第 33 卷第 9 期
2017 年 9 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.33 No.9
1547-1554

邻异丙硫基苯甲酰基和苯硫甲基铁衍生物的合成与反应

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摘要：利用异丙基苯硫醚与丁基锂反应后，再依次与羰基铁和碘反应制得了碘桥双核邻异丙硫基苯甲酰基铁配合物[(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$,而苯甲硫醚类似的反应却仅得到单核苯硫甲基铁配合物 $C_6H_5SCH_2Fe(CO)_3I$。当与亲核试剂作用时,这 2 个化合物表现出显著不同的反应活性。如双核配合物[(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$ 与 2-吡啶硫醇钠(PySNa)反应得到单核配合物(*o*-^{i}PrS)$C_6H_4COFe(CO)_2$(SPy),但单核配合物 $C_6H_5SCH_2Fe(CO)_3I$ 与 PySNa 反应导致其分解。另一方面,单核配合物 $C_6H_5SCH_2Fe(CO)_3I$ 与三苯基膦(PPh_3)反应得到羰基取代配合物 $C_6H_5SCH_2Fe(CO)_2(PPh_3)I$,但是双核配合物[(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$ 类似的反应却导致其分解,没有获得可表征的化合物。所有新合成的化合物都通过了核磁与红外光谱的表征,它们的结构也获得了 X 射线单晶衍射的确证。

关键词：硫醚；羰基铁；金属酰基配合物；吡啶；膦配体
中图分类号：O614.81$^+$1　　**文献标识码**：A　　**文章编号**：1001-4861(2017)09-1547-08
DOI:10.11862/CJIC.2017.192

Synthesis and Reactivity of *ortho*-Isopropylthiobenzoyl and Phenylthiomethyl Iron Derivatives

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Abstract: Reaction of isopropylthiobenzene with *n*-BuLi, and subsequently with iron carbonyl and iodine gave a dimeric *ortho*-isopropylthiobenzoyl iron derivative [(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$ through two iodide bridges, while similar reaction of thioanisole only yielded mononuclear phenylthiomethyl iron complex $C_6H_5SCH_2Fe(CO)_3I$. These two complexes show significantly different reactivities upon treatment with various nucleophiles. For example, reaction of [(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$ with sodium 2-pyridinethiolate (PySNa) give mononuclear complex (*o*-^{i}PrS)$C_6H_4COFe(CO)_2$(SPy), while reaction of $C_6H_5SCH_2Fe(CO)_3I$ with PySNa results in the decomposition of the starting material. On the other hand, reaction of $C_6H_5SCH_2Fe(CO)_3I$ with PPh_3 give complex $C_6H_5SCH_2Fe(CO)_2(PPh_3)I$, but no characterizable product is obtained from the similar reaction of [(*o*-^{i}PrS)$C_6H_4COFe(CO)_2I]_2$. All these newly synthesized compounds have been characterized by physico-chemical and spectroscopic methods, and their structures were unambiguously determined by X-ray crystallography. CCDC: 1545834, **1**; 1545835, **2A**; 1545836, **3**; 1545837, **4**.

Keywords: thioether; iron carbonyl; metal-acyl complex; pyridine; phosphine ligand

收稿日期:2017-06-22。收修改稿日期:2017-07-20。
国家自然科学基金(No.21372124)和天津市自然科学基金(No.14JCYBJC19700)资助项目。
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The investigation on the metal-acyl complexes continues to be an active research area in organometallic chemistry since these complexes show excellent catalytic activity in many organic transformations[1-4], and this category of complexes are proposed as the key active intermediates in numerous catalytic processes[5-8]. Recent studies have proven the practicability that the metal-acyl moiety was introduced into the main chain of polymers to form potential functional organometallic materials[9], and the organometallic aqueous colloids were formed through the self-assembly of the metal-acyl complexes[10], which markedly broaden their application fields. Among the metal-acyl complexes, the acyl iron complexes have drawn more and more attention in recent years because of the successful elucidation of the structure of [Fe]-hydrogenase[11-13], which suggests that an acyl-iron ligates to the active site of [Fe]-hydrogenase[14]. Since then a number of acyl iron complexes have been synthesized and characterized[15-20], which promotes the rapid development of acyl iron complexes. To match the electronic and steric properties of biomimetic models for the active site of [Fe]-hydrogenase, several kinds of donor-functionalized acyl ligands, such as acylphosphine[21], carbamoylpyridine[19], acylmethylpyridine[16], and acylmethylpyrazole[22-23], have been used to synthesize acyl iron complexes. Because of the introduction of the chelation-assisted donor atoms bearing different electron-donating ability, the corresponding acyl iron complexes exhibit versatile reactivity. In addition, the incorporation of the sulfur-containing ligand to the metal center of model complexes for [Fe]-hydrogenase is also important, since the sulfur atom possibly plays a role in the catalytic cycle of hydrogen activation by [Fe]-hydrogenase[24-25]. However, iron complexes with sulfur-functionalized acyl ligand[26-27] are rare in known synthetic model complexes of [Fe]-hydrogenase, in which phenylthiolate or 2-pyridinethiolate ligand is usually used to occupy the cysteine sulfur position. Other structural models with sulfur-functionalized acyl ligand should be conducive to gaining a deeper understanding of the structure and catalytic function of [Fe]-hydrogenase owing to the strong influence of the stereo-electronic environment of the iron center on the ability of the biomimic to bind hydrogen molecule. Our previous investigations showed that the different chelation-assisted donor atoms significantly affected the structure and reactivity of the corresponding acyl iron complexes[22-23]. As an extension of our investigations on this subject, herein we describe the synthesis and reactivity of thioether-based iron complexes.

1 Experimental

Solvents were dried and freshly distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of argon. NMR spectra were recorded on a Bruker 400 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts were reported with respect to the reference (internal $SiMe_4$ for ^1H and ^{13}C NMR spectra, external 85% H_3PO_4 aqueous solution for ^{31}P NMR spectra). IR spectra were recorded as KBr pellets on a Tensor 27 spectrometer. Elemental analyses were carried out on an Elementar Vario EL analyzer.

1.1 Synthesis of $[(o\text{-}^i\text{PrS})C_6H_4COFe(CO)_2I]_2$ (1)

A hexane solution of n-BuLi (1.6 mol·L^{-1}, 1.3 mL, 2 mmol) was added to the solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.2 mL, 2 mmol) in hexane (10 mL) at room temperature. After 30 min, isopropylthiobenzene (0.32 mL, 2 mmol) was added to the above-mentioned solution. The resulting mixture was stirred for 4 h at room temperature, during which time a solid was precipitated out. Then, the reaction mixture was cooled to −78 ℃, and THF (20 mL) was added, After the solid was completely dissolved, $Fe(CO)_5$ (0.26 mL, 2 mmol) was added. The reaction mixture was continuously stirred at −78 ℃ for 30 min, and allowed to reach room temperature slowly and stirred for 2 h. A solution of I_2 (0.51 g, 2 mmol) in THF (10 mL) was added dropwise. After completion of addition, the reaction mixture was stirred overnight. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica with CH_2Cl_2 as the eluent. The red eluate was concentrated to dryness to give **1** as a red solid. Yield: 0.33 g (38%). ^1H NMR: δ 1.43 (d, J=5.3 Hz, 6H, CH_3),

1.49 (d, J=5.0 Hz, 6H, CH_3), 3.20~3.35 (m, 2H, CH), 7.55~7.65 (m, 4H, C_6H_4), 7.74~7.80 (m, 4H, C_6H_4). ^{13}C NMR: δ 22.1 (CH_3), 22.4 (CH_3), 48.7 (CH), 125.2, 130.8, 131.7, 132.1, 136.4, 150.5 (C_6H_4), 195.8, 205.0 (C≡O), 246.9 (C=O). IR(cm^{-1}): ν(C≡O) 2 090, 2 030, 2 004, 1 975; ν(C=O) 1 628. Anal. Calcd. for $C_{24}H_{22}Fe_2I_2O_6S_2$ (%): C 34.48, H 2.65; Found(%): C 34.35, H 3.10.

1.2 Synthesis of (*o*-^{i}PrS)$C_6H_4COFe(CO)_2$(SPy) (2)

Sodium hydride (12 mg, 0.5 mmol) was added to a solution of 2-mercaptopyridine (56 mg, 0.5 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1 h at room temperature, followed by the addition of a solution of **1** (0.21 g, 0.25 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was continuously stirred for 6 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica with CH_2Cl_2 as the eluent. The red eluate was concentrated to dryness to afford 0.16 g (72%) of **2**. This complex consisted of two isomers (**2A/2B**) in solution. The relative ratio of isomers was *ca.* 1∶1 in $CDCl_3$ and 2∶1 in acetone-d_6, respectively, according to the integral of the corresponding protons of the methine and methyl groups. **2A**: ^{1}H NMR: δ 1.38 (d, J=6.6 Hz, CH_3), 1.49 (d, J=6.6 Hz, CH_3), 3.35~3.46 (m, CH), 3.50~3.66 (m, CH), 6.55~6.61 (m), 6.82~6.90 (m), 7.00~7.16 (m), 7.29~7.35 (m), 7.36~7.41 (m), 7.61~7.70 (m), 7.88~7.95 (m) (phenyl and pyridyl protons). ^{13}C NMR: δ 21.5, 22.0, 22.1, 22.6 (CH_3), 46.3, 46.9 (CH), 117.5, 117.9, 122.2, 122.5, 125.4, 127.4, 130.3, 130.5, 130.8, 131.4, 131.7, 131.8, 135.5, 136.1, 138.1, 138.6, 148.5, 148.7, 149.7, 151.0, 177.3, 180.8 (phenyl and pyridyl carbons), 208.8, 210.2, 210.7, 211.6 (C≡O), 260.3, 262.2 (C=O). **2B**: ^{1}H NMR (acetone-d_6): δ 1.39 (d, J=6.8 Hz), 1.41 (d, J=6.7 Hz), 1.53 (d, J=6.7 Hz), 3.55~3.65 (m), 3.68~3.83 (m), 6.77 (t, J=6.2 Hz), 6.89 (dd, J_1=2.8 Hz, J_2=8.3 Hz), 7.00~7.03 (m), 7.09~7.24 (m), 7.42 (dd, J_1=1.0 Hz, J_2=7.6 Hz), 7.89 (t, J=8.1 Hz), 8.20 (d, J=5.3 Hz). The other signals in the range of 7.48~7.70 overlapped seriously. IR(cm^{-1}): ν(C≡O) 2 023, 1 967, 1 957; ν(C=O) 1 615. Anal. Calcd. for $C_{17}H_{15}FeNO_3S_2$(%): C 50.88, H 3.77, N 3.49; Found(%): C 50.66, H 4.23, N 3.46.

1.3 Synthesis of $C_6H_5SCH_2Fe(CO)_3I$ (3)

This complex was similarly obtained using thioanisole instead of isopropylthiobenzene as above-mentioned synthesis of **1**. Yield: 39%. ^{1}H NMR: δ 3.95~4.00 (m, 2H, CH_2), 7.39 (s, br, 3H, C_6H_5), 7.53 (s, br, 2H, C_6H_5). ^{13}C NMR: δ 38.7 (CH_2), 129.8, 130.0, 130.1, 135.8 (C_6H_5), 203.8, 209.4, 210.2 (C≡O). IR: ν(C≡O) 2 077, 2 019, 1 996 cm^{-1}. Anal. Calcd. for $C_{10}H_7FeIO_3S$ (%): C 30.80, H 1.81; Found(%): C 30.92, H 2.14.

1.4 Synthesis of $C_6H_5SCH_2Fe(CO)_2(PPh_3)I$ (4)

PPh_3 (26 mg, 0.1 mmol) was added to a solution of **3** (39 mg, 0.1 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica with CH_2Cl_2/hexane (1∶2, V/V) as the eluent to give a red eluate, which was concentrated to dryness to afford 20 mg (32%) of **4** as a red solid. ^{1}H NMR: δ 3.92~4.11 (m, 2H, CH_2), 7.03~7.60 (m, 20H, C_6H_5). ^{13}C NMR: δ 36.0 (d, $J_{P\text{-}C}$=20.2 Hz, CH_2), 128.4 (d, $J_{P\text{-}C}$=9.5 Hz), 128.1, 129.0, 129.3, 130.2, 133.6, 133.9 (d, $J_{P\text{-}C}$=10.1 Hz), 135.0, 135.4, 136.0 (C_6H_5), 214.9 (d, $J_{P\text{-}C}$=17.5 Hz), 218.1 (C≡O). ^{31}P NMR: δ 40.1. IR: ν(C≡O) 2 004, 1 950 cm^{-1}. Anal. Calcd. for $C_{27}H_{22}FeIO_2PS$ (%): C 51.95, H 3.55; Found(%): C 51.80, H 3.89.

1.5 Reaction of 1 with PPh_3

Reaction of **1** with PPh_3, like that of **3** with PPh_3, resulted in the decomposition of the starting material. No characterizable product was obtained.

1.6 Crystal structure determination

Crystals of **1**, **2A**, **3** and **4** suitable for X-ray analyses were obtained by slow diffusion of hexane into their CH_2Cl_2 solutions at −18 ℃. All intensity data were collected on a Rigaku Saturn CCD detector using Mo $K\alpha$ radiation (λ=0.071 073 nm). Semi-empirical absorption corrections were applied using the Crystalclear program[28]. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL[29] by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined with riding model position parameters. A summary of the fundamental crystal data for **1**, **2A**, **3** and **4** is listed in Table 1.

Table 1 Crystal data and refinement parameters for complexes 1, 2A, 3 and 4

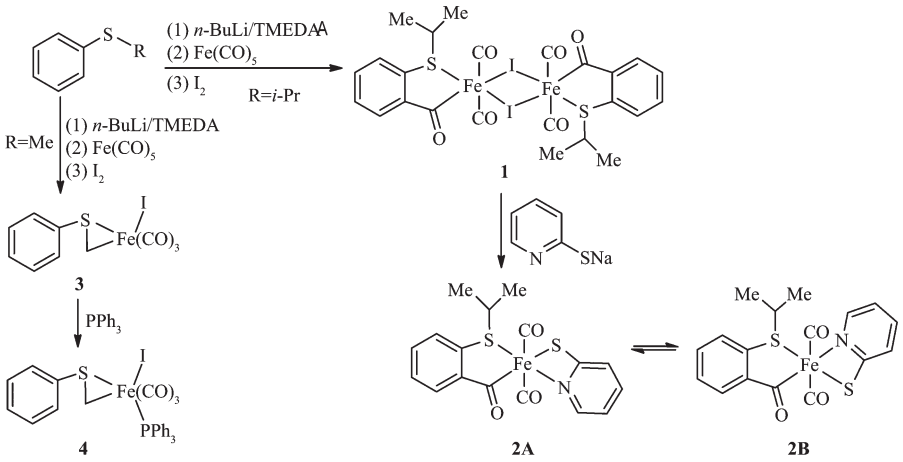
Complex	1	2A	3	4
Formula	$C_{24}H_{22}Fe_2I_2O_6S_2$	$C_{17}H_{15}FeNO_3S_2$	$C_{10}H_7FeIO_3S$	$C_{27}H_{22}FeIO_2PS$
Formula weight	836.03	401.27	389.97	624.23
Crystal size / mm	0.20×0.18×0.12	0.20×0.18×0.12	0.24×0.22×0.16	0.20×0.18×0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/n$	$P2_1/c$
a / nm	2.267 3(5)	1.166 2(2)	1.229 12(13)	1.273 57(18)
b / nm	0.961 08(19)	1.250 4(3)	0.710 29(7)	1.049 13(15)
c / nm	1.649 6(3)	1.188 6(2)	1.433 60(14)	1.871 3(2)
β / (°)	127.86(3)	95.379(2)	97.984(2)	92.063(3)
T / K	113(2)	113(2)	113(2)	113(2)
V / nm^3	2.837 8(13)	1.725 5(6)	1.239 4(2)	2.498 7(6)
Z	4	4	4	4
D_c / (g·cm^{-3})	1.957	1.545	2.090	1.659
F(000)	1 616	824	744	1 240
μ / mm^{-1}	3.381	1.130	3.863	2.009
θ range / (°)	2.40~25.02	2.34~36.37	2.05~28.71	3.20~27.52
Measured reflection	14 131	30 684	16 369	31 228
Unique reflection (R_{int})	2 513 (0.076 8)	8 160 (0.019 9)	3 210 (0.019 9)	5 749 (0.046 5)
Observed reflection with [$I>2\sigma(I)$]	2 004	7 136	3 082	5 039
Parameter	165	219	145	298
GOF	1.219	1.014	1.056	0.998
Residuals *R*, wR_2	0.076 9, 0.160 5	0.024 7, 0.063 5	0.011 5, 0.028 1	0.023 7, 0.060 0

CCDC: 1545834, **1**; 1545835, **2A**; 1545836, **3**; 1545837, **4**.

2 Results and discussion

2.1 Synthesis and reactivity of *ortho*-isopropylthiobenzoyl iron complex

It is known that isopropylthiobenzene is deprotonated with *n*-BuLi in the presence of TMEDA to give the *ortho*-lithiation product[30]. Herein, we find that reaction of this *ortho*-lithiation product with iron carbonyl followed by iodine yields a dimeric *ortho*-isopropylthiobenzoyl iron complex **1** (Scheme 1). This result is significantly different from the similar reactions of (pyrazol-1-yl)methyllithium[23] and (2-pyridyl)methyllithium[31], which only give mononuclear acyl iron complexes, revealing that different chelation-assisted

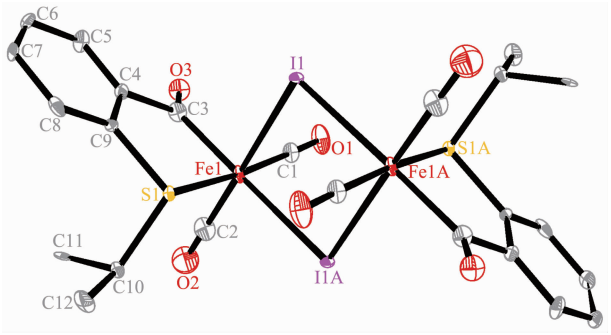


Scheme 1 Synthesis and reactivity of thiobenzoyl and thiomethyl iron complexes

donors strongly affect the fundamental structures of metal-acyl complexes. The substitution of iodide in **1** by 2-pyridinethiolate is successful, which gives mononuclear complex **2**. However, reaction of **1** with PPh_3 leads to the decomposition of the starting material. Complexes **1** and **2** are air-stable solids and their solution could be manipulated in air for a short time without notable decomposition. They have been characterized by spectroscopic methods.

The IR spectra of **1** and **2** show that the acyl carbonyl peak occurrs at 1 628 and 1 615 cm^{-1}, respectively, lower than those in polydentate acyl ligated iron complexes [22-23], but comparable to those in monodentate acyl ligated iron complexes[23]. The corresponding acyl carbon resonates at 246.9 in the ^{13}C NMR spectrum of **1**. The ^{1}H and ^{13}C NMR spectra of **2** contain two sets of proton and carbon signals, indicating that this complex possibly exists in solution as mixture of two geometric isomers (Scheme 1). The main structural difference of two isomers arises from the relative position of *ortho*-isopropylthiobenzoyl with 2-pyridinethiolate. Furthermore, the relative ratio of two isomers is variable in the $CDCl_3$ and acetone-d_6 solutions, showing that the interconversion between two isomers is possible in solution with the help of solvent, through partial dissociation of the ligands and succedent association process. Similar isomerism and interconversion have been observed in (pyrazol-1-yl) acyl iron complexes[23].

The structures of **1** and **2A** were confirmed by X-ray crystallography, and are shown in Fig.1 and 2, respectively. The selected bond distances and angles are listed in Table 2. Fig.1 shows that complex **1** consists of two unequal iodide bridges between two benzoyl iron fragments. The Fe-I(1) bond distance (0.266 8 (2) nm) is slightly shorter than the Fe-I(1A) bond distance (0.273 4(2) nm). These values are similar to those in bidentate acyl ligated iron complexes, but shorter than those in monodentate acyl ligated iron complexes[23]. Fig.2 shows that the pyridyl nitrogen atom in **2A** occupies the *cis*-position to the acyl group with the C(8)-Fe(1)-N(1) angle of 94.54(3)°. Complexes **1** and **2A** possess analogous Fe-C_{acyl} and C-C_{acyl} bond distances, which are also comparable to the correspon-



Symmetry code: A: $-x+2$, $-y+1$, $-z+1$

Fig.1　Molecular structure of **1** with 30% probability displacement ellipsoids

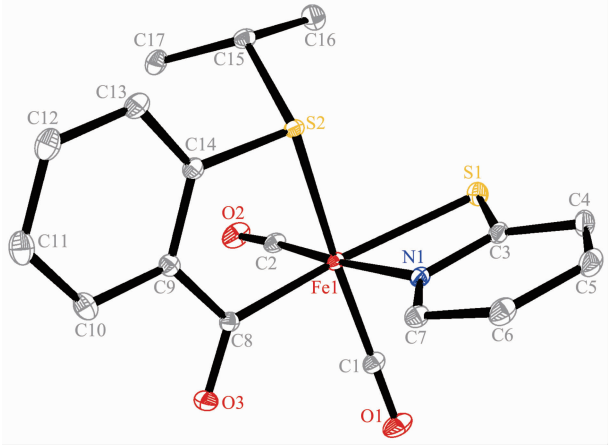


Fig.2　Molecular structure of **2A** with 30% probability displacement ellipsoids

Table 2　Selected bond distances (nm) and angles (°) for complexes 1, 2A, 3 and 4

Complex **1**					
Fe(1)-I(1)	0.266 8(2)	Fe(1)-I(1A)	0.273 4(2)	Fe(1)-S(1)	0.229 8(3)
Fe(1)-C(1)	0.178 1(13)	Fe(1)-C(2)	0.172 6(15)	Fe(1)-C(3)	0.194 8(15)
C(1)-O(1)	0.113 7(16)	C(3)-O(3)	0.126 3(16)	C(3)-C(4)	0.151 9(19)
Fe(1)-I(1)-Fe(1A)	91.82(6)	I(1)-Fe(1)-I(1A)	88.18(6)	C(2)-Fe(1)-I(1)	176.4(5)
C(3)-Fe(1)-I(1A)	174.8(4)	C(3)-Fe(1)-S(1)	87.6(4)	Fe(1)-C(3)-O(3)	124.6(11)
Fe(1)-S(1)-C(9)	99.1(4)	C(4)-C(3)-O(3)	118.5(13)	C(11)-C(10)-S(1)	113.9(9)

Continued Table 1

Complex **2A**					
Fe(1)-S(1)	0.241 60(5)	Fe(1)-S(2)	0.227 92(4)	Fe(1)-N(1)	0.200 22(8)
Fe(1)-C(1)	0.178 97(9)	Fe(1)-C(2)	0.177 37(9)	Fe(1)-C(8)	0.194 77(9)
C(1)-O(1)	0.114 1(1)	C(8)-O(3)	0.122 4(1)	C(8)-C(9)	0.151 6(1)
C(8)-Fe(1)-S(1)	164.20(2)	C(8)-Fe(1)-S(2)	88.00(3)	C(8)-Fe(1)-N(1)	94.54(3)
Fe(1)-C(3)-N(1)	101.95(5)	Fe(1)-C(8)-O(3)	125.67(7)	Fe(1)-S(1)-C(3)	77.19(3)
Fe(1)-S(2)-C(14)	99.47(3)	S(1)-Fe(1)-S(2)	87.75(1)	N(1)-Fe(1)-S(1)	69.78(2)
N(1)-Fe(1)-S(2)	81.67(2)	C(17)-C(15)-S(2)	114.68(6)		
Complex **3**					
Fe(1)-I(1)	0.265 17(3)	Fe(1)-S(1)	0.226 51(4)	Fe(1)-C(1)	0.178 6(1)
Fe(1)-C(4)	0.201 9(1)	C(4)-S(1)	0.176 1(1)		
S(1)-C(4)-Fe(1)	73.28(4)	C(1)-Fe(1)-C(4)	99.60(5)	C(2)-Fe(1)-S(1)	96.58(4)
C(2)-Fe(1)-I(1)	176.90(4)	C(4)-Fe(1)-I(1)	89.43(4)	C(4)-Fe(1)-S(1)	48.11(3)
Fe(1)-S(1)-C(4)	58.61(4)	Fe(1)-S(1)-C(5)	111.75(4)		
Complex **4**					
Fe(1)-P(1)	0.229 44(6)	Fe(1)-S(1)	0.226 54(6)	Fe(1)-I(1)	0.268 21(4)
Fe(1)-C(1)	0.175 6(2)	Fe(1)-C(3)	0.201 7(2)	C(3)-S(1)	0.176 7(2)
C(1)-Fe(1)-C(3)	87.94(9)	C(1)-Fe(1)-I(1)	171.26(6)	C(2)-Fe(1)-S(1)	148.87(7)
C(3)-Fe(1)-S(1)	48.30(6)	C(3)-Fe(1)-P(1)	154.97(6)	C(3)-S(1)-Fe(1)	58.47(7)
C(16)-P(1)-C(22)	103.62(8)	C(16)-P(1)-Fe(1)	113.49(6)	S(1)-C(3)-Fe(1)	73.22(7)
S(1)-Fe(1)-P(1)	106.88(2)	S(1)-Fe(1)-I(1)	85.15(2)	P(1)-Fe(1)-I(1)	92.87(2)

Symmetry codes: A: $-x+2$, $-y+1$, $-z+1$ for **1**.

ding values reported for monodentate acyl iron complexes[23].

2.2 Synthesis and reactivity of phenylthiomethyl iron complex

The lithiation process of thioanisole with *n*-BuLi is different from that of isopropylthiobenzene[30,32]. Thioanisole was deprotonated with *n*-BuLi to give the methyl metalation product instead of the ortho lithiation product of phenyl group[32]. Reactions of α-thiocarbanions with iron carbonyl have been investigated, which generated acyl iron intermediates and subsequently transferred to various organic and organometallic derivatives[33-34]. However, we find that reaction of phenylthiomethyllithium with iron carbonyl followed by iodine only affords phenylthiomethyl iron complex **3** (Scheme 1). No acyl iron derivatives are obtained. Reactivity of **3** is significantly different from that of **1**. For example, similar treatment of **3** with 2-pyridinethiolate results in the decomposition of **3**, rather than the substitution of iodide. In addition, reaction of alkylmetal carbonyl compounds with nucleophilic ligands, such as phosphine (PR_3), has been extensively used to form acyl metal derivatives through alkyl/carbonyl migratory insertion reaction[9], but reaction of **3** with PPh_3 only give the carbonyl substitution product **4**. No induced carbonyl insertion reaction took place, though such reaction should be able to reduce the ring strain in **3**. Complexes **3** and **4** also are air-stable solids. Their IR and NMR spectra are highly consistent with the alkyl iron structure. These two complexes only exhibit three (for **3**) or two (for **4**) absorption bands in the range of 2 077~1 950 cm^{-1} for terminal carbonyl ligands, and no acyl carbonyl absorption band is observed in their IR spectra.

Complexes **3** and **4** were also characterized by single crystal X-ray structural determination. Fig.3 and 4 reveal that the fundamental frameworks in complexes **3** and **4** are similar to each other, except

that PPh_3 locates on the trans-position of the methyl carbon in **4** instead of one carbonyl group like in **3**. The phenylthiomethyl group bonds to the iron atom in a bidentate κ^2-[C,S] chelating fashion in these two complexes, yielding a three-membered metallocyclic structure. Complexes **3** and **4** possess analogous Fe-S, Fe-I and Fe-C_{methyl} bond distances (Table 2). The Fe-S and Fe-I bond distances are also comparable to the corresponding values in **1** and **2**.

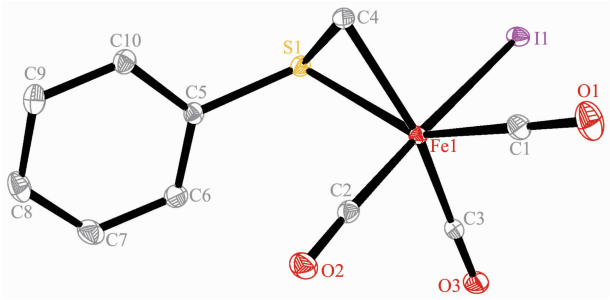


Fig.3　Molecular structure of **3** with 30% probability displacement ellipsoids

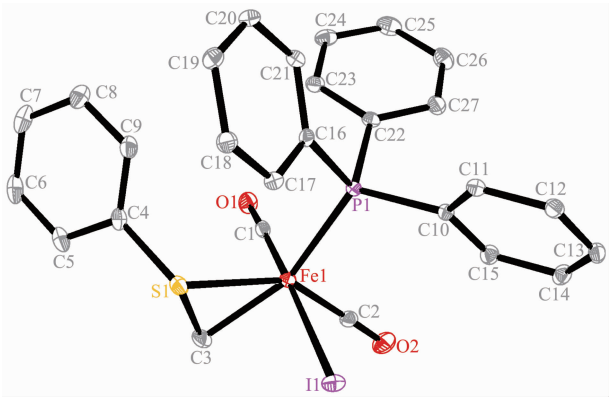


Fig.4　Molecular structure of **4** with 30% probability displacement ellipsoids

3　Conclusions

In summary, *ortho*-isopropylthiobenzoyl and phenylthiomethyl iron derivatives have been obtained by the reaction of *ortho*-isopropylthiophenyllithium or phenylthiomethyllithium with iron carbonyl followed by treatment with iodine. These complexes also show markedly different reactivities upon treatment with nucleophilic ligands.

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