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Thiosemicarbazone Organometallic Complexes of Molybdenum

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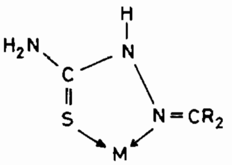
Many 'classical' coordination complexes with attached thiosemicarbazone ligands have been reported [1]. Most of these complexes contain thiosemicarbazone with bidentate coordination to the metal as shown in Fig. 1. To date no thiosemicarbazone organometallic complexes have been reported. We now report the first example of an organometallic molybdenum complex containing a thiosemicarbazone ligand.



R = alkyl, aryl etc.

Fig. 1. Metal coordination of thiosemicarbazone.

Experimental

$MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4Me\text{-}2)$ was prepared according to the method of Hayter [2], and the thiosemicarbazones by reaction of the ketone with a solution of thiosemicarbazide in water [3].

Infrared spectra were recorded by nujol mull or KBr disc on a Perkin Elmer 397 infrared spectrophotometer. The elemental analysis for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas). ^1H NMR spectra were recorded on a Perkin Elmer R12 B60 MHz NMR spectrometer (all spectra were calibrated against tetramethylsilane).

$MoCl(CO)_2\{(CH_3)_2CNNHCSNH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)$, (1)

$MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4Me\text{-}2)$ (2.00 g, 0.006 mol) was dissolved in CH_2Cl_2 (25 cm^3) with continuous stirring under a stream of dry nitrogen. To this was added $(CH_3)_2CNNHCSNH_2$ (0.81 g, 0.006 mol). The mixture was left stirring for two hours after which time a yellow precipitate was observed in the solution. This was filtered and dried under vacuum (yield 1.56 g, 70%). *Anal.* $C_{10}H_{16}MoN_3O_2Cl$. Calc.: C, 32.14; H, 4.32; N, 11.24. Found: C, 31.90; H, 4.43; N, 11.50. At room temperature the ^1H NMR spectrum in d_6-dimethyl sulphoxide showed resonances at $\delta = 0.82$ (s, 2H, *CHα*), 1.94 [s, 9H, CH_3 allylic + 2(CH_3-tsc)], 2.82 (s, 2H, *CHβ*), 7.59/8.00 [d(J = 28 Hz), 2H, NH_2] and 10.00 (s, 1H, NH).

$MoCl(CO)_2\{(CH_3\text{-}, CH_3CH_2\text{-})CNNHCSNH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)$, (2)

Following the same procedure $MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4Me\text{-}2)$ (2.00 g, 0.006 mol) was reacted with (CH_3-, CH_3CH_2-) $CNNHCSNH_2$ (0.87 g, 0.006 mol) to afford yellow crystals of $MoCl(CO)_2\{(CH_3\text{-}, CH_3CH_2\text{-})CNNHCSNH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)$ (yield 1.46 g, 63%). *Anal.* $C_{11}H_{18}MoN_3O_2Cl$. Calc.: C, 34.07; H, 4.68; N, 10.83. Found: 33.33; H, 4.55; N, 10.62. At room temperature the ^1H NMR spectrum in d_6-dimethyl sulphoxide showed resonances at $\delta = 0.83$ (s, 2H, CHα), 1.05 [t(J = 7.4 Hz), 3H, *CH₃*–CH₂–tsc], 1.91 (s, 3H, CH_3 allylic), 1.93 (s, 3H, CH_3-tsc), 2.27 [q(J = 7.4 Hz), 2H, CH₃–*CH₂*-tsc], 2.81 (s, 2H, CHβ), 7.49/8.01 [9(J = 30 Hz), 2H, NH_2] and 9.92 (s, 1H, NH).

$MoCl(CO)_2\{(CH_3\text{-}, CH_3CH_2CH_2\text{-})CNNHCSNH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)$, (3)

The same procedure was used as described for complex **1** using $MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4Me\text{-}2)$ (2.00 g, 0.006 mol) and (CH_3-, $CH_3CH_2CH_2$-)-$CNNHCSNH_2$ (0.96 g, 0.006 mol) to afford yellow crystals of $MoCl(CO)_2\{(CH_3\text{-}, CH_3CH_2CH_2\text{-})\text{-}CNNHCSNH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)$ (yield 1.57 g, 65%). *Anal.* $C_{12}H_{20}MoN_3O_2Cl$. Calc.: C, 35,87; H, 5.02; N, 10.46. Found: C, 35.11; H, 4.84; N, 10.16. At room temperature the ^1H NMR spectrum in d_6-dimethyl sulphoxide showed resonances at $\delta = 0.80$ (s, 2H, CHα), 0.84 [t(J = 7.4 Hz), 3H, *CH₃*–CH₂–CH₂tsc], 1.52 [m(J = 7.4 Hz), 2H, CH₃–*CH₂*–CH₂–tsc], 1.89 (s, 3H, CH_3-allylic), 1.93 (s, 3H, CH_3-tsc), 2.18[t(J = 7.4 Hz), 2H, CH₃CH₂*CH₂*-tsc], 2.79 (s, 2H, CHβ), 7.45/7.98 [d(J = 32 Hz), 2H, NH_2] and 9.95 (s, 1H, NH).

Results

Microanalytical and ^1H NMR data (above) together with infrared data (Table I) support the formulation of the complexes $MoCl(CO)_2(tsc)(\eta^3\text{-}C_3H_4Me\text{-}2)$ (tsc = thiosemicarbazone).

Under mild conditions MeCN is readily replaced from $MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4Me\text{-}2)$ by the chelating thiosemicarbazone ligand. X-ray crystal-

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TABLE I. Infrared Data for π-Allyl Thiosemicarbazone Complexes.[a]

Complex	νNH (cm^{-1})	νNH_2 (cm^{-1})	νCO (cm^{-1})	νC=C=C (cm^{-1})	νCH_3(allylic)/CH_2 (cm^{-1})	νCS (cm^{-1})
$MoCl(CO)_2[(CH_3\text{-})_2CNNHCSNH_2]\eta^3C_3H_4Me\text{-}2$	3400–3455s 3250s	1600s 1540s	1840s 1938s	1420–1430w	2920w 2990w	805
$MoCl(CO)_2[CH_3\text{-}, CH_3CH_2\text{-})CNNHCSNH_2]\eta^3C_3H_4Me\text{-}2$	3375s 3305s	1615s 1560s	1850s 1935s	1430s	2850w 2920w	
$MoCl(CO)_2[CH_3\text{-}, CH_3CH_2CH_2\text{-})CNNHCSNH_2]\eta^3C_3H_4Me\text{-}2$	3400b 3250	1615s 1555s	1845s 1930s	1420–1440w/s	2955w 2900w	850w

[a] s = strong, w = weak, b = broad.

lographic studies on some analogous complexes containing bidentate nitrogen [4 - 6] and oxygen [7] ligands have shown that the geometry is essentially octahedral (assuming that the π-allyl group occupies one coordination site). The infrared (Table I) and ^{1}H NMR data for the thiosemicarbazone complexes is consistent with this stereochemistry (Fig. 2). The allyl group is *trans*- to the chloride ion, the two *cis*-carbonyl groups are approximately co-planar with the thiosemicarbazone ligand. The *cis*- carbonyl groups give us two strong bands separated by about 90 cm^{-1}.

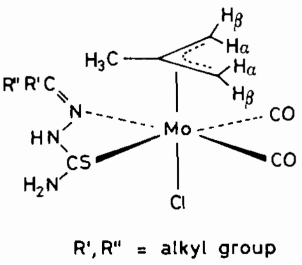

Fig. 2. The geometry of Mo–thiosemicarbazone complexes.

Thiosemicarbazones have been found to be active against influenza [8], protozoa [9], smallpox [10] and certain kinds of tumour [11], and their activity has frequently been thought to be due to their ability to chelate trace metals. The molybdenum complexes above are currently under test for any possible activity.

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