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

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A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Doctor of Philosophy
Johannesburg, 2005

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
September 2005

ABSTRACT

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

The solventless reaction of $Mn(CO)_4(PPh_3)Br$ with PPh_3 in KBr matrix using DRIFTS was also conducted and the activation enthalpy change of formation was found to be 169 ± 28 $kJ.mol^{-1}$ while the activation entropy change of formation was 204 ± 57 $J.mol^{-1}.K^{-1}$. The sample preparation method, the type of support and the particle size of the support material influenced the reaction rate. The soventless reaction $Mn(CO)_4LBr + L \rightarrow Mn(CO)_3L_2Br + CO$ [L= P(*p*-C_6H_4-R)$_3$, R = 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 $Mn(CO)_4LBr + L' \rightarrow Mn(CO)_3LL'Br + CO$ [L= P(*p*-C_6H_4-R)$_3$, R = 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, $(\eta^5\text{-}C_5H_5)_2ZrCl_2 + Na^+RCOO^-$, R = C_6H_5, p-C_6H_4-NO_2, p-C_6H_4-NH_2 → $(\eta^5\text{-}C_5H_5)_2ZrCl(RCOO)$ + NaCl did not occur but the reaction was found to take place in the NMR solvent. Single crystal XRD study of $(\eta^5\text{-}C_5H_5)_2ZrCl(RCOO)$ R = C_6H_5, p-C_6H_4-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 Cp_2ZrCl_2 / *n*-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*-BuLi.

ACKNOWLEDGEMENTS

My immediate thanks go to God Jehovah for the life that I have, all-round support with day-to-day business activities particularly on bad days, protection (inclusive of unforeseen circumstances), help and encouragement (through his word) when I felt small and helpless, and needed constant guidance.

I am greatly indebted to the following people whose input and support made this thesis possible.

- Prof. N. J. Coville, My supervisor and mentor, for his luminosity. I would not have managed to produce this document without his timely interventions, particularly when nothing seemed to work. I am privileged to have had his expert guidance. I managed to see further than others by standing on the shoulders of a giant.
- SASOL, DoE NRF and The University of The Witwatersrand Scholarships for financial support
- Prof C. B. de Koning for encouragement and optimism.
- Prof M. Rollnick for her encouragement.
- Dr E.M. Mmutlane for his friendship and incessant nagging. Your support in many ways is appreciated.
- Mrs F. Nareetsile for friendship and support in the lab. Thanks a lot sister.
- My mother, S. N. Maswanganyi for everything. I would not have been where I am without her help and support and yes her prayers.
- Miss A. Budhai for being a good friend and her support.
- Mr R. Mampa for NMR work and friendship. Mrs S. Heiss also helped with NMR work.
- Dr M. Fernandes for X-ray crystallographic work.
- Dr M. Bala, Dr O. G. Adeyemi, Dr T. Molefetse, Mr T. Magadzu, Miss K. Khoabane for assistance in the lab.
- The entire CATOMCER group, Mr K. Mokoena, Mr. L. Sikwivhilu, Miss C. Mbileni, Miss S. Mohlala, Dr S. Ndou, Dr X Liu and Dr R. Mpfundzeni.

- My friends Mr S. Molele, Mr J. Maluleke, Mr I. Khosa, Mr C. P. Sibuyi and Mrs J. Nhlapo (thanks a lot sister particularly for your encouragements and prayers)
- Mr S. Gannon and Mr B. Fairbrother for glass blowing work.
- Mr B. Chassoulas for electronic work. I appreciative your assistance with the GC (assemble and calibration), heating jacket and autoclave constructions.
- Physics workshop for autoclave modifications.
- My wife, N. B. Sekgobela, for reasons too many to mention.

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