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Co-ordinated Thioformaldehyde Monomer. Synthesis and Reactions of $[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$

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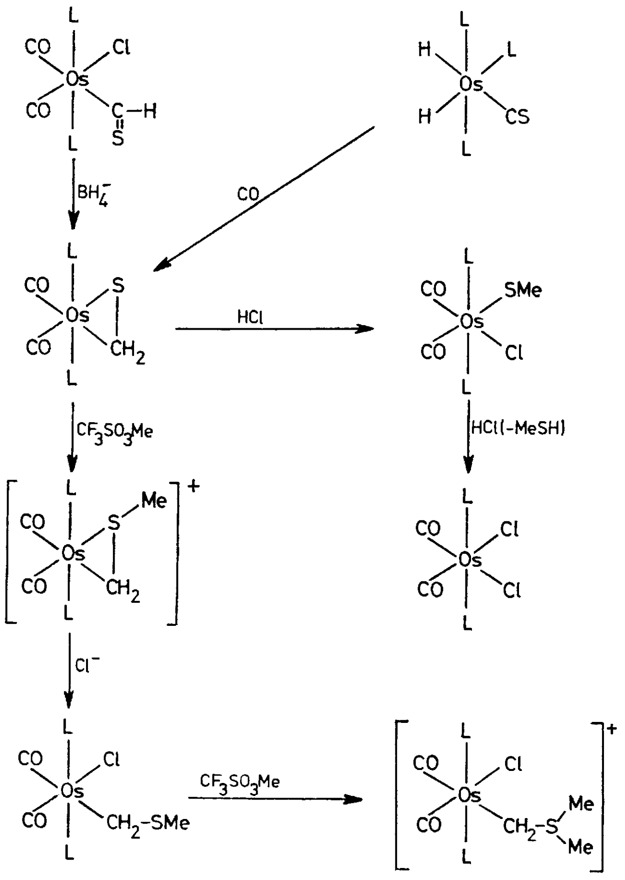
Summary A stable complex of the unstable intermediate, thioformaldehyde, results from reaction of the thioformyl complex $[Os(CHS)Cl(CO)_2(PPh_3)_2]$ with $NaBH_4$; $[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$ forms methanethiolato-derivatives with acids but is alkylated on sulphur forming methylthiomethyl- and dimethylsulphonium methylide complexes.

ALTHOUGH several thioketone complexes are known in which the ligand is bound either through sulphur[1] or through both sulphur and carbon,[2] no stable complexes of monomeric thioaldehydes or of thioformaldehyde have been described. Pure thioformaldehyde has been generated by the high temperature decomposition of 1,2,4-trithiolan[3] or methylsulphenyl chloride[4] and has been established as a constituent of the interstellar medium.[5]

We recently observed[6] that the thiocarbonyl ligand in $[IrH(CS)(PPh_3)_3]$ was completely reduced by hydrogen to the methanethiolato-ligand and suggested that likely intermediates in this process were thioformyl and thioformaldehyde complexes, corresponding to the transfer of one and two hydride ligands to the thiocarbonyl ligand, respectively. Examples of stable thioformyl complexes are now known[6,7] and we describe here the preparation of a compound in which thioformaldehyde monomer functions as a *dihapto*-ligand.

Two possible synthetic approaches were considered: (i) starting with $[OsH_2(CS)(PPh_3)_3]$[8] and inducing transfer of both hydrides through reaction with CO and (ii) reaction of the previously characterised thioformyl complex, $[Os(CHS)Cl(CO)_2(PPh_3)_2]$,[6,7] with $NaBH_4$ (see Scheme). Method (ii) produces $[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$ in high yield but method (i) requires vigorous conditions owing to the inertness of $[OsH_2(CS)(PPh_3)_3]$ and, while $[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$ was



SCHEME. L = PPh_3.

detected amongst the products, the major product was of low solubility and may have thioformaldehyde as a bridging ligand. Complex $[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$ forms colourless crystals; the thioformaldehyde protons in the ^1H n.m.r. spectrum ($CDCl_3$) appear as a triplet at τ 9·1 [^3J(H–P) 4·6 Hz] (see Table for i.r. data). Reaction with acids (probably *via* protonation at the metal) is rapid to yield methanethiolato-compounds and in a further (slower) reaction, methanethiol is liberated (see Scheme). Thus stable examples are now available for each of the intermediates postulated in the hydrogenation of CS in $[IrH(CS)(PPh_3)_3]$.[6]

TABLE. I.r. data[a] for osmium complexes.[b]

Complex	ν_{CO}/cm^{-1}
$[Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2]$	1985, 1915
$[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]^+$	2035, 1954
$[Os(\eta^1\text{-}CH_2SMe)Cl(CO)_2(PPh_3)_2]$	2025, 2005, 1952, 1934
$[Os(\eta^1\text{-}CH_2SMe_2)Cl(CO)_2(PPh_3)_2]^+$	2035, 1957
$[Os(SMe)Cl(CO)_2(PPh_3)_2]$	2038, 1950

[a] Nujol mulls. [b] All compounds have satisfactory elemental analyses and ^1H n.m.r. spectra consistent with the formulations given. Cations characterised as trifluoromethanesulphonate salts.

In contrast, alkylation with methyl trifluoromethanesulphonate occurs at the sulphur atom to yield first a *dihapto*-methylthiomethyl complex, $[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]^+$. Co-ordinating anions bring about ring-opening, forming, *e.g.* $[Os(\eta^1\text{-}CH_2SMe)Cl(CO)_2(PPh_3)_2]$. Further methylation produces the dimethylsulphonium methylide complex, $[OsCl(\eta^1\text{-}CH_2SMe_2)(CO_2)(PPh_3)_2]^+$. Palladium and platinum complexes of these ligands have been derived from oxidative addition of $ClCH_2SMe$ to $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$, respectively, followed by methylation.[9]

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