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Mössbauer Effect, ^{13}C NMR and IR Study of the Effect of Bulky Cp Substituents and CO Substitution on the Structure and Bonding of Mono- and Dinuclear Organoiron Complexes

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Abstract

A Mössbauer, IR and ^{13}C NMR study on some new thiocarboxylate derivatives of the half-sandwich iron complexes $FeCp(CO)_2SCOR$ showed that the –SCOR group is a better σ-donor, weak π-donor and probably has a weak π-acceptor property, compared to halides and SCN ligands. The study on the CO-substituted derivatives, $FeCp(CO)(EPh_3)SCOR$ (E = P, As, Sb) showed that the $SbPh_3$ is a slightly better π-acceptor ligand than $AsPh_3$. A related study showed also that the presence of the large t-butyl substituent on the Cp ring in the mononuclear complexes $FeCp(CO)_2SCOR$ and the dimeric compound $\{FeCp(CO)_2\}_2$ has a considerable effect on the structural and bonding properties of the iron complexes. These structural changes are more important in the dimeric iron compounds.

Introduction

It has been demonstrated that in the half-sandwich complexes $FeCp(CO)_2X$ and $FeCp(CO)LX$, the FeCp and Fe–CO bonds are affected by the σ-donor and π-acceptor properties of both L and X [1–14].

We have recently prepared a series of new complexes, $FeCp(CO)_2SCOR$ from the reaction of $(\mu\text{-}S_3)\{FeCp(CO)_2\}_2$ with acid chloride RCOCl [15, 16]. From these iron dicarbonyl cyclopentadienyl thiocarboxylates we chose to prepare the CO-substituted derivatives $FeCp(CO)(EPh_3)(2\text{-}Fe_6H_4)$ (E = P (**II**), As (**III**) and Sb (**IV**)) to study of the effect of EPh_3 substituents on the bonding and structural characteristics of these new mononuclear iron complexes, by Mössbauer, ^{13}C NMR and IR spectroscopy.

We also included in this work a study of the effect of a bulky Cp substituent on the bonding and structure of the new mononuclear iron complexes, $FeCp(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (**V**), $Fe(Bu^tC_5H_4)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (**VI**) and $Fe(1,3\text{-di-}Bu^tC_5H_3)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (**VII**) and the dinuclear complexes $\{FeCp(O)_2\}_2$ (**VIII**), $\{Fe(Bu^tC_5H_4)(CO)_2\}_2$ (**IX**) and $\{Fe(1,3\text{-di-}Bu^tC_5H_3(CO)_2\}_2$ (**X**) [17]. This work has been initiated because considerable interest has been focused recently on the substituted cyclopentadienyl transition metal complexes due to the substituent influence on the reactivity of metal centers, on the structural characteristics and the catalytic activity of such complexes [18–22].

Experimental

All reactions and manipulations of chemicals were performed under dry nitrogen. The cyclopentadienyl dicarbonyl iron S-bonded monothiocarboxylates **I** and **V** were prepared from the reaction of $(\mu\text{-}S_3)\{FeCP(CO)_2\}_2$ with $2\text{-}FC_6H_4COCl$ and $4\text{-}O_2NC_6H_4COCl$ respectively as described in previous work [15, 16]. The CO-substituted derivatives $FeCp(CO)(EPh_3)SCO(2\text{-}FC_6H_4)$ (E = P (**II**), As (**III**), Sb (**IV**)) were prepared by photolytic reactions of **I** with excess EPh_3 in THF as solvent using a high-pressure mercury lamp (HANAU) (240–600 nm). Each substitution reaction was monitored by IR spectroscopy and irradiation continued until the reaction had gone to completion. The reaction was considered complete when the two terminal CO bands of $FeCp(CO)_2SCO(2\text{-}FC_6H_4)$ at 2045 and 1990 cm^{-1} had disappeared and a new terminal CO band appeared at 1957 (**II**), 1950 (**III**) and 1945 (**V**) cm^{-1}. After the reaction mixture was dried under vacuum, the residue was dissolved in a minimum amount of CH_2Cl_2 and the required product purified by column chromatog-

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TABLE 1. IR and ^{13}C NMR spectral data of compounds I–X

Compound	IR (CH_2Cl_2) (cm^{-1}) $\nu(C\equiv O)$	^{13}C NMR (ppm) $C(C\equiv O)$
$FeCp(CO)_2SCO(2\text{-}FC_6H_4)$ (I)	2045, 1990	211.68
$FeCp(CO)(PPh_3)SCO(2\text{-}FC_6H_4)$ (II)	1957	214.50
$FeCp(CO)(AsPh_3)SCO(2\text{-}FC_6H_4)$ (III)	1950	219.31
$FeCp(CO)(SbPh_3)SCO(2\text{-}FC_6H_4)$ (IV)	1945	218.00
$FeCp(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (V)	2040, 1998	211.34
$Fe(Bu^tCp)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (VI)	2042, 1990	212.31
$Fe(1,3\text{-di-}Bu^tCp)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (VII)	2040, 1985	213.16
$\{FeCp(CO)_2\}_2$ (VIII)	1990, 1950, 1767[a]	211.91
$\{Fe(Bu^tCp)(CO)_2\}_2$ (IX)	1981, 1938, 1762[a]	212.72
$\{Fe(1,3\text{-di-}Bu^tCp)(CO)_2\}_2$ (X)	1975, 1935, 1760[a]	214.10

[a] Bridging CO.

raphy. The column was first eluted with 1/9 (vol./vol.) Et_2O/n-hexane to elute the unreacted EPh_3 and the product was then separated by 1/1 (vol./vol.) Et_2O/n-hexane (E = P), or 1/3 (vol./vol.) Et_2O/n-hexane for E = As and Sb. The products were recrystallized from CH_2Cl_2–n-hexane and characterized by IR and ^1H NMR spectroscopy and elemental analysis.

$FeCp(CO)(PPh_3)SCO(2\text{-}FC_6H_4)$ (**II**), yield 83%, brownish-orange crystals, melting point (m.p.) 165–166 °C. *Anal.* Calc. for $C_{31}H_{24}O_2SFPFe$: C, 65.74; H, 4.24; S, 5.65. Found: C, 65.53; H, 4.33; S, 5.70%. IR: $\nu(CO)$ 1957vs, $\nu(C=O)$ 1592s, $\nu(C\overset{\cdot\cdot}{-}S)$ 923s cm^{-1}. ^1H NMR: $\delta 4.60$ (d, 5H, C_5H_5); $\delta 6.97$ (m, 1H, 5-Ar*H*); $\delta 7.06$ (m, 1H, 4-Ar*H*); $\delta 7.34$–7.61 (m, 17H, 3-, 6-Ar*H* and PPh_3) ppm.

$FeCp(CO)(AsPh_3)SCO(2\text{-}FC_6H_4)$ (**III**), yield 63%, dark red crystals, m.p. 111–112 °C. *Anal.* Calc. for $C_{31}H_{24}O_2SFAsFe$: C, 60.98; H, 3.93; S, 5.24. Found: C, 60.76; H, 3.87; S, 5.19%. IR: $\nu(CO)$ 1950vs, $\nu(C=O)$ 1593s, $\nu(C\overset{\cdot\cdot}{-}S)$ 923s cm^{-1}. ^1H NMR: $\delta 4.68$ (s, 5H, C_5H_5), $\delta 6.93$–6.04 (m, 2H, 4-, 5-Ar*H*), $\delta 7.29$–7.49 (m, 17H, 3-, 6-Ar*H* and $AsPh_3$) ppm.

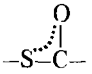
$FeCp(CO)(SbPh_3)SCO(2\text{-}FC_6H_4)$ (**IV**), yield 70%, dark violet crystals, m.p. 126–128 °C. *Anal.* Calc. for $C_{31}H_{24}O_2SFSbFe$: C, 56.66; H, 3.65; S, 4.87. Found: C, 56.61; H, 3.83; S, 4.64%. IR: $\nu(CO)$ 1945vs, $\nu(C=O)$ 1580s, $\nu(C\overset{\cdot\cdot}{-}S)$ 932m cm^{-1}. ^1H NMR: $\delta 4.75$ (s, 5H, C_5H_5), $\delta 7.32$–7.64 (m, 19H, Ar*H* and $SbPh_3$) ppm.

The compounds $Fe(Bu^tC_5H_4)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (**VI**) and $Fe(1,3\text{-di-}Bu^tC_5H_3)(CO)_2SCO(4\text{-}O_2NC_6H_4)$ (**VII**) were prepared from the reaction of $(\mu\text{-}S_3)\{Fe(Bu^tC_5H_4)(CO)_2\}_2$ and $(\mu\text{-}S_3)\{Fe(1,3\text{-di-}Bu^tC_5H_3)(CO)_2\}_2$ with $4\text{-}O_2NC_6H_4COCl$ as has been recently described [17]. $\{Fe(C_5H_5)(CO)_2\}_2$ (**VIII**) was purchased from Aldrich. The two iron dimers $\{Fe(Bu^tC_5H_4)(CO)_2\}_2$ (**IX**) and $\{Fe(1,3\text{-di-}Bu^tC_5H_3)(CO)_2\}_2$ (**X**) were prepared by the reaction of $Fe_2(CO)_9$ with $Bu^tC_5H_5$ and $1,3\text{-di-}Bu^tC_5H_4$ respectively as described in ref. 17. The IR spectra were recorded using a Pye-Unicam SP3-100 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP 80 SY spectrometer with TMS as internal standard. $CDCl_3$ was used as solvent for NMR measurements. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, AZ 85018, U.S.A. Table 1 shows the IR and ^{13}C NMR spectra of compounds **I**–**X**.

Mössbauer Measurements

The Mössbauer spectra for compounds **I**–**X** were recorded by using 20 mCi ^{57}Co diffused in a palladium matrix as a moving source which was mounted at room temperature on a standard constant acceleration drive unit. Each of the compounds was used as the absorber in the form of a polycrystalline powder sandwiched firmly and homogeneously in a thin layer between two plastic discs as a holder. The discs were 10 mm in diameter and transparent to the 14.2 keV gamma rays. The spectra of all the compounds were recorded at 77 K. The distance between the absorber and the source was chosen to be 10 cm to minimize the angle effect on the linewidth of the Mössbauer spectra. The spectrometer was calibrated with a thin α-iron foil held at room temperature. The recorded spectrum of each compound showed a quadrupole splitting of two lines. All the spectra were fitted to Lorentzian line shapes using a standard multiparameter non-linear squares program, leaving linewidths, areas and positions as free parameters. The spectra were corrected for the parabolic motion of the source. A typical spectrum of our measurement and fit is depicted in Fig. 1. Table 2 shows the Mössbauer parameters extracted from the fit for each compound. The isomer shifts were measured relative to α-iron which was held at room temperature.

Results and Discussion

The IR and ^{13}C NMR spectral data are presented in Table 1. As we have mentioned above each of the compounds **I**–**X** studied in the present work gave a well resolved quadrupole doublet spectrum in a Mössbauer spectrum. The Mössbauer effect parameters obtained at 77 K are shown in Table 2. The new iron dicarbonyl cyclopentadienyl S-bonded thiocarboxylate complexes **I** and **V** exhibit lower isomer shift values (0.159 (**I**), 0.158 (**V**)) than those reported in the literature for the mononuclear iron complexes $FeCp(CO)_2X$ {X = Cl, 0.228; Br, 0.227; I, 0.215; SCN, 0.186 mm s^{-1}} [23]. These isomer shift values for **I** and **V** indicate an increasing s-electron density at iron. The S-bonded thiocarboxylate group may be considered as a better σ-donor and a weaker π-donor ligand in comparison to X = Cl, Br, I and SCN. Another possibility is that the back-bonding from the filled d orbital at Fe into vacant  $-S-\overset{O}{C}-$ π_p^* orbitals or π–d orbitals on the sulfur atom might also contribute to the lowering of the isomer shift values in compounds **I** and **V**.

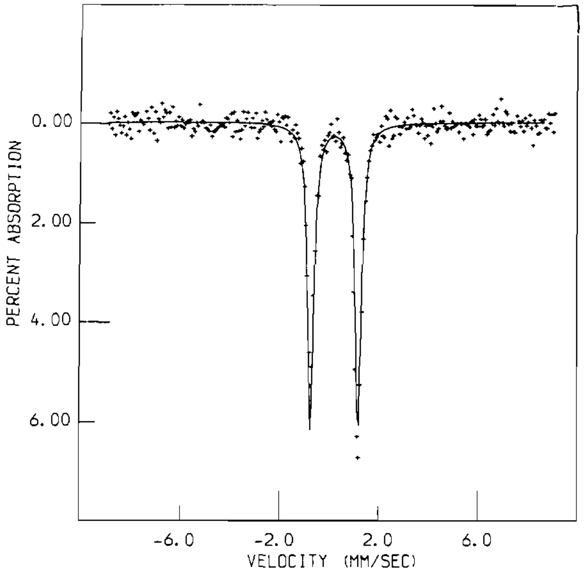


Fig. 1. The Mössbauer effect spectrum of $\{Fe(Bu^t\text{-}Cp)(CO)_2\}_2$ (**IX**) at 77 K.

Figure 2 shows the molecular structure of $FeCp(CO)_2SCO(2\text{-}O_2NC_6H_4)$ [16]. The Fe atom in all of the reported iron thiocarboxylate complexes is thought to have the same structural environment as shown in Fig. 2. Therefore the ΔE_Q values for **I** and **V** are expected to be close to each other (1.795 (**I**) and 1.805 (**V**) mm s^{-1}). This is because almost no effect is expected on changing the R group in

TABLE 2. Mössbauer parameters obtained from compounds I–X at $T = 77$ K. Isomer shift (δ) measured relative to room temperature α-iron

Compound	Isomer shift δ (mm s^{-1})	Change in δ (mm s^{-1})	Quadrupole splitting ΔE_Q (mm s^{-1})	Change in ΔE_Q (mm s^{-1})	Linewidth Γ_1 Γ_2	Area A_1 A_2
I	0.159(1)	0	1.795(7)	0	0.276(5) 0.278(5)	0.052(1) 0.062(1)
II	0.226(1)	0.069	1.817(8)	0.022	0.248(5) 0.254(5)	0.016(1) 0.016(1)
III	0.293(3)	0.134	1.827(5)	0.032	0.256(5) 0.267(5)	0.017(1) 0.018(1)
IV	0.286(4)	0.127	1.782(5)	−0.013	0.265(5) 0.257(5)	0.035(1) 0.035(1)
V	0.158(2)	0	1.805(5)	0	0.268(2) 0.265(2)	0.043(1) 0.043(1)
VI	0.161(2)	0.003	1.857(2)	0.052	0.270(2) 0.270(2)	0.036(1) 0.038(1)
VII	0.161(2)	0.003	1.903(4)	0.098	0.232(5) 0.330(5)	0.0140(1) 0.0124(1)
VIII	0.227(2)	0	1.912(5)	0	0.338(7) 0.371(2)	0.105(1) 0.126(1)
IX	0.231(4)	0.004	1.956(2)	0.044	0.289(1) 0.286(1)	0.030(1) 0.0361(1)
X	0.220(2)	−0.007	2.153(2)	0.241	0.444(5) 0.482(5)	0.043(1) 0.047(1)

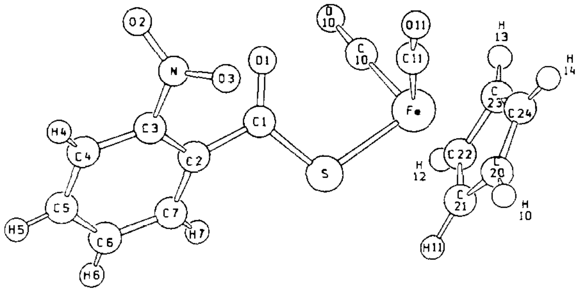


Fig. 2. The molecular structure of $FeCp(CO)_2SCO(2\text{-}O_2NC_6H_4)$ (ref. 16).

$FeCp(CO)_2SCOR$ complexes on the basic geometry around the Fe atom. When compound **I** undergoes photolytic CO substitution by EPh_3 (E = P, As, Sb) it gives the mono-substituted derivatives, $FeCp(CO)(EPh_3)(2\text{-}FC_6H_4)$ (E = P (**II**), As (**III**), Sb (**IV**)) as the only product and in very good yield. The isomer shift values of **II**, **III** and **IV** are significantly higher by an amount of 0.069, 0.136 and 0.129 mm s^{-1} respectively than that of the unsubstituted compound **I**. These results are in agreement with the weaker π-acceptor and better σ-donor properties of the group V ligands compared to the CO ligand [11–13]. The isomer shift values in the substituted derivatives **II**, **III** and **IV** (0.226, 0.293 and 0.286 mm s^{-1} respectively) are consistent with the better π-acceptor and σ-donor property of the PPh_3 ligand relative to both $AsPh_3$ and $SbPh_3$ [24]. The similar isomer shift values of complexes **III** and **IV** with the $SbPh_3$ derivative **IV** having a slightly lower isomer shift value might indicate that $SbPh_3$ has a slightly better π-acceptor property than $AsPh_3$.

The infrared spectra of compounds **II**, **III** and **IV** show that the carbonyl stretching frequencies in these compounds are in the order **II** > **III** > **IV**, which indicates an increase in the π-donation from Fe to the CO–π^* orbital in the order **IV** > **III** > **II**. However the ^{13}C NMR results for the carbonyl carbons in **II**, **III** and **IV** show that the π-donation from the iron to CO–π^* orbitals is in the order **III** > **IV** > **II**. Some authors [13,25] have demonstrated, by studying several different types of organometallic systems, that the expected increase in occupation of the antibonding π^*–carbonyl orbitals, as is observed by the decreased IR CO stretching frequency in **II**–**IV** versus **I**, shows up as an apparent deshielding of the carbonyl carbon atom which is counter to diamagnetic shielding predictions. The ^{13}C NMR results, therefore, indicate that the $SbPh_3$ ligand is probably a slightly better π-acceptor than $AsPh_3$ which agrees with the observed Mössbauer results.

The quadrupole splitting parameter ΔE_Q for compounds **I**–**IV** is relatively invariant. In related compounds Bancroft *et al.* [14] have attributed this invariance to the ability of the carbonyl and cyclopentadienyl ligands to substantially modify their bonding properties so as to neutralize the changes in electron asymmetry. It is interesting to note that $FeCp(CO)(SbPh_3)SCO(2\text{-}FC_6H_4)$ (**IV**) has relatively the lowest quadrupole splitting value. This low value could be attributed to the smaller cone angle of $SbPh_3$ relative to $AsPh_3$ and PPh_3 [26] and low ligand–ligand repulsion, which results in a geometry with a relatively reduced field gradient at the iron nucleus.

The Mössbauer effect results for the unsubstituted Cp compound, **V** and the mono- and di-t-butyl–Cp compounds, **VI** and **VII**, show that their isomer shift values are almost the same, which indicates that no significant change in s-electron density at the iron atom is observed upon adding one or two t-butyl substituents to the Cp ring. On the other hand, a significant change in quadrupole splitting value ΔE_Q is observed in **VI** and **VII** relative to **V**. The increase in ΔE_Q in **VII** relative to **V** is almost double the increase in compound **VI**, relative to **V**. This variation is mainly due to the steric repulsion between the bulky t-butyl groups and the surrounding ligands and the resulting electronic effects which explains the increase in asymmetry of the charge distribution around the Fe atom. Both IR and ^{13}C NMR spectra of compounds **V**–**VII** (Table 1) show that a slight increase in π-donation from Fe to CO has resulted upon Cp substitution. However, the unchanged s-electron density at the Fe atom in **VI** and **VII** relative to **V** could then be interpreted as a result of slight elongation of the Fe–Cp bond in **VI** and **VII** which causes a decrease in the $d\pi(Fe) \rightarrow \pi^*(Cp)$ back donation. Such an increase in the metal–Cp bond distance has been recently observed in $(1,3\text{-di-}Bu^tCp)_2TiCl_2$ [27]. This compound has an average Ti–C distance which is 0.1 Å longer than any other Ti–C bond distances of all structurally studied titanocene compounds [28]. In addition to the above work we have carried out a further study of the effect of t-butyl substituents at the Cp ring on the structure and bonding of the iron dimers **IX** and **X**. The Mössbauer results showed that the presence of one t-butyl at the Cp ring in **IX** has almost no effect on its isomer shift, but a significant effect is observed on the quadrupole splitting, ΔE_Q, which clearly indicates an increase in the asymmetry of charge distributions in the Fe atom electron shell as a result of both geometrical changes due to steric repulsions and electronic effects. The presence of two t-butyl groups on the Cp ring in compound **X** caused a decrease in the isomer shift value relative to **IX** and **VIII** and a relatively large increase of 0.24 mm s^{-1} in the quadrupole splitting value compared to **VIII**.

The IR spectra of **VIII**, **IX** and **X** showed a gradual decrease in the carbonyl stretching frequency in these compounds going from **VIII** to **X**, indicating an increased $d\pi$-donation from iron to carbonyl–π^*

orbitals. Similar results were obtained from ^{13}C NMR spectra. The large increase in the ΔE_Q value and the decrease in the isomer shift in **X** reflect a substantial change in its structure and bonding properties compared to the unsubstituted Cp dimer **VIII**. This is due to the presence of two bulky t-butyl groups on the Cp rings. The large steric repulsion between the bulky t-butyl groups on the two Cp rings in the dimer **X** results probably in a weakening of the Fe–Fe bond and a further increase in back donation from $d\pi$(Fe) to CO–π^*. These two effects together cause the increase of s-electron density in the iron atom and cause also an appreciable increase in the asymmetry of the charge distribution around the Fe atom. In our previous report [7] on the chemistry of **IX** and **X**, we observed that both compounds and in particular compound **X** are thermally unstable in comparison to **VIII**, and we have found that compounds **IX** and **X** exhibit a reactive Fe–Fe bond towards oxidative insertion of S_x ($x = 3, 4$) from S_8. Further study of their reactivities and a study of their molecular structure by X-ray diffraction are now under consideration.

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