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Preliminary communication

STRUCTURE OF A η^2-DITHIOMETHYLESTER-RUTHENIUM(II) COMPLEX AND FURTHER REACTIONS OF A η^1-DITHIOMETHYLESTER-RUTHENIUM(II) COMPLEX

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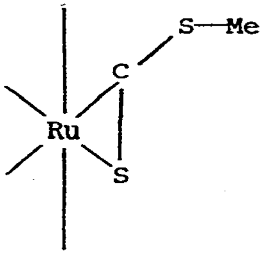
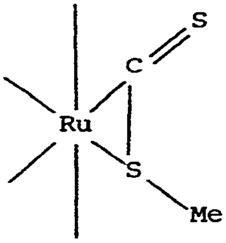
Summary

X-ray crystal structure analysis of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$ reveals that the dithioester function is co-ordinated through carbon and the un-methylated sulphur atom; the chelate ring is opened by introduction of bidentate diethyldithiocarbamate and the resulting monodentate dithioester reacts rapidly with acids producing $[Ru(\eta^2\text{-}S_2CNEt_2)(CS)(CO)(PPh_3)_2]^+$ and with MeI forming $[Ru(\eta^2\text{-}S_2CNEt_2)\{C(SMe)_2\}(CO)(PPh_3)_2]^+$.

We recently described the synthesis of dithiomethylester complexes of ruthenium and osmium by methylation of the CS_2 complexes, $M(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$ (M = Ru or Os)[1]. From the available evidence it was concluded that the dithiomethylester ligands were coordinated through both C and S but it was not possible to distinguish between the two arrangements I and II *viz.*,



I



II

The I.R. spectra of all the η^2-dithioester compounds we have made show bands near 1100 cm^{-1} (the same range as νCS for the precursor η^2-CS_2 complexes) which perhaps supports the intuitively less favourable arrangement II. To settle this question $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$ was selected for crystal structure determination. Yellow crystals from CH_2Cl_2-EtOH-cyclo-C_6H_{12} are monoclinic, a = 12.2982(8), b = 23.171(2), c = 14.781(2), β = 100.975(1), Z = 4, space group $P2_1/n$. Intensity data were collected on a Hilger-Watts 4-circle diffractometer using Ni-filtered Cu-K_α radiation. A total of 3049 unique reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier syntheses and has been partially refined by least squares techniques to R = 0.097.

The geometry of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+$ is depicted in the Figure and confirms that the dithioester group has arrangement I. The two C-S bond lengths are closely similar to one another and also to the C-S bond lengths in a η^2-thiocarboxamide Rh(III) complex[2]. It has been argued[3] that the dithioester ligand will have less tendency to be bidentate than the thiocarboxamide ligand and in keeping with this suggestion the chelate is readily opened through co-ordination of suitable anions. Cyanide ion opens the ring producing the neutral compound $Ru(CN)(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$. This molecule

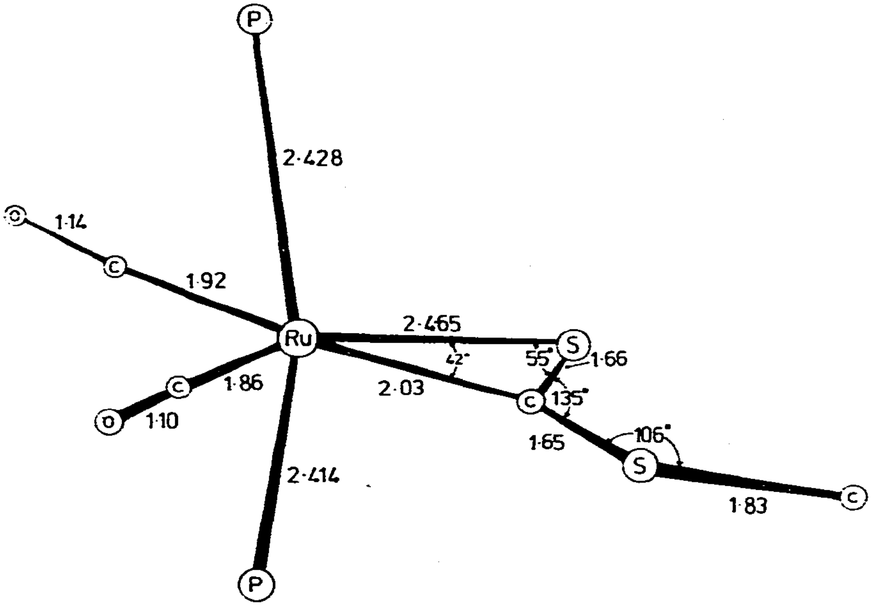


Figure. Structure of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+$

readily loses carbon monoxide giving $Ru(CN)(\eta^2\text{-}CS_2Me)(CO)(PPh_3)_2$, an analogue of the previously described halide complexes, $RuX(\eta^2\text{-}CS_2Me)(CO)(PPh_3)_2$[1], for which the dicarbonyl intermediates could not be isolated. Acetate and diethyldithiocarbamate chelate to the metal, opening the ring and expelling carbon monoxide (see Scheme). It is interesting that the corresponding thiocarboxamide cation, $[Ru\{\eta^2\text{-}CSN(p\text{-tolyl})Me\}(CO)_2(PPh_3)_2]^+$, reacts with diethyldithiocarbamate with both carbonyl and phosphine loss forming $[Ru\{\eta^2\text{-}CSN(p\text{-tolyl}\}Me)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)]$, the thiocarboxamide ligand remaining bidentate[4]. While the bidentate dithioester complexes react only slowly with acids to form thiocarbonyl complexes[1] the monodentate complexes react rapidly.

TABLE INFRARED DATA FOR NEW COMPLEXES

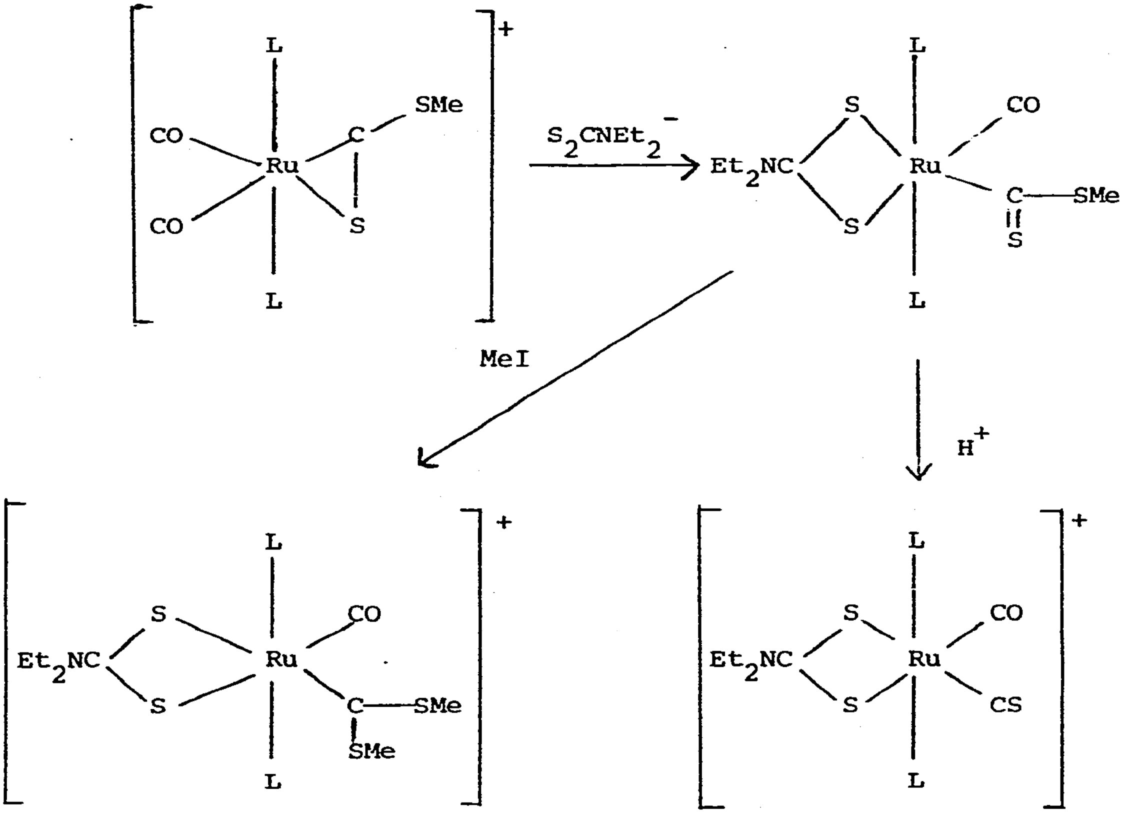
Compound[a]	CO (cm^{-1})[b]	νCS (cm^{-1})
$[Ru(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]ClO_4$	2055, 1995 (br)	1115[d]
$Ru(CN)(\eta^1-CS_2Me)(CO)_2(PPh_3)_2$	2060, 2000	980
$Ru(CN)(\eta^2-CS_2Me)(CO)(PPh_3)_2$	1930	1090[c]
$Ru(\eta^2-O_2CCH_3)(\eta^1-CS_2Me)(CO)(PPh_3)_2$	1942	1013
$Ru(\eta^2-S_2CNEt_2)(\eta^1-CS_2Me)(CO)(PPh_3)_2$	1930	998
$[Ru(\eta^2-S_2CNEt_2)(CS)(CO)(PPh_3)_2]BF_4$	2040	1310
$[Ru(\eta^2-S_2CNEt_2)\{C(SMe)_2\}(CO)(PPh_3)_2]I$	1945	-

a) All compounds have satisfactory elemental analyses.

b) Measured as nujol mulls.

c) Band partially obscured by phosphine band at 1095 cm^{-1}.

d) Band obscured by perchlorate band at 1090 cm^{-1}, value quoted is for iodide salt.



Scheme. L = PPh_3.

Recrystallisation of $Ru(\eta^2-S_2CNEt_2)(\eta^1-CS_2Me)(CO)(PPh_3)_2$ in the presence of a few drops of tetrafluoroboric acid produces the thiocarbonyl cation, $[Ru(\eta^2-S_2CNEt_2)(CS)(CO)(PPh_3)_2]^+$. Likewise, reaction with MeI is fast to give the dithiocarbene cation $[Ru(\eta^2-S_2CNEt_2)\{C(SMe)_2\}(CO)(PPh_3)_2]^+$.

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