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OSMIUM COMPLEXES
AS MODELS FOR
CO REDUCTION INTERMEDIATES

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

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ABSTRACT

This thesis is concerned with the synthesis, and aspects of the chemistry, of carbon-donor complexes of osmium as organometallic models for CO reduction intermediates.

In Chapter 1 some aspects of ligand reactivity of the carbon-donor ligands CO, CS, CSe, CTe and carbenes in transition metal complexes are reviewed. The reduction reactions of these ligands are emphasized.

The preparation and structure of the osmium η^2 -formaldehyde complex $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2$ is described in Chapter 2. This complex has proved to be a useful synthetic precursor for stable osmium formyl, hydroxymethyl, methoxymethyl and halomethyl ($-\text{CH}_2\text{X}$, X = Cl, Br, I) complexes and some facets of the reactivity of these ligands have been investigated. A general synthetic route to neutral osmium formyl complexes $\text{Os}(\text{CHO})\text{X}(\text{CO})_2(\text{PPh}_3)_2$ (X = halide or alkyl) has been developed. The facile preparation of a stable example of an intermediate formed during decarbonylation of a simple aldehyde by a transition metal, the osmium *monohapto*-acetyl-hydrido complex $\text{Os}(\eta^1\text{-C}[\text{O}]\text{CH}_3)\text{H}(\text{CO})_2(\text{PPh}_3)_2$, has been demonstrated.

A preliminary study of the reactions of the osmium iodomethyl complex $\text{Os}(\text{CH}_2\text{I})\text{I}(\text{CO})_2(\text{PPh}_3)_2$ is reported in Chapter 3. The typical reaction of this species is nucleophilic substitution;

in many respects reactivity is analogous to an electrophilic methyldene complex. Reaction with a variety of nucleophiles [e.g. OR^- , H^- , EH^- ($\text{E} = \text{S}, \text{Se}, \text{Te}$), NH_2R and PR_3] has been investigated and the ligand reactivity of some of these derivatives studied.

A synthetic route to $\eta^2\text{-CSeS}$ and $\eta^2\text{-CSe}_2$ complexes of osmium without the use of molecular CSeS or CSe_2 has been developed and the isolation of the geometrical isomers of the $\eta^2\text{-CSeS}$ complex $\text{Os}(\eta^2\text{-CSeS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2$ (arising from $\eta^2\text{-C,S}$ or $\eta^2\text{-C,Se}$ coordination) has been achieved. The synthesis of a stable osmium hydrido-selenocarbonyl complex, $\text{OsHCl}(\text{CO})(\text{CSe})(\text{PPh}_3)_2$, has allowed the direct observation of hydride transfer from metal to CSe ligand. These latter results are discussed in Chapter 4.

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LIST OF ABBREVIATIONS

<i>n</i> -Bu	<i>n</i> -butyl
<i>s</i> -Bu	<i>s</i> -butyl
<i>t</i> -Bu	<i>t</i> -butyl
CNR	<i>p</i> -tolylisocyanide (unless otherwise specified)
COD	1,5-cyclooctadiene
Cp	<i>pentahapto</i> -cyclopentadienyl
Cp'	<i>pentahapto</i> -ethyltetramethylcyclopentadienyl
Cp [*]	<i>pentahapto</i> -pentamethylcyclopentadienyl
Cy	cyclohexyl
dipy	2,2'-bipyridyl
DMF	dimethylformamide
diphos	1,2-bis(diphenylphosphino)ethylene
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
Et	ethyl
hr(s).	hour(s)
i.r.	infrared
Me	methyl
min.	minute(s)
M.p.	melting point
n.m.r.	nuclear magnetic resonance
PCHO	<i>o</i> -diphenylphosphinobenzaldehyde
Ph	phenyl
phen	1,10-phenanthroline

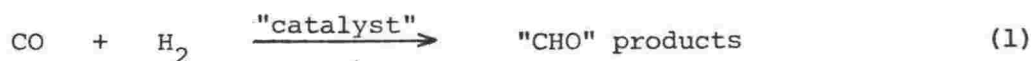
<i>i</i> -Pr	<i>iso</i> -propyl
py	pyridine
R	alkyl or aryl (unless otherwise specified)
THF	tetrahydrofuran
triflate	trifluoromethanesulphonate

PROLOGUE

THE FISCHER-TROPSCH SYNTHESIS REACTION

The drastic increase in oil prices since the end of 1973, coupled with world-wide concern regarding the rapid depletion of oil and natural gas reserves, has led to a reassessment of the role of coal as a major world energy source. Success in exploiting the world's huge reserves of coal will depend in the long run on developing technology to convert coal into liquid products and gas². One method of accomplishing this goal is via the Fischer-Tropsch reaction, in which synthesis gas - a mixture of CO and H₂ produced by burning coal in the presence of O₂ and steam - is converted into a wide range of hydrocarbon products.

The Fischer-Tropsch synthesis, which may be broadly defined as the reductive polymerization of CO, can be schematically represented as shown in equation 1. The "CHO" products are any



organic molecules containing C, H, and/or O which are stable under the reaction conditions employed in the synthesis. With most heterogeneous catalysts the primary products of the reaction are straight-chain alkanes, while the secondary products include branched-chain hydrocarbons, alkenes, alcohols, aldehydes, and carboxylic acids. The distribution of the various products depends on both the type of catalyst and the reaction conditions utilized³.

The Role of Organometallic Chemistry

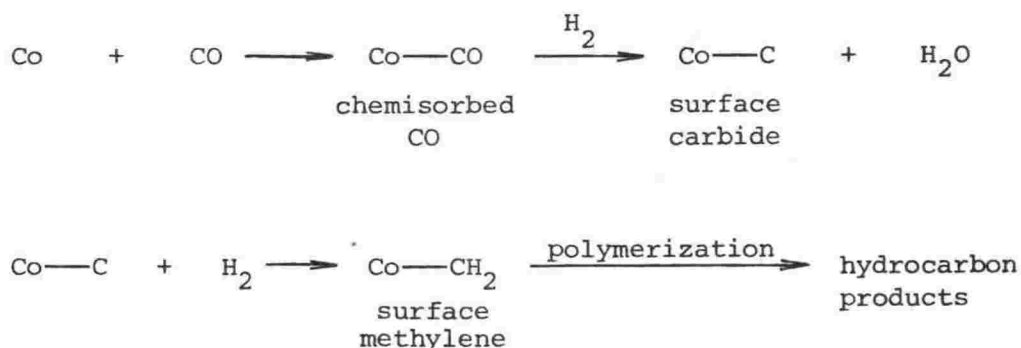
The problems for organometallic chemistry in dealing with the Fischer-Tropsch synthesis are firstly to find homogeneous catalysts and secondly to endeavour to understand the reaction.

The Fischer-Tropsch reaction is at present exclusively dependent upon heterogeneous catalysts which are not highly selective⁸ and are thus wasteful of reagents¹⁶⁸. Heterogeneous catalysts do present several advantages over homogeneous catalysts, but the key performance factor which has continued to promote efforts to find homogeneous substitutes is the high and often manipulable selectivity that is the hallmark of a successful homogeneous catalyst. Transition metal cluster complexes have been reported to function as homogeneous catalysts for the reduction of carbon monoxide. Thus, $\text{Os}_3(\text{CO})_{12}$ or $\text{Ir}_4(\text{CO})_{12}$ in toluene solution have been found¹⁶⁴ to be mildly catalytic for reduction of CO to CH_4 , and the latter⁷³ also yields ethane in a NaAlCl_4 melt at 180°C . Likewise Walker *et al.*¹⁶⁵ reported salts of the cluster anion $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ in THF or dioxane to be active for the hydrogen reduction of CO to methanol, ethylene glycol, glycerol, and propylene glycol. Several mononuclear metal complexes (for example, $\text{CoH}(\text{CO})_4$, $\text{MnH}(\text{CO})_5$ ⁶², and $\text{Ru}(\text{CO})_5$ ¹⁶⁷) have recently been shown to homogeneously catalyse the reduction of carbon monoxide by hydrogen to hydrocarbons. However, no homogeneous process is yet in use which is competitive with presently available heterogeneous processes¹⁶⁸.

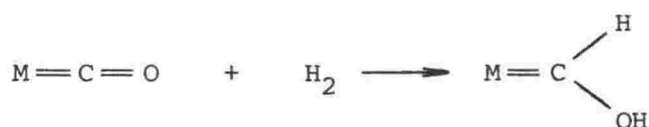
The elucidation of the mechanism of the Fischer-Tropsch synthesis (both the heterogeneously catalysed reaction and the more

recently developed homogeneous analogues) has been the aim of much research in recent years. While the mechanism of the reaction is still unknown, over the last 50 years several mechanisms have been proposed and these may be divided into three main classes principally on the basis of studies using heterogeneous catalyst systems: (a) metal-carbide mechanisms; (b) hydroxyl "carbene", $=C(OH)H$, condensation mechanisms; and (c) CO insertion mechanisms.

The earliest theory, advanced by Fischer and Tropsch in 1926⁴, proposed that the reaction proceeded via formation of intermediate metal carbides which reacted on the catalyst surface to form methylene groups. Surface polymerization of these methylene groups was then thought to occur to form hydrocarbon chains, which desorbed as saturated and unsaturated hydrocarbons. For example, the following reaction sequence was proposed for cobalt-based catalysts⁵:

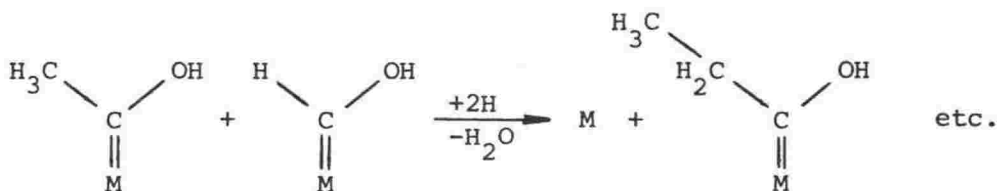
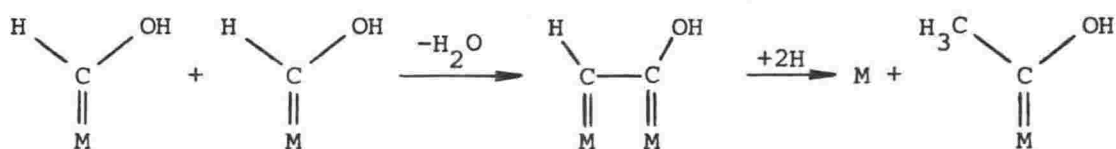


A second theory for the mechanism, proposed by Storch *et al.* in 1951⁶, suggested the formation of $=C(OH)H$ groups on the catalyst surface via hydrogenation of chemisorbed CO:

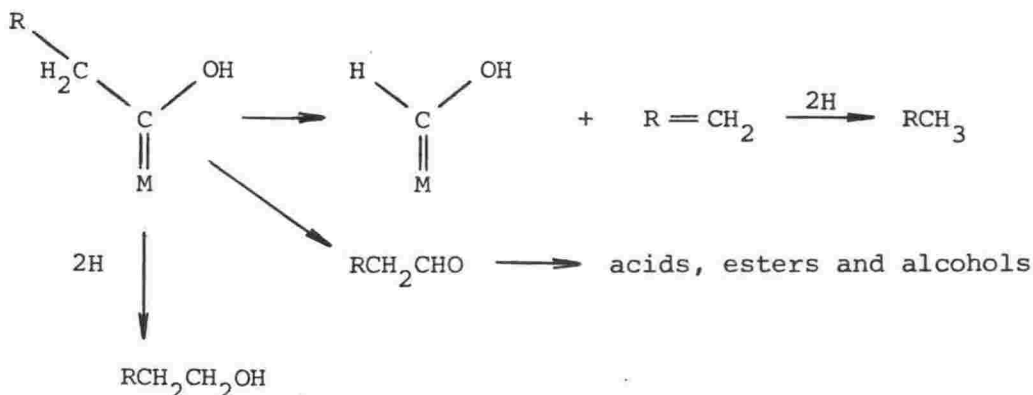


Chain growth then occurs through condensation of these groups with

concomitant elimination of water and addition of hydrogen:

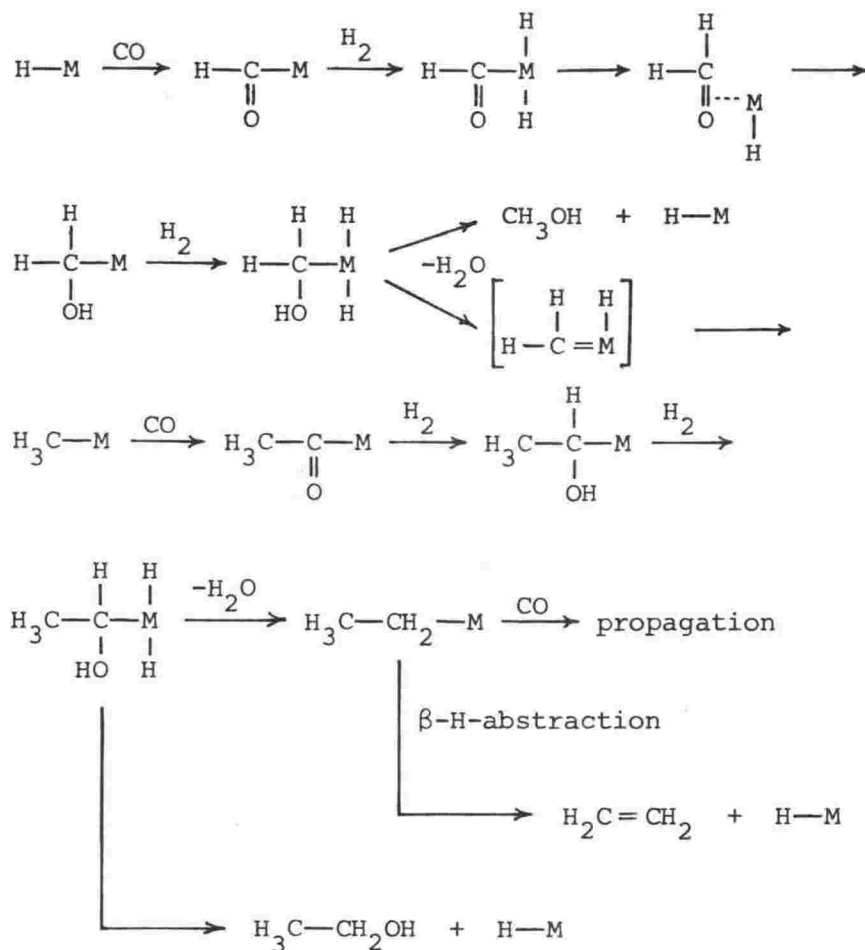


and termination by means of one of the sequences shown below:



The third class of mechanisms is that originated by Pichler and Schulz in which chain growth is accomplished by direct insertion of an absorbed CO molecule into a carbon-metal bond produced by hydrogenation of a surface carbonyl⁷. This mechanism explains all the various types of products found in the heterogeneously catalysed Fischer-Tropsch synthesis and incorporates many concepts which have now been demonstrated in organometallic chemistry. Several other mechanisms have been proposed^{8,9}; in essence these closely resemble that proposed by Pichler. The mechanism proposed recently by Henrici-Olivé and Olivé⁸ based on individual steps known to occur in

homogeneous catalysis with soluble mononuclear transition metal complexes is depicted in Scheme 1.



Scheme 1 Mechanism of the Fischer-Tropsch Reaction.

Reference 8.

A major problem associated with the investigation of the mechanism of the heterogeneously catalysed Fischer-Tropsch synthesis is understanding the nature of the molecular species which are formed and the processes which take place at the active sites of a catalytic surface. The nature of chemisorbed species has been indirectly investigated for a long time through the study of bulk properties¹⁵⁵ and some spectroscopic methods¹⁵⁶ have been used to examine the chemisorbed species which are assumed to be either precursors to or intermediates in heterogeneously catalysed reactions. But to a large extent this is an area of heterogeneous catalysis for which a fundamental knowledge is lacking.

Even the structure of metallic catalysts has been the subject of a certain amount of controversy¹⁵⁷, however work by Boudart¹⁵⁸ and others^{157,159} suggests that typical industrial metallic catalysts consist of finely divided, irregular particles of 100 or more metal atoms. This is clearly quite different from an ideal metal surface.

Polynuclear transition metal complexes or clusters containing as many as 30 metal atoms¹⁶⁰ forming a central core and bonded together in many different geometries have now been synthesized. Large numbers of such complexes have been characterized by X-ray crystallography¹⁶¹ and the size of these molecules can, in fact, approach that of particles of finely dispersed metals. Many, but the larger aggregates in particular^{161c}, have structures resembling those proposed for metal crystallites. An example of the structural relationship is offered by the hexagonally close packed structure of $[\text{Rh}_{13}\text{H}_3(\text{CO})_{24}]^{2-}$ ¹⁶². Such hcp structures are common for pure metals occurring, for example for osmium, ruthenium and, under some

conditions, cobalt; pure rhodium however is cubic close packed¹⁶³.

It appears, however, that even small transition metal cluster complexes can homogeneously catalyse the reduction of carbon monoxide by hydrogen^{73,164,165}. On the basis of this catalytic activity and other similarities, a number of workers have suggested that useful analogies may be drawn between the homogeneous stoichiometric (organometallic) chemistry of clusters and the processes which occur on the surfaces of heterogeneous catalysts¹⁶⁶. Moreover, the recent observations of homogeneous catalysis of the reduction of carbon monoxide by several mononuclear metal complexes^{62,167} suggest that it would not be unreasonable to surmise that discrete mononuclear transition metal complexes (as well as clusters) are, to a first approximation, reasonable models for metal surfaces in the heterogeneously catalysed Fischer-Tropsch synthesis reaction.

The interrelationship between surface chemistry, heterogeneous catalysis and organometallic chemistry has been discussed by several authors¹ and while the application of models for bonding and reactivity developed in organometallic chemistry to heterogeneous catalysis remains questionable (since no exact homogeneous analogue of the heterogeneous Fischer-Tropsch synthesis is known), the practice has originated through the need to draw reasonable chemical representations of surface species proposed for heterogeneous reactions. Even the utilization of organometallic models for homogeneous Fischer-Tropsch syntheses is open to question. This is particularly so when the known stoichiometric organometallic reactivity is not in agreement with the reactivity proposed for the catalytic organometallic species. However, organometallic reactivity,

in the main, has been investigated at temperatures less than 100°C while catalytic species (both homogeneous and heterogeneous) are often formed or react at much higher temperatures. Some unexpected and possibly enhanced reactivity of organometallic compounds may be anticipated at elevated temperatures.