Journal of Organometallic Chemistry, 90 (1975) C34—C36

Preliminary communication

THIOCARBONYL, h^2-DITHIOMETHYL ESTER, AND DITHIOCARBENE COMPLEXES DERIVED FROM CARBON DISULPHIDE COMPLEXES OF RUTHENIUM AND OSMIUM

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(Received March 12th, 1975)

Summary

Methyl iodide converts the π-CS$_2$ complexes $Ru(CS_2)(CO)_2(PPh_3)_2$ and $Os(CS_2)(CO)_2(PPh_3)_2$ to cationic and neutral complexes containing the bidentate (through C and S) dithiomethyl ester group which reacts further with acids to yield thiocarbonyl complexes. Excess methyl iodide with $Os(CS_2)(CO)_2(PPh_3)_2$ produces the dithiocarbene complex $[OsI\{C(SMe)_2\}(CO)_2(PPh_3)_2]^+$.

Few synthetic routes are available for the preparation of thiocarbonyl complexes [1]. The most commonly used method involves reaction of a π-CS$_2$ complex with a sulphur acceptor such as a tertiary phosphine. Unfortunately this reaction is not general. Other approaches use reaction between low-valent species and thiophosgene or derivatives of thiophosgene [2]. We report here an approach involving methylation of coordinated CS$_2$ followed by acid cleavage of the resulting dithiomethyl ester group to produce coordinated CS.

$Ru(CO)_2(PPh_3)_3$ [3] reacts rapidly with CS$_2$ to form $Ru(CS_2)(CO)_2(PPh_3)_2$. Preparation of the corresponding osmium compounds required prior formation of $Os(C_2H_4)(CO)_2(PPh_3)_2$ (from $Os(CO)_2(PPh_3)_3$ [3] and C_2H_4 in benzene in presence of sunlight) and reaction of the ethylene adduct with one equivalent of CS$_2$. The IR spectra of these CS$_2$ complexes show strong bands near 1100 cm^{-1} as expected for this type of compound [1] (see Table 1). Both CS$_2$ complexes react rapidly with methyl iodide forming the cations $[M(CS_2Me)(CO)_2(PPh_3)_2]^+$ (M = Ru or Os, isolated as both iodide and perchlorate salts) in which, to maintain octahedral coordination, the CS$_2$Me group must be bidentate. The extreme ease with which this methylation takes place is demonstrated by the fact that even methyl chloride is an effective reagent [4]. That the ligand is a dithioester (bound through C and

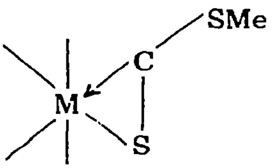
TABLE 1

INFRARED DATA FOR NEW COMPLEXES

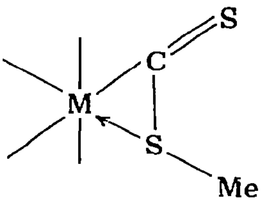
Compound [a]	ν(CO)(cm^{-1}) [b]	ν(CS)(cm^{-1})
$Ru(CS_2)(CO)_2L_2$	2010, 1945	1118
$Os(CS_2)(CO)_2L_2$	2000, 1940	1115
$[Os(CS_2Me)(CO)_2L_2]^+$ [c]	2050, 1995	1070
$RuCl(CS_2Me)(CO)L_2$	1948	1085
$RuCl_2(CO)(CS)L_2$	2050, 2040	1302
$OsCl_2(CO)(CS)L_2$	2040, 2030, 2020	1315
$[OsI\{C(SMe)_2\}(CO)_2L_2]^+$ [d]	2055, 1980	

[a] L = PPh_3. Compounds all yellow except $RuCl_2(CO)(CS)L_2$ and $OsCl_2(CO)(CS)L_2$ which are colourless. Cations were isolated as perchlorate salts and all compounds characterised by IR and NMR spectroscopy and by elemental analysis. [b] Measured as nujol mulls. [c] ^1H NMR ($CDCl_3$)τ 7.76s ppm (3H). [d] ^1H NMR ($CDCl_3$)τ 7.40s ppm (6H).

S) rather than a dithioacetate (bound through 2 S's) is shown by the following facts:
(i) the IR spectrum is unlike that reported for the dithioacetate complex $Re(S_2CMe)(CO)_4$ [5], (ii) in one instance (see below) dimethylation occurred to produce a compound with equivalent methyl groups (^1H NMR spectrum see Table 1) on each S implying that the first methylation also occurred at sulphur, and (iii) the further reaction with acid to produce thiocarbonyl and liberate methylthiol is possible only for a dithioester formulation.
There are two possible structures for a chelate dithioester viz. I or II and the



(I)



(II)

available evidence does not allow an unambiguous choice to be made between them. An X-ray structure determination of a suitable compound is in progress.

The ruthenium cation is labile with respect to displacement of CO by anionic ligands, X^-, forming $Ru(CS_2Me)X(CO)(PPh_3)_2$, but the osmium cation is inert. When any of the above dithiomethyl ester compounds are heated under reflux in ethanol with aqueous hydrochloric acid a slow reaction ensues with release of methylthiol and formation of the mixed carbonylthiocarbonyl complexes $RuCl_2(CO)(CS)(PPh_3)_2$ and $OsCl_2(CO)(CS)(PPh_3)_2$,

e.g.: $Ru(CS_2Me)Cl(CO)(PPh_3)_2 + HCl \rightarrow RuCl_2(CO)(CS)(PPh_3)_2 + MeSH$

$Os(CS_2)(CO)_2(PPh_3)_2$ also reacts directly with HCl evolving H_2S and forming $OsCl_2(CO)(CS)(PPh_3)_2$. These thiocarbonyl complexes are remarkable in that ν(CO) occurs at the very high value (for neutral Ru^{II} and Os^{II} species) of 2050 cm^{-1}. This is attributable to the marked π-acceptor capacity of the CS ligand. Because of the similarity between these thiocarbonyl complexes and the selenocarbonyl $RuCl_2(CO)(CSe)(PPh_3)_2$ of known structure [6] both $RuCl_2(CO)(CS)(PPh_3)_2$ and $OsCl_2(CO)(CS)(PPh_3)_2$ are believed to have a *trans* arrangement of phosphines and a *cis* arrangement of CO and CS. Other compounds of formula $RuCl_2(CO)(CS)(PPh_3)_2$, with quite different physical properties, have been described [7] and must be geometrical isomers.

When $Os(CS_2)(CO)_2(PPh_3)_2$ is treated with excess of methyl iodide (as solvent) both sulphur atoms of the coordinated CS_2 are methylated forming the bright yellow dithiocarbene cation, $[OsI\{C(SMe)_2\}(CO)_2(PPh_3)_2]^+$.

We thank the N.Z. Universities Grants Committee for grants towards instrumental facilities and the award of a Postgraduate Scholarship to K.R.G., the University of Toronto for granting study leave to R.O.H., and Johnson, Matthey Ltd, for a generous loan of platinum salts.

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