

Synthesis and reactivity of metal acetylide complexes

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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis and reactivity of metal acetylide complexes**” being submitted by **Sabuj Dhar** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bona fide research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Date:

Dr. Saurav Chatterjee

(Supervisor)

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Rourkela

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Date :

Abstract

Concerted research is being carried out to synthesise various types of metal acetylides. Acetylides give excellent reaction versatility towards metal counterpart. Flexibility in the molecular conformation also increases. In this project two metal acetylides of iron and tungsten have been prepared. $[LM(CO)_n C \equiv CR]$ [$\{L = \eta^5-C_5H_5, M = W, R = (\eta^5-C_5H_4)Fe(\eta^5-C_5H_5), n = 3\}, \{L = \eta^5-C_5Me_5, M = Fe, R = Ph, n = 2\}$] Then CS_2 has been incorporated in the metal acetylides prepared. Insertion of CS_2 has been observed into metal-carbon acetylide bond when exposed to mild sunlight to obtain a variety of transition metal dithiolato complexes. The tungsten complex containing ferrocenyldithiolato ligand has been very interesting due to the presence of two types of metal species bridged by a S_2C_3 unit. The resulting compound was characterised by UV-visible spectroscopy, IR, NMR. The electrochemical studies was carried out.

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“I see C_2 in the carbon arc and in the tail of Halley’s Comet. I see it in acetylene, ethylene and ethane. I see it in the lovely molecular complexes of P.Wolczanski, M.I. Bruce, G. Longoni and their co-worker’s....I see it in CaC_2 and in W. Jeitschko, A. Simon, and their co-worker’s rare –earth carbides. It’s staggering!”

Roald Hoffmann[1]

Chapter 1

Introduction

1.1 Transition metal acetylides

Complexes containing C₂hydrocarbyl ligands occupy a very important position in organometallic chemistry. Monovalent anions of alk-1-yne, [RC≡C]⁻ are isoelectronic to cyanide ion and CO. This fact prompted the first preparation of metal alkynyl complexes in 1953 [2,3]. Since then, a number of synthetic strategies have been developed and chemistry of metal acetylide complexes has grown tremendously. Alkynyl part (-C≡CR) of the metalacetylides have the ability to bind to metal centres in a variety of bonding modes. Due to this a large number of acetylide – bridged polynuclear complexes has been possible to synthesis [4-7]. The presence of metal and electron - rich C≡C moiety in acetylide complexes facilitates cluster growth reactions, and coupling of acetylide moieties to form polycarbon chains on metal frameworks [8-9]. A large majority of the acetylide – bridged mixed metal complexes contain metals of the same group of the Periodic Table. Although, several examples exist of mixed – metal acetylide complexes containing metals from groups 6, 7, 9 and 12.

Examples of metal acetylides according to the transition metal groups in the periodic table are given in Table 1.

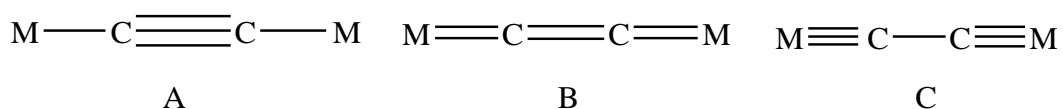
Table 1: Examples of metal acetylides according the transition metal groups in the periodic table

Transition metals (Groups in the periodic table)	Homonuclear/mononuclear acetylide complex	Mixed metal acetylide complex
Molybdenum(Gr-6) [10]	$\text{Cp}(\text{CO})_3\text{Mo}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$	
Rhenium(Gr-7) [11]		

Transition metals (Groups in the periodic table)	Homonuclear / mononuclear acetylide complex	Mixed metal acetylide complex
Iron(Gr-8)[12]	$(\text{CO})_2\text{Cp}^*\text{Fe}-\text{C}\equiv\text{C}-\text{Fe}-\text{Cp}^*(\text{CO})_2$	
Platinum(Gr-10) [14]	$[\text{Pt}(\text{C}\equiv\text{CR})_4]^{2-}$	
Copper(Gr- 11) [15]		
Mercury(Gr-12) [16]		

1.2. Structural diversity of metal acetylides and bonding modes

Several types of bonding modes are found in metal acetylides complexes. Some acetylides contain metal - carbon σ bond while others have metal - carbon π bond.



In the above examples compound **A** is having only σ bond between metal centre and acetylene carbon whereas **B** and **C** are having π bond.

Alkynes have two π bonds and hence the potential to be four-electron donors. When bonded side-on to a single metal atom, the η^2 carbon-carbon triple bond is considered as a two-electron donor, with the π^* orbitals accepting electron density from the metal atom in the same way as for alkenes. When strongly electron withdrawing groups are attached to an alkyne, the ligand can become an excellent π acceptor and displace other ligands such as phosphines. The alkyne, dimethylacetylene-dicarboxylate, $\text{CH}_3\text{CO}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$ is a good example of such type of alkynes. Substituted alkynes can form very stable polymetallic complexes in which the alkyne can be regarded as a four electron donor. For example η^2 -diphenylethyne(hexacarbonyl)dicobalt(0)(Fig.1), in which we can view one π bond as donating to one of the Cobalt atom and the second π bond as overlapping with the other Cobalt atom. In this compound, the alkyl or aryl groups present on the alkyne impart stability by lowering the tendency towards secondary reactions of the coordinated ethyne, such as loss of the slightly acidic H atom to the metal.

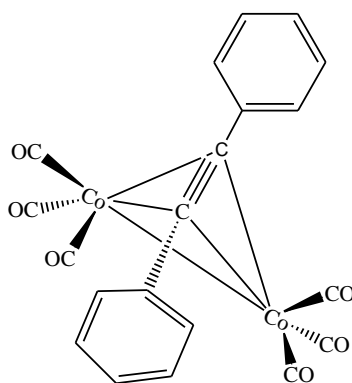


Fig.1:[η^2 -diphenylethyne(hexacarbonyl)dicobalt(0)]

Similar to alkynes, metal acetylide units are also capable of forming adduct with metal species using the π electrons of the alkynyl fragment. There are now many examples of $[\text{M}](\text{C}_2)_n[\text{M}]$ complexes, both of the smallest possible type ($n=1$), and also the higher homologues with an even numbered C_{2n} ($n=1, 2, 3, \dots$) “naked” carbon bridge between two metal centres, which have been obtained in the last two decades and described in many reviews [16]. The importance of such compounds for applications in materials synthesis, as

well as for basic research, has been outlined recently [17]. Some examples of coordination of the acetylide unit in complexes of the type $[M]_m(\mu_n-C_2)$ are shown in Fig.2.

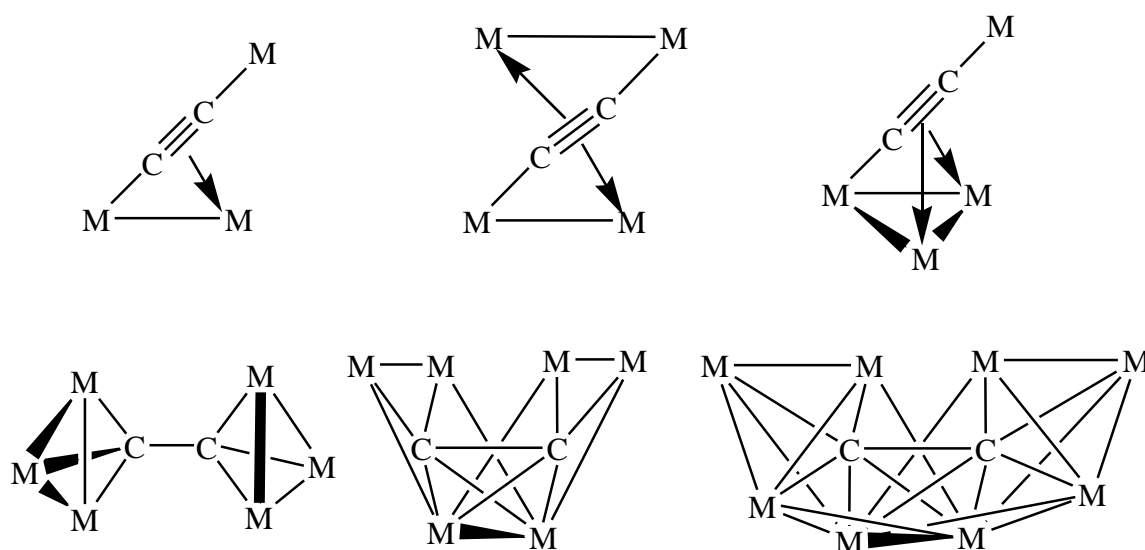


Fig.2: Different types of complexes of the type $[M]_m(\mu_n-C_2)$

Complexes of the type $[M]_2C_2$ have been frequently reported [17], but their complexation with another metal fragment $[M]$ to give discrete $[M]_3C_2$ complexes is very rare. Cluster compounds with more than three metal centres often contain the $[M]_3C_2$ subunit. There are four important interactions : a σ,π -bridging mode with a metal–metal interaction (D), an analogous mode without metal–metal bonding (E), and two modes (F and G) in which one metal centre is coordinated to one carbon atom, and two other metal centres are coordinated to the second carbon atom (Fig. 3).

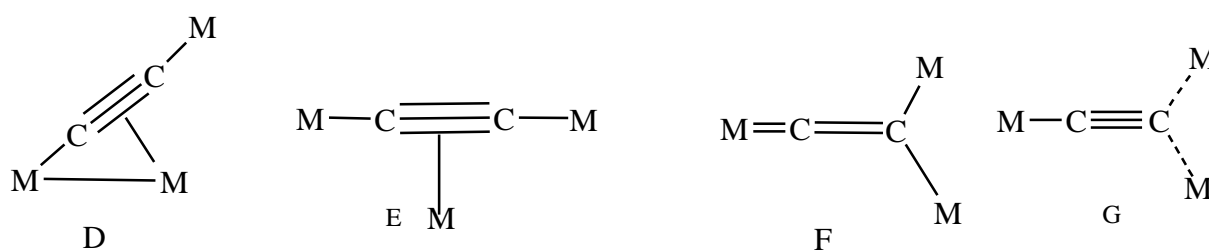


Fig.3: Different types of $[M]_3C_2$ complexes

Examples of metal acetylide containing $[M]_4C_4$ unit are less known and shows structural types as shown in Fig. 4.

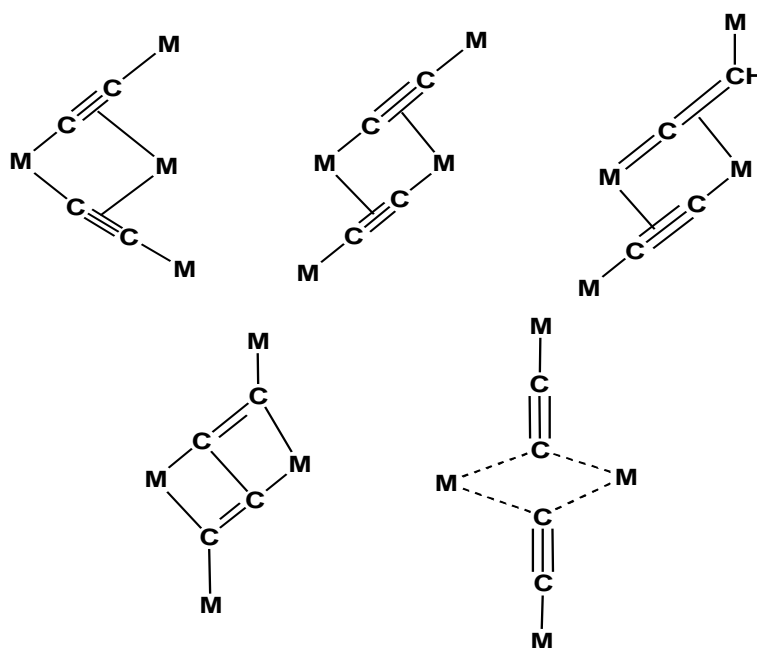


Fig.4: Different types of $[M]_4C_4$ complexes

A heteronuclear cluster acetylide with unique bonding environment has been synthesised by mathur et al from a reaction between iron chalcogen cluster and mononuclear metal acetylide in presence of trimethylamine-oxide (Fig. 5).

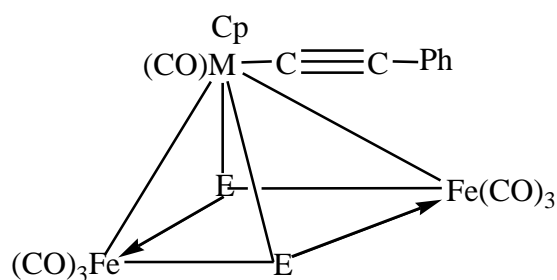
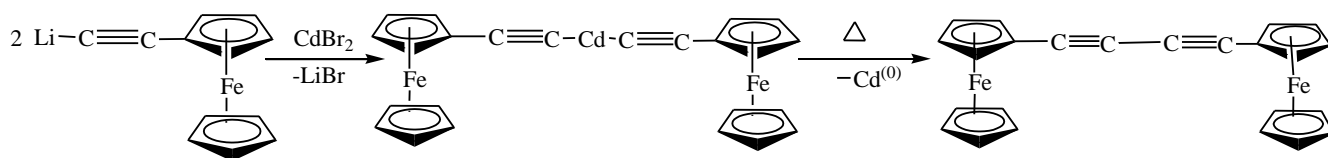


Fig.5: $[CpM(CO) C \equiv C-PhFe_2(CO)_6E_2]$ where $E=Se,Te$; $M=Mo, W$

1.3. Reactivity of metal acetylides

The reactivity of alkynes towards transition metals has been the subject of many studies, because of the versatility in the bonding properties of the acetylide group[18]. Metal acetylides possess two reactive sites, the C≡C triple bond and the metal centre itself. Combination of the former to act as an electron donating alkyne ligand and the latter to be able to effect ligand transformation in its co-ordination sphere can give rise to novel and unusual reactivity features. Large variation in the chemistry of the acetylide moieties can be achieved by incorporating into the co-ordination sphere of mixed-metal polynuclear complexes. Indeed, this strategy has been used in recent times and there exist a number of mixed-metal clusters which have been obtained from mononuclear acetylide precursors. Reactions leading to C-C bond formations with an additional C₂ fragments have constituted an important development in the study of acetylide-cluster complexes. The excellent reactivity of metal acetylides can be shown by some reactions.

The ferroceneethynyl-functionalized homoleptic cadmium complex [Cd(C≡CFc)₂] was synthesized by treatment of CdBr₂ with two equivalents of LiC≡CFc (Fc = (η⁵-C₅H₄)(η⁵-C₅H₅)Fe)[19]. This compound decomposes even at low temperature via carbon-carbon bond formation to give the all-carbon butadiyne FcC≡CC≡CFc. (scheme 1)



Scheme.1

The first ferrocenyl-functionalized bis(alkynyl) mercury compound was reported by Bassetti et al. [20] who demonstrated that quenching the reaction of [Hg(OAc)₂] and HC≡CFc with an iodine solution, immediately after addition of the mercury acetate, led to an orange precipitate, which could be identified as [Hg(C≡CFc)₂]. This molecule was formed in

quantitative yield. However, when longer reaction times (up to three days) were used then acetyl ferrocene was obtained quantitatively via intermediates like $\text{FcC}(\text{OMe}) = \text{CH}_2$ [20].

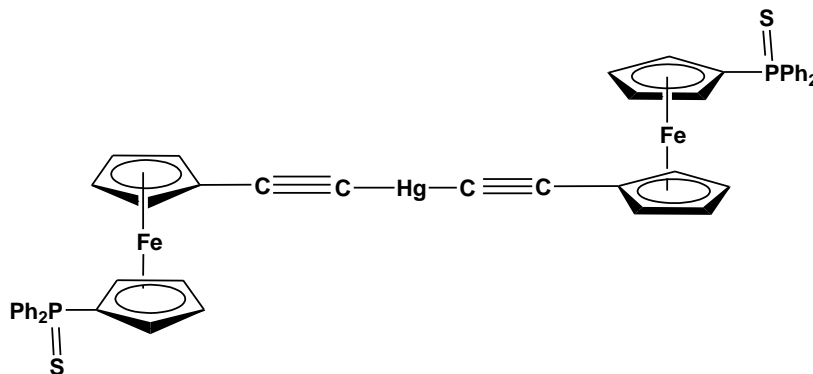


Fig.6: $[\text{Hg}\{\text{C}\equiv\text{C-Fc-P}(\text{S})\text{Ph}_2\}_2]$

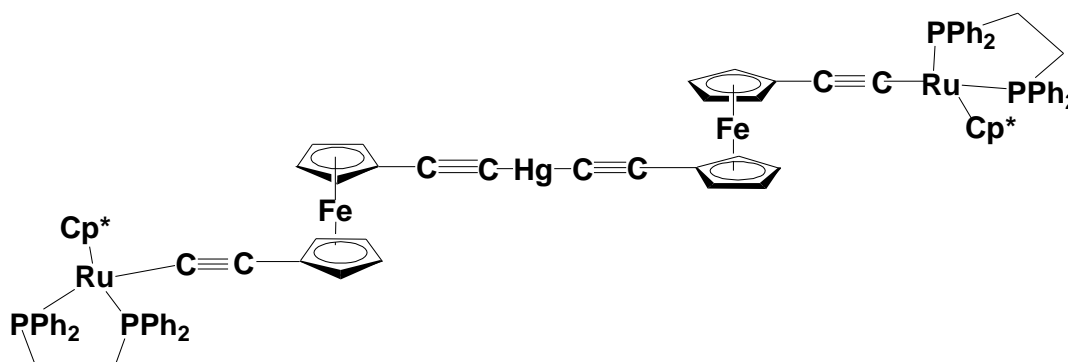


Fig.7: $[\text{Hg}\{\text{C}\equiv\text{C-Fc-C}\equiv\text{CRu}(\text{dppe})(\text{Cp}^*)\}_2]$

A similar compound featuring a diphenylthiophosphoryl group at ferrocene was recently published according to the synthesis method reported by Kutscheroff et. al. [21] in which complex $[\text{Hg}\{\text{C}\equiv\text{C-Fc-P}(\text{S})\text{Ph}_2\}_2]$ ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_4)\text{Fe}$) (Fig. 6) was obtained. Hetero trimetallic compound, $[\text{Hg}\{\text{C}\equiv\text{C-Fc-C}\equiv\text{CRu}(\text{dppe})(\text{Cp}^*)\}_2]$ could be isolated from the reaction of $[\text{Hg}(\text{OAc})_2]$ with $[\text{HC}\equiv\text{C-Fc-C}\equiv\text{CRu}(\text{dppe})(\text{Cp}^*)]$ in refluxing tetrahydrofuran as described by Bruce et. al. (Fig.7) [22].

1.4. Applications of transition metal acetylides

Among the unsaturated hydrocarbon used to bridge metal centres increasing attention has been paid to alkynyl ligands in recent years. This interest mainly arises from the favourable electronic and structural features of $C\equiv CR$ ligands via σ or σ - π networks which can be modulated by varying both or either of the R substituents and the metal centres [23]. Acetylide acts as a bridging ligand in bimetallic complexes, in which two metal centres show pronounced electronic interactions across the bridging ligand. Applications may be found in molecular electronics and as models for electron-transfer processes in biological processes [24]. These complexes can also display enhanced or unique reactivity in stoichiometric and catalytic reactions [25]. To promote the cooperative effect between the metal centres, the bridging ligand should be able to provide an electronic coupling pathway. As the degree of communication is primarily controlled by the ligand, the success on metal-metal interactions in a bimetallic complex is dependent on key ligand properties, such as flexibility and the degree of delocalization, which depends on the potential for effective orbital overlap between frontier orbitals associated with the metal and bridge fragments. For example, conjugated systems should be able to mediate the electronic interactions through their π orbitals. Acetylides are the best metal complexes having tuneable properties to fit the above mentioned applications. It is also possible to change the metals and ancillary ligand bound to the acetylene part or the metal oxidation state to induce significant chemical and physical properties to the systems [24-25].

Thus, bimetallic and polymetallic metal acetylide systems with σ -bonded bridging metal centres are attracting considerable interest. They are commonly called “carbon σ -bonded molecular wires” and possess one-dimensional semi rigid structures, which facilitates the electronic communication between the two redox active moieties. As a result, potential

applications for these systems have been suggested as molecular devices, electronic current rectifiers, and switches [26-27].

The most common example of bimetallic complexes with linear acetylene chains such as $LM-(C\equiv C)_n-ML$ are those with $n=1$ [28-29]. Whereas complexes with polyynediyl bridges $LM-(C\equiv C)_n-ML$ comprise the most fundamental class of carbon-based wires.

Example with $n=2$ and metal as iron is shown in Fig. 8.

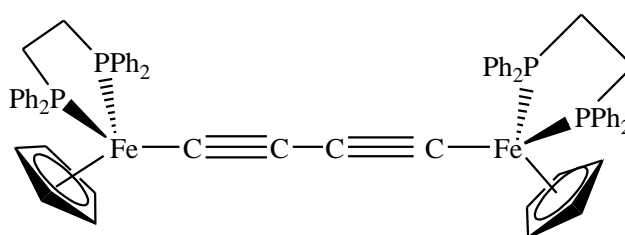
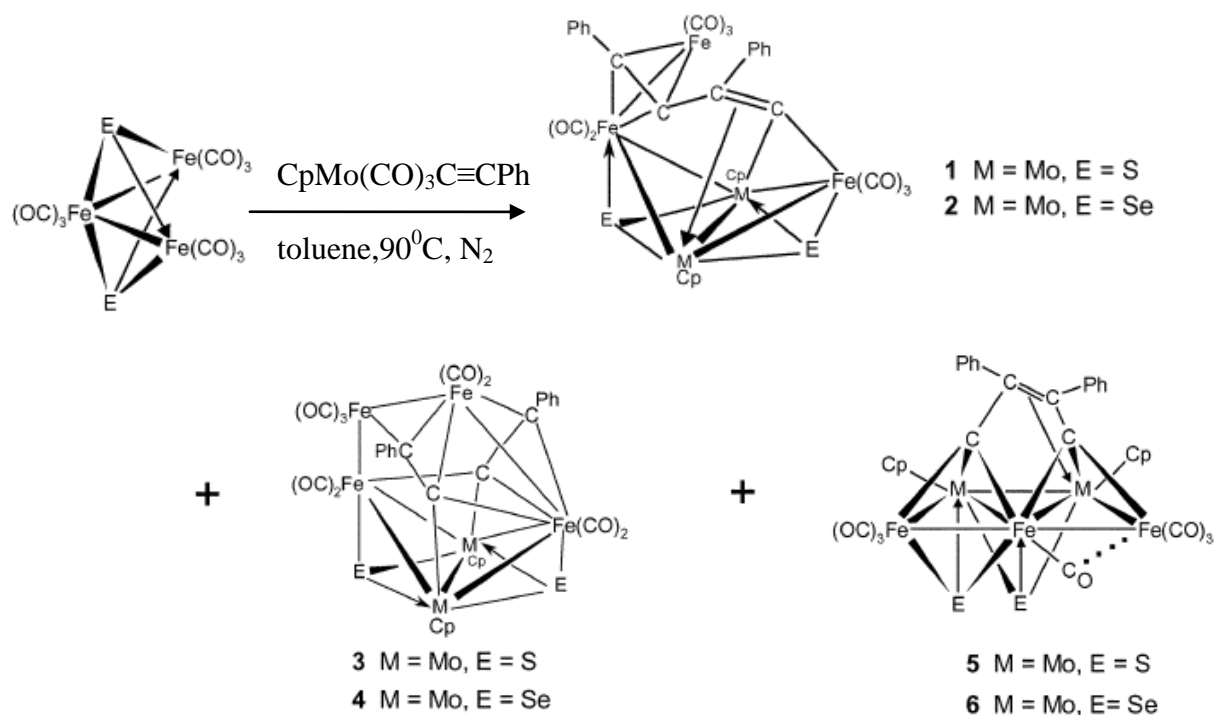


Fig.8: $(PPh_2)_2(CH_2)_2CpFe-(CC)_2-FeCp(CH_2)_2(PPh_2)_2$

Mononuclear acetylide complexes are versatile building blocks in cluster growth reactions and numerous types of mixed-metal clusters have been prepared by this route. This approach has been particularly fruitful for the formation of clusters containing multi-site bound polycarbon units resulting from coupling of acetylide units.

When a toluene solution containing $[(\eta^5-C_5H_5)Mo(CO)_3(C\equiv CPh)]$ and $[Fe_3(CO)_9(\mu_3-E)_2]$ ($E = S, Se$) is heated at $90^\circ C$ for 3 hrs., the following new acetylide-coupled mixed-metal clusters are obtained [30]: $[(\eta^5-C_5H_5)_2Mo_2Fe_3(CO)_8(\mu_3-E)_2\{\mu_5-C\equiv C(Ph)CC(Ph)\}]$ ($E = S, Se$), $[(\eta^5-C_5H_5)_2Mo_2Fe_4(CO)_9(\mu_3-E)_2(\mu_4-CCPh)_2]$ ($E = S, Se$) and $[(\eta^5-C_5H_5)_2Mo_2Fe_3(CO)_7(\mu_3-E)_2\{\mu_5-C\equiv C(Ph)C(Ph)C\}]$ ($E = S, Se$) (Scheme 2).



Scheme 2

Transition metal acetylides are also used as catalyst in various reactions. Various Nickel acetylides have been reported to show catalytic activity towards *p*-diethynyl benzene polymerization [31]. Nickel acetylides were found to be efficient initiating systems for the alkyne polymerization reactions. The polymerization proceeds under mild conditions to give soluble *p*-conjugated polymers with weight average molecular weights as high as 4.8×10^4 in yields as high as 95%.

Chapter 2

Synthesis, CS₂ incorporation and characterization of Fe and W acetylide complexes

2.1. Reactivity of acetylides towards different molecules

Acetylides have broad spectrum of reactivity towards different organic and inorganic molecules. Addition of halogens (Cl_2 , Br_2 or I_2) to ruthenium or osmium acetylide complexes result in the formation of cationic halo-vinylidene derivatives. Halogenation of the phenyl group in phenylacetylide compounds also takes readily. [32] Addition of arenediazonium or tropylium salts to ruthenium acetylide, $[\text{Ru}(\text{C}_2\text{Ph})(\text{L})_2(\eta\text{-C}_5\text{H}_5)]$, ($\text{L}_2 = (\text{PPh}_3)_2$ or DPPE) gives the corresponding cationic aryldiazovinylidene and cycloheptatrienyl-vinylidene complexes, respectively, $[\text{Ru}(\text{C}\equiv\text{CPhN}\equiv\text{NC}_6\text{H}_3\text{Me}_{2-3,4})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ and $[\text{Ru}\{\text{C}\equiv\text{CPh}(\text{C}_7\text{H}_7)\}(\text{DPPE})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$. [33] In the last decade, transition metal-acetylide compounds have been used mainly for a large number of studies on organic transformations. Some of these acetylides show unique bonding environment and structural framework and are found to be versatile synthetic intermediates for the efficient synthesis of novel organic compounds [41-44].

As an unsaturated electrophile and a potential source of C_1 chemistry, carbon disulphide has attracted a plethora of research activity, in particular on its reactivity towards transition metal complexes [34]. A diverse array of compounds are known where CS_2 bonds in η^1 -end on, η^2 -side on and bridging co-ordinating modes [35-36]. It readily inserts into metal alkyl and metal hydride bonds at room temperature or under mild thermolytic conditions to form dithiocarboxylate or dithioformate complexes where the S_2C motif is bound to the metal in either η^2 or η^3 fashion [35]. Although insertion of CS_2 into a $\text{M-C}(\text{sp}^3)$ bond is the most common, there exist some examples of CS_2 additions yielding $\eta^3\text{-S}_2\text{CR}$ ligand systems [37]. A few literatures have been reported where CS_2 insertion takes place into metal acetylide units [37-40]. In a recent investigation UV-radiation has been used for the reaction of carbon disulfide with iron and molybdenum acetylide to obtain dithiopropiolato

containing complexes. Lately Mathur et al reported the transformation of dithiopropiolato complexes to dithiole-thione derivatives, which are an important class of chemoprotective agents and used for other medicinal purposes. On the other hand, organometallic reaction using sunlight has been known to a far lesser extent and requires effective investigation for the better understanding of sunlight driven reactions [45-47]. In this report, synthesis and characterization of ferrocenyl based tungsten acetylide was carried out and reacted with CS₂ under sunlight to obtain a novel ferrocene containing alkynyl dithiocarboxylate tungsten complex.

2.2. Results and Discussions:

Ferrocene containing tungsten acetylide complex, **1** has been prepared by a slightly modified procedure, using CpW(CO)₃Cl, FcC≡CH, CuI and Et₂NH in THF solution. Iron acetylide has been prepared by literature method. A mixture of carbon-disulfide and metal acetylide, [LM(CO)_nC≡CR] [$\{L=\eta^5\text{-C}_5\text{H}_5, M = \text{W}, R = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5), n = 3\}, \{L=\eta^5\text{-C}_5\text{Me}_5, M = \text{Fe}, R = \text{Ph}, n = 2\}$] (**1-2**) in n-hexane solvent when exposed to sunlight for a few seconds results in the formation of a blue to violet coloured compound [LM(CO)_n($\eta^2\text{-S}_2\text{C}$)C≡CR], [$\{L=\eta^5\text{-C}_5\text{H}_5, M = \text{W}, R = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5), n = 2\}; \{L=\eta^5\text{-C}_5\text{Me}_5, M = \text{Fe}, R = \text{Ph}, n = 1\}$] (**3-4**) in very high yield (Scheme 1). Carbon disulfide insertion reactions have also been observed to take place in the absence of solvent.

3. Conclusions

Under the exposure of sunlight CS₂ has been incorporated in the acetylides [LM(CO)_nC≡CR] [$\{L=\eta^5\text{-C}_5\text{H}_5, M = \text{W}, R = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5), n = 3\}, \{L=\eta^5\text{-C}_5\text{Me}_5, M = \text{Fe}, R = \text{Ph}, n = 2\}$] in n-hexane solvent. The resulting CS₂ incorporated compounds [$\eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})(\eta^2\text{-$

$S_2C)C\equiv CPh]$ and $[\eta^5-C_5H_5W(CO)_2(\eta^2-S_2C)C\equiv C(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)]$ have been characterised by IR, NMR, UV spectra. The tentative structures have been drawn.

CS_2 is bonded with metal atoms in η^2 mode. To our knowledge sunlight driven reaction on transition metal acetylides are rare and requires more detail understanding particularly on ferrocenyl based acetylides.

In summary, insertion of CS_2 has been observed into metal –carbon acetylide bond when exposed to mild sunlight to obtain a variety of transition metal dithiolato complexes. The tungsten complex (**3**) containing ferrocenyldithiolato ligand has been very interesting due to the presence of two types of metal species bridged by a S_2C_3 unit. Studies are going on to understand the electronic communication between the two metal fragments and probable luminescent behaviour for their use as sensors.

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