UNIVERSITY OF ILORIN

THE ONE HUNDRED AND SIXTY-FIFTH (165TH) INAUGURAL LECTURE

"IN SEARCH OF THE ANSWER TO QUESTIONS UNKNOWN"

By

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This 165th Inaugural Lecture was delivered under the Chairmanship of:

The Vice-Chancellor

Professor AbdulGaniyu Ambali (OON)
DVM (Zaria), M.V.Sc., Ph.D. (Liverpool), MCVSN (Abuja)

24th November, 2016

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Order of Protocol
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My Lords, Spiritual and Temporal,
My Brother Knights of the Order of St. Mulumba Nigeria,
  Noble ladies of St. Mulumba,
Distinguished Guests, Gentlemen of the Fourth Estate of
  the Realm,
Great and Illustrious Nigerian Students, especially Students
  of the University of Ilorin,
Ladies and Gentlemen,

Pre-Chemistry
　　　　To HIM who sits on the throne and to the Lamb be blessing and honour and glory and might forever and ever, Amen. (Rev 5:14)
1.0　　I thank you God Almighty for the privilege you have given me to present this 165th inaugural lecture of the University of Ilorin, Nigeria. The first inaugural lecture from the Department of Chemistry was delivered by Professor M. O. Fagbule on the 15th of December, 1988 and was entitled "Colour to a Colourless World: A Chemists Modest Contribution". That Lecture was the 32nd in the series of the University of Ilorin Inaugural Lectures. The following Professors of the Department of Chemistry delivered their inaugural lectures in the chronological order shown below:　Professor J. A. Obaleye;

Professor S.A. Abdulkareem; Professor S. A. Ibiyemi; Professor G.A. Olatunji; Professor D.S. Ogunniyi; Professor F.A. Adekola and Professor E. O. Odebunmi.

Today, I am especially grateful to God for the privilege to deliver the 165th inaugural lecture of the University of Ilorin and the ninth from the Department of Chemistry. It is the first to focus on Organometallic Chemistry specialty. This lecture entitled "**In Search of the Answer to Questions Unknown**" is coming five years after my appointment to the chair of chemistry. I thank the Vice-Chancellor and the University Administration for the opportunity to deliver this inaugural lecture.

Mr. Vice-Chancellor sir, I am in love with the written word and I read from sundry sources. I have taken the title of this inaugural lecture from a Chinese poem by an anonymous author. Let me reproduce this poem in full:

> *'To sail on a dream on a crystal clear ocean*
> *To ride on the crest of the wild raging storm*
> *In search of the answer to questions unknown*
> *To be part of the movement and part of beginning to understand*
> *And then I realize*
> *To live on the land we must learn from the sea to be true as the tide*
> *And free as wind- swell*
> *Joyful and loving in letting it be'. (Anon)*

To summarize, this poetry teaches the importance of hard work, of not giving up in the face of difficulties, determined to achieve set objectives, never to manipulate outcomes, but to observe clearly. That way, our efforts yield useful dividends. Most importantly, we are to enjoy what we do.

2.0 Introduction: How it all began

After my Secondary School education at Priscilla Memorial Grammar School [PMGS] Oguta, Imo State, I arrived in the city of Ilorin in October 1978, to begin my University education. My Bachelor degree final year project was on "Synthesis and Structural Elucidation Studies of Organotin (IV) Complexes of some Schiff base Ligands". Everything about this work demanded precaution and a lot of care. To achieve successful synthesis, solvents must be dried, bench top manipulations must be avoided and micro-quantities only were to be carefully weighed out, because the reagents were expensive and not easily procurable. Even cleaning of glassware after synthesis, analysis and purification were tasks that demanded time. And so the questions began: why can't I work in the presence of air and water vapour? Why not use wet solvents like students working in other areas of research? Why must I pump out atmospheric air and vapour before a synthetic step? Why were my reagents not readily available? Why were they expensive? Why can't I clean my glassware with soap and water? Why?! Why?!! Why?!!! Well in search of answers, I first turned to journal articles most especially and to one of the few titles dealing with Organometallic Chemistry that I could find in the University library; "The Chemistry of Organotin Compounds" by R.C. Poeller. I found some answers but there were more questions, most were unknown to me at the time and therefore intriguing. Then I turned to my teacher, Prof. M.A. Mesubi, from him I learnt that the area was relatively new and growing. I continued to harbour a number of unanswered questions, had a wide and growing range of applications and had the potential to advance the frontiers of chemistry in terms of synthesis, structural elucidation studies, geometries, electronic potentials, theoretical and computational studies, industrial applications, etc. It appeared to me, conclusively, at the time, that the more answers I got, the more questions arose, such that I could say that "there are more questions than answers". It

therefore did not take me time or persuasion to pitch my tent with organometallic chemistry, especially the syntheses and structural studies of its novel compounds.

After the Mandatory National Youth Service Corps programme, I returned to the University of Ilorin to begin postgraduate studies in the area of organometallic chemistry, under the supervision of Professor M. A. Mesubi. Later, in 1987, I joined the Faculty of Science of the University of Ilorin as an Assistant Lecturer and resumed studies for my doctoral thesis in the Department of Chemistry. The peculiarities of a doctoral thesis in synthetic organometallic chemistry took me to other eminent chemists. Together they have helped to form my research direction. To them all I remain eternally grateful: Professor M. A. Mesubi for studies of organotin(IV) compounds; Professor A. R. Manning of the Department of Chemistry, University College, Dublin, Ireland for the syntheses of cobalt-tin (Co-Sn) and tin(IV)-carbon (Sn(IV)-C) bonds; Professor Ling-Kang Liu of the Institute of Chemistry Academia Sinica, Nankang, Taipei, Taiwan for the syntheses and Structural studies of new stable iron(0) compounds of the cyclopentadienyl ligand and Professor N. J. Coville of the Department of Chemistry, University of the Witwatersrand (WITS), Johannesburg, South Africa for the syntheses of organometallic systems in the non-solvent medium.

3.0   History and Basic Concepts
The First Organometallic Compounds

Organometallic Chemistry, the Chemistry of compounds containing metal-carbon bonds, has grown enormously as a field of study during the past six decades. It includes a wide variety of chemical compounds and their reactions. In this group are also compounds containing both sigma (σ) and pi (π) bonds between metal atoms and carbon, many cluster compounds, containing one or more metal-metal bonds and molecules of structural types unusual or unknown in organic chemistry.

The original discovery of the first organometallic compound took place as long ago as 1830 (Hunt, 1984), at a time, when organic chemistry was also in its infancy. The credit for this discovery goes to William Christopher Zeise, who was born in Slagelse in Denmark, and was the son of a local pharmacist. It was in 1830 that Zeise presented a paper in Latin to the University of Copenhagen, under the title "The reaction between platinum chloride and wine alcohol and on the new substances arising there from" (Zeise, 1831). This he achieved by dissolving platinic chloride ($PtCl_3$) in alcohol, evaporation of excess alcohol and reacting the residue with potassium chloride (KCl). In the manner of the time, when many newly prepared compounds were given the name of their discoverer, the compound became known as "Zeise's salt, $K[PtCl_3(C_2H_4)]H_2O$, whose anti-cancer properties have been widely investigated.

Zeise's salt
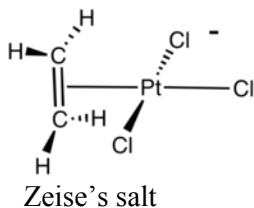
Zeise paper immediately attracted considerable attention from Berzelius, Liebig and Poggendorff. Berzelius and Poggendorff wrote Oersted the following lines to congratulate his country: "May I congratulate your country which through its latest work of Professor Zeise has been assured of a place in the history of Chemistry" (Hunt, 1984).

A little later on, the elegant chemistry embedded in Zeise's salt was to be involved in bitter controversy that continued for more than twenty years among the leading chemists of the period. Berzelius, Dumas and Liebig strongly opposed the conclusions of Ziese. Nearly a quarter of a century later Zeise's views were fully vindicated by two assistants of

Hofmann in the Royal College of Chemistry in London. Johann Griess and Carl Martins not only confirmed that ethylene was liberated when Zeise's salt was decomposed but confirmed the formulae given by Zeise in contradiction to the opinion of Liebig who believed that the ethylene moiety bore an oxygen atom in the form "C_4H_5O".

No further work was carried out on these platinum complexes for many years, but in the meantime great strides forward were made in the general subject of the combination of metals with organic substances, chiefly by Edward Frankland. His first discoveries, made in Bunsen's laboratory in Marburg in 1849, were of zinc methyl and zinc ethyl (H_3C_2-Zn-C_2H_5). It was Frankland who coined the term that describes this phase of chemistry. "I have applied the name organometallic to a family of compounds resulting from this investigation, the members of which contain a positive organic radical united directly with a metal. It serves to distinguish them from other organic compounds containing metals in which the metal and the organic radical are indirectly united or linked to each other" (Hunt, 1984). The zinc compounds discovered by Frankland have often been described in the chemical literature, and even by Frankland himself, as the first of the organometallic compounds, an obviously incorrect assessment and it seemed most probable that he was unaware of Zeise's original work. However, his own work yielded vital and valuable results in organic synthesis and he clearly foresaw the potential application that lay ahead as he would say the following in a paper to the Royal Society in London in 1852: "The extra-ordinary affinity of zinc methylithium for oxygen, its peculiar composition, and the facility with which it can be procured cannot fail to cause its employment for a great variety of transformations in organic compounds" (Frankland, 1852).

Another half century had to pass before the scientific community reached another milestone in the development of this series of compounds. Francois Auguste Victor Grignard decided

to replace the zinc of Frankland's compound with magnesium in their organic halides (RMgBr). He published his results as his doctoral thesis in 1901 (Pope and Peachy, 1909) and later in 1912, received the Nobel Prize for this work. Grignard reagents as they are called have since become active and versatile alkylating agents only second to lithium reagents (LiR).

3.1   MILESTONES:

However, between Frankland (1852) and Victor Grignard (1901) is a record of achievements in what is today formally known as organometallic chemistry: C. Friedel and J. M. Crafts for the synthesis of organochlorosilanes in 1863;

$$SiCl_4 + {}^m/_2 ZnR_3 \longrightarrow R_m SiCl_{4-m} + {}^m/_2 ZnCl_2$$
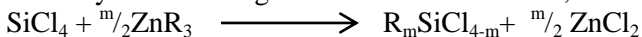
M.P. Schutzenberger records the synthesis of the first metal carbonyl complex $[Pt(CO)Cl_2]_2$ in 1868; later in 1890, L. Mond caused the synthesis of $Ni(CO)_4$, the first binary metal carbonyl. (Mond himself was the founder of Imperial Chemical Company (ICI), a renowned art collector and patron of the arts); in 1909, W.J. Pope introduced the first σ-organotransition metal compound with the formation of $(CH_3)_3PtI$; while in 1917, W. Schlenk using the method of transalkylation reaction introduced the lithium alkyls.

$$2Li + R_2Hg \rightarrow 2LiR + Hg$$
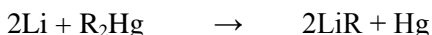
Today lithium alkyl is a versatile alkylating reagent even in organic synthesis. Indeed, organometallic chemistry continued to grow slowly and in a haphazard manner until 1951, when Kealy and Pauson and Miller, Tremaine and Tebboth working as two independent groups, published the synthesis of ferrocene. Ferrocene is known today as the first sandwich complex. (Kealy and Pauson 1951, Miller, Tebboth and Tremaine, 1952)
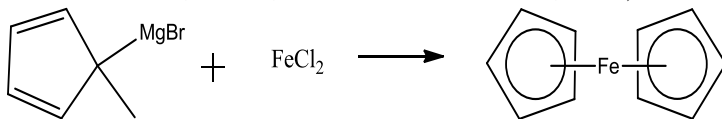
At inception, both groups had wrongly assigned the structure of metal alkyl to the novel, highly stable and fascinating compound they had just achieved.
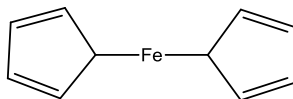
Efforts by G. Wilkinson (Wilkinson, 1975) and E.O. Fischer to establish the correct sandwich structure and explore the uniqueness of the new compound earned, for both men, the chemistry Nobel Prize in 1973. By so doing they definitively introduced a number of formalisms firmly establishing a new broad interdisciplinary field whose sphere of interest includes all compounds wherein a metal (in low oxidation state) is bonded through carbon to an organic molecule (M-C), radical or ion. Since the 1950's, organometallic chemistry has become a very active field marked by the discovery of new organometallic compounds along with their detailed structural and chemical characterization and their application as synthetic intermediates and catalysts in industrial processes.

3.2   Concepts
### 3.2.1   The Stability and Reactivity of Organometallic Compounds

The stability and reactivity of organometallic compounds are associated with the nature of the organic ligands and the metal to which they are attached (Housecroft and Sharpe, 2005). In each of the main groups of the periodic table (groups 1, 2 and 13-15), the thermal stability of a given type of organometallic compound generally decreases from the lightest to the heaviest element in a group. For example, in compounds containing group-1 metal, methyllithium ($LiCH_3$) is more stable than methylpotassium (KCH_3), and in those with group-14 metals, tetramethylsilicon $Si(CH_3)_4$ is stable in the absence of air at 500 °C whereas tetramethyllead, $Pb(CH_3)_4$ rapidly

decomposes at that temperature. This trend in stability is a consequence, in part, of the decrease in M–C bond strength on going down within a group. The trend does not hold for d-block (transition metals) elements in groups 3-12 where M–C bond strengths and stability often increase going down a group. The reactivity of organometallic compounds with water and air vary widely. The highly active main-group metals such as lithium, sodium, magnesium and aluminum form highly air- and water-sensitive organometallic compounds. For example, $Al_2(CH_3)_6$ undergoes immediate and violent reaction with water to give methane CH_4 and it bursts immediately into flame on contact with air. For the elements toward the right of the periodic table (groups 14 and 15), their organometallic compounds are not water-sensitive. Tetramethylsilicon, for instance does not react with water or air at room temperature.

3.2.2 Pi Backbonding

Pi (π) backbonding, also called, π backdonation is a concept from chemistry in which electrons move from an atomic orbital on one atom to a π* antibonding orbital on a π-acceptor ligand (Miessler and Tarr, 1999). It is especially common in the organometallic chemistry of transition metals with multi-atomic ligands such as ethylene, carbon monoxide, etc. Electrons from the metal are used to bond to the ligand, in the process relieving the metals of excess negative charge.

The non-classical chemistry of organometallics deal with metal compounds having ligands that are capable of, and even require, synergic ligand →metal σ/metal → ligand π electron flow (Mc Naught and Wilkinson, 2006). The synergic interaction arises when the σ donor ligand has a low energy π-acceptor orbital (LUMO) while the σ-acceptor in the adduct configuration has a π-donor orbital (metal, HOMO) of same symmetry

dz² metal ⟵ ligand   σ bonding.

M   L

Metal (HOMO) ligand ⟶ π bonding (LUMO)
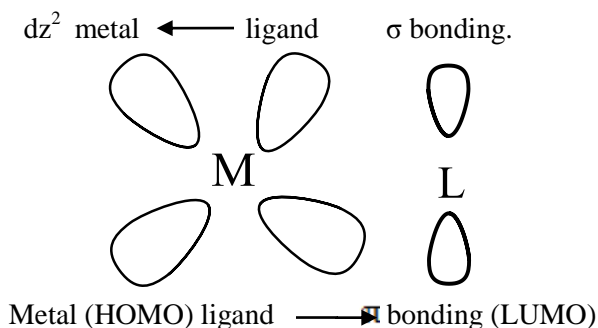
An important consequence of this two-way donor-acceptor bonding is that a bonding role can be given to otherwise non-bonding or even purely anti-bonding σ* electrons on the metal, thereby imparting greater stability to the resultant organometallic compound.

The bonding in a metal carbonyl (MCO) can be used to illustrate this. According to Mc Naught and Wilkinson (2006) and Housecroft and Sharpe (2005) the electrons are partially transferred from a d-orbital of the metal to anti-bonding molecular orbitals of CO. This electron transfer strengthens the metal–Carbon bond and weakens the C–O bond. The strengthening of the M–CO bond is reflected in increases of the vibrational frequencies for the M–C bond (often observed outside the range for the usual IR spectrophotometers). Furthermore, the M–CO bond length is shortened. The weakening of the C–O bond is indicated by a decrease in the frequency of the v_{CO} band(s) from 2143 cm^{-1}, for free CO to 2060 cm^{-1} in Ni(CO)$_4$ and 1981 cm^{-1} in Cr(CO)$_6$ and 1790 cm^{-1} in the anion [Fe(CO)$_4$]$^{2+}$. For this reason, infrared spectroscopy is an important diagnostic technique in metal carbonyl chemistry.

### 3.2.3: The Effective Atomic Number Rule (EAN)

In main group chemistry, we encounter the octet rule in which the electronic structures of many main group compounds

can be rationalized on the basis of a valence shell requirement on 8 electrons. Similarly, in organometallic chemistry, the electronic structures of many compounds are based on a total valence electron count of 18 on the central metal atom. As in the case of the octet rule, there are many exceptions to the 18 electron rule (Miessler and Tarr, 1999). Thus, the EAN rule is often referred to as the 18-or 16- electron number rule. EAN allows the systematization of much of the structural chemistry of transition metal organometallic compounds and is a useful guide to their reactions. Stable organometallic compounds of the transition metals will have total of 18-valence electrons about the metal; in other words they will have the effective atomic number of the next higher inert gas. (Elschenbroich and Salzer, 1989). However molecules having only 16-valence electrons can often be just as stable as, or even more stable than, 18-electon molecules of the same metal. This is especially true of metals at the bottom right corner of the transition metal series i.e. Rhenium to Platinium. These metals have the least tendency to be six-coordinate. Thus, in oxidation states such as Ir(I) and Pt(II) such metals can form stable 16-electron molecules.

The application of the EAN rule is quite simple. If a metal is to accommodate six adduct bond pairs and follow the EAN rule, the metal must have three electron pairs of its own. That is, the metal atom or ion involved will have a d^6 configuration and the structures of such complexes will be expected to be roughly octahedral i.e. Metals with four valence electron pairs of their own require the presence of five adduct bond pairs and should exhibit structures based on the trigonal bipyramid (tbp) or square pyramid (sp) Metals with five valence electron pairs should adopt tetrahedral square planar structures by acquisition of four ligand electron pairs i.e. d^{10} + 4 ligand bond pairs = MD_4 (Co^-, Ni^o, Cu^+) Our counting statistics model views the complexes as donor/acceptor adducts wherein each ligand is thought of as an electron pair donor and the metal as an electron pair acceptor (Miessler and Tarr, 1999).

3.2.4   Orbital Hybridization

Linus Pauling first developed the hybridization theory in 1931 in order to explain the structure of simple molecules such as methane using atomic orbitals (Pauling, 1931). The theory consists of combining atomic orbitals (s,p,d,f) into new hybrid orbitals. Pauling pointed out that a carbon atom forms four bonds by using one s and three p orbitals, so that it might be inferred that a carbon would form three bonds at right angles (using p orbitals) and a fourth weaker bond using the s orbital in some arbitrary direction. In reality, however, methane has four bonds of equivalent strength separated by the tetrahedral bond angle of 109.5°.
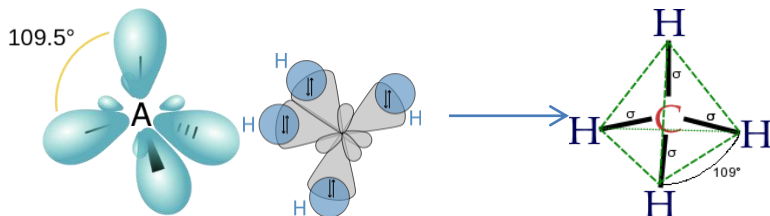
Four sp^3 orbitals

Pauling explained this by supposing that in the presence of four hydrogen atoms, the s and p orbitals form four equivalent combinations or hybrid orbitals, each denoted by sp^3 to indicate its composition which are directed along the four C–H bonds (Pauling, 1960). This concept was developed for simple chemical systems, but the approach was later applied more widely, and today it is considered an effective general strategy for rationalizing the structures of organic compounds. Orbitals are a model representation of the behaviour of electrons within molecules. In the case of simple hybridization, this approximation is based on atomic orbitals, similar to those obtained for the hydrogen atom, the only neutral atom for which the Schrodinger equation can be solved exactly. In heavier atoms, such as carbon, nitrogen, and oxygen, the atomic orbitals

used are 2s and 2p orbitals, similar to excited state orbitals for hydrogen. Hybrid, orbitals are assumed to be mixtures of these atomic orbitals, superimposed on each other in various proportions. It provides a quantum mechanical insight to Lewis structures. Hybridization theory finds its use mainly in organic chemistry and is the combining of solutions to the Schrodinger wave function for atomic orbitals to produce hybrid orbitals. The total number of orbitals available for forming bonds does not change, a new set of slightly different energy is simply formed, (Vollhardt, 2005)

$2s$ $\qquad$ $2p_z$ $\qquad$ sp hybrid
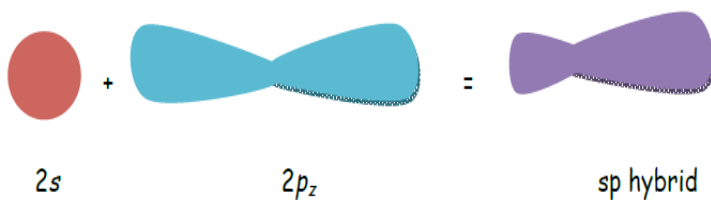
Hybridization

4.0   Applications
The continued research interest in organometallic compounds over the past sixty years has been largely due to their wide-spread applications in industry, agriculture and medicine. Details of these wide applications will not be discussed in this lecture.

5.0   My Contributions to Research
Mr. Vice Chancellor Sir, I now turn to my contributions to the development of organometallic chemistry in particular. Because, when I do coordination chemistry, it is often with the view to make a metal-carbon bond.

5.1   Organotin (IV) Complexes

My first publication came from my M.Sc. thesis. I had studied the biological activity of triorganotin(IV) compounds of *N*-protected amino-acids. (Eke, Mesubi and Bamigboye, 1988). The complexes are of the type R_3SnL (L = *N*-phthaloyl derivatives of glycine, DL-alanine, or *N*-acetyl and *N*-benzoyl-glycine and cystein).
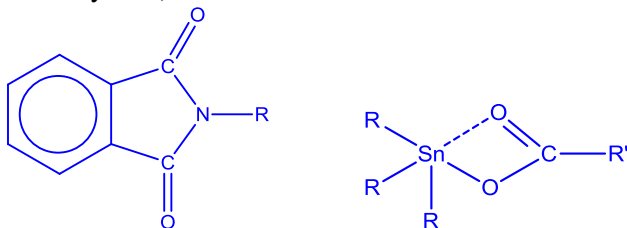
The complexes were characterized by elemental analysis, infrared and NMR spectroscopy. They are monomeric in molten camphor. The spectral data support cis five-coordinate geometry with an unsymmetrical bidentate coordination of the carboxylate group to the tin moiety.

The triorganotin(IV) complexes were found to be stomach poisons to bean weevils (*Sitophilus granaria*) even at low concentrations. They also show fungicidal activity on *Aspergilus niger* and *Helminthosporium taulosum*.

5.2   Cyclopentadienyliron Halides as Electrophiles

Vice-Chancellor sir, I now turn the attention of this audience to the chemistry of η^5-cyclopentadienyliron dicarbonyl halides (Fp-halide). In the presence of tertiary phosphines PR_3, Fp-halide and lithium alkyls (RLi, R = Me, n-Bu, Ph) react at low (-78 °C) temperatures (Eke, Luh and Liu, 1995). The reaction pattern found is that of a facile three-component reaction which effectively changes the η^5-$C_5H_5^-$ bonding mode in Fp- halide to η^4-RC_5H_5 bonding in $(\eta^4$-$RC_5H_5)Fe(CO)_2PPh_3$. Vice-Chancellor sir, the authors, (Eke, Luh and Liu, 1995) were

delighted to report the accomplishment of the following from the three-component reaction in the presence of PR_3 (i) transformation from η^5 to η^4 bonding mode for Fp- halide, (ii) synthesis of a stable Fe(0) compound from Fe(II) species, (iii) ring alkylation of a 1,4-cyclopentadiene moiety and (iv) confirmation that the three-component reaction under discussion is a one-pot synthesis that took place in a tandem fashion.

Furthermore, we studied the electron density of the Fe(0) surface as implied by the back donating ability of the Fe core to CO ligands by varying the incoming phosphine ligands (PPh_3, $PMePh_2$, PMe_2Ph and PMe_3). Treatment of equimolar amounts of Fp-Iodide and PR_3 in THF at -78 °C with a slight excess of MeLi results in the formation of $(\eta^4\text{-}MeC_5H_5)Fe(CO)_2(PR_3)$. These are identified as compounds **1-4** for $PR_3 = PPh_3$, $PMePh_2$, PMe_2Ph and PMe_3 respectively.

1-4, $PR_3 = PPh_3$, $PMePh_2$, PMe_2Ph, PMe_3
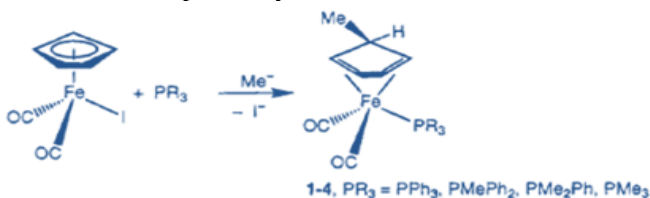
Scheme 1

Two IR absorption bands are recorded for each complex. The symmetric v_{CO} frequencies are 1958, 1962, and 1964 cm^{-1} and the asymmetric ones are 1893, 1898, 1904 cm^{-1} for **4**, **3**, **2** and **1** respectively. Our results show that, among the phosphines employed, PMe_2, is the most σ-donating while, PPh_3 is the least σ-donating moiety. Consequently, the PMe_3 derivative (compound **4**) bears the most electron-rich Fe core while, the PPh_3 congener (compound **1**) is the least electron-rich Fe centre for the corresponding complexes.

Detailed ^{31}P NMR studies of (**1-4**) revealed a regular variation in the chemical shifts of the tertiary phosphines. The

^{31}P NMR chemical shifts Δ of a tertiary phosphine were fitted to a mathematical equation:

$$\Delta = -62 + \sum_{n=1}^{3} \sigma_n^p$$

Where σ^p is the group contribution; e.g. $\sigma_{Me}^P = 0, \sigma_{Ph}^P = 18$

Mr. Vice-Chancellor, equation 1 is our handiwork,(Luh, Eke and Liu, 1995) the equation, correctly predicts the ^{31}P-NMR chemical shifts of tertiary phosphines. The calculated chemical shifts are within 2 ppm units from the observed chemical shifts as recorded in Table 1.

Table 1: Observed and calculated ^{31}P Chemical Shifts of Complexes 1-4

Complex	Δ_{obsd}, δ	Δ_{cald}, δ	diff, δ
1	28.0	26.3	1.7
2	39.2	41.6	-2.4
3	56.8	56.9	-0.1
4	73.2	72.2	1.0

The results of the X-ray structure analysis of the Ph$_2$Me analogue **2** (Fig. 1) suggest that the nucleophilic addition of Me is direct without Fe mediation and the Me is exo to the cyclopentadiene ring.
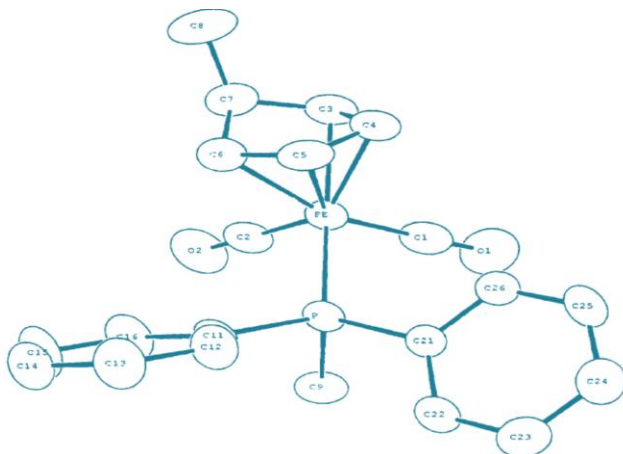
Fig. 1. Molecular plot of the Ph$_2$Me analogue 2 with atomic numbering sequences. The thermal ellipsoids are plotted at the 50% level, The H atoms are omitted for clarity (Luh *et al*., 1995).

With diphosphines, the low temperature, 3-component reaction under discussion gives complexes with one free, dangling phosphorus atom as in compound **5** with dppm in scheme 2
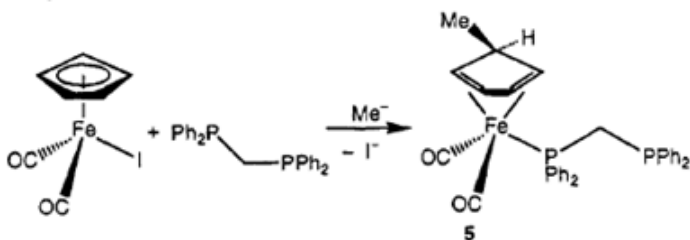
Scheme 2

When the diphosphines are dppe, dppb or dppp the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (FpI) with BuLi in 2:1 mole ratio yields products in which both rings are alkylated. The dppm arm is

17

thought to be too short to accommodate a second cyclopentadiene fragment.

n = 2-4

6-8
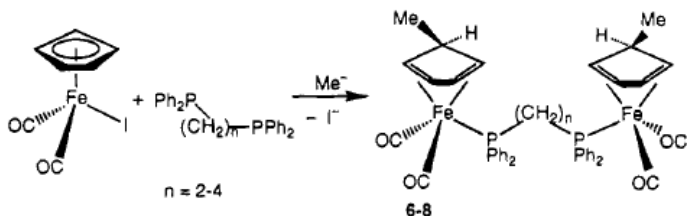
Scheme 3

Complex **6** has been investigated by a single-crystal X-ray diffraction study. Fig. 2 shows the molecular plot of **6,** in which a bridging dppe links two $[(\eta^4\text{-MeC}_5H_5)Fe(CO)_2]$ units. Given four molecules in the unit cell of *C2/c* that has eight equivalent positions, only half of the molecule is crystallographically independent, the molecule being required to possess a C_2 crystallographic symmetry. The Me group is on *exo* position on the cyclopentadiene ring. The coordination geometry around Fe is that of a distorted square pyramid with one CO placed at the apical position, $PPh_2(CH_2\text{-})$ in the basal plane trans to one of the double bonds, and the second CO ligand trans to the second double band.
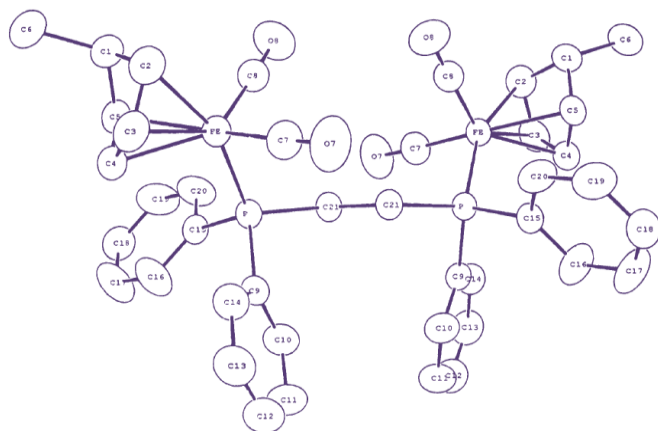
Fig. 2. Molecular plot of complex 6 with atomic numbering sequences. The thermal ellipsoids are plotted at the 50% level.

Three-Component Reaction in the Presence of NaOR/NaSR

Half-sandwich Iron carboxyl and thiocarboxyalkyls result from the reactions of NaOR/NaSR and FpI in the presence of PPh_3 (Liu, Eke and co-workers, 1995a). For instance, one equivalent of NaOMe (as alkylating agent)was added to an equimolar mixture of FpI and PPh_3, after the addition of a few drops of n-BuLi, to take advantage of the catalytic formation of $[FpPPh_3]^+I^-$ which upon formation became the virtual reactant with the nucleophile, $-OMe^-$. The $-OMe^-$ reaction yielded the methylcarboxylate $(\eta^5-C_5H_5)Fe(CO)(PPh_3)C(O)OMe$.
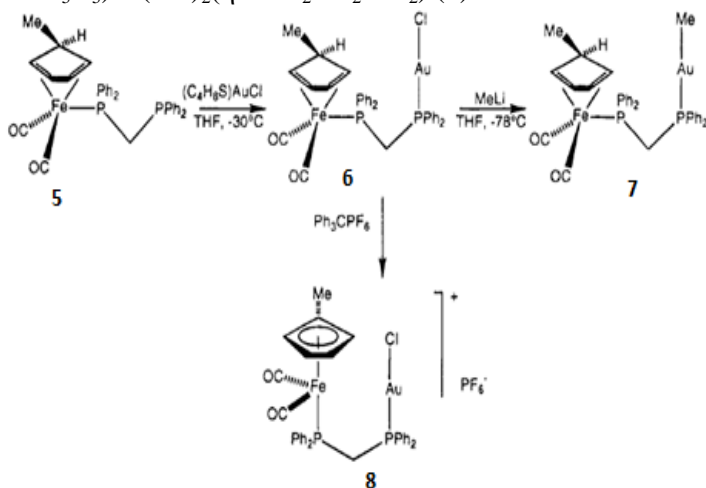
Scheme 4
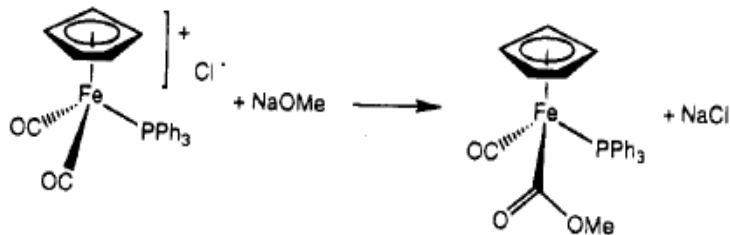
A similar pattern was observed in the -OPh⁻, -SMe⁻ and -SPh⁻ reactions, resulting in the derivatives Fe(CO)PPh₃C(O)OPh, Fe(CO)PPh₃C(O)SMe, and Fe(CO)PPh₃C(O)SPh, respectively. The metallo esters exist simultaneously, in the molecular form and the ionic form, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3]^+OR$, whereas the S analogues existed only in the ionic form.

The syntheses of heterobimetallic complexes have been of interest in view of incorporation of site-selective reactivity and synergistic effects to the bimetallic system, especially the ones with catalytic potential.

The study (Eke, Liu and co-workers, 1995b) examined the reactivity of a novel monodentate dppm complex (**Scheme 5**) $(\eta^4\text{-}MeC_5H_5)Fe(CO)_2(\eta^1\text{-}PPh_2CH_2PPh_2)$ (**5**).

Scheme 5

The ring alkylation of FpI with MeLi in the presence of dppm at -78 °C yielded **5**. Compound **5** was used as a mononuclear precursor for the construction of bimetallic complexes with dppm as a stabilizing backbone. Compound **5** then reacted with (C₄H₈S)AuCl in THF at -30 °C to give a heterobimetallic complex **6** whose Au-Cl moiety could be attacked nucleophilically by MeLi to result in compound **7**. When

complex **6** was treated with equimolar $Ph_3C^+PF_6^-$ (trityl), the endo H atom was abstracted to result in complex **8**. Interestingly, when the monodentate dppm complex **5** was allowed to react with $(Rh(CO)_2Cl)_2$ in THF/n-hexane at room temperature a novel heterobimetallic complex **9** was isolated in excellent yields. The spontaneous formation of **9** summed up sequentially a PPh_2 ligation, an endo-H elimination and post rearrangements in one treatment.
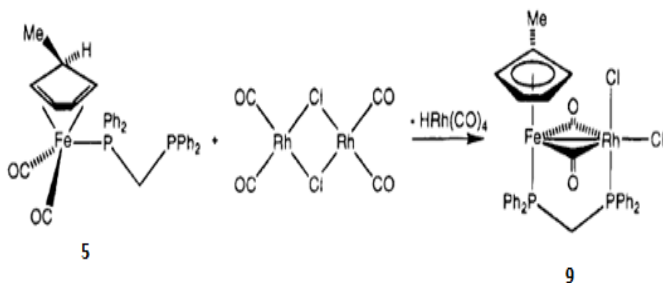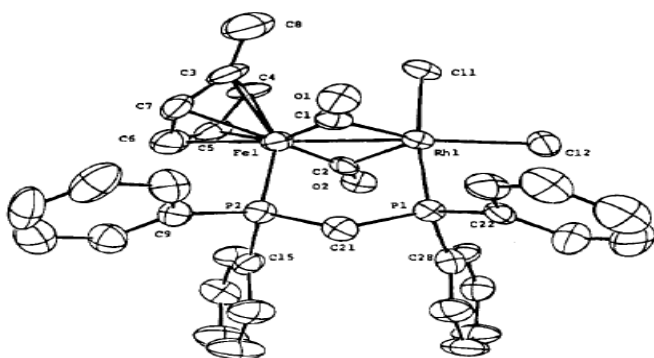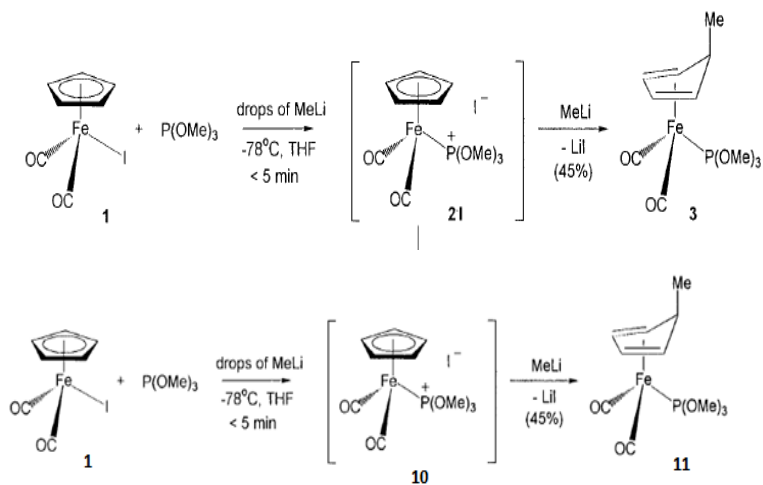
Scheme 6

Fig. 3: Molecular plots of complex **9** with atomic numbering sequence. The thermal ellipsoids were drawn at the **50%** probability level. The H atoms were omitted for clarity.

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Mr. Vice-Chancellor sir, in my continued **search for the answer to questions unknown** my research group in Academia Sinica, Taiwan, (Eke and co-workers, 1999) investigated the roles of MeLi as a reductant, nucleophile, and base. A lithiated reagent can serve as a nucleophile and a base and on many occasions, the lithium reagent works as a reductant. In this study, therefore, we report the various roles of MeLi in its reaction with a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (**1**) and $P(OMe)_3$. A mixture of **1** and $P(OMe)_3$ detects the three roles of MeLi. The addition of MeLi drop wise without delay to the 1:1 mixture results in **3**, where MeLi is both a reductant and a nucleophile.

Scheme 7

Compound **1** did not interact with $P(OMe)_3$ at -78 °C until after the addition of a few drops of MeLi when a rapid conversion to **10** was revealed. Compound **10** can be isolated as a PF_6 salt in 68% isolated yield if immediately anion exchanged in *ca.* 2 minutes. The rapidly formed **10** will proceed with the well-known Arbuzov-like reaction (Brill and Landon, 1984) on

standing for 45 minutes and produce in 70% yields the phosphonate complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(O)(OMe)_2(\mathbf{II})$ when the solution is warmed from -78 °C to room temperature.

10   12
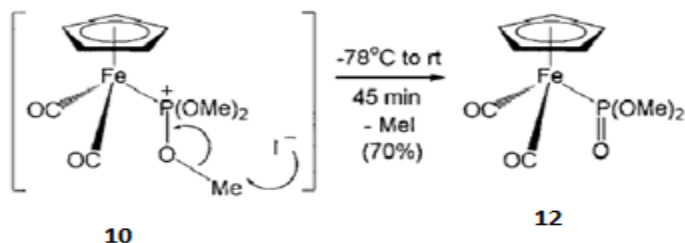
Scheme 8

The literature preparation of **11** from $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X =Cl, I) and $P(OMe)_3$ requires a long stirring at reflux or at room temperature with a large quantity of by-products $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}\{P(O)(OMe)_2\}$ (**12**) and $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}X$ (Haines *et al.*, 1970; Brown *et al.*, 1970). Compound **11** could also be prepared from the treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P\text{-}(NC_4H_8)(OMe)_2\}^+][Cl^-]$ with KOH (Nakazawa *et al.*, 1994). Thus, our procedure employing a catalytic amount of MeLi improves the method of preparation in that the reaction is at a low temperature, requires a short time, and gives a high yield.

On the other hand, the addition of a catalytic amount of MeLi to the mixture of **1** and excess $P(OMe)_3$, with a delay time applied before the MeLi/MeI sequence, results in **13**, where MeLi is both a reductant and a base as reported in Scheme 9.
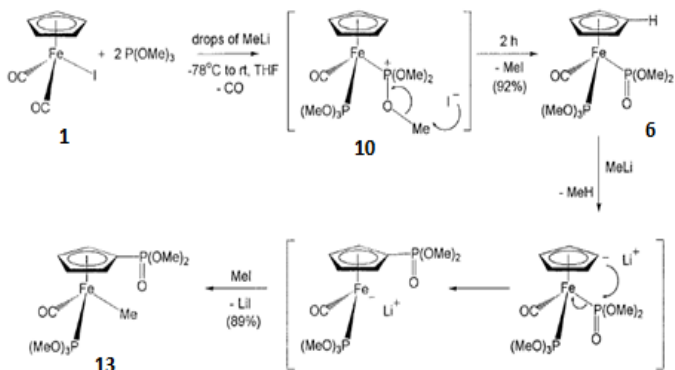
Scheme 9

5.3. Solvent-free Synthesis of the Metal-Carbon Bond

Mr. Vice-Chancellor sir, as advocates for the voiceless, Chemists speak for the poor of humanity by making new, improved and cheaper products. We develop methodologies in our laboratories to mass produce end-products and thus make them affordable to ordinary folks in society. We speak for molecules and electrons by locating them in their various places of abode in the soil as minerals, in plants as biologically active materials, etc. Chemists also speak for mother earth or nature. We do so by preaching the gospel of environmental remediation, atom economy, pollution control techniques and technologies, safe disposal of wastes, waste to wealth activities etc. Aristotle is reputed to have said that "there is no reaction without solvent''. But, Mr. Vice-Chancellor sir, the solvents that enable us to make wonder drugs and niceties of our present civilization pollute and endanger mother earth. As friends of the earth, Chemists must again worry about the safe disposal of solvents. This can be achieved by turning solvents used in synthetic manipulations into benign products. It is better still, if we can achieve synthesis in the total or near total absence of solvents. Herein therefore, lies

the main objective of our "search for the answers to questions unknown''.

5.3.1 The solid state reaction between $RhX(PPh_3)_3$ and $(\eta^5\text{-}C_5H_4Me)W(CO)_3X$ (X = halogen)

Compared to the extensive studies performed on organic complexes, organometallic chemistry in the solid state has been little studied. The studies performed have revealed that a range of reactions is possible and these include molecular rearrangements in the solid state and reactions between a solid and a gas. Reactions between two organometallic complexes in the solid state are rare. It is well known that Wilkinson's catalyst can decarbonylate both organic and organometallic carbonyl complexes (Albers and Coville, 1984) in the solution phase. Further, a study indicated that $RhCl(PPh_3)_3$ reacts with CO in the solid state to produce the stable $RhCl(CO)(PPh_3)_2$ complex in good yield (Porta *et al*., 1996) This suggested that reaction between $RhCl(PPh_3)_3$ and a metal carbonyl complex in which the CO group could readily be displaced could provide a system that would undergo mutual ligand exchange:

$RhCl(PPh_3)_3$ + $M(CO)_n$. $\rightarrow RhCl(CO)(PPh_3)_2$ + $M(CO)_{n-1}(PPh)_3$.
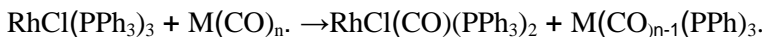
To test this possibility, the reaction between $(\eta^5\text{-}C_5H_4Me)W(CO)_3Y$ (Y = halogen) and $RhX(PPh)_3$ (X = halogen) was performed in the solid state (Eke and Coville, 2000). The W reagent was chosen since the starting material and product are relatively stable, solid state isomerisation reactions have been accomplished with substituted derivatives in both the solution and solid state and a CO group can readily be displaced from the reactant. The starting materials were prepared by literature procedures and the complexes had expected IR and NMR spectra.

Table 2: Reaction conditions and products of the reactions between $RhX(PPh_3)_3$ and $(\eta^5\text{-}C_5H_4Me)W(CO)_3X$

Reactants	Reaction conditions	Products
$RhCl(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3Cl$	THF, 16 h, reflux	cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)Cl$, trans-$RhClCO(PPh_3)_2$
$RhCl(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3Cl$	Solid state, 75°C, 24 h	cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)Cl$, trans-$RhClCO(PPh_3)_2$
$RhBr(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3Br$	Solid state, 75°C, 24 h	trans-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)Br$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)Br$, trans-$RhBrCO(PPh_3)_2$
$RhI(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3I$	Solid state, 75°C, 24 h	trans-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, trans-$RhICO(PPh_3)_2$
$RhCl(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3I$	THF, 16 h, reflux	trans-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)$Cl, trans-$RhICO(PPh_3)_2$, trans-$RhClCO(PPh_3)_2$
$RhCl(PPh_3)_3$ + $(\eta^5\text{-}C_5H_4Me)W(CO)_3I$	Solid state, 75°C, 24 h	trans-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)I$, cis-$(\eta^5\text{-}C_5H_4Me)W(CO)_2(PPh_3)$Cl, trans-$RhICO(PPh_3)_2$, trans-$RhClCO(PPh_3)_2$

Exchange reactions were performed in THF (reflux, < 16 h) and the degree of reaction was determined from the NMR spectra of the reaction mixture. Solid state reactions were performed by grinding together mixtures of the appropriate reactants and the mixture was then placed in a glass capillary tube that was sealed under dinitrogen molecule and heated in an oil bath for up to 24 h at 75 °C. At the end of the reaction the solid reaction mixture was dissolved in $CDCl_3$ and the NMR spectrum recorded (Table 2).

The solution state reaction (THF, 8 h, reflux) between $(\eta^5\text{-}C_5H_4Me)W(CO)_3Cl$ and $RhCl(PPh_3)_3$ yielded starting material (< 12%) as well as the ligand exchanged products cis-$(C_5H_4Me)W(CO)_2(PPh_3)Cl$ and trans-$RhCl(CO)(PPh_3)_2$. These products were readily characterised from their IR and NMR spectral data. The melting points of the various reagents and mixtures were recorded by DSC. From the DSC measurements a temperature of 75 °C was chosen for the solid state reactions to ensure the materials would be in the solid state. Equimolar amounts of $(\eta^5\text{-}C_5H_4Me)W(CO)_3Cl$ and $RhC(PPh_3)_3$ were then mixed together, heated in an oil bath and the solution NMR

spectra ^{31}P, ^{1}H of the reaction mixture recorded. The spectrum revealed that all the starting materials had been consumed and complete conversion to *cis*-$(\eta^5$-$C_5H_4Me)W(CO)_2(PPh_3)Cl$ and *trans*-$RhCl(CO)(PPh_3)_2$, and a small amount (6%) of an unidentified P containing complex had occurred. The reaction clearly shows that CO is efficiently transferred from the W atom to the Rh atom during the reaction. Since the W complex is stable at 75°C, it is unlikely that free CO (gas) is the reagent that displaces the PPh_3 group in the reaction. Similar mechanisms could be expected in both the solid and solution states. Two possible mechanisms are currently consistent with the data:

1. $RhCl(PPh_3)_3$ is known to contain a weakly coordinated *trans* PPh_3 ligand and it is possible that a highly reactive 'unsaturated' $RhCl(PPh_3)_2$ entity is formed at the reaction temperature. This reagent in the presence of $(\eta^5$-$C_5H_4Me)W(CO)_3Cl$, can interact with the bound CO ligand to give the exchanged product. The high yield of *cis*-$(\eta^5$-$C_5H_4Me)W(CO)_2(PPh_3)Cl$ formed suggests that the free PPh_3 may assist in the reaction.

2.   The reaction may proceed via a pentacoordinated intermediate, $RhCl(CO)(PPh_3)_3$, as proposed in a related solid state reaction between $(\eta^5$-$C_5H_4Me)W(CO)_3X$ and $RhX(PPh_3)_3$ (X = Br, I) in the solid state (Porta *et al*., 1996) which also gave the CO/PPh_3 exchanged products, but in this instance both *cis* and *trans* isomers of $(\eta^5$-$C_5H_4Me)W(CO)_2(PPh_3)X$ (X = Br, I) were formed. The isomer ratio was similar to that produced when $(\eta^5$-$C_5H_4Me)W(CO)_2(PPh_3)X$ equilibrated in the solution phase reaction between $(\eta^5$-$C_5H_4Me)W(CO)_2(PPh_3)I$ and $RhCl(PPh_3)_3$ yielded not only the CO/PPh_3 exchanged products but the halide exchanged products as well. The same mixture and product ratio was obtained from both the solution (THF, 16 h) and solid state (75 °C, 16 h) reactions.

Our results (Eke and Coville, 2000) indicated that facile solid state reactions, which entail ligand exchange between two organometallic complexes, can occur in the solid state. While the

reactions described above give the same product yields and distributions as found for the corresponding solution state reactions, this does not always have to apply.

5.3.2   The Solid-State Isomerization of *cis*- and *trans*- (η^5-$C_5H_5Me)Mo(CO)_2(P(O^iPr)_3)I$

Mr. Vice-Chancellor sir, this invited paper (Coville, Eke, Adeyemi and co-workers, 2002) is dedicated to John Osborn – who taught his students and colleagues how to live life to the full. It affords us an opportunity to further examine organometallic reactions in the solid-state.

Cyclopentadienyl molybdenum carbonyl halide complexes, $CpMo(CO)_2(L)X$, have been extensively investigated since their first preparation (L = CO) in the early 1950's. Since then modification of complexes of this type has been achieved by replacing the ring protons with other substituents or modifying the ligand set (CO, L, X), and this has resulted in the synthesis of many hundreds of complexes of this type. A significant breakthrough in this area of chemistry was the physical separation of the pure *cis* and *trans* isomers of (η^5-$C_5H_5)Mo(CO)_2(PPh_3)I$ in 1975 (Bach and Barnett, 1975). Of particular importance was the finding that these complexes underwent isomerization reactions in the solid state. Other than a short comment on the solid-state isomerization reaction of (η^5-$C_5H_5)Mo(CO)_2(PBu_3)I$ (Beach, et al, 1977) and a description of the cis/trans inter-conversion of $Cp'M(CO)_2(PMe_3)GeX_3$ (Cp' = C_5H_5, C_5Me_5; M = Mo, W) (Filipou, *et al.*, 1998) no other solid state isomerization reactions of four-legged piano stool complexes have been reported in the literature. We now report (Coville, Eke, Adeyemi and co-workers, 2002) results of the thermal solid-state isomerisation reactions of (η^5-$C_5H_4Me)Mo(CO)_2(P(O_iPr)_3)I$ to further explore the generality of the reaction.

Sold-state isomerization reactions of the title compounds were carried out using 5–20 mg of the isomers packed into

sealed NMR tubes under nitrogen and immersed in an oil bath at a pre-set temperature. Care was taken to ensure that the reactant was fully covered by the oil. Temperatures between 80 and100 °C were chosen and the reaction was monitored at 20 min intervals. The product was analyzed by TLC, solution IR and ^{1}H NMR spectroscopy. Because both isomers had similar red colours, the solid-state isomerization reactions of the complexes could not be monitored visually. NMR spectroscopy, DSC and XRD measurements were used to monitor the solid-state isomerization reaction.

The *cis*- and *trans*-$(\eta^5$-$C_5H_4Me)Mo(CO)_2(P(OiPr)_3)I$ isomers studied are stable in solution (e.g. $CHCl_3$,benzene) at room temperature for a period of several hours. However, when either one of the isomers was refluxed in benzene they quickly isomerized (< 2 h) to a thermodynamic equilibrium of isomers ([*cis*]/[*trans*] ratio, 70:30). This result shows that the solution state isomerization was bidirectional. Similar equilibrium studies on $(\eta^5$-$C_5H_5)Mo(CO)_2(L)X$ (L = PPh$_3$, PBu$_3$; X = Br, I) (Beach *et al*., 1977) and $(\eta^5$-$C_5H_4R)M(CO)_2(L)I$ (R = Me, ^{t}Bu, SiMe$_3$; L = isonitrile, phosphine, phosphite) in refluxing benzene have also been reported.

Table 3: Solid-state isomerization reactions of *cis*- and *trans*-$(\eta^5$-$C_5H_4Me)Mo(CO)_2(P(O^iPr)_3)I$ complexes.

Complex	Yield (%)[a]	DSC (°C)[b]	m.p. (°C)[c]	Reaction temperature and time	(Trans/cis) equilibrium ratio (%)[d]
cis-$(\eta^5$-$C_5H_4Me)Mo(CO)_2(P(O^iPr)_3)I$	70	113^{ex}, 124^{ex},135^{en}	122–124	90 °C, 100 min	70:30
trans-$(\eta^5$-$C_5H_4Me)Mo(CO)_2(P(O^iPr)_3)I$	70	138^{en}	126–128	90 °C, 100 min	70:30

[a] Isolated yield. [b] Melting point determined by DSC (10 °C min^{-1}): ex = exothermic. en = endothermic. [c] Melting point determined by melting point apparatus. [d] Determined by ^{1}H NMR spectroscopy

Both *cis-* and *trans-* isomers (Coville, Eke, Adeyemi and co-workers, 2002) were tested for solid state isomerization behaviour (Table 3). It was found that the thermal solid-state isomerization reaction is also *bidirectional* with an equilibrium ratio established from either isomer (equilibrium ratio: [*cis*]/[*trans*] = 30:70). This ratio differs from the solution (benzene) data, thus revealing phase dependent isomerization isomer ratios. The *k values* for the reaction were calculated assuming first order kinetics and the Arrhenius plot yielded an activation energy for the reaction = 68 ± 10 kJ mol^{-1}. This is to be compared to the value of 100 ± 9 kJ mol^{-1}, found for the (η^5-$C_5H_4Me)Re(CO)(P(OPh)_3Br_2$ complex (Bogadi, 2001). XRD data for the conversion of the *cis* to the *trans* isomer of (η^5-$C_5H_4Me)Mo(CO)_2(P(OiPr)_3)I$ (90 °C) were recorded and revealed dramatic changes in the peak positions/intensities as a function of time (Fig. 4).

Fig. 4: Powder XRD patterns of *cis*-MeCpMo(CO)$_2$P(O^{i}Pr)$_3$I (heated at 90 °C); (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min.

Particular peaks associated with the *cis* isomer are reduced in intensity, while new peaks grow (e.g. at 11° and 13°). The XRD data for the *trans* isomer were also monitored as a function of

time. Spectra showing the changes in peak intensity/position are shown in Fig. 7.
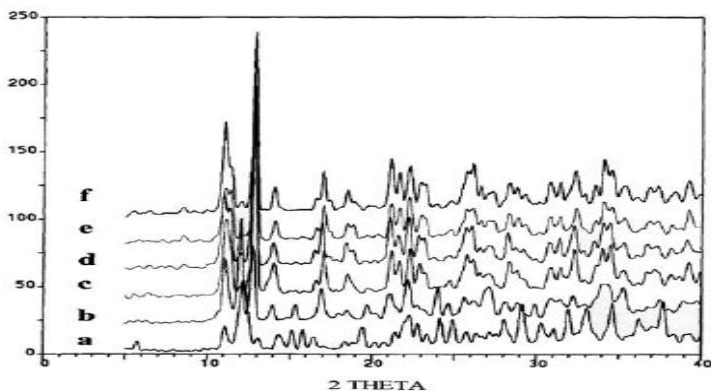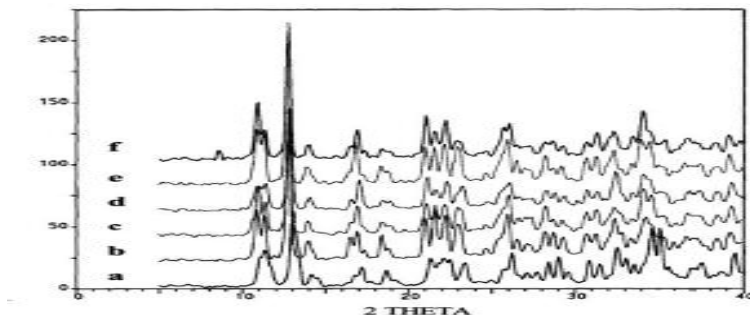

Fig. 5: Powder XRD patterns of *trans*-MeCpMo(CO)$_2$P(O^{i}Pr)$_3$I (heated at 90 °C); (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min.

Two key observations from the figures are:
(*i*)   The XRD patterns after100 min reaction are identical in the two spectra (Figs. 4 and 5) and
(*ii*)   The XRD pattern of the original *cis* and *trans* isomers are no longer present.

This is more clearly seen in Fig. 6. NMR spectra of all the above samples were recorded after the XRD experiment by solution NMR spectroscopy and the data indicated that both the *cis* and the *trans* isomers were present in the samples. The implication from the XRD and NMR data is that the *cis* isomer has converted either to a new *cis* (and *trans*) polymorph or to a new crystal form in the solid-state reaction. Heating of the *trans* isomer also yields similar changes.
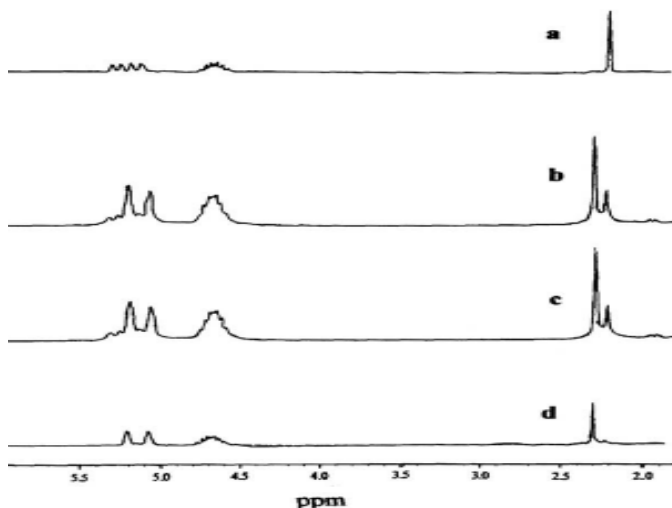
Fig. 6: ^{1}H NMR spectra of **MeCpMo(CO)$_2$P(O^{i}Pr)$_3$I after reaction in the solid state at 90 °C. Spectra of the *cis* isomer at (a)** $t = 0$ min, **(b)** $t = 100$ min. **Spectra of the *trans* isomer at (c)** $t = 100$ min, **(d)** $t = 0$ min.

This contrasts with an earlier study on $(\eta^5\text{-}C_5H_4Me)$ Re(CO)(L)Br$_2$ (L = CO, CNC$_6$H$_3$Me$_2$, P(OR)$_3$, PPh$_3$) complexes (Cheng and Coville, 1996) in which the isomerization reaction was unidirectional and no polymorphs or new crystal forms could be detected. A DSC study was carried out to obtain further information on the reaction. Data are shown in Figs. 7–9:

Fig. 7: DSC profiles of MeCpMo(CO)$_2$P(O^{i}Pr)$_3$I: (a) cis isomer, (b) trans isomer, (c) cis isomer after pre-heating to 80 °C for 1 h, (d) trans isomer after pre-heating to 80 °C for 1 h.

An initial interpretation of the DSC profile recorded at 10 °C min^{-1} (Fig. 7b) would suggest that the pure *trans* isomer m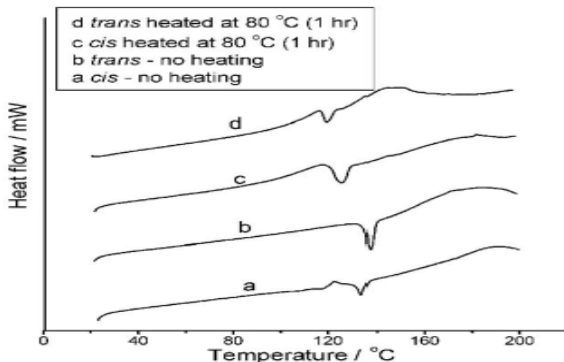elts at 138 °C. However, the NMR spectrum of the material recorded after DSC experiments were terminated (between 120 and 140 °C), revealed that in all cases the material comprises of a 30:70 *cis/trans* mixture (some decomposition was also noted in the NMR spectrum when the reaction was performed at the higher temperatures). The NMR data implied that isomerization had taken place in the solid state even though no exotherm was to be seen in the DSC profile. Samples were also preheated to 80°C for 1 h in an NMR tube and the DSC profile (Fig. 7d) and NMR spectra then recorded. The NMR spectra revealed a 30:70 *cis/trans* isomer ratio and the DSC profile revealed that the endotherm had moved to a lower temperature suggestive of the presence of a mixture. The above data (together with the XRD data) are entirely consistent with an isomerization occurring between 80 and 100 °C, but the event is not reflected in the DSC profiles.
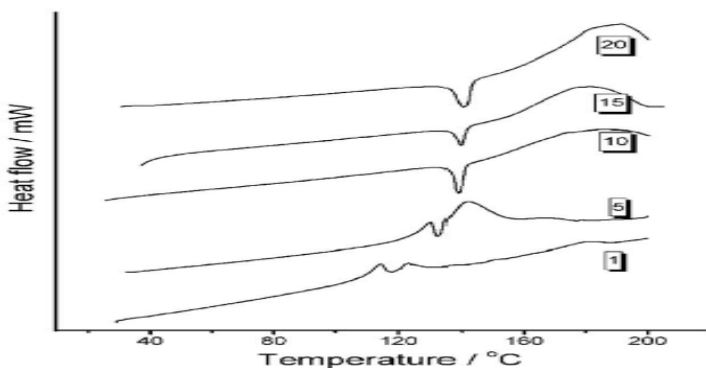
Fig. 8: DSC profiles as a function of scanning rate (°C min⁻¹): *trans*-**MeCpMo(CO)₂P(O***ᶦ***Pr)₃I (scanning rates indicated in the figure)**

DSC profiles were also measured as a function of heating rate (Fig. 8). At low heating rates of 1 °C (and 5 °C min⁻¹), more complex behaviour were detected with the endotherm (melting point) situated on top of an exotherm. A TGA profile recorded at 1 °C min⁻¹ (not shown) indicates 50% mass loss that commences at about 100 °C, indicating that the endotherm was due to a decomposition reaction. At heating rates of 10°C min⁻¹ and above, only the melting point of the mixed isomer mixture and a decomposition endotherm ($T > 140$ °C) are to be seen.

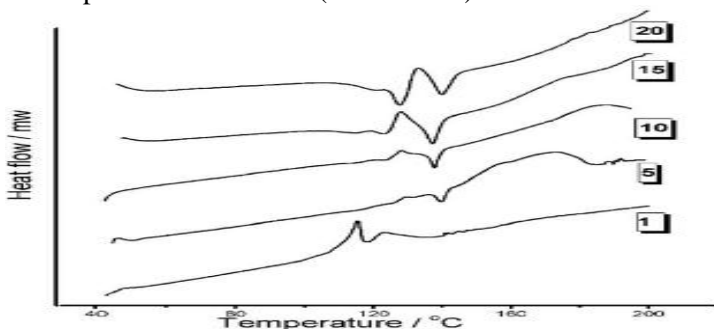**Fig.9: DSC profiles as a function of scanning rate (°C min⁻¹):** *cis*-**MeCpMo(CO)₂P(O***ᶦ***Pr)₃I (scanning rates indicated in the figure).**

The DSC profile of the *cis* isomer (at a heating rate of 10 °C min^{-1}) shows complex behaviour. Of note is the endotherm at 135 °C which is similar to that observed for the *trans* isomer. Also of note are the exotherms to be seen at 113 and 124 °C. Samples of the *cis* isomer were heated at 80 °C for 1 h and analyzed: (*i*) solution NMR spectra of a sample showed that it was comprised of a mixture of *cis/trans* isomers (ratio: 30:70) and (*ii*) a DSC profile revealed that most of the peaks below 130 °C had been eliminated (compare Fig. 7a and Fig. 7c) and only a single endotherm similar to that observed for the trans isomer (Fig. 7d) was to be seen. DSC data were recorded on the *cis* isomer as a function of DSC heating rate. At 1 °C min^{-1} the profile is similar to that recorded for the *trans* isomer (exotherm superimposed on an endotherm), again suggesting that the isomerization is bi-directional and not detected in the DSC profiles. Interestingly, the DSC profiles at 15 and 20 °C min^{-1} show a complex behaviour that arises from 70% of the *cis* isomer having to isomerize, in a *cis* matrix, to the *trans* isomer. At a heating rate of 20 °C min^{-1}, two exotherms are to be seen. It can be speculated that at this heating rate, the first melting point (endotherm) relates to the *cis* (or *cis*-rich) isomer. In conclusion, all the data were consistent with a bi-directional *cis–trans* isomerization occurring in the solid state between 70 and 100 °C, followed by product decomposition.

The data suggest, in contrast to the solution phase studies, that an understanding of the isomerisation mechanism must entail an understanding of the intramolecular forces at play in the solid state. The intermolecular forces that override the intramolecular forces, which dominate in the solution phase, could be both steric (phase rebuilding), topotatic and electronic, in nature. Thus, an understanding of the reaction will only be possible from the knowledge of solid-state packing information. Presently there are insufficient structures containing the P(O^{i}Pr)$_3$ ligand available to propose the specific arrangements of the O^{i}Pr groups that could give rise to the different polymorphs that may

have been formed in this study. The melting point measured on a Kofler melting point apparatus (10 °C min^{-1}) indicates that the trans isomer has a marginally higher melting point than the *cis* isomer (Table 3). The DSC 'melting point' data revealed a more complex issue. This arises since the Mo complex isomerizes from both directions on heating and the endotherms measured (Table 3) refer to the melting points of the equilibrium isomer mixtures. Our data, suggest that many melting point measurements that have previously been described for this class of organometallic complexes (and other complexes in general) may in actual fact relate to the melting points of an isomer mixture. Neither isomer is more stable than the other in the solid-state environment. The stable environment is the environment in which an approximate 30:70 ratio of *cis/trans* isomers is formed in the solid state for this complex. The solution (refluxing benzene) isomer ratio involving a dynamic equilibrium is quite different to that found in the solid-state. It is not clear as to whether the solid-state data refer to a dynamic equilibrium at the high temperature, or whether this is a static equilibrium determined by the most stable arrangement of isomers in the solid mixture.

In conclusion, the molybdenum complex (η^5-$C_5H_4Me)Mo(CO)_2(P(OiPr)_3)I$ (Adeyemi, Eke, Coville and Co-workers, 2002) undergoes a bidirectional thermal solid-state isomerization reaction. Both the DSC and XRD powder data are consistent with this view. Two key findings from this study are:

– DSC data alone do not allow for identification of *cis/trans* isomer reactions; and
– melting point data recorded on complexes that can undergo isomerization reactions in the solid state may relate to isomer mixtures.

Our results further suggest that thermal solid-state *cis–trans* isomerization reactions should be a common reaction type for cyclopentadienyl four-legged piano stool transition metal

complexes and for many other complexes with geometries that permit for *cis/trans* isomers.

5.4. Ruthenium(II) Compounds as Precursor to Ruthenium Organometallic Compounds and Catalysts

Mr. Vice-Chancellor sir, I now turn to another focus of my studies and manipulations with molecules. Following successful explorations with cyclopentadienyliron(II)dicarbonyls and solid-state organometallic reactivities, I now wish to consider the reactions of iron's heavier congener- Ruthenium. I do so with a goal of studying new precursor catalysts and precursor moieties to ruthenium organometallic compounds.

5.4.1 Ruthenium Complexes Containing Hydrazine and Isocynanide

The chemistry of transition metal complexes containing hydrazine (NH_2NH_2) or substituted hydrazine ($RNHNH_2$) as ligands has been widely studied. This sustained interest is partly due to the different coordination modes offered by hydrazine complexes and also to the importance of hydrazine in the dinitrogen fixation process. The coordination of hydrazine to metal centers is usually through the nitrogen in a monodentate fashion but in a few cases, a bridging bidentate coordination mode can be adopted. These reports, adopt the use of anhydrous hydrazine and substituted hydrazine in the synthesis of the desired hydrazides. Anhydrous hydrazine is a highly regulated product. Therefore, the use of hydrated hydrazine was investigated in this study (Owalude *et al*., 2013). Our studies showed that the hydrated hydrazine, a commercially available reagent, can be used to prepare Ru(II)- hydrazine complexes. The complex $[Ru(COD)(N_2H_4)_4][BPh_4]_2$ (**1**) was prepared by the reaction of polymeric species $[\{RuCl_2(COD)\}x]$ (COD = cyclo-octa-1,5-diene) and hydrazine hydrate in methanol. The structure of **1** was determined using single crystal X-ray diffraction

analysis as shown in Fig. 10. The structural analysis indicates a distorted octahedral geometry with the ruthenium compound ligated by four hydrazine and one COD molecule.
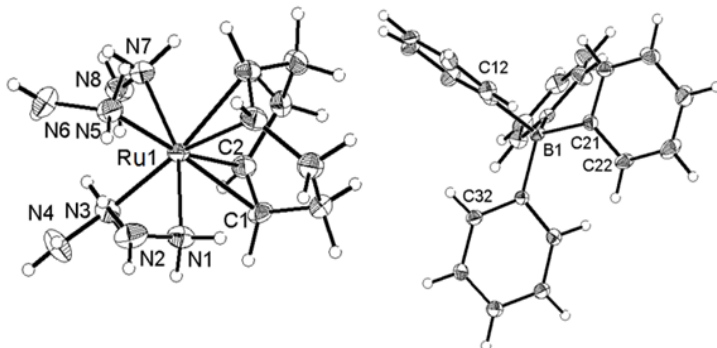
Fig. 10: Molecular diagram for [Ru(COD)(H$_2$NNH$_2$)$_4$][BPh$_4$]$_2$ with ellipsoids representing a displacement probability of 50%. Only one of the BPh$_4$ anion is shown while the molecules of solvation are removed for clarity.

Subsequent reaction of the dimeric [Ru(COD)(N$_2$H$_4$)$_4$][BPh$_4$]$_2$ in refluxing acetone with benzyl isocyanide produced [Ru(NH$_2$N:CMe$_2$)$_2$(PhCH$_2$NC)$_4$][BPh$_4$]$_2$ (**2**). The molecular structure of **2** is shown in Fig. 11.
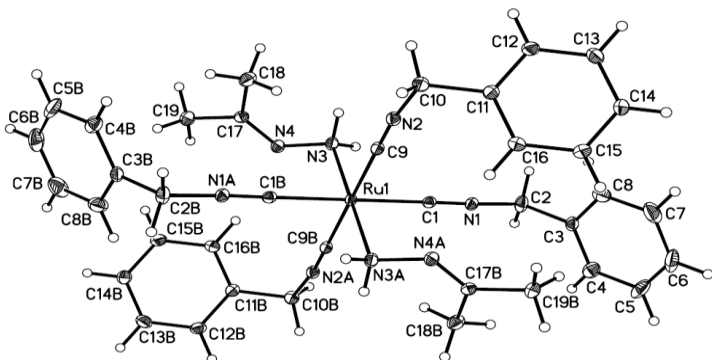
Fig. 11: Molecular structure of [Ru(CNCH$_2$C$_6$H$_5$)$_4$(H$_2$NNC:(CH$_3$)$_2$]$^{2+}$ with atom labeling. Thermal ellipsoids are drawn at the 50% probability level. The BPh$_4^-$ anions are omitted for clarity.

5.4.2 Hexakis (benzonitrile) ruthenium(II) bis [tetrafluoroborate(1-)]: a precursor to ruthenium organometallic compounds

The known compound tris (acetonitrile) tris (pyrazolyl) boratoruthenium (II) has been applied successfully as intermediate in the preparation of ruthenium catalysts and DNA binding drugs over the years due to the lability of the acetonitrile group (Underwood *et al*., 2013). The acetonitrile group in a similar compound $[CpRu(NCCH_3)_3][PF_6]$, has been exchanged with aromatic compounds to generate complexes with radiopharmaceutical potentials, or with nitrogen heterocycles to produce catalysts used in the purification of coal tar. Syntheses of these compounds required many steps which can take up to days to complete and this has limited their applications as synthons. Therefore, $[Ru(NCMe)_6]^{2+}$ $[\mathbf{1}]^{2+}$ $[\mathbf{1} = Ru(NCMe)_6]$ was developed to overcome these defects and has since been used over the years as a precursor in the synthesis of ruthenium organometallic compounds (Underwood *et al*., 2013).

The non-isolable [**1**] has been precipitated from solutions as [**1**][BF_4]$_2$ and [**1**][$ZnCl_4$]. However, these two complexes have not received the expected prominent use as starting materials for the synthesis of ruthenium(II) organometallic compounds. This is most likely because [**1**][BF_4]$_2$ requires many steps to synthesize. On the other hand, the ruthenium(II) zincate analogue [**1**][$ZnCl_4$] contains a counter anion [$ZnCl_4$]$_2$ capable of initiating side reactions with the incoming ligand(s). To address these shortcomings, and with the understanding that the benzonitrile (NCPh) complexes are more soluble in common organic solvents, the present study has therefore developed a more convenient synthetic route to the preparation of NCPh analogue [**2**][BF_4]$_2$ ([**2** = $Ru(NCPh)_6$) as a possible alternative to [**1**][BF_4]$_2$. Reported synthesis of [**2**][BF_4]$_2$ involved a combination of both electrochemical and chemical techniques in a series of steps starting from $RuCl_3$. The electrochemical route yielded [$RuX_2(NCPh)_4$] as the lowest

halide-containing moiety which was then subjected to a reaction with Ag(I) to remove a further halide resulting in $[RuX(NCPh)_5]^+$. The last halide was then removed by the reaction of $[RuX(NCPh)_5]^+$ with hot concentrated triflic acid under strictly anaerobic conditions to obtain $[Ru(NCPh)_6]^{+2}$. One major problem associated with the use of concentrated triflic acid is that it has the capacity to catalyze the polymerization of benzonitrile. To prevent polymerization, more benzonitrile is usually added to the reaction mixture and subsequent dilution with dry ether. The complex $[2][BF_4]_2$ has also been synthesized from the substitution reaction of $[Ru(H_2O)_6]^{+2}$ with benzonitrile, but the preparation of $[Ru(H_2O)_6]^{+2}$ is not easy, requiring very tedious purification procedures. In this study, $[2][BF_4]_2$ was obtained pure in a single step by the treatment of the polymer $\{[RuCl_2(COD)]_x\}$ with two equivalents of $AgBF_4$ in refluxing benzonitrile for 24 h with an overall yield of 78% compared to literature value of 66% reported for $[1][BF_4]_2$.

The complex was isolated as a bright yellow air-stable solid and has been characterized by IR and NMR spectroscopic techniques, elemental analysis, and X-ray crystallographic diffraction analysis (Owalude *et al*., 2015).

The crystal structure of the analogous homoleptic Ru(II) complex, $[1][BF_4]_2$ has been reported (Underwood *et al*., 2013), but the structure of $[2][BF_4]_2$ is the first with six NCPh ligands coordinated to a ruthenium center (Owalude *et al*., 2015). The structure of $[2][BF_4]_2$ consists of a discrete cation and anion with six N-bonded NCPh ligands coordinated in a distorted octahedral arrangement to the central Ru^{+2} ion with two BF_4 anions outside the coordination sphere (Fig. 12). The six NCPh ligands are coordinated to the ruthenium centre through the nitrogen atom as proposed from its IR spectrum. The angles around the Ru atom in $[2][BF_4]_2$ are all close to 90° in line with the octahedral coordination arrangement. The six phenyl rings in the structure have the average C–C bond distance of 1.390(6) Å and C–C–C bond angles of 120.04^o which are within the accepted values of

1.394 Å and 120° for phenyl rings (Cordero, *et al*., 2008). The average Ru–N bond length found in this structure (2.019 Å) is slightly shorter than the average value in the acetonitrile congener (2.022 Å), which suggests a stronger Ru–N bond interaction in the benzonitrile. The average Ru–N bond length of 2.019(2) Å is shorter than the sum of their covalent radii, 2.17 Å, which suggests a strong mutual attraction between Ru and N. The N–Ru–N angles between mutually trans NCPh ligands are 177.48(8)^o, 177.74(7)^o, and l79.59(9)^o. However, no chemical interactions were observed between the BF_4 anions and the $[Ru(NCPh)_6]^{+2}$ cations as was observed in the $[Ru(NCMe)_6]^{+2}$ analogue.

The potential of this compound as a viable precursor to the synthesis of active organometallic compounds of ruthenium is a subject of ongoing research.
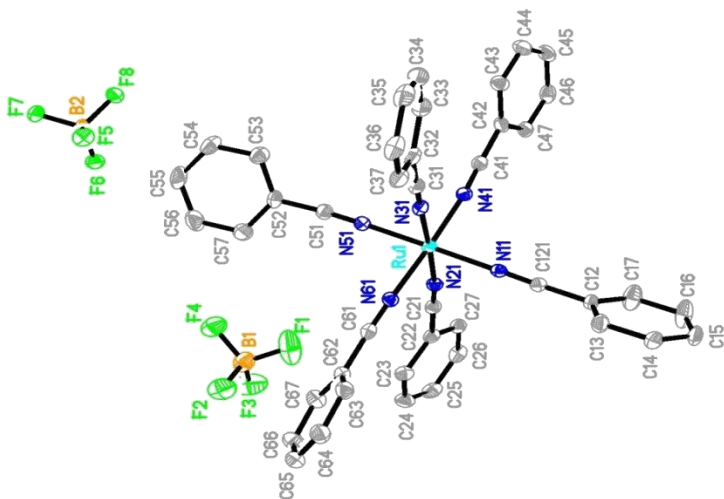

Fig. 12: ORTEP diagram of [Ru(NCPh)$_6$][(BF$_4$)$_2$] with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity

5.4.3. Catalytic Transfer hydrogenation reactions

Mr. Vice-Chancellor sir, I wish to direct the attention of this audience to a very important reaction in organometallic chemistry, *Catalytic Transfer Hydrogenation reactions*. Transfer hydrogenation can be simply defined as the addition of hydrogen (H_2) to a molecule from a source other than gaseous H_2. This reaction has been widely applied in organic synthesis and in the large scale industrial processes such as liquefaction of coal (Muñiz and Kilian, 2005). Before the discovery of this important reaction, hydrogenation reactions were being carried out using gaseous molecular hydrogen (H_2) under high temperature and pressure. This procedure required high consumption of energy making the process to be highly inconvenient and very expensive. In this regard, transition metal complexes with coordinated chiral bidentate phosphine and phosphonite ligands have remained one of the most studied systems. This is attributed to their simple synthetic methods, versatile coordination behaviour and more importantly their wide applications as catalysts for several other organic functional group transformations. Since the monodentate ligands are less expensive and more readily available than most chiral bidentate ligands, I hereby report our findings on the reaction of ruthenium starting material [RuCl$_2$(COD)(CH$_3$CN)$_2$] with the monodentate dimethylphenylphosphonite ligand P(OCH$_3$)$_2$C$_6$H$_5$, and the data on the catalytic activity of the resulting novel complex, [RuCl$_2$(NCCH$_3$)$_2${P(OCH$_3$)$_2$C$_6$H$_5$}$_2$] (**1**), in the transfer hydrogenation of ketones (Owalude *et al*. 2013).
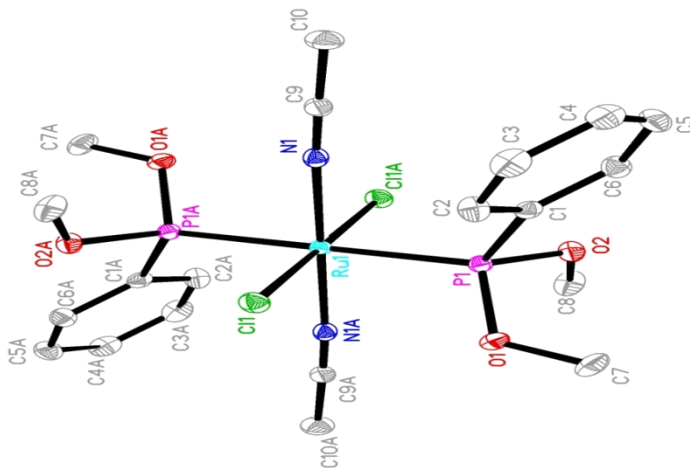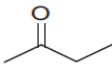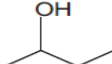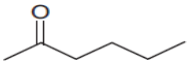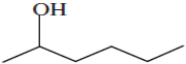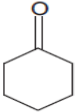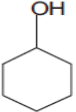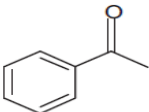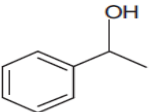
Fig. 13: ORTEP diagram of 1 with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

The structure of the ruthenium acetonitrile complex (**1**) was elucidated using both analytical and spectroscopic techniques as well as single-crystal X-ray diffraction studies. The ruthenium in the compound has almost ideal octahedral coordination geometry as depicted in Fig. 13.

The ruthenium complex **1** showed remarkable performance in the conversion of both aliphatic and aromatic ketones to alcohols and the results are presented in Table 5.

Table 5: Catalytic transfer hydrogenation of ketones catalyzed by complex 1

Entry	Substrate	Product	Yield (%)
1.			99.5
2.			97
3.			100
4.			100

Experimental conditions: ketone, 5 mmol; NaOH, 0.096 mol; catalyst loading, 0.004 mmol; 2-propanol, 15 mL; temp, 82 °C; time, 4 h. Yields were determined by GC-MS and related to the unreacted ketone.

The complex efficiently catalyzed the reduction of ethylmethyl ketone and hexanone to their corresponding alcohols with 99.5 and 97% conversion respectively. The conversion in case of both acetophenone and cyclohexanone was 100%. No transfer hydrogenation was however observed in the absence of base, suggesting loss of the chlorides to form a reactive dihydride species in a similar fashion to the formation of $RuH_2(PPh_3)_2(cydn)$ reported in the literature (Morris *et al*., 2000). Therefore, it is believed that the base facilitated the formation of a ruthenium alkoxide by abstracting the proton from the alcohol and subsequently the alkoxide underwent β-elimination to give the active species, ruthenium hydride. The ketone then coordinated to the hydride-ruthenium intermediate which eventually led to the alcohol formation. Complex **1,**

however, showed no activity toward the hydrogenation of nitrobenzene even after 48 h; therefore no further attempt was made to hydrogenate compounds with similar functional groups. The results obtained in this study are similar to those reported by Wills and co-workers with the complex [{P(OC$_{10}$H$_6$)$_2$C$_6$H$_4$Br}$_2$-RuCl$_2$(DPEN)] (DPEN = diphenylethylenediamine) for the transfer hydrogenation of acetophenone (Xu *et al*., 2004). Using the complex at 50 bar hydrogen pressure and substrate/catalyst ratio of 2000, acetophenone was fully reduced in less than 4 h. The new catalyst system **1** does not require the presence of molecular hydrogen to function; the hydrogen is rather transferred in form of hydride from isopropanol to the ketones as proposed above. Our new catalyst system is very effective and fast, achieving 100% conversion in 4 h for acetophenone, and there is no problem of chiral resolution of products with this new catalyst system.

6.0. Ongoing Studies

Mr. Vice-Chancellor sir, I have discussed the historicity of Organometallic Chemistry and my contributions to the field in the preceding chapters. Let me now say a few words on my current efforts and what the future holds. We are focusing on two major present day concerns. These are;

(i)   The provision of potable water, using bioactive macromolecules, and
(ii)   The role of bio-organometallic compounds in medicine.

Both efforts are robust and yielding results, for (ii) we are focused on CORMs (carbonmonoxide releasing molecules) (Eke and Abubakar, 2015). I am aware that CO is a dreaded silent "killer", but in the carefully trained hands of a Chemist they may become metallotherapeutic drugs with wide anti-bacterial applications amongst others (Motterlini, 2011& 2013). Our aim is to develop CORMs that act as anti-bacterial agents based on their ability to deliver CO to tissues and cells which can

bind to heme and cytochromes, impair bacteria respiration and eventual death. Our recent review (Eke and Abubakar, 2015) of this subject reveals a great potential for small gaseous molecules in the control of infectious diseases. We have synthesized several metal carbonyls. The next step in our search for "answers to questions unknown" will be to determine the suitability of the metal carbonyls in our arsenal as CORMs in Vivo.

Concluding Remarks

(i)　　Mr. Vice-Chancellor Sir, although I am a scientist, I continue to share the anxieties of other Nigerians as our country swings on the pendulum of hope, despair and near chaos. We have climbed to the precipice a few times. But thank God we did come back to the coast of hope and restraint, ready and willing to pick up and start building again. Please recall the riots in various parts of our country where lives and property were lost. On several occasions, we have visited our country and the world with these unnecessary crises because of fear! Fear of our individual tomorrow. But if we encouraged ourselves to look inward we shall find that such apprehensions are needless and baseless. We will be surprised to discover that all we need to achieve the dream of a prosperous nation is a "pair of hands" - the hand of humanity.

　　My wife will serve a dish of rice at my dinner table this night. Mr. Vice Chancellor Sir, permit me to recount for you the journey of a grain of this rice to my dinner table. One hand prepared the paddy where the grain was planted. Another hand sowed the grain and yet another hand pruned the weeds so that the tender plant could grow to maturity. Another hand harvested and threshed the grain for food and another hand packaged the now numerous grains for the market where I bought the grain that will be found on my dinner table tonight. Whether it is "Ofada", "Abakaliki", "Taraku", "Gboko ", etc or even the long grain from Thailand or any part of Asia or the world at large, I am not able to identify the "hands" feeding me tonight. The only

thing I know and I am able to identify is the "hand" of humanity. The "hands" may well have been Caucasian, Asian, or Negroid, they may even be the hands of those who take their faith in God very seriously or those of others that only get by. That I will not know, I just know that the "hand" of humanity nurtures the entire human race to live the good life that we all crave for. And so Mr. Vice-Chancellor, I dedicate this inaugural Lecture to all hands of humanity, to us, and to say that if we act together from the perspective of our various human endeavors we can build a beautiful world here on planet earth. If we go our different ways and pursue our different dreams, the result we get shall be global warming, droughts, famine, deforestation, flooding, hunger, diseases, etc.

(ii)   **If I were you**

Mr. Obizue taught me English language and literature at PMGS Oguta. Mr. Obizue was full of life, tried to influence his students, and enjoyed the job he did "teaching the English language" to youngsters. Mr. Obizue was used to the use of high sounding words for which he was nicknamed "Obizueism". I remember him at this lecture for his dictum "if I were you, you will be another person" by which he meant as he would tell us, "that if I become you, you will no longer be the person you are meant to be, but another that you may not want to be.

Mr. Vice-Chancellor Sir, I see this as part of the problem in our national polity." Our" leaders never want to give up their guidance of national discourse and control of the management of our human and natural resources. I think that this amounts to tenure perpetuation by subterfuge. This is not healthy for the modern world. The present challenges that mother earth is facing and will face in the future, require fresh ideas, informed by new knowledge. They are challenges that are global in dimension (pollution, disease, hunger, flooding, aridity, economic migration, etc.). The solution to these challenges cannot be found in the now "ancient history" of the amalgamation of Nigeria, of

the struggle for resource control, not even in the distrust that the various ethnic nationalities of Nigeria have for each other. They can only come from knowledge, new knowledge from a new Nigeria. By this I mean a new Nigeria made possible by a reorientation and re-education of society based on "Ogu" (equity), "Ofo" (justice), "ikenga" (self-esteem), "Ako" (tact) and Onyeaghala-nwanneya" (the common good). If we achieve this, we shall no longer be bogged down with electoral litigations more than one full year after an electoral contest. I think that we can avoid this shameful attitude when, as a people, we adopt the core values given above. We shall realize that social engineering is a complex contract that requires every "hand of humanity" to be on-board.

Suggestions: I can only suggest!!

1.   The education sector, via the Federal Ministry of Education must do more to create a conducive environment for the emergence of highly skilled and knowledgeable Nigerian youth. In terms of standard, the gap between primary and secondary schools run by government agencies and those of non-governmental organizations is non-permissibly too wide. Government should urgently upgrade and improve the quality of knowledge that Nigerian children receive in schools run by government agencies.

2.   The ministry of Youth and Sport has a lot to offer in the total development of the Nigerian child. Adult politicians don't seem to have learnt that in any contest, there can be only one winner. Every contestant believes he/she has the absolute right to win at all times. Should he/she loose, then the process has been rigged. That is why electoral litigation/disputations continue until the next election. The new generation should learn to compete vigorously and accept defeat when it comes. This is achievable through grassroots sports activities of the Federal Ministry of Youth and Sports development. Government should devote a lot of money to research. As the western world

continues in its stride to achieve "next generation" technologies", much of which is harmful to the earth, let the third world advocate for mother earth by studying the methodologies that will reduce or eliminate pollution. Let us reclaim our land polluted by oil exploration. Our seas polluted by excessive dumping of plastic materials and overfishing to satisfy the voracious appetite of modern man.

FROM A GRATEFUL HEART

I must pay a debt of gratitude to the very many individuals that have contributed to my wellbeing.

To Almighty God for my life and the good fortune HE has given me

To my parents and family (The Eke Akoros) for a large dose of love

To my late brother, Nicholas Columbus Eke, who answered the call of his creator so suddenly

To my late sister, Theresa Chidinma Isigwe (nee Eke); Dear sister you went so very early

To the late Rev. Fr. Dr. Edmund Okere - the Counsellor

To my teachers, from primary, secondary and university Thank you for the work you did

To Dr. J. A. Adeleke who introduced me to Prof. Ling-Kang Liu

To my mentors at the University of Ilorin

To Prof. I. O. Oloyede (OFR)

To Prof. A. G. Ambali (OON)

To Prof. M. A. Mesubi – Father of the Day

To my friends too numerous to list

To my students for their useful work

To Mr. Basil Okere and family – for standing by me at difficult moments

To my in-laws for giving me their daughter in marriage

To my children for their love at all times

To my wife Lady Rita Ugwuamaka Eke – my love, real friend and confidante

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