$$\mathrm{CH_2Cl_2} \xrightarrow{\text{i–iii}} \underset{1}{\mathrm{G{-}CH_2{-}Te^nBu}} \xrightarrow{\text{iv, v}} \mathrm{G{-}CH_2{-}E} \quad (3)$$

reaction conditions: (i) ^{n}BuTeLi, 6c, 2 h;
(ii) ^{n}BuLi, −95 °C, 10 min;
(iii) GX, −95 to +25 °C, 1 h;
(iv) ^{n}BuLi, −95 to −78 °C, 20 min;
(v) electrophile (E^+), −78 to +25 °C, 1 h

(runs 17 and 18). Bis(phenyltelluro)methane, a precursor of $\mathrm{PhTeCH_2Li}$,[8] was not suitable for this purpose.[17]

The present method is operationally simple and has wide generality, and so it will be a practical and quite useful procedure for the preparation of various heteroatom-substituted methyllithiums.

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[17] The reaction of $\mathrm{PhTeCH_2SiMe_3}$ with butyllithium gave PhLi predominantly rather than **2d** in about a 2:1 ratio (determined by trapping with PhCHO), probably because the thermodynamic stability of PhLi may be comparable to that of **2d**.

Synthesis, Structure, and Reactivity of the First Anionic Acyldihalocarbonyliron(II) Complex. Halogen-Induced Insertion of Carbon Monoxide into an Alkyl-Iron Bond

Take-aki Mitsudo,* Atsushi Ishihara, Toshiaki Suzuki, and Yoshihisa Watanabe*

Department of Hydrocarbon Chemistry
Faculty of Engineering
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Hideki Masuda

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

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Summary: The reaction of $[\mathrm{PPN}][\mathrm{RFe(CO)_4}]$ (R = $\mathrm{CH_3}$ (**1a**), $\mathrm{C_2H_5}$ (**1b**), $\mathrm{PhCH_2}$ (**1c**)) with iodine in $\mathrm{CH_2Cl_2}$ induces the insertion of carbon monoxide into the carbon–metal bond to give the first $[\mathrm{PPN}][\mathrm{RCOFe(CO)_3I_2}]$ complexes (**3a–c**). The molecular structure of **3a** was established by X-ray analysis. $[\mathrm{PPN}][\mathrm{RCOFe(CO)_4}]$ (**4a–d**) reacts with $\mathrm{I_2}$ in $\mathrm{CH_2Cl_2}$ to give $[\mathrm{PPN}][\mathrm{RCOFe(CO)_3I_2}]$ (**3a–d**) in high yield. $[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]$ (**2**) reacts with methyl iodide to give **3a**. Reactions of **3** with nucleophiles such as alcohols and amines have been investigated.

Insertion of carbon monoxide into a metal–alkyl bond, giving an acyl–metal complex, is a fundamental reaction in organometallic chemistry.[1] It is known that an anionic alkyliron complex, $[\mathrm{RFe(CO)_4}]^-$ (**1**), reacts with alcohols, amines, and water in the presence of an excess of iodine or bromine to give esters, amides, and carboxylic acids, respectively (eq 1).[2] In the course of our studies on iron

$$\underset{1}{[\mathrm{RFe(CO)_4}]^-} + \mathrm{NuH} + \mathrm{X_2} \rightarrow \mathrm{RCONu} \quad (1)$$

$$\mathrm{NuH} = \mathrm{R'OH},\ \mathrm{R'NH_2},\ \mathrm{H_2O};\ \mathrm{X_2} = \mathrm{Br_2},\ \mathrm{I_2}$$

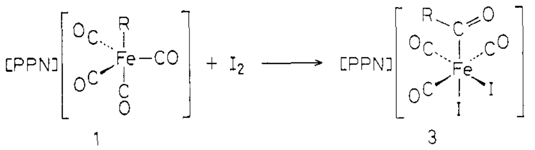
cluster carbonylates,[3] we now have found that the reaction of $[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]$ (**2**) with methyl iodide gives $[\mathrm{PPN}][\mathrm{CH_3COFe(CO)_3I_2}]$ (**3a**). This complex may be an intermediate in the reaction shown in eq 1. For this reason we also examined the reactions of $[\mathrm{RFe(CO)_4}]^-$ (**1**) with iodine and found that the same complex is formed and, thus, clear evidence for $\mathrm{I_2}$-induced CO insertion into an alkyl–metal bond was obtained. We now report the preparation, structure, and reactivities of the novel complex **3**.

$[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]$ (**2**) reacted with an excess of methyl iodide in THF under an argon atmosphere at 25 °C during the course of 5 days to give $[\mathrm{PPN}][\mathrm{CH_3COFe(CO)_3I_2}]$ (**3a**)

$$\underset{2}{[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]} + \mathrm{CH_3I} \rightarrow \underset{3a}{[\mathrm{PPN}][\mathrm{CH_3COFe(CO)_3I_2}]} \quad (2)$$

in 60% yield. Thus, the tetranuclear cluster decomposed completely to the mononuclear complex to give the first acyldiiodotricarbonylferrate(II) complex **3**.

Such complex salts also could be prepared by reaction of salts of $[\mathrm{RFe(CO)_4}]^-$ anions with iodine. For example, $[\mathrm{PPN}][\mathrm{CH_3Fe(CO)_4}]$ (**1a**), $[\mathrm{PPN}][\mathrm{C_2H_5Fe(CO)_4}]$ (**1b**), and $[\mathrm{PPN}][\mathrm{PhCH_2Fe(CO)_4}]$ (**1c**) reacted with $\mathrm{I_2}$ in $\mathrm{CH_2Cl_2}$ at −78 °C during the course of 2–4 h to give $[\mathrm{PPN}][\mathrm{CH_3COFe(CO)_3I_2}]$ (**3a**; yield 33%), $[\mathrm{C_2H_5COFe(CO)_3I_2}]$ (**3b**; yield 45%), and $[\mathrm{PPN}][\mathrm{PhCH_2COFe(CO)_3I_2}]$ (**3c**; yield 40%), respectively (eq 3). $[\mathrm{PPN}][\mathrm{RCOFe(CO)_4}]$ (**4**; R = $\mathrm{CH_3}$ (**4a**), $\mathrm{C_2H_5}$ (**4b**), $\mathrm{PhCH_2}$ (**4c**), Ph (**4d**)) also reacted with $\mathrm{I_2}$ in $\mathrm{CH_2Cl_2}$ at −78 °C to give the same products, $[\mathrm{PPN}][\mathrm{RCOFe(CO)_3I_2}]$ (yield 95% (**3a**), 75% (**3b**), 69% (**3c**), 87% (**3d**)), with evolution of carbon monoxide (eq 4).



1 3 (3)

$$\underset{4}{[\mathrm{PPN}][\mathrm{RCOFe(CO)_4}]} + \mathrm{I_2} \rightarrow \underset{3}{[\mathrm{PPN}][\mathrm{RCOFe(CO)_3I_2}]} + \mathrm{CO} \quad (4)$$

Reactions of the complex salts **1** or **4** with bromine in a similar fashion gave the corresponding anionic acyldibromotricarbonyliron complexes at −78 °C, which was confirmed by IR spectra of the reaction solutions.[4]

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[1] E.g.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 355.

[2] (a) Takegami, Y.; Watanabe, Y.; Masada, I.; Kanaya, I. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1456. (b) Masada, H.; Mizuno, M.; Suga, S.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3824. (c) Collman, J. P.; Winter, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249. (d) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

[3] Ishihara, A.; Mitsudo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *368*, 199 and references cited therein.

[4] For $[\mathrm{PPN}][\mathrm{PhCOFe(CO)_3Br_2}]$ in $\mathrm{CH_2Cl_2}$, derived from $[\mathrm{PPN}][\mathrm{PhCOFe(CO)_4}]$ (**4d**) and $\mathrm{Br_2}$ (at 0 °C), $\nu(\mathrm{C{\equiv}O})$ = 2097 (s), 2037 (vs), 1995 (s) $\mathrm{cm^{-1}}$ and $\nu(\mathrm{C{=}O})$ = 1603 (m) $\mathrm{cm^{-1}}$. This complex decomposed in $\mathrm{CH_2Cl_2}$ solution at 10 °C to give benzoyl bromide ($\nu(\mathrm{C{=}O})$ = 1773 $\mathrm{cm^{-1}}$). For $[\mathrm{PPN}][\mathrm{CH_3COFe(CO)_3Br_2}]$ in $\mathrm{CH_2Cl_2}$, derived from $[\mathrm{PPN}][\mathrm{CH_3Fe(CO)_4}]$ (**1a**) and $\mathrm{Br_2}$ (at 0 °C), $\nu(\mathrm{C{\equiv}O})$ = 2097 (s), 2031 (vs), 1995 (s) $\mathrm{cm^{-1}}$ and $\nu(\mathrm{C{=}O})$ = 1647 (m), 1628 (m) $\mathrm{cm^{-1}}$. This complex decomposed in $\mathrm{CH_2Cl_2}$ solution at 10 °C to give acetyl bromide ($\nu(\mathrm{C{=}O})$ = 1811 $\mathrm{cm^{-1}}$).

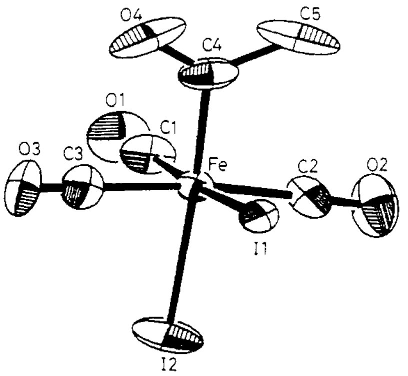


Figure 1. ORTEP drawing of [PPN][$CH_3COFe(CO)_3I_2$] (**3a**). Selected bond distances (Å) and angles (deg): Fe–C(1) = 1.782 (10); Fe–C(2) = 1.826 (9); Fe–C(3) = 1.869 (10); Fe–C(4) = 1.991 (9); Fe–I(1) = 2.632 (1); Fe–I(2) = 2.683 (1); C(4)–O(4) = 1.163 (13); C(4)–C(5) = 1.486 (17); C(1)–O(1) = 1.082 (13); C(2)–O(2) = 1.080 (13); C(3)–O(3) = 0.954 (13); C(4)–Fe–I(2) = 176.8 (3); Fe–C(4)–C(5) = 119.6 (8); Fe–C(4)–O(4) = 122.0 (9); C(1)–Fe–I(1) = 173.3 (3); C(2)–Fe–C(3) = 172.0 (5).

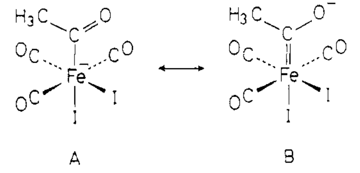
Table I. Spectral Data for the Complexes 3a and 3d

	IR (KBr), cm^{-1}		^1H NMR (270 MHz, CD_2Cl_2, TMS), δ	^{13}C NMR (67.8 MHz, CD_2Cl_2, TMS), δ
	$\nu(C{\equiv}O)$	$\nu(C{=}O)$		
3a	2074 (m)	1645 (m)	2.77 (s, 3 H, CH_3)	51.2 (q, $^1J(C-H)$ = 127.8 Hz, CH_3)
	2006 (vs)	1628 (m)	7.50 (m, 30 H, PPN)	260.0 (s, CH_3CO) 208.8 (s, $C{\equiv}O$)
	1981 (s)			213.5 (s, $C{\equiv}O$)
3d	2078 (m)	1611 (m)	7.36–7.70 (35 H, Ph, and PPN)	263.3 (s, PhCO) 208.8 (s, $C{\equiv}O$)
	2018 (vs)			214.4 (s, $C{\equiv}O$)
	1977 (s)			

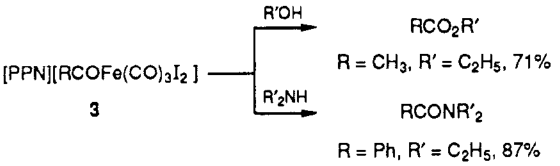
However, these complexes decomposed at ca. 10 °C and could not be isolated.

Spectral data of **3a** and **3d** shown in Table I are representative. Spectral data of **3a–d** showed that these complexes are all of the type [PPN][$RCOFe(CO)_3I_2$]. The three terminal $\nu(C{\equiv}O)$ absorptions around 2078–1977 cm^{-1} (KBr) are at higher wavenumber compared with those of [$RCOFe(CO)_4$]$^-$ (2010–1855 cm^{-1}).[5] The pattern of these absorptions showed that these complexes are *cis-mer* isomers.[6] The $\nu(C{=}O)$ absorptions of the acyl groups were found at 1611–1644 cm^{-1}. Complex **3a** has two $\nu(C{=}O)$ bands at 1647 and 1626 cm^{-1}, in CH_2Cl_2 solution as well as in the solid state (KBr, 1645 and 1628 cm^{-1}). The ^1H NMR signal of the methyl group of **3a** was found at 2.77 ppm, and the methylene groups in **3b** and **3c** were observed at lower fields, 3.20 and 4.51 ppm, respectively. ^{13}C NMR spectra exhibited signals due to the methyl group of **3a** and methylene groups in **3b** and **3c** at rather lower field, 51.2, 58.9, and 71.0 ppm, respectively. ^{13}C NMR signals due to the acyl carbonyls were observed in the range 255.0–263.3 ppm, similar to that (δ 261.5 ppm in THF) of [PPN][$C_2H_5COFe(CO)_4$].[5] Thus, the complexes **3a–d** were inferred to be bis(triphenylphosphine)nitrogen(1+) *cis-mer*-acyldiiodotricarbonylferrate(II) salts on the basis of the spectral data.

X-ray analysis established the structure of complex **3a**, which is shown in Figure 1.[7] The geometry of the complex is octahedral, and the *cis-mer* configuration was confirmed. Considering the standard deviation, the Fe–C(4) length of 1.991 (9) Å is slightly longer than those in most acyliron complexes (1.96–1.97 Å).[8] Usually, the structure of an anionic acyliron complex is represented in terms of the resonance hybrid A ↔ B, and a shorter Fe–C(acyl) distance,[9] due to the contribution of structure B, is expected. However, in this case, the electronegative iodide ion in the trans position may reduce the back-donation from the iron atom to the acyl carbon atom and the contribution of A may be greater than that of B.



[PPN][$CH_3COFe(CO)_3I_2$] (**3a**) reacted with nucleophiles such as ethanol and diethylamine to give ethyl acetate and *N*,*N*-diethylacetamide (71 and 37% yields, respectively). [PPN][$PhCOFe(CO)_3I_2$] (**3d**) also reacted with ethanol and diethylamine to give ethyl benzoate and *N*,*N*-diethylbenzamide (54 and 87% yields, respectively). It is known that [$RFe(CO)_4$]$^-$ (**1**) and [$RCOFe(CO)_4$]$^-$ (**4**) react with alcohols or amines in the presence of an excess of iodine to give esters or amides.[2] In these reactions, it has been assumed that acyl halides would be formed. In fact, in the reaction of **4** with bromine, the dibromoacyliron complex corresponding to **3** was formed below 0 °C, and it decomposed to give acyl bromide at ca. 10 °C.[4] These results suggest that, in the reactions of [$RFe(CO)_4$]$^-$ (**1**) or [$RCOFe(CO)_4$]$^-$ (**4**) with alcohols or amines in the presence of halogen,[2] [$RCOFe(CO)_3X_2$]$^-$ is formed in the initial step, followed by the formation of acyl halides, which then react with the nucleophiles to give the observed esters or amides:



(5)

Further study on the reactivities of the novel acyldiiodotricarbonyliron complex **3** is in progress.

Supplementary Material Available: Listings of atomic coordinates and isotropic temperature factors, hydrogen coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles and listings giving results of analyses and spectroscopic data and details of the reactions of **2**, **3**, and **4** (16 pages); a listing of structure factor amplitudes (F_o–F_c) (15 pages). Ordering information is given on any current masthead page.

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(7) **3a**: mp 77 °C dec. Some crystal data for **3a** are as follows: $C_{41}H_{33}FeI_2NO_4P_2$, M_r = 975.32, monoclinic, space group $P2_1/c$, a = 14.466 (3) Å, b = 18.472 (2) Å, c = 15.349 (1) Å, β = 96.35 (1)°, V = 4076.2 $Å^3$, Z = 4, D_c = 1.589 g cm^{-3}, μ(Mo Kα) = 19.84 cm^{-1}, crystal dimensions 0.3 × 0.3 × 0.4 mm. Intensity data in the range $2\theta \leq 60°$ were collected by the ω–2θ scan technique with an Enraf-Nonius CAD4 automated four-circle diffractometer. The structure was solved by direct methods (MULTAN78) and was refined by full-matrix least-squares techniques. The final R and R_w values were 0.0708 and 0.0709, respectively, for 6230 unique reflections with $|F_o| \geq 3\sigma|F_o|$. Full details are provided in the supplementary material.

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