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# Some Organometallic Complexes Containing All-Carbon Ligands

by

Paul James Low

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The Department of Chemistry

The University of Adelaide

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## - Abstract -

This thesis details the synthesis, characterisation and reactions of some transition metal complexes containing ligands derived from the diacetylenes 1,4-bis(trimethylsilyl)buta-1,3-diyne and buta-1,3-diyne. Some related chemistry of  $[\text{Ru}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$  and  $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$  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  $\text{C}_4$  chain.

The preparation of diyne ( $[\text{L}_m\text{M}]\text{C}\equiv\text{CC}\equiv\text{CR}$ ) and diyndiyne ( $[\text{L}_m\text{M}]\text{C}\equiv\text{CC}\equiv\text{C}[\text{ML}_m]$ ) complexes are described in Chapter 3. Elaboration of the diyne ligand has been achieved. Co-ordination to the  $\text{C}\equiv\text{C}$  triple bonds and incorporation of the terminal C atoms into clusters results in electron rearrangement along the  $\text{C}_4$  chain. The bis-metallated tetra-yne complexes  $\{\text{Cp}(\text{CO})_3\text{M}\}\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C}\{\text{M}'(\text{CO})_3\text{Cp}\}$  ( $\text{M}, \text{M}' = \text{Mo}, \text{W}$ ) have been prepared by oxidative coupling of the appropriate diyne precursors.

In Chapter 4 the binuclear ruthenium complexes  $[\text{Ru}]_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$  ( $[\text{Ru}] = \text{Ru}(\text{PPh}_3)_2\text{Cp}$  or  $\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cp}$ ) are shown to undergo an unprecedented 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  $\text{Ru}(\text{PPh}_3)_2\text{Cp}$  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  $[\text{Ru}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ . In all cases attack occurs at the exposed  $\text{C}_\gamma$ , and the acetylide complexes  $\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{R})(\text{PPh}_3)_2\text{Cp}$   $\{\text{R} = \text{Me}, \text{OMe}, \text{CN}, \text{C}_5\text{H}_5, \text{CH}(\text{CO}_2\text{Me})_2\}$  have been obtained. With  $\text{NHMe}_2$ , the cationic acetylide  $[\text{Ru}\{\text{C}\equiv\text{CCPh}_2(\text{NHMe}_2)\}(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$  was formed. The trienylidene ligand in  $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$  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  $\text{C}_\gamma$  and the nature of the nucleophilic reagent.