ELSEVIER

Journal of Organometallic Chemistry 489 (1995) C71–C73

Journal of Organometallic Chemistry

Preliminary communication

Synthesis and structures of the mononuclear iron(II) dialkyl FeR_2 and the iron(II) dithiolate complex $[Fe(SAr)_2(RH)]$ $[R = C(SiMe_3)_2C_5H_4N\text{-}2;\ Ar = 2,4,6\text{-}{}^tBu_3C_6H_2]$

Hung Kay Lee, Bao-Sheng Luo, Thomas C.W. Mak, Wing-Por Leung *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong

Received 23 September 1994

Abstract

The thermally stable iron(II) dialkyl, **1** was obtained in good yield from $[LiR]_2$ and $FeCl_2$. Reaction of **1** with ArSH yielded the novel neutral mononuclear iron(II) dithiolate complex **2**. An X-ray diffraction study revealed that the alkyl ligands in **1** are bonded to the metal center in a chelating manner, whereas in **2** one alkyl ligand has been converted into a neutral alkane species by ArSH, but remains coordinated to the iron(II) center via its pyridyl nitrogen atom.

Keywords: Iron; Thiolate; Pyridine; Silicon; Crystal structure

---

Iron(II) dialkyl complexes such as diethylbis(dipyridyl)iron have been known to be useful catalysts in the cyclooligomerization of butadiene and acetylene [1,2]. Owing to their low stabilities, very few iron(II) dialkyl compounds have been fully-characterized. The lability of iron–carbon σ-bond is mainly due to the small energy difference between the *d*-orbitals of the metal and the antibonding orbitals of the Fe–C bond [3]. Most of the known organoiron compounds contain supporting ligands such as CO, PR_3, $\eta^5\text{-}C_5H_5$, and bipyridine. However, use of the sterically demanding mesityl ligand to obtain a homoleptic iron(II) diaryl compound $[Fe(Mes)_2]_2$ $[Mes = 2,4,6\text{-}Me_3C_6H_2]$ was reported recently [4,5]. Sterically hindered and *N*-functionalized alkyl ligands such as $[C(SiMe_3)_2C_5H_4N\text{-}2]^-$, R, have been shown to have a stabilizing effect and exhibits unusual bonding configurations in some low-valent Main Group metal complexes [6]. We have recently reported the synthesis and characterization of a thermally stable cobalt(II) dialkyl complex CoR_2, **3** $R = C(SiMe_3)_2C_5H_4N\text{-}2$ [7]. We have now made the iron(II) dialkyl complex FeR_2 **1**, and a novel mononuclear iron(II) dithiolate complex $Fe(SAr)_2(RH)$, **2**.

The reaction of $[LiR]_2$ with $FeCl_2$ in ether gave compound **1** as yellow crystals in 80% yield (Scheme 1). Compound **1** can be sublimed at 112–116°C under vacuum (0.01 mmHg). This high thermal stability contrasts markedly with the behaviour of $FeEt_2(bipy)_2$, which decomposes to ethane and ethylene under vacuum at 120°C [2]. The stability of **1** is attributed to the presence of the alkyl ligand R which is highly hindered, nitrogen-functionalised and inert towards β-elimination.

The molecular structure of **1** determined by X-ray crystallography is shown in Fig. 1 [8]. The iron(II) center has a highly distorted tetrahedral coordination environment with each of the two alkyl ligands acting in a chelating mode. Coordination from the pyridyl nitrogens is believed to have a stabilizing effect on the metal complex. The observed Fe–C bond distances are 2.139(7) and 2.154(8) Å, which are somewhat longer than the average Fe–C single bond distance of 2.065 Å in $FeEt_2(bipy)_2$ [9] and 2.024 Å in the dinuclear $[Fe(Mes)_2]_2$ [5]. The Fe–N distances are 2.111(8) and 2.135(5) Å which are significantly longer than those of 1.937(2)–1.943(2) Å in $FeEt_2(bipy)_2$ [9]. The bite angles $\angle$C–Fe–N of 67.2(3) and 66.8(2)° in **1** are similar to the corresponding angles of 67.2(2)° in MgR_2 [6] and 59.0(2)° in SnR_2 [6]; both of these latter complexes adopting a tetrahedral geometry. The large C–Fe–C angle of 160.4(3)° in **1** is probably due to steric repul-

---

* Corresponding author.

SSDI 0022-328X(94)05254-9

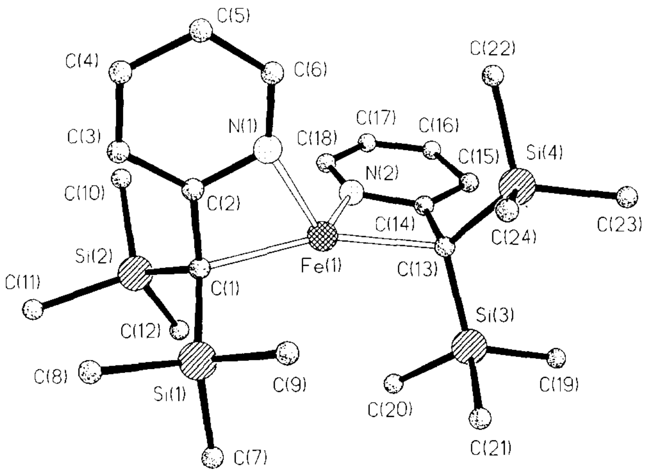


Fig. 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°]: Fe(1)–C(1) 2.154(8), Fe(1)–N(1) 2.135(5), Fe(1)–C(13) 2.139(7), Fe(1)–N(2) 2.111(8); C(1)–Fe(1)–N(1) 66.8(2), C(1)–Fe(1)–C(13) 160.4(3), N(1)–Fe(1)–C(13) 125.4, C(1)–Fe(1)–N(2) 124.1, N(1)–Fe(1)–N(2) 116.3(2), C(13)–Fe(1)–N(2) 67.2(3).

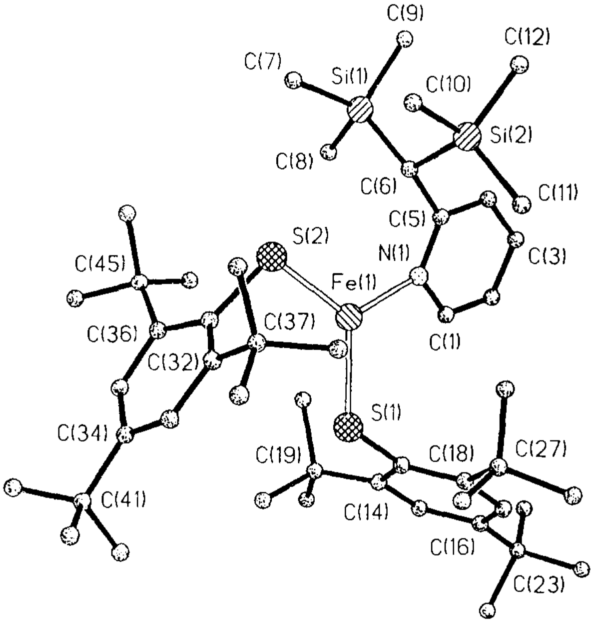
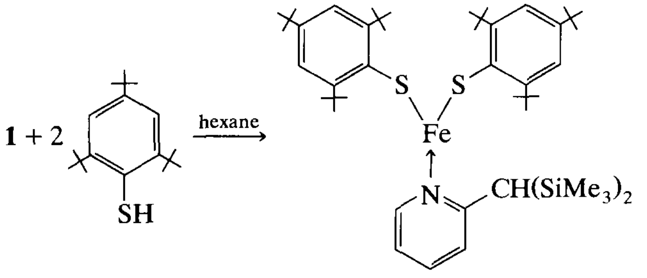


Fig. 2. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Fe(1)–N(1) 2.086(9), Fe(1)–S(1) 2.259(4), Fe(1)–S(2) 2.261(3); N(1)–Fe(1)–S(1) 118.7(2), N(1)–Fe(1)–S(2) 123.4(2), S(1)–Fe(1)–S(2) 117.8(1), Fe(1)–S(1)–C(13) 113.1(4), Fe(1)–S(2)–C(31) 101.0(3).

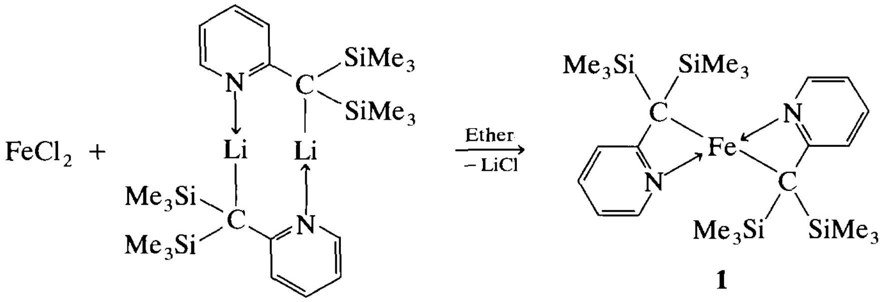
sion between the trimethylsilyl groups on the two α-carbons.

Subsequent reaction of **1** with two equivalents of ArSH in hexane yielded the monomeric iron(II) dithiolate complex $[Fe(SAr)_2(RH)]$ (**2**) (Scheme 2). Compound **2** was obtained in 65% yield as a yellow crystalline compound which decomposes above 182°C. This reaction provides an alternative method for the preparation of mononuclear metal thiolate compounds via metal alkyls. Dinuclear metal dithiolate complexes $[M(SAr)_2]_2$ [M = Mn (**4**), Fe (**5**) and Co (**6**)] have recently been prepared by the reaction of $M[N(SiMe_3)_2]_2$ with ArSH [10]. Unlike $[Cd(SAr)_2]_2$, these metal dithiolate compounds remain as dimers in solution [11]. By using a more bulky aryl substituent, Power et al. have made the mononuclear iron(II) thiolate complexes, $Fe(SAr')[N(SiMe_3)_2]$ (**7**) and $Fe(SAr')_2$ [$Ar' = 2,6\text{-}Mes_2C_6H_2$], (**8**), with two-coordinated iron(II) centers [12]. The Lewis acid centers in compounds **4**–**8** are free from nitrogen coordination in spite of the presence of a strong base $NH(SiMe_3)_2$ in solution. The mechanism for the formation of our current iron(II) dithiolate complex 2 is not wholly clear, but we suggest that an intermediate "FeR(SAr)" is first formed, and this is followed by the protonation of the second alkyl ligand to give a neutral RH molecule whose pyridine ring remains coordinated to the metal center to bring about steric congestion around the



2
65%

Scheme 2.



1
80%

Scheme 1.

metal center. The three bulky ligands ($2\mathrm{ArS}^-$ and RH) are believed to play a vital role in preventing the association of the neighbouring $\mathrm{Fe(SAr)_2}$ moieties, thus resulting in the formation of the mononuclear three-coordinated iron(II) dithiolate complex **2**.

The molecular structure of **2** as determined by X-ray crystallography is shown in Fig. 2 [8]. The dithiolate complex possesses a trigonal planar coordination geometry around the central metal atom. Owing to their bulk, the three ligands are oriented in such a way that the complex adopts a propeller-like structure. The Fe–S bond distances in **2** are 2.259(4) and 2.261(3) Å. These are similar to the terminal Fe–S distances 2.256(3) Å, but shorter than the bridging Fe–S distances, 2.365(3) and 2.366(3) Å, in complex **4** [10]. When comparison is made with the mononuclear thiolate complexes **7** and **8**, the Fe–S distances in **2** are shorter than that of 2.308(2) and 2.314(2) Å in **7**, but is comparable with that of 2.277(2) and 2.275(2) Å in **8** [12]. The Fe–N distance in **2** is 2.086 Å, which only differs from those found in the dialkyl complex **1** by 0.03 Å. The fact that the N(1)–Fe–S(2) angle of 123.4(2)° in **2** is larger than the remaining two angles in the $\mathrm{FeS_2N}$ plane, 118.7(2)° and 117.8(1)° is probably due to the repulsion of the $\mathrm{C(SiMe_3)_2}$ group and the ortho hydrogen of the pyridine ring.

Both compounds were also characterised by their mass spectra and elemental analysis. The magnetic moment, as measured by Evan's method in $\mathrm{C_6D_6}$ solution [13], are 4.24 B.M. for **1** and 5.11 B.M. for **2** at 308 K. The value for **1** lies somewhat below the normal range of 5.1–5.2 B.M. for tetrahedral iron(II) complexes, presumably owing to some spin-mixing.

Acknowledgements

This work is supported by the Hong Kong Research Grants Council under Earmarked Grant No. CUHK 22/91.

References and notes

[1] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito and Y. Uchida, *J. Am. Chem. Soc.*, *90* (1968) 1878.

[2] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Am. Chem. Soc.*, *87* (1965) 4652.

[3] M.D. Johnson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), Comprehensive Organometallic Chemistry Pergamon, Oxford, 1982, Vol. 4, Chapter 3.1.2.

[4] H. Muller, W. Seidel and H. Korls, *J. Organomet. Chem.*, *445* (1993) 133.

[5] B. Machelett, *Z. Chem.*, *16* (1976) 116.

[6] M.J. Henderson, R.I. Papasergio, C.L. Raston, A.H. White and M.F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1986) 672; L.M. Engelhardt, U. Kynast, C.L. Raston and A.H. White, *Angew. Chem. Int. Ed. Engl.*, *26* (1987) 681; L.M. Engelhardt, B.S. Jolly, M.F. Lappert, C.L. Raston and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1988) 336; T. van den Anker, B.S. Jolly, M.F. Lappert, C.L. Raston, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1990) 1006; L.M. Engelhardt, B.S. Jolly, M.F. Lappert, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1993) 2653.

[7] W.-P. Leung, H.K. Lee, Z.-Y. Zhou and T.C.W. Mak, *J. Organomet. Chem.*, *443* (1993) C39.

[8] Crystal data for **1**: $\mathrm{C_{24}H_{44}N_2Si_4Fe}$, M = 528.8, monoclinic, space group $P2_1/c$ (No. 14), $a = 23.882(5)$, $b = 16.820(6)$, $c = 16.406(4)$ Å, $\beta = 107.32(1)°$, $V = 6291(3)$ Å^3, $Z = 8$, $F(000) = 2272$, $D_c = 1.117$ g cm^{-3}, $m = 0.645$ mm^{-1}, $2\theta_{max} = 50°$, $N = 10957$, $N_0 = 4418$, $R = 0.0411$, $wR = 0.0621$; **2**: $\mathrm{C_{48}H_{81}NS_2Si_2Fe}$, $M = 848.29$, monoclinic space group $P2_1/c$ (No. 14), $a = 14.585(5)$, $b = 19.894(6)$, $c = 19.266(5)$ Å, $\beta = 111.16(1)°$, $V = 5213(3)$ Å^3, $Z = 4$, $F(000) = 1848$, $D_c = 1.081$ g cm^{-3}, $m = 0.44$ mm^{-1}, $2\theta_{max} = 45°$, $N = 6826$, $N_o = 3656$, $R = 0.0845$, $wR = 0.1251$. X-ray data were collected from single crystals sealed in 0.5 mm Lindemann glass capillaries under dinitrogen on a Nicolet P4/PC diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in the $\omega/2\theta$ scan model. N unique reflections were measured, and N_0 'observed' reflections with $|F_0| \geq n\sigma(|F_0|)$ where n = 6 for **1** and 4 for **2**, were used in the structure solution refinement. The weighing scheme $w = [\sigma^2|F_o| + 0.008|F_o|^2]^{-1}$ was used for **1** and $w = [\sigma^2|F_o| + 0.0035|F_o|^2]^{-1}$ was used for **2**. The structures were solved by direct phase determination using the computer program SHELXTL-PC on a PC 486 and refined by full matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors. Tables of atomic coordinates and thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

[9] W. Lau, J.C. Huffman and J.K. Kochi, *Organometallics*, *1* (1992) 155.

[10] P.P. Power and S.C. Shoner, *Angew. Chem. Int. Ed. Engl.*, *30* (1991) 330.

[11] M. Bochmann, K. Webb, M. Harman and M.B. Hurtshouse, *Angew. Chem. Int. Ed. Engl.*, *29* (1990) 638.

[12] J.J. Ellison, K. Ruhlandt-Senge and P.P. Power, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1178.

[13] D.F. Evans, *J. Chem. Soc.*, (1959) 2003.