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Synthesis and structure of sila-bridged bis(1-indenyl and tetrahydroindenyl) tetracarbonyl di-iron complex

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Abstract—Sila-bridged bis(1-indenyl) tetracarbonyl di-iron complexes $E[IndFe(CO)]_2(\mu\text{-}CO)_2$ ($E = Me_2Si$, **1**; $Me_2SiOSiMe_2$, **2**) have been synthesized by the reaction of $Fe(CO)_5$ and the corresponding sila-bridged bisindenyl ligands. Both **1** and **2** have *cis* and *trans* isomers. According to the different crystal shapes a small amount of pure *cis* isomer **1c** and *trans* isomer **1t** were separated mechanically. But only pure *trans* isomer **2t** was obtained by recrystallization. **1** and **2t** were hydrogenated in the presence of PtO_2 at atmospheric pressure, and the corresponding tetrahydroindenyl complexes **3** and **4t** were obtained respectively. After hydrogenation, pure *cis* isomer **3c** and *trans* isomer **3t** were separated by chromatography. The crystal structure of the *trans* isomer **1t** was determined by X-ray diffraction. It shows that the unfused moieties of six-membered rings of indenyl ligands exist as a conjugated diene system. This explains that **1** and **2** can be readily hydrogenated to the tetrahydro-indenyl complexes even at atmospheric pressure. © 1997 Elsevier Science Ltd

Keywords: di-iron complex; tetrahydroindenyl ligand; *cis* and *trans* isomer; crystal structure; column chromatography; sila-bridge.

Much attention has been focused on the synthesis and study of a variety of metal–metal bonded transition metal complexes, especially bridged binuclear complexes, due to their structural characteristics and application as catalysts [1–3]. Among them, bridged biscyclopentadienyl di-iron complexes have been studied extensively [4–8]. However, bridged bisindenyl di-iron complexes, up to now, have not been reported. In this paper we report the sila-bridged bisindenyl di-iron complexes and one of the crystal structures of them was determined by X-ray diffraction.

RESULTS AND DISCUSSION

Synthesis of sila-bridged bis(1-indenyl) tetracarbonyl di-iron **1** and **2** was achieved by heating $E(C_9H_7)_2$ ($E = Me_2Si$, $Me_2SiOSiMe_2$) with $Fe(CO)_5$ in refluxing heptane.

In comparison with cyclopentadienyl analogues, **1** and **2** are less stable. While the reactions were carried out in refluxing xylene, no desired products were produced due to serious decomposition. Owing to the asymmetry of the indenyl ligand, both **1** and **2** have *cis* and *trans* isomers. For **1**, according to the different crystal shapes a small amount of pure *cis* isomer **1c** and *trans* isomer **1t** were picked out mechanically. For **2**, after recrystallization only one isomer was obtained. Its ^1H NMR and IR spectra indicated that it is the *trans* isomer **2t**. In order to increase the stability, **1** and **2t** were hydrogenated in the presence of PtO_2 at atmospheric pressure, and the corresponding tetrahydroindenyl complexes **3** and **4t** were obtained respectively. After hydrogenation, pure *cis* isomer **3c** and *trans* isomer **3t** were separated by chromatography.

The 200 MHz ^1H NMR spectra indicate the presence of two isomers. The α, β protons of the five-membered rings of each isomer appear as two doublets. The Si-methyl protons of the *cis* isomers **1c** and **3c** appear as two singlets, but for the *trans* isomers **1t** and **3t**, they appear as singlets. For the tetramethyldisiloxane-bridged complexes **2** and **4** both the isomers appear as two singlets. In the IR spectra of **1**–**4** there are absorption peaks of bridged carbonyls

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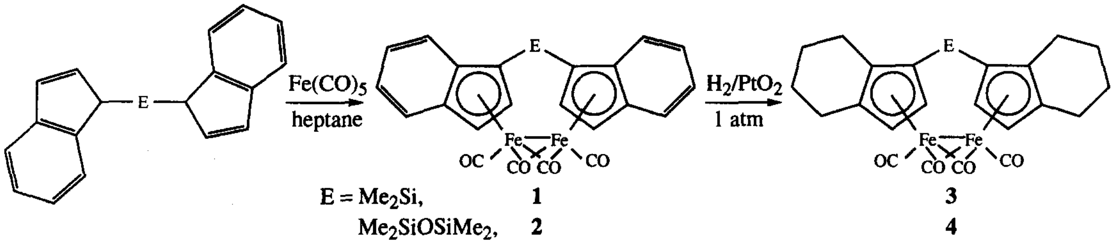

in about 1800 cm^{-1} and terminal carbonyls in the range of 1900–2000 cm^{-1}. For the *cis* isomers, the absorptions of bridged carbonyls appear as two peaks, but for the *trans* isomers, they appear as a single peak.

The molecular structure of **1t** was determined by X-ray diffraction (Fig. 1). **1t** proved to be the *trans* isomer. In the five-membered rings the C—C bond lengths are almost identical, indicating that the five-membered rings are bonded with Fe atom in the η^5-form. But in the six-membered rings the bond lengths of C(15)—C(16) (1.371 Å) and C(17)—C(18) (1.365 Å) are significantly shorter and close to the double bond length (1.34–1.35 Å). This indicates that in the six-membered rings the ring part of C(15)—C(16)—C(17)—C(18) exists as a conjugated diene system and explains that **1** and **2** can be hydrogenated to the tetrahydroindenyl complexes even under ordinary pressure.

EXPERIMENTAL

All operations were performed under purified argon. Heptane was distilled from sodium benzophenone ketyl under argon before use. IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer, while ^{1}H NMR spectra on a JEOL FX-90Q or BRUKER AC-P200 spectrometer. 1,1′-bis(1-indenyl)dimethylsilane [9] and 1,3-bis(1-indenyl) tetramethyldisiloxane [10] were synthesized according to published procedures.

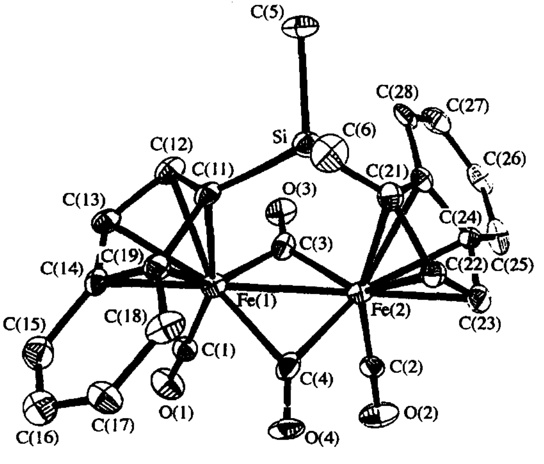

Fig. 1. The molecular structure of **1t**.

Synthesis of compound $Me_2Si[IndFe(CO)]_2(\mu\text{-}CO)_2$, **1**

1,1′-bis(1-indenyl)dimethylsilane (3.9 g, 13.52 mmol) and $Fe(CO)_5$ (3 cm^3, 22.22 mmol) were heated in heptane (50 cm^3) under reflux for 2 days. After removal of excess of $Fe(CO)_5$ and solvent *in vacuo*, the residue was extracted with dichloromethane and filtered through a silica column (3 × 30 cm). The red band was eluted with dichloromethane/petroleum ether (1 : 3), which, on evaporation, yielded brown crystals **1** (0.47 g, 6.8%) as the mixture of *cis* and *trans* isomers. According to the different crystal shapes a small amount of pure *cis* isomer **1c** and *trans* isomer **1t** were separated mechanically. **1**, Found for $C_{24}H_{18}Fe_2O_4Si$: C, 56.5; H, 3.4. Calc.: C, 56.5; H, 3.6%. ^{1}H NMR (200 MHz, $CDCl_3$): **1c**, δ_H 7.60–7.42 (m, 6H), 7.38–7.24 (m, 2H), 6.19 (d, 2.75 Hz, 2H), 5.36 (d, 2.75 Hz, 2H), 0.78 (s, 3H), 0.60 (s, 3H) ppm. **1t**, δ_H 7.60–7.42 (m, 6H), 7.38–7.24 (m, 2H), 6.19 (d, 2.75 Hz, 2H), 5.25 (d, 2.75 Hz, 2H), 0.72 (s, 6H) ppm. IR(KBr) [ν_{CO}/cm^{-1}]: **1c**, 1966.8(vs), 1925.8(s), 1810.9(m), 1786.3(vs). **1t**, 1999.6(vs), 1942.2(s), 1778.1(vs).

Synthesis of $(Me_2SiOSiMe_2)[IndFe(CO)]_2(\mu\text{-}CO)_2$, **2**

This compound was prepared in 4.7% yield by the reaction of 1,3-bis(1-indenyl) tetramethylsiloxane and $Fe(CO)_5$ using the similar method described for **1**. After recrystallization from dichloromethane/petroleum ether, the pure *trans* isomer **2t** was obtained. Found for $C_{24}H_{24}Fe_2O_5Si_2$: C, 53.2; H, 4.0. Calc.: C, 53.4; H, 4.1%. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 7.58–7.24 (m, 6H), 7.12 (d), 7.01 (d) (total 2H), 5.95 (d, 2.0 Hz, 2H), 5.19 (d, 2.0 Hz), 5.11 (d, 2.0 Hz) (total 2H), 0.57(s), 0.50(s) (total 6H), 0.26(s), 0.17(s) (total 6H) ppm. IR(KBr) [ν_{CO}/cm^{-1}]: 1983.2(vs), 1934.0 (s), 1810.9(m), 1769.9(vs). **2t**, ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 7.63–7.28 (m, 6H), 7.12 (d, 2H), 5.95 (s, 2H), 5.11 (s, 2H), 0.50 (s, 6H), 0.17 (s, 6H) ppm. IR(KBr) [ν_{CO}/cm^{-1}]: 1975.0(vs), 1925.8(s), 1778.1(vs).

Synthesis of $Me_2Si[IndH_4Fe(CO)]_2(\mu\text{-}CO)_2$, **3**

To a solution of **1** (0.22 g, 2.20 mmol) in CH_2Cl_2 (50 cm^3), PtO_2 (50 mg, 1.9 mmol) was added. The

Table 1. Summary of crystal data and data collection and refinement for **1t**

Formula	$C_{24}H_{18}Fe_2O_4Si$
M (g/mol)	510.19
Prism (mm)	0.3 × 0.3 × 0.4
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.571(1)
b (Å)	11.555(2)
c (Å)	23.889(6)
β (°)	94.11(2)
V (Å^3)	2085(1)
Z	4
D_x (g cm^{-3})	1.625
F(000)	1040
μ (Mo-K_α) (mm^{-1})	1.763
Reflections collected	2841
Independent reflections	2709
Observed reflections [$I \geq 3\sigma(I)$]	1601
Number of refined parameters	280
S	2.9
R_{int}	0.022
Final R and Rw	0.043 and 0.051
Maximum Δ/σ	0.02
Max. residual peak (e/Å^3)	0.53
Min. residual peak (e/Å^3)	−0.44

mixture was stirred under hydrogen atmosphere (1 atm) at 30°C for 24 h. After filtration the filtrate was evaporated to a small volume and chromatographed through a silica column. Eluted with CH_2Cl_2/petroleum ether (1 : 3), the first and second red bands afforded 0.143 g (64%) of *trans* isomer **3t** and 25 mg (6.5%) of *cis* isomer **3c** as dark brown crystals respectively. **3c**, Found for $C_{24}H_{26}Fe_2O_4Si$: C, 55.7 ; H, 5.2. Calc. : C, 55.6 ; H, 5.1%. ^{1}H NMR (200 MHz, $CDCl_3$) : δ_H 5.25 (d, 2.75 Hz, 2H), 4.70 (d, 2.75 Hz, 2H), 3.05–2.84 (m, 2H), 2.56–1.48 (m, 14H), 0.35 (s, 3H), 0.18 (s, 3H) ppm. IR(KBr) [ν_{CO}/cm^{-1}] : 1969.2(vs), 1930.7(vs), 1807.5(s), 1752.5(vs). **3t**, Found for $C_{24}H_{26}Fe_2O_4Si$: C, 55.6 ; H, 5.1. Calc. : C, 55.6 ; H, 5.1%. ^{1}H NMR (200 MHz, $CDCl_3$) : δ_H 5.30 (d, 2.77 Hz, 2H), 4.85 (d, 2.77 Hz, 2H), 3.01–1.45 (m, 16H), 0.26 (s, 6H) ppm. IR(KBr) [ν_{CO}/cm^{-1}] : 1970.7(vs), 1933.5(s), 1758.1(vs).

Synthesis of $(Me_2SiOSiMe_2)[IndH_4Fe(CO)]_2(\mu\text{-}CO)_2$, **4**

As similar procedure for **3**, from 0.15 g of **2t**, 50 mg of PtO_2 and 50 cm^3 of CH_2Cl_2 47 mg (31.3%) of *trans* isomer **4t** was obtained as dark red crystals. Found for $C_{24}H_{32}Fe_2O_5Si_2$: C, 52.8 ; H, 5.5. Calc. : C, 52.7 ; H, 5.4%. ^{1}H NMR (200 MHz, $CDCl_3$) : δ_H 5.10 (d, 2.57 Hz, 2H), 4.43 (d, 2.57 Hz, 2H), 3.05–2.86 (m, 2H), 2.51–1.52 (m, 14H), 0.36 (s, 6H), −0.01 (s, 6H) ppm. IR(KBr) [ν_{CO}/cm^{-1}] : 1982.5(vs), 1934.7(m), 1803.9(w), 1760.4(vs).

X-Ray crystallography

Single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/petroleum ether. Data collection were performed with Mo-K_α radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 2709 independent reflections were collected with θ_{max} = 23° by the $\omega/2\theta$ scan mode at room temperature (299 ± 1 K), of which 1601 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. The corrections for Lp factors and empirical absorptions were applied to the intensity data. The structure was solved by direct methods using the SDP-PLUS program on PDP 11/44 computer. The full-matrix least-squares method was employed for refinement. Crystal data and some details of data collection and refinement are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 2. Selected bond distances (Å) and bond angles (°) of **1t**

Fe(1)—Fe(2)	2.524(1)	Si—C(11)	1.862(6)	Si—C(21)	1.852(6)
Fe(1)—C(11)	2.159(5)	C(11)—C(12)	1.464(7)		
Fe(1)—C(12)	2.118(6)	C(11)—C(19)	1.472(8)	C(14)—C(15)	1.454(8)
Fe(1)—C(13)	2.106(6)	C(12)—C(13)	1.437(8)	C(15)—C(16)	1.371(8)
Fe(1)—C(14)	2.185(5)	C(13)—C(14)	1.460(8)	C(16)—C(17)	1.431(8)
Fe(1)—C(19)	2.214(5)	C(14)—C(19)	1.410(7)	C(17)—C(18)	1.365(9)
Fe(2)—C(21)	2.161(6)	C(21)—C(22)	1.463(8)	C(18)—C(19)	1.452(8)
Fe(2)—C(22)	2.134(6)	C(21)—C(29)	1.468(7)	C(24)—C(25)	1.437(8)
Fe(2)—C(23)	2.100(6)	C(22)—C(23)	1.397(8)	C(25)—C(26)	1.396(9)
Fe(2)—C(24)	2.181(6)	C(23)—C(24)	1.469(8)	C(26)—C(27)	1.410(9)
Fe(2)—C(29)	2.217(6)	C(24)—C(29)	1.404(8)	C(27)—C(28)	1.379(8)
Fe(1)—CEN(1)	1.770	Fe(2)—CEN(2)	1.778	C(28)—C(29)	1.438(8)
Fe(2)—PL(2)	1.7750(13)	Si—PL(1)	0.1533(27)	Fe(1)—PL(1)	1.7673(13)
PL(1)—PL(2)	83.48(30)	C(11)—Si—C(21)	106.8(2)	Si—PL(2)	0.2149(27)

PL = The plane of five-membered ring, CEN = The center of five-membered ring.

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