

**ORGANOMETALLIC CHEMISTRY OF SOME
MANGANESE AND ZIRCONIUM
COMPLEXES: A GREEN CHEMISTRY
APPROACH**

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ORGANOMETALLIC CHEMISTRY OF SOME MANGANESE AND ZIRCONIUM COMPLEXES: A GREEN CHEMISTRY APPROACH

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DECLARATION

I declare that this thesis is my own, unaided work, performed under the supervision of Professor N. J. Coville and Dr W. Meyer. It is submitted for the Degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination in any other University.

Sunnyboy Stanley Manzini

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ABSTRACT

The solventless reaction between $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ and PPh_3 as neat reagents using FTIRS was conducted and the activation enthalpy change of formation was found to be $143 \pm 19 \text{ kJmol}^{-1}$ while the activation entropy change of formation was $104 \pm 7 \text{ Jmol}^{-1}\text{K}^{-1}$. The same reaction was also carried out in chloroform and the activation enthalpy change of formation was found to be $146 \pm 8 \text{ kJmol}^{-1}$ while the activation entropy change of formation was $114 \pm 6 \text{ Jmol}^{-1}\text{K}^{-1}$. When the reaction was conducted in TCE solution, the activation enthalpy and entropy changes of formation were $137 \pm 6 \text{ kJmol}^{-1}$ and $97 \pm 5 \text{ Jmol}^{-1}\text{K}^{-1}$ respectively.

The solventless reaction of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with PPh_3 in KBr matrix using DRIFTS was also conducted and the activation enthalpy change of formation was found to be $169 \pm 28 \text{ kJ.mol}^{-1}$ while the activation entropy change of formation was $204 \pm 57 \text{ J.mol}^{-1}.\text{K}^{-1}$. The sample preparation method, the type of support and the particle size of the support material influenced the reaction rate. The solventless reaction $\text{Mn}(\text{CO})_4\text{LBr} + \text{L} \rightarrow \text{Mn}(\text{CO})_3\text{L}_2\text{Br} + \text{CO}$ [$\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{-R})_3$, $\text{R} = \text{Ph, MeO, Cl, F}$] in KBr using DRIFTS was also studied. It was found that the electronic effects of the ligand already attached on the metal complex influenced the rate of the reaction.

An optical microscopy study of the reaction $\text{Mn}(\text{CO})_4\text{LBr} + \text{L}' \rightarrow \text{Mn}(\text{CO})_3\text{LL}'\text{Br} + \text{CO}$ [$\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{-R})_3$, $\text{R} = \text{H, Ph, MeO}$] was undertaken in an attempt to reconcile the well-behaved reaction kinetics of the solventless reactions with solventless reactions by observing the microscopic behaviour of the reagents. The reactions were observed to go through a melt phase at temperatures much lower than the lowest melting point of the reagents, provided the reagents were in contact with each other. Isolated reagents neither reacted nor melted. The molten reagent thus served as a medium that allowed the diffusion of the reagents and products to ensure well-behaved kinetics. Investigation using ^{31}P NMR demonstrated that the dissociation of the attached phosphine ligands also

took place. The evidence obtained using the various techniques enabled the elucidation of the reaction mechanism.

The solventless reaction, $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2 + \text{Na}^+\text{RCOO}^-$, $\text{R} = \text{C}_6\text{H}_5$, $\text{p-C}_6\text{H}_4\text{-NO}_2$, $\text{p-C}_6\text{H}_4\text{-NH}_2 \rightarrow (\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl(RCOO)} + \text{NaCl}$ did not occur but the reaction was found to take place in the NMR solvent. Single crystal XRD study of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl(RCOO)}$ $\text{R} = \text{C}_6\text{H}_5$, $\text{p-C}_6\text{H}_4\text{-NO}_2$ revealed that the carboxylato ligand was coordinated in a bidentate fashion.

The reaction of chlorobis(η^5 -cyclopentadienyl)hexylzirconium(IV) with internal hexene isomers failed to yield terminal olefins even under harsh experimental conditions. Isomerisation reactions using substituted zirconium metallocenes also failed to produce the terminal olefin. The reaction of $\text{Cp}_2\text{ZrCl}_2 / n\text{-BuLi}$ with internal hexenes yielded a stoichiometric amount of 1-hexene. The reaction was found to be catalytic in Cp_2ZrCl_2 but limited by the amount of $n\text{-BuLi}$.

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