Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Organoiron Selenium Complexes. Synthesis and Characterization of tert-Butyl Substituted Cyclopentadienyldicarbonylselenoc Iron Complexes, $C_p{}'Fe(CO)_2SeCOR$ ($Cp' = C_5H_5$, $t\text{-}BuC_5H_4$, $1,3\text{-}t\text{-}Bu_2C_5H_3$)

Ibrahim Jibril[a] & Osama Abu-Nimreh[a]
[a] Department of Chemistry, Yarmouk University, Irbid, Jordan

To cite this article: Ibrahim Jibril & Osama Abu-Nimreh (1996): Organoiron Selenium Complexes. Synthesis and Characterization of tert-Butyl Substituted Cyclopentadienyldicarbonylselenocarboxylate Iron Complexes, $C_p{}'Fe(CO)_2SeCOR$ ($Cp' = C_5H_5$, $t\text{-}BuC_5H_4$, $1,3\text{-}t\text{-}Bu_2C_5H_3$), Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:8, 1409-1419

To link to this article: http://dx.doi.org/10.1080/00945719608005133

SYNTH. REACT. INORG. MET.-ORG. CHEM., 26(8), 1409-1419 (1996)

ORGANOIRON SELENIUM COMPLEXES. SYNTHESIS AND CHARACTERIZATION OF *tert*-BUTYL SUBSTITUTED CYCLOPENTADIENYLDICARBONYLSELENOCARBOXYLATE IRON COMPLEXES, Cp'Fe(CO)$_2$SeCOR (Cp' = C_5H_5, *t*-BuC_5H_4, 1,3-*t*-Bu$_2C_5H_3$)

Ibrahim Jibril* and Osama Abu-Nimreh
Department of Chemistry, Yarmouk University
Irbid, Jordan

ABSTRACT

The organoiron selenides $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-Se})$ (I), $[(t\text{-BuC}_5H_4)Fe(CO)_2]_2(\mu\text{-Se}_2)$ (II), and $[(1,3\text{-}t\text{-Bu}_2C_5H_3)Fe(CO)_2]_2(\mu\text{-Se}_2)$ (III) were prepared from the reaction of the organoiron dimers $[(C_5H_5)Fe(CO)_2]_2$, $[(t\text{-BuC}_5H_4)Fe(CO)_2]_2$ and $[(1,3\text{-}t\text{-Bu}_2C_5H_3)Fe(CO)_2]_2$ with elemental selenium. The above selenides (I), (II) and (III) react with acid chlorides, RCOCl to give the Se-bonded monoselenocarboxylate derivatives [Cp'Fe(CO)$_2$SeCOR] (Cp' = C_5H_5, *t*-BuC_5H_4, 1,3-*t*-Bu$_2C_5H_3$; R = 4-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$). The presence of *tert*-butyl substituents on the cyclopentadienyl ring introduces significant changes in the properties of these systems relative to the unsubstituted cyclopentadienyl analogues.

INTRODUCTION

There has been increasing interest in the synthesis, structure determination and reactivity of transition metal chalcogen complexes[1-6] due to their important biological and catalytic aspects[7-10]. In contrast to the metal sulfides which have been extensively studied[11], metal selenides received only scant attention and examples of transition metal selenide complexes remain rare. Moreover, syntheses of transition metals selenides from elemental selenium are very uncommon. The organoiron selenide $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-}Se)$ has been prepared by the reaction[12] of $[(C_5H_5)Fe(CO)_2]^-$ with Se_2Cl_2. The molybdenum and tungsten selenium complexes $(C_5Me_5)_2Mo_2Se_4$ and $(C_5Me_5)_2W_2(CO)_2Se_3$ have been prepared from the thermal reaction of $(C_5Me_5)_2M_2(CO)_4$ (M = Mo, W) with elemental selenium[13]. It is worth noting that, although much attention has been focused on the synthetic and structural aspects of metal chalcogen complexes, the understanding of the reactivity of transition metal sulfides and selenides is still at its beginning and even basic reactions have not been carried out. We have previously reported the synthesis of the organoiron polysulfides $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}S_3)$ and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}S_3)$ and their reaction with acid chlorides, RCOCl (R = alkyl or aryl)[14]. The above reaction proved to be a facile method for the synthesis of a new class of organoiron thiocarboxylate complexes $Cp'Fe(CO)_2SCOR$ (Cp' = C_5H_5, $t\text{-}BuC_5H_4$, $1,3\text{-}t\text{-}Bu_2C_5H_3$). In continuation of our efforts in this area, we report here the synthesis of the organoiron selenides $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-}Se)$, $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}Se_2)$ and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}Se_2)$ as well as their reactions with acid chlorides, RCOCl (R = $4\text{-}O_2NC_6H_4$, $3,5\text{-}(O_2N)_2C_6H_3$).

EXPERIMENTAL

All reactions were conducted under dinitrogen by Schlenk techniques. The acid chlorides were purchased from Aldrich and elemental selenium (gray) was purchased from Fluka. *Tert*-butylcyclopentadiene and 1,3-di(*tert*-butyl)cyclopentadiene were prepared as reported[15,16]. $Fe_2(CO)_9$ was prepared by photolysis of $Fe(CO)_5$ in glacial acetic acid as reported[17]. $[(C_5H_5)Fe(CO)_2]_2$ was prepared from $Fe_2(CO)_9$ and freshly prepared cyclopentadiene similar to the established procedure[18]. $[(t\text{-}BuC_5H_5)Fe(CO)_2]_2$ and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2$ were prepared as previously reported[14]. For column chromatography, silica of the particle size 0.063-0.200 mm (70 - 230 mesh ASTM) EM reagent was employed. Infrared spectra were recorded on a Pye-Unicam SP3-100 spectrophotometer and ^1H NMR spectra on a Bruker WP80SY spectrometer with Me_4Si as internal standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, USA.

Reaction of $[(C_5H_5)Fe(CO)_2]_2$ with Selenium; Preparation of $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-}Se)$ (I).

A toluene solution (80 mL) containing $[(C_5H_5)Fe(CO)_2]_2$ (0.71 g, 2 mmole) and selenium powder (0.40 g, 5 mmole) was heated with stirring at 90-95 °C. The reaction was monitored by IR spectroscopy and heating was continued untill the reaction has gone to completion (75 min), as identified by the disappearance of the bridging carbonyl band at 1767 cm^{-1} of the starting material and the appearance of two new terminal carbonyl bands at 2030 and 1980 cm^{-1}. The reaction mixture was then cooled to room temperature and the solvent was evaporated under vacuum at 20 °C. The deep-red, oily residue was taken up in CH_2Cl_2 (10 mL) and transferred to a chromatography column made up in hexane. An orange-red band was eluted with CH_2Cl_2/hexane (3:1). Evaporation of the solvent and crystallization from CH_2Cl_2 produced orange red crystals of $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-}Se)$ (I). Yield (0.39 g, 45%), m.p. 80-82 °C (dec). Anal. Found: C, 38.89; H, 2.44. Calc. for $Fe_2SeC_{14}H_{10}O_4$, (432.9): C, 38.84; H, 2.33 %. IR (CH_2Cl_2): νCO: 2030 s, 1980 vs cm^{-1}. ^1H NMR ($CDCl_3$): 5.04 ppm (s).

Reaction of $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2$ with Selenium; Preparation of $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (II).

A benzene solution (80 mL) containing (0.93 g, 2 mmole) of $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2$ and (0.40 g, 5 mmole) of selenium powder was refluxed until the reaction has gone to completion (45 min). The disappearance of the bridging carbonyl band at 1762 cm^{-1} and the appearance of two new terminal carbonyl bands at 2022 and 1975 cm^{-1} indicate the completion of the reaction. The mixture was cooled to room temperature and the solvent was evaporated under vacuum at 20 °C. The deep red oily residue was taken up in CH_2Cl_2 (10 mL) and transferred to a chromatography column made up in hexane. An orange-red band was eluted with CH_2Cl_2/hexane (5:2). Evaporation of the solvent under vacuum and crystallization from CH_2Cl_2 afforded orange-red crystals of $[(C_5H_4)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (II). Yield (0.37 g, 30%), m.p. 83-85 °C (dec.). Anal. Found: C, 42.11; H, 4.19. Calc. for $Fe_2Se_2C_{22}H_{26}O_4$ (264.1): C, 42.34; H, 4.20 %. IR(CH_2Cl_2): νCO: 2022 s, 1975 vs cm^{-1}. ^1H NMR($CDCl_3$): 1.29 (s, 18H), 4.97 (s, 8H) ppm.

Reaction of $[1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2$ with Selenium; Preparation of $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (III).

A methylene chloride (CH_2Cl_2) solution (100 mL) containing $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2$ (1.16 g, 2 mmole) and selenium powder (0.40 g, 5 mmole) was stirred at room temperature

Table I

Colors, Yields and Melting Points of the Selenocarboxylate Derivatives $Cp'Fe(CO)_2SeCOR$, (IV)-(IX).

Compound	Color	Yield , %	M.P. °C
$[(C_5H_5)Fe(CO)_2SeCO(3,5\text{-}(O_2N)_2C_6H_3)$, (IV)	orange-brown	50	128-130
$[(C_5H_5)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$, (V)	red-brown	42	108-110
$(t\text{-}BuC_5H_4)Fe(CO)_2SeCO(3,5\text{-}(O_2N)_2C_6H_3)$, (VI)	orange-brown	58	112-114
$(t\text{-}BuC_5H_4)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$, (VII)	brown	48	98 -100
$(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2SeCO(3,5\text{-}(O_2N)_2C_6H_3)$, (VIII)	orange-brown	62	113-115
$(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$, (IX)	orange-red	53	103-105

until the reaction has gone to completion (4h). The disappearance of the bridging carbonyl band at 1760 cm^{-1} and the appearance of two new terminal carbonyl bands at 2020 and 1975 cm^{-1} indicate the completion of the reaction. The solvent was then evaporated under vacuum at 20 °C and the residue was transferred to a chromatography column. An orange-red band was eluted with CH_2Cl_2/hexane (4:1). Evaporation of the solvent and crystallization from CH_2Cl_2 afforded orange-red crystals of $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (III). Yield (0.88 g, 60 %), m.p. 86-88 °C (dec). Anal. Found: C, 48.36; H, 6.00. Calc. for $Fe_2Se_2C_{30}H_{42}O_4$ (736.3): C, 48.93; H, 5.75%. IR(CH_2Cl_2): νCO: 2020 s, 1975 vs cm^{-1}. ^1H NMR($CDCl_3$): 1.30 (s, 36H), 4.84 (s, 6H) ppm.

Reaction of $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-}Se)$ (I), $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (II) and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (III) with Acid Chlorides RCOCl.

To a methylene chloride solution (50 mL) containing the organoiron selenides (I), (II) or (III) (2 mmole), a solution of the acid chloride (2.5 mmole) in CH_2Cl_2 was added slowly. The reaction mixture was refluxed for (1-2 h) until the color changes from orange-red to dark red. The solvent was then evaporated under vacuum and the residue was transferred to a chromatography column. A brown-red band was eluted with CH_2Cl_2/hexane (3:1). Crystallization from CH_2Cl_2 afforded dark red to red crystals of the corresponding

Table II

Chemical Analysis Data of the Selenocarboxylate Derivatives Cp'Fe(CO)$_2$SeCOR, (IV)-(IX).

Compound	Empirical Formula	% Found (Calc.) C	H	N
[(C$_5$H$_5$)Fe(CO)$_2$SeCO(3,5-(O$_2$N)$_2$C$_6$H$_3$), (IV)	FeSeC$_{14}$H$_8$N$_2$O$_7$	37.22 (37.25)	1.91 (1.78)	6.11 (6.21)
[(C$_5$H$_5$)Fe(CO)$_2$SeCO(4-O$_2$NC$_6$H$_4$), (V)	FeSeC$_{14}$H$_9$NO$_5$	41.31 (41.41)	2.40 (2.23)	3.26 (3.45)
(t-BuC$_5$H$_4$)Fe(CO)$_2$SeCO(3,5-(O$_2$N)$_2$C$_6$H$_3$), (VI)	FeSeC$_{18}$H$_{16}$N$_2$O$_7$	42.72 (42.63)	3.14 (3.18)	5.33 (5.52)
(t-BuC$_5$H$_4$)Fe(CO)$_2$SeCO(4-O$_2$NC$_6$H$_4$), (VII)	FeSeC$_{18}$H$_{17}$NO$_5$	47.00 (46.80)	3.77 (3.71)	3.03 (3.03)
(1,3-t-Bu$_2$C$_5$H$_3$)Fe(CO)$_2$SeCO(3,5-(O$_2$N)$_2$C$_6$H$_3$), (VIII)	FeSeC$_{22}$H$_{24}$N$_2$O$_7$	46.59 (46.91)	4.39 (4.29)	4.28 (4.97)
(1,3-t-Bu$_2$C$_5$H$_3$)Fe(CO)$_2$SeCO(4-O$_2$NC$_6$H$_4$), (IX)	FeSeC$_{22}$H$_{25}$NO$_5$	50.71 (50.96)	5.00 (4.86)	2.43 (2.70)

monoselenocarboxylates, Cp'Fe(CO)$_2$SeCOR (IV)-(IX). The colors, yields and melting points are shown in Table I. The analytical data are shown in Table II. The spectral data are presented in Table III.

RESULTS AND DISCUSSION

The organoiron selenides in Fig. 1, [(C$_5$H$_5$)Fe(CO)$_2$]$_2$(μ-Se) (I), [(t-BuC$_5$H$_4$)Fe(CO)$_2$]$_2$(μ-Se$_2$) (II) and [(1,3-t-Bu$_2$C$_5$H$_3$)Fe(CO)$_2$]$_2$(μ-Se$_2$) (III), respectively, were formed from the reactions of the iron dimers [(C$_5$H$_5$)Fe(CO)$_2$]$_2$, [t-BuC$_5$H$_4$)Fe(CO$_2$]$_2$ or [(1,3-t-Bu$_2$C$_5$H$_3$)Fe(CO)$_2$]$_2$ with elemental gray selenium.

The reaction of the organoiron dimers with elemental selenium can be represented as shown in eq. (1)[19].

$$[\mathrm{Cp'Fe(CO)_2}]_2 + x\mathrm{Se} \xrightarrow{\qquad\qquad} [\mathrm{Cp'Fe(CO)_2}]_2(\mu\text{-}\mathrm{Se}_x) \qquad (1)$$

(Cp' = C$_5$H$_5$, x = 1; Cp' = t-BuC$_5$H$_4$ or 1,3-t-Bu$_2$C$_5$H$_3$, x = 2)

Table III

IR and ^{1}H NMR Spectra of the Selenocarboxylate Derivatives Cp'Fe(CO)$_2$SeCOR (IV)-(IX).

Compound	**IR (CH_2Cl_2) (cm^{-1})**	**^{1}H NMR ($CDCl_3$) (δ, ppm)**
[(C_5H_5)Fe(CO)$_2$SeCO(3,5-(O_2N)$_2C_6H_3$), (IV)	2035 s, 1973 vs ν(CO), 1615 s ν(C=O) 1530 s, 1340 w ν(NO_2)	5.11 (s, 5H, C_5H_5), 9.20 (m, 3H, ArH)
[(C_5H_5)Fe(CO)$_2$SeCO(4-$O_2NC_6H_4$), (V)	2030 s,1965 vs ν(CO), 1590 s ν(C=O) 1525 m,1335 m ν(NO_2)	5.08 (s, 5H, C_5H_5), 8.20 (s, 4H, ArH)
(*t*-BuC_5H_4)Fe(CO)$_2$SeCO(3,5-(O_2N)$_2C_6H_3$), (VI)	2950 br, ν(C-H) 2012 s, 1970 vs ν(CO), 1590 ν(C=O) 1530 s, 1330 m ν(NO_2)	1.28 (s, 9H, C(CH_3)$_3$), 5.00 (m, 4H, C_5H_4), 9.13 (t, 1H, 4-ArH) 9.21 (d, 2H, 2,6-ArH)
(*t*-BuC_5H_4)Fe(CO)$_2$SeCO(4-$O_2NC_6H_4$), (VII)	2950 br ν(C-H) 2010 s, 1965 vs ν(CO) 1590 s, ν(C=O) 1525 m, 1335 m ν(NO_2)	1.29 (s, 9H, C(CH_3)$_3$) 4.99 (s, 4H, C_5H_4) 8.20 (s, 4H, ArH)
(1,3-*t*-Bu$_2C_5H_3$)Fe(CO)$_2$SeCO(3,5-(O_2N)$_2C_6H_3$), (VIII)	2970 br ν(C-H) 2005 s, 1965 vs ν(CO) 1605 s, ν(C=O) 1530 m, 1350 s, ν(NO_2)	1.31 (s, 18H, C(CH_3)$_3$) 4.81 (t, 1H, 2-C_5H_3) 4.95 (d, 2H, 4,5-C_5H_3) 9.15 (t, 1H, 4-ArH) 9.23 (d, 2H, 2,6-ArH)
(1,3-*t*-Bu$_2C_5H_3$)Fe(CO)$_2$SeCO(4-$O_2NC_6H_4$), (IX)	2950 br ν(C-H) 2007 s, 1960 vs ν(CO), 1600 s, ν(C=O) 1520 m, 1340 m, ν(NO_2)	1.29 (s, 18H, C(CH_3)$_3$) 4.80 (t, 1H, 2-C_5H_3) 4.94 (d, 2H, 4,5-C_5H_3) 8.20 (s, 4H, ArH)

The selenide complexes (I), (II) and (III) are fairly stable as solids, but decompose in solution in the presence of light with deposition of elemental selenium. Compounds (I), (II) and (III) were characterized by elemental analysis, IR and ^{1}H NMR spectroscopy. Although the direct route of using soluble polyselenide anions with transition metal complexes has been the primary method utilized for the synthesis of transition metal selenide complexes[20,21], the reaction of elemental selenium with organotransition metal complexes represents a

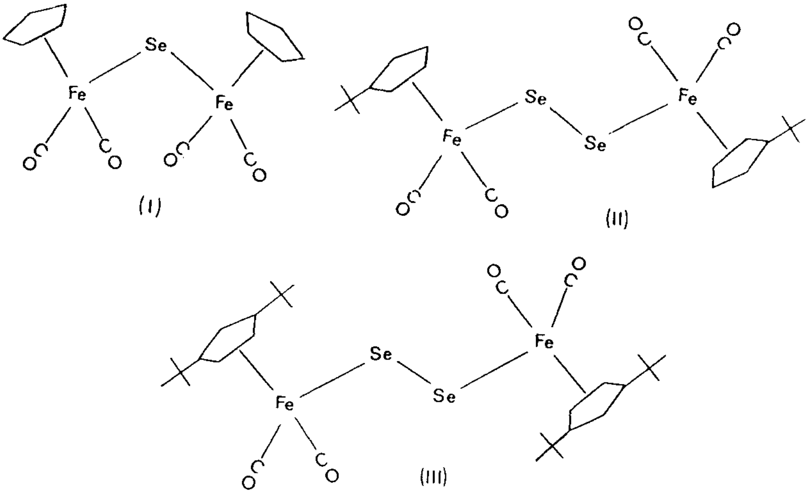

Fig.1 . Structures of the Organoiron Selenides I, II and III.

considerably successful route for the synthesis of organotransition metal selenide complexes. This method works especially well with low-valent organometallic complexes[22].

The presence of *tert*-butyl groups on the cyclopentadienyl ring of the iron dimers leads to a remarkable variation in reactivity and structure relative to the unsubstituted analogs. From the experimantal conditions needed for the formation of the selenides, it is observed that the ease of formation of the selenides is enhanced by substitution, (III) > (II) > (I). This order could be attributed to the thermal stability of the dimers which decreases on going from the unsubstituted cyclopentadienyl iron dimer to the di(*tert*-butyl)cyclopentadienyl iron dimer. This decrease in thermal stability could be attributed mainly to the electronic influence of the *tert*-butyl groups that lead to a weakening of the Fe-Fe bond. X-ray structural analysis of $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2$[23] has shown that this dimer exhibits an Fe-Fe bond distance (255.7 pm) which is longer than that of $[(C_5H_5)Fe(CO)_2]_2$ which has an Fe-Fe bond distance of 253.1 pm. It was proposed[23] that the increase in the bascity of the cyclopentadienyl ring of these dimers leads to a higher electronic repulsion between the occupied orbitals of the iron atoms.

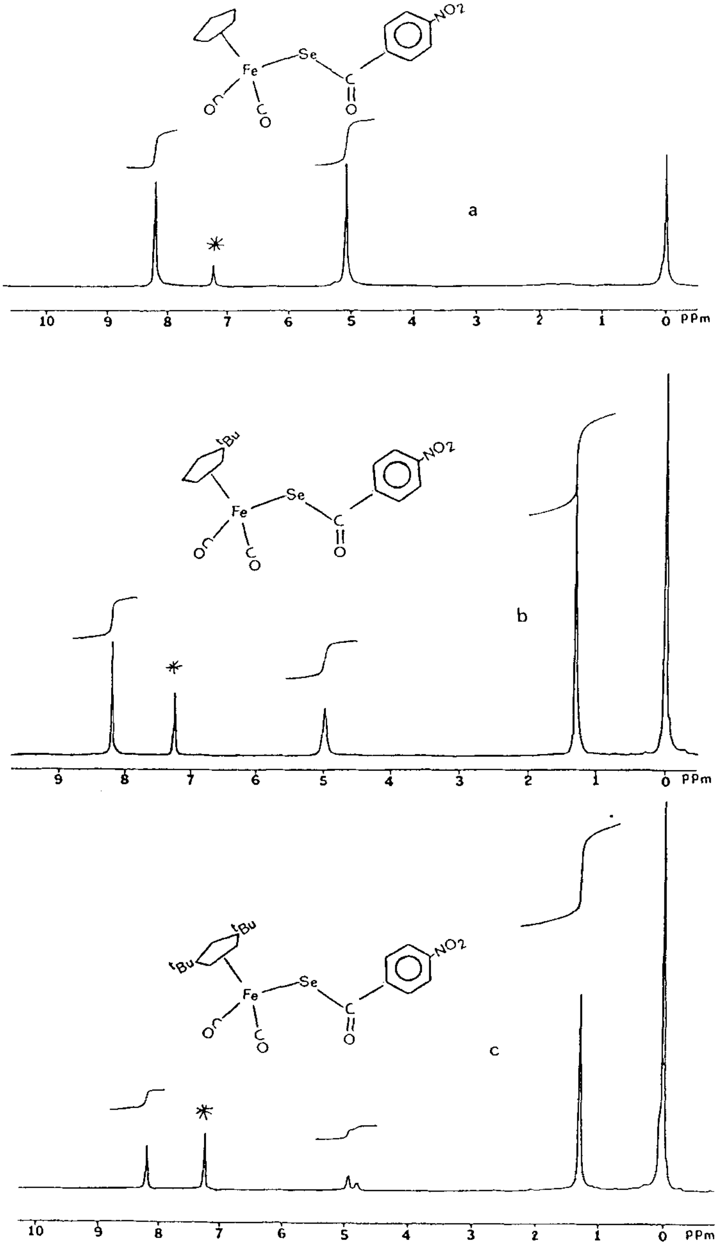

Fig. 2 .

^1H NMR Spectra of $(C_5H_5)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$ (a); $(t\text{-}Bu\text{-}C_5H_4)\text{-}Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$ (b) and $1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$ (c). (* $CDCl_3$ peak).

Besides their electonic effects which influence the reactivity of the iron dimers, the steric effects of the *tert*-butyl substituents seem to affect strongly the type of the selenide formed in these reactions. Thus, the monoselenide (I) of the unsubstituted cyclopentadienyl iron and the diselenide (III) of the di(*tert*-butyl)cyclopentadienyl iron were the only products formed in successive trials conducted on each.

IR Spectra

The IR spectra for the selenides (I), (II) and (III) show two terminal carbonyl stretching bands at 2030 and 1980, 2022 and 1975 and 2020 and 1975 cm^{-1}, respectively.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of $[(C_5H_5)Fe(CO)_2]_2(\mu\text{-Se})$ (I) shows a singlet at δ 5.04 ppm corresponding to the C_5H_5-ring protons while those of $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (II) and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}Se_2)$ (III) show a singlet at δ 1.29 (18 H) and 1.30 (36 H) ppm corresponding to the *tert*-butyl groups of (II) and (III), respectively, in addition to singlets at δ 4.97 (8 H) and 4.84 (6 H) ppm for the Cp-ring protons of (II) and (III), respectively. It has been shown[24,25] that the splitting pattern of the ring protons of *tert*-butyl substituted cyclopentadienyl complexes is highly affected by the nature of the ligands on the metal center. Comparison of the ^{1}H NMR spectra of (II) and (III) with those of the trisulfides $[(t\text{-}BuC_5H_4)Fe(CO)_2]_2(\mu\text{-}S_3)$ (IIa) and $[(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2]_2(\mu\text{-}S_3)$ (IIIa) shows that the Cp-ring protons in the above sulfides are not equivalent but appear as two triplets at δ 5.17 and 5.02 ppm in (IIa) and as a doublet and a triplet at δ 5.30, 5.21 ppm in (IIIa)[14], while in the case of the selenides (II) and (III) the Cp-ring protons are equivalent and appear as singlets at δ 4.97 and 4.84 ppm, respectively. This result indicates a remarkable structural difference between the organoiron sulfides and selenides which is attributed to the size difference of the chalcogen atoms.

Reactions with Acid Chlorides

The organoiron selenides (I), (II) and (III) react with acid chlorides, RCOCl, to give the Se-bonded monoselenocarboxylate derivatives (IV)-(IX). Their colors, yields, melting points and elemental analyses are presented in Tables I and II. The organoironselenides in this reaction bear a close resemblance to their sulfide analogs and the reactivity of the organoiron selenides toward acid chlorides as electrophiles has been attributed to the presence of selenium atoms which are considered as nucleophilic centers in the bridged organoiron complexes[26]. In view of the work established on organoiron sulfides[27], the reaction of the organoiron selenides with acid chlorides can be represented in eqs. (2) and (3).

$$\mathrm{Cp'Fe(CO)_2\text{-}Se_x\text{-}Fe(CO)_2Cp' + RCOCl \longrightarrow Cp'Fe(CO)_2Se_xCOR + Cp'Fe(CO)_2Cl} \quad (2)$$

$$\mathrm{Cp'Fe(CO)_2Se_xCOR \longrightarrow Cp'Fe(CO)_2SeCOR + (x\text{-}1)Se} \qquad (x > 1) \quad (3)$$

Although there are other options suggested for this reaction[27], eqs. (2) and (3) represent the only possible route that explains the formation of monoselenocarboxylate derivatives from both mono- and diselenides. This reaction respresents a facile method for the synthesis of a new class of organoiron monoselenocarboxylate complexes. The new selenocarboxylate complexes (IV)-(IX) are fairly stable as solids and in solution. Their IR spectra (Table III) show two terminal carbonyl bands in the range 2030-2005 and 1973-1960 cm^{-1}, and a band in the range 1615 - 1590 cm^{-1} corresponding to the (C=O) band of the carboxylate moiety. Moreover, the C-Se stretching band appears in the range[28] 895 - 870 cm^{-1}. Their ^1H NMR spectra (Table III) show the characteritic protons in their expected chemical shift regions Fig. 2 shows the ^1H NMR spectra of $(C_5H_5)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$, $(t\text{-}BuC_5H_4)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$ and $(1,3\text{-}t\text{-}Bu_2C_5H_3)Fe(CO)_2SeCO(4\text{-}O_2NC_6H_4)$.

ACKNOWLEDGMENT

Financial support from Yarmouk University is gratefully acknowledged. Thanks are due to Miss Fadwa Bani Hani for typing this manuscript.

REFERENCES

1. L. C. Roof and J. W. Kolis, Chem. Rev., 93, 1937 (1993).
2. M. Draganjac and T. B. Rauchfuss, Angew. Chem. Int. Ed. Engl., 24, 742 (1985).
3. J. Wachter, Angew. Chem. Int. Ed. Engl., 28, 1613 (1989).
4. A. Muller and E. Diemann, Adv. Inorg. Chem., 31, 89 (1987).
5. M. A. Ansari and J. A. Ibers, Coord. Chem. Rev., 100, 223 (1990).

6. W. A. Herrmann, Angew. Chem. Int. Ed. Engl., 25, 56 (1986).

7. R. H. Holm, S. Ciurli and J. A. Weigel, Prog. Inorg. Chem., 38, 1, (1990).

8. D. Coucouvanis, Acc. Chem. Res., 24, 1 (1991).

9. R. R. Chianelli, Catal. Rev. Sci. Engl., 26, 361 (1984).

10. H. Toposoe and B. S. Clausen, Catal. Rev. Sci. Engl., 26, 395 (1984).

11. I. G. Dance, Polyhedron, 5, 1037 (1986).

12. W. A. Herrmann, J. Rohrmann and H. Hecht, J. Organomet. Chem., 290, 53 (1985).

13. H. Brunner, J. Wachter and H. Wintergerst, J. Organomet. Chem., 235, 77 (1982).

14. M. A. El-Hinnawi, M. Y. El-Khatib, I. Jibril and S. T. Abu-Orbai, Synth. React. Inorg. Met-Org. Chem., 19, 809 (1989).

15. R. Riemschneider and R. Nehring, Z. Naturforsch. Teil B, 18, 463 (1963).

16. L. Knothe, H. Prinzbach and E. Hadicke, Chem. Ber., 114, 1656 (1981).

17. E. Speyer and H. Wolf, Chem. Ber., 60, 1424 (1927).

18. B. F. Hallam, O. S. Mills and P. L. Pauson, J. Inorg. Nucl. Chem., 1, 313 (1955).

19. H. Brunner, N. Janietz, W. Meer, J. Wachter, E. Herdtweck, W. A. Herrmann, O. Serhadli and M. L. Ziegler, J. Organomet. Chem., 347, 237 (1988).

20. S. C. O'Neal, W. T. Pennington and J. W. Kolis, Inorg. Chem., 29, 590 (1990).

21. M. Draganijac, S. Dhingra, S. P. Huang and M. G. Kanatzidis, Inorg. Chem., 29, 590 (1990).

22. W. Chen, L. Y. Goh and E. Sinn, Organometallics, 7, 245 (1988).

23. M. Scheer, K. Schuster, U. Becker, A. Krug and H. Hartung, J. Organomet. Chem., 460, 105 (1993).

24. I . Jibril, S. T. Abu-Orabi, S. A. Klaib, L. Zsolnai and G. Huttner, J. Organomet. Chem., 467, 189 (1994).

25. I. Jibril, F. T. Esmadi, H. Al-Masri, L. Zsolnai and G. Huttner, J. Organomet. Chem., in press.

26. M. A. El-Hinnawi, A. A. Aruffo, B. D. Santarisiero, D. R. McAlister and V. Schomaker, Inorg. Chem., 22, 1385 (1983).

27. M. A. El-Hinnawi and A. M. Al-Ajlouni, J. Organomet. Chem., 332, 321 (1987).

28. S. Kato, H. Ishihara, K. Ibi, H. Kageyama and T. Murai, J. Organomet. Chem., 386, 313 (1990).

Received: 3 July 1995
Accepted: 30 May 1996

Referee I: W. P. Giering
Referee II: G. C. DeFotis