Rochester.

[‡] Max-Planck-Institut für Bioorganische Chemie.

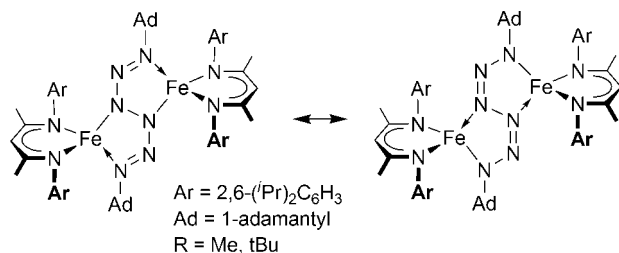


Figure 3. Two possible resonance structures for $L^R\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^R$ that assign the compound as a formal diiron(II) complex.

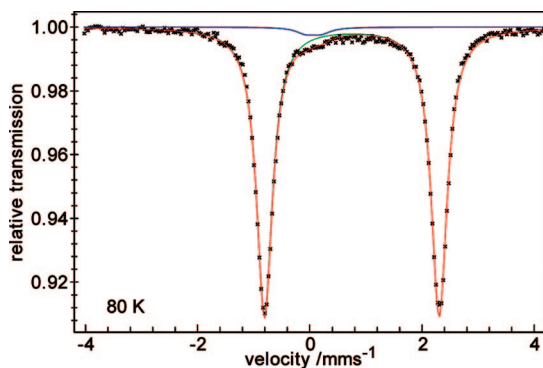


Figure 4. Mössbauer spectrum of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$. The majority of the signal (98% of total iron) was fit with values of $\delta = 0.75(1)$ mm/s and $\Delta E_Q = 3.12(2)$ mm/s, and the remaining impurity (2%) was fit with $\delta = 0.06(4)$ mm/s and $\Delta E_Q = 0.27(8)$ mm/s. The lines represent the Lorentzian doublets of the subspectra and their superposition (red).

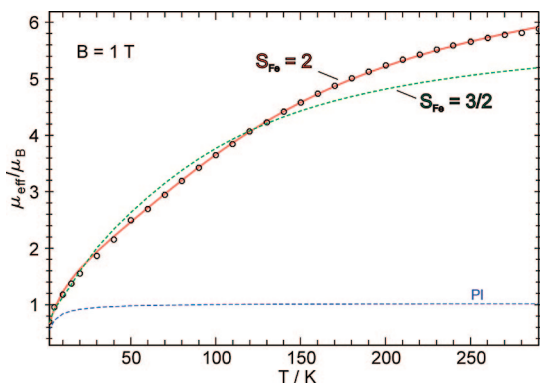


Figure 5. Variable-temperature magnetic susceptibility of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$. The simulation (solid red line) is obtained using $H_{\text{exch}} = -2J(S_1 \cdot S_2)$ with $S_1 = S_2 = S_{\text{Fe}} = 2$, $J = -21(1)$ cm⁻¹, $D_{\text{Fe}} = 24(1)$ cm⁻¹, $g_{\text{Fe}} = 2.2(1)$, and 3% paramagnetic impurity ($S = 5/2$). The contribution from this paramagnetic impurity is shown as a blue dashed line. The green dashed line is an alternative fit with $S_{\text{Fe}} = 3/2$ and the same parameters, showing that an iron(I) model does not fit as well as an iron(II) model.

by tris(phosphino)borate ligands,¹² and in iron–sulfur clusters.¹³ The alternative high-spin iron(I) formulation cannot be excluded on the basis of the Mössbauer measurements because low-valent iron(II) and iron(I) sites can have similar isomer shifts,¹⁴ presumably because of compensating effects originating from the changes in the number of valence electrons and in back-bonding.

Finally, the magnetic susceptibility of solid $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ was studied at temperatures from 2 to 290 K. Figure 5 shows that the value of μ_{eff} gradually decreases with lower temperature to a minimum of less than 1 μ_B . The data were successfully fit to a model of two exchange-coupled high-spin iron(II) ($S_{\text{Fe}} = 2$) with coupling constant $J = -21(1)$ cm⁻¹ and large single-ion zero-field splitting parameter $D_{\text{Fe}} = 24(1)$ cm⁻¹ (Figure 5, red line). The best fit for a high-spin iron(I) dimer with $S_{\text{Fe}} = 3/2$ deviates

considerably from the data (dashed line). Thus the combined crystallographic, spectroscopic, and magnetic data indicate that there are two high-spin iron(II) centers, which are antiferromagnetically coupled to give a diamagnetic ground state.

Because of the formal oxidation of iron(I) to iron(II) in the reaction of $L^R\text{FeNNFeL}^R$ to $L^R\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^R$, we view the hexazine ligand as being derived from reductive azide coupling. We are not aware of any other published examples of reductive coupling of two azides.

To our knowledge, these are the first transition metal complexes with a hexa-nitrogen $R_2N_6^{2-}$ ligand. Although they contain a locally high concentration of nitrogen atoms, they are remarkably inert as long as they are protected from O₂ and moisture. Under N₂, the solid complexes slowly decompose to a black residue only above 140 °C in the solid state and do not explosively decompose when struck with a hammer. This contrasts with several examples of explosive 1,4-pentaazadien-3-ide complexes.¹⁵ Treatment of $L^{\text{Me}}\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-AdN}_6\text{Ad})\text{FeL}^{\text{Me}}$ with neutral donor ligands (*tert*-butylisocyanide, 4-*tert*-butylpyridine), irradiation (200 W mercury lamp for 70 min),¹⁶ or extended heating (100 °C for 5 days, slurry in C₆D₆) does not result in a color change or the appearance of new paramagnetically shifted peaks in the ¹H NMR spectrum. This stability contrasts greatly with metal-free hexazenes, which decompose within minutes upon heating or irradiating.^{4a–c} This difference demonstrates the importance of iron coordination in stabilizing the catenated nitrogen atoms.

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Supporting Information Available: Synthetic, structural, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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