

## ABSTRACT

Haloalkyl transition metal complexes can be precursors for a wide range of useful complexes. In Chapter 1, the bromohexyl iron complex,  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{Br}\}]$  has been prepared and new information on electrochemical and thermal behaviour of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{Br}\}]$  has been obtained from cyclic voltammetry and differential scanning calorimetry respectively. The chemical reactivity of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{Br}\}]$  with various reagents including NaOMe, a cobaloxime anion, MeLi,  $\text{NaN}_3$ , magnesium metal, phenol derivatives ( phenol, resorcinol, 4-hydroxybenzyl alcohol and 3,5-dihydroxybenzyl alcohol ), trityl salt,  $\text{PPh}_3$ , and  $\text{CO}/\text{AgBF}_4$  has also been studied. The new complexes that we obtained are namely:  $[\text{CpFe}(\text{CO})(\text{L})\{\text{C}=\text{O}(\text{CH}_2)_6\text{Br}\}]$  (  $\text{L} = \text{CO}$  and  $\text{PPh}_3$  ) from the reactions with  $\text{CO}/\text{AgBF}_4$  and  $\text{PPh}_3$  respectively,  $[\text{CpFe}(\text{CO})_2\{\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{Br}\}]\text{PF}_6$  from the reaction with the trityl salt, and  $\omega$ -functionalized hexyl iron complexes. All these new complexes have been characterized by standard analytical and spectroscopic methods. The results showed that chemoselective reactions of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{Br}\}]$  can occur at either the metal centre or the  $\omega$ -functional group. The results are also compared to those obtained for alkyl and functionalized alkyl iron complexes.

In Chapter 2, a series of new  $\omega$ -hydroxyalkyl transition metal complexes of the type  $[\text{L}_m\text{M}\{(\text{CH}_2)_n\text{OH}\}]$  ( where  $\text{L}_m\text{M} = \text{CpFe}(\text{CO})_2$ ,  $\text{Cp}^*\text{Fe}(\text{CO})_2$  and  $\text{CpRu}(\text{CO})_2$ ;  $n = 2, 3$  and  $4$  ), have been prepared. These new complexes have been characterized by microanalysis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and mass spectroscopy. The unusually high CO absorption bands of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_2\text{OH}\}]$  in IR spectroscopy are discussed. Also, significantly low chemical shifts of  $\alpha$  carbons in  $\omega$ -hydroxypropyl metal complexes were observed in  $^{13}\text{C}$  NMR spectra. This effect has been investigated by comparison with a series of  $\omega$ -functionalized propyl iron complexes and a new mode of interaction

between iron and  $\omega$ -functional group is proposed. The mass spectrum of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_2\text{OH}\}]$  shows a new fragmentation pathway and this is discussed. In Chapter 3, the reactivity of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_3\text{OH}\}]$  with various reagents, including silyl chlorides ( $\text{Me}_3\text{SiCl}$ ,  $t\text{-BuMe}_2\text{SiCl}$  and  $t\text{-BuPh}_2\text{SiCl}$ ),  $\text{PPh}_3/\text{CBr}_4$ , 4-nonyloxybenzoyl chloride,  $\text{Ph}_3\text{CPF}_6$  and  $\text{PPh}_3$  is described. Cyclic voltammetry and differential scanning calorimetry are also employed to investigate the electrochemical behaviour and the thermal properties of  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_3\text{OH}\}]$ . The results are compared with those obtained for  $[\text{CpFe}(\text{CO})_2\{(\text{CH}_2)_6\text{Br}\}]$ .

In Chapter 4, we describe the synthesis of a series of new organometallic dendrimers. These dendrimers have been prepared by the convergent approach and contain organometallic functional groups, namely  $\text{CpRu}(\text{CO})_2$ , which lie exclusively at the surface of the dendritic structure. The construction of these dendrimers starts from the reaction of haloalkyl metal complexes,  $[\text{CpM}(\text{CO})_2\{(\text{CH}_2)_3\text{Br}\}]$  ( $\text{M} = \text{Fe}$  and  $\text{Ru}$ ), with the building block 3,5-dihydroxybenzyl alcohol, followed by the activation reaction with  $\text{PPh}_3/\text{CBr}_4$  to give the first generation dendritic wedge. Through consecutive reaction cycles, we have prepared a dendritic wedge up to the fourth generation. This reacts with 1,1,1-tris(4-hydroxyphenyl)ethane to give a fourth generation dendrimer. This dendrimer contains 48 ruthenium metal atoms, and has a nominal molecular weight of 18438 amu. As far as we know, this dendrimer is the largest organotransition metal complex ever prepared. The thermal properties of the series of dendrimers have also been studied by differential scanning calorimetry and the results are discussed.

The experimental details are given in Chapter 5.