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Preliminary communication

GEOMETRICAL ISOMERISM ARISING FROM C,S- OR C,Se-COORDINATION OF CARBON SELENIDE SULPHIDE AND THE CONVERSION OF A THIOCARBONYL LIGAND TO A SELENOCARBONYL LIGAND

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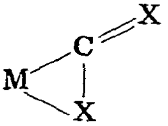
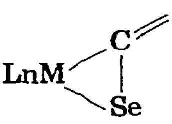
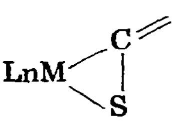
Summary

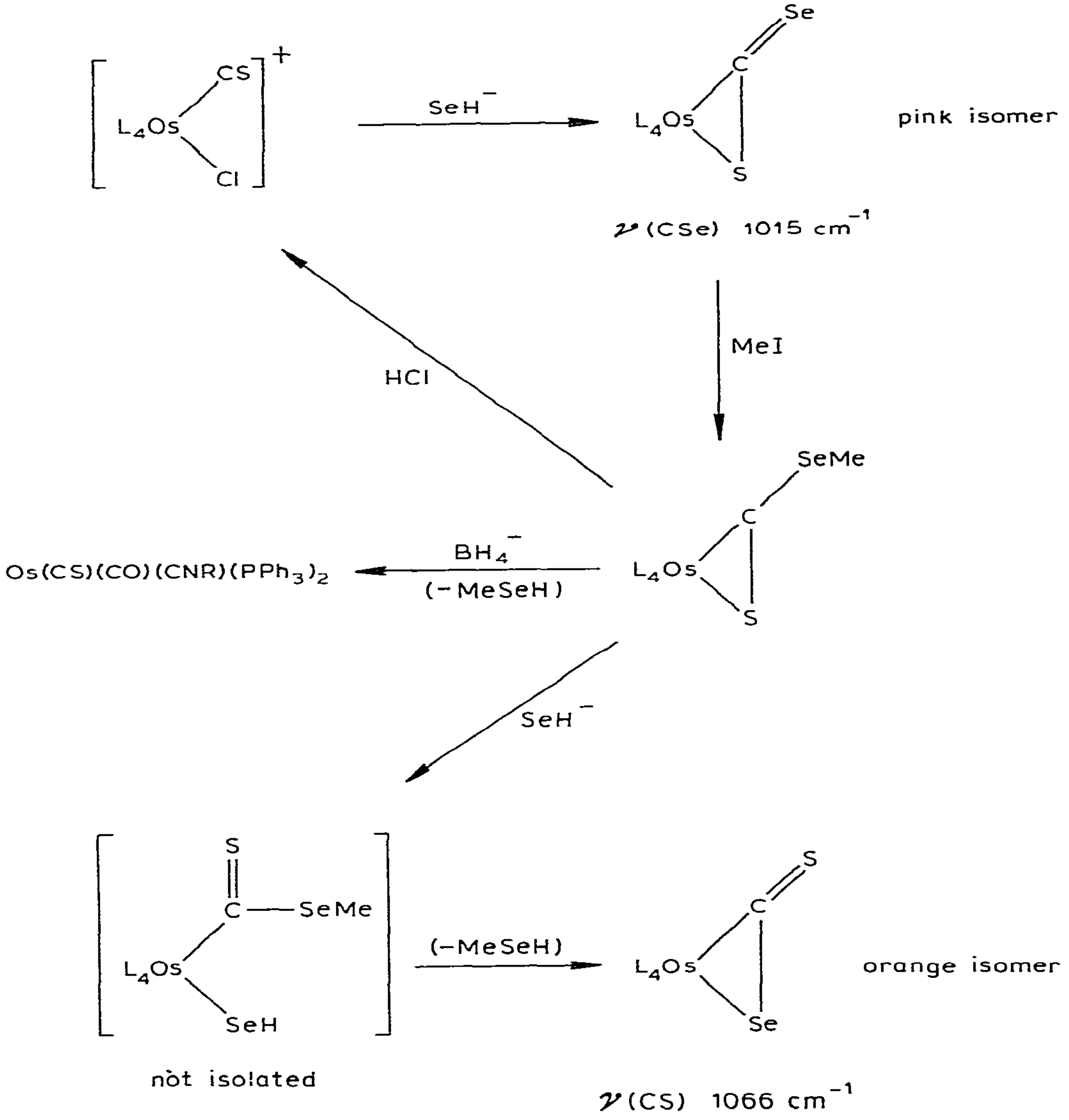
Reaction sequences commencing with nucleophilic attack on the CS ligand in the cationic species $[MCl(CS)(CO)(CNR)(PPh_3)_2]^+$, (M = Ru or Os; R = *p*-tolyl) by SeH^- lead to each of the geometrical isomers $M(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ and $M(\eta^2\text{-CSSe})(CO)(CNR)(PPh_3)_2$. For $Ru(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ reaction with MeI followed by HCl leads to $RuCl_2(CSe)(CNR)(PPh_3)_2$ which overall represents a four-step conversion of a thiocarbonyl ligand to a selenocarbonyl ligand.

The carbon dichalcogenides CX_2 (X = O, S, or Se) all coordinate to low-valent centres through the attachment of a CX bond viz.:



Some well-characterised examples include $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ [1] (Cy = cyclohexyl), $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ [2] and $Ru(\eta^2\text{-}CSe_2)(CO)_2(PPh_3)_2$ [3]. The mixed carbon dichalcogenides, COS and CSeS, present the opportunity of coordinating in two distinctly different ways although for COS, C,S-coordination is likely to be favoured over C,O-coordination and the known complexes $Pt(\eta^2\text{-COS})(PPh_3)_2$ [4], $Rh(\eta^2\text{-COS})Cl(PCy_3)_2$ [5], and $Ni(\eta^2\text{-COS})(dipy)$ (dipy = 2,2'-bipyridyl) [6] are certainly C,S-bound. For CeS the possibility of isolating both isomers viz.:  and  is much greater since both CS_2 and CSe_2 bind strongly to low-valent metal centres and rapid interconversion of isomers is unlikely because $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ has been demonstrated by ^{13}C NMR to be a non-fluxional molecule [7]. The only previous report of coordinated CSeS in $M(\eta^2\text{-CSeS})(\eta^5\text{-C}_5H_5)(PMe_3)$, (M = Co or Rh) [8] did not discuss the geometrical isomer possibilities. We describe herein synthetic procedures which allow isolation of both isomers of $Os(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$, i.e. $Os(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ and $Os(\eta^2\text{-CSSe})(CO)(CNR)(PPh_3)_2$.

The ruthenium analogues are also described although only the C,Se-bound isomer $Ru(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$, has been isolated in a pure form and this compound after methylation on sulphur and reaction with HCl gives $RuCl_2(CSe)(CNR)(PPh_3)_2$. Since $Ru(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ is made from $RuCl_2(CS)(CNR)(PPh_3)_2$, overall this represents the conversion of a CS ligand to a CSe ligand in four reasonably high-yield steps.



SCHEME 1. Preparation of geometrical isomers of $Os(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ (L_4 = $(CO)(CNR)(PPh_3)_2$).

The phosphine ligands in all of these complexes are assumed to be arranged *trans* as has been demonstrated for numerous other η^2-adducts of $M(CO)_2(PPh_3)_2$ and $M(CO)(CNR)(PPh_3)_2$ [9]. Additional isomer possibilities arise from the relative positioning of CO and CNR with respect to the η^2-CSeS ligand. We do not yet have information on the precise arrangement of the CO and CNR ligands and in the reaction schemes, therefore, we have not depicted complete stereochemistry, but restricted attention to the geometry of attachment of the various mixed Se,S-fragments.

We have previously described reaction between the osmium(II) cation, $[OsCl(CS)(CO)(CNR)(PPh_3)_2]^+$, and SH^- which leads to a mixture of $Os(\eta^2\text{-}SCNR)(CS)(CO)(PPh_3)_2$ and $Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$ [10]. When this same cation was treated with SeH^- [11] the exclusive product was $Os(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$ (see Scheme 1). This is a pink crystalline material with an infrared absorption at 1015 cm^{-1} (see Table 1 for other IR spectral data) which we assign to ν(CSe) of the *exo*-CSe group, i.e., this is the C,S-bound isomer $Os(\eta^2\text{-}CSSe)(CO)(CNR)(PPh_3)_2$. This structural assignment is fully supported by further reactions of this compound. Methylation occurs readily with MeI giving a *dihapto*-methylselenothioester complex and that this methylation occurs on Se (indicating *exo*-Se for the pink isomer) is proved by the further reactions:

(i) with HCl to return $[OsCl(CS)(CO)(CNR)(PPh_3)_2]^+$ and

(ii) with $NaBH_4$ which leads to loss of MeSeH and formation of a zerovalent thiocarbonyl complex, $Os(CS)(CO)(CNR)(PPh_3)_2$. The preparation of $Os(CS)(CO)_2(PPh_3)_2$ from $[Os(CS_2Me)(CO)_2(PPh_3)_2]^+$ and $NaBH_4$ via $OsH(CS_2Me)(CO)_2(PPh_3)_2$ has been reported previously [12]. The effectiveness of the methylselenato function as a leaving group, demonstrated by the transfor-

TABLE 1

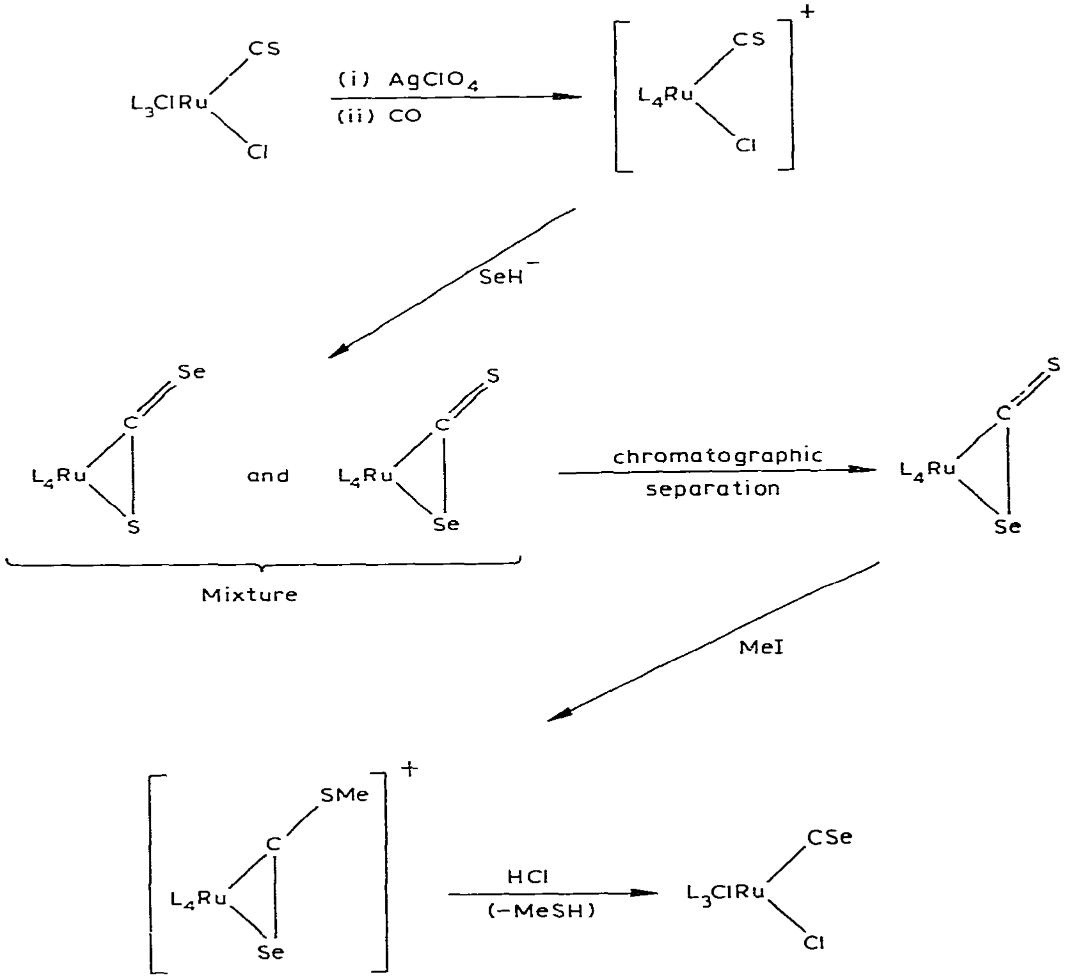
IR DATA[a] FOR RUTHENIUM AND OSMIUM COMPLEXES

Compound[b]	ν(CO)	ν(CN)	ν(CS)	ν(CSe)
$RuCl_2(CS)(H_2O)(PPh_3)_2$			1293	
trans-$RuCl_2(CS)(CNR)(PPh_3)_2$		2187	1270	
cis-$RuCl_2(CS)(CNR)(PPh_3)_2$		2155	1295	
$[RuCl(CS)(CO)(CNR)(PPh_3)_2]^+$	2075	2200, 2160	1135	
$[OsCl(CS)(CO)(CNR)(PPh_3)_2]^+$	2060	2205	1323	
$Ru(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$	1938	2110	1063m	
$Ru(\eta^2\text{-}CSSe)(CO)(CNR)(PPh_3)_2$[c]				1027m
$Os(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$	1908	2125	1066m	
$Os(\eta^2\text{-}CSSe)(CO)(CNR)(PPh_3)_2$	1908	2125		1015m
$[Ru(\eta^2\text{-}CSeSMe)(CO)(CNR)(PPh_3)_2]^+$	1972	2163	1050m	
$[Os(\eta^2\text{-}CSeSMe)(CO)(CNR)(PPh_3)_2]^+$	1956	2160	1045m	
$[Os(\eta^2\text{-}CSSeMe)(CO)(CNR)(PPh_3)_2]^+$	1954	2160		1032m
$Os(CS)(CO)(CNR)(PPh_3)_2$	1890, 1865	2060, 2036	1232, 1222	
$RuCl_2(CSe)(CNR)(PPh_3)_2$		2175		1134
$[RuCl(CSe)(CO)(CNR)(PPh_3)_2]^+$	2070	2201		1135
$Ru(\eta^2\text{-}CSe_2)(CO)(CNR)(PPh_3)_2$	1918	2129		945

[a] cm^{-1} measured as Nujol mulls. All bands strong unless indicated otherwise. [b] All compounds with the exception noted below have satisfactory elemental analyses. Cations characterised as perchlorate salts. [c] Infrared data for this compound extracted from the IR spectrum of the mixture of $Ru(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$ and $Ru(\eta^2\text{-}CSSe)(CO)(CNR)(PPh_3)_2$.

mations detailed above, suggested an experimental route to the C,Se-bound isomer. It was anticipated that reaction of the cation $[Os(\eta^2\text{-}CSSeMe)(CO)(CNR)(PPh_3)_2]^+$ with SeH^- would lead to coordination of SeH^- with rearrangement of the *dihapto*-methylselenothioester group to a *monohapto* form (see Scheme 1). Such an intermediate was not isolated, but the reaction led to the expected elimination of MeSeH and formation of an orange crystalline product with ν(CO) and ν(CN) IR absorptions identical to those of the pink isomer (see Table 1). However, the IR band at 1015 cm^{-1} assigned to ν(CSe) in the pink isomer was replaced, in the orange isomer, by a band at 1066 cm^{-1} assigned to ν(CS) of the *exo*-CS group i.e., the orange compound is $Os(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$.

$Os(\eta^2\text{-}CSeS)(CO)(CNR)(PPh_3)_2$ is methylated on S to give $[Os(\eta^2\text{-}CSeSMe)(CO)(CNR)(PPh_3)_2]^+$. We expected this cation to react with HCl with MeSH elimination and formation of a selenocarbonyl complex, but the acid reaction was very slow and accompanied by other reactions, and led to traces



SCHEME 2. Conversion of a CS ligand to a CSe ligand (L_3 = $(CNR)(PPh_3)_2$ and L_4 = $(CO)(CNR)(PPh_3)_2$).

only of selenocarbonyl-containing species as judged from IR spectra. Much greater success in this respect was achieved with the ruthenium system.

We describe first the sequence of reactions which lead to the required cation, $[RuCl(CS)(CO)(CNR)(PPh_3)_2]^+$. The reaction between $RuCl_2(PPh_3)_3$ and CS_2 is complicated and can lead to a variety of products [13]. However, we find that in xylene under reflux the major product from this reaction is $RuCl_2(CS)(H_2O)(PPh_3)_2$. This is probably the isomer with *trans*-phosphines and *trans*-chlorines since only one ν(Ru—Cl) at 324 cm^{-1} is evident in the IR spectrum and replacement of H_2O by CNR gives the yellow *trans*-isomer of $RuCl_2(CS)(CNR)(PPh_3)_2$. Isomerization to a colourless *cis*-isomer occurs in toluene under reflux, and the colourless isomer reacts with $AgClO_4$ giving $Ru(OClO_3)Cl(CS)(CNR)(PPh_3)_2$, which in turn gives upon carbonylation $[RuCl(CS)(CO)(CNR)(PPh_3)_2]ClO_4$.

Reaction of $[RuCl(CS)(CO)(CNR)(PPh_3)_2]^+$ with SeH^- gives a mixture of $Ru(\eta^2\text{-CSSe})(CO)(CNR)(PPh_3)_2$ and $Ru(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ (see Scheme 2 and Table 1). Chromatography of this mixture on silica gel allows isolation of the pure C,Se-bound isomer $Ru(\eta^2\text{-CSeS})(CO)(CNR)(PPh_3)_2$ as orange crystals. This compound is cleanly methylated on S with MeI to afford $[Ru(\eta^2\text{-CSeSMe})(CO)(CNR)(PPh_3)_2]^+$, and this cation, when treated with aqueous HCl in toluene/ethanol solution under reflux, liberates MeSH and forms $RuCl_2(CSe)(CNR)(PPh_3)_2$ in high yield. This compound can be converted into the cation $[RuCl(CSe)(CO)(CNR)(PPh_3)_2]^+$ through reaction with $AgClO_4$ followed by CO, and reaction with SeH^- leads to $Ru(\eta^2\text{-CSe}_2)(CO)(CNR)(PPh_3)_2$. This constitutes a novel synthesis of an $\eta^2\text{-CSe}_2$ complex which avoids the need to handle free CSe_2.

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