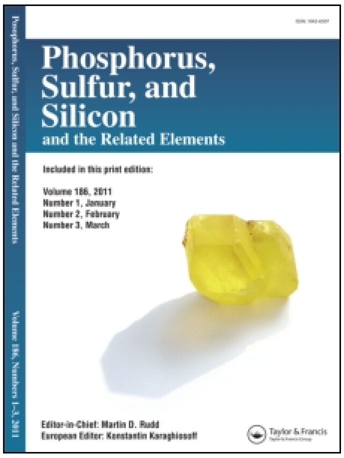

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BINUCLEAR COMPLEXES CONTAINING THIOSEMICARBAZONE LIGANDS. η^3-ALLYL DICARBONYL COMPLEXES WITH ATTACHED FERROCENE-CARBALDEHYDETFFLOSEMICARBAZONE LIGANDS

Atanas K. Tomov[a]; Kurti S. Kurtev[a]; Michel J. M. Campbell[b]
[a] Department of Organic Synthesis, Higher Institute of Chemical Technology, Burgas, Bulgaria [b] The University of Greenwich, Woolwich Campus, London, United Kingdom

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BINUCLEAR COMPLEXES CONTAINING THIOSEMICARBAZONE LIGANDS. η^3-ALLYL DICARBONYL COMPLEXES WITH ATTACHED FERROCENE-CARBALDEHYDETHIOSEMICARBAZONE LIGANDS

ATANAS K. TOMOV* and KURTI S. KURTEV
Higher Institute of Chemical Technology, Department of Organic Synthesis,
1 Professor Yakimov Street, 8010 Burgas, Bulgaria

and

MICHEL J. M. CAMPBELL
The University of Greenwich, Woolwich Campus, Wellington Street,
London SE18 6PF, United Kingdom

(Received December 13, 1994)

η^3-Allyl-bis-acetonitrilechlorodicarbonylmolybdenum(II) reacts with the thiosemicarbazones Fc—CH—N=NH—C(S)—NH—R [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5] in dichloromethane to give the complexes {$(\eta^3\text{-}C_3H_5)MoCl(CO)_2$[Fc—CH=N—NH—C(S)—NH—R]} [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5], by displacement of the acetonitrile ligands. When the reaction is carried out in ethanol in the presence of sodium ethanolate, the complexes {$(\eta^3\text{-}C_3H_5)Mo(CO)_2$[Fc—CH=N—NH—C(S)—NH—R]} [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5] are prepared by displacement of the acetonitrile ligands and a substitution of the chlorine ligand.

Key words: Bimetallic complexes, thiosemicarbazones, molybdenum, ferrocenecarbaldehyde thiosemicarbazone.

INTRODUCTION

The co-ordination chemistry of thiosemicarbazones has been well explored for transition metal complexes,[1,2] but there have been only a few reports of thiosemicarbazone organometallic compounds.[3–5] Data about bimetallic organotransition metal complexes, containing thiosemicarbazone ligands are very scarce.

Thiosemicarbazones and some of their transition metal complexes 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 1 and 2).

On the other hand a number of ferrocene containing organic[6,7] and organometallic[8] compounds has been reported as systems having potential non-linear optical properties.

The stereochemistry adopted by thiosemicarbazone ligands while interacting with

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*Author to whom all correspondence should be directed; Fax: (+0359 56) 686-141.

transition metal ions may be affected by the presence of an additional co-ordination centre in the ligand moiety and by the charge on the ligand. This in turn is influenced by thione-thiol tautomerism. In solution thiosemicarbzones probably consist of an equilibrium mixture of thione and thiol tautomers. The thione reacts as a neutral bidentate ligand, while the loss of the thiol proton (in basic media) yields a singly charged bidentate ligand.

In the most of the complexes studied the thiosemicarbazone function co-ordinates to the metal ion in the *cis*-configuration as a bidentate ligand through the sulphur atom and the hydrazine nitrogen atom.

The present study was undertaken to prepare bimetallic organomolybdenum complexes, containing ferrocenecarbaldehyde thiosemicarbazones as co-ordinated ligands in both neutral or deprotonated form and to compare their properties. Thus in recent years, many efforts have been made to investigate compounds whose metal atoms are not directly linked by metal-metal bonds, but are held at a close distance with the help of an appropriate ligand system.[9,10]

Although a wide range of mononuclear organomolybdenum thiosemicarbazone complexes has been published by Campbell *et al.*,[3] organomolybdenum thiosemicarbazone complexes, containing ferrocenecarbaldehyde thiosemicarbazones as co-ordinated ligands both in neutral and deprotonated form have not previously been studied.

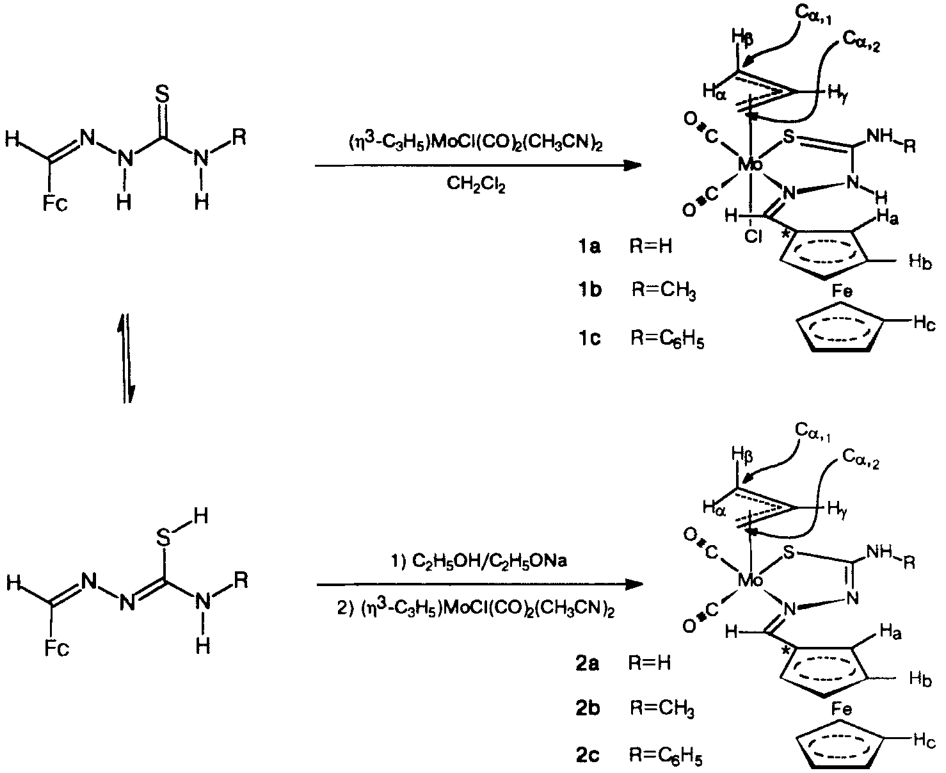
RESULTS AND DISCUSSION

The reaction of η^3-allyl-bis-acetonitrile-bis-carbonylchloromolybdenum(II) with the ferrocenecarbaldehyde thiosemicarbazones Fc—CH=N—NH—C(S)—NH—R [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5], in boiling dichloromethane gives high yields of the solid compounds **1a**–**1c** {$(\eta^3\text{-}C_3H_5)MoCl(CO)_2$[Fc—CH=N—NH—C(S)—NH—R]} [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5] by displacement of the acetonitrile ligands (Scheme I). The orange-red complexes are insoluble in nonpolar and very soluble in polar solvents such as ethanol, acetone and dimethylsulphoxide. They are air- and water-stable in the solid state at room temperature, but slowly decompose in solution.

When the reaction of η^3-allyl-bis-acetonitrile-bis-carbonylchloromolybdenum(II) and the above mentioned thiosemicarabazones is carried out in boiling ethanol in presence of equimolar quantities of sodium ethanolate, the complexes **2a**–**2b** {$(\eta^3\text{-}C_3H_5)Mo(CO)_2$[Fc—CH=N—NH—C(S)—NH—R]} [Fc = $(\eta^5\text{-}C_5H_5)_2Fe$; R = H, CH_3, C_6H_5] are prepared. In this case the ferrocenecarbaldehyde thiosemicarbzones react as bidentate anionic ligands, diplacing the acetonitrile and substituting the chlorine ligands (Scheme I). Complexes **2a**–**2c** which are soluble in dimethylsulphoxide and N,N-dimethylformamide, are air- and water stable in the solid state at room temperature but partially decompose in solution.

Complexes **1a**–**1c** and **2a**–**2c** were fully characterized by elemental analysis (Table I), FT-IR spectroscopy (Table II), ^{1}H-NMR and ^{13}C-NMR spectroscopy (Experimental part). The ^{13}C-NMR spectrum of compound **2b** was not of good quality due to its relatively poor solubility.

It has been previously mentioned by Campbell *et al.*[3] that η^3-allyl-bis-carbon-



SCHEME I. Preparation of the binuclear complexes **1a–1c** and **2a–2b**.

TABLE I

Analytical data for complexes **1a–1c** and **2a–2b**

Compl No	**Formula**	**Yield %**	**Found (Calcd.), % C**	**H**	**N**
1a	$[(\eta^3\text{-}C_3H_5)MoCl(CO)_2(FcCHNNHC(S)NH_2)]$	63	39.54	3.45	7.70
			(39.59)	(3.53)	(8.15)
1b	$[(\eta^3\text{-}C_3H_5)MoCl(CO)_2(FcCHNNHC(S)NHCH_3)]$	48	39.21	4.19	8.67
			(40.80)	(3.81)	(7.94)
1c	$[(\eta^3\text{-}C_3H_5)MoCl(CO)_2(FcCHNNHC(S)NHC_6H_5)]$	44	44.47	3.57	6.49
			(46.60)	(3.92)	(7.09)
2a	$[(\eta^3\text{-}C_3H_5)Mo(CO)_2(FcCHNNHC(S)NH_2)]$	55	42.18	3.71	8.52
			(42.60)	(3.58)	(8.77)

TABLE 1 (*Continued*)

Compl No	Formula	Yield %	Found (Calcd.), % C	H	N
2b	$[(\eta^3\text{-}C_3H_5)Mo(CO)_2(FcCHNNHC(S)NHCH_3)]$	40	43.19	3.95	8.39
			(43.83)	(3.89)	(8.52)
2c	$[(\eta^3\text{-}C_3H_5)Mo(CO)_2(FcCHNNHC(S)NHC_6H_5)]$	40	49.88	3.94	7.57
			(49.65)	(3.99)	(7.57)

TABLE II

Selected FT-IR spectral data for complexes **1a**–**1c** and **2a**–**2b**

Compl. No	R	ν_{NH} cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\delta_{NH2\,(NH)} + \nu_{C-N}$ cm^{-1}	$\nu_{C=S} + \delta_{N-N}$ cm^{-1}
1a	H	3422 m	1963 v.s.	1617 s	825 w
		3262 m	1844 s	1541 s	
		3171 m			
1b	CH_3	3432 s	1934 v.s	1581 s	824 - 842 w
		3204 s	1841 v.s	1544 s	
1c	C_6H_5	3446 s	1929 v.s	1563 s	823 - 833 w
		3156 s	1833 v.s	1526 s	
				1497 s	
2a	H	3477 s	1949 - 1932 v.s	1594 s	823 w
		3378 s	1861 - 1845 v.s	1529 w	
		3355 s			
2b	CH_3	3446 s	1930 v.s	1604 m	796 - 758 w
		3361 s	1855 - 1832 vs	1580 v.s	
2c	C_6H_5	3369 s	1942 - 1928 v.s	1605 - 1593 v.s	803 w
		3289 s	1829 v.s	1523 m	

ylchlorothiosemicarbazone molybdenum complexes exist in a configuration in which the carbonyl ligands are in *cis*-position to each other and the allyl group is located face to face towards them. This configuration was confirmed for the complexes **1a**–**1c** and **2a**–**2c** too.

The ^{1}H-NMR spectra of compounds **1a** and **2a** show different signals for the protons in the NH_2 groups, which is due to the restriction of the free rotation of these groups about the C—NH_2 bonds. The splitting of these proton signals (110.7 Hz for **1a** and 375.3 Hz for **2b**) confirms that the NH_2 protons are located in different magnetic environments. The ^{1}H-NMR signals for the hydrazine N—**H** protons of **1a**, **1b**, and **1c** are strongly displaced to lower fields (11.7 ppm, 11.23 ppm and 11.60 ppm respectively), compared with these signals in thiosemicarbazido-organomolybdenum complexes,[4] which is probably due to the p-π and π-π electron delocation in the thiosemicarbazone ligands, which include the nitrogen atoms, the thiocarbonyl and ferrocene groups.

The restrictions of the free rotation of NH—R groups as well as the presence of double N═C(H)Fc bonds in the complexes **1a**–**1c** and **2a**–**2c** make possible the existence of diastereomerizm of the co-ordinated thiosemicarbazone ligands. There are four possible diastereomers for these compounds (Figure 1), except for complexes **1a** and **2a** for which they are only two. The ferrocene groups in compounds **1a**–**1c** are probably located in *syn*-position toward the nitrogen atoms, because of

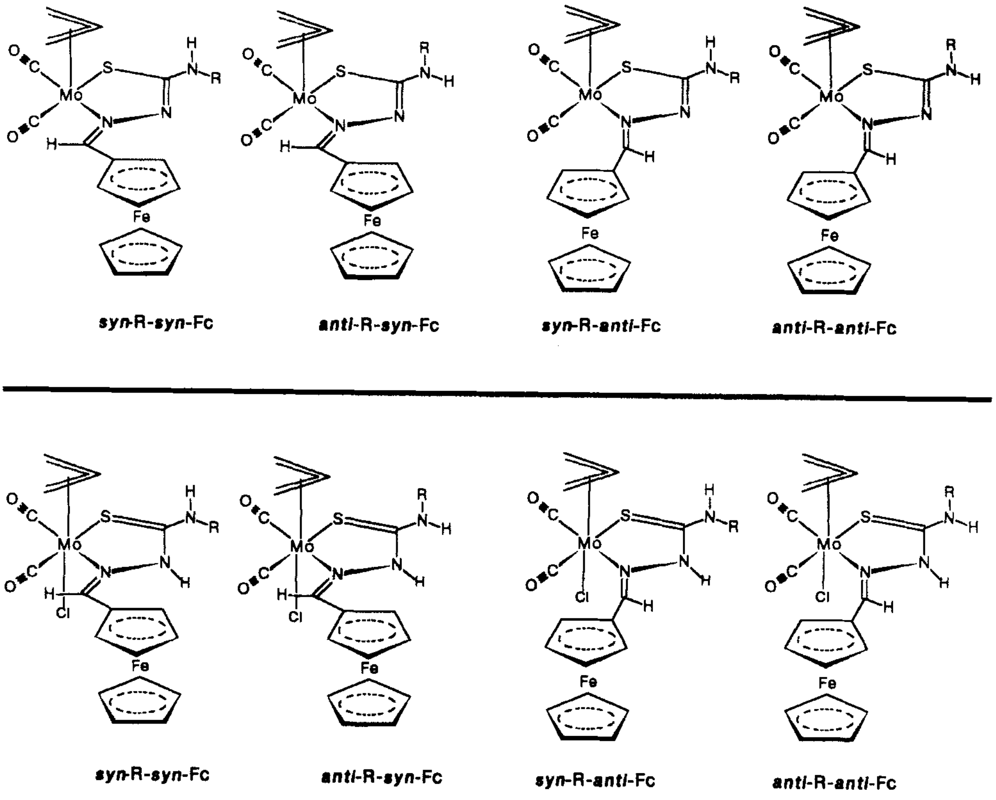


FIGURE 1 Structure of the four possible diastereomers for complexes **2b**, **2c** and **1b**, **1c**.

the steric repulsion between the bulky chlorine and ferrocene groups. The ^{1}H-NMR signals for CH_3 and $N(CH_3)$—**H** in compound **1b** are split(J = 4.4 Hz and 5.4 Hz respectively), which may be attributed to a spin-spin coupling between N—**H** and CH_3. The higher spin-spin coupling constant for $\mathbf{H}_\alpha$—**C**—$\mathbf{H}_\alpha$ in the ^{1}H-NMR spectrum of this compound is due to the steric influence of the *anti*-located CH_3 group.

In compound **1c** the phenyl ring is located in *syn*-position toward the nitrogen atoms, probably because of a steric repulsion from the allyl group. The ^{1}H-NMR spectra of the complexes **1a**–**1c** show only small changes compared with the free ligands, although the FT-IR spectra confirm the co-ordination of the ligands to the molybdenum atoms.

The ^{13}C-NMR spectra of **1a**–**1c** confirm their structure too. Two different signals were found for the terminal allyl carbon atoms in **1c**, which is apparently due to the different distance between each of these carbons and molybdenum. This may be attributed to the steric repulsion between the phenyl ring and the allyl ligand.

It was found out that only compound **2b** consists in all four possible diastereomers, while compound **2a** exists as *syn*-Fc diastereomers and **2c**—as *anti*-Ph-*anti*-Fc diastereomer. The temperature dependent ^{1}H-NMR spectroscopy of **2b** showed that the concentrations of the four diastereomers change with the temperature. Thus the ratio of *syn*-CH_3-*anti*-Fc to *anti*-CH_3-*anti*-Fc is approximately 2:1, at room temperature, while at 60°C it is 1:1. The relation between *syn*-Fc and *anti*-Fc is less dependent on temperature.

The co-ordination of the ferrocenecarbaldehyde thiosemicarbazones as anionic ligands gives rise to changes in the NMR spectra of their complexes, because of an electronic density rearrangement. The bond order between the inner hydrazine nitrogen and the carbon atom is closer to a double bond, thus increasing the electronic conjugation between the ferrocene group and the thiosemicarbazone moiety.

It is worth noting that the ^{13}C-NMR spectra of complexes **1c**, **2a** and **2c** show different signals for the two terminal allyl atoms ($C_{\alpha,1}$ and $C_{\alpha,2}$). This difference is clearly visible for **2a** where the allyl group is bonded in a fashion closer to that of a η^1-η^2 ligand, showing two very different signals for the terminal allyl carbon atoms at 18.2 and 55.2 ppm.

EXPERIMENTAL

All reactions were carried out under dry nitrogen. $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ was prepared according to Hayter's method.[11] Ferrocenecarbaldehyde-4-methylthiosemicarbazone and ferrocenecarbaldehyde-4-phenylthiosemicarbazone were prepared by the method described by Wiles and Suprunchuk.[12] FT-IR spectra were recorded as KBr discs on a Perkin-Elmer 1700 FT-IR spectrophotometer. The elemental analysis for C, H and N were recorded on a Carlo-Erba Elemental Analyser MOD 1106 (using helium as the carrier gas). ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 270 MHz on a JEOL 270 MHz FT-NMR spectrometer using TMS as an internal standard.

Preparation of $\{(\eta^3\text{-}C_3H_5)MoCl(CO)_2[FcCHNN(H)C(S)NH_2]\}$

A solution of 0.50 g (1.6 mmol) $((\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ and 0.45 g (1.6 mmol) ferrocenecarbaldehyde thiosemicarbazone is 15 ml dichloromethane was refluxed under nitrogen for 30 min. The orange-red precipitate was filtered off, washed with dichloromethane (2 × 10 ml) and dried at 40°C under vacuum (1 mm Hg). Yield—0.52 g.

The ^{1}H-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 0.97 (d{J^2_{H-H} = 8 Hz}, 2H, H_α); 3.30 (s, 2H, H_β; 4.19 (s, 5H, H_c); 4.40 (s, 2H, H_b); 4/72 (s, 2H, H_a); 7.60 (s, 1H, N(H)—$\mathbf{H}_{anti}$); 7.89 (s, 1H, N=C(Fc)—**H**); 8.01 (s, 1H, N(H)—$\mathbf{H}_{syn}$); 11.17 (s, 1H, N—N(**H**)—C).

The ^{13}H-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 58.9 - C_α; 67.5 - C_b; 68.8 - C_c; 69.2 - C_γ; 69.2 - C_a; 78.8 - C*; 143.2 - N—**C**—Fc; 176.5 **C**—S.

Preparation of $\{(\eta^3\text{-}C_3H_5)MoCl(CO)_2[FcCHNN(H)C(S)NHCH_3]\}$

A solution of 0.25 g (0.8 mmol) ferrocenecarbaldehyde-4-methylthiosemicarbazone and 0.25 g (0.8 mmol) $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ in 10 ml dichloromethane was stirred under nitrogen at room temperature for 1 hour and after that refluxed for 10 min. Adding of 15 ml *n*-heptane to the cooled reaction mixture gave a dark orange-red solid, which was filtered, washed with *n*-heptane (2 × 5 ml) and dried at 30°C under vacuum (1 mm Hg). Yield—0.21 g).

The ^{1}H-NMR spectrum in d_6-DMSO at 20°C showed resonances δ (ppm) = 0.97 (d{J^2_{H-H} = 13.5 Hz}, 2H, H_α); 2.99 (d{$J_{\mathbf{H}-C-N-\mathbf{H}}$ = 4.4 Hz}, 3H, CH_3); 3.42 (br. s, 2H, H_β); 4.20 (s, 5H, H_c); 4.31 (s, 1H, H_γ); 4.41 (s, 2H, H_b); 4.73 (s, 2H, H_a); 7.89 (s, 1H, N=C(Fc)—**H**); 8.18 (d{$J_{\mathbf{H}-N-C\cdots\mathbf{H}}$ = 5.4 Hz}, 1H, N(CH_3)—**H**); 11.23 (s, 1H, N—N(**H**)—C).

The ^{13}C-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 30.6 - CH_3; 580 - C_α; 67.4 - C_b; 68.8 - C_c; 69.6 - C_γ; 69.8 - C_a; 79.0 - C*; 142.6 - N=**C**—Fc; 176.7 - **C**=S.

Preparation of $\{(\eta^3\text{-}C_3H_5)MoCl(CO)_2[FcCHNN(H)C(S)NHC_3H_5]\}$

A solution of 0.25 g (0.7 mmol) ferrocenecarbaldehyde-4-phenylthiosemicarbazone and 0.21 (0.7 mmol) $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ in 10 ml dichloromethane was refluxed under nitrogen for 20 min and after that the solvent was evaporated to 5 ml to give a dark orange-red solid, which was filtered off with dichloromethane (2 × 7 ml) and dried at 40°C under vacuum (1 mm Hg). Yield—0.20 g.

The ^{1}H-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 0.98 (d{J^2_{H-H} = 8.8 Hz}, 2H, H_α); 3.32 (br.s, 2H, H_β); 4.23 (s, 5H, H_c); 4.45 (s, 1H, H_b); 4.83 (s, 2H, H_a); 5.75 (s, 1H, H_γ); 7.18 (t, 1H, H_{para}); 7.36 (t, 2H, H_{meta}); 7.62 (d{J^2_{H-H} = 8.8 Hz}, 2H, H_{ortho}); 8.02 (s, 1H, N=C(Fc)—**H**); 9.77 (s, 1H, N(C_6H_5)—**H**); 11.60 (s, 1H, N—N(**H**)—C).

The ^{13}C-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 54.8 - $C_{\alpha,1}$; 59.0 - $C_{\alpha2}$; 67.8 C_b; 68.9 - C_c; 69.3 - C_γ; 70.1 - C_a; 78.6 - C*; 124.9 - C_{para}; 125.1 - C_{meta}; 127.9 - C_{ortho}; 138.9 - N—$\mathbf{C}_{Ph}$; 144.1 - N=**C**—Fc; 174.6 - **C**=S.

$\{(\eta^3\text{-}C_3H_5)Mo(CO)_2[FcCHNN(H)C(S)NH_2]\}$

A solution of 0.50 g (1.7 mmol) ferrocenecarbaldehyde thiosemicarbazone and 0.12 g (1.7 mmol) sodium ethanolate in 25 ml ethanol was stirred at room temperature under nitrogen for 10 min, and 0.53 g (1.7 mmol) of $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ were added. The resulting solution was refluxed under nitrogen for 20 min to give an orange-red precipitate. After cooling the solution to 0°C, the solid was filtered off, washed with water (2 × 5 ml) and ethanol (2 × 10 ml), and dried at 45°C under vacuum (1 mm Hg). Yield—0.33 g.

The ^{1}H-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 1.06 (t, 2H, H_α); 3.35 (br.s, 2H, H_β); 3.98 (br.s, 1H, H_γ); 4.27 (s, 5H, H_c); 4.45 (s, 2H, H_b); 4.79 (s, 2H, H_a); 7.36 (br.s, 2H, N(H)—$\mathbf{H}_{syn}$ + N=C(Fc)—**H**); 8.75 (br.s, 1H, N(H)—$\mathbf{H}_{anti}$).

The ^{13}C-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 18.2 - $C_{\alpha,1}$; 55.2 - $C_{\alpha,2}$; 67.8 - C_γ; 68.9 - C_b; 69.1 - C_c; 69.9 - C_a; 73.2 - C*; 143.3 - N=C—Fc; 176.7 - **C**=S; 229.0 - **C**≡O.

Preparation of $\{(\eta^3\text{-}C_3H_5)Mo(CO)_2[FcCHNN(H)C(S)NHCH_3]\}$

A solution of 0.25 g (0.8 mmol) ferrocenecarbaldehyde-4-methylthiosemicarbazone and 0.06 g (0.9 mmol) sodium ethanolate in 20 ml ethanol was stirred at room temperature under nitrogen for 15 min and 0.25 g (0.8 mmol) of $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ were added. The reaction mixture was refluxed under nitrogen for 20 min to give an orange precipitate which was filtered off, washed with water (2 × 5 ml), ethanol (2 × 10 ml) and dried at 40°C under vacuum (1 mm Hg). Yield—0.23 g.

The ^{1}H-NMR spectrum in d_6-DMSO at 60°C showed resonances at δ (ppm) = 1.13 (m, H_α); 2.77 (d{J = 4.8 Hz}, CH_3, *syn at Fc-syn*); 2.84 (d{J = 4.4 Hz}, CH_3, *syn at Fc-anti*); 2.95 (s, CH_3, *anti at Fc-syn*); 3.00 (d{J = 4.8 Hz}, CH_3, *anti at Fc-syn*); 3.22 (br.s, H_β); 3.80 (m, H_γ, *at* CH_3*-syn*); 4.00 (m, H_γ, *at* CH_3*-anti*); 4.20 (s, H_c *at Fc-anti*); 4.26 (s, H_c *at Fc-syn*); 4.43 (s, H_b *at Fc-syn*); 4.47 (s, H_b *at Fc-anti*); 4.77 (s, H_a *at Fc-syn*); 5.13 (s, H_a *at Fc-anti*); 6.46 (s, N=C(Fc)—H_{anti}); 6.54 (s, N(CH_3)—H_{syn} *at Fc-syn*); 6.60 (s, N(CH_3)—$\mathbf{H}_{syn}$ *at Fc-anti*); 7.71 (s, N=C(Fc)—$\mathbf{H}_{syn}$); 8.76 (s, N(CH_3)—H_{anti}).

Preparation of $\{(\eta^3\text{-}C_3H_5)Mo(CO)_2[FcCHNN(H)C(S)NHC_6H_5]\}$

A solution of 0.25 g (0.7 mmol) ferrocenecarbaldehyde-4-phenylthiosemicarbazone and 0.05 g (0.7 mmol) sodium ethanolate in 10 ml ethanol was refluxed under nitrogen as long as the solid was dissolved. The $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$, (0.13 g 0.7 mmol) then were added and the reaction mixture was refluxed under nitrogen for 20 min. The resulting dark orange-red solid was filtered off, washed with water (2 × 5 ml), ethanol (2 × 10 ml) and dried at 40°C under vacuum (1 mm Hg). Yield—0.16 g.

The ^{1}H-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 1.06 (t, 2H, H_α); 3.31 (d$\{J = 5.5$ Hz$\}$, 2H, H_β); 3.86 (br. s, 1H, H_γ); 4.24 (s, 5H, H_c); 4.49 (s, 2H, H_b); 5.11 (s, 2H, H_a); 6.94 (t, 1H, H_{para}); 7.25 (t, 2H, H_{meta}); 7.66 (d$\{J^2_{H-H} = 9.0$ Hz$\}$, 2H, H_{ortho}), 7.83 (s, 1H, N═C(Fc)—**H**); 9.09 (s, 1H, N(C_6H_5)—**H**).

The ^{13}C-NMR spectrum in d_6-DMSO at 20°C showed resonances at δ (ppm) = 56.0 - $C_{\alpha,1}$; 60.2 - $C_{\alpha,2}$; 69.93 - C_a; 71.4 - C_b; 72.5 - C*; 73.6 - C_γ; 74.8 - C_c; 119.8 - C_{meta}; 121.5 - C_{para}; 128.2 - C_{ortho}; 141.4 - N—C_{Ph}; 155.6 - N═**C**(Fc)—H; 169.9 - **C**═S.

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