Inorg. Chem. **2008**, *47*, 1889−1891

Inorganic Chemistry
Communication

Monovalent Iron in a Sulfur-Rich Environment

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A series of low-coordinate, paramagnetic iron complexes in a tris(thioether) ligand environment have been prepared. Reduction of ferrous {[$PhTt^{tBu}$]FeCl}$_2$ [**1**; $PhTt^{tBu}$ = phenyltris((*tert*-butylthio)-methyl)borate] with KC_8 in the presence of PR_3 (R = Me or Et) yields the high-spin, monovalent iron phosphine complexes [$PhTt^{tBu}$]Fe(PR_3) (**2**). These complexes provide entry into other low-valent derivatives via ligand substitution. Carbonylation led to smooth formation of the low-spin dicarbonyl [$PhTt^{tBu}$]Fe(CO)$_2$ (**3**). Alternatively, replacement of PR_3 with diphenylacetylene produced the high-spin alkyne complex [$PhTt^{tBu}$]Fe(PhCCPh) (**4**). Lastly, 2 equiv of adamantyl azide undergoes a 3 + 2 cycloaddition at **2**, yielding high-spin dialkyltetraazadiene complex **5**.

The monovalent oxidation state of iron is receiving increasing attention because of its implication in biocatalytic hydrogen and ammonia production and its potential in promoting group-transfer reactions. The iron-only hydrogenase enzymes reduce protons to H_2 at an active site of composition $Fe_2(CO)_3(CN)_2(\mu\text{-}S_2(CH_2)_2X)$.[1] The unusual organometallic diiron subcluster is proposed to redox cycle via a number of states including reduced states that are formally iron(I).[2] The more structurally complex iron molybdenum cofactor of nitrogenase is a metallocluster featuring low-coordinate iron sites in sulfur-rich environments that facilitate N_2 reduction.[3] These developments have stimulated a high level of activity within the coordination chemistry community[4,5] wherein emphasis can be placed on elucidating fundamental aspects of the geometric and electronic structure and establishing how such structural features dictate chemical reactivity. Our interests in this regard are the preparation and examination of high-spin monovalent iron complexes[5,6] in a sulfur-rich ligand environment. While the spectroscopic characteristics of heme and nonheme iron complexes have been extensively examined, similar data for low-coordinate, i.e., CN < 5, low-valent, high-spin complexes are limited. Thus, a comparison with the data derived from the examination of metalloproteins is tenuous. Herein, we present the synthesis, structure, electron paramagnetic resonance (EPR), Mössbauer and magnetic properties of a series of monovalent iron complexes supported by the tris(thioether)borate ligand [$PhTt^{tBu}$].[7] Ligand substitution allows for the introduction of a range of donors including those that are potentially redox-active and, thus, confounds simple electronic structure descriptions.[8]

In contrast to the synthesis of [$PhTt^{tBu}$]MX derivatives of Ni, Co, Zn, and Cd, entry into [$PhTt^{tBu}$]-ligated iron chemistry is quite sensitive to the nature of the metal salt.[7,9] After canvassing a number of potential precursors, we established that $FeCl_2(THF)_{1.5}$ leads to the target complex, albeit in a stepwise fashion. The addition of [$PhTt^{tBu}$]Tl to $FeCl_2(THF)_{1.5}$ in THF generates the colorless "ate" complex {[κ^2-$PhTt^{tBu}$]$FeCl_2$}Tl·THF (see the Supporting Information for details). Removal of the volatiles followed by dissolution in toluene precipitates TlCl, generating light-yellow {[$PhTt^{tBu}$]FeCl}$_2$ (**1**). Unlike the Co, Ni, and Zn analogues, **1** is dimeric in the solid state as revealed by X-ray diffraction (Figure S6 in the Supporting Information, SI). The magnetic susceptibility of **1** (SQUID; Figure S1 in the SI) follows the Curie law, with $\mu_{\text{eff}} = 5.1\ \mu_B$ per Fe (10–290 K), indicating no detectable exchange coupling between the metals. The 4.5 K Mössbauer parameters of **1**, at $\delta = 0.96(3)$ mm/s and $\Delta E_Q = 3.45(2)$ mm/s, are in the range expected for a high-spin ferrous site and similar to those of ferrous rubredoxin.[10]

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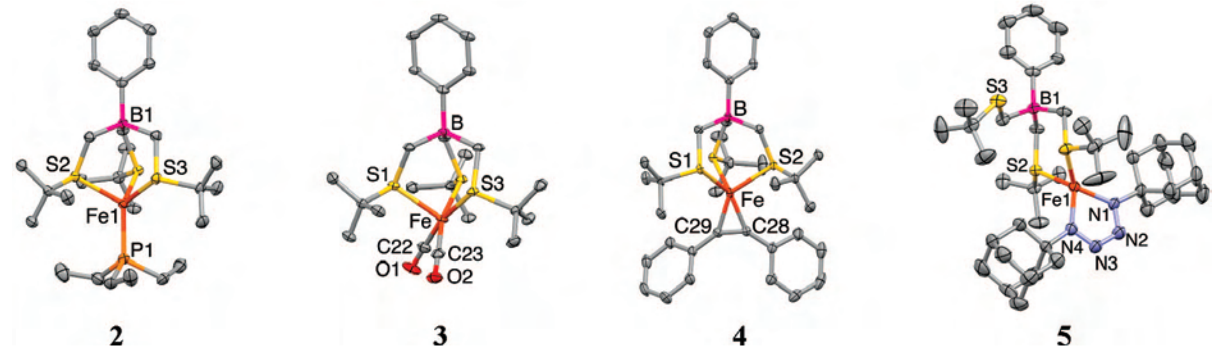
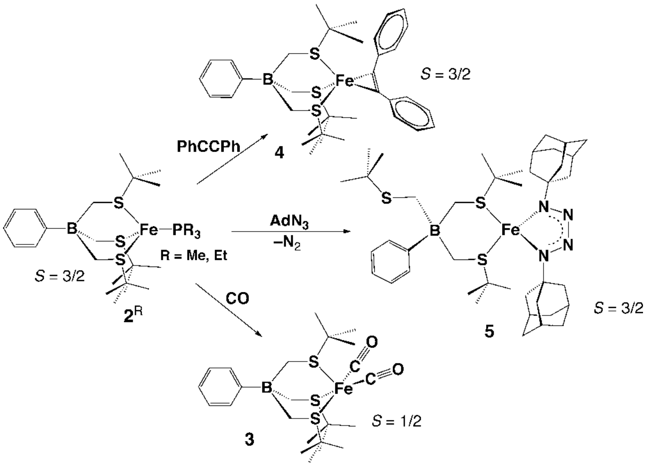


Figure 1. Molecular structures of **2**−**5** as determined by X-ray diffraction. Thermal ellipsoids are at the 30% level, and H atoms are omitted.

Scheme 1



The addition of 3 equiv of PR$_3$ (R = Me or Et) to **1** generates a light-yellow solution. Subsequent stirring over KC$_8$ produces a deep-blue solution from which monovalent [PhTt^{tBu}]Fe(PR$_3$) (**2^R**) is isolated in moderate yields. The molecular structure of **2^{Et}** is depicted in Figure 1. The molecule is pseudo-C_3-symmetric, with the phosphine residing on the 3-fold axis. The phosphine complexes display μ_{eff} = 3.9(1) μ_B for **2^{Me}** and 4.1(1) μ_B for **2^{Et}**, consistent with three unpaired electrons, i.e., $S = {}^3/_2$. Both derivatives exhibit axial EPR signals at 5 K with effective g values of 4.26 and 2.05 and $E/D = 0$ (Figure S2 in the SI). There is no discernible superhyperfine coupling to the ^{31}P NMR nucleus, suggesting that little unpaired spin density resides on that nucleus. The EPR spectrum of $S = {}^1/_2$ [PhTt^{tBu}]Ni(PMe$_3$) also does not display such coupling.[11] Mössbauer spectra of **2^{Me}** exhibit $\delta = 0.76(3)$ mm/s and $\Delta E_Q = 1.88(3)$ mm/s at 4.5 K. The isomer shift is higher than those reported for the few iron(I) complexes published.[5]

2 has proven to be a useful synthon via ligand substitution for the preparation of derivatives containing the [PhTt^{tBu}]Fe fragment (Scheme 1). Exposure of a pentane solution of **2** to a CO atmosphere results in conversion to the dicarbonyl, **3**. The IR spectrum contains two intense ν_{CO} bands at 1984 and 1911 cm^{-1}, which appear at 1938 and 1867 cm^{-1} in samples prepared from ^{13}CO. For comparison, Peters' [PhBP$_3$]Fe(CO)$_2$ exhibits nearly identical values, ν_{CO} = 1979 and 1914 cm^{-1},[6a] whereas Chirik's formally iron(0) complexes have expectedly lower energy bands.[12] The molecular structure of **3** (Figure 1) is that of a square pyramid, with two thioether sulfurs and two carbonyls defining the equatorial plane. The apical thioether bond length is longer, at Fe−S1 = 2.361(2) Å, than the equatorial Fe−S bonds, 2.307(2) and 2.327(2) Å. This observation is surprising given the strong trans influence of CO ligands. In [PhBP$_3$]Fe(CO)$_2$, the apical Fe−P bond length is shorter than the equatorial ones. The room temperature magnetic moment of **3**, determined in solution by the method of Evans,[13] is μ_{eff} = 1.7(1) μ_B, consistent with an $S = {}^1/_2$ spin state. Moreover, complex **3** displays an isomer shift of 0.21 mm/s (162 K), consistent with a low-spin complex and a rhombic EPR signal, g = 2.13, 2.07, and 2.00 (Figure S3 in the SI), similar to the signal reported for the oxidized state of the H cluster of hydrogenase II, g = 2.078. 2.027, and 1.99.[14] A sample of **3** prepared with ^{13}CO exhibits superhyperfine coupling to the two ^{13}C nuclei, with A_1 = 30 MHz, A_2 = 30.5 MHz, and A_3 = 36 MHz.

The addition of diphenylacetylene to **2** generates an olive-green alkyne complex, **4**. The geometry at the iron is square pyramidal, τ = 0.06, [15] when considering the alkyne carbons in two of the equatorial positions. The Fe−C bond lengths, 1.971(3) and 1.961(3) Å, reflect symmetric alkyne coordination. The C−C bond length, 1.280(4) Å, of the diphenylacetylene ligand is lengthened compared to the free alkyne, 1.210(3) Å.[16] The C−C bond length is indistinguishable from that in (^{iPr}PDI)Fe(PhCCPh)[17] while somewhat longer than that found in several lower coordinate β-diketiminate derivatives.[6b] The ν_{CC} mode at 1804 cm^{-1} is at much lower energy than for the free ligand, 2217 cm^{-1}.[18] Thus, there is significant electronic back-donation to the diphenylacetylene ligand, with the ferrous state relevant. The paramagnetically shifted ^{1}H NMR spectral features of **4** are more similar to those of other ferrous

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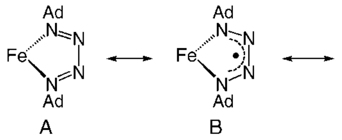

Figure 2. Resonance structures of **5**: high-spin iron(I) with $(N_4Ad_2)^0$ (A), high-spin iron(II) with an antiferromagnetically coupled N_4Ad_2 radical anion (B), and intermediate-spin iron(III) with $(N_4Ad_2)^{2-}$ (C).

complexes, i.e., **1** and [PhTt^{tBu}]Fe(Me),[19] than to those of the monovalent species **2** and **3**. **4** is high-spin, $S = {}^{3}/_{2}$, as indicated by its magnetic moment, $\mu_{eff} = 4.1(1)\ \mu_B$, and rhombic EPR signals, $g = 6.42$, 1.64, and 1.29 and $E/D = 0.228$ (Figure S4 in the SI). Preliminary Mössbauer spectra of **4** reveal $\delta = 0.62(3)$ mm/s and $\Delta E_Q = 1.62(2)$ mm/s, which do not contradict its assignment as an iron(I) $S = {}^{3}/_{2}$ species. The pseudo-three-coordinate LFe(PhCCH) prepared by Holland et al. displays parameters $\delta = 0.44(2)$ mm/s and $\Delta E_Q = 2.02(2)$ mm/s.[5b]

Lastly, we are interested in preparing higher valent complexes of [PhTt^{tBu}]Fe, specifically imidoiron(III), using the group-transfer approach.[6a,20] It was surprising that the addition of 1-adamantyl azide to **2** did not yield imidoiron(III) [PhTt^{tBu}]Fe(NAd). Instead, the dark-orange diadamantyltetraazadiene, **5**, was isolated. **5** has an $S = {}^{3}/_{2}$ ground state as indicated by its magnetic moment, $\mu_{eff} = 3.8(1)\ \mu_B$ and its rhombic EPR spectrum with $g = 5.47$, 2.28, and 1.57 and $E/D = 0.305$ (Figure S4 in the SI). The similarities between the EPR and spectral data of **4** and **5** provide empirical evidence for similar degrees of charge transfer onto the ligands PhCCPh and Ad_2N_4, respectively.

The molecular structure of **5** (Figure 1) features a four-coordinate iron site of roughly tetrahedral stereochemistry with the [PhTt^{tBu}] ligand coordinated in a κ^2 fashion. The Ad_2N_4 unit binds symmetrically through its 1 and 4 nitrogens, Fe$-$N1 = 1.943(3) Å and Fe$-$N4 = 1.947(3) Å. The resulting five-membered metallacycle is planar with N$-$N bond lengths of N1$-$N2 = 1.324(4) Å, N3$-$N4 = 1.317(4) Å, and N2$-$N3 = 1.337(5) Å. The similarity of the N$-$N bond distances suggests a resonance structure with electron delocalization across the ring [Figure 2 (resonance form B)].[21] These structural parameters are inconsistent with limiting resonance contributors in which the Ad_2N_4 ligand is either neutral (A) or dianionic (C) because each predicts localized N$-$N and N$=$N bonds. Interestingly, the electronic spectrum of **5** contains a low-energy absorption band in the near-IR, $\lambda_{max} = 950$ nm ($\epsilon = 112\ M^{-1}\ cm^{-1}$). A similar feature was reported for the 19-electron anions, [CpCo(1,4-R_2N_4)]$^-$, in which the unpaired electron was determined to reside in a delocalized π^* orbital of the metallacycle based on Xα calculations.[22] While we consider resonance form B as a description consistent with the experimental data, it can be problematic to overemphasize such assignments. As noted by Trogler, "... tetrazabutadiene complexes defy a simple description."[21] Recent reports of the complex redox behavior and electronic structures of iron α-diimine complexes highlight this cautionary note.[8] Experiments aimed at the characterization of the electronic structures of **4** and **5**, augmented by density functional theory calculations, are in progress.

A plausible reaction pathway leading to tetraazadiene complexes was proposed first by Stone et al.[23] The formation of **5** would initiate with group transfer to iron(I) generating a putative imidoiron(III) intermediate, [PhTt^{tBu}]Fe(NAd). Clear precedents of similar adducts are available in the systematic studies of Peters and co-workers that demonstrate that four-coordinate imidoiron complexes may be accessed in the ferrous, ferric, and iron(IV) oxidation states.[24] In the present case, the imidoiron(III) intermediate reacts further with a second 1 equiv of AdN_3 via a 3 + 2 cyclization, leading to **5**. This last step may be favored because of the ability of [PhTt^{tBu}] to deligate one thioether substituent, thus providing sufficient space for the 3 + 2 cycloaddition to proceed. Additional studies are warranted to further investigate the mechanism of this reaction.

In summary, we have established entry into monovalent iron coordination complexes in a sulfur-rich ligand environment. High-spin iron(I) complex **2** is a synthon for a number of new complexes via ligand substitution. While **2** and **3** appear to be bona fide monovalent iron species, high-spin **4** and **5** exhibit distinct spectral and structural characteristics indicative of back-donation to the alkyne and tetraazadiene ligands, respectively. The interesting and more complex electronic structures of **4** and **5** are the subject of ongoing studies.

Acknowledgment. We thank the NSF (CHE-0518508 to C.G.R. and CHE-0421116 to C.V.P.) for financial support. S. Bobev, S. Xia, and P. Tobash are thanked for assistance in acquiring the SQUID data for **1**, M. Hendrich is thanked for the use of the program *SpinCount* and for the simulations of the EPR spectra of **4** and **5**, and J. Dykins and H. B. Linden are thanked for collection of the LIFDI-MS data.

Supporting Information Available: Synthetic procedures and characterization data including EPR and Mössbauer spectra (PDF) and X-ray diffraction refinement data for **1**$-$**5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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