SUBSTITUTION KINETICS OF THE

PENTACARBONYLBIS(TRIMETHYLSILYL)ETHYNETUNGSTEN(0) WITH

TRIPHENYLBISMUTHINE

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Approval of the Graduate School of Natural and Applied Sciences

_____

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ABSTRACT

SUBSTITUTION KINETICS OF THE
PENTACARBONYLBIS(TRIMETHYLSILYL)ETHYNETUNGSTEN(0) WITH
TRIPHENYLBISMUTHINE

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The reaction between pentacarbonylbis(trimethylsilyl)ethynetungsten(0), $W(CO)_5(\eta^2\text{-btmse})$, and triphenylbismuthine, $Bi\emptyset_3$, yields pentacarbonyltriphenylbismuthinetungsten(0), $W(CO)_5(Bi\emptyset_3)$, as the sole product. The kinetics of the substitution of btmse by $Bi\emptyset_3$ was studied by means of quantitative FT-IR Spectroscopy.

The starting complex was prepared photochemically from hexacarbonyltungsten, $W(CO)_6$, in the presence of excess btmse in n-hexane and

identified by FT-IR and NMR Spectroscopies. The substitution reactions were performed in cyclohexane solutions at different concentrations of both leaving and entering ligand to observe the dependence of observed rate constant, k_{obs}, on the concentration of entering and leaving ligands and also, at different temperatures to evaluate the activation enthalpy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$).

The IR extinction coefficients for CO stretching were determined for both the starting complex $W(CO)_5(\eta^2\text{-btmse})$, and the product $W(CO)_5(Bi\text{\O}_3)$. Quantitative IR Spectroscopy does not show any significant reduction in the total amount of substance (material balance). Formation of $W(CO)_6$ (in small amount) was attributed to the decomposition of the product, $W(CO)_5Bi\text{\O}_3$.

From the evaluation of kinetic data, a mechanism was proposed in which the rate determining step is the cleavage of btmse ligand from the starting complex, $W(CO)_5(\eta^2\text{-btmse})$ and the formation of solvated complex, $W(CO)_5(\text{solvent})$. Thus, the reaction is essentially dissociative. The large positive value of activation entropy ($\Delta S^{\neq}$) and large value of activation enthalpy ($\Delta H^{\neq}$) are indicative of a dissociative mechanism.

Keywords : Substitution kinetics , tungsten , carbonyl , triphenylbismuthine , bis(trimethylsilyl)ethyne.

ÖZ

PENTAKARBONİLBİS(TRİMETİLSİLİL)ETİNTUNGSTEN(0) KOMPLEKSİNİN TRİFENİLBİZMUTİN İLE YERDEĞİŞTİRME KİNETİĞİ

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Pentakarbonilbis(trimetilsilil)etintungsten(0), $W(CO)_5(\eta^2\text{-btmse})$, ile trifenilbizmutin, $BiØ_3$, tepkimeye girerek tek ürün olan pentakarboniltrifenilbizmutintungsten(0), $W(CO)_5(BiØ_3)$, kompleksini verir. Btmse'nin $BiØ_3$ ile yerdeğiştirme kinetiği nicel FT-IR Spektroskopisi ile incelendi.

Başlangıç kompleksi, hekzakarboniltungsten(0), $W(CO)_6$ ile fazla miktardaki btmse'nin n-hekzan içindeki fotokimyasal tepkimesi ile hazırlandı ve FT-IR ve

NMR Spektroskopileri ile tanımlandı. Yerdeğiştirme tepkimeleri siklohekzan çözeltisi içinde, gözlenen hız sabitinin giren ve çıkan ligand derişimlerine bağlı olarak değişimini gözlemek için değişik giren ve çıkan ligand derişimlerinde ve ayrıca, aktivasyon entalpisi ve aktivasyon entropisini hesaplamak için değişik sıcaklıklarda gerçekleştirildi.

Başlangıç kompleksi, $W(CO)_5(\eta^2\text{-btmse})$, ve ürün, $W(CO)_5(Bi\O_3)$, için CO-gerilme titreşimlerine ait molar soğurma katsayısı hesaplandı. Nicel IR-spektroskopisi ile toplam madde miktarında önemli bir azalma olmadığı görüldü (madde dengesi). Çok az miktardaki $W(CO)_6$ oluşumu, ürünün bozunmasından kaynaklanmaktadır.

Kinetik verilerin değerlendirilmesinden önerilen mekanizmada btmse ligandının başlangıç kompleksinden ayrılması ve çözücü kompleksi oluşumunun hız belirleyen basamak olduğu görüldü. Buna göre, tepkimenin mekanizması ayrışmalı mekanizmadır. Aktivasyon entropisinin yüksek artı değeri $(\Delta S^{\neq})$ ve aktivasyon entalpisinin $(\Delta H^{\neq})$ yüksek olması da ayrışmalı mekanizmanın işaretidir.

Anahtar Kelimeler : Yerdeğiştirme kinetiği , tungsten , karbonil , trifenilbizmutin , bis(trimetilsilil)etin.

To the memory of my father, Rıza BAYRAM

ACKNOWLEDGMENTS

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ϕ or $\emptyset$……………………………..……………………….(C_6H_5)

M………………………………………………….…..…...Metal

L………………………………………….…………………Ligand

CHAPTER 1

INTRODUCTION

The subject of Organometallic Chemistry covers both inorganic and organic chemistry since it deals with the substances having at least one metal-carbon interaction.[1] Examples of such compounds date back to 18th century. In 1760 the French chemist L.C. Cadet was attempting to make invisible inks from arsenate salts which, a repulsively smelling liquid, was later identified as dicacodyl (=stink), $As_2(Me)_4$.[2] This salt was the first example of compounds having M-C direct interaction, but, in 1827 W.C. Zeiss, a Danish pharmacist, synthesized the first metal-olefin complex, $K[(C_2H_4)PtCl_3]$.[3] After this discovery, the first metal-carbonyl complex was prepared about 40 years later by Schutzenberger as $[PtCl_2(CO)]_2$.[4]

Recognition of the sandwich structure of dicyclopentadienyl iron (ferrocene) by using X-Ray diffraction technique in 1952 by Wilkinson, Rosenblum, Whiting and Woodward[5] was in fact, the starting point of the development of the Organometallic Chemistry, although the ferrocene was synthesized a year before the elucidation of its structure by two independent groups, Kealy and Pauson[6] and Miller.[7]

Homogeneous catalysis, with advantages in selectivity, milder conditions for reactions and economy in reagents, will become more important as resources diminish.[8] There are a number of processes that appear to be homogeneously

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catalyzed by organometallic complexes.[9] In recent years, owing to the development of organometallic chemistry, many interesting homogeneous catalysts have been developed. Most of the organometallic compounds catalyze many important industrial processes.[10] The polymerization of alkenes with metal halides activated by aluminium alkyls (Ziegler-Natta catalysis) is now one of the most important industrial processes.[2]

The great expansion of synthetic organometallic chemistry has been accompanied to a lesser extend by an interest in the kinetics and mechanism of organometallic reactions. Among the most basic reactions of these are ligand substitution processes at low-valent transition-metal centers. The information obtained is not only useful in systematic organometallic synthesis, but also quite relevant to the design and operation of homogeneous catalysis.[11]

The majority of studies of organometallic substitution reactions have been accomplished on transition metal carbonyl complexes[12] which are one of the most important classes of organometallic complexes. The metal carbonyl complexes serve as useful starting materials for other organometallic complexes in which a metal-carbonyl system forms an integral part of the structure,[10] as stoichiometric reagents in numerous organic transformations and as a catalyst precursors for important catalytic processes.[13] The binary metal carbonyls are readily prepared and purified. They are quite stable and have very characteristic absorption bands for CO stretching in the infrared spectra that allow quantitave analysis.[8] The first known binary metal-carbonyl was synthesized by Ludwig Mond in 1890 as $Ni(CO)_4$ which led to a commercial process for refining nickel.[14] $Fe(CO)_5$[15] and $Mo(CO)_6$[16] was synthesized again by Ludwig Mond. Hexacarbonyl-chromium and hexacarbonyl-tungsten were synthesized about 40 years later by Job et.al.[17] in 1927.

Although in recent years ^{13}C-NMR spectroscopy has became increasingly valuable, it is still true that infrared (IR) spectroscopy is the preeminent physical method for characterizing metal-carbonyls.[18] The vibrational spectra of metal-

carbonyls have proved particularly informative. Metal complexes containing one or more CO ligands bound to a single metal atom show one or more intense infrared bands between 2200 and 1800 cm^{-1}, which are assigned to the carbon-oxygen stretch of the coordinated CO. The CO stretching bands observed in the infrared are sharp, sensitive to environment and commonly intense. The number and pattern of these bands give information about molecular symmetry and geometry, while the positions of the bands are related to bonding. Therefore, the study of these bands is highly rewarding.[19]

Alkene or alkyne substituted group-6 metal-carbonyls occupy a significant fraction in the specific area of metal π-complexes. But, alkyne substituted metal-carbonyls take more attention than alkenes due to the reactivity of triple bond they bear. The first metal-carbonyl alkyne complexes have been generated upon UV-irradiation of alkane solution of $Mo(CO)_6$ and $W(CO)_6$ in the presence of an alkyne, detected IR-spectroscopic observation in solution.[20] After this pioneering work, various alkyne complexes of group-6 metal-carbonlys have been synthesized and isolated. The complexes indicate different coordination geometry due to the variable number of electron donated by alkyne: $Cr(\eta^2- C_2Ph_2)_2(dmpe)$ (dmpe:dimethylphosphinoethane)[21] , $Cr(CO)_2(\eta^2-BTMSE)_2$[22-23], $W(CO)(\eta^2-3-$hexyne)$_3$[24], $W(CO)(\eta^2-C_2Ph_2)_3$[25] are four coordinate carbonyl complexes with multiple alkyne ligands. The examples of five coordination are $Cr(CO)_2(P(OMe)_3)_2(\eta^2-C_2Ph_2)$[26] , $Cr(CO)_2(\eta^2-C_4Ph_4)(\eta^2-C_2Ph_2)$.[27] There are six coordinate alkyne complexes that contain five carbonyl and one alkyne, such as phenyl acetylene[28], thiobenzaldehyde[29], and bis(trimethyl)silylethyne (btmse)[30] with tungsten.

Photochemically generated $M(CO)_5(alkyne)$ complexes are labile towards nucleophilic substitution. For instance, $W(CO)_5(\eta^2-btmse)$, isolated from the UV irradiation of $W(CO)_6$ and btmse in n-hexane at room temperature, has shown unusual reactivity toward ligand substitution with ligands $(CN-C_6H_{11})$, $(CN-^iC_3H_7)$, $(CN-^tC_4H_9)$, $(\eta^2 - C_2H_4)$, $(\eta^2 -1,3-butadiene)$[31] , $(\eta^2 - (E)-cyclooctene)$[32], and tricyclohexylphosphine.[33] Btmse is an alkyne, bearing strong electron

donating groups providing stability for the $M(CO)_5$-moiety just enough to be isolated. Yet, when attached to a group-6 metal center especially to a tungsten, namely $W(CO)_5(\eta^2$-btmse) complex, is the one with the highest potential of a good starting material for ligand substitution reactions in the sense that it is less sensitive to air oxidation and easy to handle when compared to other group-6 members.[31]

Although substituted group-6 metal carbonyl complexes containing ligands having group-15 and 16 donor atoms have been widely studied[34] and remains one of the most active areas of coordination chemistry,[35] relatively little work has been reported on simple substitution products of ligands containing the heavier elements in these groups.[36] This may be, due to fact that, like their aliphatic analogues, for example, triarylbismuthine compounds appear to have ver weak nucleophilic or donor character.[37] Also very weak σ-donor ability of bismuth, the ease with which Bi-C bonds break in the presence of many metal centres[38] and steric effects due to the bismuth itself and of substituents[18] are the reasons why the reported coordination chemistry of triarylbismuth is rather meager.

In this study, the reaction between $W(CO)_5(\eta^2$-btmse) complex and triphenylbismuthine, $BiØ_3$, will be investigated and the products of the reaction will be identified. If a substitution reaction is observed, then, the kinetics of that reaction will also be studied and a mechanism for the substitution reaction will be proposed after the evaluation of kinetic data. This mechanism will be supported with the calculated activation parameters.

This is the first study in the field of investigation of the reaction between pentacarbonylalkynemetal(0) complex with a triarylated heavy group-15 donor ligand. For the starting complex, btmse (Figure 1.1) was used as a source of alkyne which bears strong electron donating groups and provides stability for $M(CO)_5$-moiety, just enough to be isolated. Tungsten was chosen as a central metal atom due to the reactivity of isolated $W(CO)_5(\eta^2$-btmse) complex, which has pseudo-octahedral coordination geometry with an eclipsed btmse to one of

the OC-W-CO axes[39-40] (Figure 1.2). This complex is very labile towards substitutions in the presence of a potential ligand.[31] The complex $W(CO)_5(\eta^2\text{-}$btmse) undergoes not only the replacement of btmse, but also substitution of the CO groups cis to the btmse ligand, as the four electron donor btmse ligand with bulky $SiMe_3$ groups labilize the four cis CO ligands. Thus, it can yield eventually $W(CO)L_5$ complex through a variety of substitution products.
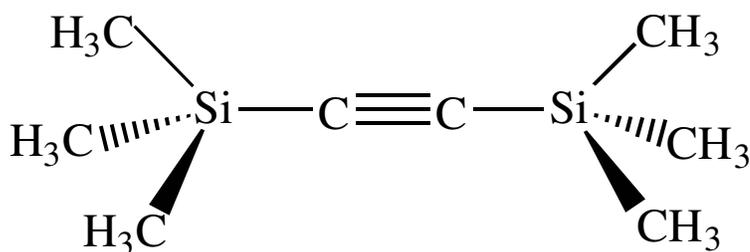
Figure 1.1. Bis(trimethyl)silylethyne (btmse)
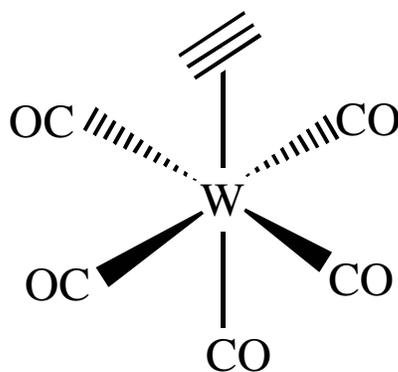
Figure 1.2. Eclipsed form of $W(CO)_5(\eta^2\text{-}$btmse). The btmse ligand is denoted by a triple bond

In this study, the formation of $W(CO)_5(Bi\emptyset_3)$ complex as a product of the reaction between the $W(CO)_5(\eta^2\text{-}$btmse) complex and $Bi\emptyset_3$ ligand is expected. According to the IR observation, the reaction of $W(CO)_5(\eta^2\text{-}$btmse) with $Bi\emptyset_3$ yields almost solely the monosubstitution product $W(CO)_5(Bi\emptyset_3)$. This indicates

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that $W(CO)_5(\eta^2\text{-btmse})$ undergoes only btmse substitution with $Bi\text{Ø}_3$ and the reaction ceases after monosubstitution. $W(CO)_5(Bi\text{Ø}_3)$ complex has already been synthesized by UV irradiation of $W(CO)_6$ in THF, isolated and fully characterized.[35]

CHAPTER 2

BONDING

2.1. Metal-Carbonyl Bonding

One of the most commonly encountered ligand in organotransition metal chemistry is carbon monoxide which forms complexes with these metals known as metal-carbonyls. Its primary mode of attachment to the metal is through the C atom.[41]

The bonding of CO to a metal can be described in terms of two synergic compounds; The more σ-donation by the carbonyl, the stronger π-back-bonding by the metal:[41]

i)   σ-dative bonding: Two electron donation of the lone pair on carbon into a vacant metal d-orbital; This electron donation makes the metal more electron rich and in order to compensate for this increased electron density, a filled metal d-orbital may interact with empty π^*-orbital on the carbonyl ligand to relieve itself of the added electron density.

ii)   π-back-bonding: Effective overlap of the metal d-orbital and carbon monoxide π^*-orbital results in an extensive back-bonding.These interactions are shown diagramatically in Figure 2.1.
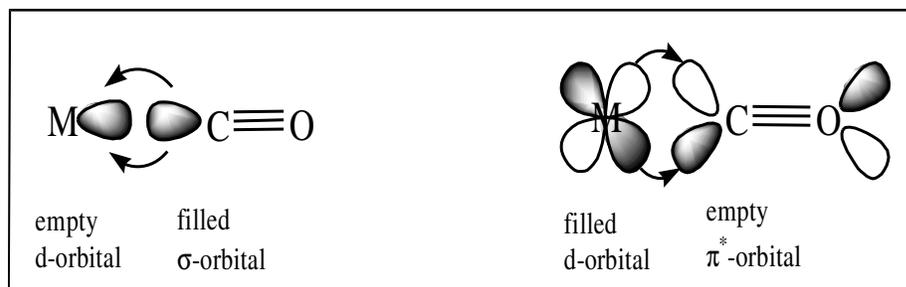
Figure 2.1. Molecular orbital description of metal-carbonyl interaction

Since π-back-bonding depends crucially on the electron density of the metal, it not only strengthens the M-CO bond, but provides a very sensitive probe for the electronic characteristics of the metal center. Extensive back bonding in electron rich complexes lowers the CO stretching frequency. This is consistent with the bonding model, an increase in the electron density on the metal atom is delocalized over the CO ligands, by populating the carbonyl π^*-orbital thus weakening the CO bond. Nevertheless, the converse is true if the complex is positively charged. Also other strong σ-donor and π-acceptor ligands attached trans to CO ligand in a mixed metal ligand carbonyl weakens M-CO bond and strengthen C≡O bond simultaneously.[41] This weakening or strenthening is due to the sharing of the same d-orbital by the carbonyl and the L ligand, trans to that carbonyl (π-competition) (Figure 2.2)
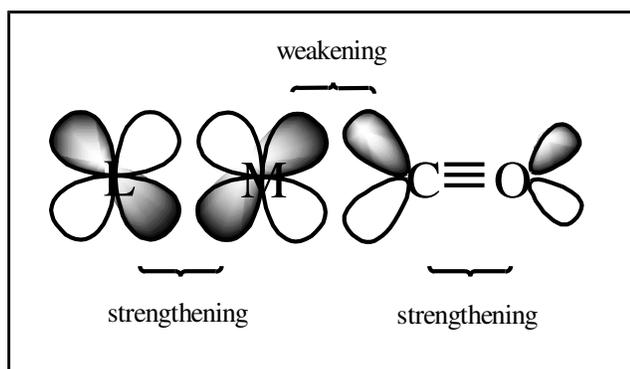
Figure 2.2. Competition for π-bonding in metal-carbonyl derivatives

2.2. Metal-Alkyne Bonding

Alkynes (acetylenes) form complexes with transition metals in a similar way to alkenes and similar bonding schemes can be applied. However, characteristic differences can be summarized as follows;[42]

- C≡C bonds are more reactive than C=C bonds
- Alkynes are stronger π-acceptors than alkenes
- Alkynes have 2 orthogonal π^*-systems that can act as 2- as well as 4-electron donor ligands.

The metal-alkyne bonding is explained by Dewar[43], Chatt and Duncanson[44] MO description. In this description the bonding is assumed to consist of 2 components as shown in Figure 2.3. First the formation of σ-bond between the π-orbital of the alkyne and σ-type d-orbital on the metal atom. In σ-bond electron is donated by the alkyne. π-back-bonding is the result of the overlap of filled π-type d-orbital of the metal and empty π^*-orbital of the acetylene.
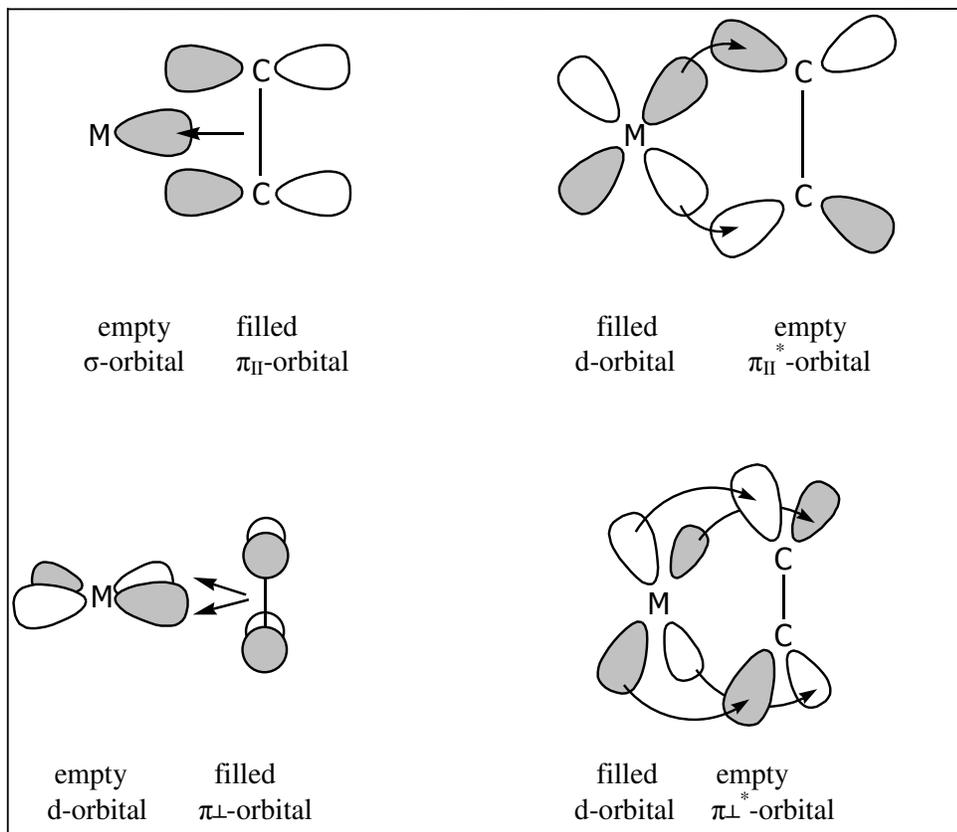
Figure 2.3. Molecular orbital description of metal-acetylene interaction

2.3. Metal-Bismuthine Bonding

Phosphines (PR_3) and Phosphites ($P(OR_3)$) are neutral, 2 electron donor ligands that bind to transition metals via their lone pairs.[45] Since bismuth is also the element of group-15 as phosphorus, similar bonding schemes to metal centres could be applied. The bonding in bismuthine ligands have 2 important components as carbonyl ligand (Figure 2.4) but, differ in the π-accepting orbitals. The primary component is sigma donation of the bismuthine lone pair to an empty orbital of metal with σ-symmetry. The second component is back-donation from a filled metal orbital to a bismuthine ligand. The π-back-bonding differs from that for CO in that the π-acceptor orbitals are the bismuth *6d* orbitals. Hence the bonding designated as d_π-d_π whereas that of CO is d_π-p_π. The extend of σ-donation and π-acception depends on the nature of the groups attached to Bi.[18] When the ligand L ($L=PR_3$, BiR_3 etc.) are attached to a metal center in a position

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trans to CO ligand, π-competition between the CO and the ligand is observed due to the same d-orbital sharing for π-back-donation. As a result, bond strength of the M-L, M-C and C≡O synergitically increase or decrease. For example, the greater σ-donation and π-acceptance of phosphorus, the stronger M-P bond[46] and synergitically weaker M-C bond and stronger C≡O bond which can be observed via IR spectroscopy.
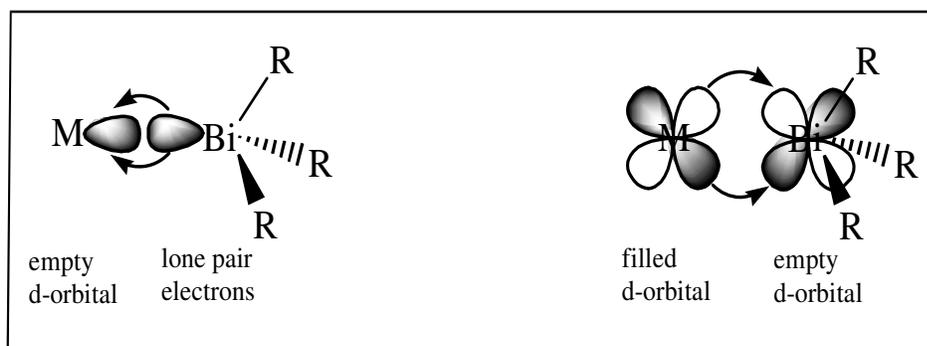
Figure 2.4. Molecular orbital description of metal-bismuthine interaction

CHAPTER 3

EXPERIMENTAL

3.1. Basic Techniques

Most of the organometallic compounds are air sensitive and tend to decompose if not handled properly. In many cases oxidation occurs at a significant rate at room temperature. This sensitivity to oxygen and water is usually more in solution than in solid state. Therefore handling and all reactions of organometallic compounds should be carried out under dry and deoxygenated atmosphere.

Organometallics may be handled almost as easily as ordinary compounds if the reactions are carried out in the absence of oxygen. For this reason dry and deoxygenated nitrogen atmosphere is created by passing through nitrogen gas when the organometallic substances are open to air. Circulated nitrogen gas passes through some purification steps as shown in Figure 3.1
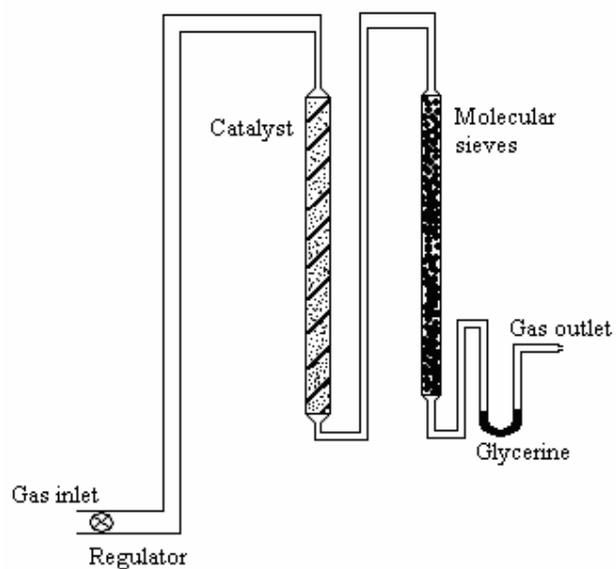
Figure 3.1. Nitrogen gas purification steps

Firstly, nitrogen gas passes through a catalyst (BASF R3.11, Ludwigshafen, Germany) heated up to 120°C to remove oxygen and then dried molecular sieves to remove its moisture and lastly glycerine to bubble the flowing gas.

Solvents used were purified and solvated oxygen was removed by refluxing over metallic sodium under nitrogen atmosphere for 3 to 4 days before use.

Hexacarbonyltungsten and bis-(trimethyl)silylethyne (btmse) were purchased from Aldrich®, triphenylbismuthine was purchased from Fluka® and used without further purification.

Photochemical reactions were performed in a special apparatus with a Mercury-Arc Lamp (Hg-Tauchlampe TQ-150) as described in detail, in the literature.[47]

3.2. Infrared Spectroscopy

Both the syntheses and the kinetic reactions of the complexes were followed by means of Infrared Spectroscopy. Infrared spectra of the complexes were recorded from their cyclohexane solutions on a Nicolet 510 FTIR Spectrophotometer using Omnic software.

During the kinetic experiments Specac Variable Temperature Cell P/N 21500 was used to keep the temperature constant throughout the kinetic measurements.

3.3. NMR Spectroscopy

^{13}C-NMR spectra of the complexes were taken from chloroform-*d* solution on a Bruker Spectroscopin, DPX-400 Ultra Shield FT-NMR with Avance software.

3.4. Syntheses of the Complexes

3.4.1. Synthesis of $W(CO)_5(\eta^2$-btmse)

$W(CO)_5(\eta^2$-btmse) was prepared photochemically as described in the literature[31] with minor modifications. In 200 ml *n*-hexane, 1 gram (2.85 mmol) $W(CO)_6$ and 5.82 gram (34.2 mmol) $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ (btmse) were dissolved in the photochemical reaction vessel. The solution was irradiated for 7 hours with stirring at room temperature. Then the solvent was evaporated down to 20 ml at room temperature, under vacuum (10^{-3} mbar). The unreacted $W(CO)_6$ was crystallized out during the volume reduction and filtered off. The rest of the solvent was completely stripped off and the excess of the ligand was sublimed over a cold-finger cooled to -30°C by using cryostat under vacuum. The remaining solid dissolved in 15 ml n-hexane and recrystallized at dry ice temperature. This yielded yellow-needle like crystals of $W(CO)_5(\eta^2$-btmse). IR (cyclohexane) $v(CO) = 2080.1 , 1988.3 , 1960.4 , 1953.1 , 1938.6$ cm^{-1} , $v(C{\equiv}C)$

= 1906.0 cm^{-1} ; ^{13}C-NMR (chloroform-d) δ = 201.65 (CO$_{ax}$, J(^{183}W–^{13}C) = 148 Hz) , 198.10 (CO$_{eq}$, J(^{183}W–^{13}C) = 126 Hz) , 95.97 (-C≡C-) , 0.43 (-CH$_3$) ppm.

3.4.2. Synthesis of W(CO)$_5$(BiØ$_3$)

W(CO)$_5$(BiØ$_3$) was prepared photochemically as described in the literature[35] with minor modifications. 1.0 gram (2.83 mmol) W(CO)$_6$ was dissolved in 200 ml THF in the photochemical reaction vessel and irradiated with stirring for 1 hour at room temperature. To the yellow coloured-solution formed, 0.9 gram (1.92 mmol) BiØ$_3$ was added and the solution stirred under nitrogen for 1 hour to form a pale-yellow solution. Then all solvent was stripped off and the residue was dissolved in n-hexane, filtered and the solvent again removed to leave a yellow solid which was recrystallized from n-hexane at dry ice temperature. IR (cyclohexane) ν(CO) = 2074.1 , 1949.3 , 1943.2 cm^{-1} ; ^{13}C-NMR (chloroform-d) δ = 198.13 (CO$_{ax}$, J(^{183}W–^{13}C) = 183 Hz) , 197.24 (CO$_{eq}$, J(^{183}W–^{13}C) = 126 Hz)

3.5. Kinetic Measurements

The rate of substitution of btmse in W(CO)$_5$(η^2-btmse) with BiØ$_3$ was determined by using quantitative FTIR-Spectroscopy at various temperatures. The thermal substitution reactions were performed in the Specac Variable Temperature Cell.

All kinetic spectral measurements and identification spectral measurements were recorded in cyclohexane solutions. Variable Temperature IR cell has a width of 0.020 cm with CaF$_2$ windows. IR extinction coefficients (ε) of both complexes, W(CO)$_5$(η^2-btmse) and W(CO)$_5$(BiØ$_3$) were determined from the standard solutions prepared by dissolving the known amount of pure complexes in cyclohexane. A calibration curve was obtained by plotting absorbance at the highest frequency peak of the reactant or product versus concentrations (Figure 3.2 and Figure 3.3). These plots gave molar extinction coefficients which are given in Table 3.1 at the given wavelengths. By using these values, the

concentrations of the starting material and the product could be calculated from the measured IR absorbance values at any stage of the reaction.
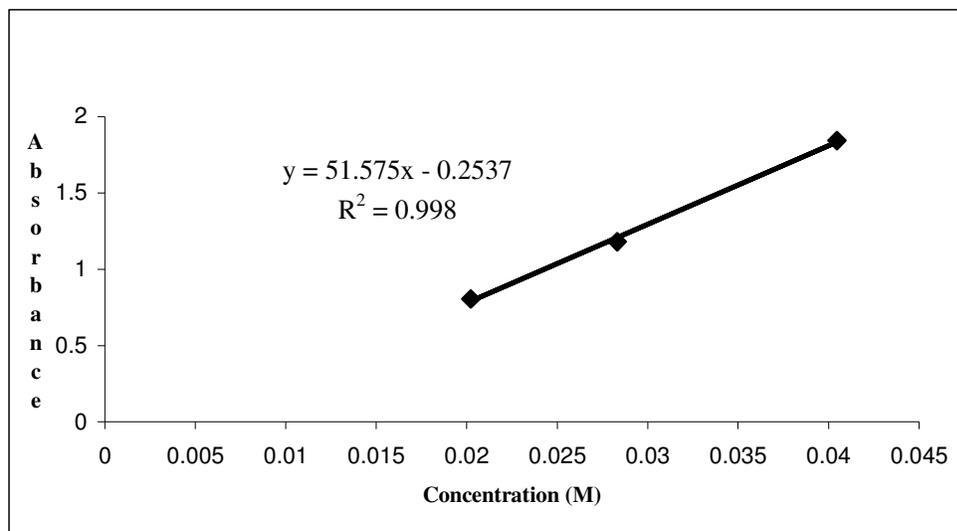
Figure 3.2. Beer's plot for $W(CO)_5(\eta^2\text{-btmse})$
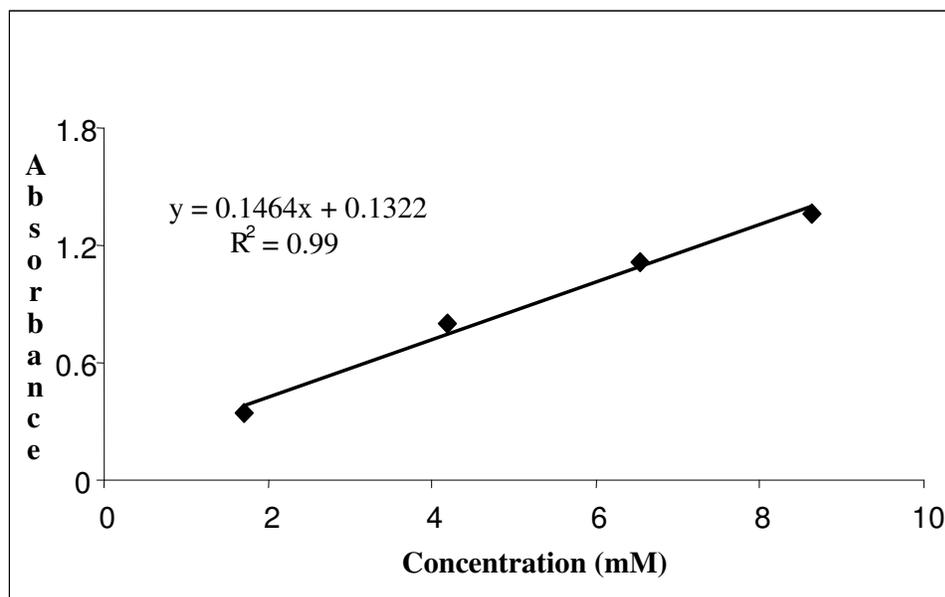
Figure 3.3. Beer's plot for $W(CO)_5(Bi\text{Ø}_3)$

Table 3.1. The molar extinction coefficients of complexes at given IR frequencies

Complex	ε (mol/L.cm)	v (cm^{-1})
$W(CO)_5(\eta^2\text{-btmse})$	2578	2080.1
$W(CO)_5(Bi\text{Ø}_3)$	7320	2074.1

For each set of kinetic experiment, a 10 ml round-bottomed schlenk glass was used for mixing reactants. Firstly, 10 mg of $W(CO)_5(\eta^2\text{-btmse})$ was dissolved in cyclohexane and the certain amount of $Bi\text{Ø}_3$ was added into the solution and stirred under nitrogen atmosphere for 2-3 minutes. After 2-3 minutes of stirring with magnetic stirrer, the solution was transferred into an IR cell which is placed inside the Specac Variable Temperature Cell in which the rest of the reaction was maintained. The rate of the reactions were determined by following the disappearance of the highest frequency peak of the reactant, since it is the most distinct peak which does not overlap with any peak of the product. By this way quantitative data on the rates of reactions was obtained easily and accurately. The graphical evaluation of the data with respect to time gave the observed rate constants.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Preparation and Identification of the complexes

4.1.1. Pentacarbonylbis(trimethylsilyl)ethynetungsten(0) , W(CO)$_5$(η^2-btmse)

The pentacarbonylbis(trimethylsilyl)ethynetungsten(0) complex was prepared by irradiation of hexacarbonyltungsten(0) in the presence of excess bis(trimethylsilyl)ethyne as described in the literature[31] and identified by FT-IR Spectroscopy and ^{13}C-NMR Spectroscopy.

The IR spectrum of W(CO)$_5$(η^2-btmse) exhibits 4 prominent bands in the CO stretching vibrational region (Figure 4.1) instead of typical three band-pattern commonly observed for M(CO)$_5$L fragments of local C$_{4v}$ symmetry with three IR active 2A$_1$ and E modes.[19] Obviously, the degeneracy of the E mode is lifted, due to the presence of an alkyne ligand, as a result, five IR active CO stretching vibrations, 3A$_1$, B$_1$, B$_2$ are predicted for the M(CO)$_5$ unit under C$_{2v}$ symmetry (Figure 4.2). However one of the A$_1$ mode should be intrinsically weak in intensity, and may remain unobserved or barely observable.[48]

The IR spectrum of W(CO)$_5$(η^2-btmse) reveals the stretching of C$\equiv$C fragment with a weak signal at 1906.0 cm^{-1}. The remarkable change in v(C$\equiv$C) frequency

compared to that of free btmse molecule, 2017 cm^{-1} [49] is due to the alkyne-transition metal bonding which decreases the bond order and lowers the C≡C stretching frequency of the alkyne.
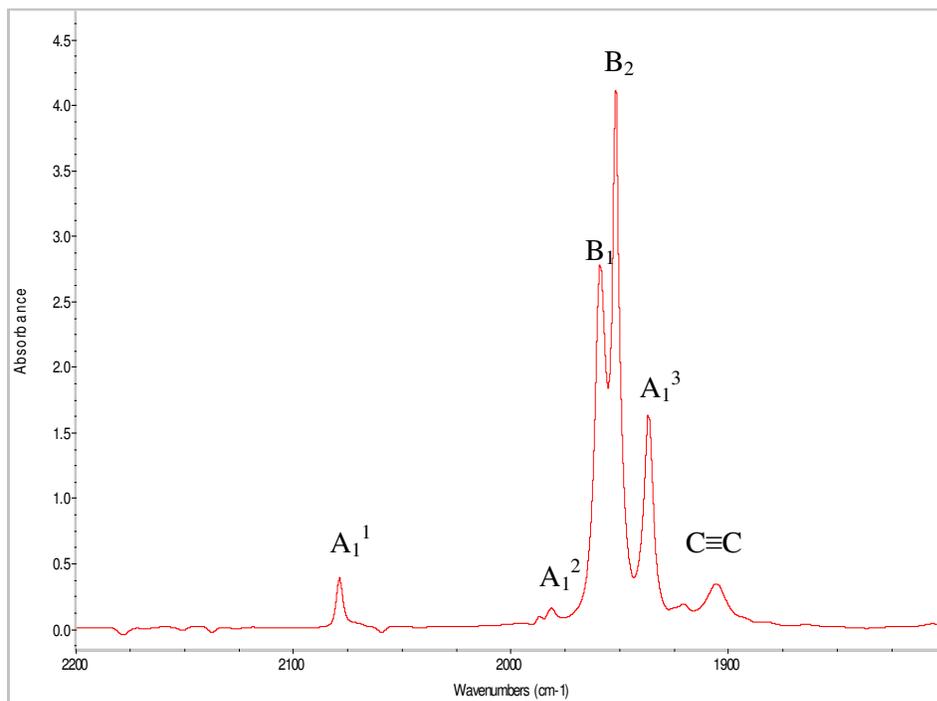
Figure 4.1. Infrared Spectrum of W(CO)$_5$(η^2-btmse) in the CO stretching region (taken in cyclohexane)

Table 4.1. CO stretching frequencies of the complex W(CO)$_5$(η^2-btmse) in cyclohexane

Complex	v(CO)				
	A_1^1	A_1^2	B_1	B_2	A_1^3
W(CO)$_5$(η^2-btmse)	2080.1	1988.3	1960.5	1953.2	1938.6

19
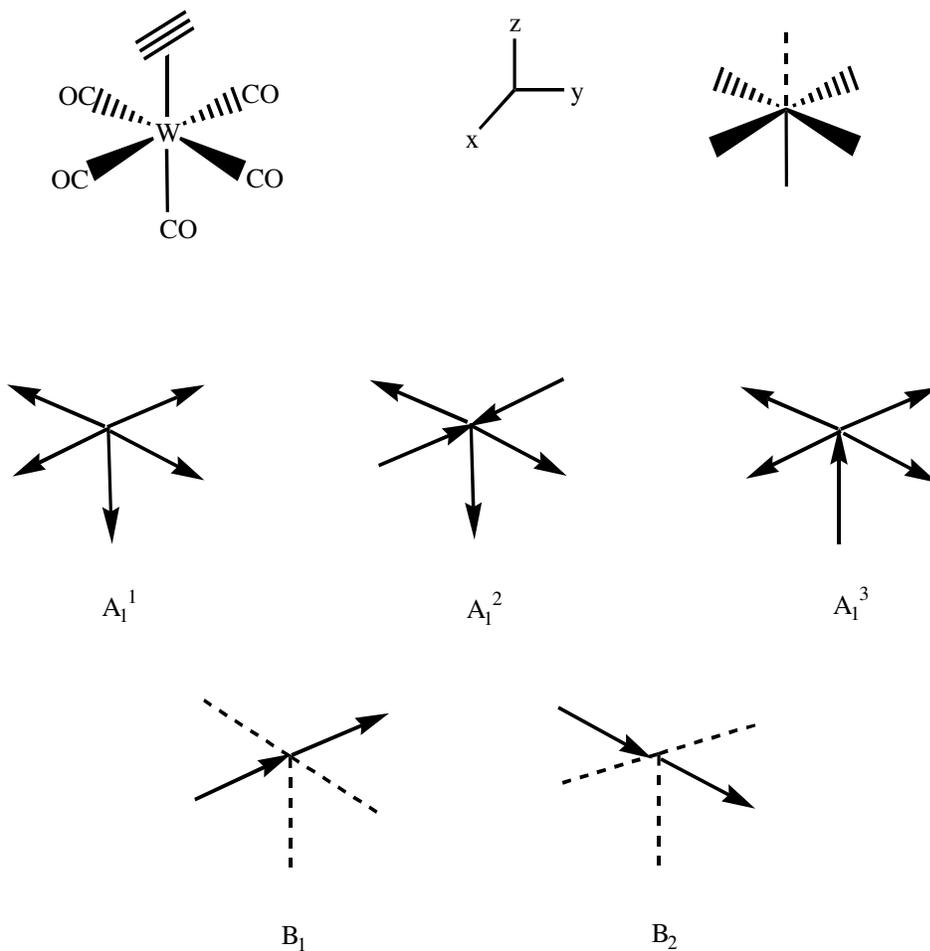
Figure 4.2. CO stretching vibrations of $W(CO)_5(\eta^2\text{-btmse})$. The btmse ligand is denoted by a triple bond

Table 4.2. ^{13}C-NMR chemical shifts of the complex $W(CO)_5(\eta^2\text{-btmse})$ in ppm at 25 °C in *d*-chloroform

Complex	$\delta(CO_{ax})$	$\delta(CO_{eq})$	C≡C	-CH$_3$
$W(CO)_5(\eta^2\text{-btmse})$	201.57	198.66	96.26	0.43

The ^{1}H-NMR spectra of the $W(CO)_5(\eta^2$-btmse) is uninformative for the identification of the complex. However, ^{13}C-NMR gives the information about the structure. In the CO resonance region of the ^{13}C-NMR spectra, two singlets with an approximate ratio of 1:4 were observed. Four equatorial CO groups are equal and appear as a singlet; Remaining one CO trans to BTMSE ligand also appears as a singlet (CO_{ax}, $J(^{183}W-^{13}C) = 148$ Hz ; CO_{eq}, $J(^{183}W-^{13}C) = 126$ Hz).

4.1.2. Pentacarbonyltriphenylbismuthinetungsten(0) , $W(CO)_5(Bi\emptyset_3)$

Thermal substitution of btmse in $W(CO)_5(\eta^2$-btmse) by $Bi\emptyset_3$ yields $W(CO)_5(Bi\emptyset_3)$ which was isolated and then identified by FT-IR Spectroscopy and ^{13}C-NMR Spectroscopy by comparing with the spectral data given in the literature.[35]

The IR spectrum of $W(CO)_5(Bi\emptyset_3)$ exhibits three bands in the CO stretching vibrational region (Figure 4.3) as a typical $M(CO)_5L$ fragment with C_{4v} symmetry giving three IR active CO stretching modes of $2A_1+E$. Two bands are close to each other. Thus, the weaker A_1 band is observed as a shoulder of the E band. The expected stretching modes of the molecule is shown in the Figure 4.5.

The ^{13}C-NMR spectrum gives two signals at 198.13 and 197.24 ppm for the carbonyl ligands in the complex $W(CO)_5(Bi\emptyset_3)$ with a relative intensity ratio of 1:4. (CO_{ax}, $J(^{183}W-^{13}C) = 183$ Hz ; CO_{eq}, $J(^{183}W-^{13}C) = 126$ Hz). Carbon atoms of the phenyl groups attached to bismuth appears at 139.12 , 136.13 , 130.98 and 130.02 ppm (Figure 4.4).

Due to the fluxionality of bulky $Bi\emptyset_3$ ligand, four equatorial CO ligands lie in the same plane and appear as a singlet at 197.24 ppm in the ^{13}C-NMR spectrum; Remaining signal at 198.13 is the CO group trans to the $Bi\emptyset_3$ ligand and this signal seems to be close to the equatorial CO signal due to the fact that trans influence of bismuth is very low when compared with a wide range of ligands and this is consistent with the low σ-donor ability of bismuth.[35]
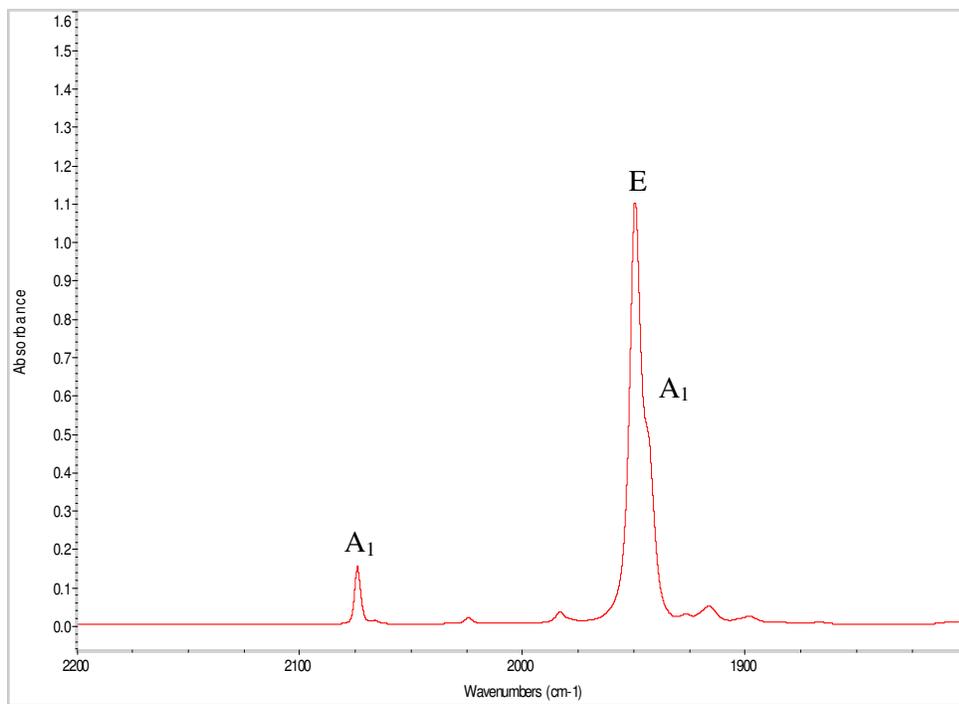
Figure 4.3. Infrared Spectrum of $W(CO)_5(Bi\emptyset_3)$ in the CO stretching region
(taken in cyclohexane)
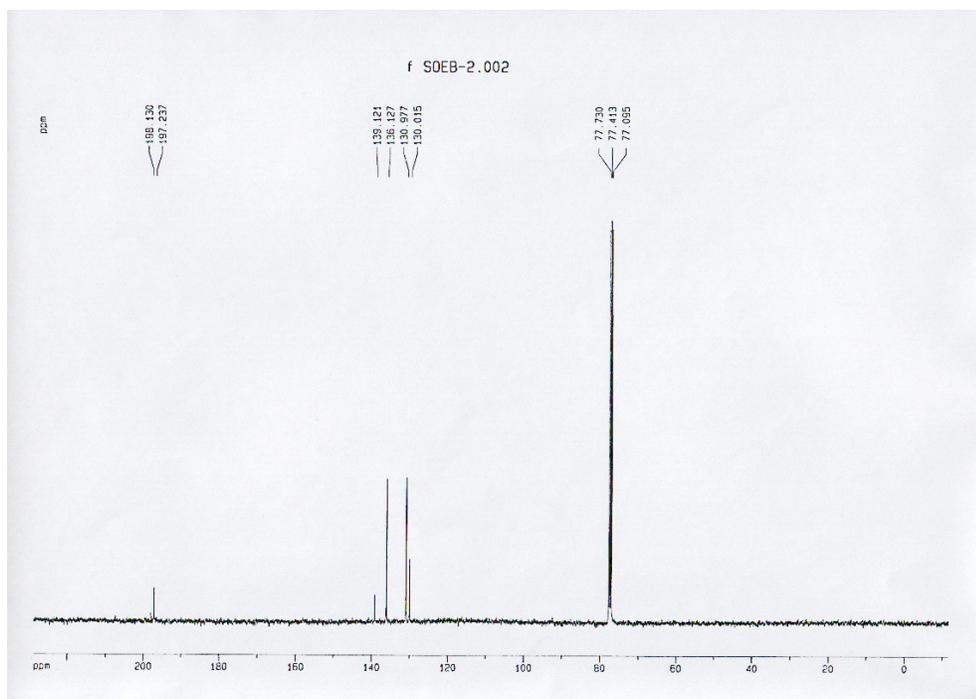
Figure 4.4. ^{13}C-NMR Spectrum of $W(CO)_5(Bi\emptyset_3)$
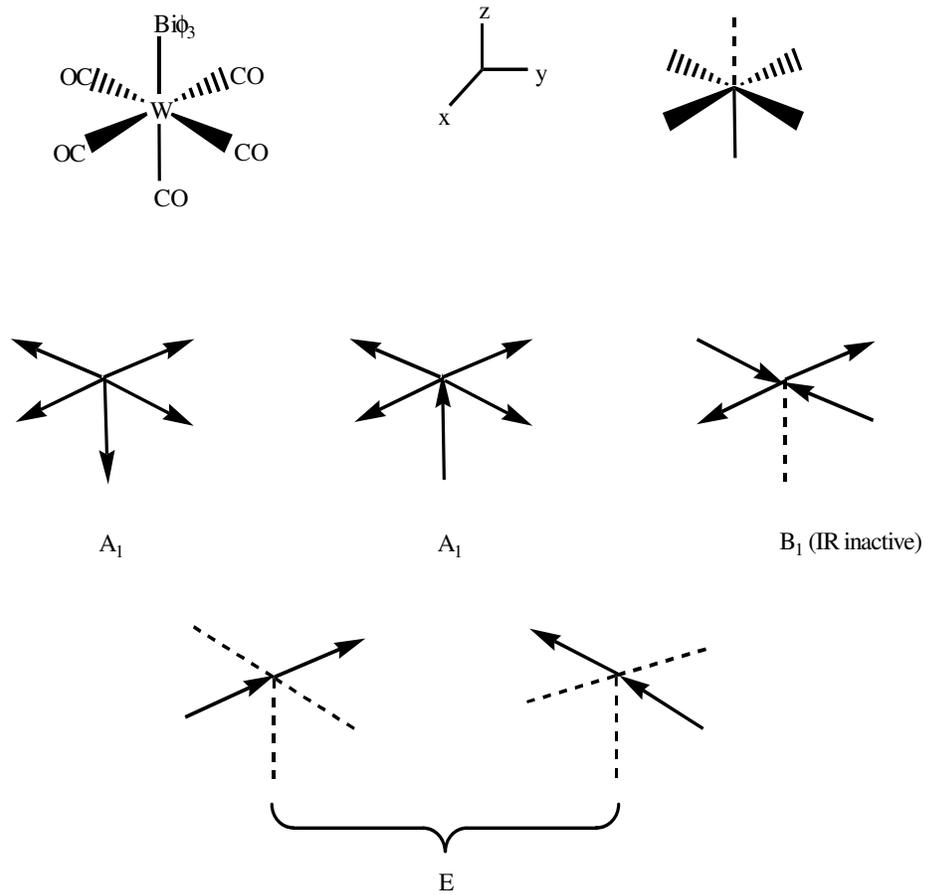
Figure 4.5. CO stretching vibrations of $W(CO)_5(Bi\emptyset_3)$

The crystal structure of the $W(CO)_5(Bi\emptyset_3)$ has already been determined by single crystal X-ray diffraction[35] and shown in Figure 4.6
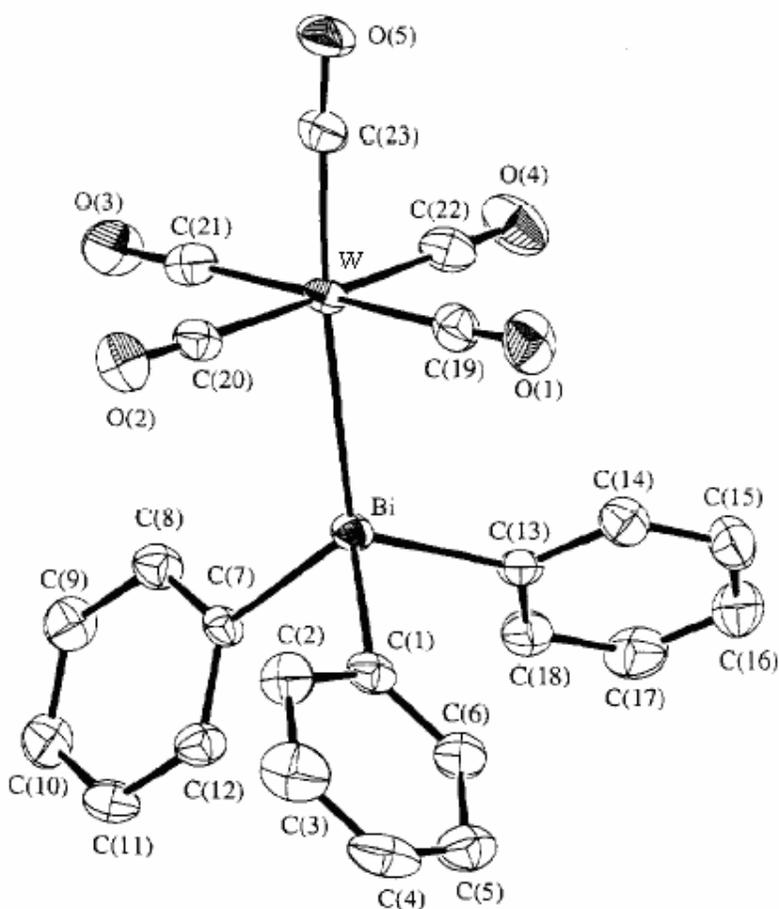
Figure 4.6. Crystal structure of $W(CO)_5(BiØ_3)$ taken from the literature[35]

(H atoms are omitted for clarity)

4.2. Reactivity of $W(CO)_5(\eta^2\text{-btmse})$

The starting complex, $W(CO)_5(\eta^2\text{-btmse})$, has been shown to be very labile towards the substitution of btmse or CO ligand in the presence of a potential ligand.[31] Figure 4.7 illustrates the possible reaction routes and products of the reaction between $W(CO)_5(\eta^2\text{-btmse})$ and $BiØ_3$.

The complex $W(CO)_5(\eta^2\text{-btmse})$ can undergo either the substitution of btmse or CO ligand. The substitution of btmse with $BiØ_3$ yields $W(CO)_5(BiØ_3)$. Additionally, one of the four CO groups cis to btmse can be replaced by $BiØ_3$.

The CO substitution product cis-$W(CO)_4(\eta^2$-btmse)$(Bi\emptyset_3)$ may isomerizes into its trans- form or may undergo btmse substitution to form cis-$W(CO)_4(Bi\emptyset_3)_2$, which may also isomerizes into its trans form. The product cis-$W(CO)_4(\eta^2$-btmse)$(Bi\emptyset_3)$ may undergo further CO substitution to yield either cis- or trans-$W(CO)_3(\eta^2$-btmse)$(Bi\emptyset_3)_2$. These disubstitution products may also loose the btmse ligand to yield either mer- or fac-$W(CO)_3(Bi\emptyset_3)_3$. Since btmse ligand labilizes the four cis-CO group, substitution of these four CO groups by $Bi\emptyset_3$ may be expected in the presence of excess $Bi\emptyset_3$. The substitution reaction may proceed until there stays only one CO group trans to btmse which may also loose the btmse to form $W(CO)(Bi\emptyset_3)_4$ eventually.

Experiments showed that the reaction of $W(CO)_5(\eta^2$-btmse) with triphenylbismuthine in cyclohexane at temperature between 30-50°C yields almost solely the btmse substitution product, $W(CO)_5(Bi\emptyset_3)$. The results of a kinetics investigation of this reaction will be discussed in what follows.
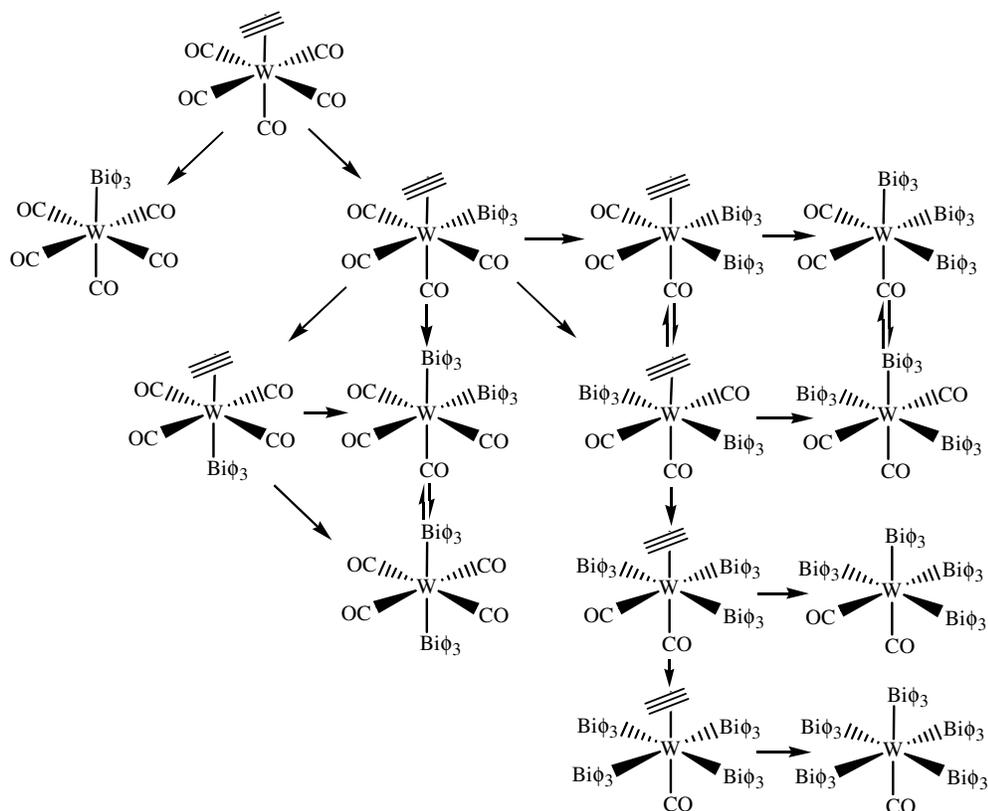
Figure 4.7. Expected reaction routes and products of the reaction between
$W(CO)_5(\eta^2\text{-btmse})$ and $Bi\emptyset_3$

4.3. Kinetics and Mechanism of the Thermal Substitution Reaction

The thermal substitution reaction of btmse in $W(CO)_5(\eta^2\text{-btmse})$, with $Bi\emptyset_3$
was followed by means of quantitative FT-IR Spectroscopy.

As the substitution reaction proceeds, the absorption bands in the CO
stretching vibrational region of the reactant are replaced gradually by the signals
of the product. As an example, the IR spectra taken at different stages of
substitution reaction of $W(CO)_5(\eta^2\text{-btmse})$ with $Bi\emptyset_3$ at 50°C is depicted in
Figure 4.8.
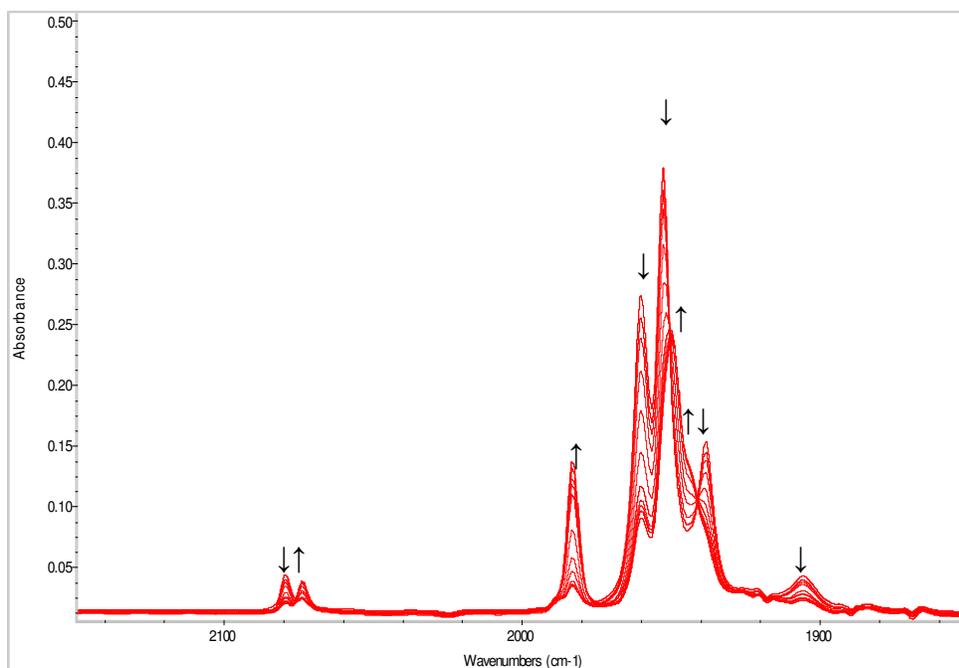
Figure 4.8. Infrared spectra of the reaction between $W(CO)_5(\eta^2\text{-btmse})$ and $Bi\emptyset_3$ taken at the different stages of the reaction at $50°C$

The formation of nice isosbestic points indicates a straightforward conversion of the reactant into the product without any side or subsequent reaction.[50]

It is inferred from the spectra that highest energy bands of the reactant and product do not overlap and resolved clearly throughout the reaction with a nice isosbestic point. Therefore these two bands were selected to follow the consumption of the reactant and the formation of the product, respectively.

The plot of the concentrations of $W(CO)_5(\eta^2\text{-btmse})$ and $W(CO)_5(Bi\emptyset_3)$ versus time at $50°C$ (Figure 4.9) shows the exponential decay of the reactant, $W(CO)_5(\eta^2\text{-btmse})$ and the exponential growth of the product, $W(CO)_5(Bi\emptyset_3)$. When the natural logarithm of the normalized concentration (the ratio of concentration of the reactant to its initial concentration) is plotted against time (Figure 4.10) one obtains a straight line, indicating that the substitution reaction is

first order with a correlation coefficient greater than 0.990, while the slope of the straight line gives the observed rate constant, k_{obs} (s^{-1})
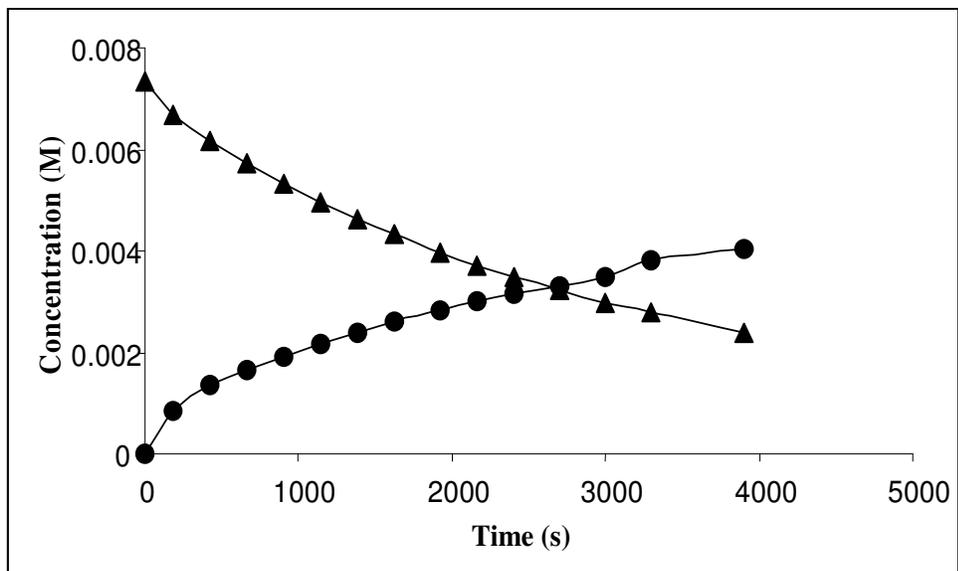
Figure 4.9. Concentration versus time plot for the substitution reaction of
$W(CO)_5(\eta^2\text{-btmse})$ with $Bi(\emptyset)_3$ at 50°C in cyclohexane

▲ : $W(CO)_5(\eta^2\text{-btmse})$ ● : $W(CO)_5(Bi(\emptyset)_3)$
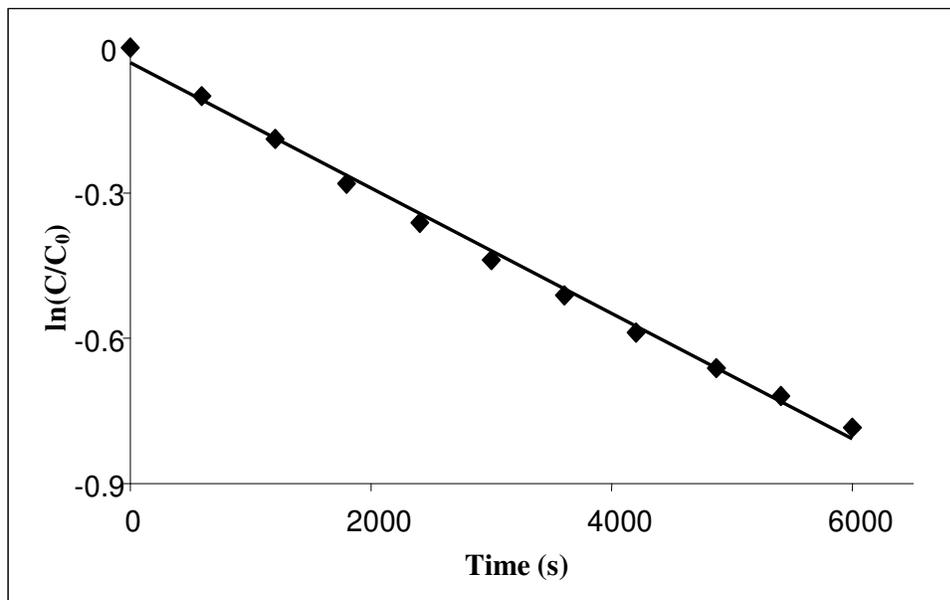
Figure 4.10. Plot of the first order reaction kinetics for the substitution of btmse
in $W(CO)_5(\eta^2\text{-btmse})$ with $Bi(\emptyset)_3$ at 50°C in cyclohexane

Figure 4.11 shows time versus natural logarithm of the normalized concentration plot for the dissociation of btmse from $W(CO)_5(\eta^2\text{-btmse})$ by $Bi\emptyset_3$ at different temperatures and it may be concluded that the substitution reaction is highly temperature dependent.
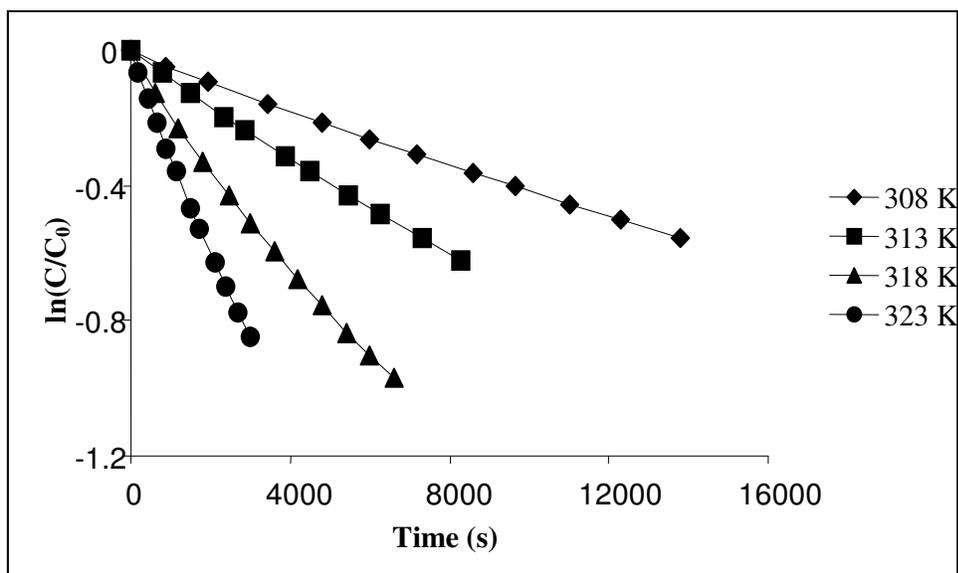
Figure 4.11. Time versus absorbance plot for the reaction of
$W(CO)_5(\eta^2\text{-btmse})$ with $Bi(\emptyset)_3$ at various temperatures
$[W(CO)_5(\eta^2\text{-btmse})]_0 = 3.37\text{mM}$, $[Bi(\emptyset)_3]_0 = 33.7\text{mM}$

Table 4.3. The observed rate constants obtained at different temperatures in the presence of 5 fold excess of $Bi\emptyset_3$

T(K)	$k_{obs} \times 10^5$ (s^{-1})
308	3.95±0.20
313	7.43±0.37
318	12.97±0.65
323	26.36±1.32

Study of the kinetics of a ligand substitution reaction would only be possible if one considers the effect of the both entering and leaving ligands on the reaction rate and mechanism. So, the substitution reaction of $W(CO)_5(\eta^2\text{-btmse})$ with $Bi\emptyset_3$ was studied by varying the $Bi\emptyset_3$ concentration as 5-10-20 fold excess for constant $W(CO)_5(\eta^2\text{-btmse})$ concentration. To observe the effect of leaving ligand on the observed rate constant, 5-10 fold excess of btmse was addedto the eraction mixture while keeping the concentrations of $W(CO)_5(\eta^2\text{-btmse})$ and $Bi\emptyset_3$ constant.

Detailed study on the IR spectrum taken at the different stages of the reaction (Figure 4.8) reveals that, monosubstitution of btmse ligand with free $Bi\emptyset_3$ occurs. CO stretching peaks of $W(CO)_5(\eta^2\text{-btmse})$ are gradually replaced by the CO stretching peaks of the $W(CO)_5(Bi\emptyset_3)$ and also the formation of $W(CO)_6$ is observed in small amount as monitored by the absorption band at 1982 cm^{-1}. The formation of $W(CO)_6$ may be attributed to the decomposition of $W(CO)_5(Bi\emptyset_3)$ complex, which is not stable in solution at temperatures above 0°C. Also very small amount of decomposition of the reactant $W(CO)_5(\eta^2\text{-btmse})$ may be expected since it is not stable in solution unless an excess of btmse is present. But it is expected that as soon as the $W(CO)_5$-moiety is formed, free $Bi\emptyset_3$ ligand attaches to the $W(CO)_5$-moiety since $Bi\emptyset_3$ ligand is present in excess amount in solution. Addition of free btmse ligand also inhibits the formation of $W(CO)_6$. The material balance for the substitution reaction given in the appendix, shows that the total mass remains greater than 85% until about 50% conversion of $W(CO)_5(\eta^2\text{-btmse})$ into $W(CO)_5(Bi\emptyset_3)$. Although excess $Bi\emptyset_3$ exists in the solution, $W(CO)_5(Bi\emptyset_3)$ is not stable above the 0°C, may be, due to the weak coordination ability of bismuth. The proposed mechanism for the substitution of btmse in $W(CO)_5(\eta^2\text{-btmse})$ with $Bi\emptyset_3$ is given in the Figure 4.12

$$\begin{array}{ccc}
\textbf{A} & & \textbf{B} \qquad \textbf{C} \\
W(CO)_5(\eta^2\text{-btmse}) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & W(CO)_5(\text{solvent}) + \text{btmse}
\end{array}$$

$$k_2 \Big\downarrow \quad Bi\phi_3 \qquad \textbf{D}$$

$$W(CO)_5(Bi\phi_3) \qquad \textbf{E}$$
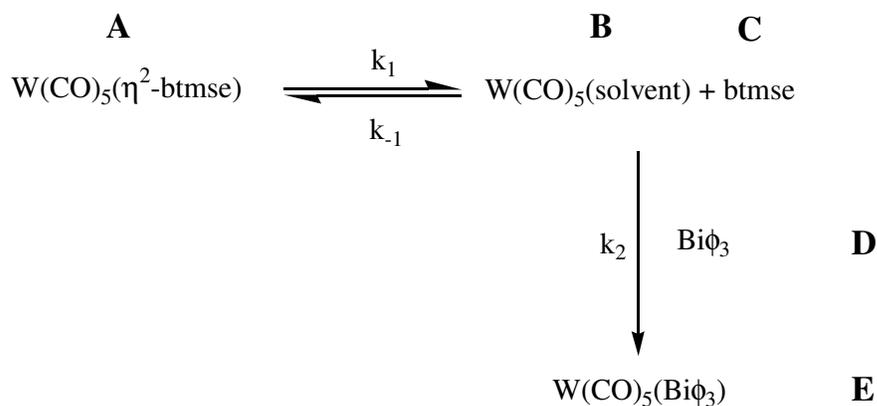
Figure 4.12. Proposed mechanism for the substitution reaction of
$W(CO)_5(\eta^2\text{-btmse})$ with $BiØ_3$

The $W(CO)_5(\eta^2\text{-btmse})$ complex has been shown to be very labile with respect to the btmse replacement.[31] In solution, it forms the solvated complex $W(CO)_5(\text{solvent})$ which can readily react with an incoming ligand such as $BiØ_3$, tricyclohexylphosphine[33] etc. Therefore, dissociation of btmse from the complex is assumed to be the rate determining step. The metal-alkyne bond is cleaved to yield the intermediate which is a solvated complex, that can either reconvert itself into the starting material or can go on to the next step of the mechanism, which is the attachment of the free $BiØ_3$.

The question whether a $[W(CO)_5(\text{solvent})]$ molecule or coordinatively unsaturated $[W(CO)_5]$ complex is the species involved in the further reaction has been addressed through studies of mechanism and catalysis employing photogenerated intermediates.[51] Mechanistic studies have shown that the replacement of the solvent from $[W(CO)_5(\text{solvent})]$ intermediate is much slower (nanosecond to milisecond)[52] than the attack of $[W(CO)_5]$ by solvent (picosecond).[53] Therefore, it is conceivable that $[W(CO)_5(\text{solvent})]$ is formed as intermediate upon the reversible, thermal detachment of btmse from $W(CO)_5(\eta^2\text{-btmse})$. This intermediate undergoes solvent replacement by either btmse yielding the starting complex, $W(CO)_5(\eta^2\text{-btmse})$, or $BiØ_3$ forming the product, $W(CO)_5BiØ_3$ as shown in Figure 4.12.

The rate law for the reaction is derived by applying the steady-state approximation for the intermediate **B**.

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B][C] \tag{1}$$

Steady State Approximation

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B][C] - k_2[B][D] = 0 \tag{2}$$

$$[B] = \frac{k_1[A]}{k_{-1}[C] + k_2[D]} \tag{3}$$

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}\left(\frac{k_1[A]}{k_{-1}[C] + k_2[D]}\right)[C] \tag{4}$$

$$-\frac{d[A]}{dt} = \frac{k_1 k_2[D]}{k_{-1}[C] + k_2[D]}[A] \tag{5}$$

$$\text{Rate} = k_{obs} \cdot [A] \tag{6}$$

$$k_{obs} = \frac{k_1 k_2[Bi\varnothing_3]}{k_{-1}[btmse] + k_2[Bi\varnothing_3]} \tag{7}$$

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Rearrange for $\dfrac{1}{k_{obs}}$;

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \left(\frac{k_{-1}}{k_1 k_2} \cdot \frac{[btmse]}{[Bi\varnothing_3]} \right) \qquad \textbf{(8)}$$

The concentration of entering ligand, $Bi\varnothing_3$ plays an important role on the rate of reaction via the observed rate constant. As the concentration of $Bi\varnothing_3$ increases, k_{obs} increases and approaches a limiting value at high concentrations of $Bi\varnothing_3$ (Figure 4.13). Equation **9** shows that this limiting value of k_{obs} equal to k_1 at an infinite concentration of entering ligand, $Bi\varnothing_3$.

$$\lim_{[Bi\varnothing_3] \to \infty} k_{obs} = k_1 \qquad \textbf{(9)}$$
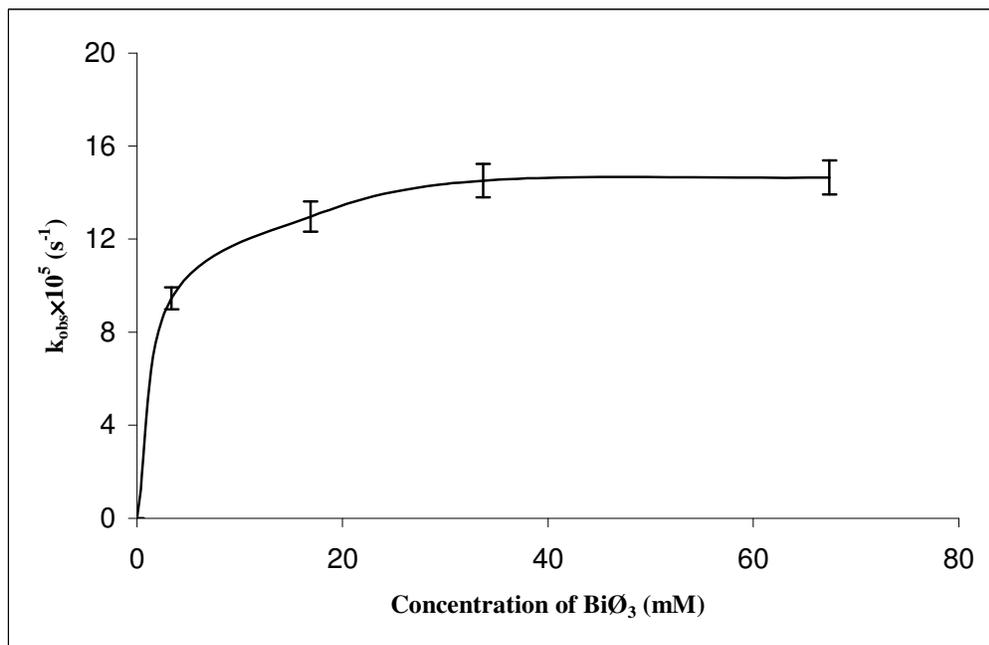
Figure 4.13. The variations in the observed rate constant k_{obs}, with the concentration of the entering ligand, $Bi\varnothing_3$ at $45\,^{\circ}\mathrm{C}$

$[W(CO)_5(\eta^2\text{-btmse})]_0 = 3.37\text{mM}$

The concentration of the leaving ligand, btmse also plays an important role on the rate of reaction via the observed rate constant. Five and ten folds of free btmse addition was studied at 45°C. It was found that the k_{obs} value decreases with the increasing btmse concentration (Table 4.4). Obviously, the addition of free btmse inhibits the formation of the $W(CO)_5(Bi\emptyset_3)$ complex, thus, lower k_{obs} values. Equations **6** and **7** also suggest that the substitution reaction slows down when the concentration of btmse increased. According to the mechanism proposed, two potential ligands, $Bi\emptyset_3$ and btmse, competes with each other for the attacment to the $W(CO)_5$-moiety in the intermediate solvated complex, $W(CO)_5$(solvent). However, the higher coordination ability of btmse and yet its higher concentration favor the coordination of btmse to the $W(CO)_5$-moiety over $Bi\emptyset_3$. Thus, the formation of $W(CO)_5(Bi\emptyset_3)$ is inhibited by the increasing concentration of the leaving btmse ligand.

Table 4.4. Change in the k_{obs} values at constant $W(CO)_5(\eta^2\text{-btmse})$ and $Bi\emptyset_3$ concentration with varying btmse concentration at 45°C

$[W(CO)_5(\eta^2\text{-btmse})]_0 = 3.37mM$, $[Bi\emptyset_3]_0 = 33.7mM$

$k_{obs} \times 10^5$ (s^{-1})	[btmse] (mM)
12.97±0.65	---
9.06±0.45	16.9
5.51±0.28	33.8

The equation **8**, can be used to determine the k_1 value from the observed rate constant values, k_{obs}, for the substitution reactions of $W(CO)_5(\eta^2\text{-btmse})$ with $Bi\emptyset_3$ for variable concentrations of $Bi\emptyset_3$ at constant temperature. A straight line was obtained when drawing the plot of $1/k_{obs}$ versus $1/[Bi\emptyset_3]$ and the intercept of this line on the vertical-axis gives $1/k_1$ values (Figure 4.14). Evaluated k_1 values are given in the Table 4.5. Remaining individual rate constants, k_{-1} and k_2 could not be determined experimentally. However, their ratio k_{-1}/k_2 could be estimated from the slope of the $1/k_{obs}$ versus $1/[Bi\emptyset_3]$ line, as the k_1 value and the [btmse] concentration are known. By employing the k_1 value obtained from the intercept

of the line and using the known concentration of btmse, the k_{-1}/k_2 ratio could be estimated. The estimated values of k_{-1}/k_2 are in the range of 0.3-0.5. It is not suprising that the k_{-1} and k_2 rate constants do not differ from each other significantly, as both of them are dealing with the attachment of a highly reactive 16-electron intermediate $W(CO)_5$ by potential ligands btmse or $BiØ_3$. Of course they may differ from each other slightly as the k_{-1}/k_2 ratio points out. Ideally, these two rate constants can be determined by flash photolysis combined with time resolved IR spectroscopy. The reaction of photochemically generated $W(CO)_5$ from the flash photolysis of $W(CO)_6$ in the presence of either btmse or $BiØ_3$ will be followed by time resolved IR spectroscopy to give the value of k_{-1} or k_2 respectively.
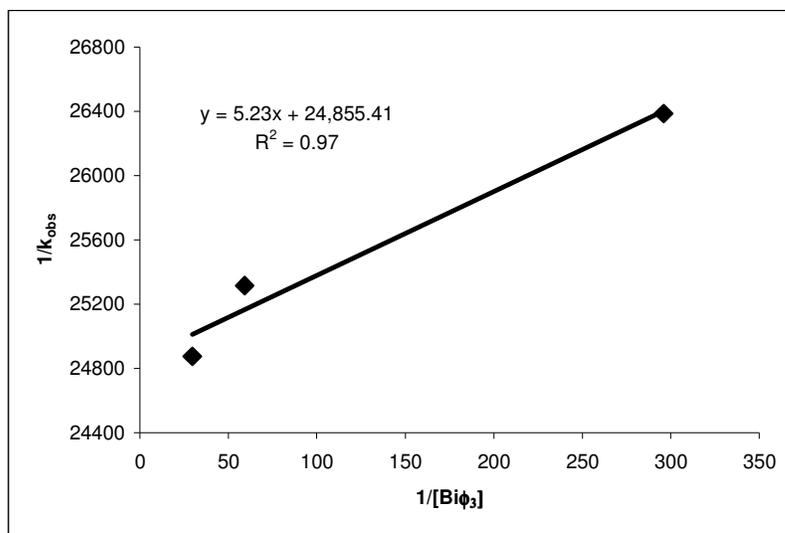
(a)
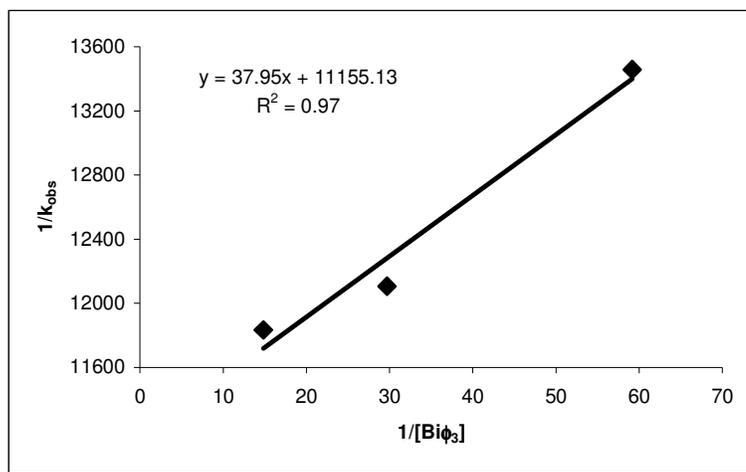
(b)
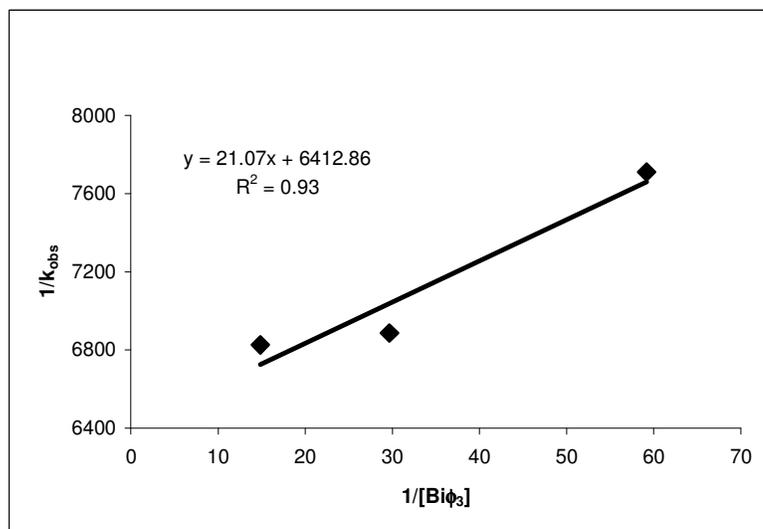
(c)
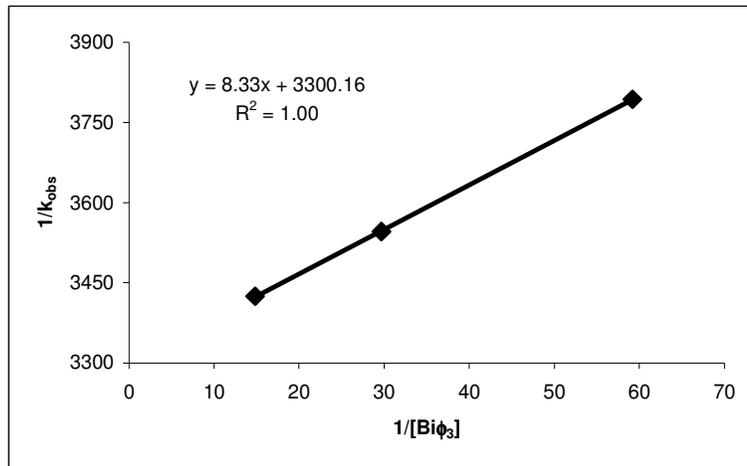
(d)

Figure 4.14. $1/k_{obs}$ versus $1/[BiØ_3]$ graph of the substitution of btmse in

$W(CO)_5(\eta^2\text{-btmse})$ with $Bi(Ø)_3$ at different temperatures

(a)35 ℃ , (b)40 ℃ , (c)45 ℃ , (d)50 ℃

Table 4.5 Evaluated k_1 values of the substitution of btmse in $W(CO)_5(\eta^2\text{-btmse})$

with $Bi(Ø)_3$ from the graph of $1/k_{obs}$ versus $1/[BiØ_3]$

Temperature (K)	$k_1 \times 10^5$ (s^{-1})
308	4.02±0.20
313	8.96±0.45
318	15.59±0.78
323	30.30±1.52

In order to evaluate the activation parameters, thermal substitution reactions were performed at four different temperatures, 35° , 40° , 45° and 50°C in the presence of 5 fold of $BiØ_3$, to achieve pseudo-first order condition.

In 1889 Arrhenius pointed out that the k and T data for many reactions fit the expression ;

$$k = A.e^{-\frac{Ea}{RT}} \qquad \textbf{(10)}$$

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where A and E_a are constants characteristics of the reaction and R is the gas constant. E_a is the Arrhenius activation energy and A is the pre-exponential factor.[54]

Taking the natural logarithm of equation **10**, we get ;

$$\ell nk = \ell nA - \left(\frac{E_a}{RT}\right) \qquad \textbf{(11)}$$

The plot of ℓnk_1 versus $\frac{1}{T}$ is a straight line with a slope of $\left(-\frac{E_a}{R}\right)$ shown in Figure 4.15.

$$y = -13.085x + 43.912$$
$$R^2 = 0.9945$$
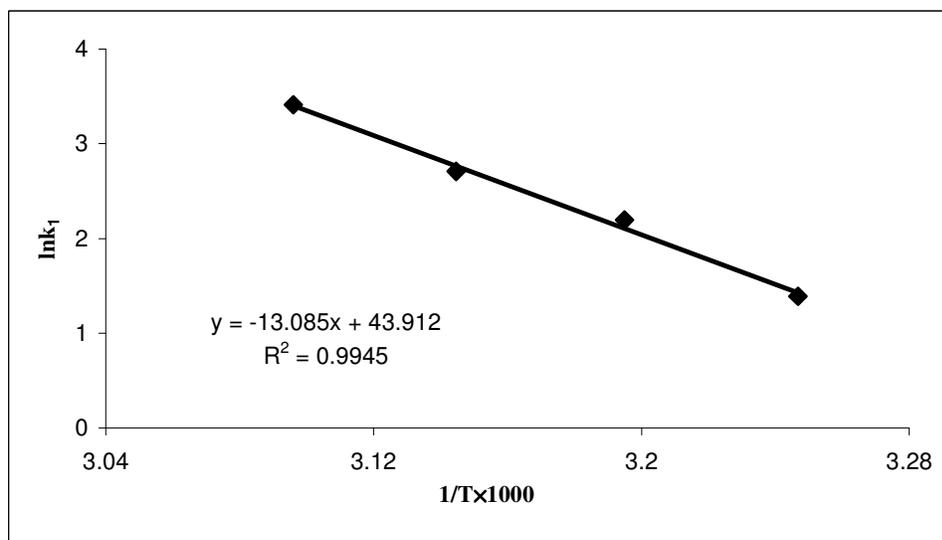
Figure 4.15. Arrhenius plot for the substitution of btmse in $W(CO)_5(\eta^2$-btmse) by $BiØ_3$ at different temperatures

From the slope of the Arrhenius plot, the activation energy, E_a, for the dissociation of btmse from $W(CO)_5(\eta^2$-btmse) was calculated to be 109 ± 2 kJ/mol.

Activation parameters are the basis for the determination of the nature of a mechanism.[55] The enthalpy of activation, $\Delta H^{\neq}$, and the entropy of activation, $\Delta S^{\neq}$, were calculated according to the equation **12** by drawing the graph of $\ell n\left(\dfrac{k_1}{T}\right)$ versus $\dfrac{1}{T}$.

$$\ell n\left(\frac{k_1}{T}\right) = -\frac{\Delta H^{\neq}}{RT} + \ell n\left(\frac{k^{'}}{h}\right) + \frac{\Delta S^{\neq}}{R} \qquad\qquad \textbf{(12)}$$

y = -12.77x + 37.158
R^2 = 0.9942
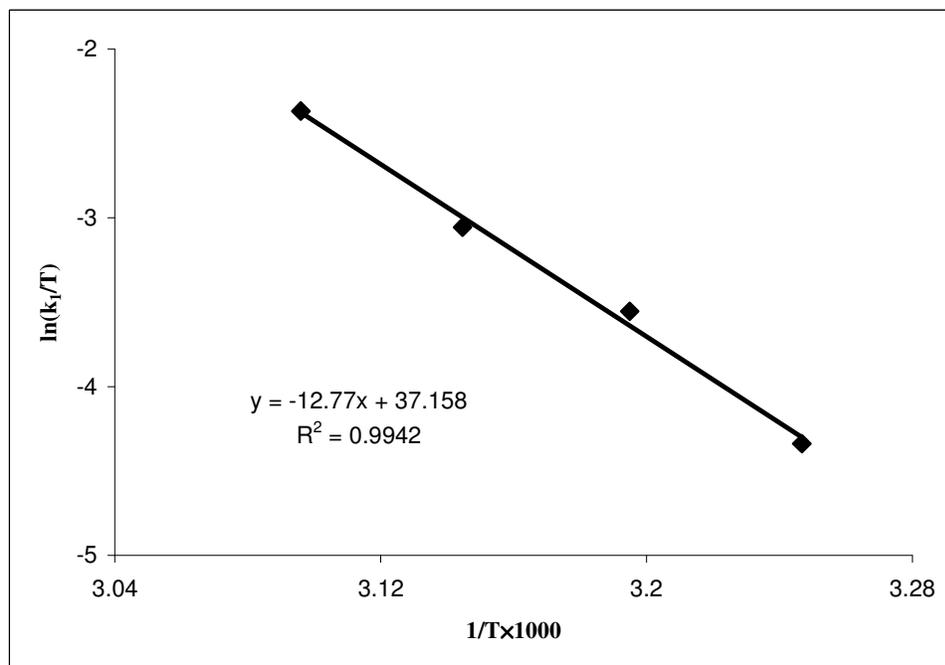
Figure 4.16. Eyring plot for the substitution of btmse in $W(CO)_5(\eta^2\text{-btmse})$ by $Bi\varnothing_3$ at different temperatures

From the Eyring plot, the enthalpy of activation for substitution of btmse by $Bi\varnothing_3$ in $W(CO)_5(\eta^2\text{-btmse})$ was evaluated to be 106±2 kJ/mol, while the entropy of activation value is 111±6 J/K.mol (Table 4.6).

Table 4.6. The activation parameters for $W(CO)_5(\eta^2\text{-btmse})$

Complex	$\Delta H^{\neq}$	$\Delta S^{\neq}$
$W(CO)_5(\eta^2\text{-btmse})$	106±2 kJ/mol	111±6 J/K.mol

Although associative mechanism in the transition state may be expected due to the tungsten metal center with large atomic size which may allow possible seven-coordination, large positive entropy of activation ($\Delta S^{\neq}$ = 111±6 J/K.mol) was observed which implies a dissociative mechanism in the transition state.

Another parameter which can give clue about the nature of mechanism is the enthalpy of activation which is closely related to the dissociation enthalpy of the bond between the metal and the leaving group. The rate determining step involves only bond breaking of W-btmse in the dissociative mechanism whereas, it is both the cleavage of W-btmse and formation of W-Bi bond in the associative mechanism. Thus, it is estimated that, the activation enthalpy should approach the bond dissociation enthalpy of the metal-alkyne bond in $W(CO)_5(\eta^2\text{-btmse})$ arising from a possible dissociative mechanism in the transition state. The enthalpy of activation would be much smaller than the bond dissociation enthalpy of metal-alkyne bond in an associative mechanism.

There exists no experimental data on the bond dissociation enthalpy of a tungsten-olefin bond. However, the analoguous molybdenum-olefin bond dissociation energy has been determined to be 108 kJ/mol for Mo-cyclooctadiene and 111.6 kJ/mol for Mo-norbornadiene.[56] Tungsten-olefin bond dissociation enthalpy is expected to be close to that of molybdenum-olefin. Also, because of higher electron density in alkyne, tungsten-alkyne bond dissociation enthalpy is expected to be slightly larger than the value of tungsten-olefin bond. The activation enthalpy of the activated complex was found experimentally to be 106.2±0.2 kJ/mol, a value which is close to the expected tungsten-alkyne bond dissociation energy. Thus, this implies a dissociative mechanism in the transition state.

CHAPTER 5

CONCLUSION

The bis(trimethylsilyl)ethyne ligand (btmse) in $W(CO)_5(\eta^2\text{-btmse})$ is substituted by triphenylbismuthine $Bi\emptyset_3$ to yield $W(CO)_5(Bi\emptyset_3)$ as the sole product.

$$W(CO)_5(\eta^2\text{-btmse}) + Bi\phi_3 \xrightarrow{\Delta} W(CO)_5(Bi\phi_3) + btmse$$

The kinetics of the substitution reaction of $W(CO)_5(\eta^2\text{-btmse})$ with $Bi\emptyset_3$ was studied by quantitative FTIR-Spectroscopy. Both the reactant and product were identified by means of FT-IR and ^{13}C-NMR Spectroscopies.

The results of the kinetic experiments directed us to propose a mechanism for the displacement of the alkyne ligand by triphenylbismuthine. The rate determining step in the proposed mechanism is the cleavage of metal-alkyne bond forming the solvated complex $W(CO)_5(\text{solvent})$.

$$W(CO)_5(\eta^2\text{-btmse}) + Bi\phi_3 \rightleftharpoons W(CO)_5(\text{solvent}) + btmse$$
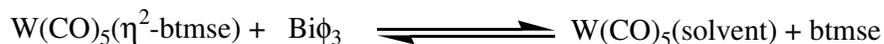
When steady state approximation is applied to the intermediate, the solvated complex, $W(CO)_5(\text{solvent})$, the rate law could be derived from the mechanism.

41

$$rate = k_{obs}.[\text{W(CO)}_5(\eta^2\text{-btmse})]$$

$$k_{obs} = \frac{k_1 k_2 [Bi\varnothing_3]}{k_{-1}[btmse] + k_2 [Bi\varnothing_3]}$$

A pseudo-first order dependence of reaction rate on the concentration of $\text{W(CO)}_5(\eta^2\text{-btmse})$ was observed. The magnitude of k_{obs} also depends upon the concentration of entering and leaving ligands. For the entering ligand, $Bi\varnothing_3$, the k_{obs} value increases and approaches a limiting value, while for the leaving ligand, btmse, it decreases up to zero in the infinite concentration of btmse. These two observations are parallel to the predictions from the mechanism proposed.

The activation parameters for the substitution reaction was evaluated by using the kinetic data collected. According to these calculations, the enthalpy of activation, $\Delta H^{\neq}$, was found to be 106±2 kJ/mol. The entropy of activation, $\Delta S^{\neq}$, value for the complex is 111±6 J/K.mol. The positive entropy of activation and large value of activation enthalpy suggest a dissociative mechanism in the transition state for the substitution reaction.

We can finally conclude that, the substitution of btmse in the complex, $\text{W(CO)}_5(\eta^2\text{-btmse})$ by triphenylbismuthine proceeds through a dissociative mechanism in which the cleavage of the metal-alkyne bond is the rate determining step. The dissociative nature of the reaction may be attributed to the presence of quite bulky entering and leaving ligands which inhibit the possible formation of seven-coordinate complex in the transition state.

Only one of the individual rate constants, k_1, k_{-1}, and k_2 could be determined from the evaluation of the experimantal data. However, it is assumed that k_{-1} and k_2 values are comparable since their ratio is close to one (0.3-0.5) which was estimated by employing the slope and intercept of the $1/k_{obs}$ versus $1/[Bi\varnothing_3]$ graph. Namely, the value of k_1, the rate constant for the rate determining step, could be obtained from the graphical evaluation of k_{obs} versus the concentration

of the entering ligand. From the same graph, one can obtain the k_{-1}/k_2 ratio too. These two rate constants need to be determined by flash photolysis combined with time resolved IR spectroscopy.

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APPENDIX - 1

The kinetic data and calculated k_{obs} values for the substitution of btmse in $W(CO)_5(\eta^2$-btmse) with $BiØ_3$ at different temperatures and different concentrations of entering ligands and the material balance of the substitution reaction to give an idea about the stoichiometry of the reaction is represented.

0.0202mmol $W(CO)_5(\eta^2$-btmse) , 35°C , 0.1010mmol $BiØ_3$

$k_{obs} = 3.95*10^{-5}$ s^{-1}

Time (sec)	Net ABS of $W(CO)_5(\eta^2$-btmse)	Concentration of $W(CO)_5(\eta^2$-btmse) (M)	Net ABS of $W(CO)_5(BiØ_3)$	Concentration of $W(CO)_5(BiØ_3)$ (M)	TOTAL
0	0.457	0.00886	0.000	0.00000	100.00
720	0.439	0.00851	0.074	0.00051	101.80
1440	0.424	0.00822	0.099	0.00068	100.45
2400	0.406	0.00787	0.130	0.00089	98.90
3600	0.386	0.00749	0.165	0.00113	97.22
5160	0.362	0.00702	0.208	0.00142	95.28
6420	0.345	0.00669	0.238	0.00163	93.87
7860	0.327	0.00634	0.271	0.00185	92.47
9000	0.313	0.00607	0.293	0.00200	91.11
10200	0.300	0.00582	0.316	0.00216	90.03
11460	0.287	0.00557	0.339	0.00232	88.96
12600	0.277	0.00537	0.356	0.00243	88.08

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, $35°C$, 0.2020mmol $BiØ_3$

$k_{obs} = 4.02*10^{-5}$ s^{-1}

Time (sec)	Net ABS of $W(CO)_5(\eta^2\text{-btmse})$	Concentration of $W(CO)_5(\eta^2\text{-btmse})$ (M)	Net ABS of $W(CO)_5(BiØ_3)$	Concentration of $W(CO)_5(BiØ_3)$ (M)	TOTAL
0	0.494	0.00958	0.000	0.00000	100.00
900	0.469	0.00910	0.094	0.00064	101.65
1920	0.449	0.00871	0.130	0.00089	100.17
3420	0.421	0.00817	0.180	0.00123	98.07
4800	0.399	0.00774	0.221	0.00151	96.54
6000	0.380	0.00737	0.255	0.00174	95.11
7200	0.362	0.00702	0.287	0.00196	93.75
8580	0.344	0.00667	0.320	0.00219	92.46
9660	0.330	0.00640	0.346	0.00236	91.48
11040	0.313	0.00607	0.375	0.00256	90.11
12300	0.299	0.00580	0.400	0.00273	89.05

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, $40°C$, 0.1010mmol $BiØ_3$

$$k_{obs} = 7.43*10^{-5} \text{ s}^{-1}$$

Time (sec)	Net ABS of $W(CO)_5(\eta^2\text{-btmse})$	Concentration of $W(CO)_5(\eta^2\text{-btmse})$ (M)	Net ABS of $W(CO)_5(BiØ_3)$	Concentration of $W(CO)_5(BiØ_3)$ (M)	TOTAL
0	0.386	0.00749	0.000	0.00000	100.00
720	0.359	0.00696	0.106	0.00072	102.63
1500	0.334	0.00648	0.148	0.00101	99.98
2400	0.311	0.00603	0.192	0.00131	98.04
3240	0.291	0.00564	0.228	0.00156	96.15
4200	0.270	0.00524	0.265	0.00181	94.08
5280	0.248	0.00481	0.301	0.00206	91.67
6000	0.236	0.00458	0.322	0.00220	90.48
6900	0.222	0.00431	0.346	0.00236	89.04
7680	0.210	0.00407	0.363	0.00248	87.48
8700	0.198	0.00384	0.386	0.00264	86.47
9300	0.190	0.00369	0.397	0.00271	85.40
10020	0.182	0.00353	0.409	0.00279	84.43

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, $40°C$, 0.2020mmol $Bi\emptyset_3$

$k_{obs} = 8.26 \times 10^{-5}$ s^{-1}

Time (sec)	Net ABS of $W(CO)_5(\eta^2$-btmse)	Concentration of $W(CO)_5(\eta^2$-btmse) (M)	Net ABS of $W(CO)_5(Bi\emptyset_3)$	Concentration of $W(CO)_5(Bi\emptyset_3)$ (M)	TOTAL
0	0.640	0.01241	0.000	0.00000	100.00
780	0.598	0.01160	0.171	0.00117	102.87
1500	0.563	0.01092	0.240	0.00164	101.20
2340	0.526	0.01020	0.312	0.00213	99.38
2880	0.504	0.00978	0.353	0.00241	98.20
3900	0.468	0.00908	0.425	0.00290	96.53
4500	0.448	0.00869	0.463	0.00316	95.50
5460	0.417	0.00809	0.518	0.00354	93.68
6240	0.395	0.00766	0.561	0.00383	92.61
7320	0.367	0.00712	0.612	0.00418	91.04
8280	0.344	0.00667	0.650	0.00444	89.54
8880	0.309	0.00598	0.652	0.00445	84.10

0.0202mmol W(CO)$_5$(η^2-btmse) , 40°C , 0.4040mmol BiØ$_3$

k$_{obs}$ = 8.45*10^{-5} s^{-1}

Time (sec)	Net ABS of W(CO)$_5$(η^2-btmse)	Concentration of W(CO)$_5$(η^2-btmse) (M)	Net ABS of W(CO)$_5$(BiØ$_3$)	Concentration of W(CO)$_5$(BiØ$_3$) (M)	TOTAL
0	0.456	0.00884	0.000	0.00000	100.00
600	0.425	0.00824	0.124	0.00085	102.83
1500	0.391	0.00758	0.192	0.00131	100.62
2400	0.360	0.00698	0.252	0.00172	98.46
3000	0.341	0.00661	0.288	0.00197	97.07
3600	0.325	0.00630	0.322	0.00220	96.19
4320	0.305	0.00592	0.358	0.00245	94.58
5040	0.289	0.00561	0.393	0.00268	93.77
5820	0.270	0.00524	0.426	0.00291	92.15
6600	0.253	0.00491	0.456	0.00311	90.74
7380	0.238	0.00462	0.483	0.00330	89.54
9000	0.212	0.00411	0.535	0.00365	87.85

0.0202mmol W(CO)$_5$(η^2-btmse) , 45°C , 0.1010mmol BiØ$_3$

k$_{obs}$ = 12.97*10^{-5} s^{-1}

Time (sec)	Net ABS of W(CO)$_5$(η^2-btmse)	Concentration of W(CO)$_5$(η^2-btmse) (M)	Net ABS of W(CO)$_5$(BiØ$_3$)	Concentration of W(CO)$_5$(BiØ$_3$) (M)	TOTAL
0	0.571	0.01107	0.000	0.00000	100.00
600	0.517	0.01003	0.214	0.00146	103.78
1200	0.473	0.00917	0.295	0.00202	101.07
1800	0.432	0.00838	0.366	0.00250	98.27
2400	0.397	0.00770	0.430	0.00294	96.09
3000	0.369	0.00716	0.486	0.00332	94.64
3600	0.342	0.00663	0.610	0.00417	97.56
4200	0.317	0.00615	0.571	0.00390	90.77
4860	0.295	0.00572	0.610	0.00417	89.32
5400	0.278	0.00539	0.638	0.00436	88.07
6000	0.261	0.00506	0.659	0.00450	86.39

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, 45°C , 0.2020mmol $Bi\emptyset_3$

$k_{obs} = 14.52*10^{-5} \text{ s}^{-1}$

Time (sec)	Net ABS of $W(CO)_5(\eta^2\text{-btmse})$	Concentration of $W(CO)_5(\eta^2\text{-btmse})$ (M)	Net ABS of $W(CO)_5(Bi\emptyset_3)$	Concentration of $W(CO)_5(Bi\emptyset_3)$ (M)	TOTAL
0	0.377	0.00731	0.000	0.00000	100.00
600	0.333	0.00646	0.128	0.00087	100.45
1200	0.300	0.00582	0.189	0.00129	97.39
1800	0.271	0.00526	0.247	0.00169	95.11
2460	0.245	0.00475	0.292	0.00199	92.41
3000	0.226	0.00438	0.326	0.00223	90.55
3600	0.208	0.00403	0.359	0.00245	88.85
4200	0.192	0.00372	0.389	0.00266	87.41
4800	0.177	0.00343	0.414	0.00283	85.76
5400	0.163	0.00316	0.433	0.00296	83.82
6000	0.153	0.00297	0.453	0.00309	83.04
6600	0.143	0.00277	0.468	0.00320	81.78

0.0202mmol W(CO)$_5$(η^2-btmse) , 45°C , 0.4040mmol BiØ$_3$

k$_{obs}$ = 14.65*10^{-5} s^{-1}

Time (sec)	Net ABS of W(CO)$_5$(η^2-btmse)	Concentration of W(CO)$_5$(η^2-btmse) (M)	Net ABS of W(CO)$_5$(BiØ$_3$)	Concentration of W(CO)$_5$(BiØ$_3$) (M)	TOTAL
0	0.600	0.01760	0.000	0.00000	100.00
600	0.544	0.01595	0.210	0.00143	98.79
1200	0.497	0.01457	0.354	0.00242	96.55
1800	0.453	0.01328	0.386	0.00264	90.46
2400	0.417	0.01223	0.462	0.00316	87.41
3000	0.383	0.01123	0.528	0.00361	84.31
3600	0.351	0.01029	0.585	0.00400	81.19
4260	0.321	0.00941	0.643	0.00439	78.44
4800	0.298	0.00874	0.686	0.00469	76.28
5400	0.276	0.00809	0.725	0.00495	74.13
6000	0.256	0.00751	0.760	0.00519	72.15
6600	0.238	0.00698	0.794	0.00542	70.47

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, 50°C , 0.1010mmol $BiØ_3$

$k_{obs} = 26.36*10^{-5} \text{ s}^{-1}$

Time (sec)	Net ABS of $W(CO)_5(\eta^2\text{-btmse})$	Concentration of $W(CO)_5(\eta^2\text{-btmse})$ (M)	Net ABS of $W(CO)_5(BiØ_3)$	Concentration of $W(CO)_5(BiØ_3)$ (M)	TOTAL
0	0.496	0.00962	0.000	0.00000	100.00
300	0.439	0.00851	0.192	0.00131	102.14
480	0.414	0.00803	0.239	0.00163	100.44
720	0.383	0.00743	0.297	0.00203	98.30
960	0.355	0.00689	0.351	0.00240	96.49
1200	0.331	0.00642	0.397	0.00271	94.92
1440	0.308	0.00597	0.437	0.00298	93.12
1740	0.284	0.00551	0.478	0.00327	91.20
2040	0.262	0.00508	0.515	0.00352	89.39
2400	0.239	0.00464	0.549	0.00375	87.17
2700	0.224	0.00434	0.425	0.00290	75.34

0.0202mmol $W(CO)_5(\eta^2$-btmse) , 50°C , 0.2020mmol BiØ$_3$

$k_{obs} = 28.20*10^{-5}$ s^{-1}

Time (sec)	Net ABS of $W(CO)_5(\eta^2$-btmse)	Concentration of $W(CO)_5(\eta^2$-btmse) (M)	Net ABS of $W(CO)_5(BiØ_3)$	Concentration of $W(CO)_5(BiØ_3)$ (M)	TOTAL
0	0.496	0.00962	0.000	0.00000	100.00
180	0.464	0.00900	0.157	0.00107	104.69
420	0.429	0.00832	0.227	0.00155	102.61
660	0.400	0.00776	0.287	0.00196	101.02
900	0.371	0.00720	0.341	0.00233	99.01
1140	0.347	0.00673	0.390	0.00266	97.65
1500	0.311	0.00603	0.454	0.00310	94.94
1740	0.292	0.00566	0.491	0.00335	93.73
2100	0.265	0.00514	0.541	0.00370	91.84
2400	0.246	0.00477	0.577	0.00394	90.57
2700	0.228	0.00442	0.606	0.00414	89.00
3000	0.212	0.00411	0.631	0.00431	87.54

0.0202mmol $W(CO)_5(\eta^2\text{-btmse})$, $50°C$, 0.4040mmol $Bi\emptyset_3$

$k_{obs} = 29.20*10^{-5} \text{ s}^{-1}$

Time (sec)	Net ABS of $W(CO)_5(\eta^2\text{-btmse})$	Concentration of $W(CO)_5(\eta^2\text{-btmse})$ (M)	Net ABS of $W(CO)_5(Bi\emptyset_3)$	Concentration of $W(CO)_5(Bi\emptyset_3)$ (M)	TOTAL
0	0.378	0.00733	0.000	0.00000	100.00
180	0.344	0.00667	0.122	0.00083	102.39
420	0.317	0.00615	0.199	0.00136	102.42
660	0.295	0.00572	0.241	0.00165	100.51
900	0.275	0.00533	0.281	0.00192	98.95
1140	0.255	0.00495	0.316	0.00216	96.92
1380	0.239	0.00464	0.349	0.00238	95.76
1620	0.223	0.00433	0.380	0.00260	94.42
1920	0.205	0.00398	0.415	0.00283	92.91
2160	0.192	0.00372	0.439	0.00300	91.71
2400	0.179	0.00347	0.461	0.00315	90.32
2700	0.166	0.00322	0.486	0.00332	89.21
3000	0.154	0.00299	0.509	0.00348	88.18