

Preliminary communication

NEUTRAL AND CATIONIC DITHIOCARBONYL COMPLEXES OF OSMIUM(II)

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Summary

$\text{Os}(\eta^2\text{-CS}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$ and $[\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ have been derived from $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ and the dithioester-complex reacts with acids to give $\text{OsX}_2(\text{CS})_2(\text{PPh}_3)_2$ or, after introduction of diethyldithiocarbamate, to give the dithiocarbonyl cation $[\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})_2(\text{PPh}_3)_2]^+$. Reaction of this last species with borohydride gives a thioformyl complex, $\text{Os}(\text{CHS})(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})(\text{PPh}_3)_2$.

Although a rapidly increasing number of thiocarbonyl complexes is being reported these all contain just one thiocarbonyl ligand. Some years ago $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CS})_2(\text{CO})$ was reported¹ but in only 20% yield and both $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CS})_3$ and $\text{Ni}(\text{CS})_4$ ² have been detected by spectroscopic methods only. By utilising the zerovalent thiocarbonyl compound, $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ ³, in the previously reported thiocarbonyl synthesis⁴ (via methylation of a $\eta^2\text{-CS}_2$ complex and acid hydrolysis of the resulting dithioester complex), we have been able to systematically and in high yield introduce a second thiocarbonyl ligand into several osmium complexes.

$\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ reacts with CS_2 in benzene solution to give golden-yellow crystals of $\text{Os}(\eta^2\text{-CS}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$ in quantitative yield. Like $\text{Os}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2$ ⁴ this is rapidly methylated by $\text{CF}_3\text{SO}_3\text{CH}_3$ to $\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2\text{CF}_3\text{SO}_3$. Reaction of this salt, or of $\text{Os}(\eta^2\text{-CS}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$ directly with aqueous HX (X = Cl or Br) in benzene-ethanol (2:1) under reflux results in loss of CO and MeSH (or H₂S) and quantitative formation of the dithiocarbonyl complexes $\text{OsX}_2(\text{CS})_2(\text{PPh}_3)_2$. The pale yellow

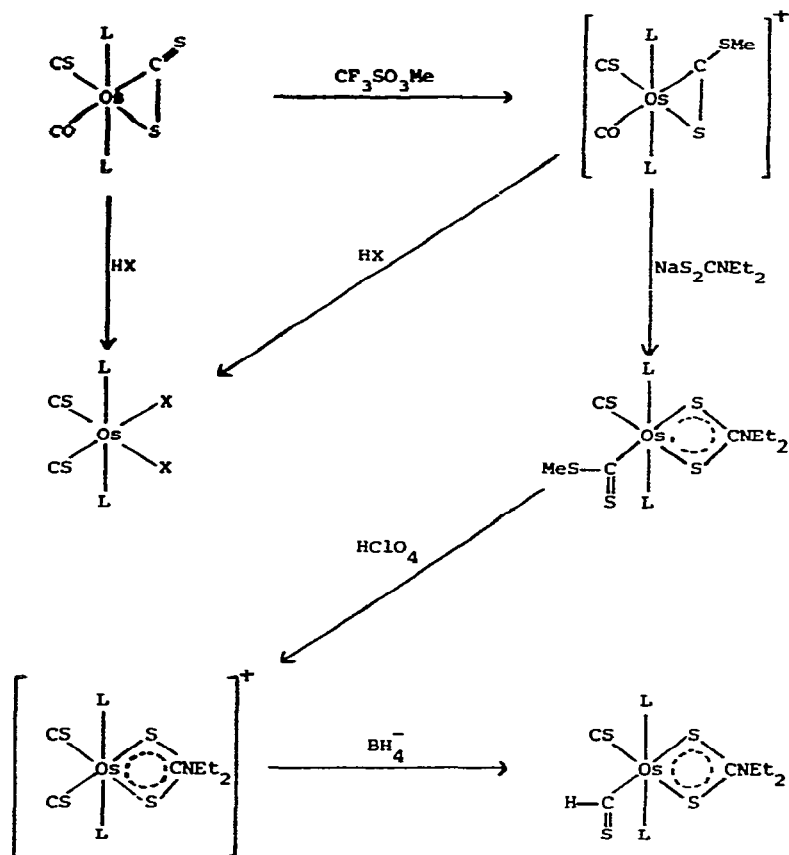
TABLE I. R DATA FOR OSMIUM THIOCARBONYL COMPLEXES

Compound ^a	$\nu_{CS}(\text{cm}^{-1})$, ^b	$\nu_{CO}(\text{cm}^{-1})$	Other bands (cm^{-1})
$\text{Os}(\eta^2\text{-CS}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$	1280	2020, 1995, 1975, 1965 ^c	ν_{CS_2} , 1112(s), 664(m)
$[\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]$	1300	2070, 2040, 1997 ^c	
$\text{OsCl}_2(\text{CS})_2(\text{PPh}_3)_2$	1370, 1260		
$\text{OsBr}_2(\text{CS})_2(\text{PPh}_3)_2$	1360, 1260		
$\text{Os}(\eta^1\text{-S}_2\text{CNET}_2)(\eta^1\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2$	1290	2030	$\nu_{CS_2\text{Me}}$, 1012(m)
$\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\eta^1\text{-CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$	1268		$\nu_{CS_2\text{Me}}$, 970(m)
$[\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})_2(\text{PPh}_3)_2][\text{ClO}_4]$	1350, 1265		
$\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CHS})(\text{CS})(\text{PPh}_3)_2$	1270		ν_{CHS} , 978(m)

^a All compounds have satisfactory elemental analyses.

^b Nujol mulls, all ν_{CS} and ν_{CO} absorptions are strong.

^c The structuring of the ν_{CO} band may be due to solid-state splitting of the various isomer possibilities or both.



Scheme L = PPh_3 , X = Cl, Br

complexes have a *cis* arrangement of the thiocarbonyl ligands as indicated by the appearance of two strong ν_{CS} bands (see Table).

The bidentate dithioester ligand in $[\text{Os}(\eta^2\text{-CS}_2\text{Me})(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+$ is opened by introduction of the diethyldithiocarbamate ligand forming $\text{Os}(\eta^1\text{-CS}_2\text{Me})(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})(\text{PPh}_3)_2$ via an isolatable intermediate $\text{Os}(\eta^1\text{-CS}_2\text{Me})(\eta^1\text{-S}_2\text{CNET}_2)(\text{CS})(\text{CO})(\text{PPh}_3)_2$. By comparison with $\eta^2\text{-CS}_2\text{Me}$ ligands, the $\eta^1\text{-CS}_2\text{Me}$ ligands are rapidly cleaved by reaction with acids and $\text{Os}(\eta^1\text{-CS}_2\text{Me})(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})(\text{PPh}_3)_2$ with HClO_4 gives the dithiocarbonyl cation $[\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})_2(\text{PPh}_3)_2]^+$, where the CS ligands are again *cis* (see Table).

Thiocarbonyl cations are interesting species in that opportunities for nucleophilic attack at the CS ligand will be greater than in neutral species. In illustration of this we have found that $[\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CS})_2(\text{PPh}_3)_2]^+$ reacts with NaBH_4 forming the stable thioformyl complex, $\text{Os}(\eta^2\text{-S}_2\text{CNET}_2)(\text{CHS})(\text{CS})(\text{PPh}_3)_2$. (^1H N.M.R. (CDCl_3), τ , -7.78, triplet, $^3\text{J}(\text{H-P}) = 2\text{Hz}$). An osmium thioformyl $\text{Os}(\text{CHS})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ has been previously prepared⁵ but by a migratory-insertion reaction rather than by direct hydride attack at CS.

References

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