Kinetics of the Substitution of Norbornadiene in Tetracarbonyl(norbornadiene)molybdenum(0) by 2,2'-Bipyridine

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The kinetics of the thermal substitution of norbornadiene (nbd) by 2,2'-bipyridine (2,2'-bipy) in $(CO)_4Mo(C_7H_9)$ was studied by quantitative FT-IR and UV-VIS spectroscopy. The reaction rate exhibits first-order dependence on the concentration of the starting complex, and the observed rate constant depends on the concentration of both leaving nbd and entering 2,2'-bipy ligand. The mechanism was found to be consistent with the previously proposed one, where the rate determining step is the cleavage of one of the two Mo-olefin bonds. The reaction was performed at four different temperatures (35 - 50 °C) and the evaluation of the kinetic data gives the activation parameters which now support an associative mechanism in the transition states.

Introduction

The tetracarbonyl(η -diene) complexes of the group 6 elements have been known for over three decades [1] and used as $M(CO)_4$ transfer reagents to prepare a variety of $M(CO)_4L_2$ compounds (L = donor ligand). Furthermore, $M(CO)_4(\eta$ -diene) complexes have been shown to be the intermediates in the catalytic transformations of dienes using $M(CO)_6$ [2]. The lability of the coordinated dienes is very important in designing homogeneous catalytic processes. Despite of this, very little work has been performed on the displacement of dienes in $M(CO)_4$ (*n*-diene) complexes and most of the available studies deal with the displacement of diene by two monodentate ligands [3, 4]. These studies revealed that the cleavage of one of the M-olefin bonds is the rate determining step in the proposed mechanism [5, 6]. The substitution of diene in the same complex with a bidentate ligand, has recently been studied using bis(diphenylphosphino)alkane as a ligand and provided more information about the mechanism [7 - 10]. At this point, we thought that it is interesting to change the donor atoms of the entering bidentate ligand from phosphorus to nitrogen and see whether there will be any change in the reaction mechanism. It is well established that irradiation of group 6 metal carbonyl solutions containing an excess of a diimine ligand (e. g. 2,2'-bipyridine or 1,10 phenanthroline) results in stable tetracarbonyl derivatives [11]. This reaction is thought to proceed via a two step process: initial photochemical formation of $M(CO)_5(N-N)$ (N-N = diimine ligands), and subsequent thermal extrusion of a second CO ligand to form $M(CO)_4(N-N)$.

$$\begin{split} M(CO)_6 + N\text{-}N \xrightarrow{h\nu} M(CO)_5(N\text{-}N) + CO \\ M(CO)_5(N\text{-}N) \xrightarrow{\Delta} M(CO)_4(N\text{-}N) + CO \\ N\text{-}N = 1,4\text{-}diazabutadiene, 2,2'-bipyridine, \\ or pyridine-2-carbaldehyde \end{split}$$

The formation of chelate complexes M(CO)₄-(NN) was followed by UV-VIS spectroscopy and kinetic data were reported [12 - 14]. The unstable intermediates M(CO)₅(NN) could not be isolated, but the formation of the chelate complexes $M(CO)_4(NN)$ was assumed to proceed through the formation of M(CO)₅(NN) [15, 16]. Later on, $M(CO)_5(N-N)$ (NN = 1,4-diazabutadiene) complexes were isolated and the kinetics of the ringclosure reactions were studied [17]. This type of chelate ring-closure reaction is very fast in the case of 2,2'-bipyridine, and therefore $M(CO)_5(NN)$ (NN = 2,2'-bipyridine) could not be isolated [18 - 20]. The displacement of one bidentate ligand (norbornadiene) by another (2,2'-bipyridine) may give valuable insight into the substitution kinetics. Therefore, in this work, we studied the ligand displacement kinetics of norbornadiene (nbd) in tetra-

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carbonyl($\eta^{2:2}$ -nbd)molybdenum(0) with 2,2'-bipyridine (2,2'-bipy) according to the following reaction:

 $M(CO)_4(nbd) + 2,2'-bipy \xrightarrow{\Delta} M(CO)_4(2,2'-bipy) + nbd$

The process was studied by quantitative FT-IR spectroscopy. Since both the reactant and the product give sharp bands of the CO stretching, the intensity of which is generally very sensitive to changes in concentration, the use of IR spectroscopy enables one to follow the reaction precisely and to control the material balance and the yield at any conversion up to 80 - 90%. For comparison the kinetics were also followed by UV-VIS spectroscopy in the presence of a 10-fold excess of 2,2'-bipy.

Experimental Section

All reactions and manipulations were carried out either in vacuum or under a dry and deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for 3 - 4 d and stored until used. Hexacarbonylmolybdenum(0), norbornadiene and 2,2'-bipyridine were purchased from Aldrich Chemical Co., Ltd, Dorset, England and used without further purification. NMR spectra were recorded on a Bruker DPX 400 Spectrometer. Infrared spectra were recorded from 1,2-dichloroethane solution using a Perkin Elmer PC-16 FTIR or a Nicolet 510 FTIR spectrometers.

Tetracarbonyl($\eta^{2:2}$ -norbornadiene)molybdenum(0): Mo(CO)₄(nbd) (1)

1 was prepared according to the procedure described in the literature [21, 22] with minor modifications. 6 g (22.7 mmol) of Mo(CO)₆ is dissolved in 70 ml of isooctane and 8 ml (78.4 mmol) of nbd is added with stirring and refluxed for 3 h until the color of the solution turns to yellow. The reaction solution is evaporated to dryness and the residue is washed several times with *n*-hexane in order to remove the starting material. Crystallization yields yellow crystals (70%). – IR (1,2-dichloroethane): ν (C=O) 2039, 1959.0, 1913.0 cm⁻¹. – ¹³C-{1H}NMR (100 MHz, C₇D₈): δ = 78.5 (=CH-), 48.8 (-CH₂), 64.8 (CH), 217.70 (C=O), 213.80 (C=O).

Tetracarbonyl(2,2'-bipyridine)molybdenum: *Mo*(*CO*)₄(2,2'-bipy) (**2**)

A hexane solution (30 ml) containing $Mo(CO)_6$ (0.017 mmol) and 2,2'-bipy (0.017 mmol) is deoxygenated (gentle N₂ purging for 10 min) in a 100 ml roundbottom flask. The solution is irradiated with a 200 W Hg lamp for approximately 30 min with continued purging (gentle N₂ stream) and constant stirring. Upon long irradiation the solution turns orange and precipitation starts. Cooling in an ice bath for 15 min yields the orange colored product. It is purified by washing the residue with *n*-hexane several times. (60%) (17). – IR(1,2-dichloroethane): $\nu = 2015$ (C=O), 1905.0, 1876.8, 1831.8 cm⁻¹. ¹³C{1H} NMR (100 MHz, d₆-dmso): $\delta = 155.01$ (C=N), 153.73 (HC=N), 141.37 (HC=), 128.73 (HC=), 126.60 (HC=).

Kinetic measurements

All spectral measurements were recorded in 1,2-dichloroethane with a Specac variable temperature IR cell with 0.109 mm path length and calcium fluoride windows. The molar extinction coefficients of 1834 L·cm·⁻¹·mol⁻¹ at 2039 cm⁻¹ for **1**, and 1115 L·cm·⁻¹·mol⁻¹ at 2015 cm⁻¹ for **2** were determined from 1,2-dichloroethane solutions of the pure complexes by plotting the absorbance of the ν_{CO} IR band, with the highest frequency, versus the concentration of the respective complex in the standard solutions prepared. By using these values, the concentration of **1** and **2** during the reaction of Mo(CO)₄(nbd) with 2,2'-bipy could be determined from the measured IR absorbances at any stage of the reaction.

Samples of the solution for IR measurements were taken periodically. The initial concentration of 1 was $C_0(1) = 8 \cdot 10^{-3}$ molar when it was added into the preheated solution of 2,2'-bipy in 1,2-dichloroethane. The reaction rates were determined by following the disappearance of the highest frequency peak of the starting material, since it was the only distinct peak which does not overlap with the peak of the product. The graphical evaluation of the data gave the rate constants. To study the dependence of the rate constants on the concentration of the entering and leaving ligands, kinetic experiments were performed first, by varying the concentration ratio of 2,2'-bipy to 1 ([2,2'-bipy]/[1] = 0, 10, 20, 40, 60,80) with no added nbd; second, keeping the concentration ratio 2,2'-bipy to 1 constant ([2,2'-bipy]/[1] = 1) and varying the concentration ratio of nbd to 1 ([nbd]/[1] = 0,2, 4, 6).

The activation parameters were obtained from the temperature dependence of the rate constant in the range of 35 - 50 °C by an increment of 5 °C.

Results and Discussion

The IR absorption spectrum of $Mo(CO)_4(\eta^{2:2})_{-1}$ nbd) dissolved in 1,2-dichloroethane (Fig. 1a) shows three absorption bands in the CO stretching region corresponding to a local C_{2v} symmetry of its $Mo(CO)_4$ moiety $(2A_1 + B_1 + B_2)$ [23].



Fig. 1. IR spectra of (a) $Oo(CO)_4(\eta^{2:2}-nbd)$, (b) Mo-(CO)₄($\eta^{2:2}$ -nbd) and Mo(CO)₄-(2,2'-bipy) during the substitution reaction and (c) Mo(CO)₄(2,2'-bipy) in 1,2dichloroethane.

Two of the four bands expected obviously overlap. The ¹³C-¹H-NMR spectrum of Mo(CO)₄ ($\eta^{2:2}$ nbd) shows three signals for the nbd ligand and two for the carbonyl groups. The carbonyl signal at lower field is assigned to the CO groups trans to each other [24]. Thermal substitution of nbd in Mo(CO)₄($\eta^{2:2}$ -nbd) by 2,2'-bipy yields the complex Mo(CO)₄(2,2'-bipy). The IR absorption spectrum of Mo(CO)₄(2,2'-bipy) again shows four absorption bands in the CO stretching region (C_{2v} symmetry for the Mo(CO)₄ part). The ¹³C-¹H-NMR spectrum of Mo(CO)₄(2,2'-bipy) gives two signals in a 1:1 ratio for two carbonyl groups and five signals for the 2,2'-bipy system indicating that two aromatic rings remain equivalent.

The kinetics of the substitution was followed by quantitative FT-IR spectroscopy. In the CO stretching region of the IR spectrum the three absorption



Fig. 2. Time dependent behavior of concentrations of $Mo(CO)_4(\eta^{2:2}-nbd)$ and $Mo(CO)_4(2,2'-bipy)$: (a) Concentration *versus* time plot (\bigstar : $Mo(CO)_4(\eta^{2:2}-nbd)$; \blacksquare : $Mo(CO)_4(2,2'-bipy)$); (b) plot of the first order reaction kinetics for the substitution reaction.

bands of Mo(CO)₄($\eta^{2:2}$ -nbd) are gradually replaced by the bands of Mo(CO)₄(2,2'-bipy) during the reaction (Fig. 1 a-c). When the reaction is conducted at 45 °C isosbestic points indicate a straightforward conversion of the reactant into product without side or subsequent reactions [25].

An inspection of the spectra in Fig. 1 shows that the highest frequency bands of the reactant and product at 2043.0 and 2014 cm⁻¹, respectively, do not overlap and remain well resolved during the whole reaction. Therefore, these two IR bands are selected to follow the consumption of the educt, 1, and the growth of the product 2.

Fig. 2a shows a plot of concentration *versus* time for the thermal reaction at 45 °C for which the time resolved spectra are given in Fig. 1. This graph shows an exponential decay for 1 and an exponential growth for 2 (Fig. 2a). The logarithmic plot of the concentration of 1 against time gives a straight line (Fig. 2b) for the reaction. This indicates that



the displacement of nbd from $Mo(CO)_4(\eta^{2:2}\text{-nbd})$ by 2,2'-bipy obeys pseudo-first order kinetics with a correlation coefficient around 0.99. The slope of the straight line gives the observed rate constant, k_{obs} (s⁻¹).

From previous studies [7 - 9] we assume that dissociation of nbd from the complex is the rate determining step: One of the two olefin-metal bonds is cleaved to yield intermediate I (Scheme 1). The next steps involve associative or dissociative processes to form III or the very labile intermediate II, which immediately reacts with 2,2'-bipy to form the product. Dissociation of the olefin from intermediate III and ring closure of 2,2'-bipy give the product as well. There is no evidence for the formation *cis*-M(CO)₄(η^2 -nbd)₂ from intermediate I upon reversible coordination of a second nbd molecule, even though similar complexes have already been isolated [26].



Fig. 3. Variations of the observed rate constant with the concentration of 2,2'-bipyridine at $45 \text{ }^{\circ}\text{C}$.

By application of the well known steady state approximation for intermediates I and II the rate is found to be

Rate =
$$k_{obs}$$
[1],
 $k_{obs} = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_5 + k_3 [NN] - \frac{k_5}{1 + k_6 [NN]/k_{-5} [nbd]}}$

The proposed mechanism was shown to be in agreement with the experimental results. When the complex is dissolved in 1,2-dichloroethane and left at 45 °C in the absence of the entering ligand 2,2'-bipy for about 2 - 3 h, there is no noticeable change in the concentration of the complex. The limit of k_{obs} approaches zero, when the concentration 2,2'-bipy goes to zero as the proposed mechanism predicts:

$$\lim_{(NN)\to 0} (k_{obs}) = 0.$$

As the concentration of the entering ligand increases gradually, k_{obs} increases and reaches a finite value at very high concentrations (Fig. 3):

$$\lim_{(NN)\to\infty} (k_{obs}) = k_1 = 1.24 \cdot 10^{-3}.$$

The effect of the leaving group nbd on the rate of the substitution reaction was also studied by varying the concentration of nbd but keeping the concentration of 2,2'-bipy constant ($8 \cdot 10^{-3}$ molar). The plot of k_{obs} versus nbd is curved downward, with positive intercept, indicating the presence of a complex mechanism [27] in which the increasing concentration of nbd causes a decrease in k_{obs}. This clearly suggests that the substitution rate of nbd in **1** is retarded by the presence of excess nbd. As the concentration of nbd goes to infinity, k_{obs} approaches a limit value which can be obtained from Fig. 4:



Fig. 4. Variations of the observed rate constant with the concentration of norbornadiene at 45 $^{\circ}$ C.



Fig. 5. First order kinetics for the displacement reaction of nbd from Mo(CO)₄($\eta^{2:2}$ -nbd) by 2,2'-bipy in the temperature range 35 - 50 °C.

$$\lim_{[nbd]\to\infty} (k_{obs}) = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_3 [NN]} = 9.3 \cdot 10^{-5}.$$

On the other hand, as the concentration of nbd goes to zero, k_{obs} approaches another limit value which can also be seen from Fig. 4:

$$\lim_{[nbd]\to 0} (k_{obs}) = k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_5 + k_3 [NN]} = 1.25 \cdot 10^{-4}.$$

In order to evaluate the activation parameters thermal substitution reactions were performed at four different temperatures (35, 40, 45, 50 °C) in the presence of 10-fold excess ($8.0 \cdot 10^{-2}$ molar) of 2,2'-bipyridine to provide pseudo-first order con-

Table 1. The rate constants (k_{obs}) obtained at different temperatures and free energy of activation values determined from IR and UV-VIS data.

T(K)	$k_{obs} [10^{-4} sec^{-1}]$		⊿G [≠] [kJ/mol]	
	IR	UV-VIS	IR	UV-VIS
308	2.24	2.00	96.9	97.2
313	3.48	2.91	97.3	98.4
318	4.62	3.70	98.2	98.8
323	5.47	4.70	99.3	99.7



Fig. 6. Eyring plot for the substitution of nbd in Mo-(CO)₄($\eta^{2.2}$ -nbd) in the presence of a 10 fold excess of 2,2'-bipy (followed by IR spectroscopy).

ditions. The observed rate constant values (Fig. 5) as well as the free energy of activation calculated are given in Table 1. From the Eyring plot the enthalpy and the entropy of activation are found to be $\Delta H^{\neq} = 46.5(\pm 7) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^{\neq} = -86.9(\pm 18) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively (Fig. 6). The negative value of ΔS^{\neq} is consistent with an S_N2 or associative mechanism in the transition state [27].

For comparison with the IR spectroscopic results, the formation of **2** (*ca*. $6 \cdot 10^{-4}$ molar in hexane solution) was also monitored by quantitative UV-VIS spectroscopy in the presence of a 10-fold excess of 2,2'-bipyridine. From the increase in the concentration of product as a function of time k_{obs} is found for a pseudo-first order reaction. The rate of formation of **2** ($\lambda = 470$ nm), is comparable with the result obtained from FT-IR for the disappearance of **1** (Table 1). The activation parameters, calculated using UV data, ΔH^{\neq} , and ΔS^{\neq} are 43.8(±3) kJ·mol⁻¹ and $-96(\pm 10)$ J·mol⁻¹·K⁻¹, respectively. The results compare well with those obtained by quantitative IR spectroscopy.

In a dissociative S_N1 mechanism, the rate de-

termining step involves only bond breaking, while in an associative mechanism (S_N2), the rate determining step involves both bond breaking and bond formation [28]. It is expected that the enthalpy of activation, ΔH^{\neq} , would approach the M-nbd bond energy for a predominantly dissociative processes and be rather independent of the nature of the entering ligand, whereas for an associative process ΔH^{\neq} is expected to be smaller than the M-nbd bond energy. Single Mo-nbd bond energy is reported to be 111.6 kJ·mol⁻¹ [29], but $\Delta H^{\neq} = 46.5$ kJ·mol⁻¹ is

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found experimentally. This also clearly indicates that substitution reaction of $Mo(CO)_4(\eta^{2:2}-nbd)$ with 2,2'-bipy has an $S_N 2$ or associative mechanism in the transition state.

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