# THE SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE MONODENTATE (S) THIOSEMICARBAZIDE AND THIOSEMICARBAZONE COMPLEXES [ $Fe(CO)_2L(\eta^5-C_5H_5)$ ][ $PF_6$ ]

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Abstract—Reaction of  $[Fc(CO)_2(OCMe_2)(\eta^5-C_5H_3)][PF_6]$  with 1 equivalent of L  $(L = H_2NNHCSNH_2 \text{ or } R'R''CNNHCSNH_2 \text{ where } R' = R'' = Me; R' = H, R'' = Ph;$  $\mathbf{R}' = \mathbf{H}, \mathbf{R}'' = p$ -NO<sub>2</sub>Ph;  $\mathbf{R}' = \mathbf{M}e, \mathbf{R}'' = p$ -MePh;  $\mathbf{R}'\mathbf{R}'' = C_{5}H_{10}$  in CHCl<sub>3</sub> at 50°C gave good yields of  $[Fe(CO)_2L(\eta^5-C_5H_5)][PF_6]$  by displacement of the acetone. The crystal structure of  $[Fe(CO)_2(PhCHNNHCSNH_2)(\eta^5-C_5H_5)][PF_6]$  was determined by single crystal X-ray diffraction studies refined to R = 0.067 for 1389 reflections above background. The coordination geometry about the iron may best be described in terms of a "piano stool" or pseudo-octahedral structure. The  $C_5H_5^-$  ligand occupies three sites in the octahedron with the carbonyls and the sulphur atom of the thiosemicarbazone in the other three sites. The Mössbauer isomer shifts of these compounds have values which lie between that of  $[Fe(CO)_3(\eta^5-C_5H_5)]^-$  and those for  $[Fe(CO)_2X(\eta^5-C_5H_5)]$  showing the thiosemicarbazone sulphur to be a poorer  $\pi$ -acceptor than CO and a better  $\pi$ -acceptor than the halides. The similarity of the spectroscopic data for all the compounds suggests that they all have the same structure. The monodentate S-bonded nature of the thiosemicarbazide in solutions of  $[Fe(CO)_2(NH_2NHCSNH_2)(\eta^5-C_5H_5)][PF_6]$  is confirmed by its reaction with benzaldehyde to give the compound [Fe(CO)<sub>2</sub>(PhCHNNHCSNH<sub>2</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>].

Since 1934 when the first thiosemicarbazide complexes of nickel(II) were reported,<sup>1</sup> a wide range of "classical" coordination compounds formed by transition metal ions with thiosemicarbazides and thiosemicarbazones have been described.<sup>2</sup> Thiosemicarbazones have a wide range of pharmacological activity against, amongst other things, protozoa, influenza, smallpox, leprosy and certain kinds of tumour, and have been suggested as possible pesticides and fungicides (see references cited in the two reviews<sup>2</sup>). Following Liebermeister's demonstration that copper ions enhanced the antitubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone,<sup>3</sup> the role of metal ions in thiosemicarbazone has been either proved or suspected in many other cases.

Most "classical" coordination compounds formed by thiosemicarbazides and thiosemicarba-

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zones are with first row transition metal ions in the +2 and +3 oxidation states, i.e. with hard or marginally soft acids, and the other ligands in the coordination sphere, where present, are usually halides. In most of the compounds these ligands are bidentate and coordinate through sulphur and the hydrazinic nitrogen.<sup>2</sup> In a small number of cases thiosemicarbazide and thiosemicarbazones have been shown to coordinate as monodentate ligands through the sulphur atom. In these cases the metal ion is a soft acid, e.g. Ag<sup>I</sup>, Hg<sup>II</sup> and Co<sup>II</sup> in CoI<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>CHNNHCSNH<sub>2</sub>)<sub>2</sub>.<sup>2,4</sup>

In organotransition metal compounds the metal centre is normally soft and most of the ligands bound to it are  $\pi$ -acceptors. Such compounds might therefore prove suitable to test the conditions under which thiosemicarbazones form monodentate complexes. We have previously described<sup>5</sup> the first organotransition metal compounds,  $[MoX(CO)_2]$ (thiosemicarbazone) $(\eta^3 - C_3H_4R)$ ], containing a thiosemicarbazone as an attached ligand. In these compounds the thiosemicarbazone is found to be bidentate. We have also reported<sup>6</sup> the corresponding semicarbazone compounds [MoX(CO)<sub>2</sub> (semicarbazone)( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>R)] and here too the semicarbazone ligand is bidentate. Preliminary results of our work describing the first organoiron thiosemicarbazide and thiosemicarbazone complexes [Fe(CO)<sub>2</sub>L( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>], where L is  $NH_2NHCSNH_2$  or  $R_1R_2CNNHCSNH_2$  and is found to be monodentate, have already been published.<sup>7</sup> In this paper we wish to describe this work in full and to report the X-ray structure of [Fe  $(CO)_2(C_6H_5CHNNHCSNH_2)(\eta^5-C_5H_5)][PF_6].$ 

#### **EXPERIMENTAL**

The reactions described in this paper were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The complex  $[Fe(CO)_2(OC Me_2)(\eta^5-C_5H_5)][PF_6]$  was prepared by the literature method,<sup>8</sup> and the thiosemicarbazone ligands by the method described by Sah and Daniels.<sup>9</sup> All other chemicals were purchased from commercial sources.

The elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 using helium as the carrier gas. IR spectra were recorded, as KBr discs on a Perkin–Elmer 397 IR spectrophotometer. The <sup>1</sup>H NMR spectra were recorded either on a Bruker WH 400 MHz spectrometer at the University of Warwick or on a Jeol GX-270 at Thames Polytechnic (all spectra were calibrated against tetramethylsilane). The Mössbauer spectra were recorded on a Cryophysics microprocessor controlled Mössbauer spectrometer and spectra were calibrated against Fe-57 enriched iron foil.

## (1) $[Fe(CO)_2(H_2NNHCSNH_2)(\eta^5-C_5H_5)][PF_6]$

H<sub>2</sub>NNHCSNH<sub>2</sub> (0.06 g, 0.66 mmol) was added to a stirred solution of  $[Fc(CO)_2(OCMe_2)(\eta^5-C_5H_5)][PF_6]$  (0.25 g, 0.66 mmol) in CHCl<sub>3</sub> (20 cm<sup>3</sup>) warmed to 50°C. After 90 min the yellow  $[Fe(CO)_2(H_2NNHCSNH_2)(\eta^5-C_5H_5)][PF_6]$  which had separated was filtered, washed with CHCl<sub>3</sub> (3 × 5 cm<sup>3</sup>) and dried in a desiccator over silica gel (0.16 g, 59%).

### (2) $[Fe(CO)_2(cy-C_5H_{10}CNNCSNH_2)(\eta^5-C_5H_5)][PF_6]$

The cy-C<sub>5</sub>H<sub>10</sub>CNNHCSNH<sub>2</sub> (0.09 g, 0.53 mmol) was added to a stirred solution of [Fe(CO)<sub>2</sub>(OC Me<sub>2</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>] (0.20 g, 0.53 mmol) in CHCl<sub>3</sub> (20 cm<sup>3</sup>) warmed to 50°C. After 2 h the orange [Fe(CO)<sub>2</sub>(cy-C<sub>5</sub>H<sub>10</sub>CNNHCSNH<sub>2</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>] which had separated was filtered, washed with CHCl<sub>3</sub> (3 × 5 cm<sup>3</sup>) and dried in a desiccator over silica gel (0.18 g, 72%).

The thiosemicarbazone complexes (3-6) were prepared in an analogous manner by reaction of  $[Fe(CO)_2(OCMe_2)(\eta^5-C_5H_5)][PF_6]$  with an equimolar quantity of L [L = R'R"CNNHCSNH<sub>2</sub>, where R' = R" = Me (3); R' = H, R" = Ph (4); R' = H, R" = p-NO\_2Ph (5) and R' = Me, R" = p-MePh (6)] in CHCl<sub>3</sub> at 50°C. For colours, yields and decomposition points see Table 1.

Reaction of  $[Fe(CO)_2(H_2NNHCSNH_2)(\eta^5-C_5H_5)]$ [PF<sub>6</sub>] with PhCHO

PhCHO (0.04 g, 0.24 mmol) was added to a stirred solution of  $[Fe(CO)_2(H_2NNHCSNH_2)(\eta^5-C_5H_5)][PF_6]$  (0.10 g, 0.24 mmol) in CHCl<sub>3</sub> (20 cm<sup>3</sup>) warmed to 50°C. After 2 h the orange solid [Fe (CO)<sub>2</sub>(PhCHNNHCSNH<sub>2</sub>)(\eta^5-C\_5H\_5)][PF\_6] which had separated was filtered, washed with Et<sub>2</sub>O (2 × 5 cm<sup>3</sup>) and dried in a desiccator (0.06 g, 50%). Found : C, 34.5; H, 2.9; N, 9.8. C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>FeO<sub>2</sub>PS requires C, 35.9; H, 2.8; N, 8.4%.

v(max) (KBr) 3500 m, 3371 m, 3319 m and 3126 w (NH), 3026 (CH), 2060 s and 2024 s (CO), 1591 s and 1544 s (NH<sub>2</sub>), 1429 w and 1017 w (C--C or ring def.) and 846 s br cm<sup>-1</sup> (PF<sub>6</sub>).

#### **RESULTS AND DISCUSSION**

The ligands L (L = NH<sub>2</sub>NHCSNH<sub>2</sub> or R<sub>1</sub>R<sub>2</sub> CNNHCSNH<sub>2</sub>) do not displace CO from [Fe( $\eta^{5}$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>3</sub>][PF<sub>6</sub>] even with UV irradiation but

Ligand L <sup>b</sup>	Yield (%)	Decomposition point (°C)	C(%)	H(%)	N(%)
$H_2NNHCSNH_2$ (1)	59	100	22.7	2.4	10.6
			(23.6)	(2.4)	(10.2)
$C_5H_{10}CNNHCSNH_2$ (2)	72	137	33.8	3.6	8.1
			(34.1)	(3.7)	(8.5)
$(CH_3)_2 CNNHCSNH_2$ (3)	61	108	30.1	3.2	9.0
			(29.2)	(3.1)	(9.3)
$C_6H_5CHNNHCSNH_2$ (4)	65	160	35.2	2.8	7.9
			(35.9)	(2.8)	(8.4)
$p-NO_2C_6H_4CHNNHCSNH_2$ (5)	58	_	33.0	2.4	9.9
			(33.0)	(2.4)	(10.1)
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> )NNHCSNH <sub>2</sub> (6)	51	_	38.8	3.4	7.9
			(38.7)	(3.5)	(7.9)
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHNNHCSNH <sub>2</sub> (7)	50	154	36.6	3.2	7.2
			(37.3)	(3.1)	(8.2)
$p-ClC_6H_4CHNNHCSNH_2$ (8)	80	150	32.4	2.3	7.1
· · · · · · · · · · · · · · · · · ·			(33.6)	(2.4)	(7.8)

Table 1. Analytical (C, H and N) data,<sup>*a*</sup> yields and decomposition points of the complexes  $[Fe(CO)_2L(\eta^5-C_5H_5)][PF_6]$ 

<sup>a</sup>Calculated values in parentheses.

<sup>b</sup> All compounds are orange except 1 which is yellow.

they will displace a labile group S from species  $[Fe(\eta^{5}-C_{5}H_{5})(CO)_{2}S]^{+}$ . When S is H<sub>2</sub>O the yields are very poor, *ca* 1%, but when S is Me<sub>2</sub>CO good yields from 50 to 80% are obtained on refluxing  $[Fe(\eta^{5}-C_{5}H_{5})(CO)_{2}(Me_{2}CO)][PF_{6}]$  with the ligand L in CHCl<sub>3</sub>. Attempts to prepare these compounds

from  $Fe(\eta^5-C_5H_5)(CO)_2I$  in the presence of  $NaBF_4$ or  $AgBF_4$  were unsuccessful. Surprisingly there was no evidence at all that the thiosemicarbazone displaces I from this complex. The compounds (1– 8) (see Table 1) have been fully characterized by microanalysis (Table 1), IR (Table 2), <sup>1</sup>H NMR

Table 2. IR absorption frequencies (in cm<sup>-1</sup>) of v(CO) in the complexes  $[Fe(CO)_2L(\eta^5-C_5H_5)][PF_6]$ 

Complex	Solvent	$v(CO) (cm^{-1})$	
$[Fe(CO)_{3}(\eta^{5}-C_{5}H_{5})][PF_{6}]^{a,b}$	(CH <sub>3</sub> ) <sub>2</sub> CO	2130	2078
$[Fe(CO)_2(SC_4H_9)^{a,c}(\eta^5-C_5H_5)][PF_6]$	CHCl <sub>3</sub>	2061	2016
1	$(CH_3)_2CO$	2052	2006
	KBr	2047	2011
2	KBr	2049	1998
3	KBr	2058	2002
4	CHCl <sub>3</sub>	2060	2025
	KBr	2061	2024
5	(CH <sub>3</sub> ) <sub>2</sub> CO	2054	2009
	KBr	2060	2016
6	KBr	2057	2009
7	KBr	2050	2009
8	(CH <sub>3</sub> ) <sub>2</sub> CO	2053	2008
	KBr	2052	2014
$[Fe(CO)_2(C_6H_5CHNNHCONH_2)(\eta^5-C_5H_5)][PF_6]$	KBr	2077	2038

" Included for reference.

<sup>b</sup> Reference 16.

<sup>c</sup> Reference 17.

Complex	(C <sub>5</sub> H <sub>5</sub> )	R	R <sup>1</sup>	NH <sub>2</sub> NH	NH <sub>2</sub> CS	NH
í	5.49d			8.30s <sup>b</sup>	9.80s	11.21s
	( —	—	_	4.43s	7.31, 8.63	8.63s) <sup>c</sup>
2	5.48s	1.60(6H)	2.33, 2.47, 2.55	(4H)	8.46s	11.61s
	( —	1.56(6H)	2.23-2.41	(4H)	7.74d	10.15s)
3	5.49s	2.08s	2.08s		8.60d	11.32s
	( —	1.93s	1.93s	_	7.15d	8.98s)
4	5.60s	$7.53 - 7.92 \text{m} (C_6 \text{H}_5)$	8.28s(CH)	_	8.97d	12.51s
	( —	$7.42 - 8.10 \text{m} (C_6 H_5)$	8.23s(CH)	_	7.42–8.10m	11.55)
5	5.55/5.72d	8.21	8.65m	_	8.21-8.65m	12.86s
	( —	8.09-8.31m(ring)	8.47s		8.09–8.31m	11.79s)
6	5.78s	7.37-7.71m(ring)	2.66s(CCH <sub>3</sub> )	_	7.37–7.71m	10.27s
		$2.04s(p-CH_3)$				
	( —	7.18/7.21(ring)	2.32s(CCH <sub>3</sub> )	_	7.90–8.27d ( $J = 3.7$ Hz)	10.18s)
		7.81/7.84m				
		$2.28s(p-CH_3)$				
7	5.26s	7.10/7.36m(ring)	8.27s		8.69d	12.62s
		7.80/8.06				
		2.41s ( <i>p</i> -CH <sub>3</sub> )				
	( —	7.22/7.25m	8.15s		8.09d	11.42s)
		7.69/7.72				
		2.33s ( <i>p</i> -CH <sub>3</sub> )				
8	5.52s	7.58–7.95m	8.28s		8.97d (J = 4.1  Hz)	12.65s
	( —	7.42-8.10m	8.23s		7.42-8.10m	11.55s)
<b>9</b> <sup>d</sup>	5.78s	7.37	7.72m		6.51s	10.29s
	( —	7.41–7.52m	7.76-7.92m		6.54s	10.45s)

Table 3. <sup>1</sup>H NMR data  $(\sigma)^{a}$  of the complexes [Fe(CO)<sub>2</sub>( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>]

<sup>a</sup> Spectra recorded in d<sub>6</sub>-DMSO.

<sup>b</sup> s---singlet, d---doublet, m---multiplet.

<sup>c</sup> Values in parentheses are for corresponding free ligand L.

<sup>d</sup> Compound 9 is  $[Fe(CO)_2(C_6H_5CHNNHCONH_2)(\eta^5-C_5H_5)][PF_6]$ .

(Table 3) and Mössbauer spectroscopy (Table 4). The complexes are stable in air in the solid state and only slowly decompose in solution. The compounds are insoluble in non-polar solvents, and only sparingly soluble in  $CH_2Cl_2$  and  $CHCl_3$ . They are, however, very soluble in  $Me_2SO$ .

### Crystallography

Crystals of the title compound suitable for X-ray investigation were obtained from CHCl<sub>3</sub> as orange plates.

Crystal data  $[C_{15}H_{14}N_{3}O_{2}SFe]^{+}[PF_{6}]^{-}$ , M =

Complex	Isomer shift (mm s <sup>-1</sup> )	Quadrupole splitting (mm s <sup>-1</sup> )	Temperature (K)
$[Fe(CO)_3(\eta^5-C_5H_5)][PF_6]$	0.05	1.88	78ª
$[Fe(CO)_2Cl(\eta^5-C_5H_5)]$	0.24	1.88	78"
1	0.18	1.73	293
2	0.13	1.72	78
3	0.16	1.75	78
4	0.20	1.76	293
5	0.21	1.78	293
6	0.17	1.69	78
7	0.15	1.71	78
[Fe(CO) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CHNNHCONH <sub>2</sub> )][PF <sub>6</sub> ]	0.18	1.95	78

<sup>a</sup> Reference 18.

500.16, monoclinic, a = 7.103(1), b = 18.637(3), c = 15.193(2) Å,  $\beta = 90.76(1)$ , U = 2011.1 Å<sup>3</sup>, space group  $P2_1/c$ , Z = 4,  $D_c = 1.652$  g cm<sup>-3</sup>, F(000) = 788,  $\mu$ (Mo- $K_{\alpha}$ ) = 9.9 cm<sup>-1</sup>.

#### Data collection

Accurate unit cell parameters were measured on an Enraf-Nonius CAD4 diffractometer using 25 accurately centred reflections  $(13^{\circ} < \theta < 15^{\circ})$  from a crystal of dimensions  $0.4 \times 0.4 \times 0.1$  mm. Reflection data were collected to a  $\theta$ -limit of 24° using graphite-monochromated Mo- $K_{\alpha}$  radiation in a  $\omega$ -2 $\theta$  scan mode. 3555 reflections were measured which after averaging and rejection of systematic absences reduced to 3142 (1389 for which  $I > 3\sigma(I)$ were considered observed). No decay of the crystal was noted during the total X-ray exposure time (71 h). No absorption correction was applied.

#### Structure determination and refinement

The structure was solved using a combination of MULTAN<sup>10</sup> and Fourier techniques. The three heaviest peaks from a default run of Multan were assumed to correspond to the iron, phosphorus and sulphur atoms. Two cycles of Fourier/structure factor calculations located all the remaining nonhydrogen atoms with R = 0.23. Full-matrix leastsquares refinement was carried out using isotropic thermal parameters and an empirical absorption correction. DIFABS<sup>11</sup> was applied (minimum correction 0.757, maximum 1.184, average 0.993) prior to refinement with anisotropic thermal parameters. Because of limitations in the SDP package<sup>12</sup> used for the calculations, hydrogen atoms could not be included. The weighting scheme  $\omega = 1/[\sigma^2(F_o) + 0.07(F_o)^2]$  gave a satisfactory agreement analysis and refinement was terminated with a final R and  $R_w$  of 0.067 and 0.087.

Selected bond lengths and angles are given in Table 5. Fractional atomic coordinates, anisotropic temperature factors, a complete list of bond lengths and angles, and  $F_o/F_c$  tables have been deposited as supplementary data with the Editor.

The structure and the numbering scheme are shown in Fig. 1. The structure consists of discrete cations and  $[PF_6]^-$  anions. Within the cation, the coordination geometry about the iron atom is best described in terms of a "piano-stool" or pseudooctahedron. The  $C_5H_5$  moiety occupies three sites, with the two carbonyls and the sulphur atom of the thiosemicarbazone occupying the remainder. Although the Cambridge Crystallographic Database reveals almost 100 complexes containing coordinated thiosemicarbazones, there appear to be only two reported examples of monodentate Sbonded thiosemicarbazones. One of these is bis (acetophenonethiosemicarbazone)cobalt(II) iodide<sup>4(i)</sup> while the other is an organometallic compound, acetone thiosemicarbazone pentacarbonyl tungsten(0), W(CO)<sub>5</sub>(TSCAC).<sup>13</sup> In the present case, as in the case (above) of the cobalt(II) iodide complex, the reason for the monodentate binding of the thiosemicarbazone is probably stereochemical, further coordination through N(3)being effectively blocked by the remaining ligands. Thus, the thiosemicarbazone is found with the -N—N=C group in an essentially extended linear conformation. The Fe-S(1) dis-

tance (2.279(4) Å) compares favourably with that

Table 5. Selected bond lengths (Å) and angles (°)

Bond lengths			
Fe—S(1)	2.279(4)		
FeC(1)	1.71(2)		
FeC(2)	1.79(2)		
Fe-(C <sub>5</sub> H <sub>5</sub> )	2.08(2) <sub>av</sub>		
Bond angles			
C(1)—Fe—C(2)	92.8(8)	C(2)—Fe—C(11)	155.2(8)
C(1)—Fe— $S(1)$	93.9(5)	C(2)—Fe— $C(12)$	116.4(9)
C(2)—Fe— $S(1)$	86.8(6)	C(2)—Fe—C(13)	88.3(9)
C(1)—Fe—C(11)	96.3(8)	C(2)—Fe—C(14)	99.1(9)
C(1)—Fe—C(12)	93.5(7)	C(2)—Fe—C(15)	135.0(1)
C(1)-Fe-C(13)	126.4(8)	S(1)-Fe-C(11)	115.4(8)
C(1)—Fe—C(14)	160.9(7)	S(1)—Fe—C(12)	155.2(6)
C(1)—Fe—C(15)	132.4(9)	S(1)—Fe—C(13)	139.6(7)
		S(1)—Fe—C(14)	101.6(6)
		S(1)-Fe-C(15)	90.8(6)



Fig. 1. The structure and numbering scheme for  $[Fe(CO)_2(PhCHNNHCSNH_2)(\eta^5-C_5H_5)][PF_6]$ .

found in other iron complexes with bidentate ligands,<sup>14,15</sup> but the Fe—S(1)—C(3) angle is much more obtuse (111.3°) compared with the value of about 98° generally found for the M—S—C angle. Other bond lengths and angles in the thiosemicarbazone moiety are similar to values reported for other complexes. In particular, they are identical within experimental error to those found for W(CO)<sub>5</sub>(TSCAC).<sup>13</sup>

## IR data

The IR spectra of the complexes show absorptions characteristic of the thiosemicarbazide moiety, that is v(NH) between 3500 and 3100 cm<sup>-1</sup>,  $\delta(NH_2)$  in the 1650–1600 cm<sup>-1</sup> region, various coupled modes in the 1600–1000 cm<sup>-1</sup> region, as well as a strong absorption due to  $PF_6^-$  at about 845 cm<sup>-1</sup> which masks the mainly v(CS) vibration in the 700–800 cm<sup>-1</sup> region. The similarity of the spectra suggest that the thiosemicarbazide/-one ligand is bound to the iron in the same way in all these complexes, i.e. through sulphur as shown by the X-ray diffraction study of 4.

The expected two v(CO) absorptions are found in all the spectra. The band positions in solution and in the solid (KBr) differ by only a few cm<sup>-1</sup>. The values of the v(CO) absorptions (in cm<sup>-1</sup>) are significantly lower than those found in the spectrum of [Fe(CO)<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>] but similar to those found for [Fe(CO)<sub>2</sub>(SC<sub>4</sub>H<sub>9</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>]. This suggests that CO is a better  $\pi$ -acceptor than C=S or CS<sup>-</sup>. The IR spectrum of the semicarbazone analogue of 4, [Fe(CO)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CHNNHCONH<sub>2</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)] [PF<sub>6</sub>], clearly shows that the semicarbazone is not bonded through the C=O group, the v(C=O),  $\delta$ (NH<sub>2</sub>) and amide II frequencies being identical to those of the free ligand (1690, 1651 and 1598 cm<sup>-1</sup>, respectively), whereas in the IR spectra of the molybdenum semicarbazone complexes<sup>6</sup> the v(C=O) band frequency is 20–30 cm<sup>-1</sup> lower than in the free ligands. The semicarbazone must therefore be bound through the hydrazine nitrogen

$$\left(-N=C\right)$$
. The position of the carbon monoxide

stretching frequencies (see Table 2) is higher than for the thiosemicarbazone compounds, which is compatible with -N=C < being a better  $\pi$ acceptor than S=C <.

#### <sup>1</sup>H NMR data

In the NMR spectrum of complex 1 the proton resonances of the thiosemicarbazide ligand are all shifted downfield by several ppm relative to their positions in the free ligand (see Table 3), which indicates that a net decrease in electron density has occurred. Similarly, a downfield shift, although somewhat smaller, is observed for the proton resonances of the thiosemicarbazone ligands in complexes 2–8. In the spectrum of the semicarbazone ligand [Fe(CO)<sub>2</sub>(PhCHNNHCONH<sub>2</sub>)( $\eta^5$ -C<sub>3</sub>H<sub>5</sub>)][PF<sub>6</sub>], on the other hand, the proton resonances of the semicarbazone ligand all show an upfield shift, those of the semicarbazide moiety being between 2 and 3 ppm. This would indicate a net increase in electron density on the ligand.

Since the bonding between iron and either  $\infty$  or C N can involve both an L-M  $\sigma$ bond and an M—L  $\pi$ -bond, the net change in electron density on complex formation will depend on the relative importance of the two components. The net decrease in electron density in the complexed thiosemicarbazide/-one ligands shows that back donation is less important than the  $\sigma$ -bonding. The relatively large size of the sulphur and the positive charge on the iron(II) undoubtedly leads to poor overlap between the  $C = S \pi^*$ -orbital and the appropriate *d*-orbital, i.e. to an energy mismatch. In the case of the semicarbazone ligand the ≻C==N group may well be a poorer  $\sigma$ -donor than but is clearly a better  $\pi$ -acceptor, since there is an overall increase in electron density on complex formation.

#### Mössbauer data

The Mössbauer parameters of compounds 1–7, together with those of [Fe(CO)<sub>2</sub>(PhCHNNH  $\text{CONH}_2$ )( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>], [Fe(CO)<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>] and  $[Fe(CO)_2(\eta^5-C_5H_5)Cl]$  which are included for comparison, are shown in Table 4. The isomer shift values of compounds 1-7 are more positive than the value for  $[Fe(CO)_3(\eta^5-C_5H_5)][PF_6]$ but less positive than that of  $[Fe(CO)_2(\eta^5-C_5H_5)Cl]$ , i.e. the s-electron density at the  ${}^{57}$ Fe nucleus is less than in  $[Fe(CO)_3(\eta^5-C_5H_5)][PF_6]$  and more than in  $[Fe(CO)_2(\eta^5-C_5H_5)Cl]$ . The ligand contributes to the total s-electron density at the <sup>57</sup>Fe nucleus by  $\sigma$ -donation which increases the 4s electron density and by  $\pi$ -acceptance which removes 3d-electrons and thus decreases the shielding of the s-electrons. Hence, the thiosemicarbazide/-one ligands of 1-7 must either be better  $\sigma$ -donors or poorer  $\pi$ -acceptors than CO. The IR and NMR evidence (see above) indicates that they are poorer  $\pi$ -acceptors. The isomer shift of  $[Fe(CO)_2(PhCHNNHCONH_2)(\eta^5-C_5H_5)]$  $[PF_6]$  is virtually the same, within experimental error, as that of its sulphur analogue, 4. Again, the net effect of  $\sigma + \pi$  bonding is a decrease in s-electron density but in this case the IR and NMR evidence (see above) shows it to be a better  $\pi$ -acceptor than 4 so that it must be a poorer  $\sigma$ donor. The electric field gradient at the iron nucleus arises largely from the  $\pi$ -bonding ligands, but for compounds such as those considered containing two or three such ligands it is difficult to relate changes to a single factor. The only significant point is that the quadruple splitting (QS) values of 1-7 are smaller than that of [CpFe(CO)<sub>3</sub>][PF<sub>6</sub>], while the QS value of the semicarbazone analogue of 4 is larger.

#### Reactions

It is significant that compound 1,  $[Fe(CO)_2 (NH_2NHCSNH_2)(\eta^5 - C_5H_5)][PF_6]$ , reacts smoothly with benzaldehyde in trichloromethane at 50°C to give the benzaldehyde thiosemicarbazone, 4. This confirms that the thiosemicarbazide is monodentate and S-bonded even in solution, since thiosemicarbazone formation occurs by reaction of the hydrazinic-NH<sub>2</sub> group with the carbonyl group of the aldehyde or ketone. Furthermore, in compound 1 the ---NH<sub>2</sub> must be sterically unhindered. However, attempts to prepare alkyl thiosemicarbazone complexes such as 3 by reaction of 1 with the corresponding ketone failed, only starting material being recovered.

The compound  $[Fe(CO)_2(PPh_3)(\eta^5-C_5H_5)][PF_6]$ reacts with NaBH<sub>4</sub> to give  $[Fe(CO)_2(PPh_3)(C_5H_6)]$ , while  $[Fe(CO)_3(\eta^5-C_5H_5)][PF_6]$  reacts to give  $[Fe(CO)_2(\eta^5-C_5H_5)]_2$  as the main product.<sup>15</sup> Reaction of 4 with sodium borohydride yielded three fractions after chromatographic separation, of which the major one proved to be  $[Fe(CO)_2(\eta^5-C_5H_5)]_2$ . Clearly the thiosemicarbazone is more readily displaced from the coordination sphere than PPh<sub>3</sub> and the reaction may go via the formation of a hydride such as  $[Fe(CO)_2H(\eta^5-C_5H_5)]_2$ .

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