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Organoruthenium sulfur complexes. Synthesis of (μ-S_5) $[RuCp(CO)_2]_2$ and its reaction with acid chlorides. Preparation of $RuCp(CO)_2SCOR$ and molecular structure of $RuCp(CO)_2SCO(2\text{-}O_2NC_6H_4)$

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Abstract

The binuclear pentasulfur bridged organoruthenium complex, (μ-S_5) $[RuCp(CO)_2]_2$ (I), and other organoruthenium polysulfanes have been prepared by reaction of $[RuCp(CO)_2]_2$ with elemental sulfur upon refluxing or photolysis in benzene. These organoruthenium sulfanes readily react with acid chlorides, RCOCl, to give the *S*-bonded monothiocarboxylate derivatives, $RuCp(CO)_2SCOR$ (R = 1-$C_{10}H_7$ (II), 2-FC_6H_4 (III), 4-$O_2NC_6H_4$ (IV), 3,5-$(O_2N)_2C_6H_3$ (V), 2-$O_2NC_6H_4$ (VI), $C_6H_4COSFeCp(CO)_2$ (VII)). The crystal structure of VI has been determined. Compound VI crystallizes in the monoclinic system, space group $C2/c$ with a 1488.0(5), b 1359.4(3), c 1651.6(5) pm; β 115.68(2)°: $Z = 8$; $R_1 = 0.027$; $R_2 = 0.027$.

Introduction

Simple neutral binuclear sulfur-bridged organometallic complexes of the type $L_nMS_xML_n$ (metallosulfanes, ($x \geqslant 1$) in which the polysulfide dianion S_x^{2-}, serves as bidentate bridging ligand, have attracted much attention in recent years [1–10]. The reaction of elemental sulfur with dimeric organometallic complexes has been used for the synthesis of such organometallic sulfur complexes [3–5,10], which have been also produced from the reaction of a reactive organometallic species such as $[FeCp(CO)_2]^-$ or $WCp(CO)_3H$ with sulfur-containing reagents such as SCl_2 or SO_2

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[3,5,6–9]. Such sulfane complexes are exemplified by (μ-S_x) $[FeCp(CO)_2]_2$ ($x = 1$–4) [3], (μ-S_2) $[MCp(CO)_3]_2$(M = Mo, W) (5), (μ-S) $[WCp(CO)_3]_2$ (6, 7), (μ-S_x)-$[(Me_3P)_2(CO)_2Re]_2$ ($x = 1, 4$) (8, 9), and (μ-S_4) $[RuCp^{\star}(CO)_2]_2$ ($Cp^{\star} = \eta^5$-C_5Me_5) (10). We report here the synthesis of (μ-S_5) $[RuCp(CO)_2]_2$ and its reactions with acid chlorides to give the S-bonded monothiocarboxylate ruthenium derivatives $RuCp(CO)_2SCOR$. The crystal structure of $RuCp(CO)_2SCO(2$-$O_2NC_6H_4)$ has been determined.

Experimental

Materials and methods

All reactions were conducted under nitrogen by conventional Schlenk techniques. Solvents were dried and purified as previously described [3]. $Ru_3(CO)_{12}$ and acid chlorides were purchased from Aldrich. The ruthenium dimer $[RuCp(CO)_2]_2$ was prepared from $Ru_3(CO)_{12}$ as described previously [11], ^1H NMR spectra were recorded on a Bruker WP 80 SY spectrometer with TMS as internal standard. Infrared spectra were recorded on Pye-Unicam SP3-100 spectrophotometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

Thermal reaction of $[RuCp(CO)_2]_2$ with elemental sulfur; preparation of (μ-S_5)$[RuCp(CO)_2]_2$

Refluxing of $[RuCp(CO)_2]_2$ (0.89 g, 2 mmol) with elemental sulfur, S_8 (5 mmol, excess) in benzene for 14–16 h gave an olive green solution. The solvent was removed in vacuo, and the residual dark green oil was extracted with 20 cm^3 of CH_2Cl_2. Column chromatography (70–230 mesh silica gel, 3/1 (v/v) CH_2Cl_2/petroleum ether) gave a yellowish-green broad band. TLC examination (CH_2Cl_2) indicated that the band contained a mixture of compounds with $R_f = 0.78$, 0.70, and 0.64. The mixture exhibited ^1H NMR resonances ($CDCl_3$) at δ 5.53, 5.56, and 5.57 ppm. The IR spectrum (CH_2Cl_2) exhibited ν(CO) band at 2040(s) and 1980(vs) cm^{-1}. After numerous attempts we were able to separate pale green microcrystals of the pentasulfane, (μ-S_5)$[RuCp(CO)_2]_2$ (I) by fractional crystallization of the second fraction from the TLC separation. Compound I (yield 27%) was characterized by elemental analysis, IR and ^1H NMR. Anal. Found: C, 28.22; H, 1.66; S, 25.87. $C_{14}H_{10}O_4S_5Ru_2$ calcd.: C, 27.81; H, 1.65; S, 26.51%. IR: ν(CO) (CH_2Cl_2) 2038(s), 1981(vs) cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.53 ppm (s, C_5H_5); M.p. 71°C. The other two compounds in the green oil are believed to be structurally related to pentasulfane I, but with different number of bridging sulfur atoms. This was confirmed by the reaction of the oil with acid chloride, which gave the monothiocarboxylate derivatives, $RuCp(CO)_2SCOR$, as described below.

Photochemical reaction of $[RuCp(CO)_2]_2$ with S_8

A mixture of a benzene solution of $[RuCp(CO)_2]_2$ (0.89 g, 2 mmol) with elemental sulfur, S_8 (0.77 g, 2 mmol) was irradiated with a high-pressure mercury lamp (HANAU, 240-600 nm) for 4–5 h. The reaction was monitored by TLC and IR spectroscopy. The disappearance of the bridging CO band of the ruthenium dimer and its replacement by two strong terminal CO bands at 2042 and 1981 cm^{-1}, indicated complete reaction. Drying of the solvent, extraction of the residue by CH_2Cl_2 and then chromatographic separation (1/1) (v/v) CH_2Cl_2/n-hexane) afforded mainly a mixture of ruthenium sulfanes with other, unidentified, decomposition products. Use of the procedure described for the thermal reaction gave crystals of the $(\mu\text{-}S_5)[RuCp(CO)_2]_2$ (I) (yield 15%).

Reaction of $(\mu\text{-}S_5)[RuCp(CO)_2]_2$ with acid chlorides, RCOCl and the preparation of the monothiocarboxylate derivatives, $RuCp(CO)_2SCOR$

In a typical procedure, a 150 cm^3 Schlenk flask was charged with $(\mu\text{-}S_5)[RuCp(CO)_2]_2$ (2 mmol) and diethyl ether (50 cm^3). A solution of the acid chloride RCOCl (2.5 mmol) in diethyl ether (10 cm^3) was added slowly to the orange-yellow solution and the mixture was then stirred for 2 h at room temperature during which the color changed from orange-yellow to light yellow. A sample of the mixture was examined by TLC (Silica, CH_2Cl_2) which showed the presence of two yellow products and these were separated by column chromatography (CH_2Cl_2). The yellow product from the first band was recrystallized from CH_2Cl_2/n-hexane as yellow crystals, and shown to be $RuCp(CO)_2Cl$ [12] (yield 15%) m.p. 100–101° C. Anal. Found: C, 32.8; H, 2.16; Cl, 13.59. $C_7H_5O_2ClRu$ calcd.: C, 32.60; H, 1.95; Cl, 13.78%. IR (CH_2Cl_2): ν(CO) 2040s, 1985s cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.44 (s, C_5H_5). The product from the second band was obtained as yellow crystals from CH_2Cl_2/n-hexane and identified as $RuCp(CO)_2SCOR$. Table 1 shows the analytical data, melting points, yields and colors of the monothiocarboxylate derivatives with various R groups and Table 2 gives the IR and ^1H NMR spectral data.

Crystal structure analysis for $RuCp(CO)_2SCOR(2\text{-}O_2NC_6H_4)$ (VI)

Crystals suitable for the X-ray study were obtained by recrystallization from CH_2Cl_2/n-hexane. Compound VI crystallizes in the monoclinic system, space group $C2/c$ (No. 15) [13] with a 1488.0(5), b 1359.4(3), c 1651.6(5) pm, β 115.68(2)°,

Table 1

Analytical data, colors, melting points, and yields for the complexes $RuCp(CO)_2SCOR$

$RuCp(CO)_2SCOR$	Color	Yield (%)	M.p. (°C)	Analysis (Found (calcd.)%)			
				C	H	S	N
R = 1-$C_{10}H_7$ (II) (1-naphthyl)	yellow	47	149–150	52.76 (52.81)	3.04 (2.95)	7.73 (7.83)	
R = 2-FC_6H_4 (III)	yellow	71	105–106	44.41 (44.56)	2.49 (2.40)	8.61 (8.50)	
R = 4-$O_2NC_6H_4$ (IV)	yellow	63	137–138	41.49 (41.58)	2.35 (2.24)	7.81 (7.93)	3.44 (3.46)
R = 3,5-$(O_2N)_2C_6H_3$ (V)	yellow	55	194–195	37.26 (37.42)	1.86 (1.79)	7.19 (7.14)	6.06 (6.23)
R = 2-$O_2NC_6H_4$ (VI)	yellow	76	104–105	41.45 (41.58)	2.36 (2.24)	7.78 (7.93)	3.51 (3.46)
R = $C_6H_4C(=O)SFeCp(CO)_2$ (VII)	reddish-orange	66	130 (decomp.)	42.10 (42.04)	2.50 (2.47)	11.18 (11.23)	

Table 2

IR and ^{1}H NMR spectral data for the complexes $RuCp(CO)_2SCOR$

$RuCp(CO)_2SCOR$	$IR(CH_2Cl_2)$ (cm^{-1})	^{1}H NMR ($CDCl_3$) δ (ppm)
R = 1-$C_{10}H_7$ (II)	2038 vs, 1980 vs (ν(CO)) 1604 s (ν(C=O) 915 m (νC$\cdots$S))	5.47 (s, 5H, C_5H_5) 7.33–8.36 (m, 7H, ArH)
R = 2-FC_6H_4 (III)	2040 vs, 1985 vs (ν(CO)) 1601s (ν(C=O)) 925 s (ν(C$\cdots$S))	5.47 (s, 5H, C_5H_5) 7.0–7.42 (m, 3H, 3-, 4-,5-ArH)
R = 4-$O_2NC_6H_4$ (IV)	2050 vs, 1980 vs (ν(CO)) 1601 s (ν(C=O)) 1528 s, 1360 vs (ν(NO_2)) 935 s (ν(C$\cdots$S))	5.49 (s, 5H, C_5H_5) 8.24 (s, 4H, ArH)
R = 3,5-$(O_2N)_2C_6H_3$ (V)	2045 vs, 1990 vs (ν(CO)) 1610 s (ν(C=O)) 1538 s, 1348 vs (ν(NO_2)) 922 m (ν(C$\cdots$S))	5.51 (s, 5H, C_5H_5) 9.10 (t, 1H, 4-ArH) 9.27 (d, 2H, 2-,6-ArH)
R = 2-$O_2NC_6H_4$ (VI)	2038 vs, 1980 vs (ν(CO)) 1603 s (ν(C=O)) 1523 s, 1348 s (ν(NO_2)) 929 s (ν(C$\cdots$S))	5.52 (s, 5H, C_5H_5) 7.46–7.66 (m, 3H, 3-,4-,5-ArH) 7.86–7.96 (m, 1H, 6-ArH)
R = $C_6H_4C(=O)SFeCp(CO)_2$ (VII)	2038 vs, 1980 vs (ν(CO)) 1604-1590 s (br) (ν(C=O)) 910 s (ν(C$\cdots$S)	5.06 (s, 5H, C_5H_5(Fe)) 5.46 (s, 5H, C_5H_5(Ru)) 8.09 (s, 4H, ArH)

Table 3

Atomic coordinates for compound VI, with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}
Ru(1)	0.5286(2)	0.24235(2)	0.5542(2)	0.0369(1)
S(1)	−0.00253(7)	0.13733(8)	0.42765(7)	0.0525(4)
C(1)	−0.1262(3)	0.1653(3)	0.3633(2)	0.040(1)
O(1)	−0.1746(2)	0.2309(2)	0.3744(2)	0.062(1)
C(2)	−0.2498(3)	0.0293(2)	0.2771(2)	0.040(1)
C(3)	−0.2949(3)	−0.0336(3)	0.2055(2)	0.051(2)
C(4)	−0.2656(3)	−0.0304(3)	0.1371(3)	0.057(2)
C(5)	−0.1924(3)	0.0345(3)	0.1416(2)	0.053(2)
C(6)	−0.1472(3)	0.0958(3)	0.2151(2)	0.044(2)
C(17)	−0.1745(3)	0.0943(2)	0.2855(2)	0.036(1)
N(1)	−0.2844(3)	0.0246(2)	0.3484(2)	0.052(2)
O(2)	−0.2246(3)	0.0361(3)	0.4256(2)	0.082(2)
O(3)	−0.3727(2)	0.0085(3)	0.3255(2)	0.078(2)
C(8)	−0.0607(3)	0.1770(3)	0.5949(3)	0.059(2)
C(9)	−0.0703(3)	0.2794(3)	0.5934(3)	0.058(2)
C(10)	0.0198(3)	0.3179(3)	0.6581(3)	0.053(2)
C(11)	0.0841(3)	0.2398(3)	0.6993(2)	0.056(2)
C(12)	0.0347(3)	0.1518(5)	0.6599(3)	0.059(2)
C(13)	0.1861(3)	0.2171(3)	0.5770(3)	0.049(2)
O(13)	0.2668(2)	0.2016(2)	0.5929(2)	0.075(2)
C(14)	0.0439(3)	0.3531(3)	0.4837(3)	0.051(2)
O(14)	0.0367(3)	0.4215(3)	0.4427(2)	0.085(2)

Table 4

Bond distances (Å) for compound VI

Ru(1)–S(1)	2.380(1)	C(2)–C(3)	1.375(5)
Ru(1)–C(8)	2.242(5)	C(2)–C(7)	1.386(5)
Ru(1)–C(9)	2.236(5)	C(3)–C(4)	1.375(7)
Ru(1)–C(10)	2.213(5)	C(4)–C(5)	1.379(6)
Ru(1)–C(11)	2.214(4)	C(5)–C(6)	1.384(5)
Ru(1)–C(12)	2.229(5)	C(6)–C(7)	1.389(6)
Ru(1)–C(13)	1.887(5)	C(2)–N(1)	1.477(6)
Ru(1)–C(14)	1.885(4)	N(1)–O(2)	1.208(4)
S(1)–C(1)	1.722(3)	N(1)–O(3)	1.219(5)
C(1)–O(1)	1.209(5)	C(8)–C(9)	1.399(6)
C(1)–C(7)	1.516(4)	C(8)–C(10)	1.404(5)
C(13)–O(13)	1.132(6)	C(10)–C(11)	1.394(6)
C(14)–O(14)	1.127(6)	C(11)–C(12)	1.406(6)
		C(8)–C(12)	1.401(5)

$V = 3010.81 \times 10^6$ pm^3, $d_{cal.}$ 1.78 g cm^{-3} μ 11.74 cm^{-1}, $Z = 8$, T 298 K, ω-Scan, $\Delta\omega$ 0.75°, 2.4° $< \omega <$ 29.3° min^{-1} 2.0° $< 2\theta <$ 54.0°, 2129 independent significant reflections ($I \geqslant 2\sigma(I)$). The cell constants and reflections were measured on a Syntex-P3-diffractometer with a graphite monochromator, λ(Mo-K_α 71.073 pm. The structure was solved by use of the program SHEL-XTL-PLUS [14] by direct methods. Hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at $R_1 = 0.027$ and $R_2 = 0.027$. A list of atomic coordinates with LS-computed standard deviations is given in Table 3. Bond distances and bond angles are given in Tables 4 and 5, respectively.

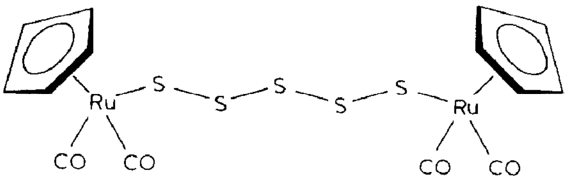
Table 5

Bond angles (°) and torsional angles for compound VI

(X(1A) = center of C_5H_5 ring)			
S(1)–Ru(1)–C(14)	89.4(1)	S(1)–C(1)–O(1)	128.1(3)
S(1)–Ru(1)–C(13)	91.1(1)	C(7)–C(1)–O(1)	120.2(3)
C(13)–Ru(1)–C(14)	92.7(2)	C(2)–N(1)–O(3)	117.5(4)
S(1)–Ru(1)–X(1A)	122.0	C(2)–N(1)–O(2)	118.9(4)
C(13)–Ru(1)–X(1A)	125.6	O(2)–N(1)–O(3)	123.5(5)
C(14)–Ru(1)–X(1A)	125.8	Ru(1)–C(13)–O(13)	177.7(4)
Ru(1)–S(1)–C(1)	106.4(1)	Ru(1)–C(14)–O(13)	177.1(4)
S(1)–C(1)–C(7)	111.7(3)		
X(1A)–Ru(1)–S(1)–C(1)	65.0		
Ru(1)–S(1)–C(1)–O(1)	6.5		
Ru(1)–S(1)–C(1)–C(7)	−172.6		
C(14)–Ru(1)–S(1)–C(1)	−69.5		
X(1A)–S(1)–C(1)–O(1)	29.3		
C(14)–S(1)–C(1)–O(1)	−28.7		
C(13)–S(1)–C(1)–O(1)	−11.7		
C(13)–Ru(1)–S(1)–C(1)	−162.2		
O(1)–C(1)–C(7)–C(2)	−65.0		

Results and discussion

The reaction of $[RuCp(CO)_2]_2$ with elemental sulfur in refluxing benzene for 14–16 h or upon irradiation in benzene for 4–5 h gives an oily olive-green mixture of sulfur bridged products, $(\mu\text{-}S_x)[RuCp(CO)_2]_2$, $x \geqslant 1$ as the only isolable products. From this mixture, the pentasulfane product $(\mu\text{-}S_5)[RuCp(CO)_2]_2$ (I) was isolated by fractional crystallization of the product from one of the chromatographic bands. Numerous attempts to separate the other ruthenium sulfane products were unsuccessful.



(I)

The new organoruthenium pentasulfane I was characterized by elemental analysis, ^1H NMR and IR. Its ^1H NMR spectrum showed a singlet at δ 5.53 ppm due to the Cp protons, and its solution (CH_2Cl_2) IR spectrum showed two strong terminal carbonyl bands, at 2038 and 1981 cm^{-1}. The IR spectrum of the olive-green mixture also showed two strong terminal carbonyl bands at 2040 and 1980 cm^{-1}, but the ^1H NMR spectrum $(CDCl_3)$ exhibited three singlets at δ 5.53, 5.56, and 5.57 ppm, showing the presence of three structurally related ruthenium sulfane compounds, one of them the pentasulfane. We obtained analogous results for the reaction between S_8 and $[FeCp(CO)_2]_2$ in the synthesis of $(\mu\text{-}S_x)[FeCp(CO)_2]_2$, $(x = 1\text{–}4)$ [3]; one difference is that complete transformation of the iron dimer into a mixture of iron-sulfanes requires only 50–60 minutes in refluxing benzene. This clearly indicates the expected lower reactivity of the Ru–Ru bond in $[RuCp(CO)_2]_2$ towards oxidative insertion of S_x ligand $(x \geqslant 1)$ compared with that of the Fe–Fe bond in $[FeCp(CO)_2]_2$. In addition, refluxing $[FeCp(CO)_2]_2$ with elemental sulfur in benzene for more than 6 h gave the iron-sulfur cubane, $[FeCpS]_4$ [15], whereas, as observed, refluxing $[RuCp(CO)_2]_2$ with S_8 in benzene for 14–16 h gives a mixture of ruthenium sulfanes along with minor amounts of decomposition products. This provides a further example of the reluctance of $RuCp(CO)_2X$ compounds to undergo carbonyl substitution reactions [16], and compound I is the first sulfane example of a ruthenium sulfane with an unsubstituted cyclopentadienyl ring. Recent results were reported by T.B. Rauchfuss for the reaction of the organoruthenium dimer $[RuCp^{\star}(CO)_2]_2$ $(Cp^{\star} = C_5Me_4Et)$ with elemental sulfur in toluene or upon photolysis (toluene). These reactions produced the compounds $Cp^{\star}_2Ru_2S_5(CO)$ (red), $Cp^{\star}_2Ru_2S_6(CO)_2$ (black-green) and $Cp^{\star}_2Ru_2S_2(CO)_2$ (turqoise) [17]. The reaction of $[RuCp^{\star}(CO)_2]_2$ $(Cp^{\star} = C_5Me_5)$ with an excess of sulfur upon irradiation in THF solution has recently been shown to give the bridged tetrasulfide ruthenium complex, $(\mu\text{-}S_4)$ $[RuCp^{\star}(CO)_2]_2$ in addition to $Cp^{\star}_2Ru_2(CO)_3S_4$, $Cp^{\star}_2Ru_2(CO)S_5$ and $Cp^{\star}Ru_2(CO)_2S_6$ [10], but when the above reaction was carried out in boiling toluene the ruthenium tetrasulfide $(\mu\text{-}S_4)[RuCp^{\star}(CO)_2]_2$ and $Ru_2Cp^{\star}(CO)S_5$ were the only products obtained. Although the type of products and their proportions formed in a reaction of a given organometallic compound with S_8

vary with the conditions used [10,18], the effect of electron-releasing substituents at the Cp ring of the ruthenium dimer on its reactivity and the products formed is very obvious in the reactions described in ref. 10 and 17.

The formulation of the ruthenium pentasulfane I was further confirmed by its reaction with PPh_3 (excess), which gave the ruthenium dimer and Ph_3PS, as shown in eq. 1.

$$Cp(CO)_2Ru\text{-}S_5\text{-}RuCp(CO)_2 + 5\ PPh_3 \xrightarrow{THF} [RuCp(CO)_2]_2 + 5\ Ph_3PS \tag{1}$$

The olive-green mixture of structurally related ruthenium sulfanes reacts completely with an excess of PPh_3 to give the ruthenium dimer and Ph_3PS.

Addition of RCOCl to I or to the olive-green mixture of ruthenium sulfanes in diethyl ether at room temperature quickly gave the ruthenium thiocarboxylate derivatives $RuCp(CO)_2SCOR$ ($R = 1\text{-}C_{10}H_7$ (II), $2\text{-}FC_6H_4$ (III), $4\text{-}O_2NC_6H_4$ (IV), $3,5\text{-}(O_2N)_2C_6H_3$ (V), $2\text{-}O_2NC_6H_4$ (VI), $C_6H_4COSFeCp(CO)_2$ (VII)) in good yield (47–76%). The ruthenium-iron monothioterphthalate $RuCp(CO)_2SCOC_6H_4COSFe(CO)_2Cp$ (VII) was prepared by reaction of ruthenium pentasulfane I with $Cp(CO)_2FeSCOC_6H_4COCl$ [19*]; the latter was obtained by reaction of (μ-S_3)$[FeCp(CO)_2]_2$ with an excess of $ClCOC_6H_4COCl$ as orange crystals. The new ruthenium thiocarboxylates were isolated as yellow crystals from CH_2Cl_2/n-hexane, and are reasonably stable as solids and in solution. Their physical and spectral data are reported in Tables 1 and 2. From the reaction of I with acid chlorides, $RuCp(CO)_2Cl$ was isolated in low yield. The reactivity of the ruthenium sulfanes as well as the iron sulfanes [20,21] towards acid chlorides is attributed to the presence of reactive sulfur atom(s) in the bridging S_x group. A reaction pathway similar to that suggested for the reaction of $Fp\text{–}S_3\text{–}Fp$ ($Fp = FeCp(CO)_2$) with acid chloride [21] can be assumed for the reaction of the ruthenium pentasulfane I with acid chlorides. The intermediate formation of unstable species such as $RuCp(CO)_2S_xCOR$ ($x > 1$) and $RuCp(CO)_2S_xCl$ ($x \geqslant 1$), which readily give the more stable $RuCp(CO)_2SCOR$ and $RuCp(CO)_2Cl$ respectively and elemental sulfur, can also be assumed. The IR spectra of the thiocarboxylate derivatives II–VII show the characteristic strong terminal metal carbonyl bands in the ranges 2040–2062 and 1998–1985 cm^{-1} and C=O and C$\doteq$S stretching frequencies of *S*-bonded monothiocarboxylate group at ca. 1600 and 920 cm^{-1} respectively [22,23]. Their ^1H NMR spectra show a singlet due to Cp protons in the range 5.46–5.52 ppm. The dinuclear iron-ruthenium thiocarboxylate compound VII exhibits two singlets at 5.06 and 5.46 ppm due to the two Cp protons at Fe and Ru respectively. The ^1H NMR spectra of these compounds show also the characteristic peaks due to R protons (see Table 2).

Molecular structure of $RuCp(CO)_2(2\text{-}O_2NC_6H_4)$ (VI)

The molecular structure of compound VI is shown in Fig. 1. Bond distances and selected bond angles and torsional angles are shown in Table 4 and 5, respectively [24*]. The thiocarboxylate ligand is *S*-bonded to the ruthenium atom in the $RuCp(CO)_2$ unit, with a *cis* disposition of the Ru–S relative to the C=O bond. A similar planar *cis* conformation was found in the recently reported Fe analogue [21] (see Fig. 2) and in organic esters and a silylmonothioacetate [25,26]. The *cis*

* Reference number with asterisk indicates a note in the list of references.

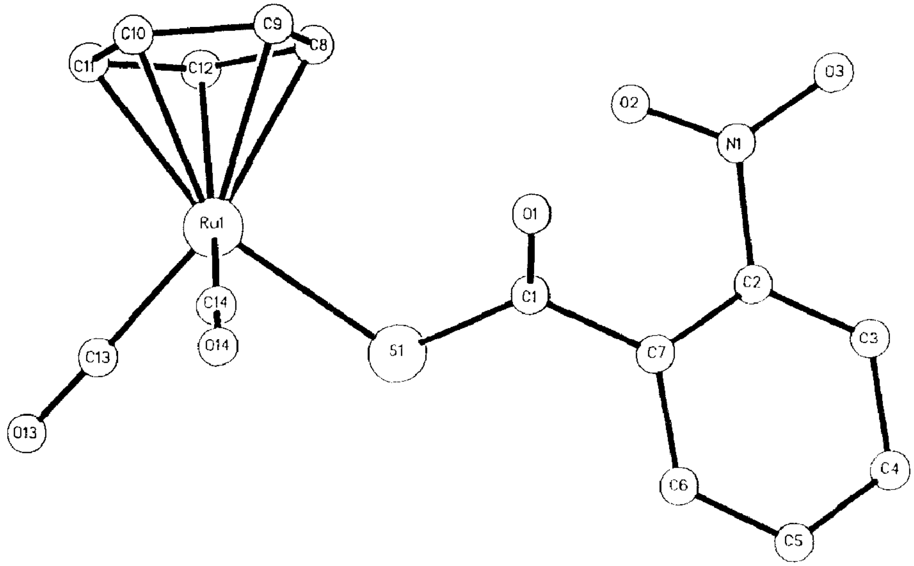


Fig. 1. Molecular structure of $RuCp(CO)_2SCO(2\text{-}O_2NC_6H_4)$ (VI).

relationship between the Ru–Cp bond and C–S bonds contrasts with the corresponding *trans*-relationship observed for the Fe analogue. The angles S(1)–Ru(1)–C(14), S(1)–Ru(1)–C(13) and C(13)–Ru(1)–C(14) are 91.1, 89.4 and 92.7° respectively, and are smaller than the corresponding angles in the analogous Fe Complex (93.6°, 94.1° and 94.2°); the smaller angles at the metal in VI are essentially due to the larger size of the ruthenium atom. The size of the Ru(1)–S(1)–C(1) angle of 106.4 is close to that of Fe–S–C (108.0) in the iron analogue, with almost sp^3 hybridization of the sulfur atom in both complexes. The NO_2 group points in the same direction as the thiocarboxylate C=O group. The Ru(1)–S(1) bond distance of 2.38 Å is in the normal range of single Ru–S bond distance though it seems to be slightly smaller than that (2.40 Å) in the octahedral conflex [Ru(SCOPh)$_2$ (Phen)(PMe$_2$Ph)$_2$] and related species [27].

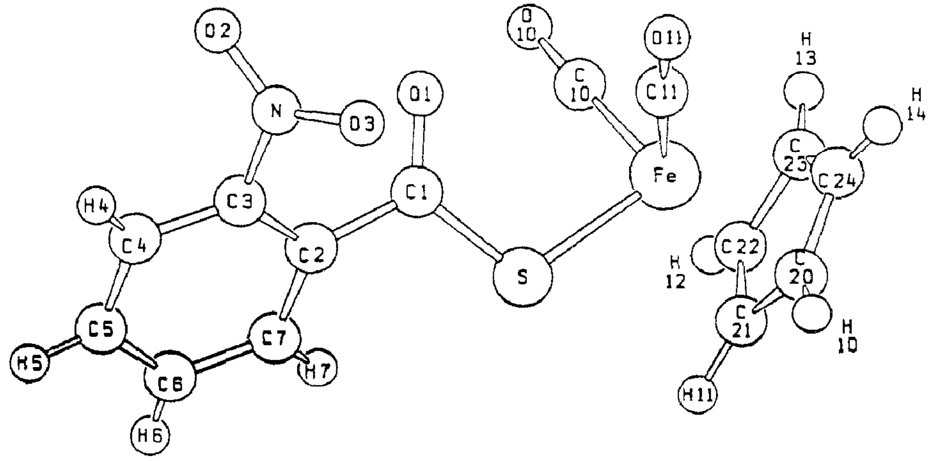


Fig. 2. Molecular structure of $FeCp(CO)_2SCO(2\text{-}O_2NC_6H_4)$ (from ref. 21).

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19 $Cp(CO)_2FeSCOC_6H_4COCl$ (yield 55%) orange crystals, m.p. 115–116 °C. Anal. Found: C, 47.72; H, 2.41; S, 8.56; Cl, 9.37. $C_{15}H_9O_4SClFe$ calcd.: C, 47.83; H, 2.39; S, 8.50; Cl, 9.43%. IR (CH_2Cl_2): ν(CO) 2035 vs, 1997 vs cm^{-1}, ν(C=O) (COCl) 1752 s cm^{-1}, ν(C=O) (SCO) 1595 s cm^{-1}; ν(C=S) 918 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.08 (s, 5H, C_5H_5), 8.04–8.27 (m, 4H, Ar–H).
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