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Preliminary communication

A FLUOROCHLOROCARBENE COMPLEX OF OSMIUM, $OsCl_2(CFCl)(CO)(PPh_3)_2$ AND THE STRUCTURE OF A FLUOROALKOXYCARBENE COMPLEX OF RUTHENIUM, $RuCl_2(CFOCH_2CMe_3)(CO)(PPh_3)_2$

S.V. HOSKINS, R.A. PAUPTIT, W.R. ROPER* and J.M. WATERS

Department of Chemistry, University of Auckland, Auckland (New Zealand)

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Summary

$OsCl_2(CFCl)(CO)(PPh_3)_2$ results from reaction between $OsCl_2(CCl_2)(CO)(PPh_3)_2$ and $Cd(CF_3)_2(DME)$. The CFCl ligand is converted into $CFNMe_2$ and CFSEt ligands through reaction with Me_2NH and NaSEt, respectively. The crystal structure of $RuCl_2(CFOCH_2CMe_3)(CO)(PPh_3)_2$ reveals the following dimensions about the carbene—carbon atom: Ru—C, 1.914(5) Å; C—O, 1.303(7) Å; C—F, 1.307(6) Å; Ru—C—F, 127.1(4)°; Ru—C—O, 125.5(4)°; F—C—O, 107.4(5)°.

Difluorocarbene complexes have now been isolated for both ruthenium(II) [1] and ruthenium(0) [2], and dichlorocarbene complexes are known for iron(II) [3], ruthenium(II) [4], osmium(II) [5] and iridium(III) [6]. In compounds exhibiting higher oxidation states (II and III) these ligands are characteristically electrophilic and undergo various substitution reactions [1,4–6]. On the other hand, in zerovalent complexes the CF_2 ligand has reduced electrophilicity and may even react with some electrophiles [2]. Fuller understanding of the reactivity of dihalocarbene ligands will be assisted by the development of synthetic routes to mixed dihalocarbene ligands and we describe here an osmium complex containing the fluorochlorocarbene ligand and a single crystal X-ray diffraction study of a fluoroalkoxycarbene complex of ruthenium.

The dimethoxyethane adduct of bis(trifluoromethyl)cadmium has been shown to be an efficient fluorinating agent for acyl halides, e.g., acetyl bromide is converted into acetyl fluoride in 90% yield [7]. The reactivity of complexes containing the CCl_2 ligand resembles in many ways that of an acid halide, e.g., the reactivity of $RuCl_2(CCl_2)(CO)(PPh_3)_2$ and $IrCl_3(CCl_2)(PPh_3)_2$ may be usefully compared with that of phosgene. It is not surprising, therefore, that $Cd(CF_3)_2 \cdot$ DME converts $OsCl_2(CCl_2)(CO)(PPh_3)_2$ into $OsCl_2(CFCl)(CO)(PPh_3)_2$ (see Scheme 1). The CFCl ligand has strong ν(CF) and ν(CCl) bands in the IR

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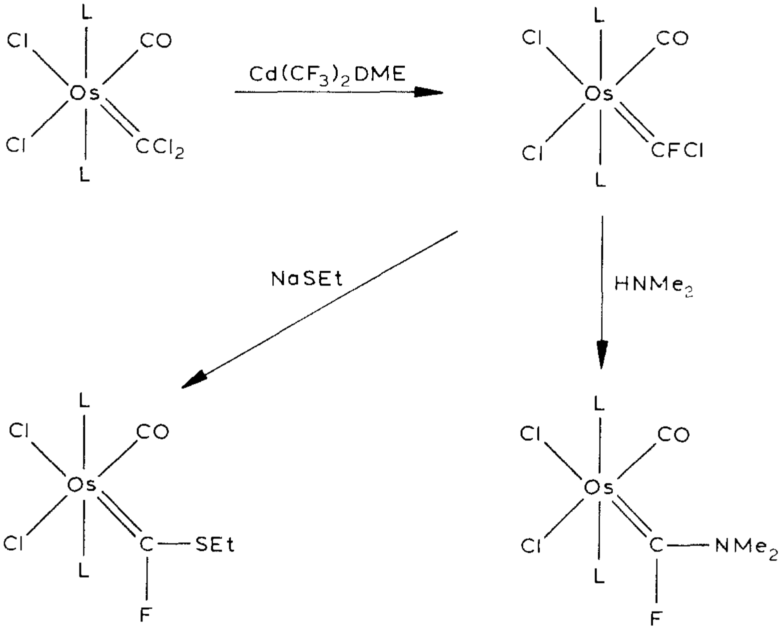

SCHEME 1. Synthesis and reactions of $OsCl_2(CFCl)(CO)L_2$ ($L = PPh_3$).

spectrum (see Table 1). The neutral CFCl complex is easily converted into a cationic complex through reaction with $AgSbF_6$ in acetonitrile. When $OsCl_2(CFCl)(CO)(PPh_3)_2$ reacts with dimethylamine, substitution at the C—Cl bond gives $OsCl_2(CFNMe_2)(CO)(PPh_3)_2$. Similarly, reaction with NaSEt replaces chloride to give the mixed fluorothiocarbene complex, $OsCl_2(CFSEt)(CO)(PPh_3)_2$.

Other monofluorocarbene complexes have been made by the addition of fluoride to suitable carbyne complexes and a structure determination of one of these compounds, $CpMn(CFPh)(CO)_2$ revealed [8] unusual geometry with a long C—F distance of 1.39 Å and a small Mn—C—F angle of 117.5°. We chose a ruthenium complex containing a fluoroalkoxy ligand, $RuCl_2(CFOCH_2CMe_3)(CO)(PPh_3)$ (derived from $RuCl_2(CF_2)(CO)(PPh_3)_2$ [1] through reaction with $HOCH_2CMe_3$) for structure determination. $RuCl_2(CFOCH_2CMe_3)(CO)(PPh_3)_2$ forms colourless triclinic crystals, space group $P\bar{1}$ with a 11.304(1), b 12.461(2), c 17.971(3) Å, α 109.76(2), β 103.84(1), γ 77.31(1)° and $Z = 2$, Mo-K_α radia-

TABLE 1

IR DATA[a] FOR FLUOROCARBENE COMPLEXES

Compound[b]	ν(CO)	ν(CF)	ν(CCl)	ν(CN)
$OsCl_2(CFCl)(CO)L_2$	2008,1990	1124	885	
$[OsCl(CFCl)(MeCN)(CO)L_2]^+$	2018	1125	909	
$OsCl(CFNMe_2)(CO)L_2$	1948,1928			1561
$[OsCl(CFNMe_2)(MeCN)(CO)L_2]^+$	1956			1523
$OsCl_2(CFSEt)(CO)L_2$	1975			
$RuCl_2(CFOCH_2CMe_3)(CO)L_2$	1982			

[a] In cm^{-1} measured as Nujol mulls. [b] $L = PPh_3$. All compounds have satisfactory elemental analyses.

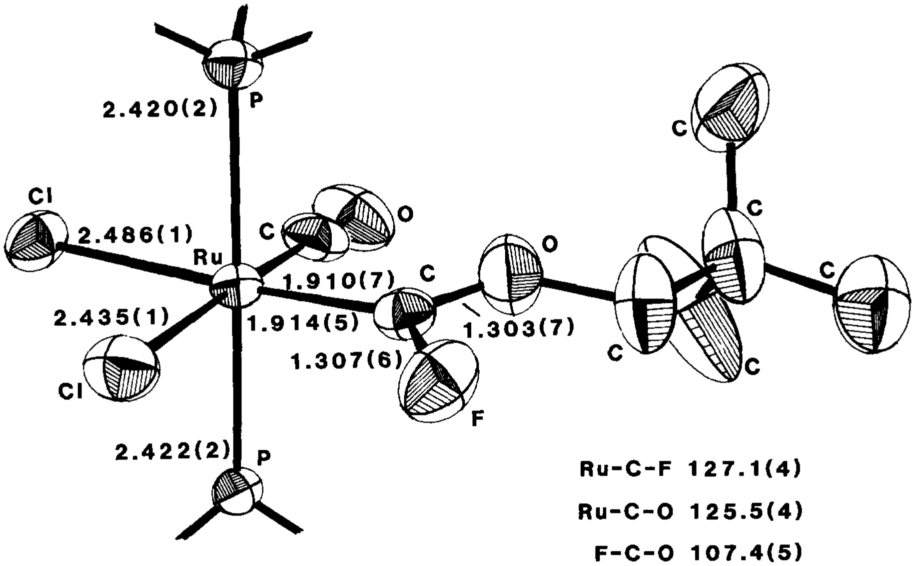

Fig. 1. Molecular structure of $RuCl_2(CFOCH_2CMe_3)(CO)(PPh_3)_2$ with phenyl groups omitted for clarity.

tion. The structure was solved by conventional heavy atom methods and refined by full-matrix least-squares assuming anisotropic thermal parameters for all non-hydrogen atoms except those in the phenyl rings, which were refined as rigid groups until the last two refinement cycles. The present *R* value is 4.80% for 5465 observed reflections. A tetrachloroethane solvent molecule is included in the asymmetric unit. The molecular structure is depicted in Fig. 1.

It can be seen that the Ru—C distances for the carbene and carbonyl ligands are comparable. This contrasts with the zerovalent difluorocarbene complex $Ru(CF_2)(CO)_2(PPh_3)_2$ for which the Ru—C distance to the carbene ligand was significantly shorter than for the CO ligand [2]. This lengthening of the Ru—carbene distance must be attributed to effective π-donation from the OCH_2CMe_3 group and less effective π-donation from ruthenium(II) thus reducing the Ru—C bond order. The C—F distance is much shorter than that in the Mn complex [8] and the bond angles are quite regular. A pronounced *trans*-influence of the carbene ligand is evident in the Ru—Cl distances.

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