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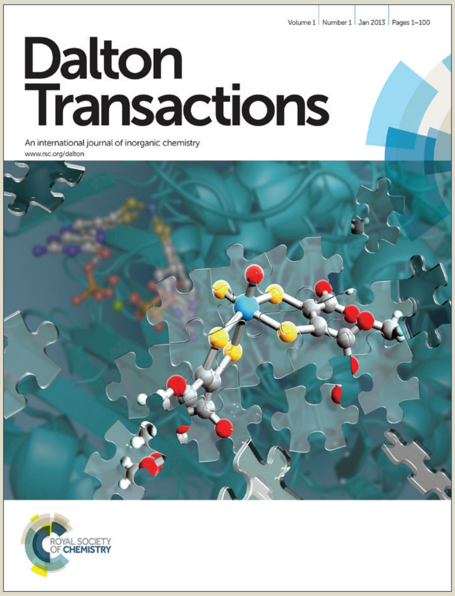

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Synthesis of Carboxylate-bridged Iron-thiolate Clusters from Alcohols/Aldehydes or Carboxylate salts

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ABSTRACT: A series of novel carboxylate-bridged cyclopentadienyl diiron complexes [Cp*Fe(μ-SEt)$_2$(μ-η^2-OOCR)FeCp*][PF$_6$] (**2**, R = H; **3**, R = Me; **4**, R = Et; **5**, R = Pr-*n*; **6**, R = Ph; **7**, R = *p*-Me-C$_6$H$_4$; **8**, R = PhCH=CH; **9**, CH≡C) were obtained from alcohols/aldehydes or sodium carboxylates at room temperature. These eight complexes were fully characterized by spectroscopy, and some of them (**3**, **4**, **7** and **8**) were further defined by X-ray crystallography. In addition, the electrochemical properties of clusters **2** and **6** are also discussed.

Introduction

Metalloproteins perform a variety of functions in biological systems. The catalysis of several remarkable chemical transformations occurs at metal centers embedded in the active sites of metalloenzymes.[1] Among numerous metalloproteins, enzymes containing carboxylate-bridged diiron cores, such as Ribonucleotide reductase (RNR),[2] Δ^9 desaturase (Δ^9 D)[3] and soluble methane monooxygenase (sMMO)[1a, 4] *etc*., play a variety of critical roles in biology. The studies show that the diiron active sites in those metalloproteins are responsible for activation and transformation of small molecules.[5] The carboxylate bridge plays a key role in maintaining the structural integrity of the diiron center during catalysis.[6] As a consequence, the structural and functional mimicking of these diiron complexes has been a growth spurt in the past decades because of their unique functions.[7] Generally, carboxylate-bridged diiron complexes were prepared by reaction of iron salts or iron complexes containing multidentate N or O ligands with carboxylate salts.[8]

Furthermore, the method based on the *in situ* oxidation of alcohol or aldehyde to form carboxylate-bridged or oxalate-bridged metal complexes has attracted the interest of inorganic chemists.[9] The aromatic aldehydes could be oxidized to aromatic carboxylates to give carboxylate-bridged cobalt, manganese and nickel complexes.[9a-9c] The oxidation reaction of alcohol are also proceeded in the presence of Mn(III),[9e] manganese[9e, 9g] and cobalt.[9f] However, so far, there has been no report about diiron-thiolate clusters with carboxylates as ligands generated by *in situ* oxidation of alcohols or aldehydes.

In 1960's, the first diiron-sulfur core complex with Cp as ligand, [Cp$_2$Fe$_2$(μ-SMe)$_2$(CO)$_2$] (Cp = cyclopentadienyl), was prepared and characterized by King's group.[10] In the following decades, a series of studies on the diiron-sulfur core [Cp$_2$Fe$_2$(μ-SR)$_2$L]$^{n+}$ and [Cp*$_2$Fe$_2$(μ-SR)$_2$L]$^{n+}$ complexes (R = alkyl or aryl), of their redox and/or their crystal structures have been reported.[11] [Cp$_2$Fe$_2$(μ-SEt)$_2$L(MeCN)]$^{2+}$ could react with dppm, dppf, CO, ^{t}BuNC *etc*. because of labile MeCN ligand.[11e] Cp$_2$*Fe$_2$(μ-SAr)$_2$ (Ar = PhSiMe$_3$)[11g] and Cp*$_2$Fe$_2$(SR)$_3$ (R = Et, Me)[12c] work as effective catalysts toward the reduction of hydrazines into ammonia on the sulfur-bridged diiron skeleton, which is likely observed at the active site of nitrogenase. It can be seen that diiron complexes with -SR and Cp or Cp* should be good candidates for mimicking metalloenzymes.

Recently, our group aims at the synthesis and reactivity of diiron-sulfur clusters with Cp* as ancillary ligands, which can provide bimetallic reaction sites and simulate biological metalloproteins to active small molecules. The introduction of Cp* group into the cluster can increase the electron density at the metal centers and cause the cluster to be more reactive. A series of thiolate-bridged diiron complexes which can catalyze the cleavage of the N–N bond of hydrazines and activate the C-Cl bond, terminal alkynes and CS$_2$ have been documented.[12] As an extension of the work in this field, herein, we present the formation of carboxylate-bridged cyclopentadienyl diiron complexes by reacting [Cp*Fe(μ-SEt)$_2$(MeCN)$_2$FeCp*][PF6]$_2$ (**1**) with alcohols/aldehydes under air or carboxylate salts at room temperature. As far as we know, this is the first example of carboxylate-bridged diiron complexes with Cp* ligand.

Results and discussion

Synthesis

Carboxylate-bridged diiron complexes from alcohols

When we explored the properties of diiron-sulfur cluster, a formate-bridged diiron complex [Cp*Fe(μ-SEt)$_2$(μ-OOCH)FeCp*][PF$_6$] (**2**) was generated from a solution of [Cp*Fe(μ-

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SEt)$_2$(MeCN)$_2$FeCp*][PF$_6$]$_2$ (**1**) containing MeOH and base while it was exposed to air. Further study showed that the color of the solution changed smoothly from brown to green when a mixture of **1**, MeONa and MeOH was stirred under air at room temperature and **2** was isolated as a green solid in 75% yield after 24 h (Scheme 1). Moreover, the structure of **2** was confirmed by IR, NMR and MS. The ^{1}H NMR spectrum of **2** in CDCl$_3$ exhibits four resonances at δ 5.24, 2.01, 1.74 and 1.40 ppm corresponding to OOCH, CH$_3$, CH$_2$ and Cp*. Notably, the value of chemical shift of two equivalent CH$_3$ (2.01 ppm, triplet) of -SEt group was larger than that of two equivalent CH$_2$ (1.74 ppm, quartet) of -SEt group. This abnormal result is caused by shielding effect of Fe-Fe-O-C-O cycle. The IR (KBr) spectrum of **2** shows a strong band at 1567 cm^{-1} ascribed to C=O stretching.

Scheme 1 is placed here.

Furthermore, EtOH could react with **1** under air to give the targeted product [Cp*Fe(μ-SEt)$_2$(μ-OOCMe)FeCp*][PF$_6$] (**3**) as a green solid in 48% yield when NEt$_3$ takes the place of MeONa. The ^{1}H NMR spectra of **3** in CDCl$_3$ shows four resonances at δ 2.01, 1.70, 1.40 and 1.20 ppm. Notably, the chemical shifts of 2.01 and 1.70 ppm are attributed to CH$_3$ and CH$_2$ protons of -SEt respectively. Similar to **2**, it also shows abnormal chemical shift between CH$_2$ and CH$_3$ of -SEt due to shielding effect of Fe(1)-Fe(1A)-O(1A)-C(13)-O(1) cycle, which is fully consistent with the X-ray structure of **3**. The IR spectrum of **3** exhibits C=O stretch at 1534 cm^{-1}.

The reaction could not proceed without base. Subsequently, various bases, including *t*-BuOK, NHEt$_2$, NEt$_3$ and RONa, were tested in ROH (R = Me, Et). The results showed that base was essential to the reaction, MeONa and NEt$_3$ are best for oxidation of MeOH and EtOH respectively. When Et$_3$N was used, Et$_3$NH·PF$_6$ was detected by ^{1}H NMR. So it could be seen that Et$_3$N serves as base to neutralize acid. It should be noted that the reaction did not proceed under Ar atmosphere, which illustrated that air was crucial. We also tried to investigate if other alcohol, such as *n*-propanol, *n*-butanol and 2-(2-methoxyethoxy)ethanol, could be converted to corresponding products under air. However, **1** was almost insoluble in those alcohols. Thus no product was detected even after 48 h. Although we added other solvents (such as CH$_2$Cl$_2$ or MeCN) to increase its solubility, no product was yet isolated. Treatment of **1** with NEt$_3$ in ethylene glycol at room temperature under air gave complicated products, which were hard to be characterized exactly.

Carboxylate-bridged diiron complexes from aldehydes

Besides alcohols, we also examined the conversion of aldehydes to form carboxylate-bridged complexes. The results indicated that the conversion of aldehydes were easier than alcohols. As outlined in Scheme 2, when a solution of **1** in propionaldehyde was stirred at room temperature in the presence of NEt$_3$ under air, color changed gradually from brown to yellow-green. After 0.5 h, the excess propionaldehyde was removed in vacuum, and [Cp*Fe(μ-SEt)$_2$(μ-OOCEt)FeCp*][PF$_6$] (**4**) was obtained as a green solid in 90% yield. The ^{1}H NMR spectrum of **4** in CDCl$_3$ shows two broad singlets at δ 2.00 and 1.66 ppm attributed to two equivalent CH$_3$ protons and equivalent CH$_2$ protons of -SEt group respectively, which was also affected by the shielding effect of Fe(1)-Fe(2)-O(2)-C(25)-O(1) cycle. The characteristic C=O stretching absorption is observed at 1528 cm^{-1}.

Scheme 2 is placed here.

Similarly, treatment of *n*-butylaldehyde with **1** and NEt$_3$ afforded the complex [Cp*Fe(μ-SEt)$_2$(μ-OOCPr-*n*)FeCp*][PF$_6$] (**5**) as a green solid in 80% yield, which was unambiguously characterized by all spectra. The resonance of two equivalent CH$_3$ of -SEt is found at δ 2.01 ppm while two equivalent CH$_2$ of -SEt at δ 1.68 ppm. The IR spectrum clearly indicates the C=O stretching band at 1529 cm^{-1}. In addition, the reactions of aryl aldehydes were also explored. To a solution of complex **1** in benzaldehyde or *p*-tolualdehyde, NEt$_3$ was added, and the solution turned from brown to yellow-green. After workup, [Cp*Fe(μ-SEt)$_2$(μ-OOCPh)FeCp*][PF$_6$] (**6**) or [Cp*Fe(μ-SEt)$_2$ (μ-OOCC$_6$H$_4$Me-*p*)FeCp*][PF$_6$] **(7)** was isolated in 57% and 28% yield, respectively. The low yield may result from the poor solubility of **1** in corresponding aldehyde. Similar to others, the ^{1}H NMR spectra of **6** and **7** have also unusual chemical shifts for CH$_2$ and CH$_3$ of –SEt, which is attributed to the same reasons. The IR spectra of **6** and **7** exhibit C=O stretch at 1525 and 1519 cm^{-1} respectively.

Similar to the oxidation of alcohol mentioned above, the oxidation of aldehyde could not perform to give carboxylate-bridged diiron complex under Ar atmosphere, which illustrated that oxygen was crucial. And no reaction occurred without a base. Thus, various bases including *t*-BuOK, NHEt$_2$ and NEt$_3$ were examined. The results show that most of the bases were efficient for the conversion of aldehydes and NEt$_3$ was the best among them. Similar with the reaction of EtOH, Et$_3$NH·PF$_6$ was also detected by ^{1}H NMR.

Carboxylate-bridged diiron complexes from sodium carboxylates

The carboxylate-bridged complexes derived from alcohols and aldehydes could also be synthesized by the reaction of [Cp*Fe(μ-SEt)$_2$(MeCN)$_2$FeCp*][PF$_6$]$_2$ (**1**) with corresponding carboxylic salts (Scheme 3). Based on this strategy, other carboxylate-bridged complexes can be obtained. The reaction of [Cp*Fe(μ-SEt)$_2$(MeCN)$_2$FeCp*][PF$_6$]$_2$ with sodium cinnamate (PhCH=CHCOONa, 1.2 equiv) in anhydrous CH$_3$CN afforded greenish solid of diiron complex, [Cp*Fe(μ-SEt)$_2$(μ-OOCCH=CHPh)FeCp*][PF$_6$] (**8**), in modest yield (55%). The ^{1}H NMR spectrum of **8** in CDCl$_3$ displays two broad singlets at δ 2.00 and 1.69 ppm corresponding to two equivalent CH$_3$ protons and equivalent CH$_2$ protons of -SEt respectively. The protons chemical shift of (μ-OOCCH=CHPh) are located at 6.47 and 5.64 respectively. The IR absorptions observed at 1576 cm^{-1} and 1976 cm^{-1} are assigned to C=C and C=O stretching vibration.

Scheme 3 is placed here.

Meanwhile, complex **10** (Fig. 1) was tested for the same oxidation reaction, however no carboxylate-bridged diiron complex was generated. There was also no aimed product even if the stronger oxidants were used (H$_2$O$_2$, *t*-BuOOH and *t*-BuOO*t*-Bu). The proposed reason for this is that it is difficult for the ligands CO to dissociate from the complex **10** even if its structure is similar to the complex **1**, which is bearing two liable ligands MeCN. So, we proposed the unique reaction activity of complex **1** is probably attributed to its characteristic diiron center and the two weakly coordinating MeCN ligands, which were easily dissociated from iron centers and vacated the coordination sites and then form carboxylate-bridged diiron complexes. Et_3N or MeONa is necessary for this oxidation reaction and Et_3NHPF_6 is detected by ^1H NMR. So, it could be seen that Et_3N serves as base to neutralize acid. But the detailed mechanism of this reaction is not very clear. We proposed one possible reason is that the substrates (alcohols or aldehydes) and dioxygen were coordinated and activated at the two iron centers. Another possible pathway is that O_2 destroys some of complex **1** to give ferric salts that catalyze the oxidation to give carboxylates, which then attach to the un-destroyed complex **1** to give the target products. Obviously, in both cases, the characteristic diiron center is the key point for the formation of the carboxylate-bridged diiron complexes.

Fig. 1 is placed here.

Crystal structures

The structures of **3**, **4**, **7** and **8** are unambiguously characterized by single crystal X-ray diffraction analysis, and their spectral features are fully consistent with their crystal structures. Their crystallographic data are listed in Table 1. The ORTEP drawings of **3**, **7** and **4**, **8** and their selected bond distances and angles are shown in Fig. 2, Fig. 3 and Fig. S1, Fig. S2 (ESI) respectively.

Table 1 is placed here.

These four complexes have similar structures. The two Fe(III) center are bridged by a μ-1,3 carboxylate ligand and two -SEt ligands. In complex **4**, the distance of Fe–Fe 2.6166(9) Å falls in the 2.5-2.8 Å range which indicates a single bond between the two iron atoms.[13] The two Cp* ligands coordinating to Fe centers are in mutually *cis*- orientation with dihedral angle being 54.646(204)°. The Fe2S2 ring is substantially puckered with a dihedral angle of 172.042(40)° along the Fe(1)–Fe(2) vector. The distance of Fe–O are 1.978(3) Å and 1.980(3) Å, respectively. The angle of O(1)–C(25)–O(2) is 125.4(4)°. The dihedral angle between $\{Fe_2(\mu\text{-}O_2)\}^{2+}$ plane and O(1)–C(25)–O(2) plane being 0.881(422)° indicates they are almost on the same plane. From the structure, we can also see that the two equivalents CH_2 of -SEt locate in the chemical shielding zone of Fe(1)-Fe(2)-O(2)-C(25)-O(1) cycle, which makes CH_2 of -SEt shift to up-field in ^1H NMR spectrum.

Fig 2 and **Fig 3** are placed here.

3, **7** and **8** contain a carboxylate-bridged diiron (III) centers with Fe–Fe distance of 2.6188(7), 2.6072(10) and 2.6196 (7) Å, respectively. Notably, The dihedral angle of complex **7** between $\{Fe_2(\mu\text{-}O_2)\}^{2+}$ plane and O(1)–C(25)–O(2) plane is 5.569(345)°, which is larger than that in **3**, **4** and **8** (0.881(422)°, 0.348(62)° and 3.128(462) respectively).

Electrochemistry studies of clusters 2 and 6

Due to the similarity in chemical structures, we took **2** and **6** as examples to investigate their cyclic voltammograms (CV) in THF-0.1 M $[n\text{-}Bu_4N][PF_6]$, shown in Fig. S3 and Fig. S4. The CV of **2** shows three quasi- reversible redox peaks. The process observed at $E_{1/2}$ = +0.52 V *vs*. Fc/Fc^+ is assigned to $[Fe^{III}Fe^{III}]/[Fe^{III}Fe^{IV}]$, the second one at $E_{1/2}$ = -0.92 V results from $[Fe^{II}Fe^{III}]/[Fe^{III}Fe^{III}]$, and the third one at $E_{1/2}$ = -1.32 V is ascribed to $[Fe^{II}Fe^{II}]]/[Fe^{II}Fe^{III}]$. Analogous to **2**, three quasi-reversible redox processes of **6** are also observed at $E_{1/2}$ = +0.53 V, $E_{1/2}$ = -0.93 V and $E_{1/2}$ = -1.34 V, which is corresponding to $[Fe^{III}Fe^{III}]/[Fe^{III}Fe^{IV}]$, $[Fe^{II}Fe^{III}]/[Fe^{III}Fe^{III}]$ and $[Fe^{II}Fe^{II}]]/[Fe^{II}Fe^{III}]$, respectively. The quite close redox potentials of formic and benzoic demonstrate that carboxylic ligands have a negligible effect on the electrochemistry of the diiron complexes.

Magnetic properties

A series of the carboxylate-bridged diiron complexes have been reported[14], such as $[Fe_2(\mu\text{-}O_2CAr^{Tol})_2(O_2CAr)L1]$,[14a] $[Fe_2(\mu\text{-}O_2CAr^{Tol})_4L2]$,[14b] $[Fe_2(\mu\text{-}O_2Cglu)_4L3]$[14c] and $[Fe_2(\mu\text{-}O_2CCH_3)_2L4]$.[14d] We learnt that the distance of Fe-O (carboxylate) of these complexes is almost in the range of 2.00-2.10 Å and also learnt that they show high-spin state with S = 3/2, 2 or 5/2. However, the distances of Fe-O (carboxylate) of the complexes in this context were almost 1.97 Å, smaller than the distance of 2.00-2.10 Å, which showed they were probably different from the previous carboxylate-bridged diiron complexes. According to the standard Evans method,[15] the molar paramagnetic susceptibility was calculated to be 0, so S = 0, n = 0 (see ESI for details). It could be concluded that carboxylate-bridged complex **2** was diamagnetic with low spin state. Because of the structural similarity of complexes **2** to **9**, we speculated they were low spin states with n = 0 and S = 0.

Conclusions

In summary, we have synthesized eight carboxylate-bridged diiron complexes $Cp^*Fe(\mu\text{-}SEt)_2(\mu\text{-}\eta^2\text{-}OOCR)FeCp^*][PF_6]$ (**2**, R = H; **3**, R = Me; **4**, R = Et; **5**, R = *n*-Pr; **6**, R = Ph; **7**, R = *p*-Me-C_6H_4; **8**, R = PhCH=CH; **9**, CH≡C) from alcohols/aldehydes oxidation or sodium carboxylates. It is noteworthy that this is the first example of carboxylate-bridged diiron complexes with Cp* ligand. The unique reaction activity of $[Cp^*Fe(\mu\text{-}SEt)_2(MeCN)_2FeCp^*][PF_6]_2$ (**1**) is attributed to its characteristic diiron center and the two weakly coordinating MeCN ligands.

Experiment

All aldehydes (propionaldehyde, *n*-butylaldehyde, benzaldehyde and *p*-tolualdehyde) were shaked with sodium hydroxide solid, separated, and freshly distilled under argon. MeOH and EtOH were shaked with sodium hydroxide solid, separated, and freshly distilled over magnesium under argon. NEt_3 and MeONa were used as received. Infrared spectra were recorded on a NEXUSTM FT-IR spectrometer. The ^1H NMR spectra were performed on a Bruker 400 Ultra Shield spectrometer. The MS were measured on a LTQ Orbitrap XL TM spectrometer. Element analyses were performed on a Vario EL analyser. Compound $[Cp^*Fe(\mu\text{-}SEt)_2(MeCN)_2FeCp^*][PF_6]_2$ (**1**) was prepared according to our previous work.[12c] Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 $mV\cdot s^{-1}$. Cyclic voltammogram was obtained in a three-electrode cell in THF-0.1 M $[n\text{-}Bu_4N][PF_6]$. The working electrode was a glassy carbon disk (diameter 3mm), the reference electrode was a non-aqueous Ag/$AgNO_3$ electrode, and the auxiliary electrode was a platinum wire.

X-Ray Crystallography Crystals suitable for X-ray crystallography were obtained by recrystallization from a mixture of Et_2O and THF. The data were obtained on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Empirical absorption corrections were performed using the SADABS program.[16] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 using Shelx97.[17] All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were generated and refined in ideal positions.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCH)FeCp*][PF$_6$] (2) To a solution of **1** (88 mg, 0.1 mmol) in MeOH (1 mL) was added MeONa (11 mg, 0.2 mmol). The brown solution was stirred at room temperature under air and the colour changed smoothly to yellow-green. After 24 h, the obtained green solution was evaporated under reduced pressure. Then, the residue was extracted with THF (1 mL). After removal of the solvent in vacuum, the residue was washed with H_2O (1 mL) and Et_2O (1 mL × 2) to give **2** as a green solid (55 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.24 (s, 1H, -OOC*H*), 2.01 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, -SCH$_2$C*H*$_3$), 1.74 (q, $J_{H\text{-}H}$ = 7.2 Hz, 4H, -SC*H*$_2$CH$_3$), 1.40 (s, 30H, Cp*-C*H*$_3$). IR (KBr, cm^{-1}): 2967 (s), 2927 (s), 1567 (s), 1455 (m), 1378 (s), 1342 (m), 1267 (w), 1235 (w), 1124 (w), 1083 (m), 1017 (m), 913 (m), 838 (s), 736 (m), 702 (w). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 549.1252; calcd. value for $C_{25}H_{41}Fe_2S_2O_2$: 549.1247. Anal. Calcd for $C_{25}H_{41}F_6Fe_2S_2O_2P$: C, 43.24; H, 5.95. Found: C, 43.26; H, 5.86.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCMe)FeCp*][PF$_6$] (3) The reaction was carried out analogously to the procedures described for **2** by treatment of **1** (88 mg, 0.1 mmol) with NEt_3 (29 μL, 0.2 mmol) and EtOH (1 mL), and gave **3** as a green solid (34 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (t, $J_{H\text{-}H}$ = 7.6 Hz, 6H, -SCH$_2$C*H*$_3$), 1.70 (q, $J_{H\text{-}H}$ = 7.6 Hz, 4H, -SC*H*$_2$CH$_3$), 1.40 (s, 30H, Cp*-C*H*$_3$), 1.20 (s, 3H, -OOCC*H*$_3$). IR (KBr, cm^{-1}): 2972 (s), 2919 (s), 2867 (s), 2267 (m), 1534 (s), 1489 (s), 1452 (s), 1377 (s), 1231 (m), 1074(m), 1022 (w), 970 (w), 908 (m), 835 (s), 730 (m), 692 (w). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 563.1391; calcd. value for $C_{26}H_{43}Fe_2S_2O_2$: 563.1403. Anal. Calcd for $C_{26}H_{43}F_6Fe_2S_2O_2P$: C, 44.08; H, 6.12. Found: C, 43.80; H, 5.82.

General procedures for preparation of [Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCR)FeCp*][PF$_6$] (4 - 7) from aldehyde

To a solution of **1** (88 mg, 0.1 mmol) in corresponding aldehyde (0.3 mL) was added NEt_3 (29 μL, 0.2 mmol). The brown solution was stirred at room temperature under air and the colour changed smoothly to yellow-green. After 0.5 h, the obtained green solution was filtered. Then, the volatile of the filtrate was removed under reduced pressure and the residue was washed with Et_2O (1 mL × 2) to give a solid, which was extracted with THF. After removal of the solvent in vacuum, the residue was washed with Et_2O (1 mL × 2) and H_2O (1 mL) to obtain the product as a green solid.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCEt)FeCp*][PF$_6$] (4) Green solid (65 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.00 (br, 6H, -SCH$_2$C*H*$_3$), 1.66 (br, 4H, -SC*H*$_2$CH$_3$), 1.35 (br, 2H, -OOCC*H*$_2$CH$_3$), 1.40 (s, 30H, Cp*-C*H*$_3$), 0.4 (br, 3H, -OOCCH$_2$C*H*$_3$). IR (KBr, cm^{-1}): 2972 (s), 2919 (s), 2275 (m), 1528 (s), 1461 (m), 1376 (s), 1302 (w), 1228 (w), 1018 (m), 913 (m), 838 (s), 731 (m). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 577.1538; calcd. value for $C_{27}H_{45}Fe_2S_2O_2$: 577.1560. Anal. Calcd for $C_{27}H_{45}F_6Fe_2S_2O_2P$: C, 44.89; H, 6.28. Found: C, 44.74; H, 6.18.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCPr-*n*)FeCp*][PF$_6$] (**5**) Green solid (59 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (t, $J_{H\text{-}H}$ = 7.6 Hz, 6H, -SCH$_2$C*H*$_3$), 1.68 (t, $J_{H\text{-}H}$ = 7.6 Hz, 4H, -SC*H*$_2$CH$_3$), 1.37 (br, 2H, -OOCC*H*$_2$CH$_2$CH$_3$), 1.40 (s, 30H, Cp*-C*H*$_3$), 0.81 (br, 2H, -OOCCH$_2$C*H*$_2$CH$_3$), 0.52 (t, $J_{H\text{-}H}$ = 7.6 Hz, 3H, -OOCCH$_2$CH$_2$C*H*$_3$). IR (KBr, cm^{-1}): 2958 (s), 2926 (s), 2868 (w), 1529 (s), 1497 (w), 1438 (m), 1421 (m), 1404(m), 1376 (s), 1316 (s), 1234 (m), 1073 (m), 1022 (s), 876 (m), 842 (s), 786 (w). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 591.1695; calcd. value for $C_{28}H_{47}Fe_2S_2O_2$: 591.1716. Anal. Calcd for $C_{28}H_{47}F_6Fe_2S_2O_2P$: C, 45.66; H, 6.43. Found: C, 45.48; H, 6.22.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCPh)FeCp*][PF$_6$] (**6**) Green solid (43 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, $J_{H\text{-}H}$ = 7.2 Hz, 1H, Ph-*H*), 7.10 (m, 2H, Ph-*H*), 6.95 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H, Ph-*H*), 1.93 (t, $J_{H\text{-}H}$ = 7.6 Hz, 6H, -SCH$_2$C*H*$_3$), 1.63 (q, $J_{H\text{-}H}$ = 7.6 Hz, 4H, -SC*H*$_2$CH$_3$), 1.46 (s, 30H, Cp*-C*H*$_3$). IR (KBr, cm^{-1}): 2962 (s), 2923 (w), 2868 (w), 1525 (s), 1455(m), 1402 (s), 1377 (w), 1234 (m), 1160 (w), 1072 (m), 1019 (s), 914 (s), 840 (s), 722 (s), 694 (m). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 625.1560; calcd. value for $C_{31}H_{45}Fe_2S_2O_2$: 625.1560. Anal. Calcd for $C_{31}H_{45}F_6Fe_2S_2O_2P$: C, 48.33; H, 5.89. Found: C, 47.98; H, 5.58.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCC$_6$H$_4$Me-*p*)FeCp*][PF$_6$] (**7**) Green solid (22 mg, 28%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.88 (m, 4H, Ph-*H*), 2.24 (s, 3H, Ph-C*H*$_3$), 1.93 (t, $J_{H\text{-}H}$ = 7.6 Hz, 6H, -SCH$_2$C*H*$_3$), 1.63 (q, $J_{H\text{-}H}$ = 7.6 Hz, 4H, -SC*H*$_2$CH$_3$), 1.47 (s, 30H, Cp*-C*H*$_3$). IR (KBr, cm^{-1}): 2924 (s), 1609 (m), 1575 (m), 1519 (s), 1497 (m), 1455 (w), 1404 (s), 1376 (w), 1235 (m), 1178 (s), 1020 (s), 910 (m), 840 (s), 762 (m), 728 (m). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 639.1704; calcd. value for $C_{32}H_{47}Fe_2S_2O_2$: 639.1716. Anal. Calcd for $C_{32}H_{47}F_6Fe_2S_2O_2P$: C, 48.99; H, 6.04. Found: C, 48.63; H, 5.75.

General procedures for preparation of [Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCR)FeCp*][PF$_6$] from sodium carboxylates.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-O$_2$CCH=CHPh)FeCp*][PF$_6$] (**8**) Sodium cinnamate (14 mg, 0.08mmol) was added to a solution of [Cp*Fe(*μ*-SEt)$_2$(MeCN)$_2$FeCp*][PF$_6$]$_2$ (60 mg, 0.68 mmol) in CH_3CN (4 mL) allowed to react for 24 h at room temperature. After filtration, the solution was removed in *vacuum*. Then, the residue was extracted with CH_2Cl_2 (2 mL). After removal of the solvent in *vacuum*, the residue was extracted with THF (2 mL). After removal of the solvent, the residue was washed with Et_2O (1 mL × 2) to give green solid (30 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (br, 5H, Ph*H*), 6.47 (br, 1H, CH=C*H*), 5.64 (br, 1H, C*H*=CH), 2.01 (br, 6H, -SCH$_2$C*H*$_3$), 1.68 (br, 4H, -SC*H*$_2$CH$_3$), 1.47 (s, 30H, Cp*-C*H*$_3$). IR (KBr, cm^{-1}): 2962 (s), 2927 (s), 1976 (s), 1576 (m), 1514 (s), 1497 (s), 1375 (w), 1261 (w), 1240 (m), 1073 (s), 1019 (s), 981 (m), 876 (s), 839 (s), 775 (m), 748 (m), 720 (s), 686 (m). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 651.1718; calcd. value for $C_{33}H_{47}Fe_2S_2O_2$: 651.1716. Anal. Calcd for $C_{33}H_{47}F_6Fe_2S_2O_2P$: C, 49.76; H, 5.95. Found: C, 49.48; H, 5.80.

[Cp*Fe(*μ*-SEt)$_2$(*μ*-OOCC≡CH)FeCp*][PF$_6$] (**9**) Green solid (68%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s，1H, C≡C*H*), 2.07 (br, 6H, -SCH$_2$C*H*$_3$), 1.81 (br, 4H, -SC*H*$_2$CH$_3$), 1.43 (s, 30H, Cp*-C*H*$_3$); IR (KBr, cm^{-1}): 3281 (s), 2962 (s), 2923 (s), 1535 (s), 1497 (s), 1429 (m), 1408 (m), 1376 (w), 1313 (w), 1261 (m), 1096 (s), 1021 (s), 841 (s). ESI-HRMS (*m/z*): [M-PF$_6$]$^+$ 573.1247; calcd. value for $C_{27}H_{41}Fe_2O_2S_2$:

573.1246. Anal. Calcd for $C_{27}H_{41}F_6Fe_2S_2O_2P$: C, 45.14; H, 5.75. Found: C, 44.85; H, 5.93.

[Cp*Fe(μ-SEt)$_2$(μ-OOCH)FeCp*][PF$_6$] (**2**) Green solid (61%). The characterization data (^{1}H NMR, HR-MS and IR) is the same as the product obtained from MeOH.

[Cp*Fe(μ-SEt)$_2$(μ-OOCMe)FeCp*][PF$_6$] (**3**) Green solid (66%). The characterization data (^{1}H NMR, HR-MS and IR) is the same as the product obtained from EtOH.

[Cp*Fe(μ-SEt)$_2$(μ-OOCPh)FeCp*][PF$_6$] (**6**) Green solid (89%). The characterization data (^{1}H NMR, HR-MS and IR) is the same as the product obtained from benzaldehyde.

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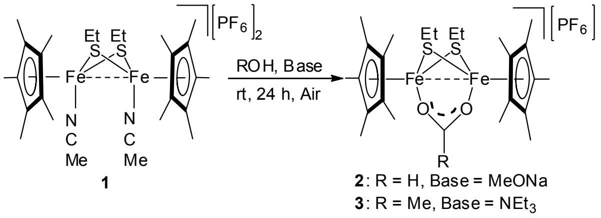
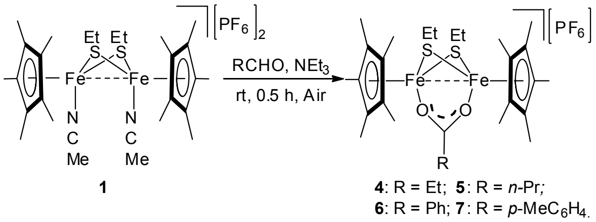
Table 1 Crystal Data and Structure Refinement for complexes **3** and **7**.

	3	**7**
Formula	$C_{26}H_{43}F_6Fe_2O_2PS_2$	$C_{32}H_{47}F_6Fe_2O_2PS_2$
Formula weigh	708.39	784.49
Crystal dimensions (mm^3)	0.36×0.20×0.04	0.22×0.26×0.18
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1$/c
a (Å)	12.034(3)	15.844(3)
b (Å)	15.336(4)	13.974(2)
c (Å)	17.019(5)	16.746(3)
α (Å)	90.00	90.00
β (Å)	91.739(4)	108.737(3)
γ (Å)	90.00	90.00
Volume ($Å^3$)	3139.5(14)	3511.1(10)
Z	4	4
T (K)	298(2)	298(2)
D calcd (g cm^{-3})	1.499	1.484
μ (mm^{-1})	1.166	1.051
F (000)	1472	1632
No. Of rflns. collected	7926	18590
No. Of indep. Rflns. /Rint	2759 / 0.0288	6178 / 0.0358
No. Of obsd. Rflns. [$I > 2\sigma(I)$]	2383	4818
Data / restraints / parameters	2759 / 0 / 171	6178 / 0 / 390
R_1, [a] /wR_2 [b] [$I > 2\sigma(I)$]	0.0514 / 0.1343	0.0448 / 0.1322
R_1, [a] /wR_2 [b] (all data)	0.0596 / 0.1387	0.0599 / 0.1413
GOF (on F^2)	1.000	1.000
Largest diff. Peak and hole (e $Å^{-3}$)	0.645 / -0.521	0.705 / -0.522

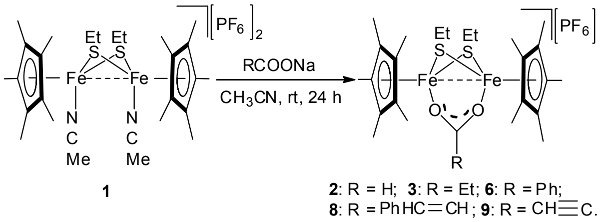
[a] $R_1 = \Sigma Fo\ - |F_c\ /\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



Scheme 1 Synthesis of **2** and **3** from alcohols.



Scheme 2 Synthesis of **4** to **7** from aldehydes.



Scheme 3 Synthesis of **2**, **3**, **6**, **8** and **9** from carboxylate salts.

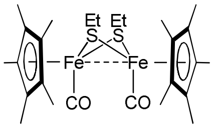


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Fig 1. The structure of **10**.

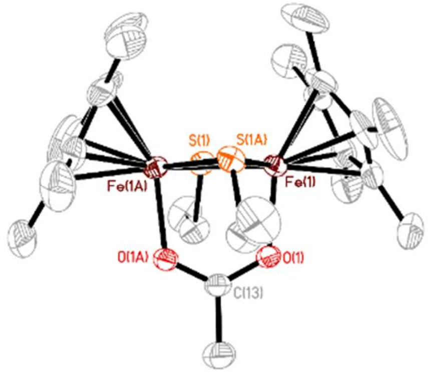

Fig 2 ORTEP (ellipsoids at 30% probability) diagram of **3**. All hydrogen atoms as well as the PF_6^- anions are omitted for clarity. Selected bond length (Å), Bond Angles and Plane Angles (deg):Fe(1A)–Fe(1) 2.6072(10), Fe(1A)–S(1A) 2.2113(13), Fe(1A)–S(1) 2.1989(13), Fe(1A)–O(1A) 1.9769(27), Fe(1)–S(1A) 2.1990 (13), Fe(1)–S(1) 2.2113(13), Fe(1)–O(1) 1.9769 (27), Fe(1)–S(1A)–Fe(1A)

72.47(4), Fe(1)–S(1)–Fe(1A) 72.81(3), O(1)–C(13)–O(1A) 125.3(5), Cp*(1)-Cp*(2) 56.107(136), S(1A)Fe(1)Fe(1A)-Fe(1)O(1)O(1A)Fe(1A) 86.480(47), O(1)C(13)O(1A)-Fe(1)O(1)O(1A)Fe(1A) 0.348(62).

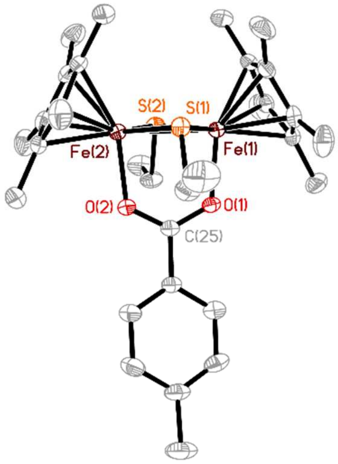

Fig. 3 ORTEP (ellipsoids at 30% probability) diagram of **7**. All hydrogen atoms as well as the PF_6^- anions are omitted for clarity. Selected bond length (Å), Bond Angles and Plane Angles (deg): Fe(1)–Fe(2) 2.6188(7), Fe(1)–S(1) 2.2152(12), Fe(1)–S(2) 2.1999(10), Fe(1)–O(1) 1.9796(22), Fe(2)–S(1) 2.2043(10), Fe(2)–S(2) 2.2127(12), Fe(2)–O(2) 1.9725 (21), Fe(2)–S(1)–Fe(1) 72.68(3), Fe(2)–S(2)–Fe(1) 72.81(3), O(2)–C(25)–O(1) 124.6(3), Cp*(1)-Cp*(2) 55.258(106), S(1)Fe(2)Fe(1)-Fe(2)O(2)O(1)Fe(1) 85.477(54), O(2)C(25)O(1)-Fe(2)O(2)O(1)Fe(1) 5.569(345).

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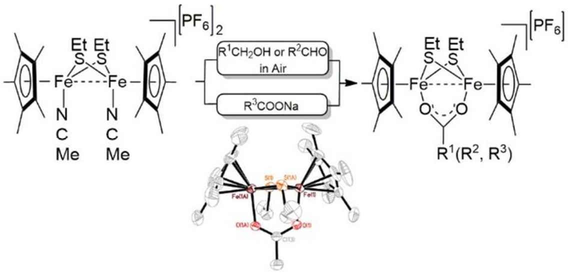

Carboxylate-bridged iron-thiolate clusters were formed from alcohols/aldehydes in air or sodium carboxylates at room temperature.