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Journal of Organometallic Chemistry 691 (2006) 3267-3273

www.elsevier.com/locate/jorganchem

Substitution kinetics of $W(CO)_5(\eta^2$ -bis(trimethylsilyl)ethyne) with triphenylbismuthine

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Received 27 February 2006; received in revised form 27 March 2006; accepted 27 March 2006 Available online 25 April 2006

Abstract

The labile complex $W(CO)_5(\eta^2$ -btmse) undergoes replacement of bis(trimethylsilyl)ethyne, btmse, by triphenylbismuthine in cyclohexane solution at an observable rate in the temperature range of 35–50 °C yielding almost solely $W(CO)_5(BiPh_3)$ as the final product. The kinetics of this substitution reaction was studied in cyclohexane solution by quantitative FT-IR spectroscopy. The substitution reaction obeys a pseudo-first-order kinetics with respect to the concentration of the starting complex. The observed rate constant, k_{obs} , was determined at four different temperatures and three different concentrations of the entering ligand BiPh₃ in the range 16.8–65.4 mM. From the evaluation of kinetic data a possible reaction mechanism was proposed in which the rate determining step is the cleavage of metal–alkyne bond in the complex $W(CO)_5(\eta^2$ -btmse). A rate law was derived from the proposed mechanism. From the dependence of k_{obs} on the entering ligand concentration, the rate constant k_1 for the rate determining step was estimated at all temperatures. The activation enthalpy $(106 \pm 2 \text{ kJ mol}^{-1})$ and the activation entropy $(111 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1})$ were determined for this rate determining step from the evaluation of k_1 values at different temperatures. The large positive value of the activation entropy is consistent with the dissociative nature of reaction. The large value of the activation enthalpy, close to the calculated tungsten–alkyne bond dissociation energy, also supports this dissociative rate-determining step of the substitution reaction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Tungsten; Carbonyl; Bis(trimethylsilyl)ethyne; Triphenylbismuthine; Kinetics; Substitution; FT-IR spectroscopy

1. Introduction

Pentacarbonyl(η^2 -bis(trimethylsilyl)ethyne)tungsten(0), W(CO)₅(η^2 -btmse), has been shown to be stable enough to be isolated as yellow crystals from the hydrocarbon solution [1]. Although this complex survives in solution even in the absence of btmse at room temperature under argon atmosphere at room temperature, it is labile towards ligand substitution. It can undergo both CO and alkyne substitution depending on the incoming ligand [2]. For example, it gives only alkyne substitution product with ethene and 1,3-butadiene, while the btmse and one CO ligand are concomitantly replaced by two molecules of *E*-cyclooc-

* Corresponding author. Fax: +90 312 210 1280. E-mail address: sozkar@metu.edu.tr (S. Özkar). tene [3]. In the case of tricyclohexylphosphine, the formation of mono and disubstitution products has been observed [4]. This lability of W(CO)₅(η^2 -btmse) makes it a useful starting material for the syntheses of some inaccessible tungsten-carbonyl derivatives, similar to how $Cr(CO)_5(\eta^2 - Z$ -cyclooctene) serves as a convenient $Cr(CO)_5$ source [5]. These results motivated us to examine the kinetics of the substitution reaction of $W(CO)_5(\eta^2$ -btmse) with triphenylbismuthine for which there is relatively little work has been reported either on simple synthesis or substitution reactions [6]. Although substituted group 6 metal-carbonyl complexes containing ligands having group 15 and 16 donor atoms have been widely studied [7] and remains one of the most active areas of coordination chemistry [8], the reported coordination chemistry of triarylbismuthine is rather meager due to the fact that it has very weak nucleophilic or donor character [9]. Furthermore, the

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bismuth-carbon bond breaks easily in the presence of many metal centres [10]. Thus, the coordination of triphenylbismuthine to a transition metal requires milder condition. Using the labile complex, $W(CO)_5(\eta^2$ -btmse) provides a versatile synthetic route to the carbonyl-tungsten complexes of BiPh₃. The reaction between $W(CO)_5(\eta^2$ -btmse) and BiPh₃ yields solely the alkyne substitution product, W(CO)₅(BiPh₃). The latter complex was also isolated from the reaction of photogenerated W(CO)₅(thf) with triphenylbismuthine in tetrahydrofuran (thf) and identified [8]. Herein, we report the results of a kinetic study on the ligand substitution reaction between pentacarbonyl(η^2 bis(trimethylsilyl)ethyne)tungsten(0) and triphenylbismuthine in cyclohexane solution. This is the first kinetic study of substitution reaction of a group 6 metal pentacarbonylalkyne complex with a bismuthine ligand. The ligand substitution reaction could be followed quantitatively by FT-IR spectroscopy.

2. Experimental

All of reactions and manipulations were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3-4 days and stored under nitrogen until used. Hexacarbonyltungsten(0) and bis(trimethylsilyl)ethyne were purchased from Aldrich[®], triphenylbismuthine was purchased from Fluka[®] and used without further purification. The thermal reactions and other treatments of organometallic compounds such as purification and crystallisation were followed by taking IR spectra at appropriate time intervals. NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for ¹H, and 100.613 MHz for ⁻¹³C). TMS was used as internal reference for ¹H and ¹³C NMR chemical shifts. Infrared spectra of the complexes were recorded from their cyclohexane solutions on a Nicolet 510 FT-IR Spectrophotometer using Omnic software. Photochemical reactions were carried out in an immersion-well apparatus [11] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high-pressure mercury lamp, which was cooled by circulating water. The thermal substitution reactions were performed in the Specac Variable Temperature Cell in combination with a circulating thermostat bath (Heto CB 11e).

 $W(CO)_5(\eta^2$ -btmse) [1] and $W(CO)_5(BiPh_3)$ [8] were prepared according to procedures given in the literature.

2.1. Kinetic measurements

The substitution rate of btmse in $W(CO)_5(\eta^2$ -btmse) with BiPh₃ in cyclohexane was determined by using quantitative FT-IR spectroscopy at various temperatures. The thermal substitution reactions were performed in the IR cell with the Specac Automatic Temperature Controller P/N 20120 to maintain a constant temperature throughout the reaction.

The kinetic measurements were recorded in cyclohexane solutions in an IR cell with a 0.20 mm path length with calcium fluoride windows. Since the substitution reaction does not proceed at an observable rate at room temperature, the mixture of reactants were stirred in a Schlenk tube under nitrogen atmosphere for 1-2 min to obtain a homogeneous mixture of the reactants. It was then transferred into an IR liquid sample cell, which is placed inside the cell holder of the thermostat in which the rest of the reaction mixture is maintained. The reaction rates were determined by following the disappearance of the highest frequency peak of the reactant at 2080.1 cm^{-1} , because it is the most distinct peak that does not overlap with any peak of the product, and the growth of the highest frequency peak of the product at 2074.1 cm⁻¹, which also remains well resolved throughout the reaction. Thus, the material balance could also be checked at any point of conversion. The observed rate constants were obtained as a result of the graphical evaluation of the data for the substitution reactions in the temperature range of 35-50 °C by an increment of 5 °C.

Kinetic experiments were also performed by varying the concentration of BiPh₃ (16.8, 33.7, and 67.4 mM, corresponding to 5-, 10- and 20-fold the initial concentration of the complex) at all the aforementioned temperatures, 35, 40, 45 and 50 °C, in order to study the dependence of the observed rate constants on the concentration of entering ligand. Moreover, kinetic experiments were also conducted by varying the concentration of btmse (0, 16.8, and 33.7 mM, corresponding to 0-, 5- and 10-fold the initial concentration of the complex) at 45 °C in order to study the dependence of the observed rate constants on the concentration of the complex of the observed rate constants on the concentration of the complex of the observed rate constants on the concentration of leaving ligand.

The IR molar extinction coefficients of W(CO)₅(η^2 btmse) and W(CO)₅(BiPh₃) 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 concentration of the respective complex in the range 2–10 and 20–100 mM, respectively. The slope of these lines gave molar extinction coefficients as $\varepsilon = 2578 \text{ mol L}^{-1} \text{ cm}^{-1}$ at 2080.1 cm⁻¹ for W(CO)₅(η^2 -btmse) and $\varepsilon = 7320 \text{ mol L}^{-1} \text{ cm}^{-1}$ at 2074.1 cm⁻¹ for W(CO)₅(BiPh₃).

3. Results and discussion

The complex $W(CO)_5(\eta^2$ -btmse) (1), prepared and identified as described in the literature [1], reacts with triphenylbismuthine, BiPh₃ at temperatures in the range of 35–50 °C to yield the complex $W(CO)_5(BiPh_3)$ (2) as the sole substitution product according to the following equation

$$W(CO)_{5}(\eta^{2}\text{-btmse}) + BiPh_{3}$$

$$\stackrel{\Delta}{\to} W(CO)_{5}(BiPh_{3}) + btmse$$
(1)

The product complex **2** was also isolated and identified by IR and 13 C NMR spectroscopy [8].

The kinetics of the thermal substitution reaction in cyclohexane solution were studied by using the quantitative FT-IR spectroscopy at temperatures between 35 and 50 °C. The IR spectrum initially shows five prominent absorption bands at 2080.1, 1988.3, 1960.4, 1953.1, and 1938.6 cm⁻¹ due to the CO stretching along with a weak feature at 1906.0 cm⁻¹ due to the $\tilde{C}\equiv C$ stretching for W(CO)₅(η^2 btmse). These bands were gradually replaced by the new absorptions at 2074.1, 1949.3, and 1943.2 cm⁻¹ due to the CO stretching for the corresponding product $W(CO)_5(BiPh_3)$ in the course of the displacement reaction. The gradual change in the IR spectrum during the reaction of 1 with BiPh₃ at 45 °C in cyclohexane is depicted in Fig. 1 as an example. The observation of nice isosbestic points indicates an almost straightforward conversion of the reactant into the product without any side or subsequent reactions [12], except the formation of $W(CO)_6$ in small amount. Another point emerging from the inspection of the IR spectra at first glance is that the highest frequency v(CO) bands of the reactant and product do not overlap and well resolved throughout the substitution reaction. Therefore, these two IR bands were selected to follow the consumption of the reactant and the growth of the product, respectively.

Although one expects three IR active v(CO) modes, 2A₁ + E (the B₂ mode is IR inactive), for the product complex **2** based on the C_{4v} symmetry of W(CO)₅ skeleton [13], only two v(CO) bands have been given in the full characterisation paper reporting a coincidence of A₁ and E modes [8]. However, in our study we also observed the A₁ mode as a shoulder to the E band at around 1943 cm⁻¹.

In this thermal substitution reaction of the labile complex 1 with BiPh₃, only the replacement of the btmse ligand occurs. In all experiments, $W(CO)_6$ was formed in small amount as monitored by the growing absorption band at 1982 cm^{-1} (however, totally less than 5%). The formation of $W(CO)_6$ may be due to the decomposition of both the reactant and product complexes. The product complex 2 is known to be slightly unstable in solution at temperatures above 0 °C due to the weak coordination ability of bismuth [8]. Also very small amount of decomposition of the reactant complex 1 may be anticipated since the detachment of the alkyne ligand generates the reactive intermediate $W(CO)_5$. However, the $W(CO)_5$ fragment will be attacked by BiPh₃ which is in large excess in solution. Hence, formation of $W(CO)_6$ in small amount may be mostly attributed to the decomposition of the product complex 2.

The logarithmic plot of concentration of the reactant versus time gives a straight line for the aforementioned reaction in the presence of triphenylbismuthine in large excess at all temperatures, as illustrated in Fig. 2 for the reaction at 45 °C starting with $[W(CO)_5(\eta^2-btmse)]_0 = 3.37 \text{ mM}$ and $[BiPh_3]_0 = 65.4 \text{ mM}$. This indicates that the displacement of btmse in 1 obeys the pseudo-first-order kinetics with a correlation constant greater than 0.99. The slope of the straight line gives the observed rate constant, k_{obs} (s⁻¹), for the pseudo-first-order thermal substitution reaction at the respective temperature. The k_{obs} values obtained for the substitution of btmse in 1 by triphenylbismuthine at various temperatures and initial concentration of BiPh₃ are listed in Table 1.

It has been shown that rapid and complete conversion of 1 into $W(CO)_6$ occurs upon treatment of an alkane solution of 1 with carbon monoxide and this reaction is significantly



Fig. 1. The FT-IR spectra taken in the course of the thermal substitution reaction of $W(CO)_5(\eta^2$ -btmse) with BiPh₃ in cyclohexane solution at 45 °C with the initial concentrations of $[W(CO)_5(\eta^2$ -btmse)]_0 = 3.37 mM and $[BiPh_3]_0 = 67.4 mM$.



Fig. 2. Logarithmic plot of the reacting complex concentration versus time for the pseudo-first-order substitution of btmse in $W(CO)_5(\eta^2$ -btmse) with BiPh₃ at 45 °C in cyclohexane. The initial concentrations are $[W(CO)_5(\eta^2$ -btmse)]_0 = 3.37 mM and $[BiPh_3]_0 = 67.4 mM$.

Table 1

Observed rate constants $(k_{obs} \times 10^5)$ for the pseudo-first-order thermal substitution reaction of W(CO)₅(η^2 -btmse) with BiPh₃ in cyclohexane solution at different temperatures in the presence of BiPh₃ in various concentration

[BiPh3]0 (mM)	35 °C	40 °C	45 °C	50 °C
16.8	3.95	7.43	12.97	26.43
33.7	4.02	7.71	14.52	28.20
67.4	4.10	8.45	14.64	29.20

The initial concentration of **1** is $[W(CO)_5(\eta^2 \text{-btmse})]_0 = 3.37 \text{ mM}.$

retarded if carried out in the presence of an excess of btmse [1,2]. It is most likely that a dissociative mechanism involves the facile reversible loss of the alkyne ligand yielding the $W(CO)_5$ species as an intermediate which will be attacked by a nucleophile present in the solution. The question whether a W(CO)₅(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 [14]. Mechanistic studies have shown that the replacement of the solvent from W(CO)₅(solvent) intermediate is much slower (microsecond timescale) [15] than the attack of W(CO)₅ by solvent (\sim 3 ps) [16]. Therefore, it is conceivable that W(CO)₅(solvent) is formed as intermediate upon the reversible, thermal detachment of btmse in $W(CO)_5(\eta^2$ -btmse). This intermediate undergoes solvent replacement by either btmse yielding the starting complex

1, or $BiPh_3$ forming the product complex 2, as shown in Scheme 1.

Assuming a steady-state approximation for the intermediate, $W(CO)_5$ (solvent), the rate law corresponding to proposed mechanism can be derived as

$$-\frac{[W(CO)_5(\eta^2-btmse)]}{dt} = k_{obs}[W(CO)_5(\eta^2-btmse)]$$
(2)

$$k_{\rm obs} = \frac{k_1 k_2 [\text{BiPh}_3]}{k_{-1} [\text{btmse}] + k_2 [\text{BiPh}_3]}$$
(3)

The concentration of entering ligand, BiPh₃ plays an important role on the rate of reaction via the observed rate constant. Fig. 3a shows how the observed rate constant varies with the concentration of BiPh₃ at 45 °C. As the concentration of BiPh₃ increases, k_{obs} increases and approaches a saturation value at high concentrations of BiPh₃ at all temperatures. This limiting value is the rate constant k_1 for the displacement of btmse from the complex W(CO)₅(η^2 -btmse)

$$\lim_{[\mathsf{BiPh}_3]\to\infty} k_{\mathsf{obs}} = \lim \frac{k_1 k_2 [\mathsf{BiPh}_3]}{k_{-1} [\mathsf{btmse}] + k_2 [\mathsf{BiPh}_3]} = k_1 \tag{4}$$

Due to the limited solubility of triphenylbismuthine in cyclohexane, it is not possible to increase the BiPh₃ concentration beyond the 20-fold excess. However, Eq. (3) can be rearranged into a form (Eq. (5)), which will permit us to estimate the k_1 value from the present data obtained by working at available concentration of BiPh₃

W(CO)₅(
$$\eta^2$$
-btmse) $\xrightarrow{k_1/-btmse}$ W(CO)₅(solvent) $\xrightarrow{k_2/+BiPh_3}$ W(CO)₅(BiPh₃)

Scheme 1. Mechanism proposed for the substitution reaction of $W(CO)_5(\eta^2$ -btmse) with triphenylbismuthine in cyclohexane solution.



Fig. 3. (a) The variations in the observed rate constant k_{obs} with the concentration of the entering ligand, BiPh₃, for the substitution of btmse in W(CO)₅(η^2 -btmse) with BiPh₃ at 45 °C in cyclohexane. [W(CO)₅(η^2 -btmse)]₀ = 3.37 mM. (b) $1/k_{obs}$ versus $1/[BiPh_3]$ graph for the same reaction.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \left(\frac{k_{-1}}{k_1 k_2} \times \frac{[\text{btmse}]}{[\text{BiPh}_3]}\right)$$
(5)

The k_1 values obtained by employing $1/k_1$ versus $1/[BiPh_3]$ graph for all temperatures are given in Table 2.

In order to study the effect of concentration of the leaving ligand, btmse, reaction was performed by adding free btmse in large excess at 45 °C. As expected from Eq. (3), the k_{obs} value decreases with the increasing btmse concen-

Table 2

 k_1 Values for the rate determining step in the substitution of btmse in W(CO)₅(η^2 -btmse) with BiPh₃ evaluated from the graph of $1/k_{obs}$ versus $1/[BiPh_3]$

Temperature (°C)	$k_1 \times 10^5 (s^{-1})$	
35	4.02 ± 0.20	
40	8.96 ± 0.45	
45	14.98 ± 0.78	
50	30.30 ± 1.52	

tration (Table 3). Obviously, the addition of free btmse inhibits the formation of the $W(CO)_5(BiPh_3)$ complex, thus, lowers k_{obs} values. According to the mechanism proposed, two potential ligands, BiPh₃ and btmse, compete with each other for the attachment to the $W(CO)_5$ -moiety in the intermediate complex, $W(CO)_5$ (solvent). However, the higher coordination ability of btmse and yet its higher

Table 3

 k_{obs} Values depending on the initial concentration of btmse for the substitution reaction of W(CO)₅(η^2 -btmse) with BiPh₃ at 45 °C in cyclohexane

$\frac{1}{k_{\rm obs} \times 10^5 ({\rm s}^{-1})}$	[btmse] (mM)	
12.97 ± 0.65	0	
9.06 ± 0.45	16.8	
5.51 ± 0.28	33.7	

The initial concentrations of reactants are $[W(CO)_5(\eta^2-btmse)]_0 = 3.37 \text{ mM}$ and $[BiPh_3]_0 = 33.7 \text{ mM}$.



Fig. 4. Eyring plot for the rate determining step of the substitution of btmse in $W(CO)_5(\eta^2$ -btmse) by BiPh₃ at different temperatures in cyclohexane.

concentration favor the coordination of btmse to the $W(CO)_5$ -moiety over BiPh₃. Thus, the formation of **2** is inhibited by increasing concentration of the leaving btmse ligand (see Fig. 4).

The calculated k_1 values at four different temperatures are used to calculate the activation parameters of the dissociation of btmse from the complex 1 and the formation of the solvated complex, $W(CO)_5$ (solvent). The activation enthalpy and entropy were found to be $106 \pm 2 \text{ kJ mol}^{-1}$ and $111 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Although associative mechanism in the transition state may be expected due to the tungsten metal centre with large atomic size which may allows possible seven-coordination, large positive entropy of activation ($\Delta S^{\neq} = 111 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$) was observed implying a dissociative mechanism in transition state. For a dissociative reaction like the displacement of btmse from the complex 1, the enthalpy of activation is expected to be close (ideally equal) to the metal-ligand bond dissociation enthalpy [17]. Unfortunately, there exists no report on the tungsten-alkyne bond dissociation enthalpy in hydrocarbon solution. Only the tungsten-acetylene bond dissociation enthalpy (105.9 kJ mol⁻¹) has been calculated in the gas phase [18].

The rate constants k_{-1} and k_2 for the other two individual steps have not been reported so far in the literature. Their determination would require the performance of the reaction between the W(CO)₅(solvent) complex, photogenerated by using flash photolysis, and the respective ligand. However, their ratio k_{-1}/k_2 could be estimated from the slope of the $1/k_{obs}$ versus $1/[BiØ_3]$ line by employing the k_1 value obtained from the intercept of the line and using the known concentration of ligands. The estimated values of k_{-1}/k_2 are in the range of 0.3–0.5. It is not surprising 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 BiØ₃.

4. Conclusion

Although W(CO)₅(η^2 -btmse) can undergo replacement of alkyne and/or CO ligand depending on the entering group, its substitution reaction with BiPh₃ yields almost solely W(CO)₅(BiPh₃) in cyclohexane solution at an appreciable rate in the temperature range of 35-50 °C. The kinetics of this ligand substitution reaction was studied by using quantitative FT-IR spectroscopy. A firstorder dependence of reaction rate on the concentration of $W(CO)_5(\eta^2$ -btmse) was observed under the pseudofirst-order conditions. The results of the kinetic experiments directed us to propose a mechanism for the substitution of the btmse ligand by triphenylbismuthine involving the reversible loss of alkyne as the rate determining step. The dissociative nature of the reaction may be attributed to the presence of quite bulky entering and leaving groups which inhibit the possible formation of seven-coordinate complex in transition state.

Acknowledgement

Partial support of this work by Turkish Academy of Sciences is gratefully acknowledged.

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