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Preliminary communication

Synthesis of Low-valent Thiocarbonyl Complexes via 1,2-Elimination of Methylthiol from cis-Metal-hydrido-dithiomethylester Complexes. $Os(CS)(CO)_2(PPh_3)_2$ and $IrCl(CS)(PPh_3)_2$

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SUMMARY

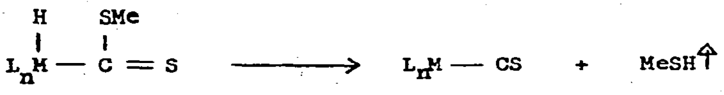
$[Os(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+$ and $[Ir(\eta^2\text{-}CS_2Me)Cl(CO)(PPh_3)_2]^+$ react with $NaBH_4$ giving $OsH(CS_2Me)(CO)_2(PPh_3)_2$ and $IrH(CS_2Me)Cl(CO)(PPh_3)_2$ respectively; These compounds contain mutually cis hydride and η^1-dithiomethylester ligands and upon heating undergo 1,2-elimination of MeSH producing $Os(CS)(CO)_2(PPh_3)_2$ and $IrCl(CS)(PPh_3)_2$.

We have described the synthesis of thiocarbonyl complexes of ruthenium(II) and osmium(II) by acid cleavage of dithiomethylester ligands,[1] e.g. $RuCl(CS_2Me)(CO)(PPh_3)_2 + HCl \longrightarrow RuCl_2(CS)(CO)(PPh_3)_2 + MeSH$. It occurred to us that by incorporating a hydride ligand into a complex containing a dithiomethylester ligand it might be possible to bring about 1,2-elimination of methylthiol with simultaneous production of a thiocarbonyl ligand, *viz.*,

Table I.R. [a] (cm^{-1}) AND ^1H N.M.R. [b] (τ) DATA FOR OSMIUM AND IRIDIUM COMPLEXES

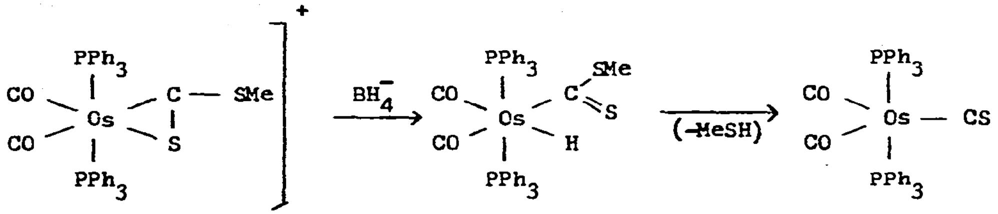
Compound [c]	νCO	νCS	Chemical Shifts
$[Os(CS_2Me)(CO)_2(PPh_3)_2]^+$	2050, 1995	1070	7.76s (SMe)
$OsH(CS_2Me)(CO)_2(PPh_3)_2$	2055, 1970	1005 [d]	14.35t J(H-P) = 20 Hz (Os-H); 8.57s (SMe)
$Os(CS)(CO)_2(PPh_3)_2$	1955, 1890	1230	
$[Ir(CS_2Me)Cl(CO)(PPh_3)_2]^+$	2020	1153	7.84s (SMe)
$IrH(CS_2Me)Cl(CO)(PPh_3)_2$	2040	985 [d]	22.0t J(H-P) = 14 Hz (Ir-H); 8.0s (SMe)
$IrCl(CS)(PPh_3)_2$		1332	

[a] Nujol mulls [b] $CDCl_3$ solution [c] All compounds reported have satisfactory elemental analyses. Cations characterised as both perchlorate and trifluoromethylsulphonate salts. [d] Medium intensity. All other bands strong.



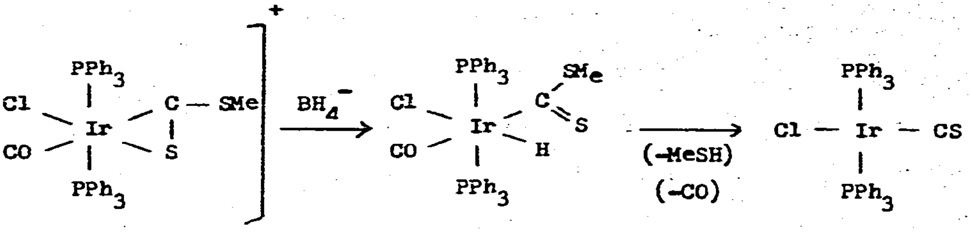
$$L_nM(H)\text{—}C(SMe){=}S \longrightarrow L_nM\text{—}CS + MeSH\uparrow$$

An advantage of such a reaction is that it is accompanied by a reduction of the metal oxidation state by two units. Thus an osmium(II) hydridodithiomethylester complex should yield an osmium(0) thiocarbonyl complex. To test this idea we reacted the cation $[Os(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+$ (ref. 1) with $NaBH_4$ so producing $OsH(CS_2Me)(CO)_2(PPh_3)_2$. Two νCO bands are observed in the I.R. spectrum of this hydride (see Table) together with νCS at $1005 cm^{-1}$, a position which we have found to be characteristic of monodentate dithiomethylester complexes. The hydride ligand appears as a 1:2:1 triplet in the ^1H NMR spectrum and the geometry of the complex is, therefore, as depicted below.



A solution of this hydride when heated under reflux in 2-methoxyethanol eliminates methylthiol and gives the pale yellow zerovalent complex $Os(CS)(CO)_2(PPh_3)_2$.

The same method can be used for a very simple, high yield, conversion of $IrCl(CO)(PPh_3)_2$ to the known thiocarbonyl analogue, $IrCl(CS)(PPh_3)_2$.[2,3] The $\eta^2\text{-}CS_2$ complex formed by $IrCl(CO)(PPh_3)_2$ is very unstable [4] but if $IrCl(CO)(PPh_3)_2$ is dissolved in CS_2 and reacted with methyl trifluoromethylsulphonate, $[Ir(CS_2Me)Cl(CO)(PPh_3)_2]\ CF_3SO_3$ results in quantitative yield. Reaction with $NaBH_4$ yields $IrH(CS_2Me)Cl(CO)(PPh_3)_2$ (see Table) and a suspension of this hydride when heated under reflux in t-butanol releases methylthiol and gives $IrCl(CS)(PPh_3)_2$.



Similar 1,2-elimination of methylthiol from appropriate starting materials could be a useful route to other low-valent complexes of CS, CO, or CNR ligands.

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