COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Binuclear iron(II) complex from a linked-bis(amidinate) ligand: synthesis and its reaction with carbon monoxide

Hiroyuki Kawaguchi* and Tsukasa Matsuo

Coordination Chemistry Laboratories, Institute for Molecular Science and CREST, Japan Science and Technology Corporation (JST), Myodaiji, Okazaki 444-8585, Japan. E-mail: hkawa@ims.ac.jp

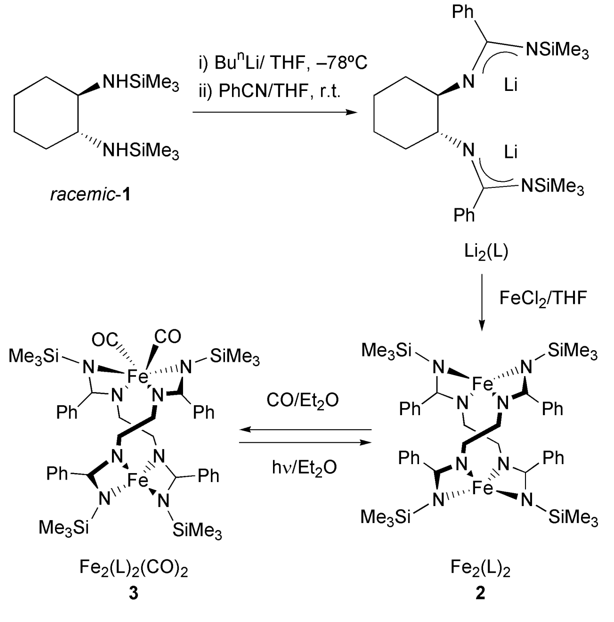
Received (in Cambridge, UK) 21st December 2001, Accepted 18th March 2002
First published as an Advance Article on the web 3rd April 2002

Binuclear iron(II) complexes supported by a cyclohexane-linked bis(amidinate) ligand have been isolated and structurally characterized.

Bimetallic complexes offer the potential to promote chemical transformations that could not be achieved in mononuclear systems.[1] On the other hand, many examples of bimetallic complexes are not able to show high reactivity, due to undesired bridging interactions between metals or due to the lack of an available coordination site. Thus, ligands should be designed to fix two metal centers having sites for binding and activating substrates. In this context, we chose to employ the linked bis(amidinate) as a binucleating ligand, because amidinate complexes display a wide variety of reactivity.[2] However, complexes with the linked bis(amidinate) ligand have yet to be explored.[3–5] Herein we describe binuclear iron(II) complexes supported by a cyclohexane-linked bis(amidinate) ligand.

The linked benzamidinate was synthesized in three steps that are entirely analogous to those employed for the preparation of functionalized benzamidinates $\mathrm{Li[Me_3NSiC(Ph)NR]}$ (Scheme 1).[5,6] The silylamine *trans*-$\mathrm{(Me_3SiNH)_2C_6H_{10}}$ **1** was prepared by the reaction of racemic *trans*-1,2-diaminocyclohexane with $\mathrm{ClSiMe_3}$ and $\mathrm{NEt_3}$ in $\mathrm{Et_2O}$. Treatment of **1** with 2 equiv. of $\mathrm{Bu^nLi}$, followed by addition of 2 equiv. of benzonitrile in THF, yielded the 1,2-cyclohexanediyl-linked bis(benzamidinate) salt $\mathrm{Li_2[\{Me_3SiNC(Ph)N\}_2C_6H_{10}]}$ [$\mathrm{Li_2(L)}$]. The THF solution of $\mathrm{Li_2(L)}$ was used in the synthesis of amidinate complexes, although we found that the dilithium salt $\mathrm{Li_2(L)}$ could be isolated as a THF adduct.

Reaction of $\mathrm{FeCl_2}$ with 1 equiv. of $\mathrm{Li_2(L)}$ in THF afforded a red, homogeneous solution from which a paramagnetic binuclear iron(II) amidinate complex $\mathrm{Fe_2(L)_2}$ **2** was obtained as yellow crystals in 47% yield.† Complex **2** is air- and moisture-sensitive, is very soluble in common organic solvents, and is crystallized from $\mathrm{Et_2O}$. Since the racemic $\mathrm{L^{2-}}$ ligand is used, the product is expected to consist of a heterochiral binuclear complex $[\mathrm{Fe_2(L^{\mathit{RR}})(L^{\mathit{SS}})}]$ and a racemic mixture of homochiral binuclear complexes $[\Lambda,\Lambda\text{-}\mathrm{Fe_2(L^{\mathit{RR}})_2}$ and $\Delta,\Delta\text{-}\mathrm{Fe_2(L^{\mathit{SS}})_2}]$. However, the ^{1}H NMR spectrum indicates the formation of a single species in solution. X-Ray analysis of several crystals eventually revealed that the product is a racemic mixture of homochiral binuclear species in the unit cell.‡ An intriguing aspect of this reaction is ligand self-recognition, resulting in the formation of two stereospecific complexes, $\Lambda,\Lambda\text{-}\mathrm{Fe_2(L^{\mathit{RR}})_2}$ and $\Delta,\Delta\text{-}\mathrm{Fe_2(L^{\mathit{SS}})_2}$.



Scheme 1

The linked amidinate ligand acts as a binucleating ligand (Fig. 1). The molecule possesses a crystallographically imposed 2-fold axis passing through two iron atoms. The cyclohexyl spacer adopts a chair conformation, and the amidinate groups are in equatorial positions. Each iron atom assumes a distorted tetrahedral geometry defined by four N atoms of the amidinate units, which is similar to those of the monomeric bis(amidinate) iron(II) complexes $\mathrm{Fe[FcC(NCy)_2]_2}$ (Fc = ferrocenyl)[7] and $\mathrm{Fe[Bu^tC(NCy)_2]_2}$.[8] The benzamidinate groups form four-membered rings almost coplanar with the iron atoms [torsion angles Fe–N–C–N of the $\mathrm{FeN_2C}$ rings = 5.1(2)° for Fe(1) and 2.4(2)° for Fe(2)]. The average Fe–N(1, 4) distances attached to the $\mathrm{SiMe_3}$ group (2.066 Å) are slightly longer than those attached to the cyclohexyl bridging unit [Fe–N(2, 3), 2.046 Å]. The separation of the iron atoms is 3.516(1) Å, indicative of no metal–metal interaction. The closely related, linked bis(amidinate) ligand was reported to coordinate solely to one titanium metal center.[3]

To test the robustness of the binuclear structure of **2**, we carried out the reaction of **2** with carbon monoxide. Complex **2** was found to readily react with 1 atm of CO even in the solid

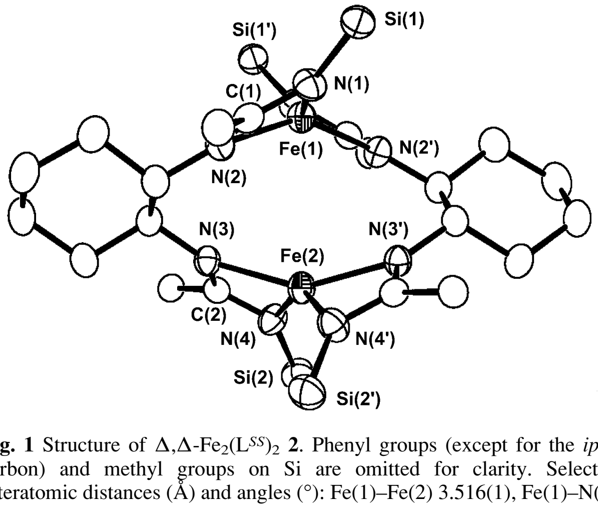


Fig. 1 Structure of $\Delta,\Delta\text{-}\mathrm{Fe_2(L^{\mathit{SS}})_2}$ **2**. Phenyl groups (except for the *ipso* carbon) and methyl groups on Si are omitted for clarity. Selected interatomic distances (Å) and angles (°): Fe(1)–Fe(2) 3.516(1), Fe(1)–N(1) 2.069(2), Fe(1)–N(2) 2.043(2), Fe(2)–N(3) 2.049(2), Fe(2)–N(4) 2.062(2), N(1)–C(1) 1.346(3), N(2)–C(1) 1.320(3), N(3)–C(2) 1.321(3), N(4)–C(2) 1.339(3); N(1)–Fe(1)–N(2) 66.03(7), N(3)–Fe(2)–N(4) 66.19(7), N(1)–C(1)–N(2) 114.4(2), N(3)–C(2)–N(4) 115.2(2).

DOI: 10.1039/b111651g

state as well as in Et$_2$O to afford a paramagnetic orange compound Fe$_2$(L)$_2$(CO)$_2$ **3** quantitatively. Irradiation of **3** resulted in regeneration of **2** concomitant with the loss of CO. According to X-ray analysis (Fig. 2),‡ the homochiral binuclear frame was retained during the reaction. A crystallographic C_2 axis again runs though the two iron atoms. Complex **3** contains the two different iron atoms: one iron atom [Fe(1)] is placed in the center of a disordered octahedron defined by four nitrogen atoms of two benzamidinate groups and two carbonyl ligands; the other iron atom [Fe(2)] adopts a distorted tetrahedral geometry with two amidinate groups. The solid structure of **3** is consistent with its ^{1}H NMR spectrum in solution, which shows two SiMe$_3$ protons as well as 16 resonances attributable to phenyl and cyclohexane groups. In the IR spectrum, the ν(CO) bands of **3** are observed at 2018 and 1944 cm^{-1} and are shifted to higher frequencies than those of Fe[Bu^{t}C(NCy)$_2$]$_2$(CO)$_2$ (1999, 1929 cm^{-1}).[8]

The dihedral angles between the two Fe–amidinates of 85.4 and 84.8° for Fe(1) and Fe(2) in **3** are lager than those of **2** (59.9 and 68.1°). The geometrical parameters within the FeN$_2$C rings in **3** are comparable to those found in **2**. However, the tethering of the amidinate groups in **3** restricts the N(4)–Fe(2)–N(4′) angle at the tetrahedral iron site, which is 128.9(2)° and acute compared with the corresponding angles at **3** [154.2(1) and 140.2(1)°]. The Fe–Fe separation of **3** was elongated by 0.94 Å compared with that of the parent complex **2**, indicating that the size of the cage created by the L^{2-} ligands is flexible. The stability of **3** deserves comment. Although **3** contains a 14-electron iron site, it is found to be stable in the solid state for a few minutes under air. In contrast, **2** immediately decomposes in air. This is ascribed to the rigid conformation, which is locked by the CO ligands and prevents **3** from undergoing further reaction. This reason is related to the formation of **3**, and coordination of additional CO is hampered in the remaining tetrahedral iron site. Studies of the reactivity of binuclear iron complexes **2** and **3** are in progress.

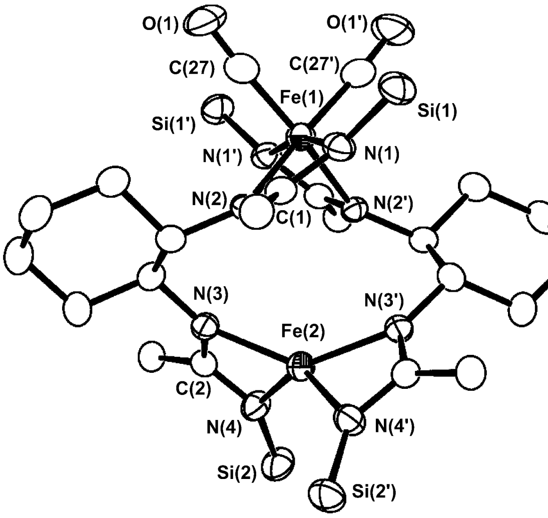


Fig. 2 Structure of Δ,Δ-Fe$_2$(L^{SS})$_2$(CO)$_2$ **3**. Phenyl groups (except for the *ipso* carbon) and methyl groups on Si are omitted for clarity. Selected interatomic distances (Å) and angles (°): Fe(1)–Fe(2) 4.4550(10), Fe(1)–N(1) 2.029(3), Fe(1)–N(2) 2.036(3), Fe(2)–N(3) 2.034(3), Fe(2)–N(4) 2.076(3), N(1)–C(1) 1.344(4), N(2)–C(1) 1.313(4), N(3)–C(2) 1.322(4), N(4)–C(2) 1.340(4), Fe(1)–C(27) 1.764(4), C(27)–O(1) 1.146(4); N(1)–Fe(1)–N(2) 65.77(11), N(3)–Fe(2)–N(4) 65.80(11), N(1)–C(1)–N(2) 112.3(3), N(3)–C(2)–N(4) 114.0(3), Fe(1)–C(27)–O(1) 176.1(3), C(27)–Fe(1)–C(27′) 87.2(2).

Notes and references

† Preparation of **2**: all manipulations were carried out under an atmosphere of argon. A solution of Li$_2$(L) (2.31 mmol) in THF (40 mL) was added to a slurry of FeCl$_2$ (0.29 g, 2.31 mmol) in THF (20 mL) at 0 °C. The solution was stirred for 18 h. The solvent was evaporated to dryness, and the red residue was extracted with Et$_2$O. Concentration and cooling to −30 °C gave 0.56 g of **2** as yellow crystals in 47% yield. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 127.8 (2H), 31.6 (2H), 21.1 (4H, Ph), 13.3 (4H, Ph), 10.6 (2H), 5.9 (2H), 2.5 (18H, SiMe$_3$ + 2H), 2.0 (2H). Anal. calc. for C$_{52}$H$_{76}$N$_8$Si$_4$Fe$_2$: C, 60.21; H, 7.39; N, 10.80. Found: C, 59.67; H, 7.33; N, 10.51%.

Preparation of **3**: a solution of **2** (0.14 g, 0.14 mmol) in Et$_2$O (20 mL) was stirred under 1atm of CO at room temperature for 16 h, after which the solvent was removed *in vacuo*. The remaining orange crystalline solid was rinsed with hexane and dried to give 0.14 g of **3** in 95% yield. IR (Nujol, KBr)/cm^{-1}: 2018 (s), 1944 (s). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 127.5 (1H), 26.3 (1H), 23.5 (2H, Ph), 22.8 (1H), 19.3 (2H, Ph), 11.0 (1H), 3.6 (9H, SiMe$_3$), 2.6 (1H), 2.0 (1H), 0.9 (1H), 0.2 (2H, Ph), 0.1 (2H, Ph), −0.1 (1H), −2.0 (9H, SiMe$_3$), −4.4 (1H), −5.6 (1H), −6.8 (1H), −7.6 (1H). Anal. calc. for C$_{54}$H$_{76}$N$_8$O$_2$Si$_4$Fe$_2$: C, 59.33; H, 7.01; N, 10.25. Found: C, 59.02; H, 6.85; N, 9.89%.

‡ *Crystal data*: for **2**: C$_{52}$H$_{76}$N$_8$Si$_4$Fe$_2$, M = 1037.26, monoclinic, space group $C2/c$, a = 23.6648(9), b = 18.6585(9), c = 13.5164(5) Å, β = 92.4516(10)°, V = 5962.7(4) Å^3, Z = 4, T = 193 K, μ(Mo-Kα) = 6.05 cm^{-1}, Rigaku Mercury, 28 006 measured reflections (2$\theta_{\max}$ = 55°), 6822 unique, 337 variables, $R1$ = 0.038 [$I > 2\sigma(I)$], $wR2$ = 0.111 (all data), and GOF = 1.03.

For **3**: C$_{54}$H$_{76}$N$_8$O$_2$Si$_4$Fe$_2$, M = 1093.28, monoclinic, space group $C2/c$, a = 23.912(4), b = 18.384(2), c = 13.4886(5) Å, β = 92.6946(9)°, V = 5923.0(9) Å^3, Z = 4, T = 193 K, μ(Mo-Kα) = 6.15 cm^{-1}, Rigaku Mercury, 27 945 measured reflections (2$\theta_{\max}$ = 55°), 6690 unique, 355 variables, $R1$ = 0.041 [$I > 2\sigma(I)$], $wR2$ = 0.127 (all data), and GOF = 1.00. All structures were solved by direct methods and refined on F^2 by full-matrix, least squares using the CrystalStructure software package.

CCDC reference numbers 176896 and 176897. See http://www.rsc.org/suppdata/cc/b1/b111651g/ for crystallographic data in CIF or other electronic format.

1 *Polynuclear Metal Cluster Complexes*, R. D. Adams and F. A. Cotton, ed., Wiley-VCH, New York, 1998N. Wheatly and P. Kalck, *Chem. Rev.*, 1999, **99**, 3379.
2 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; R. Gómes, R. Duchateau, A. N. Chernega, J. H. Teuben, F. T. Edelmann and M. L. H. Green, *J. Organomet. Chem.*, 1995, **491**, 153; M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125; E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2000, 497; P. Berno, S. Hao, R. Minhas and S. Gambarotta, *J. Am. Chem. Soc.*, 1994, **116**, 7417; J. R. Hagadorn and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1997, 3087.
3 J. R. Hagadorn and J. Arnold, *Angew. Chem., Int. Ed.*, 1998, **37**, 1729.
4 J. R. Hagadorn, *Chem. Commun.*, 2001, 2144; G. D. Whitener, J. R. Hagadorn and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1999, 1249.
5 S. Bambirra, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2001, **20**, 782.
6 M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Eur. J. Inorg. Chem.*, 1998, 1867; D. Doyle, Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2000, 4093.
7 J. R. Hagadorn and J. Arnold, *Inorg. Chem.*, 1997, **36**, 132.
8 B. Vendemiati, G. Prini, A. Meetsma, B. Hessen, J. H. Teuben and O. Traverso, *Eur. J. Inorg. Chem.*, 2001, 707.