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A Review on the Characterization of Dinitrogen Substituted Cyclopentadienyl Manganese Tricarbonyl ($CpMn(CO_3)N_2$)

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Abstract

This review details the use of Fourier Transform Infrared (FTIR) and Raman Spectroscopic methods, to characterize dinitrogen complexes formed following the photolysis of cyclopentadienyl manganese tricarbonyl ($(\eta^5\text{-}C_5H_5)Mn(CO)_3$), in the presence of N_2. The review was performed to explore the information relating to the structure and bonding modes of dinitrogen to the metal Centre. The main aim here was to explore the utilization of Raman spectroscopy in complimenting the application of Infrared spectroscopy in the characterization of organometallic complexes.

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1.0 Introduction

The Photochemistry of organometallic complexes is important for wide range of applications. These include; catalytic CO_2 reduction, (Easun *et al.*, 2014; Yang *et al.*, 2009) probe of DNA damage, (Smith, *et al.*, 2011) the study of reactive intermediates, (Johnson, *et al.*, 1991; Kemnitz, *et al.*,2011) reaction pathways e.g. oxidative addition,(Hill & Wrighton, 1987) and photochemically generated dinitrogen complexes which are shown to serve as the precursors of organometallic alkanes complexes through lower energy irradiation (Calladine *et al.*, 2010). Understanding photochemical reaction mechanisms is a prerequisite of full understanding of processes and a variety of techniques such as Infrared and Raman spectroscopy. Vibrational spectroscopy is often used to characterize reaction intermediates and unstable complexes, as they provide structural information and are not limited in terms of spectroscopic timescales in the same way, more traditional approaches such as NMR are.

Carbonyl ligands deserve special attention in organometallic chemistry because they can be easily probed by infrared spectroscopy and can therefore offer great insight into the bonding in many organometallic compounds. As one of the most common ligands in organometallic compounds, carbon monoxide serves as the only ligand in binary carbonyls and is found in combination with other ligands in a vast number of compounds (Butler & Harrod, 1989). The bonding in metal carbonyls can be appreciated by studying the vibrational frequencies of the carbonyls in various transition metal environments using both IR and Raman spectroscopic methods. Through its highest occupied molecular orbitals (HOMO), the carbon atom of the carbonyl ligand can donate electron density to the partially filled d-orbital of the metal, while the metal

back donates its d-electrons to the lowest unoccupied molecular orbital (LUMO) of the carbon atom. This π-back bonding weakens the CO bond and hence lowers its vibrational frequency. For example, □(CO) in uncoordinated CO is 2143 cm^{-1}, while it was found to be 2000 cm^{-1} in $Cr(CO)_6$ (Butler & Harrod, 1989). The vibrational frequencies of the CO ligand are also sensitive to the number of bonds present in a complex. An example of this is through the formation of bridging and triply bridging carbonyl ligands, where the vibrational frequencies are reported to be 1850 and 1750, or 1750 and 1620 cm^{-1} depending on the ligand environment (Cotton, *et al.*, 1995; Durig, *et al.*, 1969). For many complexes ultraviolet (UV) light can be used to photolyze metal carbonyl complexes, causing the loss of a carbonyl ligand which results in the formation of a coordinatively unsaturated 16-electrons transient intermediate. In solution this would normally react very rapidly with the solvent and subsequently reacting substance, parent material or with a photo-ejected CO. This reactive intermediate in most photophysical and photochemical studies can be studied by either ultrafast time-resolved spectroscopic techniques or stabilization e.g. matrix isolation, so that it can be monitored through conventional spectroscopic methods such as FTIR and Raman spectroscopy (Murphy, 2015; Yang, 2003).

1.1 Infrared and Raman Spectroscopy of metal carbonyls

Infrared spectroscopic methods can easily be employed for the characterization of coordinatively unsaturated transition-metal carbonyls in the gas, solution or supercritical phase. Because many of these unsaturated carbonyls are extremely photo-labile and their UV-visible spectra are broad, featureless and provide very little structural information. As mentioned above, the infrared spectra of unsaturated transition metal carbonyls can exhibit strong absorption bands in the CO stretching vibrational region, which as previously mentioned are sensitive to changes in electron density around the metal center (George & Turner, 1998; Zhou, *et al.*, 2001).

Infrared spectroscopic measurements are based on the absorption of radiation from the infrared region of the electromagnetic spectrum, typically the mid-IR region i.e. 400 – 4000 cm^{-1}, (Brian, 2011) by a chemical substance in the solid, liquid or gaseous form. This measurement is routinely carried out using Fourier Transform Infrared Spectrophotometers (FTIR). The Raman Effect was first demonstrated experimentally in 1928 by Chandrashekhara Venkata Raman, an Indian physicist who discovered that of a small fraction visible light can be scattered by certain molecules resulting in a shift in the scattered light's wavelength which depends on the chemical nature of the molecule and its vibrational modes. For his discovery Raman was awarded Nobel Prize in physics in 1931 (Butler & Harrod, 1989; Das & Agrawal, 2011; Miessler & Donald, 2014).

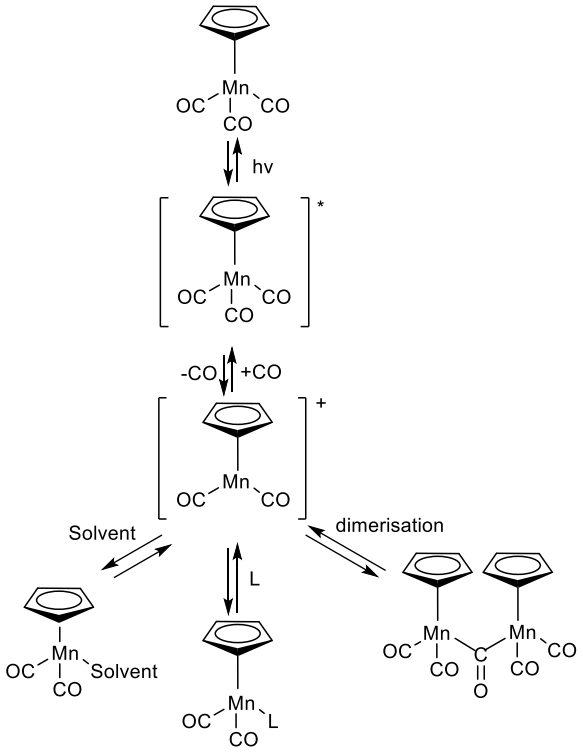
According to selection rules a molecular vibration is IR active if the dipole moment changes during the vibration. Hence, a molecular vibration can be IR active, Raman active or both. However, totally symmetric vibrations are always Raman active. (Das & Agrawal, 2011) Also, the nature of chemical bond indicates the change in polarizability for a given vibration, as the more covalent in character a bond, the more polarizable and hence strongly Raman active its associated vibration is. On the other hand, bonds with ionic character are less polarizable and have a large change in dipole moment, and can therefore be strongly IR active. For covalent compounds, the polarizability increases with increasing bond order (Ferraro & Nakamoto, 1994). Raman spectroscopy has been used by Easun, *et. al.*, 2014 to show the formation of *mer*.Re(diimine)$(CO)_3$Cl from *fac*.Re(diimine)$(CO)_3$Cl, the process was illustrated by clear decrease in the parent peak intensity around 1600 and 1500 cm^{-1} in the Raman, and the subsequent appearance of product bands at a lower wavenumber, illustrating the conversion of the fac. isomer to mer (Easun *et al.*, 2014). This research clearly demonstrates the complimentary use of Raman and FTIR spectroscopic methods in the study of photochemical reaction intermediates and products. In a related studies Durig and co-workers investigated the vibrational frequencies of $(\eta^5{-}CH_3COC_5H_4)V(CO)_4$ and $(\eta^5{-}C_5H_5)V(CO)_4$ in solid KBr and cyclohexane solution, using FTIR and Raman spectroscopic methods. The results showed no significant difference in the position of the vibrational bands for FTIR method in both medium (KBr and cyclohexane solution). The studies using Raman spectroscopy shows the appearance of narrow bands compared in the FTIR in active region (Durig *et al.*, 1969; Kariuki & Kettle, 1976).

1.1.1 Infrared and Raman Spectroscopy of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$

The vibrational spectra of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ compounds can be best described using local symmetry proposed by Cotton *et. al.* 1995, which assumed the little interaction between the $Mn(CO)_3$ and the cyclopentadienyl ring. The ring possesses C_{5v} symmetry while the $Mn(CO)_3$ moiety has C_{3v} symmetry (Adams & Squire, 1973; Hyams, *et al.*, 1967; Parker & Stiddard, 1968). However, a differing number of □(CO) bands are observed in the solution and solid phase of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in the IR and Raman spectra. These can be described based on the extent of interaction between Cp–Mn and the $Mn(CO)_3$ moieties. The solid-state spectra can be described using factor group, site symmetry or unit cell models. The site symmetry model predicts the conversion of the $Mn(CO)_3$ moiety from a C_{3v} to a Cs point group, causing the splitting of

degenerate E-mode of the C_{3v}, hence more than three peaks are reported in both the Raman and IR spectrum. In the liquid phase, the spectra can be described using the oriented gas model in which each molecule is assumed to behave independently, hence the $Mn(CO)_3$ moiety will have C_{3v} point group as predicted and two □(CO) peaks of the A_1 and E modes are visible in the IR and Raman spectrum (Fitzpatrick, *et al.,* 1981a, 1981b; Kettle, 2007).

According to scheme 1.0, during photolysis of the (η^5-C_5H_5)$Mn(CO)_3$ complex, absorption of light of right wavelength causes the ejection of one or more carbonyl ligand to form a coordinatively unsaturated carbonyl intermediate which can react in various ways to form different photoproducts. These can be monitored through vibrational spectroscopy, because the vibrational frequencies of carbonyl ligands are sensitive to the change in electron density on the metal centre. As evident from the figure 1, if the complex is in N_2 matrix, or in an inert matrix in the presence of N_2 gas, UV photolysis can produce a dinitrogen complex as one of the photo products (Hitam, *et al.,* 1984).



Scheme 1.0: Photochemical pathways of (η^5-C_5H_5)$Mn(CO)_3$ showing various possible photoproducts. Adapted from (Hitam *et al.,* 1984)

1.2 Dinitrogen Complexes and their carbonyl vibrational frequencies

The occurrence of transition metal dinitrogen complexes was first reported in 1965 through the synthesis of $[Ru(N_2)(NH_3)_5]^{2+}$ (Chatt, *et al.,* 1978; Grills, *et al.,* 2006). This process was deemed a promising development in the search of an alternative chemical nitrogen fixation route to the Haber–Bosch process. The Haber–Bosch process involves a reaction between nitrogen and hydrogen gas over an iron catalyst at high temperature and pressure to produce gaseous ammonia, however, these conditions are energy intensive. The goal of immerging chemical nitrogen fixation is to produce a metal-based nitrogen catalyst that can efficiently convert gaseous nitrogen under mild conditions into industrially useful and environmentally friendly compounds, by mimicking the biological nitrogen fixation process (Childs, Colley, *et al.,* 2000; Grills *et al.,* 2006). Some promise has been shown by the polymeric dinitrogen complex of (η^5-C_5H_5)$Mn(CO)_3$ which is highly stable compared to the monomeric analogue (Kurimura *et al.,* 1981), the property that makes it a potential nitrogen fixation catalyst.

Figure 1 shows the various bonding modes by which dinitrogen can bind to the metal centre which include; end-on mononuclear, end-on binuclear, side-on binuclear and side-on and end-on binuclear, among which the end-on mononuclear mode is the most commonly reported for weakly activated 18-electron complexes (Das & Agrawal, 2011).

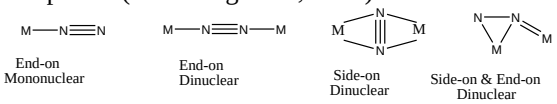


Figure 1: Binding modes of dinitrogen on metal centres. Adapted from (Childs, *et al.,* 2000)

Comparing the vibrational frequencies of carbonyls and dinitrogen in transition metal complexes, it is evident that dinitrogen is a better σ electron donor and a weaker π-electron acceptor, while carbonyl is a stronger π electron acceptor than dinitrogen in carbonyls complexes. This can be observed from the decrease in the carbonyl vibrational frequencies, due to the increase in back donation to the remaining ligands, when one of the carbonyls is substituted by dinitrogen (Fitzpatrick & Mathews, 1973).

The dinitrogen complexes can be synthesized through the formation of photogenerated dicarbonyl intermediates in hydrocarbon solvents, inert gases, supercritical fluids or polymer matrices at room or very low temperatures (Yang, 2003). These reactive complexes tend to have a very short lifetime due to their high reactivity, and are therefore often present in very low concentrations within the reaction mixture. The study of reactive intermediates therefore requires the use of techniques that can either extend the lifetime of the transient species by cooling the reaction down, e.g. through matrix isolation, or by observation of the intermediates immediately when they are formed, by time-resolved spectroscopy (Fitzpatrick & Mathews, 1973; George *et al.,* 2003; Yang, 2003).

1.3 Matrix Isolation Technique

Matrix isolation is a technique used to obtain detailed information about the structure of a reactive intermediate by prolonging its lifetime once formed through the use of low temperature and inert (or relatively inert) matrix, this allows spectroscopic measurements to take place on a reasonable timescale (Hitam *et al.,* 1984). These unstable intermediates are generated either by gas phase reactions, and then immobilising them on cold window, or by decomposing already stabilised molecules and isolating them from further reactions such as recombination, intermolecular electron transfer, and so on, while in inert gases (Calladine *et al.*, 2009; Sun *et al*., 1997), hydrocarbon solvents (Calladine *et al.,* 2010; Calladine *et al.,* 2009; Childs, *et al.,* 2000), polymer discs (Childs, *et al.,* 2000; *Clarke*, *et al.,* 2000; Clarke, *et al.,* 1994) and supercritical fluids (Banister *et al.,* 1994; Calladine *et al.,* 2010). Some form of irradiation (e.g. UV photolysis) (Murphy, 2015), is also used to generate the unstable intermediate.

The development of various matrix isolation techniques makes it more versatile, in that the restriction imposed by one method can be overcome by the other. For example, the problem associated with gas matrices such as site symmetry splitting, volatility at high temperature and so on, can be managed by using hydrocarbon solvents or a polymer matrix. In turn, the hydrocarbon solvent and polymer matrix have the disadvantages of strong absorption bands which may interfere with the bands of the substance of interest, this can also be solved by use of supercritical fluids or an inert gas matrix (Cooper *et al.,* 1993; Murphy, 2015).

1.3.1 Noble or Inert Gas Matrices

The term 'inert' in chemical a process is generally referring to non-reactive. Therefore, a gas is inert if its atoms do not combine with other atoms in a chemical reaction under relevant set conditions. Noble gases are traditionally referred as inert because they were believed to be unreactive, due to their stable octet of valence electrons. The interesting chemistry of these elements from the second most abundant element; Helium (He), through to the third most abundant component of dry air; Argon (Ar), to the radioactive; Radon (Rn) are now widely studied.(Miessler & Donald, 2014) The chemistry of noble gases started in the late 1940s when the first compounds containing noble gases known as clathrates were synthesized. The compounds were believed to contain Argon, Krypton and Xenon. (Miessler & Donald, 2014). Among these elements Xe is observed to have rich chemistry, since the observation of its first compound by Bertlett in 1962 (Murphy, 2015).

Some of the early matrix isolation studies in noble gas matrices were performed by Perutz and Turner, (Perutz & Turner, 1975) since then noble gasses are shown to be promising matrices and are extensively used to study various reactive intermediates due to their transparency in the IR and UV regions of the spectrum and can be liquefied at moderate pressures and low temperature (Perutz & Hall, 1996). But the comparable solvating properties to heavier hydrocarbons and high cost, limit their wider application for study of reactive intermediates (Bloyce *et al.,* 1990; Calladine *et al.,* 2009). Metal carbonyl complexes are reported to dissolve in liquid noble gasses at low temperatures thereby serving as a reaction medium where the complexes react with dopant molecules such as N_2 and H_2. For example, Maier and coworkers synthesised $Ni(CO)_3N_2$ in liquid krypton at 114 K from $Ni(CO)_4$ (Hitam *et al.,* 1984; Maier, *et al.,* 1982). Later the same group identified $Cr(CO)_3Xe$ in liquid Xe-doped Kr at cryogenic temperature as first evidence of formation of noble gas complexes with significantly longer lifetimes in solution, which could be attributed to the increase in the energy of visible absorption band of the unsaturated fragment with the series of noble gases (i.e. Xe>Kr>Ar>SF6>Ne) indicating strong interaction with Xe (Simpson, *et al.,* 1983). Frozen gas matrices at 12 K were also shown to stabilise the transient reactive intermediates after photo-ejection of CO through UV photolysis.(Bloyce *et al.,* 1990; Hitam *et al.,* 1984) Recently, supercritical fluids have largely replaced liquid and gaseous noble gases matrices, because they can be used to study reactive intermediates at room temperature under high pressure. However, it is important to know at this point that gaseous substances used as matrix materials should be the highest purity to minimize the number of possible side reactions with impurities and unstable intermediates at low temperature (Hitam *et al.,* 1984).

1.3.2 Supercritical Fluids

A Supercritical fluid is formed when the exerted pressure and temperature of a fluid exceed its critical values i.e. P_c and T_c, (Sun *et al.,* 1997) unlike conventional solvents, gases like hydrogen are miscible in supercritical fluids, this property provides an avenue for hydrogenation reactions.(Yang, 2003) Due to the high solubility of H_2 in supercritical Xe, it was reported to react with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ under ambient condition to produce a stable dihydrogen complex,(Howdle & Poliakoff, 1989) also nitrogen gas was shown for the first time by Howdle and Polliakoff to react with $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in supercritical Xe and produced mono, di and trisubstituted complexes, products that were not reported in conventional solvents.(Howdle, *et al.,* 1989) Supercritical fluids (s_c) have been demonstrated to be an environmentally more acceptable analytical solvent than hydrocarbon solvents. For example, supercritical CO_2 is used for impregnation of polyethylene disk with a (η^5-

$C_5H_5)Mn(CO)_3$ complex (Cooper *et al.,* 1993), this helps to reduce the number of interferences observed in the vibrational spectra, caused by persistent nature of hydrocarbon solvents. Bannister et. al. also reported the UV photolysis of metal complexes in supercritical CO_2, Xe and C_2H_6 with high pressure of N_2, leading to photo-substitution of CO by N_2. A comparison of product bands in a $scCO_2$ and scXe solvent clearly indicates no significant difference between the products obtained in both solvents, thus scCO2 can serve as the potential alternative to the more expensive scXe (Banister *et al.,* 1994; Leitner, 2002). Furthermore, scXe was reported by Sun, et. al., to stabilised the transient $(\eta^5\text{-}C_5H_5)Re(CO)_3$ through formation of $(\eta^5\text{-}C_5H_5)Re(CO)_2(Xe)$, the remarkable stability of this complex was good enough to make its observation through NMR spectroscopy (Sun *et al.,* 1997). $(\eta^5\text{-}C_5H_5)Re(CO)_2(Xe)$ was also observed to be more stable than $(\eta^5\text{-}C_5H_5)Re(CO)_2(Kr)$ toward CO dissociation in scKr solution doped with Xe at room temperature.(George *et al.,* 2003; Sun *et al.,* 1997).

1.3.3 Hydrocarbon Solutions

IR spectroscopy was also shown to be a powerful tool for the study of organometallic alkane complexes, particularly those which include carbonyl ligands (Murphy, 2015; Perutz & Turner, 1975). Organometallic alkane complexes of transition metal carbonyls have been reviewed extensively (Calladine *et al.,* 2009; Murphy, 2015; Sun *et al.,* 1997). From the work of Kelly and Gustorf in 1973 on $Cr(CO)_6$ in cyclohexane at room temperature, since then various hydrocarbon solvent matrices were used in the study of different carbonyl intermediates(Kelly & Gustorf, 1973).

The stability of photogenerated unsaturated reactive intermediate was found to be dependent on the nature of hydrocarbon solvents, various studies have revealed that longer chain and cyclic hydrocarbons can stabilise an intermediate more than their small chain counterparts. Thus, CH_4 has a weaker binding energy toward a metal centre than any other hydrocarbon matrix (Murphy, 2015). The $(\eta^5\text{-}C_5H_5)Re(CO)\ (CO)_2$ intermediate was reported by Callidine and co-workers to be stabilized by cyclopentane and n-heptane at room temperature to form $(\eta^5\text{-}C_5H_5)Re(CO)_2$(cyclopentane) and (η5-C5H5)(Re)$(CO)_2$(n-heptane) respectively.(Calladine *et al.,* 2009) These intermediates have longer lifetimes than all the hydrocarbon intermediates studied and were the first to be characterised by NMR spectroscopy.(Childs, Colley, *et al.,* 2000; Cowan & George, 2008; Torres, *et al.,* 2015) Recently, TRIR and NMR studies of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in ethane and isopentane at 135 K yields relatively stabilised reactive intermediates. Subsequent characterisation by NMR revealed the compounds possessed different isomerised photoproducts (Torres *et al.,* 2015). Perflourinated alkanes were also shown to be promising in that they can stabilise the reactive intermediates more than some hydrocarbon solvents. Although, some complexes are reported to have low solubility in perflourinated alkanes, this limitation has been overcome by doping with alkanes or noble gases such as Xe (Murphy, 2015).

1.3.4 Polymer Matrices

Different photoproducts are observed as a result of a reaction between photo-generated $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ in the polyethylene (PE) matrix and the pendent olefinic C=C bond along the polymer chain (Cooper *et al.,* 1993). Clarke and Co-workers later observed the formation of four different $(\eta^5\text{-}C_5H_5)Mn(CO)_2$(C=C) complexes, where $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ intermediate is bound to the polyethylene matrix through the vinyl, pendent or internal C=C bond in the PE chain, the formation of which competes with other reactants such as H_2 and N_2, hence inhibiting the synthesis of important complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ in the polymer matrix.(Clarke *et al.,* 1994).

To overcome the above problem, the same group demonstrated the use of $Fe(CO)_5$ and $W(CO)_6$ as photo-isomerization catalysts can reduce alkene bonds in PE the application of which is promising due to the ease of purification, where the complex is dissolved in supercritical scCO2, thereby producing a PE matrix that is practically inert. Therefore, subsequent impregnation of the PE disc with complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ results in almost no detectable polymer bound complex (Clarke *et al.,* 2000)

1.4 Time Resolved Spectroscopy

Time resolved spectroscopy involves rapid detection of photochemically generated reactive intermediates as they are formed. This can be achieved through the process of a "pump probe" method, which involves flash photolysis coupled with vibrational spectroscopic monitoring, thereby allowing the immediate detection of reactive unsaturated species generated from milliseconds to picoseconds timescales. However, with recent development in the methods of generating fast laser pulses, very rapid detection of up to femtoseconds levels are possible (Murphy, 2015, George & Turner, 1998). When the FTIR detection method is employed the process is known as Time Resolved Infrared Spectroscopy (TRIR). TRIR is a powerful technique that has been used for many decades in the study of the properties of various reactive intermediates. The design of a TRIR system in 1982 permitted the determination of IR absorptions and the kinetics of transient intermediates with picosecond lifetimes in solution, and its application in a study of the photochemistry and secondary thermal reactions of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (Hermann, *et al.,* 1982) Later Creaven and Co-workers show that the combination of UV-Vis. detection and TRIR spectroscopy can serve as the powerful tool in the study

of organometallic reaction mechanisms and it can complement low temperature matrix isolation techniques.(Creaven, 1987) This was demonstrated through the detection of the decay of a $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ intermediate generated following the UV photolysis of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, the technique was able to show the growth of bands related to the reaction with the solvent and dimerisation. The continuous developments in TRIR and matrix isolation provide insights into well-studied systems such as IR evidence for the previously unknown dicarbonyl intermediates; $[(\eta^5\text{-}C_5H_5)Mn(CO)_2Et\ldots\ldots solv.]$ and $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(CH_2CH_2\text{-}\mu\text{-}H)]$ [M=Mo or W], both in methane matrices at 13K and in solution at room temperature (Johnson *et al.*, 1991).

Development of different approaches to TRIR measurements such as point by point, step-scan and scanning dispersive TRIR has increased the quality of spectra in terms of the signal to noise ratio and time resolution, the properties that ultimately increase the scope of the number of reactive intermediates that can be probed by this method (George *et al.*, 2003; Sun, *et al.*, 2002).

2.0 Conclusion

The review covered the synthesis of dinitrogen complexes of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ through UV photolysis in hydrocarbon solvents and polyethylene matrices at room and low temperatures, and its characterisation. This revealed information on the synthesis and characterisation using FTIR and TRIR techniques, but used of other techniques such as Raman spectroscopic method have not been reported.

Conflict of Interest

The authors have no conflict of interest to declare.

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