Thioformyl and Formyl Complexes of Osmium(II)

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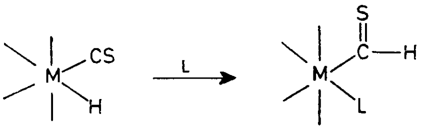
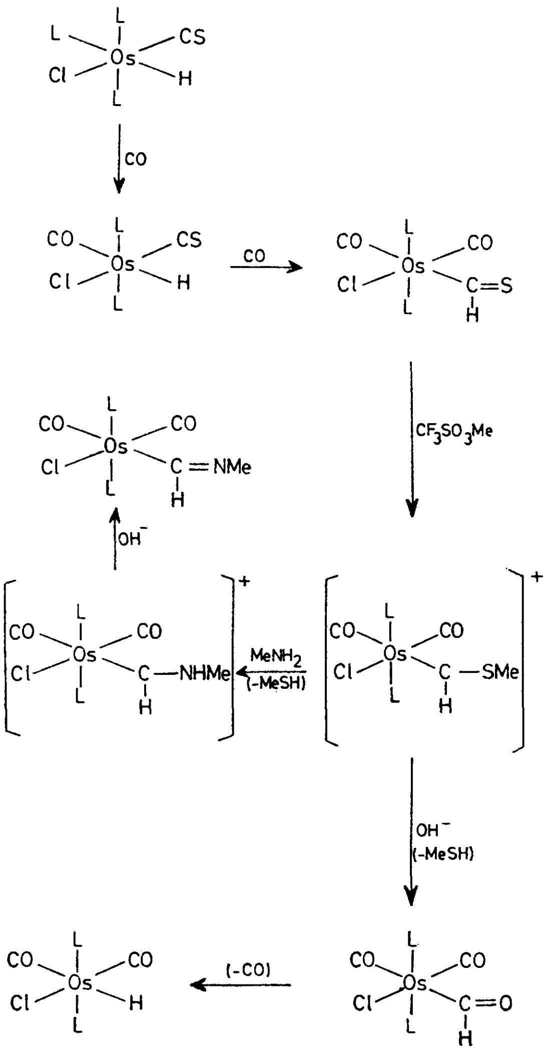
Summary $[OsHCl(CS)(PPh_3)_3]$ reacts with CO giving a blue thioformyl complex $[Os(CHS)Cl(CO)_2(PPh_3)_2]$; this is readily methylated on sulphur forming a secondary thiocarbene complex which upon hydrolysis yields a formyl complex, $[Os(CHO)Cl(CO)_2(PPh_3)_2]$.

Formyl complexes resulting from interligand reaction between hydride and carbonyl ligands have been proposed as intermediates to explain the unusual lability of transition metal carbonyl hydrides.[1] However, the first isolated and characterised formyl complex was prepared not in this way but by formylation of $[Fe(CO)_4]^{2-}$ with acetic formic anhydride.[2] An alternative synthesis of the same complex, $[Fe(CHO)(CO)_4]^-$ is from $[Fe(CO)_5]$ and trialkoxyborohydrides.[3] Hydride transfer from metal to ligand has been achieved for co-ordinated isocyanide[4] and the nitrosyl ligand,[5] and it seemed likely that by preparing a hydridothiocarbonyl complex of appropriate stereochemistry it would be possible to induce a migratory-insertion reaction to produce a thioformyl group.



To this end we have prepared, by a multi-step synthesis,[6] $[OsHCl(CS)(PPh_3)_3]$. The stereochemistry of this molecule follows from the ^1H n.m.r. spectrum and is as depicted in the Scheme. Hydride and thiocarbonyl are mutually *cis* as required for migration. Reaction with CO in benzene first



SCHEME: L = PPh_3

replaces the labile phosphine *trans* to hydride and further reaction gives a blue solution from which can be isolated blue crystals of the thioformyl complex $[Os(CHS)Cl(CO)_2(PPh_3)_2]$.

The thioformyl proton, in the ^1H n.m.r. spectrum, appears at the very low-field position of τ −6·93 [t, ^3J(P–H) 2·2 Hz]. Alkylation of the sulphur atom by methyl trifluoromethanesulphonate is rapid, giving a sulphur-substituted secondary carbene complex. This cation is hydrolysed by water to a formyl complex, $[Os(CHO)Cl(CO)_2(PPh_3)_2]$, and aminolysis gives secondary amino-carbene complexes, *e.g.* $[OsCl(CHNHMe)(CO)_2(PPh_3)_2]^+$ with $MeNH_2$. The formyl complex is characterised by ν_{CO} at 1610s cm^{-1}, and ν_{CH} at 2540w and 2620w cm^{-1}. Solutions of this complex are unstable at room temperature evolving CO and forming $[OsHCl(CO)_2(PPh_3)_2]$. This same formyl complex may be involved in the fast reaction of $[Os(CO)_3(PPh_3)_2]$ with HCl which gives $[OsCl_2(CO)_2(PPh_3)_2]$. We had previously suggested[7] that this reaction proceeded *via* $[OsHCl(CO)_2(PPh_3)_2]$ but this hydride is extremely inert towards HCl and cannot, therefore, be involved.

TABLE. I.r. data (in cm^{-1})[a] for osmium complexes[b]

	ν_{CO}	ν_{CS}	ν_{CN}
$[OsHCl(CS)(PPh_3)_3]$	—	1280	—
$[OsHCl(CS)(CO)(PPh_3)_2]$ ..	2050	1295	—
$[Os(CHS)Cl(CO)_2(PPh_3)_2]$ ..	2050, 1970	1010	—
$[OsCl(CHSMe)(CO)_2(PPh_3)_2]^+$	2050, 1996	965	—
$[Os(CHO)Cl(CO)_2(PPh_3)_2]$[c] ..	2020, 1960	—	—
$[OsCl(CHNHMe)(CO)_2(PPh_3)_2]^+$	2060, 1982	—	1610
$[OsCl(CHNMe)(CO)_2(PPh_3)_2]$	2030, 1953	—	1589

[a] Nujol mulls. [b] All compounds have satisfactory elemental analyses and ^1H n.m.r. spectra consistent with the formulations given. Cations characterised as perchlorate salts. [c] ν_{CO} (formyl) 1610 cm^{-1}.

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