

Preliminary communication

HYDRIDO-THIOCARBONYL COMPLEXES AS PRECURSORS OF LOW-VALENT
 THIOCARBONYL COMPLEXES

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Summary

The hydrido-thiocarbonyl osmium(II) complexes

$\text{OsH}_2(\text{CS})(\text{PPh}_3)_3$, $\text{OsHCl}(\text{CS})(\text{PPh}_3)_3$, $\text{OsH}(\text{OCIO}_3)(\text{CS})(\text{PPh}_3)_3$,
 $\text{OsHCl}(\text{CS})(\text{CNR})(\text{PPh}_3)_2$ and $[\text{OsH}(\text{CS})(\text{CO})(\text{PPh}_3)_3]^+$, (R = *p*-tolyl),
 have been derived from $\text{OsCl}_2(\text{CS})(\text{PPh}_3)_3$ and $[\text{OsH}(\text{CS})(\text{CO})(\text{PPh}_3)_3]^+$,
 the latter can be deprotonated to give the zerovalent complex,
 $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3^-$.

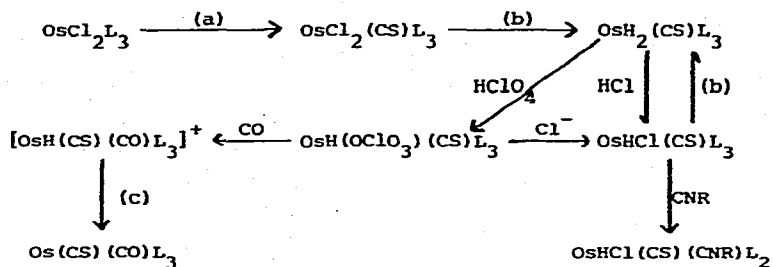
The limited number of synthetic routes available for the preparation of thiocarbonyl complexes has restricted development of this area of chemistry and in particular compounds in which thiocarbonyl ligands occur in combination with hydrido-, alkyl-, or σ -bound aryl-ligands are rare or unknown. Exceptions are provided by $[\text{W}(\text{CS})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ which results from protonation of $\text{W}(\text{CS})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$, and the iridium compounds $\text{IrH}(\text{CS})(\text{PPh}_3)_3$ and $[\text{IrH}_2(\text{CS})(\text{CO})\{\text{P}(\text{c-hexyl})_3\}_2]^+$. In order to explore the possibility of hydride migration to the thiocarbonyl ligand⁴ and also to develop synthetic routes to low-valent thiocarbonyl complexes, we have prepared and characterised various hydrido-thiocarbonyl complexes of osmium(II) and we describe these here.

Treatment of $\text{OsCl}_2(\text{PPh}_3)_3$ ⁵ with CS_2 and excess PPh_3 in benzene under reflux affords $\text{OsCl}_2(\text{CS})(\text{PPh}_3)_3$ in high yield (see Scheme). This reacts with NaOH and 2-methoxyethanol under reflux to produce $\text{OsH}_2(\text{CS})(\text{PPh}_3)_3$ which has the same stereochemistry as the well-known CO analogue $\text{OsH}_2(\text{CO})(\text{PPh}_3)_3$ (see Table for I.R. and N.M.R. data). Reaction of this dihydride with strong acids results in cleavage of one hydride ligand and formation of $\text{OsHX}(\text{CS})(\text{PPh}_3)_3$. One phosphine ligand in $\text{OsHX}(\text{CS})(\text{PPh}_3)_3$ is labile and readily displaced by other

TABLE I. R. AND N. M. R. DATA FOR THIOCARBONYL COMPLEXES

Compound ^a	$\nu_{\text{CO}}(\text{cm}^{-1})$, ^b	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{OS}}(\text{cm}^{-1})$	Chemical Shift (τ), OS-H
$\text{OsCl}_2(\text{CS})(\text{PPh}_3)_3$		1290			
$\text{OsH}_2(\text{CS})(\text{PPh}_3)_3$		1233	2070, 1895		d
$\text{OsHCl}(\text{CS})(\text{PPh}_3)_3$		1280	2100		15.5, $^2J(\text{H-P trans})$, 93Hz; $^2J(\text{H-P cis})$, 24.5Hz.
$\text{OsH}(\text{OCIO}_3)(\text{CS})(\text{PPh}_3)_3$		1295	2070		15.2, $^2J(\text{H-P trans})$, 82Hz; $^2J(\text{H-P cis})$, 24.5Hz.
$\text{OsHCl}(\text{CS})(\text{CNR}(\text{PPh}_3)_2)$		1280	2150	1955	12.75, $^2J(\text{H-P})$, 19Hz.
$[\text{OsH}(\text{CS})(\text{CO})(\text{PPh}_3)_3]^+$	2045	1310			17.9, $^2J(\text{H-P trans})$, 30Hz; $^2J(\text{H-P cis})$, 22Hz.
$\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$	1890, 1870	1230			

a) Satisfactory elemental analyses obtained for all compounds. b) Measured as nujol mulls. c) In CDCl_3 solution.
d) ^1H NMR spectrum typical of $\text{M}_2\text{X}(\text{PPh}_3)_3$ with meridional phosphine ligands and cis hydride ligands.



SCHEME: L = PPh₃, R = *p*-tolyl

(a) CS₂ + PPh₃ in benzene; (b) NaOH in 2-methoxyethanol;

(c) NaOH in MeOH.

neutral ligands, e.g. CNR to give OsHX(CS)(CNR)(PPh₃)₂.

For X = ClO₄, OsHX(CS)(PPh₃)₃ reacts with CO to provide a cationic hydrido-complex, [OsH(CS)(CO)(PPh₃)₃]ClO₄. This cation is an ideal precursor of a tris-phosphine-substituted zerovalent complex and is readily deprotonated to Os(CS)(CO)(PPh₃)₃ which is formed as red-brown crystals. This complex, with three bulky phosphine ligands can provide, through phosphine dissociation, the reactive, co-ordinatively unsaturated entity, Os(CS)(CO)(PPh₃)₂, and indeed reaction with C₂H₄ or PhC≡CPh leads to the adducts Os(C₂H₄)(CS)(CO)(PPh₃)₂ and Os(PhC≡CPh)(CS)(CO)(PPh₃)₂, respectively. The further chemistry of these and other zerovalent complexes and adducts is being studied.

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