Some Organometallic Complexes Containing All-Carbon Ligands

by

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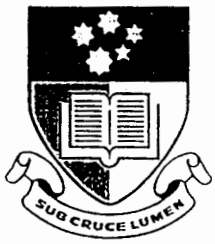

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- Abstract -

This thesis details the synthesis, characterisation and reactions of some transition metal complexes containg ligands dervived from the diacetylenes 1,4-bis(trimethylsilyl)buta-1,3-diyne and buta-1,3-diyne. Some related chemistry of $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp]PF_6$ and $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]PF_6$ is also described.

A brief review of the literature dealing with metal complexes of all-carbon ligands is given in Chapter 1.

A number of metal complexes derived from 1,4-bis(trimethylsilyl)buta-1,3-diyne are reported in Chapter 2. Further reactions afford mixed metal complexes in which the heterometallic fragments are linked by a C_4 chain.

The preparation of diynyl ($[L_mM]C{\equiv}CC{\equiv}CR$) and diyndiyl ($[L_mM]C{\equiv}CC{\equiv}C[ML_m]$) complexes are described in Chapter 3. Elaboration of the diynyl ligand has been achieved. Co-ordination to the C≡C triple bonds and incorporation of the terminal C atoms into clusters results in electron rearrangement along the C_4 chain. The bis-metallated tetra-yne complexes $\{Cp(CO)_3M\}C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C\{M'(CO)_3Cp\}$ (M, M' = Mo, W) have been prepared by oxidative coupling of the appropriate diynyl precursors.

In Chapter 4 the binuclear ruthenium complexes $[Ru]_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ ([Ru] = $Ru(PPh_3)_2Cp$ or $Ru(PMe_3)(PPh_3)Cp$) are shown to undergo an unprecendented series of four, one-electron oxidation processes. The nature of the electronic structure of the carbon bridge in these oxidised complexes has been probed using spectroelectrochemical techniques. Three of the $Ru(PPh_3)_2Cp$ series have been prepared by chemical oxidation and isolated.

The final Chapter begins with a description of the reactions between various nucleophiles and the allenylidene complex $[Ru(C=C=CPh_2)(PPh_3)_2Cp]PF_6$. In all cases attack occurs at the exposed C_γ, and the acetylide complexes $Ru(C\equiv CCPh_2R)(PPh_3)_2Cp$ {R = Me, OMe, CN, C_5H_5, $CH(CO_2Me)_2$} have been obtained. With $NHMe_2$, the cationic acetylide $[Ru\{C\equiv CCPh_2(NHMe_2)\}(PPh_3)_2Cp]PF_6$ was formed. The trienylidene ligand in $[Ru(C=C=C=CH_2)(PPh_3)_2Cp]PF_6$ reacts with various nucleophiles to give compounds containing allenylidene, vinyl acetylide, ethynylquinoline or azabuta-1,3-diene ligands. These observations have been rationalised in terms of initial attack at C_γ and the nature of the nuclephilic reagent.