



Structures and reactivity of doubly-bridged dicyclopentadienyl dinuclear iron complexes



Bo-Lin Zhu*, Xiao-Ting Hao, Wei Shi

Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, People's Republic of China

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ABSTRACT

The molecular structure of the doubly-bridged bis(cyclopentadienyl) diiron complex $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1b**) was determined, and compared with that of the other analogue $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_4$ (**1a**). The former involves two bridging and two terminal carbonyls, and a normal Fe–Fe bond distance, while the latter contains all-terminal carbonyls and a longer than normal Fe–Fe bond distance. The possible reason for different coordination modes is discussed. Complexes (**1a–b**) react with I_2 to give the corresponding diiodo products $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{EMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_4\text{I}_2$ (E = C, **2a**; E = Si, **2b**) and with phenylacetylene to give the bridging $\mu\text{-C}\equiv\text{CHPh}$ products $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{EMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-C}\equiv\text{CHPh})$ (**3a–b**). Reaction of **1a** with Na/Hg, then with MeI yields the unexpected desilylated product $[(\eta^5\text{-C}_5\text{H}_4)_2(\text{CMe}_2)]\text{Fe}_2(\text{CO})_2\text{Me}_2$ (**5a**). Reaction of **1b** with LiBHET_3 affords the bridging methylene product $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$ (**6b**). The molecular structures of **2a** and **3b** were also determined by X-ray diffraction.

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1. Introduction

Reactions of doubly-bridged dicyclopentadienes with transition metal complexes have attracted a considerable amount of attention [1–7]. A major reason is that doubly-linked ligands would lock two metals in close proximity, which may promote novel chemical reactivity [8]. Recently, we reported a series of reactions of the doubly-bridged dicyclopentadienes $(\text{C}_5\text{H}_4(\text{CMe}_2))(\text{C}_5\text{H}_4(\text{SiMe}_2))$ with transition metal carbonyls $(\text{Fe}(\text{CO})_5, \text{Ru}_3(\text{CO})_{12}, \text{Mo}(\text{CO})_6,$ and $\text{W}(\text{CO})_6)$ [9–11]. One of the products is the normal doubly-bridged bis(cyclopentadienyl) dinuclear complex $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{M}_2(\text{CO})_n$ (M = Fe, Ru, $n = 4$; or M = Mo, W, $n = 6$). The most obvious feature of these complexes is that all of them contain unusually long M–M bonds, which distinguishes them from their respective non-bridged and singly-bridged analogues (Table 1). We have studied the reactivity of dinuclear ruthenium and molybdenum complexes as part of our continuing investigation of doubly-bridged system [11,19]. In this paper, we compare the structures and reactivity of the doubly-bridged dinuclear iron complex $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_4$ (**1a**) and another known analogue $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1b**), as well as their non-bridged and single-bridged analogues.

2. Results and discussion

2.1. Crystal structure of $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1b**)

Although complex **1b** was prepared early as 1992 [7], its detailed structure has not been determined. In order to compare the structures of **1b** and the known analogue **1a**, a single crystal X-ray structural determination of **1b** was carried out (Fig. 1). The molecular structure of **1b** has approximate C_{2v} symmetry, which is reflected in a small twist around the $\text{Fe}(1)\text{--Fe}(1A)$ axis ($\angle\text{Cp}(\text{centroid})\text{--Fe}(1)\text{--Fe}(1A)\text{--Cp}(\text{centroid}) = 2.8^\circ$). The fold angle between the planes of the Cp rings of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ ligand is relatively small (110.6°), compared to that (126.9°) found in **1a** [9], which results in a normal Fe–Fe single bond distance (2.4910 (9) Å), which is significantly shorter than that (2.7747 (6) Å) in **1a**, but compares very well with those in the corresponding non-bridged and singly-bridged analogues (Table 1). One of the most noticeable structural differences between **1a** and **1b** lies in the coordination mode of the carbonyl ligands. In **1a**, each iron atom carries two terminal carbonyls; while in **1b**, the two iron atoms each carry a terminal carbonyl ligand, but are bridged by two carbonyl ligands (Chart 1). Different coordination patterns of carbonyls in **1a** and **1b** are consistent with the different Fe–Fe bond distance, because the bridging carbonyl groups tend to shorten the metal–metal distance, while the all-terminal arrangement

* Corresponding author. Tel.: +86 15122117047; fax: +86 22 23766532.

E-mail address: hxyzb1@gmail.com (B.-L. Zhu).

Table 1
M–M bond distance comparison for non-bridged, singly-bridged, and doubly-bridged dicyclopentadienyl dinuclear complexes.

	Fe complexes	Refs.	Fe–Fe (Å)	Ru complexes	Ru–Ru (Å)	Refs.
Non-bridged	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\mu\text{-CO})_2$	[12]	2.531	$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2(\mu\text{-CO})_2$	2.735(2)	[14]
Singly-bridged	$[(\eta^5\text{-C}_5\text{H}_4)_2(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$	[13]	2.512(3)	$[(\eta^5\text{-C}_5\text{H}_4)_2(\text{SiMe}_2)]\text{Ru}_2(\text{CO})_2(\mu\text{-CO})_2$	2.706(1)	[15]
Doubly-bridged	$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_4$ (1a)	[9]	2.7747(6)	$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Ru}_2(\text{CO})_4$	2.8420(8)	[11]
	Mo complexes		Mo–Mo (Å)	W complexes	W–W (Å)	
Non-bridged	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$	[16]	3.235(1)	$[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$	3.222(1)	[16]
Singly-bridged	$[(\eta^5\text{-C}_5\text{H}_4)_2(\text{CH}_2)]\text{Mo}_2(\text{CO})_6$	[17]	3.1406	$[(\eta^5\text{-C}_5\text{H}_4)_2(\text{SiMe}_2)]\text{W}_2(\text{CO})_6$	3.196(1)	[18]
Doubly-bridged	$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Mo}_2(\text{CO})_6$	[10]	3.433(1)	$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{W}_2(\text{CO})_6$	3.403(2)	[10]

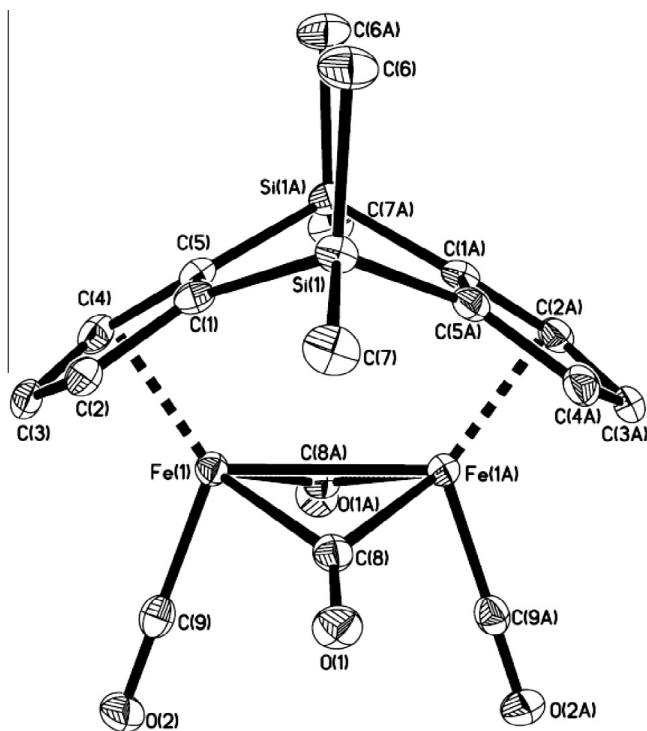
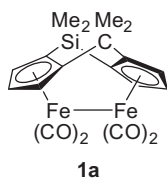
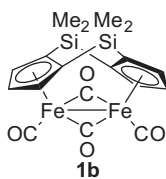


Fig. 1. Thermal ellipsoid drawing of $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1b**) showing the labeling scheme and 50% probability level. Hydrogens are partly omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Fe(1)–Fe(1A) 2.4910(9), Fe(1)–C(8) 1.933(2), Fe(1)–C(9) 1.753(2), Fe(1)–Cp(centroid) 1.752, $\angle\text{C}(1)\text{–Si}(1)\text{–C}(5\text{A})$ 98.77(9), $\angle\text{Fe}(1)\text{–C}(8)\text{–Fe}(1\text{A})$ 80.32(8), $\angle\text{Fe}(1\text{A})\text{–Fe}(1)\text{–C}(8)$ 49.76(6), $\angle\text{Fe}(1\text{A})\text{–Fe}(1)\text{–C}(9)$ 109.31(6), $\angle\text{C}(9)\text{–Fe}(1)\text{–Fe}(1\text{A})\text{–C}(9\text{A})$ 3.0, $\angle\text{Cp}(\text{centroid})\text{–Fe}(1)\text{–Fe}(2)\text{–Cp}(\text{centroid})$ 2.8, $\angle\text{Cp}\text{–Cp}$ 110.6.



all terminal carbonyls,
long Fe–Fe bond distance



terminal&bridging carbonyls,
normal Fe–Fe bond distance

Chart 1. Di-iron complexes of doubly-bridged dicyclopentadienes ($\text{C}_5\text{H}_4(\text{SiMe}_2)(\text{C}_5\text{H}_4(\text{EMe}_2))$).

favors a long metal–metal distance. Some other doubly-bridged dicyclopentadienyl diiron complexes have been reported in our previous papers (Table 2). Some of them have structures similar to that of **1a** with four terminal carbonyl groups and a longer than normal Fe–Fe bond; some of them have structures that are similar to that of **1b** with two bridging and two terminal carbonyl groups and a normal Fe–Fe bond distance. By analysis and comparison of

Table 2
Fe–Fe bond distance comparison for a series of doubly-bridged dicyclopentadienyl diiron complexes.

Doubly bridged Fe complexes	Fe–Fe (Å)	Refs.
$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_4$ (1a)	2.7747(6)	[1]
$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (1b)	2.4910(9)	this work
$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)(\text{SiPh}_2)]\text{Fe}_2(\text{CO})_4$ (1c)	2.8406(7)	[20]
$[(\eta^5\text{-C}_5\text{H}_2^t\text{Bu})_2(\text{SiMe}_2)_2]\text{Fe}_2(\text{CO})_4$ (1d)	2.8205(9)	[9]
$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CH}_2)(\text{SiMe}_2)]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (1e)	2.483(1)	[9]
$[(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{GeMe}_2)]\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (1f)	2.482(2)	[9]

compositions and structures of doubly-bridged ligands, a relationship between the ligands and the Fe–Fe bond distances in their structures is tentatively proposed: the flexibility of doubly-bridged ligands controls the Fe–Fe bond distance and the coordination mode of the carbonyl ligands. Doubly-bridged ligands that are less flexible and difficult to bend tend to form the products containing long Fe–Fe bonds and only terminal carbonyls; ligands that are more flexible and relatively easy to bend are inclined to give products with normal Fe–Fe bonds and bridging carbonyl ligands. In contrast to the ligand $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$, a shorter bridge (CMe_2) in $(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)$ results in more strain when folding the ligand; so complex **1a** adopts an all-terminal arrangement and a longer than normal Fe–Fe bond to avoid a greater bending of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)$ ligand, while $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ in **1b** is flexible enough to achieve a normal Fe–Fe bond distance. However, the introduction of bulky groups (Ph or ^tBu) on the bridging silicon atom (**1c**) or cyclopentadienyl rings (**1d**) of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ ligand increases the difficulty of bending the ligand [9,20], which leads to complexes (**1c** and **1d**) with an all-terminal CO arrangement and longer than normal Fe–Fe bonds. On the contrary, decreasing the steric size of groups on bridging atoms (**1e**) or increasing the radius of bridging atom (**1f**, exchange Si for Ge) on $(\eta^5\text{-C}_5\text{H}_3)_2(\text{CMe}_2)(\text{SiMe}_2)$ ligand results in greater flexibility of the doubly-bridged ligand, which allows complexes (**1e** and **1f**) to achieve a normal Fe–Fe bond distance (Table 2) [9]. Similar arguments may also be applied to non-bridged and singly-bridged dicyclopentadienyl diiron complex as cyclopentadienyl and singly-bridged bis(cyclopentadienyl) ligands are remarkably flexible as compared to doubly-bridged bis(cyclopentadienyl) ligands, which therefore favors the formation of diiron complexes with normal Fe–Fe distances and bridging carbonyl structures (Table 1) [9,12,13].

In view of the different structures of **1a** and **1b**, a series of reactions of **1a–b** with I_2 , phenylacetylene, Na/Hg, and LiBHET_3 were explored, for the purpose of comparing the reactivity of **1a** and **1b**, as well as the corresponding non-bridged and singly-bridged dicyclopentadienyl diiron analogues.

2.2. Reactions of **1a–b** with I_2

It is well-known that the dimeric $\text{Cp}'_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) complexes readily undergo oxidative reactions with halogens to give metal (II) halide carbonyl complexes $\text{Cp}'\text{M}(\text{CO})_2\text{X}$ [21].

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