Solid state transformation of *cis* and *trans* methylcyclopentadienyl molybdenumdicarbonyltriphenylphosphineiodide on pelleting utilizing different diluents

Olalere G. Adeyemi[*], **Umaru Salami**

Department of Chemical Sciences, Redeemer's University, Redemption City, Nigeria
Email: [*]drlereadeyemi@yahoo.com, adeyemio@run.edu.ng

ABSTRACT

[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I] undergoes solid state transformation on the formation of a good pellet for FT IR measurement. There was a formation of the products mixture on pelleting using different diluents of group I metal salts on either the *cis* or the *trans* isomer of the [(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I] complex. The *cis* or the *trans* isomer gave the same IR spectra *i.e.* a mixture of *cis* and *trans* isomer of the complex. It does not matter the isomer started with in the course of solid state transformation reaction, an equilibrium ratio of 30/70 (*trans/cis*) will still be achieved. The solid state IR spectra show very strong peaks at v_{co} 1957, 1947 and strong peaks at 1867, 1853 cm^{-1}. The individual IR *cis/trans* isomer will therefore show at 1947 and 1853/1957 and 1867 cm^{-1}. The solution IR spectra gave, *cis* = 1961, 1875 and *trans* = 1963, 1882 cm^{-1} in dry CHCl$_3$. Hence, most of the solid state IR measurement of the organometallic complex of the type (η^5-C$_5$H$_4$Me)Mo(CO)$_2$(PPh$_3$)I on pelleting will give isomer mixture.

Keywords: Solid State;
cis/trans-[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I]; Pelleting;
Diluents; FT IR

1. INTRODUCTION

Inorganic diluents or dispersants that are insoluble in the melt have been known as additives to control the rate of solid-solid reactions. Addition of a high melting point inert solid to a melt can be used to control the rate of a solvent-free reaction just as the rates of some reactions are controlled by solvents. A good example is in a solventless substitution reaction of Mn(CO)$_4$(PPh$_3$)Br with PPh$_3$, a range of dispersants or diluent (KBr, Al$_2$O$_3$, Na$_2$SO$_4$,

NaNO$_2$, SiO$_2$, Na$_2$CO$_3$, NaC$_2$H$_3$O$_2$, NaNO$_3$, sucrose and TiO$_2$) are ground and filtered only to provide a comparable particle size. The reaction was investigated and monitored by in situ DRIFTS. The result of the above study showed that the chemical nature of the diluent matrix influenced the rate of the solventless reaction. Therefore, when the reaction was carried out in sucrose and SiO$_2$, the rate of the reaction was fastest. When Al$_2$O$_3$ and TiO$_2$ were used, the reaction was slower [1]. Also the role of the nature of the solid dispersant or diluent has been investigated in solventless reactions involving thallium salts of tris (pyrazolylborate). The grinding of thallium salts of tris (pyrazolylborate), Tp with Mn(II), Co(II) and Ni(II) salts in an agate mortar has been reported to yield Mn, Co and Ni tris (pyrazolylborate) metal complexes of the type TpMCl via a substitution type of reaction [2]. Supramolecular complexes of the formula [Co^{III}(η^5-C$_5$H$_4$COOH) (η^5-C$_5$H$_4$COO)]$_2$·M$^+$X$^-$ were formed when organometallic zwitterion [Co^{III}(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)] reacts quantitatively as a solid polycrystalline phase with a number of crystalline alkali salts MX (M = K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$; X = Cl$^-$, Br$^-$, I$^-$, PF$_6^-$ [1].

In the same vein, manual grinding of the organometallic complex [Fe(η^5-C$_5$H$_4$COOH)$_2$] with a number of solid bases, namely 1,4-diazabicyclo[2.2.2]octane, C$_6$H$_{12}$N$_2$, 1,4-phenylenediamine, *p*-(NH$_2$)$_2$C$_6$H$_4$, piperazine, HN(C$_2$H$_4$)$_2$NH, *trans*-1,4-cyclohexanediamine, *p*-(NH$_2$)$_2$C$_6$H$_{10}$, and guanidinium carbonate [(NH$_2$)$_3$C]$_2$[CO$_3$], generates quantitatively the corresponding adducts,

[HC$_6$H$_{12}$N$_2$][Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)],
[HC$_6$H$_8$N$_2$][Fe(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)],
[H$_2$C$_4$H$_{10}$N$_2$][Fe(η^5-C$_5$H$_4$COO)$_2$],
[H$_2$C$_6$H$_{14}$N$_2$][Fe(η^5-C$_5$H$_4$COO)$_2$]· 2H$_2$O, and
[C(NH$_2$)$_3$]$_2$[Fe(η^5-C$_5$H$_4$COO)$_2$]· 2H$_2$O, respectively [3].
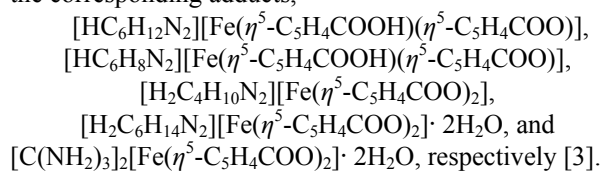
Therefore, environmental concerns in synthetic chemistry have led to a reconsideration of reaction methodologies. This has resulted in investigations into atom economy, the use of supercritical CO$_2$, ionic liquids, and

[*]Corresponding author.

other procedures to reduce the disposal problems associated with most chemical reactions. One obvious route to reduce waste entails generation of chemicals from reagents in the *absence* of solvents [4]. Little is known about reactivity patterns of organometallic complexes in the solid state, until it was discovered that organometallic complexes, of the type CpML4, undergo *cis-trans* ligand isomerization reactions in the solid state [5-8].

Hence, in this study we report on the effect of pelleting on organometallic compounds, *trans-* and *cis-*[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I]. Attempt were made on the effect of diluents on iron organometallic complexes [(η^5-C$_5$H$_5$)Fe(CO)$_2$ PPh$_3^+$][PF$_6^-$], as its influenced the products formed after pellet formation. Hence these diluents KBr, KCl, NaCl, CaCl$_2$, NaNO$_3$, BaSO$_4$, CaCO$_3$ and Al$_2$O$_3$ were screened for either good pellet formation or set out reactions with the complexes. It was observed that BaSO$_4$, CaCO$_3$ and Al$_2$O$_3$ could not form a good pellet for FT IR measurement of the complexes. A simple process of forming a good pellet for FT IR measurement could generate a reaction because of high amount of energy involved. In general, when two solids are ground together, the heat generated in the grinding process may be sufficient to either create a melt at the surface or completely melt the solid reagents. This could arise from the generation of a "hot spot" (an exotherm) [1,9] that could lead to a self-sustaining reaction.

2. EXPERIMENTAL

2.1. General

(η^5-C$_5$H$_4$Me)Mo(CO)$_3$I were prepared by the standard procedures used to synthesise other ring-substituted analogues [10,11]. TrimethylamineN-oxide dihydrate (Aldrich) was used as received. All reactions were carried out using standard Schlenk techniques under nitrogen.

2.2. Preparation of a Mixture of *trans-* and *cis-*[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I]

A mixture of the *cis* and *trans* isomers were prepared in good yield by following a standard procedure in the literature [11].

2.3. Preparation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$ PPh$_3^+$][PF$_6^-$]

The procedures are the same for the preparation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$ PPh$_3^+$][PF$_6^-$] in the literature [12].

2.4. Refractometric Measurement to Ascertain the Purity of the Salts

Abbe Refractometer (Optic Ivymen) was used to determine the purity of the samples.

2.5. Pellets Formation

The diluents were dried for 12 hrs in an oven to ensure complete removal of moisture. About 10 mg of pure diluents (e.g. NaCl) were crushed to fine powder using an agate mortar and pestle. About 2 mg of the solid organometallic complex was added and gently ground together with diluents until fully mixed. The die set was assembled and the mixture was added into the die and goes between two stainless-steel discs and pressed to form a good, thin and transparent pellet. Opaque pellets gave poor spectra and white spots in the pellets.

3. RESULTS AND DISCUSSIONS

3.1. Preparation of the Complexes *trans-* and *cis-*[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I]

The method developed by Blumer *et al*. [13] for the synthesis of the related unsubstituted compounds was adopted for the synthesis of *trans-* and *cis-*[(η^5-C$_5$H$_4$Me)Mo(CO)$_2$PPh$_3$I]. Isomer separation was achieved by dissolving the crude material in CH$_2$Cl$_2$ followed by mixing with a small quantity of silica gel. The yellow powder left after removing the CH$_2$Cl$_2$ was chromatographed on a silica gel column (60 cm) with a 1:10 CH$_2$Cl$_2$/hexane mixture to afford the desired complexes [14].

3.2. Preparation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$ PPh$_3^+$][PF$_6^-$]

The preparation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$ PPh$_3^+$][PF$_6^-$], follows the ETC PPh$_3$ ligand replacement for I$^-$ on (η^5-C$_5$H$_5$)Fe(CO)$_2$I to obtain the complexes [12]. The yield and spectroscopic information were not at variant with the established results in the literature.

3.3. Purity of the Salts

Before the formation of a good pellet suitable for FTIR measurement, the diluents were carefully dried at 105°C until a constant weight obtained. This is to remove moisture and other volatile component in the diluents. The refractive index of the salts at the specified temperature, 33.4°C depicts the state of high purity of the salts when compared with reference refractive indexes.

3.4. Effect of Pelleting on v_{co} in Methylcyclopentadienyl Molybdenum Dicarbonyl Triphenylphosphine Iodide Using Different Diluents
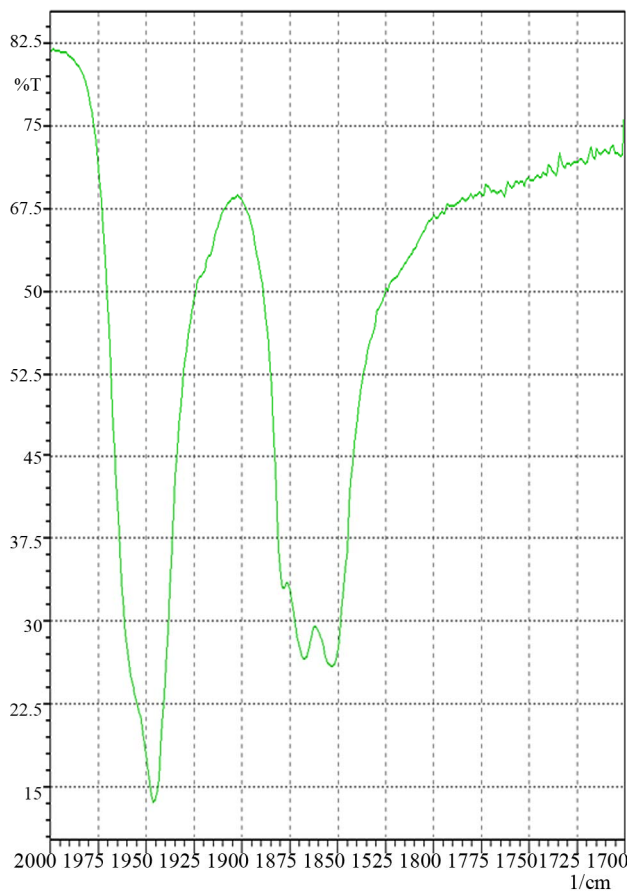
We reported earlier a thermal transformation of *cis-* or *trans-*(η^5-C$_5$H$_4$Me)Mo(CO)$_2$(PPh$_3$)I in the solid state where the color and shape of the starting materials showed no visible change and no obvious decomposition during the heating process [11]. The *cis* and *trans* products was

achieved by means of TLC, and solution IR and NMR spectroscopy on the products after the reaction, revealed the formation of the isomer materials. The isomerisation reactions for the new complexes were studied and the general trend was for the isomerisation reaction to occur from the *trans* to the *cis* isomer dependent on electronic factors associated with ligand orientation effects. An extension of the work was on the formation of the products mixture on pelleting either the *cis* or the *trans* isomer of the complex. **Figure 1** shows the isomerisation reaction during the formation of a suitable pellet for FT IR spectroscopy. While **Figure 2** shows the FT IR mixture of the *cis* or the *trans* isomer of the complex.

The *cis* or the *trans* isomer gave the same IR spectra i.e a mixture of *cis* and *trans* isomer of the complex.
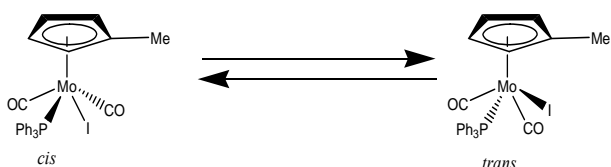
Figure 1. Solid state *cis/trans* isomerisation reaction of $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2(PPh_3)I$ during pelleting.

Therefore, it does not matter the isomer started with in the course of solid state transformation reaction, an equilibrium ratio of 30/70 (*trans/cis*) will still be achieved. This result shows that the solid state isomerisation of $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2(PPh_3)I$ still maintain a bidirectional reaction process. The IR spectra show very strong peaks at v_{co} 1957, 1947 and strong peaks at 1867, 1853 cm^{-1}. As shown in **Figures 2** and **3**.

The individual IR *cis/trans* isomer will therefore show at 1947 and 1853/1957 and 1867 cm^{-1}. The solution IR spectra gave, *cis* = 1961, 1875 and *trans* = 1963, 1882 cm^{-1} in dry CHCl$_3$ [11]. It should be noted that the same isomerisation products were obtained for the halide salts of group I investigated, namely, KCl, KBr and NaCl, **Figure 3**.

It is therefore possible to draw out some information on pelleting in the IR measurement of this complex:

1) Most of the solid state IR measurement of the organometallic complex of the type $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2$ (PPh$_3$)I on pelleting will give isomer mixture.

2) It can results in facile synthesis of *cis/trans*-$(\eta^5\text{-}C_5H_4Me)$ Mo(CO)$_2$(PPh$_3$)I.

3) It can leads to isomerisation reaction as in this process.

Figure 2. shows the FT IR spectrum of the isomer mixture in the solid state in NaCl.
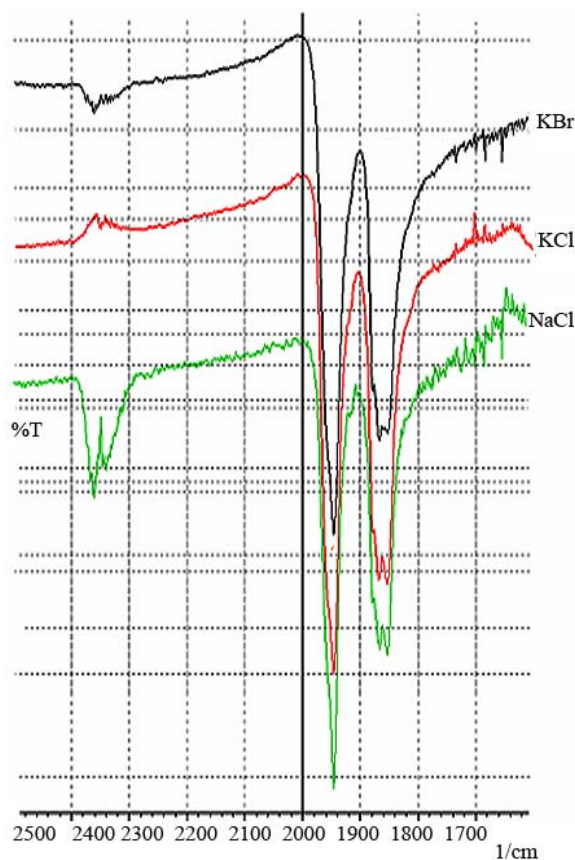
**Figure 3.** shows the FT IR spectra of the isomer mixture in the solid state in different diluents.

4) It is a fast reaction.

5) It is a neat and greener reaction.

Hence, when two solids are ground or pelleting together, the heat generated in the process set out a reaction to generate an exotherm that could then lead to a self-sustaining reaction [1,9]. It is not unlikely that no other product(s) formed during the creation of a suitable pellet for IR measurement. It is also not unlikely that there is halides exchange, a possibility of Iodide in the complex exchange for Chloride or Bromide in the diluents during the formation of a good pellet for FT IR measurement. Supporting evidence in **Figure 3** revealed that there is a change in the absorption intensity especially when pelleting the complex with KBr, while the intensities of NaCl and KCl remain constant.

A non isomeric organometallic product of the type $[\eta^5\text{-}(C_5H_5)Fe(CO)_2PPh_3]^+[PF_6]^-$ was investigated to determine the effect of the diluents through FT IR measurement and as a control for whether the solid state transformation of the $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2(PPh_3)I$ complex actually occurred. **Figure 4** shows the spectrum of the $[\eta^5\text{-}(C_5H_5)Fe(CO)_2PPh_3]^+[PF_6]^-$ complex in NaCl diluent after pelleting.

It was observed that very strong peaks at ν_{co} 2008 and 2049 cm^{-1} correspond to the absorption of CO attached to the iron centre. A lower wave number of this kind reflects the degree of back bonding to the carbon monoxide ligand. The peaks position in the solid state is not significantly different from the peaks position in solution IR that occurred at 2014 and 2062 cm^{-1} in dry CHCl$_3$ [12] **Figure 5** depicts the behaviour of complex in different diluents.
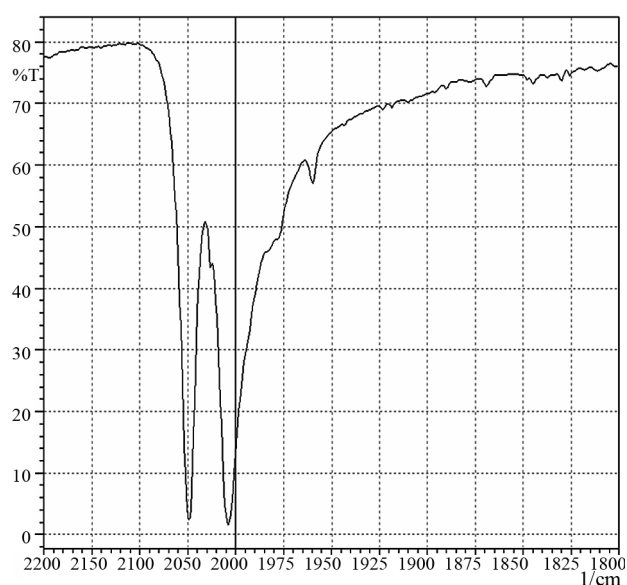
Figure 4. FTIR Spectrum of $[\eta^5\text{-}(C_5H_5)Fe(CO)_2PPh_3]^+[PF_6]^-$ in NaCl.
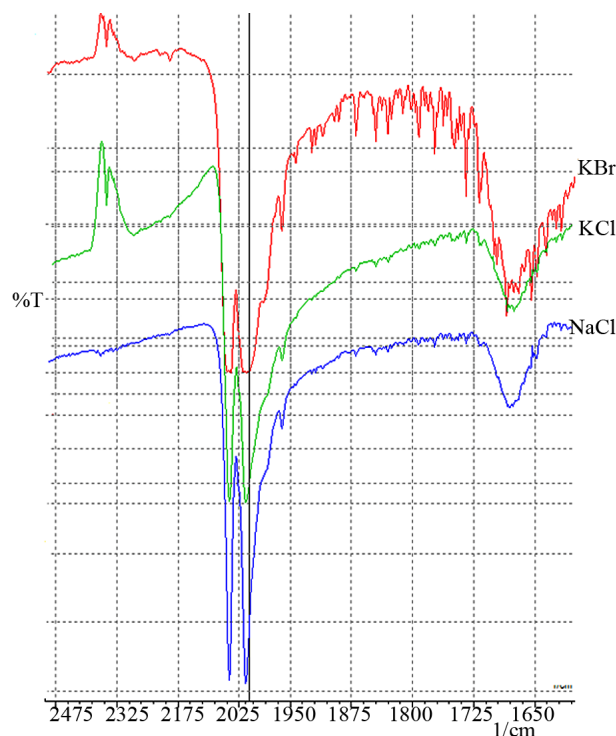
Figure 5. FTIR Spectra of $[\eta^5\text{-}(C_5H_5)Fe(CO)_2PPh_3]^+[PF_6]^-$ in different diluents.

The same pattern was therefore observed in the diluents used. This could informed that these diluents are suitable for the formation of good pellet for IR without decomposition. It is therefore possible that the anion exchange reaction, (where Cl$^-$ or Br$^-$ exchange for PF$_6^-$ did not occur because from our experience the halide counter anion are not very stable as the PF$_6^-$ anion. It could therefore infered that isomerization actually took place on pelleting *cis/trans*-$(\eta^5\text{-}C_5H_4Me)Mo(CO)_2(PPh_3)I$ and no isomerisation on $[\eta^5\text{-}(C_5H_5)Fe(CO)_2PPh_3]^+[PF_6]^-$ during pelleting.

4. CONCLUSION

It was established that pelleting can generate enough heat to set up a chemical reaction. Therefore on forming a suitable pellet using different diluents of group I metal salts leads to the isomerisation reactions of transforming *cis* to *trans* and the reverse, until isomeric mixture of *cis/trans* (30/70) is achieved.

5. ACKNOWLEDGEMENTS

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