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Synthesis, structure and stability of *fac*-$[Fe^{II}(CO)_3X_3]^{1-}$ (X = Br, I)

Jianfeng Jiang [a,*], Wenfeng Lo [b], Peter Müller [c], Noam D. Fine [a], Myrium Maruani [a], Alexander Raytman [a]

[a] Department of Chemistry, Yeshiva University, New York, NY 10033, USA
[b] Department of Chemistry, Boston College, Chestnut Hill, MA 02467, USA
[c] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

fac-$[Fe^{II}(CO)_3X_3]^{1-}$ (X = Br, I) are synthesized and their structures have been determined. They are the first crystallographically characterized iron tricarbonyl trihalide complexes. *fac*-$[Fe^{II}(CO)_3X_3]^{1-}$ (X = Br, I) are fairly thermally stable and therefore lead themselves as excellent starting materials for the preparation of various iron carbonyl complexes since both the halide and carbonyl ligands are substitutionally labile.

Metal carbonyl halides are one of the most fundamental complexes in inorganic and organometallic chemistry. The feasible ligand substitution of carbonyls and/or halides can yield a great number of metal carbonyl complexes. Since the discovery that both carbonyl and cyanide are naturally occurring ligands at the active sites of hydrogenases [1–4], iron carbonyl halides have gained significant attention since they are excellent starting materials for the preparation of structural analog complexes of the hydrogenase enzyme active sites as well as other complexes.

Although not very robust, *cis*-$Fe^{II}(CO)_4X_2$ (X = Cl, Br and I) were synthesized about 80 years ago [5,6]; these compounds are the only iron carbonyl halides to have been characterized in detail. Their infrared spectroscopic properties and reactions with phosphines or other ligands have been extensively studied [7–10]. The existence of iron tricarbonyl trihalide have been noted in the past, but the work was based only on the infrared and elemental analysis data [11,12]. We have found that *fac*-$[Fe^{II}(CO)_3X_3]^{1-}$ (X = Br, I) can be readily synthesized by the reaction of iron pentacarbonyl with bromine or iodine in the presence of bromide or iodide under ambient condition [13]. The products are acquired in about 80% yield. X-ray diffraction experiments [14] and infrared studies have established that the products are the *facial* isomer. In addition, *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ can also be made by the equal molar reaction between *cis*-$Fe^{II}(CO)_4I_2$ and iodide.

Due to its C_{3v} symmetry, IR spectrum of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ in CH_2Cl_2 shows two IR-allowed CO stretches at 2044 cm^{-1} and 2098 cm^{-1}. IR spectrum of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3I_3]$ in CH_2Cl_2 also shows two IR-allowed CO stretches, but at lower frequencies: 2025 cm^{-1} and 2078 cm^{-1}. Since iodide is a better electron-donor than bromide, all CO peaks shift to lower frequencies when bromides were replaced by iodides. In both complexes, the lower frequency stretches are assigned to the degenerate asymmetric mode E and the higher frequency stretches are assigned to the symmetric mode A_1. The CO stretching frequencies of *fac*-$[Fe^{II}(CO)_3X_3]^{1-}$ (X = Br, I) do not show any significant change in different solvents.

$[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ was synthesized by adding 1 equivalent of Br_2 to $Fe(CO)_5$ in the presence of 1 equivalent of Et_4NBr in dichloromethane or acetonitrile at room temperature [13]. We postulate that the reaction proceeds in two steps: (1) the addition of Br_2 to $Fe(CO)_5$ generates *cis*-$Fe^{II}(CO)_4Br_2$ (reaction (1)) and *cis*-$Fe^{II}(CO)_4Br_2$ subsequently reacts with Br^- to form *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ (reaction (2)).

$$Fe(CO)_5 + Br_2 \rightarrow cis\text{-}Fe^{II}(CO)_4Br_2 \quad (1)$$

$$cis\text{-}Fe^{II}(CO)_4Br_2 + Br^- \rightarrow fac\text{-}[Fe^{II}(CO)_3Br_3]^{1-} \quad (2)$$

In order to test our hypothesis, the reaction between Br_2 and $Fe(CO)_5$ in the absence of Et_4NBr was monitored by IR in CH_2Cl_2 solution at room temperature. It is found that *cis*-$Fe^{II}(CO)_4Br_2$ was the major product and no *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ was observed. When an equivalent of Et_4NBr was added after the addition of Br_2, *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ was generated, but with a much lower yield, likely because part of the *cis*-$Fe^{II}(CO)_4Br_2$ had decomposed at room temperature before Br^- was added. The infrared spectra of the reaction between $Fe(CO)_5$, halogen (Br_2 or I_2) in the absence or presence of added halide are shown in Fig. 1.

The synthesis shows that the halide ion has the ability to substitute one CO ligand *cis* to the two halides in *cis*-$Fe^{II}(CO)_4X_2$. This

* Corresponding author. Tel.: +1 7186195819.
E-mail address: Jiang@yu.edu (J. Jiang).

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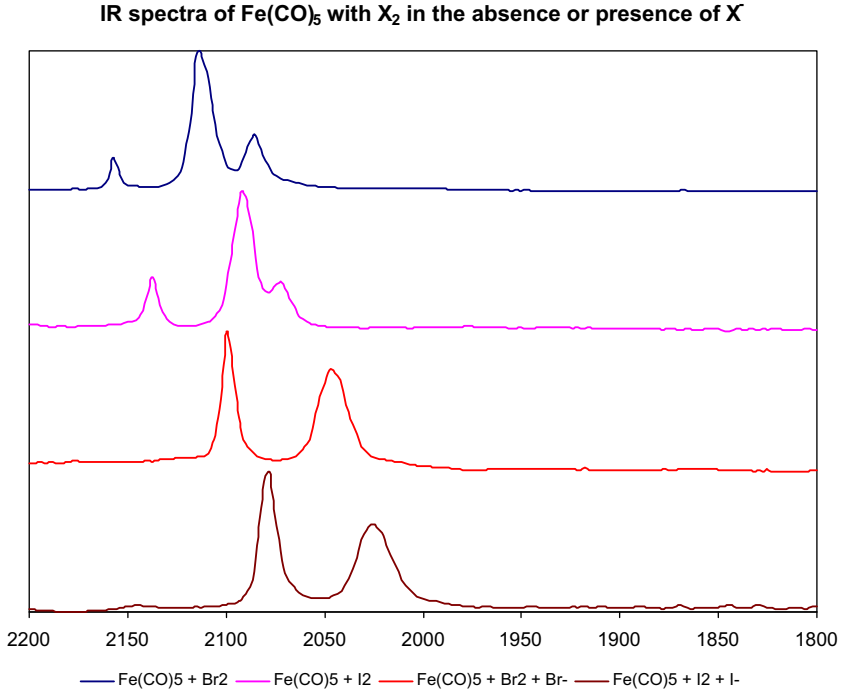

Fig. 1. IR spectra of $Fe(CO)_5$ with X_2 in the absence or presence of X^-.

observation is consistent with the substitution of isonitrile or phosphine in *cis*-$Fe^{II}(CO)_4X_2$ [7,15].

$[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ crystallizes in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit. All atoms of the *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ anion are disordered in a way that the two independent but mutually exclusive Fe positions are about 0.4 Å apart. This disorder can be described as an approximate mirror operation about a plane *ca.* 0.2 Å from and almost parallel to the Fe-C(2)C(3)–Br(1)Br(3) equatorial plane, leading to an almost overlap of the equivalent atoms of the four equatorial ligands (two Br atoms and two carbonyl groups) and the mixed overlap of the two axial ligands (twice a carbonyl group coming close to a Br atom). The four ethyl groups of the Et_4N^+ cation are disordered in such a fashion that the methyl groups superimpose, while the methylene groups occupy opposite sites of imaginary lines between the nitrogen atom and the methyl carbons. The ratios between the two components of both disorders were refined freely and converged at 0.853(3) for the $[Et_4N]$ ion and 0.841(2) for the $[Fe(CO)_3Br_3]$ moiety. Bond lengths and angles between atoms of the major components of the disorders are determined with significantly higher accuracy than for those between the corresponding atoms of the minor components. Therefore, the selected bond distances and angles listed in Table 1 for the structure of (Et_4N)*fac*-$[Fe^{II}(CO)_3Br_3]$ are those of the major component. $[Ph_4P]$*fac*-$[Fe^{II}(CO)_3I_3]$ crystallizes in the monoclinic space group $P2_1/n$ with one molecule per asymmetric unit. The structure of *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ anion is also disordered but not as severe as those in *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$. Only I1 and its *trans*-C(1)O(1) disordered in opposite positions. The major component is refined to 0.918(2) occupancy. The OETEP drawing of *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ and *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ anions are shown in Figs. 2 and 3.

fac-$[Fe^{II}(CO)_3Br_3]^{1-}$ is considerably more thermally stable than *cis*-$Fe^{II}(CO)_4Br_2$. $[Et_4N]$*fac*-$[Fe(CO)_3Br_3]$ is stable in the dark at 0 °C

Table 1
Bond distances (Å) for $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ and $[Ph_4P]$*fac*-$[Fe^{II}(CO)_3I_3]$.

	X = Br	X = I
Fe(1)–X(1)	2.452(3)	2.626(2)
Fe(1)–X(2)	2.448(2)	2.635(2)
Fe(1)–X(3)	2.446(2)	2.629(2)
Fe(1)–C(1)	1.826(5)	1.839(12)
Fe(1)–C(2)	1.790(6)	1.815(16)
Fe(1)–C(3)	1.787(6)	1.782(14)
C(1)–O(1)	1.080(9)	1.066(13)
C(2)–O(2)	1.120(7)	1.080(16)
C(3)–O(3)	1.126(7)	1.109(15)

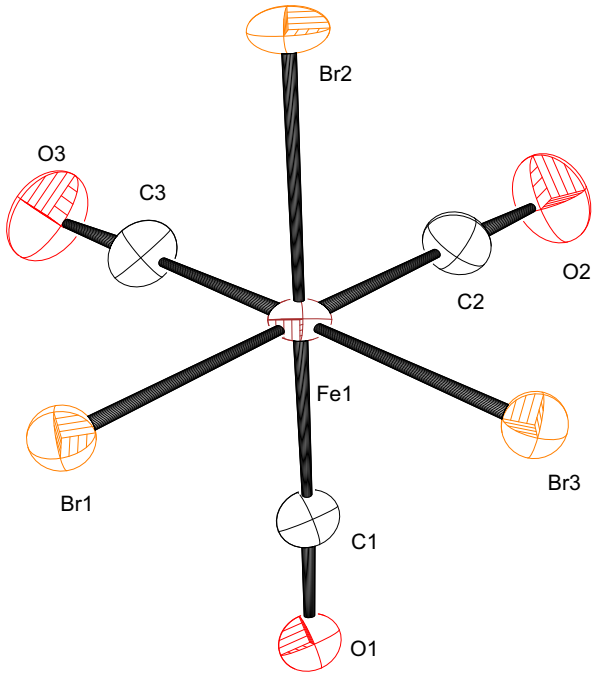

Fig. 2. ORTEP drawing of *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ at 50% probability level.

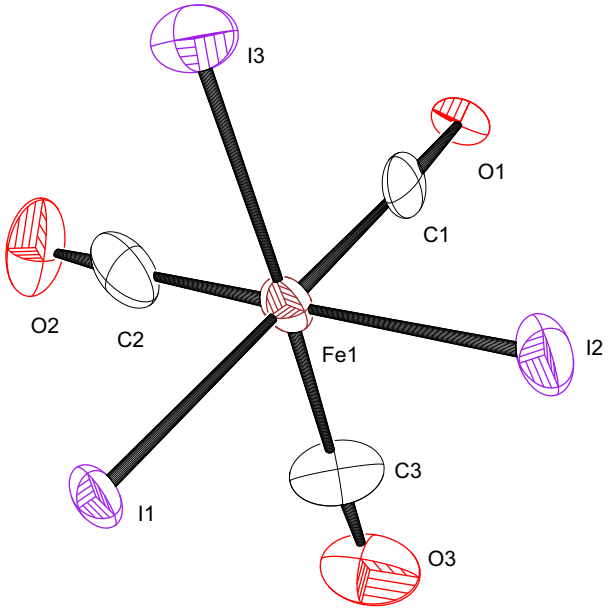

Fig. 3. ORTEP drawing of *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ at 50% probability level.

as crystalline material. Elemental analysis data show that the composition of C, H and N does not change over two months at 0 °C. However, when the crystals of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ are immersed in mineral oil under high intensity illuminator light, the color of the crystals darkens with evolution of gas bubbles, suggesting that the compound is decomposing by loss of CO. $[Et_4N]$-*fac*-$[Fe^{II}(CO)_3Br_3]$ is soluble in water but reacts with water to evolve gas at room temperature. $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ is stable in acetonitrile at room temperature in the dark but decomposes under light. On the other hand, *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ has similar thermal stability as *cis*-$Fe^{II}(CO)_4I_2$.

The reactivity of *fac*-$[Fe^{II}(CO)_3Br_3]^{1-}$ and *fac*-$[Fe^{II}(CO)_3I_3]^{1-}$ with other ligands, especially with cyanide, is currently under investigation. One encouraging observation is that cyanide can stepwise replace halides without replacing CO under certain condition [16,17]. The resulting $[Fe(CO)_3(CN)_mX_{(3-m)}]^{1-}$ ($m = 1$ and 2) complexes would be excellent tunable intermediates to make structural analog complexes for the active sites of both Ni–Fe and Fe–Fe hydrogenase [18].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.04.006.

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[13] Synthesis of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$: A solution of 3.20 g (0.020 mol) Br_2 in 20 mL dichloromethane was added dropwise over 15 min to a mixture of 2.70 mL (1.5 g/mL, 0.021 mol) $Fe(CO)_5$ and 4.20 g (0.020 mol) Et_4NBr in 50 mL dichloromethane at room temperature. The color of the mixture turned from light yellow to dark orange and bubbled vigorously. The solution was allowed to stir at room temperature for another 5 min until no bubbles formed. 100 mL diethyl ether was added to the reaction mixture and brown-orange crystalline materials precipitated. The precipitation was collected by filtration and washed with 20 mL diethyl ether 3 times and dried under vacuum to give a weight of 8.86 g (87% yield). IR (acetonitrile): ν(CO) 2044 cm^{-1}(s), 2098 cm^{-1}(s), Absorption spectrum (acetonitrile): [λ_{max}, nm (ε, M^{-1} cm^{-1})] 433 (1400). Elem. Anal. (C, H, N, Br analysis performed by Robertson Microlit Lab) Calculated: Br 47.06%, C 25.88%, H 3.92%, N 2.75%. Found: Br, 47.40% C, 25.85%, H, 4.06%, N, 3.11%. The synthesis of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3I_3]$ is very similar to that of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ excerpt a solution of 2.54 g (0.010 mol) I_2 in 50 mL dichloromethane was added to a mixture of 1.35 mL (0.0105 mol) $Fe(CO)_4I_2$ and 2.57 g (0.010 mol) Et_4NI in 50 mL dichloromethane at room temperature. Yield 4.97 g (77%). IR (acetonitrile): ν(CO) 2025 cm^{-1}(s), 2078 cm^{-1}(s), Absorption spectrum (acetonitrile): [λ_{max}, nm (ε, M^{-1} cm^{-1})] 365 (1100).
[14] X-ray diffraction experiment: Suitable crystals of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ and $[Ph_4P]$*fac*-$[Fe^{II}(CO)_3I_3]$ were obtained by vapor diffusion of diethyl ether into its dichloromethane solution at 0 °C. Low temperature (193 or 100 K) diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing ω-scans. The unit cell was determined with the goniometer control software SMART [19] and refined using SAINT [20] based on all observed reflections in the range of $3° < 2\theta < 57°$ for $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ and $3° < 2\theta < 53°$ for $[Ph_4P]$*fac*-$[Fe^{II}(CO)_3I_3]$. Data reduction was performed with SAINT, absorption correction and scaling was applied with SADABS [21], following a procedure first described by Blessing [22] The space group was assigned unambiguously by analysis of systematic absences with the help of XPREP [23]. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97 [24]. The disorders of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$ were refined with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. In addition, the nearly overlapping Fe and Br atoms were constrained to have identical anisotropic displacement parameters with their respective equivalent atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Cell parameter of $[Et_4N]$*fac*-$[Fe^{II}(CO)_3Br_3]$: $a = 12.885(6)$ Å, $b = 8.718(4)$ Å, $c = 16.679(8)$ Å, $\beta = 109.115(8)°$, $V = 1770(2)$ Å^3. $R_1 = 0.0453$, $wR_2 = 0.1170$. Cell parameter of $[Ph_4P]$*fac*-$[Fe^{II}(CO)_3I_3]$: $a = 12.583(2)$ Å, $b = 16.716(3)$ Å, $c = 14.353(2)$ Å, $\beta = 107.251(2)°$, $V = 2883.2(8)$ Å^3. $R_1 = 0.0652$, $wR_2 = 0.1681$.
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