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FLUOROCARBENE COMPLEXES
OF
RUTHENIUM AND OSMIUM

A thesis presented to the
University of Auckland
for the degree of
Doctor of Philosophy in Chemistry

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December 1983

A B S T R A C T

This thesis is concerned with the synthesis and properties of fluorocarbene complexes of ruthenium and osmium. Chapter 1 is a review of transition metal CF_3 -complexes and illustrates a number of unusual features of these compounds which makes them suitable for modification into CF_2 -complexes.

To place the fluorocarbene complexes into context, Chapter 2 contains a brief review of transition metal carbene complexes with the emphasis on other halocarbene species.

As described in Chapter 3, CF_3 -complexes of ruthenium can be prepared by the addition of $\text{Hg}(\text{CF}_3)_2$ to $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$. The x-ray crystal structure of $\text{Ru}(\text{HgCF}_3)(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ shows longer C-F bonds in the ruthenium bound CF_3 -group than in the mercury bound CF_3 -group.

Reactions of fluorocarbon complexes with Lewis acids have been explored and $\text{RuCl}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ reacts with BCl_3 to form the known $\text{RuCl}_2(\text{CO})(\text{CCL}_2)(\text{PPh}_3)_2$. Similarly $\text{OsCl}(\text{CF}_2\text{H})(\text{CO})_2(\text{PPh}_3)_2$ reacts with one equivalent of BCl_3 to form initially a cationic carbene complex in which the carbene carbon atom substitutes first into a benzene ring of one PPh_3 -ligand and, through further reaction with BCl_3 , into a ring of the second PPh_3 -ligand. The x-ray crystal structures of $\text{OsCl}(\text{CO})_2(\text{PPh}_2\text{C}_6\text{H}_4\text{CHCl})\text{PPh}_3$ and $\text{OsCl}(\text{CO})_2(\text{PPh}_2\text{C}_6\text{H}_4\text{CH})(\text{PPh}_2\text{C}_6\text{H}_4)$ are reported.

$\text{RuCl}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ in many of its reactions behaves as a CF_2 -complex precursor and Chapter 4 describes the reaction between the related $\text{RuCl}(\text{CF}_3)(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2$ and Me_3SiCl to form the first isolable CF_2 -complex, $\text{RuCl}_2(\text{CO})(\text{CF}_2)(\text{PPh}_3)_2$.

$\text{RuCl}_2(\text{CO})(\text{CF}_2)(\text{PPh}_3)_2$ contains an electrophilic carbene ligand and reacts

rapidly with hard, oxygen and nitrogen containing nucleophiles. A comparison of the reactivity of $\text{RuCl}_2(\text{CO})(\text{CF}_2)(\text{PPh}_3)_2$ and $\text{RuCl}_2(\text{CO})(\text{CCL}_2)(\text{PPh}_3)_2$ is presented and reasons for the differing reactivities proposed.

Chapter 5 shows that d^8 CF_2 -complexes can be prepared directly from reaction between the more active CF_3 -transfer reagent, $\text{Cd}(\text{CF}_3)_2$ -glyme, and various zerovalent complexes. The x-ray crystal structures of $\text{M}(\text{CO})_2(\text{CF}_2)(\text{PPh}_3)_2$ $\text{M} = \text{Ru}, \text{Os}$ and $\text{OsCl}(\text{NO})(\text{CF}_2)(\text{PPh}_3)_2$ are described and the bonding characteristics of the CF_2 -ligand discussed. The carbene ligand of $\text{M}(\text{CO})_2(\text{CF}_2)(\text{PPh}_3)_2$ $\text{M} = \text{Ru}, \text{Os}$ has some nucleophilic character and reacts readily with electrophiles, for example reaction with HCl yields $\text{MCl}(\text{CF}_2\text{H})(\text{CO})_2(\text{PPh}_3)_2$ $\text{M} = \text{Ru}, \text{Os}$.

A comparison between $\text{RuCl}_2(\text{CO})(\text{CF}_2)(\text{PPh}_3)_2$ and $\text{Ru}(\text{CO})_2(\text{CF}_2)(\text{PPh}_3)_2$ reveals that the reactivity of the carbene ligand is controlled by the electron density at the metal centre, *i.e.* is oxidation state dependent.

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ABBREVIATIONS

Me	methyl
Et	ethyl
<i>i</i> _{Pr}	isopropyl
<i>n</i> _{Bu}	<i>n</i> -butyl
<i>t</i> _{Bu}	tertiary butyl
Ph	phenyl
py	pyridine
en	ethylenediamine
Cp	<i>pentahapto</i> -cyclopentadiene
bae	N,N-bis(acetylacetonato)ethylenediamine
Bipy	bipyridyl
COD	1,5-cyclooctadiene
diphos	(1,2-dipenylphosphino)ethane
dmGH	dimethylglyoxime
DMP	N,N'-dimethylpiperazine
DMSO	dimethylsulphoxide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
EtPO	4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
PPN	μ -nitrido-bis(triphenylphosphine)
TPP	tetraphenylporphyrin
m	minute
s	second
M.p.	melting point