*Inorg. Chem.* **2007**, *46*, 366–368

Inorganic Chemistry
Communication

# Chelating or Bridging? Halide-Controlled Binding Mode of Diamido Donor Ligands in Iron(III) Complexes

**Anjan Kumar Das, Zohreh Moatazedi, Garry Mund, Andrew J. Bennet, Raymond J. Batchelor, and Daniel B. Leznoff***

*Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada*

Received September 26, 2006

In a series of iron(III) halide complexes of the form $\{FeX[MesN(SiMe_2)]_2O\}_2$ (Mes = mesityl; X = Cl, Br, I), the ancillary diamidosilylether ligand can either chelate to one metal or instead bridge two metal centers, as a function of the halide coligand. The complexes are prepared from diamidosilyletheriron(II) precursors, which are oxidized with iodine, benzyl bromide, or $PhICl_2$ to yield the appropriate iron(III) halide. The bromide analogue can also be synthesized by reacting the iron(II) precursor with a bromonium transfer agent (stabilized by adamantylideneadamantane). The latter reaction may proceed via an iron(IV) intermediate, which can oxidize the normally noncoordinating, inert $[B(Ar_F)_4]^-$ counteranion [$Ar_F = 3,5\text{-}(CF_3)_2Ph$].

The use of chelating diamido ligands has recently played an increasingly important role in transition-metal catalyst design,[1] spurred on by the desire to find alternative ancillary ligands to the ubiquitous cyclopentadienyl-based systems.[2] Diamido and diamidodonor ligands, which usually act as chelates, are particularly attractive ligands for high-valent metal centers because of their strong $\pi$-donating ability and their versatility toward steric and electronic modification (via the nitrogen substituent).[3−9] In combination with zirconium(IV) and titanium(IV) centers, they display high activities toward olefin polymerization,[4] while dinitrogen activation chemistry occurs with chelating diamidophosphine-based metal complexes.[5] We herein describe a series of iron(III) halide complexes in which the ancillary diamidosilylether ligand, as a function of the halide coligand, can either chelate to one metal or instead *bridge* two metal centers.

The addition of the diamidosilylether ligand $\{Li_2[MesN(SiMe_2)]_2O\}$[8,9] (Mes = mesityl) to $FeCl_2$ generates amido-bridged $\{Fe[MesN(SiMe_2)]_2O\}_2$ (**1**), along with LiCl as a biproduct.[10] Each iron(II) center exhibits a distorted trigonal geometry (Figure 1) in which each Fe atom is bound by one

---

* To whom correspondence should be addressed. E-mail: dleznoff@sfu.ca. Tel.: 1-604-291-4887. Fax: 1-604-291-3765.

(1) Gade, L. H. *Chem. Commun.* **2000**, 173.

(2) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(3) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. Love, J. B.; Clark, H. C.; Cloke, F. G. N.; Green, J. C.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 6843. Athimoolam, A.; Gambarotta, S.; Korobkov, I. *Organometallics* **2005**, *24*, 1996. Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415.

(4) Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795. Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. Graf, D. D.; Schrock, R. R.; Davis, W. M.; Stumpf, R. *Organometallics* **1999**, *18*, 843. Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. Liang, L.-C.; Schrock, R. R.; Davis, W. M. *Organometallics* **2000**, *19*, 2526.

(5) Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 3234. MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 3836.

(6) Elias, A. J.; Roesky, H. W.; Robinson, W. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1993**, 495. Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

(7) Mund, G.; Batchelor, R. J.; Sharma, R. D.; Jones, C. H. W.; Leznoff, D. B. *J. Chem. Soc., Dalton Trans.* **2002**, 136.

(8) Mund, G.; Vidovic, D.; Batchelor, R. J.; Britten, J. F.; Sharma, R. D.; Jones, C. H. W.; Leznoff, D. B. *Chem. Eur. J.* **2003**, *9*, 4757.

(9) Mund, G.; Gabert, A. J.; Batchelor, R. J.; Britten, J. F.; Leznoff, D. B. *Chem. Commun.* **2002**, 2990. Leznoff, D. B.; Mund, G.; Jantunen, K. C.; Bhatia, P. H.; Gabert, A. J.; Batchelor, R. J. *J. Nucl. Sci. Technol.* **2002**, Nov (Supplement 3), 406.

(10) See the Supporting Information for synthetic procedures and characterization details. Crystal data for compound **1**: $C_{44}H_{68}Fe_2N_4O_2Si_4$, $M = 909.08$, triclinic, space group $P\bar{1}$, $a = 11.468(3)$ Å, $b = 11.575(4)$ Å, $c = 19.840(4)$ Å, $\alpha = 74.48(3)°$, $\beta = 77.39(2)°$, $\gamma = 74.71(3)°$, $V = 2416.6$ Å$^3$, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.734$ mm$^{-1}$, $T = 293$ K, 6362 unique reflections, 3207 observed [$I_0 > 2.5\sigma(I_0)$]. The final $R_F = 0.0390$ and $R_{WF} = 0.0354$ (obsd data). Crystal data for compound **2**: $C_{22}H_{34}FeIN_2OSi_2$, $M = 581.44$, orthorhombic, space group *Pbca*, $a = 16.098(2)$ Å, $b = 15.199(2)$ Å, $c = 21.481(2)$ Å, $V = 5255.8$ Å$^3$, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.840$ mm$^{-1}$, $T = 293$ K, 4400 unique reflections, 1729 observed [$I_0 > 2.5\sigma(I_0)$]. The final $R_F = 0.0423$ and $R_{WF} = 0.0476$ (obsd data). Crystal data for compounds **3** and **3a**. Prepared using the bromonium reagent (**3a**): $C_{22}H_{34}FeBr_{0.63}Cl_{0.37}N_2OSi_2$, $M = 518.43$, monoclinic, space group $P2_1/c$, $a = 15.9792(13)$ Å, $b = 12.0218(11)$ Å, $c = 15.0858(13)$ Å, $\beta = 116.730(2)°$, $V = 2588.3$ Å$^3$, $Z = 4$, $\mu(\text{Cu K}\alpha) = 7.169$ mm$^{-1}$, $T = 293$ K, 8010 unique reflections, 2028 observed [$I_0 > 2\sigma(I_0)$]. The final $R_F = 0.0541$ and $R_{WF} = 0.0648$ (obsd data). Prepared using benzyl bromide (**3**): $C_{22}H_{34}FeBrN_2OSi_2$, $M = 533.98$, monoclinic, space group $P2_1/c$, $a = 15.990(7)$ Å, $b = 12.009(2)$ Å, $c = 15.105(5)$ Å, $\beta = 117.06(3)°$, $V = 2583.0$ Å$^3$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 2.239$ mm$^{-1}$, $T = 293$ K, 3614 unique reflections, 1453 observed [$I_0 > 2.5\sigma(I_0)$]. The final $R_F = 0.0482$ and $R_{WF} = 0.0431$ (obsd data). Unit cell data for compound **4**: primitive monoclinic, $a = 15.932(9)$ Å, $b = 11.970(5)$ Å, $c = 14.973(8)$ Å, $\beta = 116.31(2)°$, $V = 2559.6$ Å$^3$. For detailed X-ray crystallographic experimental information, see the deposited composite CIF files for **1**−**3** and **3a**.

10.1021/ic061832m CCC: $37.00

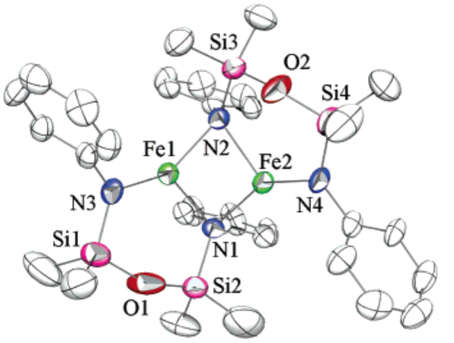


**Figure 1.** Molecular structure of **1** (ORTEP, 33% ellipsoids; methyl groups on aryl rings excluded for clarity). Selected bond lengths (Å) and angles (deg): Fe1−Fe2 2.5479(13), Fe1−N1 2.128(4), Fe1−N2 2.055(4), Fe2−N1 2.049(5), Fe2−N2 2.111(4), Fe1−N3 1.912(4), Fe2−N4 1.902(5), Si1−N3 1.694(5), Si2−N1 1.747(5), Si3−N2 1.751(5), Si4−N4 1.702(5), Si1−O1 1.634(4), Si2−O1 1.616(4), Si3−O2 1.594(4), Si4−O2 1.625(4); N1−Fe1−N2 93.09(16), N1−Fe1−N3 120.34(18), N2−Fe1−N3 143.56(18), Si1−O1−Si2 149.5(3), Si3−O1−Si4 154.8(3).

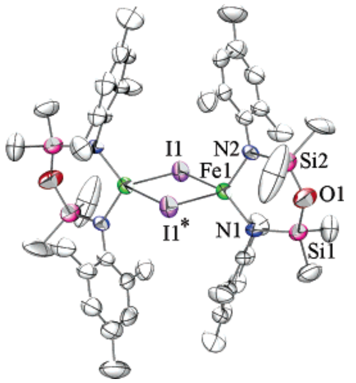


**Figure 2.** Molecular structure of **2** (ORTEP, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Fe1−Fe1* 3.749(3), Fe1−I1 2.6622(17), Fe1−I1* 2.7657(17), Fe1−N1 1.887(8), Fe1−N2 1.898(8), Si1−O1 1.630(9), Si1−N1 1.737(8), Si2−O1 1.582(8), Si2−N2 1.719(8); Fe1−I1−Fe1* 87.36(5), I1−Fe1−I1* 92.64(5), N1−Fe1−N2 110.6(4), I1−Fe1−N1 120.1(3), I1−Fe1−N2 112.5(3), I1*−Fe1−N1 112.4(3), I1*−Fe1−N2 106.5(3), Si1−O1−Si2 144.4(5). * = −*x*, −*y* + 1, −*z*.

terminal and two bridging amido groups; the silylether donor is not bound. The Fe−Fe distance is 2.5479(13) Å. The structure of **1** and its metrical parameters are comparable to those of the related iron(II) dimer $\{Fe[^tBuN(SiMe_2)]_2O\}_2$, with the exception that the silylether donor is bound to the iron center in the $^t$Bu analogue.[7]

The reaction of **1** with iodine resulted in an immediate color change from pale yellow to dark purple, and large diamond-shaped crystals of $\{FeI[MesN(SiMe_2)]_2O\}_2$ (**2**) were isolated.[10] To eliminate the presence of a chloride impurity in **2** (from trace unseparated LiCl in the synthesis of **1)**, the precursor **1** was prepared from $FeI_2$ (thereby generating only a LiI biproduct). The structure of **2** (Figure 2) clearly reveals an iron(III) iodide-bridged dimer in the solid state, with each four-coordinate, roughly tetrahedral iron center coordinated to two terminal amido donors and two bridging iodides; the Fe−Fe distance is 3.749(3) Å, precluding any direct metal−metal interaction. The diamidosilylether ligands are chelating the iron centers in **2**, although the central silylether donor remains unbound; a six-membered chelate ring is thereby formed. The $Fe_2(\mu\text{-}I)_2$ core is slightly asymmetric, as indicated by the Fe1−I1 and Fe1−I1* bond lengths of 2.6622(17) and 2.7657(17) Å, respectively. These distances are longer than those in the few reported iodoiron(III) complexes that contain terminal Fe−I bond lengths.[11,12]

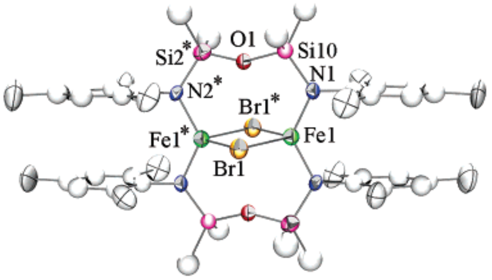


**Figure 3.** Molecular structure of **3** (ORTEP view, 50% probability ellipsoids are shown). Selected bond lengths (Å) and angles (deg): Fe1−Fe1* 3.232(3), Fe1−Br1 2.471(2), Fe1−Br1* 2.503(2), Fe1−N1 1.864(8), Fe1−N2 1.880(7), Si10−O1 1.651(9), Si11−O1 1.600(10), Si2*−O1 1.626(6), Si10−N1 1.761(10), Si11−N1 1.755(11), Si2*−N2* 1.740(8); Br1−Fe1−Br1* 98.96(7), Br1−Fe1−N1 105.5(2), Br1*−Fe1−N1 109.5(2), Si10−O1−Si2* 154.0(5), Si11−O1−Si2* 148.3(5). * = −*x* + 1, 1 − *y* − 1, −*z* + 1.

The analogous dark-red iron(III) bromide complex $\{FeBr_{1-x}(Cl)_x[MesN(SiMe_2)]_2O\}_2$ (**3a**) can be prepared[10] by the reaction of **1** with the bromonium ($Br^+$) transfer reagent $[AdAdBr][B(Ar_F)_4]$ [AdAd = adamantylideneadamantane; $Ar_F = 3,5\text{-}(CF_3)_2Ph$].[13] However, this product also contained a chloride impurity ($x < 0.37$), even in the single crystals. In this case, incorporation of chloride was avoided by reacting **1** with an excess of benzyl bromide,[14] which yielded pure $\{FeBr[MesN(SiMe_2)]_2O\}_2$ (**3**)[10] (the reaction of $FeBr_2$ with $\{Li_2[MesN(SiMe_2)]_2O\}$ did not generate **1** cleanly). The structure of **3** (Figure 3) shows a bromide-bridged dimer with a symmetric $Fe_2(\mu\text{-}Br)_2$ core (Fe−Br = 2.471(2) and 2.503(2) Å) and a shorter Fe−Fe distance of 3.232(3) Å. However, the most unusual feature is that each diamidosilylether ligand does not chelate each iron center as in iodo complex **2** but instead *bridges to both Fe atoms* and the silylether donors remain unbound and remote from the metal centers. This binding mode for diamidodonor-type ligands is extremely rare;[15] related ligands such as para-N,N′-disilyated bis(amido)benzene do bridge metal centers but, because of the para arrangement of the amido donors, cannot act as chelates.[16] An intramolecular $\pi-\pi$-stacked amidoaryl array (centroid−centroid = 3.770 Å) is also present in **3** but is absent in sterically strained **2**.

Indeed, the smaller size of bromide vs iodide (van der Waals radii for Br/I are 1.85/1.96 Å)[17] appears to be a key

---

(11) Stokes, S. L.; Davis, W. M.; Odom, A. L.; Cummins, C. C. *Organometallics* **1996**, *15*, 4521.

(12) Pohl, S.; Bierbach, U.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *26*, 776.

(13) Nagra, H. K.; Batchelor, R. J.; Bennet, A. J.; Einstein, F. W. B.; Lathioor, E. C.; Pomeroy, R. K.; Wang, W. *J. Am. Chem. Soc.* **1996**, *118*, 1207 and references cited therein.

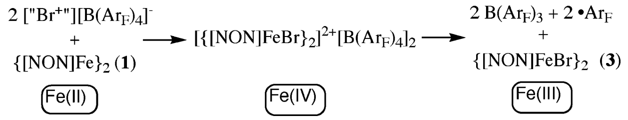
(14) Fryzuk, M. D.; Leznoff, D. B.; Ma, E. S. F.; Rettig, S. J.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 2313.

(15) Jiménez, M. V.; Sola, E.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2005**, *24*, 2722. Hitchcock, P. B.; Huang, Q.; Lappert, M. F.; Wei, X.-H.; Zhou, M. *Dalton Trans.* **2006**, 2991.

(16) Zhao, B.; Li, H.; Shen, Q.; Zhang, Y.; Yao, Y.; Lu, C. *Organometallics* **2006**, *25*, 1824. Daniele, S.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 1909.

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

**Scheme 1.** Proposed Route for the Bromonium Reaction with Iron(II) Diamidoether Complex **1**, via an Iron(IV) Intermediate ([NON] = [MesN(SiMe$_2$)]$_2$O)



factor that influences the binding mode: the larger steric strain of adjacent amidoaryl groups in the chelating form (as exemplified by the long Fe−Fe bonds in **2**) can be relieved by a switch to the bridging mode, as is observed in **3**. Consistent with this concept, the same bridging mode is also observed for the chloride analogue {FeCl[MesN(SiMe$_2$)]$_2$O}$_2$ (**4**), which can be prepared by reacting **1** with PhICl$_2$.[10] The $^1$H NMR spectra of these iron(III) complexes have very broad, featureless peaks consistent with their paramagnetism, and their intense colors are attributable to a halide-to-metal charge transfer that shifts to lower energy from Cl−Br−I (424 to 485 to 670 nm, respectively).

The large size and polarizability of iodides are known to uniquely impact the catalyst reactivity but not necessarily the catalyst structure.[18] In the {FeX[MesN(SiMe$_2$)]$_2$O}$_2$ system, it is the *smaller* halides (X) that significantly perturb the structure from the expected arrangement. Unfortunately, the absence of characteristic NMR or other spectroscopic data in solution renders an examination of the actual solution structures difficult, but the fact that both chelating and bridging binding modes are observed for {FeX[MesN(SiMe$_2$)]$_2$O}$_2$ as a function of halide in the solid state indicates that there is only a small energy difference between the two forms. As a comparison, ligands such as dialkylphosphinomethanes, which are usually designed to bridge metal centers, can be induced to chelate a single metal by altering the alkyl/aryl group steric properties; however, a single such ligand has not been observed to be capable of supporting both binding modes as a function of the coligand.[19] On the other hand, *ansa*-metallocenes can act either as chelates or bridging "fly-over" ligands depending on the coligands.[20]

The formation of **3** via the bromonium reagent, a formally two-electron oxidant, may proceed via an iron(IV) intermediate of the form {FeBr[MesN(SiMe$_2$)]$_2$O}$^+$[B(Ar$_F$)$_4$]$^-$ (or its dimer), which then undergoes intramolecular electron transfer to form the final iron(III) product (Scheme 1). In agreement with this proposal are the following observations: (1) the oxidation product B(Ar$_F$)$_3$ was isolated (which emphasizes the noninnocent nature of the noncoordinating, "inert" counterion);[21] (2) if the bromonium addition reaction is conducted in tetrahydrofuran (THF), rapid solvent polymerization occurs, but if **3** is prepared using benzyl bromide, no polymerization occurs; (3) complexes **1**−**4** are stable in THF once formed. Together, these points suggest the presence of a highly reactive intermediate.

The bridging binding motif for diamidodonor ligands reported here may have implications in the design of future diamido-supported and other chelating ligand-supported metal catalysts because it should not be assumed that a "chelating ligand" will always chelate.

**Acknowledgment.** We are grateful to NSERC of Canada (A.J.B. and D.B.L.) and Simon Fraser University (SFU) for financial support and to Michael J. Katz (SFU) for assistance with X-ray crystallography.

**Supporting Information Available:** Synthetic procedures and characterization data for **1**−**4** and crystallographic data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.jacs.org.

IC061832M

---

(18) Maitlis, P. M.; Haynes, A.; James, B. R.; Catellani, M.; Chiusoli, G. P. *Dalton Trans.* **2004**, 3409.

(19) Pamplin, C. B.; Rettig, S. J.; Patrick, B. O.; James, B. R. *Inorg. Chem.* **2003**, *42*, 4117. Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(20) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811. Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. Qiao, K.; Fischer, R. D.; Paolucci, G. *J. Organomet. Chem.* **1993**, *456*, 185.

(21) Konze, W. V.; Scott, B. L.; Kubas, G. J. *Chem. Commun.* **1999**, 1807.