Synthesis of organoiron thio- and seleno-terephthaloyl chloride derivatives and their reactions with organoiron polychalcogen complexes

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A series of organoiron thio and seleno-terephthaloyl chloride complexes of the type Cp'Fe(CO)2ECO(C6H4)COCl (Cp' = C5H5, Bu-C5H4; E = S, Se) have been prepared by the reaction of the corresponding poly sulphides or polyselenides [Cp'Fe(CO)2]2(μ-Ex) (x = 1-3) with excess terephthaloyl chloride under suitable chosen conditions and characterized. The reactions of (Bu-C5H4)Fe(CO)2ECO(C6H4)COCl with some organoiron polysulphides and polyselenides afforded the bimetallic terephthalate complexes (Bu-C5H4)Fe(CO)2ECO(C6H4)COE(CO)2FeCp' in fairly good yields.

Although much attention has been focused on the synthetic and structural aspects of metal chalogen complexes, the understanding of their reactivity is still at its beginning. Organometallic complexes containing sulphur or selenium bridges are known to undergo certain reactions due to the presence of lone pairs of electrons on the sulphur or the selenium atoms, and this may be the reason for their reactivity in general.

We have previously shown that the organoiron sulphides and selenides as well as their organoruthenium analogues [Cp'M(CO)2]2(μ-Ex)(M = Fe, Ru; Cp' = C5H5, Bu-C5H4, 1,3-Bu2-C5H3; E = S, Se; x = 1-5) react smoothly with acid chlorides to give mono-thio- and seleno-carboxylate derivatives Cp'M(CO)2ECOR (R = alkyl or aryl).

In continuation to our efforts in this area, we report here a convenient synthesis of some organoiron mono-thio- and monoseleno-terephthaloyl chloride complexes Cp'(CO)2ECO(C6H4)COCl as well as their reactions with organoiron polysulphides and polyselenides [Cp'Fe(CO)2]2(μ-Ex).

Experimental
All reactions were conducted under dinitrogen by schlenk techniques. Terephthaloyl chloride was puri-

Preparation of (C5H5)Fe(CO)2SCO(C6H4)COCl (I)
To a refluxing solution of methylene chloride (CH2Cl2) (30 ml) containing terephthaloyl chloride (0.22 g, 1.0 mmol), a solution of [(C5H5)Fe(CO)2]2(μ-S3) (0.11 g, 0.24 mmol) in CH2Cl2 (100 ml) was added dropwise over a period of 2 h. The reaction mixture was cooled to room temperature and the solvent evaporated in vacuo at 20°C. The residue was taken in CH2Cl2 and transferred to a chromatography column made up in n-hexane. An orange band was eluted with CH2Cl2-n-hexane (1:2). Evaporation of the solvent and recrystallization from CH2Cl2 afforded orange crystals of compound (I), yield (75%); m.p. (dec.) 115-117°C. [Found: C, 47.81; H, 2.29; S, 8.26; Cl, 9.60; Calc. for C16H9O4SCIFe: C, 47.84; H, 2.41; S, 8.50; Cl, 9.41%]. IR(KBr): v(CO) 2030(s), 1970(vs); v(CIC=O) 1750(s); v(SC=O) 1580 cm⁻¹. 

1H NMR (CDCl3): 5.05 (s, 5H); 8.17 (m, 4H) ppm.

Preparation of (Bu-C5H4)Fe(CO)2SCO(C6H4)COCl (II)
In a similar procedure as described above, [(Bu-C5H4)Fe(CO)2]2(μ-S3) (0.15 g, 0.27 mmol) in CH2Cl2 was added to the refluxing terephthaloyl chloride (0.25 g, 1.2 mmol) solution and compound (II) was obtained, yield (70%); m.p. (dec.) 60-62°C. [Found: C, 53.02; H, 4.18; S, 7.12; Cl, 7.86; Calc. for C19H17O4SClFe: C, 52.74; H, 3.93; S, 7.41; Cl, 8.19%]. IR(KBr): v(CO) 2030(s), 1970(vs); v(CIC=O) 1750(s); v(SC=O) 1580 cm⁻¹. 1H NMR (CDCl3): 1.30 (s, 9H); 5.00 (m, 4H); 8.17 (m, 4H) ppm.
Preparation of $(\text{C}_5\text{H}_5)\text{Fe}((\text{CO})_2\text{Se})\text{CO(C}_6\text{H}_4)\text{COCI} \ (\text{III})$

In a similar procedure, $[(\text{C}_5\text{H}_5)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.11 \text{ g}, 0.25 \text{ mmol})$ in CH$_2$Cl$_2$ was added to the refluxing terephthaloyl chloride (0.22 g, 1.0 mmol) solution, and compound (III) was obtained, yield (62%); m.p. (dec.) 64-66°C. [Found : C, 42.62; H, 2.40; Cl, 8.13; Calc. for C$_{25}$H$_{30}$O$_7$SFe : C, 42.54; H, 2.14; Cl, 8.37%]. IR (KBr) : $\nu$(CO) 20408(s), 1975(vs); $\nu$(CIC=O) 1750(s); $\nu$(SeC=O) 1610(s). $^1$H NMR (CDCl$_3$): 5.08 (s, 5H); 8.14 (m, 4H) ppm.

Preparation of $(\text{tBu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{Se})\text{CO(C}_6\text{H}_4)\text{COCI} \ (\text{IV})$

In a similar procedure $[(\text{tBu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}_2] \ (0.15 \text{ g}, 0.24 \text{ mmol})$ in CH$_2$Cl$_2$ was added to the refluxing terephthaloyl chloride (0.22 g, 1.0 mmol) solution and compound (IV) was obtained, yield (67%); m.p. (dec.) 84-86°C. [Found : C, 47.75; H, 3.76; Cl, 7.16; Calc. for C$_{31}$H$_{34}$O$_7$S$_2$Fe : C, 47.58; H, 3.57; Cl, 7.39%]. IR (KBr) : $\nu$(CO) 2020(s), 1970(vs); $\nu$(CIC=O) 1760(s); $\nu$(SeC=O) 1620(s). $^1$H NMR (CDCl$_3$): 1.25 (s, 9H); 4.99 (m, 4H); 8.14 (m, 4H) ppm.

Reactions of $(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{SCO(C}_6\text{H}_4)\text{COCI} \ (\text{II})$ with organoiron polysulphides and polselenides

**Reaction of $(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{SCO(C}_6\text{H}_4)\text{COCI} \ (\text{II})$ with $[(\text{C}_5\text{H}_5)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.10 \text{ g}, 0.22 \text{ mmol})$**

A benzene solution (80 ml) containing $[(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.10 \text{ g}, 0.23 \text{ mmol})$ and compound II (0.10 g, 0.23 mmol) was refluxed. The reaction was monitored by IR spectroscopy and refluxing was continued until the reaction was complete (2 h). This was identified by the disappearance of the strong band at 1750 cm$^{-1}$ of the acid chloride group (CIC=O) of the terephthaloyl chloride complex (II). The solvent was removed in vacuo at 20°C and the residue was taken in CH$_2$Cl$_2$ and transferred to a chromatography column made up in n-hexane. An orange-red band was eluted with CH$_2$Cl$_2$-ether (9:1). Evaporation of the solvent in vacuo and recrystallization from CH$_2$Cl$_2$ afforded orange crystals of compound (V), yield (65%); m.p. (dec.) 130-132°C. [Found : C, 52.45; H, 3.59; S, 10.37; Calc. for C$_{28}$H$_{35}$O$_7$SSeFe : C, 51.51; H, 3.65; S, 10.57%]. IR (KBr) : $\nu$(CO) 2010(s), 1970(vs); $\nu$(SC=O) 1590(s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.25 (s, 9H); 4.99 (m, 4H); 8.08 (m, 4H) ppm.

**Reaction of $(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{SCO(C}_6\text{H}_4)\text{COCI} \ (\text{II})$ with $[(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.13 \text{ g}, 0.23 \text{ mmol})$**

In a similar procedure as described above, a benzene solution (80 ml) containing $[(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.13 \text{ g}, 0.23 \text{ mmol})$ and compound II (0.10 g, 0.23 mmol) was refluxed for 2 h when compound (VI) was obtained, yield (63%); m.p. (dec.) 148-150°C. [Found : C, 54.52; H, 4.84; S, 9.67; Calc. for C$_{30}$H$_{30}$O$_7$S$_2$Fe : C, 54.40; H, 4.56; S, 9.68%]. IR (KBr) : $\nu$(CO) 2020(s), 1960(vs); $\nu$(C=O) 1580 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.29 (s, 18H); 4.98 (s, br, 8H); 8.08 (s, 4H) ppm.

**Reaction of $(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{SCO(C}_6\text{H}_4)\text{COCI} \ (\text{II})$ with $[(\text{tBu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.15 \text{ g}, 0.24 \text{ mmol})$**

In a similar procedure, a benzene solution (80 ml) containing $[(\text{tBu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.15 \text{ g}, 0.24 \text{ mmol})$ and compound II (0.10 g, 0.23 mmol) was refluxed for 3 h and compound (VII) was obtained, yield (55%); m.p. (dec.) 156-158°C. [Found : C, 50.64; H, 4.00; Calc. for C$_{30}$H$_{30}$O$_7$SeSFe : C, 50.80; H, 4.26%]. IR (KBr) : $\nu$(CO) 2010(s), 1960(vs); $\nu$(SeC=O) 1590 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.29 (s, 18H); 4.99 (m, 8H); 8.08 (s, 4H) ppm.

**Reaction of $(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2\text{SCO(C}_6\text{H}_4)\text{COCI} \ (\text{II})$ with $[(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.12 \text{ g}, 0.22 \text{ mmol})$**

In a similar procedure, a benzene solution (80 ml) containing $[(\text{Bu-C}_5\text{H}_4)\text{Fe}((\text{CO})_2)\text{Se}]_2(\mu-\text{Se}) \ (0.12 \text{ g}, 0.22 \text{ mmol})$ and compound II (0.10 g, 0.23 mmol) was refluxed for 3 h when compound (VIII) was obtained, yield (53%); m.p. (dec.) 118-120°C. [Found : C, 48.22; H, 3.50; Calc. for C$_{26}$H$_{22}$O$_7$SeFe : C, 47.81; H, 3.40%]. IR (KBr) : $\nu$(CO) 2010(s), 1970(vs); $\nu$(SC=O) 1590(s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): 1.29 (s, 9H); 4.97 (s, br, 4H); 5.05 (s, 5H); 8.08 (s, 4H) ppm.
1970(vs); v(C=O) 1585(s). $^1$H NMR (CDCl3): 1.29 (s, 9H), 5.07 (m, 8H); 8.08 (m, 4H) ppm.

Reaction of $^{t}$Bu-C$_5$H$_4$Fe(CO)$_2$SeCO(C$_6$H$_4$) COCl (IV) with $^{t}$Bu-C$_5$H$_4$Fe(CO)$_2$(μ-Se$_2$). Preparation of $^{t}$Bu-C$_5$H$_4$Fe(CO)$_2$SeCO(C$_6$H$_4$) COSe(CO)$_2$Fe $^{t}$Bu-C$_5$H$_4$ (IX)

In a similar procedure, a benzene solution (80 ml) containing ($^{t}$Bu-C$_5$H$_4$Fe(CO)$_2$(μ-Se$_2$) (0.13 g, 0.21 mmol) and compound IV (0.10 g, 0.21 mmol) was refluxed for 4h, when compound (IX) was obtained, yield (48%); m.p. (dec.) 166-168 °C [Found: C, 47.9; H, 4.13; Calc. for C$_{30}$H$_{30}$Se$_2$Fe$_2$: C, 47.65; H, 4.00%]. IR(KBr): v(C=O) 2020(s), 1970(v ); v(SeC=O) 1590(s) em".

Results and discussion

Synthesis and characterization of organoiron thio- and seleno-terephthaloyl chloride complexes.

The organoiron monothieterphthaloyl chloride complexes (C$_3$H$_5$)(Fe(CO)$_2$SCO(C$_6$H$_4$) COCl (I), (tBu-C$_5$H$_4$)Fe(CO)$_2$SCO(C$_6$H$_4$) COCl (II) and the organoiron monoseleno-terephthaloyl chloride complexes (C$_3$H$_5$)Fe(CO)$_2$SeCO(C$_6$H$_4$) COCl (III), (tBu-C$_5$H$_4$)Fe(CO)$_2$SeCO(C$_6$H$_4$) COCl (IV) were synthesized in fairly good yields from the reaction of the corresponding sulphides and selenides [(Cp'Fe(CO)$_2$)$_2$(μ-Ex) (Cp'=C$_3$H$_5$, tBu-C$_5$H$_4$; E=Se, Se; x = 1-3) with terephthaloyl chloride (CICO(C$_6$H$_4$)COCl). In this reaction, the sulphides or the selenides were dissolved in a large amount of solvent (100 ml CH$_2$Cl$_2$) and added dropwise over a period of 2-3 h to an excess amount (five fold excess) of terephthaloyl chloride dissolved in a small amount of solvent (30 ml CH$_2$Cl$_2$). These conditions can be considered as the optimum conditions that lead to the formation of the terephthaloyl chloride derivatives Cp'Fe(CO)$_2$ECO(C$_6$H$_4$) COCl without the formation of any measurable amount of the terephthalate complexes Cp'Fe(CO)$_2$ECO(C$_6$H$_4$) COE(CO)$_2$FeCp' that might be expected from this reaction. Reversing the addition afforded the terephthalate product as the major product irrespective of the presence of excess terephthaloyl chloride. It has been recently reported that the reaction of Cp$_2$Ru$_2$(CO)$_3$Se$_3$ with excess terephthaloyl chloride in acetonitrile afforded both terephthaloyl chloride CpRu(CO)$_2$SeCO(C$_6$H$_4$) COCl and terephthalate CpRu(CO)$_2$SeCO(C$_6$H$_4$) COSe(CO)$_2$Ru complexes$^{14}$. The reactivity of organoiron sulphides and selenides towards acid chlorides as electrophiles has been attributed to the reactivity of the sulphur and selenium atoms as electron donors$^{13}$. Moreover, the reactivity of organoiron selenides has been shown to be less than that of the analogous organoiron sulphides on the bases of nucleophilicity$^{11}$.

There are two acceptable possible routes for the reaction of sulphides and selenides with acid chlorides as represented in the following equations$^{11,13}$.

Cp'Fe(CO)$_2$Ex-RCOCI → Cp'Fe(CO)$_2$ExCOR +Cp'Fe(CO)$_2$Cl ...(1)

Cp'Fe(CO)$_2$Ex-RCOCI → Cp'Fe(CO)$_2$ExCOR +Cp'Fe(CO)$_2$Cl +x-1E ...(2)

Both routes lead to the formation of the same final products namely, monothio- or monoseleno-complex Cp'Fe(CO)$_2$ECOR and the chloride derivative Cp'Fe(CO)$_2$Cl which were isolated and characterized.

The organoiron terephthaloyl chloride complexes (I-IV) prepared in this work were characterized by elemental analysis, IR and $^1$H NMR spectra. Their IR spectra exhibit two bands in the ranges 2020-2040 and 1790-1980 cm$^{-1}$ corresponding to the two terminal carbonyl groups. The (C=O) stretching band of the acid chloride (CICO-O) moiety appears in the range 1750-1760 cm$^{-1}$, while the (C=O) stretching band of the thio- or seleno- carboxylate moiety (EC=O) appears in the range 1580-1610 cm$^{-1}$. The assignment of the latter v(EC=O) band was made on the basis of the reported results of organoiron thio- and selenocarboxylate derivatives$^{10,11}$. The IR and
$^1$H NMR spectra of the complexes show the characteristic bands in their respective positions.

Reaction of organoiron thio- and seleno-terephthaloyl chloride complexes ($Cp'$Fe(CO)$_2$ECO(C$_6$H$_4$) COCl) with organoiron sulphides and selenides [($Cp'$Fe(CO)$_2$)$_2$($\mu$-$\text{Ex}$)]$_2$($\mu$-$\text{Ex}$)

The presence of a free acid chloride group in the previously mentioned terephthaloyl chloride complexes (I-IV) makes them valuable precursors for many reactions. An important reaction of these complexes would be the reaction with organometal sulphides and selenides. Such a reaction offers a facile method for the synthesis of a large variety of homo- and hetero bimetallic bithio-, biseleno- and thio-seleno- terephthalate complexes. Scheme 1, represents the synthesis of some organoiron terephthalate complexes conducted in this work.

The reactions of ($^{1}$Bu-$C_5$H$_4$)Fe(CO)$_2$SCO ($C_6$H$_4$)COCl with [(Bu-$C_5$H$_4$)Fe(CO)$_2$]$_2$($\mu$-$S_3$), [(Bu-$C_5$H$_4$)Fe(CO)$_2$]$_2$($\mu$-$S_3$) and [(Bu-$C_5$H$_4$)Fe(CO)$_2$]$_2$($\mu$-$S_2$) in refluxing benzene afforded respectively the terephthalate complexes

$^{(1)}$Bu-$C_5$H$_4$)Fe(CO)$_2$SCO ($C_6$H$_4$) COS(CO)$_2$ Fe ($C_5$H$_5$), V

$^{(1)}$Bu-$C_5$H$_4$)Fe(CO)$_2$SCO ($C_6$H$_4$) COS(CO)$_2$ Fe ($^{(1)}$Bu-$C_5$H$_5$), VI and,

$^{(1)}$Bu-$C_5$H$_4$)Fe(CO)$_2$SCO ($C_6$H$_4$) COSe(CO)$_2$Fe ($^{(1)}$Bu-$C_5$H$_5$), VII. Moreover, the reactions of

$^{(1)}$Bu-$C_5$H$_4$)Fe(CO)$_2$SCO ($C_6$H$_4$) COCl with [(C$_5$H$_5$)Fe(CO)$_2$]$_2$
(μ-S₃), (Bu₅C₅H₄)Fe(CO)₂(μ-Se₂) and [(Bu₅C₅H₄)Fe(CO)₂]₂(μ-S₃) afforded respectively (Bu₅C₅H₄)Fe(CO)₂SeCO(C₆H₄)COS(CO)₂Fe(Bu₅C₅H₄) VIII, (Bu₅C₅H₄)Fe(CO)₂SeCO(C₆H₄)COS(CO)₂Fe(Bu₅C₅H₄) IX and compound VII.

These reactions are straightforward and can be easily characterized by IR spectroscopy. The disappearance of the ν(C=O) stretching band of the acid chloride in the range 1750-1760 cm⁻¹ is a clear indication of the completion of the reaction.

The terephthalate complexes (V-IX) are fairly stable as solids and in solution. They were characterized by elemental analysis, IR and ¹H NMR spectra. Their IR spectra show two bands in the ranges 2010-2020 and 1970-1980 cm⁻¹ for the terminal carbonyl groups and a strong band in the range 1580-1590 cm⁻¹ characteristic of thio- and seleno-carboxylate moieties. The band of the tert-butyl group of the substituted cyclopentadienyl complexes appears in the range 2800-3000 cm⁻¹. Their ¹H NMR spectra show the characteristic protons in their expected chemical shift regions.

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References