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Preliminary communication

COORDINATED CARBON MONOSELENIDE AND CARBON DISELENIDE. PREPARATION AND STRUCTURE OF THE MIXED CARBONYL–SELENOCARBONYL COMPLEX, $RuCl_2(CO)(CSe)(PPh_3)_2$

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Summary

Coordinated CSe_2 in $Ru(CSe_2)(CO)_2(PPh_3)_2$ has been converted to a diselenomethyl ester group which reacts with HCl forming the stable selenocarbonyl complex $RuCl_2(CO)(CSe)(PPh_3)_2$. Structure determination reveals a pronounced *trans* influence of the CSe ligand.

Carbon monoxide and carbon monosulphide are both familiar ligands although the synthetic routes available for thiocarbonyl complexes, and hence the number of such complexes which are well-characterised, is somewhat limited. The successful stepwise conversion of π-bonded carbon disulphide to thiocarbonyl in ruthenium and osmium compounds [1] led us to investigate the possibility of coordinating carbon diselenide and to attempt a similar conversion to a carbon monoselenide or selenocarbonyl complex.

CSe_2 reacts readily with $Ru(CO)_2(PPh_3)_3$ [2] to form yellow-green $Ru(CSe_2)(CO)_2(PPh_3)_2$. Like the sulphur analogue this compound is rapidly methylated by methyl iodide and further reaction with iodide ion leads to the yellow, neutral diselenomethyl ester complex $Ru(CSe_2Me)I(CO)(PPh_3)_2$. IR data for this and the corresponding bromide and chloride are given in Table 1. Reaction with hydrochloric or hydrobromic acid proceeds slowly with evolution of MeSeH and formation of colourless $RuCl_2(CO)(CSe)(PPh_3)_2$ and $RuBr_2(CO)(CSe)(PPh_3)_2$ respectively. These selenocarbonyl complexes are quite stable to air and moisture. The IR spectra show a characteristic very strong absorption for coordinated CSe at 1125 cm^{-1} (see Table 1). To confirm the presense of the CSe ligand and to gain information about the bonding features of this ligand an X-ray structure determination was undertaken.

The crystals are monoclinic, $a = 10.470(1)$, $b = 23.446(2)$, $c = 14.507(2)$ Å, β 94.75(1)°, $Z = 4$, space group $P2_1/n$. Intensity data were collected on a Hilger–Watts 4-circle diffractometer using Ni-filtered Cu-K_α radiation. A total of 2214 unique reflections with $I > 3\sigma(I)$ were recorded. The structure was

TABLE 1

INFRARED DATA FOR SELENOCARBONYL COMPLEXES AND PRECURSORS

Compound[a]	ν(CO)(cm^{-1})[b]	ν(CSe)(cm^{-1})
$Ru(CSe_2)(CO)_2L_2$	2020, 1950	953
$Ru(CSe_2Me)Cl(CO)L_2$	1945	950
$Ru(CSe_2Me)Br(CO)L_2$	1945	950
$Ru(CSe_2Me)I(CO)L_2$[c]	1945	940
$RuCl_2(CO)(CSe)L_2$	2030	1125
$RuBr_2(CO)(CSe)L_2$	2030	1125
$RuI(OH)(CO)(CSe)L_2$	2070	1137

[a] L = PPh_3. All compounds were characterized by IR and NMR spectroscopy and by elemental analysis. [b] Measured as nujol mulls. [c] ^{1}H NMR ($CDCl_3$) τ 7.98s ppm (3H).

solved by Patterson and Fourier syntheses and has been partially refined by least-squares techniques to $R = 0.077$. The benzene rings of the triphenylphosphine ligands have been constrained as rigid groups, all other non-hydrogen atoms have been assigned anisotropic thermal parameters.

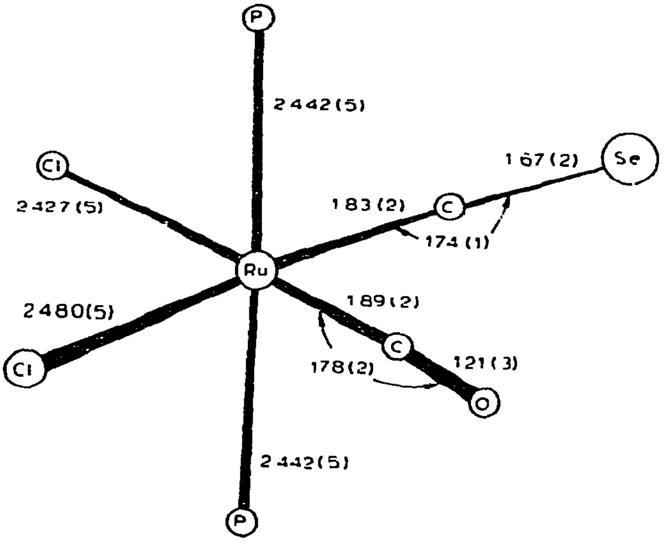

Fig.1. Bond lengths (Å) and angles in $RuCl_2(CO)(CSe)(PPh_3)_2$.

The complex is monomeric, with an octahedral coordination about the ruthenium atom consisting of *cis*-carbonyl and -selenocarbonyl, *cis*-chloride and *trans*-phosphine ligands. This geometry is outlined in Fig.1. Ru—P bonds are of normal length but both Ru—Cl distances are long compared with the range of 2.29-2.39 Å reported for other ruthenium complexes [3]. The Ru—Cl distance *trans* to CSe is particularly long, demonstrating strong *trans*-influence for this ligand. The chemical behaviour of the complexes bears this out, e.g. if $RuI_2(CO)(CSe)(PPh_3)_2$ is chromatographed on alumina the hydroxide $RuI(OH)(CO)(CSe)(PPh_3)_2$ is formed.

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