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Iron guanidinate complexes and formation of a novel dinuclear iron(II) species with a dianionic μ-$\eta^2:\eta^2$ (biguanidinate) ligand

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Reaction of the lithium salt of *N,N′,N″*-triisopropylguanidinate with Fe(III) or Fe(II) halides led to isolation of the new species $[(Pr^iN)_2C(HNPr^i)]_2FeCl$ (1) and $[\mu\text{-}\eta^2\text{-}(Pr^iN)_2C(HNPr^i)]_2\{Fe[\eta^2\text{-}(Pr^iN)_2C(HNPr^i)]\}_2$ (2); attempted alkylation of 1 with 1 equiv. of a variety of reagents produced 2; the reaction of 2 with $LiCH_2SiMe_3$ resulted in a coupling reaction between the two bridging ligands to yield $[(\mu\text{-}\eta^2:\eta^2\text{-}(Pr^iN)_2C)_2NPr^i)]\{Fe[\eta^2\text{-}(PrN^i)_2C(HNPr^i)]\}_2$.

Amidinate anions are well established as versatile ligands for a variety of transition metal complexes and particularly for compounds for the early transition metals.[1,2] In contrast, the isoelectronic *N,N′,N″*-trialkylguanidinate anions have received very limited attention as ligands in organometallic and coordination chemistry (Fig. 1).[3,4] We anticipate that these species will exhibit the same flexibility in coordination properties as amidinates and that the presence of the third nitrogen center should lead to novel coordination properties. Furthermore, the added potential of generating dianionic species, by deprotonation of the second N–H function, may yield a unique, conjugated π system.

The scarcity of Fe complexes supported with anionic nitrogen-centered ligands warrants exploration of guanidinate ligands in this regard. Interestingly, the first transition metal complexes with dianionic guanidinate ligands are represented by the dinuclear iron complexes $[\mu^2\text{-}(RN)_3C][Fe(CO)_3]_2$ (R = Cy, Pr^i).[5] These species were formed by the reaction of the appropriate carbodiimide with $Fe(CO)_5$ and remain the sole examples of guanidinate anions employed in Fe chemistry.

We wish to report our initial exploration into the use of *N,N′,N″*-trisubstituted guanidinates as supporting ligands for Fe(II) and Fe(III). This necessarily requires the development of fundamental ideas regarding the introduction of these ligands into the metal coordination sphere as well as definition of the reactivity of these species.[3,4,6]

The *N,N′,N″*-tri(alkyl)guanidinatolithium $[[(RN)_2C(HNR)]Li$ (R = Pr^i, Cy) starting materials were formed by direct reaction of the guanidine with 1 equiv. of either MeLi or Bu^nLi.[4] In all cases, metathesis reactions with iron halides were carried out with freshly prepared solutions of lithium guanidinate in ether or THF (Scheme 1). Addition of 0.5 equiv. $FeCl_3$ to a solution of $[(Pr^iN)_2C(HNPr^i)]Li$ followed by recrystallization from pentane resulted in isolation of the new bis(guanidinate)iron(III) chloride complex $[(Pr^iN)_2C(HNPr^i)]_2FeCl$, **1** (Scheme 1).[7] The solid state structure of **1** revealed a monomer with two monoanionic chelating bidentate guanidinate ligands yielding planar M–N–C–N cycles as depicted in Scheme 1.[8] The coordination sphere of the metal is completed by a terminal chloride to generate a distorted pseudo-trigonal bipyramidal geometry for **1** with approximate C_2 symmetry. The average $Fe–N_{ax}$ bond distances of 2.085(3) Å are slightly longer than the average $Fe–N_{eq}$ distances of 2.008(3) Å. The C–N bond distances within the chelate rings (average 1.34, 1.36 Å) are consistent with partial double bond character within the NCN moiety. The central C atoms of the guanidinates, the Cl ligand and the Fe center are coplanar.

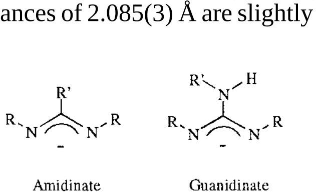
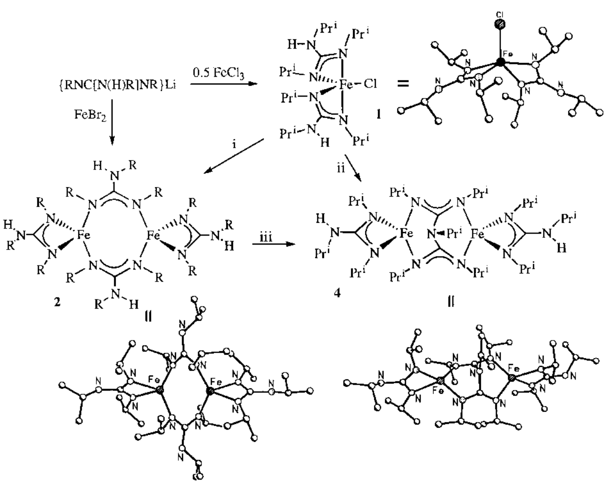


Fig. 1



Scheme 1 Reaction scheme for the preparation of **1**, **2** and **4** and the structures of these complexes. *Reagents and conditions*: i, LiMe, $LiCH_2(SiMe_3)$, $ZnEt_2$, or BzMgCl; ii, 2 $LiCH_2(SiMe_3)$; iii, $LiCH_2(SiMe_3)$.

Attempts to exchange the chloro ligand of **1** with an alkyl group using a variety of reagents including RLi (R = Me, $CH_2(SiMe_3)$), $ZnEt_2$, and BzMgCl were examined. In all cases, reduction of the metal center from Fe(III) to Fe(II) was observed and complex **2** was isolated in 40–80% yields.[7] Single crystal X-ray analysis of this new product showed it to be a dinuclear species with two bridging guanidinate ligands and two chelating bidentate ligands with formula $Fe_2[\mu\text{-}\eta^2\text{-}(Pr^iN)_2C(HNPr^i)]_2[\eta^2\text{-}(Pr^iN)_2C(HNPr^i)]_2$ (Scheme 1).[8] Another route to the Fe(II) dinuclear species **2** was *via* direct reaction of $FeBr_2$ with 2 equiv. of $[(Pr^iN)_2C(HNPr^i)]Li$ in THF followed by recrystallization from ether. This method led to isolation of **2** in 82% yield.

The coordination sphere for each Fe center is composed of four nitrogen centers of the two different ligands. The N–Fe–N bond angles exhibit a broad range of values from 63.3 to 132.3° with an average of 106°. The Fe–N bond distances vary from 2.056(6) to 2.127(7) Å. The two chelating bidentate ligands in **2** are planar and exhibit bonding parameters reminiscent of other complexes with chelating monoanionic guanidinates such as **1**. In contrast the bridging ligands appear to be quite distorted. The central C atoms of both of these groups are planar and the four N centers deviate only slightly from planarity. The CN bond distances within the bridging groups are indicative of delocalized π-bond (av. 1.33 Å). Furthermore, the average $C–N(H)Pr^i$ distance of 1.41 Å is consistent with a CN single bond. However, the bridging ligands coordinate to the two Fe centers with a decided twist that can be described by the dihedral angle α represented in Fig. 2. In **2** these angles are 67.2 and 70.3°.

A similarly distorted bridging ligand was observed in the case of the benzamidinate complex $Fe_2(\mu\text{-}DPhBz)_2(DPhBz)_2$ (**A**).[9]

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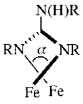
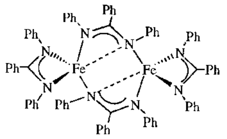


Fig. 2

In **A** the severe distortion of the bridging ligands was attributed to a weak intramolecular Fe$\cdots$N interaction at a distance of 2.477(4) Å. In the case of **2** the two closest non-coordinated N atoms to the Fe centers are at distances of 2.970 and 3.007 Å. These distances are considerably further than in **A** and seem unlikely to be the result of an interaction between these atoms. The possibility of an Fe–Fe bond in **2** can be excluded based on the large iron–iron separation of 3.264 Å.



A

We have further evidence that the bonding features observed for **2** may be general for this ligand system. In a reaction scheme similar to that used in the preparation of **2**, $FeBr_2$ was reacted with 2 equiv. of $[(CyN)_2C(HNCy)]Li$ in ether to successfully generate the cyclohexyl analogue, $Fe_2[\mu\text{-}\eta^2\text{-}(CyN)_2C(HNCy)]_2[\eta^2\text{-}(CyN)_2C(HNCy)]$ **3**. The resemblance of the metrical parameters of **3** with those of **2** was confirmed through a structural analysis.[10] Complex **3** displayed a similar orientation for the bridging ligands with the dihedral angles α of 70.0 and 73.6°. In **3**, the closest non-coordinated N centers for each Fe were even further away than in **2** (*i.e.* 3.050 and 3.190 Å) and a long Fe–Fe separation (3.161 Å) ruled out a metal–metal bonding interaction.

It is worthwhile to note that for the molybdenum complex $Mo_2[\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh]_4$, all four of the triaryl guanidinate ligands bridge the two metal centers resulting in the formation of a metal–metal bond and none of the bridging ligands demonstrate the distortion exhibited by complex **2**.[11]

Reaction of complex **1** with a variety of alkylating reagents led to reduction of the Fe(III) center and formation of the dinuclear structure **2**. When either **2** or **1** are allowed to react with additional $LiCH_2SiMe_3$ a reaction involving the guanidinate ligands was observed (Scheme 1). For example, reaction of **1** with 2 equiv. of $LiCH_2SiMe_3$ resulted in formation of the Fe(II) complex **4**. Examination of single crystals of **4** by X-ray diffraction provided the structure displayed in Scheme 1.[8]

The obvious result of the added lithium reagent is a coupling of the two bridging guanidinates to yield a bridging biguanidinate dianion. A likely pathway for the transformation of **2** to **4** begins with the deprotonation of one of the bridging ligands with the added lithium reagent to generate a nitrogen-centered anion. Subsequent attack of this nucleophilic center at the central carbon of the second bridging ligand and release an amido anion would generate the new dianionic ligand, $\{[(Pr^iN)_2C]_2NPr^i\}^{2-}$ observed for **4**.

Bonding parameters within the $\{[(Pr^iN)_2C]_2NPr^i\}^{2-}$ moiety are consistent with the resonance representation in Scheme 1. In particular, the π bonds within this species appear to be delocalized as depicted. Furthermore, the $C(NPr^i)_3$ carbon centers are planar ($\Sigma = 360°$) and the N atoms bonded to iron deviate only slightly from planarity ($\Sigma = 357°$). The two Fe atoms in **4** are separated by a distance of 4.945 Å.

The utility of *N,N′,N″*-trialkylguanidine ligands in the preparation of new Fe(II/III) complexes has been established. Attempts to alkylate bis(guanidinato)iron(III) chloride resulted in reduction of Fe(III) to Fe(II) and formation of dinuclear species. Complexes **1**–**4** demonstrate the versatility in coordination behavior for these ligands. Transformation of guanidinate ligands can be prompted by deprotonation and in the case of **2** led to the tetradentate biguanidinate dianion $\{[(Pr^iN)_2C]_2NPr^i\}^{2-}$. Our continuing efforts are directed toward understanding the details that dictate the formation of mono- *vs.* dianionic ligands and the intramolecular interactions exhibited by these ligands.

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7 The paramagnetic complexes **1**–**4** have been fully characterized by IR spectroscopy, magnetic susceptibility and elemental analysis. Connectivity for all of these species have been established through single crystal X-ray diffraction studies. In all cases suitable crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. The structures were solved using direct methods and refined by full-matrix least-squared on F^2.

8 Crystals of **1** were obtained from pentane. *Crystal data* for $C_{20}H_{44}ClFeN_6$ **1**: M = 459.91 monoclinic, a = 9.631(2), b = 14.350(2), c = 19.259(3) Å, β = 98.581(3)°, U = 2631.9(7) Å^3, T = 238 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 0.690 mm^{-1}, reflections measured 20672 unique 3212 [R(int) = 0.1274] which were used in all calculations. Final R indices [$I > 2\sigma(I)$] $R1$ = 0.0470, $wR2$ = 0.0995. Crystals of **2** were obtained from hexane. *Crystal data* for $C_{40}H_{88}Fe_2N_{12}(hexane)_{0.5}$ **2**: M = 892.01, triclinic, a = 10.342(2), b = 12.080(2), c = 21.651(4) Å, α = 92.435(4), β = 98.115(3), γ = 106.672(4)°, U = 2555.6(8) Å^3, T = 223 K, space group $P1$, Z = 2, μ(Mo-Kα) = 0.608 mm^{-1}, reflections measured 16200, unique 11406 [R(int) = 0.0300] which were used in all calculations. Final R indices [$I > 2\sigma(I)$] $R1$ = 0.0381, $wR2$ = 0.0883. Crystals of **4** were obtained from pentane. *Crystal data* for $C_{37}H_{79}Fe_2N_{11}$ **4**: M = 789.81, orthorhombic, a = 19.572(6), b = 12.747(4), c = 18.649(6) Å, U = 4653(3) Å^3, T = 238 K, space group *Pccn*, Z = 4, μ(Mo-Kα) = 6.59 mm^{-1}, reflections measured 29549, unique 2444 [R(int) = 0.2975] which were used in all calculations. Final R indices [$I > 2\sigma(I)$], $R1$ = 0.0488, $wR2$ = 0.1076. CCDC 182/1711. See http://www.rsc.org/suppdata/cc/b0/b003547p/ for crystallographic files in .cif format.

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