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A STUDY OF
GROUP VIII
METAL-CARBON
MULTIPLE BONDS

A thesis presented to the
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ABSTRACT

Molecules containing transition metal-carbon multiple bonds have been recognised as active species in catalytic reactions and key intermediates in stoichiometric reactions. It is therefore important to gain an understanding of the reactivity of these functional groups.

The metal-carbon double bond is introduced in Chapter 1 with a literature review and the following two chapters are concerned with the synthesis and properties of a new class of Group VIII metal carbene complexes containing the prototype carbene ligand, $=CH_2$. The synthetic route to the first of these complexes involves a new low-valent osmium complex $OsCl(NO)(PPh_3)_3$. The synthesis of this complex from a reformulated complex containing the novel peroxycarbonyl ligand is discussed in Chapter 2, followed by simple reactions including the synthesis of a range of acetylene, allene and heteroallene π -adducts. The reactions establish that $OsCl(NO)(PPh_3)_3$ reacts as the osmium analogue of $IrCl(CO)(PPh_3)_2$.

The methylene-ligand synthesis involves the addition of diazomethane to $OsCl(NO)(PPh_3)_3$ to give the structurally characterised $Os(CH_2)Cl(NO)(PPh_3)_2$. The reaction has been extended to give the first isolable ruthenium and iridium methylene complexes. The reactions of these complexes establish the nucleophilicity of the double bond and two Lewis acid adducts, $Os(CH_2AuI)Cl(NO)(PPh_3)_2$ and $[Os(CH_2S(O)O)Cl(NO)(PPh_3)_2]ClO_4$, have been structurally characterised. The reaction with CO and isocyanides to form ketene and ketenimine ligands illustrates a different mode of reaction that is interpreted in terms of the non-innocent participation of the nitrosyl ligand.

The change from nucleophilicity to electrophilicity of the double bond with a reduction of metal electron density is illustrated by reactions of

$\text{Os}(\text{CH}_2\text{Cl})\text{Cl}_2(\text{NO})(\text{PPh}_3)_2$ which implicate $[\text{Os}(\text{CH}_2)\text{Cl}_2(\text{NO})(\text{PPh}_3)_2]^+$ as an intermediate. $\text{Os}(\text{CH}_2\text{Cl})\text{Cl}_2(\text{NO})(\text{PPh}_3)_2$ is formed by addition of Cl_2 to $\text{Os}(\text{CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$.

In Chapter 4 a different type of metal-carbon double bond is discussed. The complexes contain the relatively uncommon dichlorocarbene ligand and the synthesis of the first such iridium complex, $\text{Ir}(\text{CCl}_2)\text{Cl}_3(\text{PPh}_3)_2$ is described. The utility of the dichlorocarbene ligand in the synthesis of a range of carbene ligands including monochlorocarbene complexes is illustrated.

The most useful single reaction of the dichlorocarbene complexes is that forming a metal-carbon triple bond. A review of the literature concerning carbyne complexes is presented in Chapter 5 and the synthesis and reactions of a number of carbyne complexes is discussed in Chapter 6.

Like the methylene complexes, the carbyne complexes such as $\text{Os}(\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ contain nucleophilic metal-carbon bonds and $\text{Os}(\text{CHPh})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ resulting from HCl addition has been structurally characterised. However, just as the reactivity can be changed with the methylene complexes, the reduction of metal electron density in complexes such as $[\text{Os}(\text{CR})\text{Cl}_2(\text{CNR}')(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{R} = \text{C}_6\text{H}_4\text{-4-NMe}_2$, $\text{R}' = \text{C}_6\text{H}_4\text{-4-Me}$) makes the triple bond electrophilic. Two methods for synthesising these octahedral carbyne complexes are described. One, involving a reaction of complexes such as $\text{Os}(\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with oxygen and the formation of another peroxy carbonyl ligand, the other a reaction with iodine to give complexes such as $\text{Ru}(\text{CPh})\text{ClI}_2(\text{PPh}_3)_2$. Reactions with chlorine by contrast lead to a group of reactive chlorophenyl carbene complexes.

Where appropriate, the reactivity of the complexes described is interpreted in terms of frontier-orbital and charge controlled reactions using the current models for the carbene and carbyne complexes.

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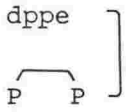
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ABBREVIATIONS

Me	:	methyl
Et	:	ethyl
Pr	:	propyl
Bu	:	butyl
Ph	:	phenyl
Cp	:	cyclopentadienyl
cod	:	cyclooctadiene
dppe 	:	bisdiphenylphosphinoethane
dmpe	:	bisdimethylphosphinoethane
ETPO	:	4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
TDPME	:	1,1,1-trisdiphenylphosphinomethylethane
dam	:	bisdiphenylarsinomethane
tmeda	:	tetramethylethylenediamine
HMPA	:	hexamethylphosphoramide
THF	:	tetrahydrofuran
TMS	:	tetramethylsilane
PPN	:	$[(\text{Ph}_3\text{P})_2\text{N}]^+$
PY	:	pyridine