

Preliminary Communication

REARRANGEMENT OF σ -ARYL-THIOCARBONYL COMPLEXES TO *dihapto*-THIOACYL COMPLEXES.
 STRUCTURE OF $\text{Os}[\eta^2\text{-C(S)R}](\eta^1\text{-O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$

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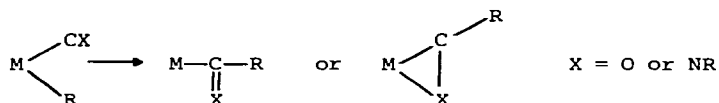
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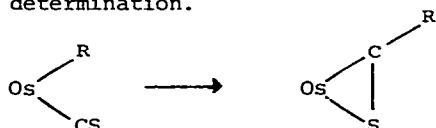
SUMMARY

Octahedral osmium complexes of the type $\text{OsRX}(\text{CS})\text{L}(\text{PPh}_3)_2$ ($\text{R} = p\text{-tolyl}$; $\text{X} = \text{Cl}$, Br , I or O_2CCF_3 ; $\text{L} = \text{CO}$ or CNR), which have adjacent R and CS ligands, undergo rearrangement to *dihapto*-thioacyl complexes $\text{Os}[\eta^2\text{-C(S)R}]\text{XL}(\text{PPh}_3)_2$, and the X-ray structure determination of a representative example $\text{Os}[\eta^2\text{-C(S)R}](\eta^1\text{-O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$, is reported.

Migratory-insertion reactions involving σ -bound organic groups and either carbonyl or isocyanide ligands are an established feature of organometallic chemistry:



The resulting acyl or iminoacyl ligands are usually *monohapto*- (the rearrangement being accompanied by uptake of an additional ligand), but several examples of *dihapto*-arrangements for both acyl (ref. 1-3) and iminoacyl (ref. 4-6) have recently been reported. For the thiocarbonyl ligand no corresponding insertion reaction has been reported, nor have any suitable σ -alkyl or σ -aryl thiocarbonyl precursors been described. We have prepared several compounds of the type $\text{OsRX}(\text{CS})\text{L}(\text{PPh}_3)_2$ and observed rearrangement to complexes containing thioacyl ligands for which a *dihapto*-arrangement has been verified by X-ray structure determination.



The *p*-tolyl ligand was introduced into a thiocarbonyl complex using di-*p*-tolyl mercury (ref. 3). $\text{OsHCl}(\text{CS})(\text{PPh}_3)_3$ (ref. 7) reacts with HgR_2 in toluene

under reflux to deposit Hg and afford a deep crimson solution from which crimson crystals of $\text{OsRCl}(\text{CS})(\text{PPh}_3)_2$ can be isolated (ca. 90%). The highly-coloured solution of this five co-ordinate complex lightens rapidly on addition of CO, CNR, or the potentially bidentate anion trifluoroacetate, forming respectively colourless $\text{OsRCl}(\text{CS})(\text{CO})(\text{PPh}_3)_2$, $\text{OsRCl}(\text{CS})(\text{CNR})(\text{PPh}_3)_2$ or yellow $\text{OsR}(\eta^2\text{-O}_2\text{CCF}_3)(\text{CS})(\text{PPh}_3)_2$. The last compound reacts with CO forming colourless $\text{OsR}(\eta^1\text{-O}_2\text{CCF}_3)(\text{CS})(\text{CO})(\text{PPh}_3)_2$ (see scheme). Solutions of these complexes, $\text{OsRX}(\text{CS})\text{L}(\text{PPh}_3)_2$, in CH_2Cl_2 , C_6H_6 or C_7H_8 turn red at rates varying from minutes at room temperature to hours at reflux depending upon X and L. The red products have elemental analyses identical to those of the colourless precursors and are formulated as *dihapto*-thioacyl complexes. I.R. data (see Table) are consistent with this formulation and a complete X-ray structure determination of $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}](\eta^1\text{-O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$ provides confirmation. Crystals of $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}]\text{Br}(\text{CO})(\text{PPh}_3)_2$ proved unsatisfactory for X-ray analysis, but suitable crystals of the trifluoroacetate were eventually obtained.

The burgundy-coloured crystals are orthorhombic, $a = 11.584(1)$, $b = 19.184(2)$, $c = 18.900(2)$ Å $Z = 4$, space group $P2_12_12_1$. The structure has been deduced from 2880 observed reflections [$I > 3 \sigma(I)$] collected on a Hilger-Watts 4-circle diffractometer with copper $K\alpha$ radiation. At the present stage of refinement with only the Os, S and P atoms assigned anisotropic thermal parameters, R is 0.073.

The geometry of the monomeric complex is depicted in the figure. The Os atom is bonded in an approximately trigonal bipyramidal arrangement to two triphenylphosphine ligands, one CO, a *monohapto*-trifluoroacetate, and a *dihapto*-thioacyl.

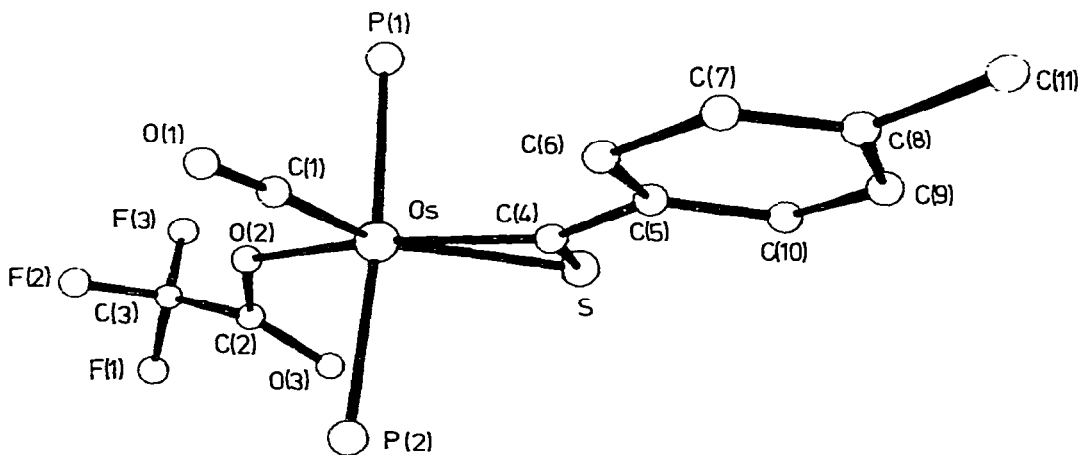
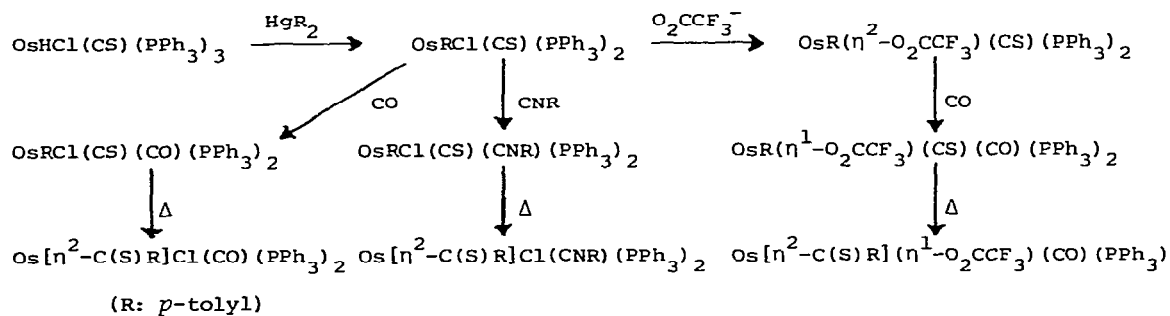


Figure. Geometry of $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}](\eta^1\text{-O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$

The plane defined by Os,C(4),S is tilted 5.6° to that defined by Os,C(1),O(2). The Os-P and Os-CO bond lengths of 2.412, 2.416(2), 1.86(2) Å are normal. The Os-O(2) bond is 2.22(2) Å.

The *dihapto*-thioacyl is characterised by distances Os-S 2.510(8), Os-C(4) 1.97(4), C(4)-S 1.76(4), C(4)-C(5) 1.48(4) Å and angles S-Os-C(4) $44.2(11)^\circ$, Os-S-C(4) $51.4(12)^\circ$, Os-C(4)-S $84.5(3)^\circ$, Os-C(4)-C(5) $149.1(8)^\circ$, S-C(4)-C(5) $124.7(10)^\circ$. There are few other structures with which these can be directly compared, but we can note that the Os-C distance is shorter than values observed for Os-C bonds of bond order 1 (ref. 8) which range from 2.06 to 2.16 Å, the Os-S distance is long compared with values of 2.426, 2.442(4) Å for the methylated disulphide ligand in $[\text{Os}(\eta^2\text{S}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ (ref. 9) and the C(4)-S bond is quite long although the standard deviations are such as to preclude definitive statements at this time.



Scheme

In an effort to convert the $\eta^2\text{-C}(\text{S})\text{R}$ ligand to an $\eta^1\text{-C}(\text{S})\text{R}$ ligand $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was reacted with the powerful chelating ligand diethyldithiocarbamate. The surprising result was the retention of the *dihapto*-thioacyl and displacement of a phosphine ligand to give $\text{Os}[\eta^2\text{-C}(\text{S})\text{R}](\eta^2\text{-S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)$. The sulphur atom of the thioacyl is slowly alkylated by methyl triflate providing a route to various thiocarbene complexes, a typical example of which is $\text{OsCl}_2[\text{C}(\text{SMe})\text{R}](\text{CNR})(\text{PPh}_3)_2$.

TABLE

I.R. Data^a for osmium thiocarbonyl derivatives

Compound ^b	Colour	VCS	VCO	VCN	Other I.R. bands
OsRCl(CS)(PPh ₃) ₂	red	1290			
OsPCl(CS)(CO)(PPh ₃) ₂	colourless	1300	2055		
OsRCl(CS)(CNR)(PPh ₃) ₂	colourless	1290		2142	
OsR(η ² -O ₂ CCF ₃)(CS)(PPh ₃) ₂	yellow	1290			1603(η ² -O ₂ CCF ₃)
OsR(η ¹ -O ₂ CCF ₃)(CS)(CO)(PPh ₃) ₂	colourless	1300	2035		1690(η ¹ -O ₂ CCF ₃)
Os[η ² -C(S)R]Cl(CO)(PPh ₃) ₂	red		1902		
Os[η ² -C(S)R]Cl(CNR)(PPh ₃) ₂	red			1940 ^c	
Os[η ² -C(S)R](η ¹ -O ₂ CCF ₃)(CO)(PPh ₃) ₂	red		1910		1691(η ¹ -O ₂ CCF ₃)
Os[η ² -C(S)R](η ² -S ₂ CNEt ₂)(CO)(PPh ₃)	red		1893		
OSCl ₂ [C(SMe)R](CNR)(PPh ₃) ₂	red			2095, 2060	

^a cm⁻¹, measured as nujol mulls.^b All compounds have satisfactory elemental analyses and ¹H NMR data consistent with the formulations given.^c very broad band.

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