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Kinetic Study of Ligand Exchange Reactions of Bis(1,5-cyclooctadiene)nickel(0) with 2,2′-Bipyridine, 4,4′-Dimethyl-2,2′-bipyridine, and 4,4′,5,5′-Tetramethyl-2,2′-bipyridine

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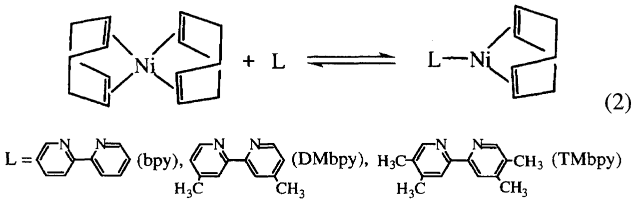
Ligand exchange reactions of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, with bpy, DMbpy, and TMbpy (bpy = 2,2′-bipyridine, DMbpy = 4,4′-dimethyl-2,2′-bipyridine, TMbpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine) in THF and DMF have been investigated kinetically. The reaction obeys the pseudo first-order kinetics, $R = -\mathrm{d}[Ni(cod)_2]/\mathrm{d}t = k_{obs}[Ni(cod)_2]$, with respect to the concentration of $Ni(cod)_2$ in both the solutions. In THF, the k_{obs} value linearly increases with [L] at a low concentration region of the exchanging ligand L; but it levels off at high concentrations of L and approaches a limiting value (e.g., about 1.0×10^{-4} s^{-1} at 25 °C). Addition of cod to the THF solution accelerates the exchange reaction. On the other hand, in DMF, the rate of the reaction (R) obeys the second-order rate law, $R = k[Ni(cod)_2][L]$, over a wide range of [L]. In DMF, the k value is independent of the concentration of cod added. Based on the kinetic results and NMR analysis, a reaction mechanism involving coordination of bpy, cod, or DMF to $Ni(cod)_2$ to form a 20 e intermediate complex is proposed. DMbpy and TMbpy have a reactivity comparable to that of bpy in THF. In DMF, their reactivity increases in the order of bpy < DMbpy < TMbpy at 25 °C.

Among various low valent transition metal complexes, bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$,[1] is one of the most important and widely used zerovalent organotransition metal complexes. The ligand exchange reaction of $Ni(cod)_2$ with neutral ligands provides a convenient route for the preparation of various zerovalent complexes such as Ni(cod)(bpy), $Ni(bpy)_2$, and $Ni(cod)(PPh_3)_2$.[1—3]

$$Ni(cod)_2 + nL \longrightarrow Ni(cod)L_n + cod \qquad n = 1 \text{ or } 2 \qquad (1)$$

$Ni(cod)_2$ itself and these zerovalent nickel complexes thus obtained have been used as important starting materials for organometallic and organic syntheses. For example, they have been utilized to prepare organonickel complexes like nickelacyclic complexes,[4] and they are effective for dehalogenative dimerization of organic halides such as aryl halide, vinyl halide, allylic halide, and benzyl halide.[1,5,6] Recently, another type of utilization of the Ni(0) complexes for dehalogenative polycondensation of dihaloaromatic compounds to give the π-conjugated polymers has also been reported.[7—9]

In spite of the presence of such numerous reports on the reaction of $Ni(cod)_2$ with substrates, kinetic aspects of the ligand exchange reaction of $Ni(cod)_2$ have attracted less attention. In this paper we report results of the kinetic studies on the ligand exchange reaction of $Ni(cod)_2$ with the following 2,2′-bipyridines.



(2)

For several other nickel complexes including zerovalent nickel and organonickel(II) complexes, kinetic studies on their ligand exchange reactions have been reported.[1,10—13] Especially, Schindler and his coworkers recently reported kinetic studies on for replacement of the cod ligand of Ni(cod)(bpy) by aldehydes.[10] The present kinetic studies have been carried out in two kinds of solvents: i.e., in a less polar solvent, THF ($\varepsilon = 7.6$), and in a polar solvent, DMF ($\varepsilon = 36.7$). Both are typical solvents used for the reactions of $Ni(cod)_2$.[1—9]

Experimental

Materials and Measurements. Manipulation of complexes and the reactions were carried out by using standard Schlenk techniques under argon or nitrogen atmosphere. $Ni(cod)_2$ was synthesized according to a previously published procedure.[3] 2,2′-Bipyridine was purified by recrystallization from petroleum ether before use. Commercial grade 4,4′-dimethyl-2,2′-bipyridine was used as purchased. 4,4′,5,5′-Tetramethyl-2,2′-bipyridine was kindly donated by Prof. T. Saji of our university. 1,5-Cyclooctadiene was dried, distilled, and stored under argon or nitrogen atmosphere in a Schlenk-type flask. UV-vis spectra were measured on a Shimadzu UV-3100PC or JASCO Ubest-35 spectrophotometer by using a

Schlenk-type optical cell. NMR spectra were obtained with JEOL EX-400 and JEOL GX-500 spectrometers.

Temperature Variable NMR Measurement. Temperature variable ^{1}H NMR spectra of Ni(cod)$_2$ with and without added cod were measured in THF-d_8, DMF-d_7, and toluene-d_8, respectively. Samples for temperature variable NMR measurements were prepared by the following method. The solvent (about 0.7 cm^3) was added to a NMR tube containing Ni(cod)$_2$ (about 2.5 mg) by a trap-to-trap distillation under vaccum, and the NMR tube was sealed. When necessitated, cod (0.025 cm^3) was added to a NMR tube containing Ni(cod)$_2$ (about 2.5 mg) and solvent (about 0.7 cm^3), and the NMR tube was sealed.

NMR Tube Reaction of Ni(cod)$_2$ with Bpy. NMR tube reactions of Ni(cod)$_2$ with bpy were carried out in THF-d_8 and DMF-d_7. A typical experimental procedure is as follows: THF-d_8 (0.67 cm^3) was added to a NMR tube containing Ni(cod)$_2$ (2.3 mg), bpy (4.5 mg), and cod (0.015 cm^3) by a trap-to-trap distillation under vaccum, and the NMR tube was sealed.

The reaction is completed after 48 h, and Ni(cod)(bpy) is selectively formed. The equilibrium constant of the ligand exchange reaction was estimated from peak areas of Ni(cod)$_2$, Ni(cod)(bpy), bpy and cod in the ^{1}H NMR spectrum taken after 48 h reaction time.

Kinetic Study. A typical experiment was carried out as follows. THF (6 cm^3) was added to a Schlenk-type optical cell containing Ni(cod)$_2$ (about 1 mg) by trap-to-trap distillation. Cod (0.032 cm^3) was added into the Schlenk-type optical cell and then a THF solution of bpy ([cod] = 0.044 M, 1 M = 1 mol dm^{-3}) was added. The reaction system was warmed to room temperature and the optical cell was set in UV-vis spectrometer equipped with a water jacket for circulating thermostated water. Kinetic data were obtained by periodically measuring the absorption spectrum.

As for the kinetic study in DMF, a DMF solution of Ni(cod)$_2$ ([Ni(cod)$_2$] = 4×10^{-4} M; [cod] = 0.044 or 0.011 M) and the bpy solution (containing cod; [cod] = 0.044 or 0.011 M) were added into the Schlenk-type optical cell with a syringe.

Results and Discussion

1. Ligand Exchange in THF.

Equilibrated Forms of Ni(cod)$_2$ and Ni(cod)(bpy) in THF: Basic Information for Kinetic Study. Although ^{1}H NMR data of Ni(cod)$_2$ in a solvent (presumably in benzene-d_6)[14)] have been reported,[1b)] ^{1}H NMR spectra under various conditions were measured to give bases for the present studies. The temperature dependent ^{1}H NMR spectrum of Ni(cod)$_2$ in THF-d_8 without added cod shows H^a signal of the coordinated cod ligand at $\delta = 4.31$, whereas the H^b and H^c protons give rise to a multiplet signal at $\delta = 2.1$ (Chart 1).[15)] The spectrum also shows peaks of free cod. Such peaks are small in a temperature range of −70—25 °C, however, indicating that Ni(cod)$_2$ essentially exists as a complex fully coordinated by cod (namely, Ni(η^4-cod)$_2$). On addition of excess cod, the ^{1}H NMR spectrum simply exhibits peaks of Ni(cod)$_2$ and free cod, and no additional peak was observed even at −60 °C.

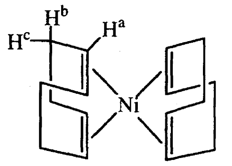


Chart 1.

The ^{1}H NMR spectrum of the reaction mixture obtained by a 1 : 3.6 reaction between Ni(cod)$_2$ (1.2×10^{-2} M) and bpy (4.3×10^{-2} M), in the presence of excess cod (0.18 M) in THF-d_8

$$\begin{array}{ccccccc} \mathrm{Ni(cod)_2} & + & \mathrm{bpy} & \xrightarrow{\mathrm{THF}} & \mathrm{Ni(cod)(bpy)} & + & \mathrm{cod} \\ 1 & : & 3.6 & & & & \mathrm{(excess)} \end{array} \tag{3}$$

shows that Ni(cod)(bpy) is selectively formed. No sign is observed for the formation of other bpy-coordinated species like Ni(bpy)$_2$ under the reaction conditions.

Although there remains weak peaks of Ni(cod)$_2$, the relative ratio between Ni(cod)$_2$ and Ni(cod)(bpy) reveals that the following equilibrium is shifted to the right side with the K value of about 400 at 26 °C:

$$K = [\mathrm{Ni(cod)(bpy)}][\mathrm{cod}]/[\mathrm{Ni(cod)_2}][\mathrm{bpy}] \tag{4}$$

$$\mathrm{Ni(cod)_2} + \mathrm{bpy} \overset{K}{\rightleftarrows} \mathrm{Ni(cod)(bpy)} + \mathrm{cod} \tag{5}$$

From the ^{1}H NMR spectrum of the finally obtained mixture, [bpy], [cod], and [Ni(cod)(bpy)]/[Ni(cod)$_2$] are estimated at 3.1×10^{-2} M, 0.19 M, and 65, respectively, which give the K value of about 400.

Selective Formation of Ni(cod)(bpy) under Kinetic Conditions. As described below, the kinetic study was carried out by UV-vis spectroscopy, which was performed under conditions different from those used for the NMR analysis. However, the selective formation of Ni(cod)(bpy) in the kinetic study has also been confirmed. Figure 1 depicts changes of the UV-vis spectrum during the ligand exchange reaction. As shown in Fig. 1, the reaction of Ni(cod)$_2$ with bpy causes rises of three peaks at 370, 565, and 825 nm,[16)] which seem assignable to MLCT (Ni → bpy) bands in view of their molar absorption coefficients (ε = ca. 3100, 4900, and 2100 M^{-1} cm^{-1}, respectively).

The ligand exchange reaction between Ni(cod)$_2$ and bpy was followed by the change of the UV-vis spectrum with time, and the equilibrium is also considered to be shifted to the direction of Ni(cod)(bpy) in the final reaction product. For example, the reaction conditions shown in Fig. 1 will give [bpy] of about 5×10^{-3} M and [cod] of 0.044 M as their final concentrations, and consequently

$$\begin{array}{lclcl} \mathrm{Ni(cod)_2} & + & \mathrm{bpy} \xrightarrow{\mathrm{THF}} \mathrm{Ni(cod)(bpy)} & + & \mathrm{cod} \\ C_0 = & & C_0 = & & C_0 = \\ 3.5\times10^{-4}\ \mathrm{M} & & 5.36\times10^{-3}\ \mathrm{M} & & 0.044\ \mathrm{M} \end{array} \tag{6}$$

C_0 = initial concentration (cf. Fig. 1)

the ratio between Ni(cod)$_2$ and Ni(cod)(bpy) is estimated at about 1 : 45 from the K value.

$$[\mathrm{Ni(cod)(bpy)}]/[\mathrm{Ni(cod)_2}] = K\frac{[\mathrm{bpy}]}{[\mathrm{cod}]} = \text{ca. } 45. \tag{7}$$

As shown in Fig. 2, the height of the peak at 565 nm after the completion of the reaction increases with the concentration of added bpy, even when the reaction is carried out with the same concentration of Ni(cod)$_2$. However, the extent of

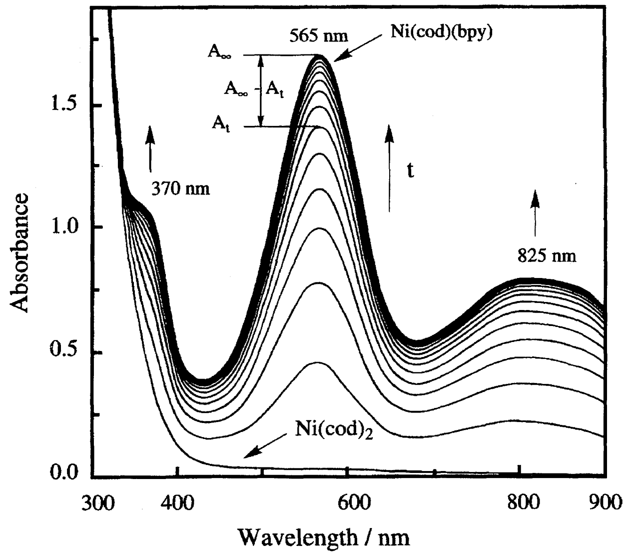


Fig. 1. Changes in the UV-vis spectrum during the ligand exchange reaction of $Ni(cod)_2$ with bpy in THF. $[Ni(cod)_2] = 3.5\times10^{-4}$ M. [cod] = 0.044 M. $[bpy] = 5.36\times10^{-3}$ M. At 25 °C. The spectrum is recorded with every 60 min.

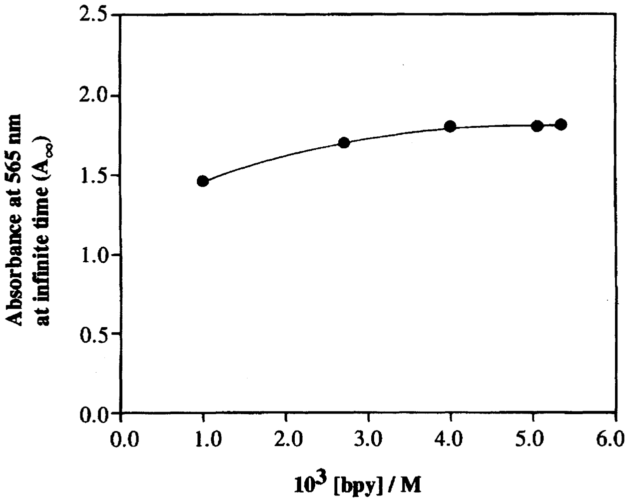


Fig. 2. Plots of A_∞ at 565 nm (cf. Fig. 1) against added [bpy]. $[Ni(cod)_2] = 3.7\times10^{-4}$ M. [cod] = 0.044 M. At 25 °C.

the increase is small, supporting the conclusion that essentially all of $Ni(cod)_2$ is converted into Ni(cod)(bpy) under the conditions used for the kinetic study.

2. Kinetic Study in THF. **Exchange with bpy.** The kinetic study has been carried out by following the increase of absorbance (A_t) of the peak at 565 nm (cf. Fig. 1) with time. In order to maintain [bpy] and [cod] constant during the reaction, excess amounts of bpy and cod, compared with the amount of $Ni(cod)_2$, are added. However, as discussed above, even in the presence of excess cod, the equilibrium in the final product is shifted to the direction of Ni(cod)(bpy).

As exemplified in Fig. 3, plots of $\ln((A_\infty - A_t)/A_\infty)$ (cf. Fig. 1 for A_∞ and A_t) against time gives straight lines under various conditions, indicating that the rate of the reaction is proportional to the concentration of $Ni(cod)_2$.

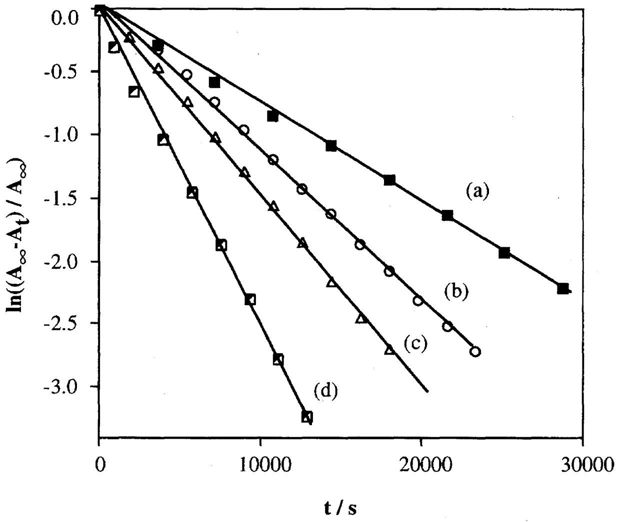


Fig. 3. Pseudo first-order plots of the ligand exchange reaction of $Ni(cod)_2$ with bpy in THF. $[Ni(cod)_2] = 0.1$—0.3 mM. [cod] = 0.044 M. (a): 25 °C, $[bpy] = 5.36\times10^{-3}$ M. (b): 30 °C, $[bpy] = 5.36\times10^{-3}$ M. (c): 35 °C, $[bpy] = 4.05\times10^{-3}$ M. (d): 40 °C, $[bpy] = 4.05\times10^{-3}$ M.

$$d[Ni(cod)(bpy)]/dt = -d[Ni(cod)_2]/dt = k_{obs}[Ni(cod)_2] \quad (8)$$

The k_{obs} value increases with [bpy] at a low concentration region of bpy and it levels off at high [bpy]. The reciprocal plots of the k_{obs} give straight lines in a temperature range of 25—40 °C, as depicted in Fig. 4.

On the other hand, it has also been observed that the increase in the concentration of added cod, [cod], also leads to an increase in k_{obs}; the reciprocal plots of the k_{obs} vs. [cod] data are shown in Fig. 5. The effect of cod may be (i) an outward one owing to a contribution of a reverse reaction ($Ni(cod)(bpy) + cod \rightarrow Ni(cod)_2 + bpy$) to k_{obs}[10,17a] or (ii) due to real enhancement of the ligand exchange by cod.

Since the equilibrium is largely shifted to the direction of Ni(cod)(bpy) (vide ante), the contribution of the reverse

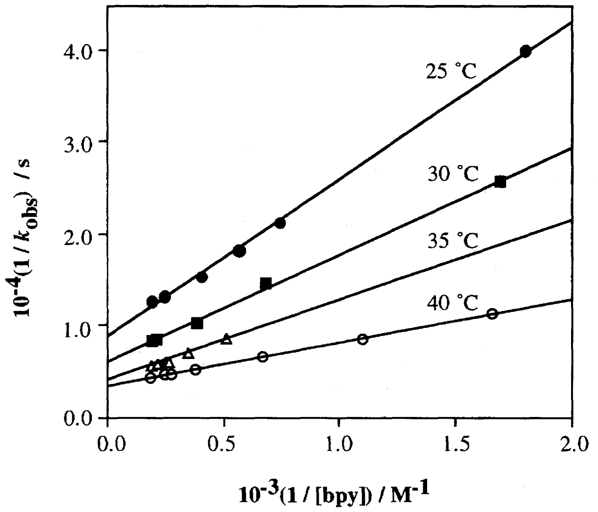


Fig. 4. Reciprocal plots of $1/k_{obs}$ against 1/[bpy]. [cod] = 0.044 M.

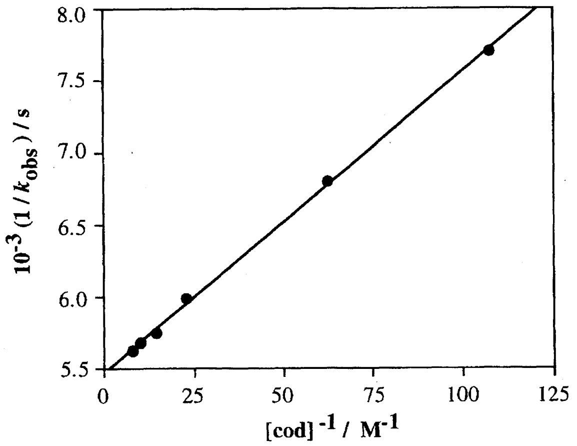
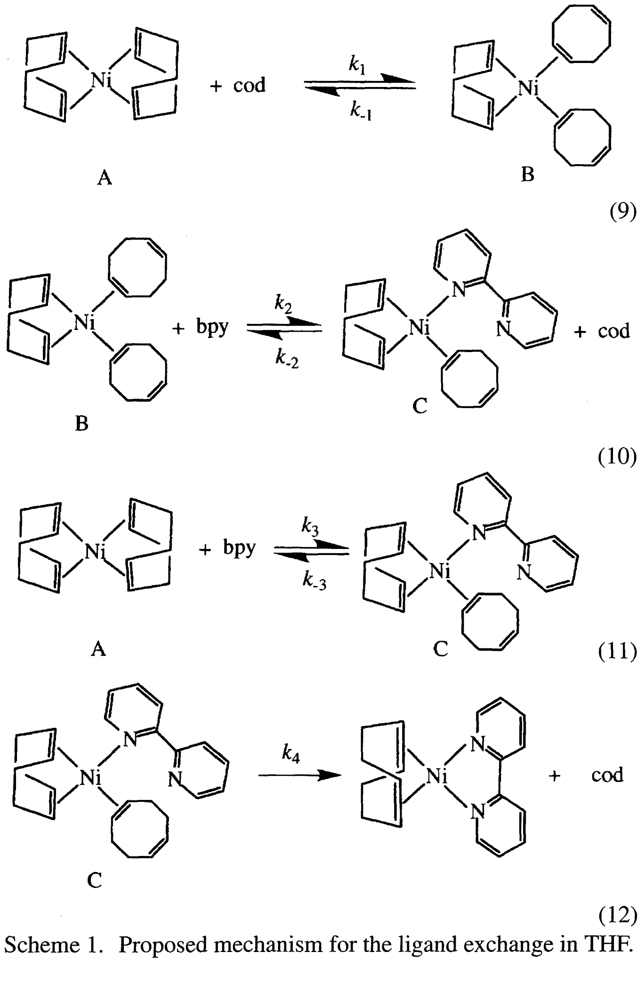


Fig. 5. Effect of added cod on the ligand exchange reaction of Ni(cod)$_2$ with bpy in THF at 40 °C. [bpy] = 2.72×10^{-3} M. Reciplocal plots are shown.

reaction is negligible.[17] In addition, the rate of the exchange reaction in the absence of cod was considerably slower.[18] On this basis, the following reaction mechanism is proposed (Scheme 1). It involves a cod-assisted formation of Ni(η^4-cod)(η^2-cod)$_2$, B (Eq. 9), replacement of the unidentate cod ligand by bpy to give an intermediate C (Eq. 10), and the eventual formation of Ni(cod)(bpy) (Eq. 12). Direct formation of the intermediate C by a direct reaction of A with bpy (Eq. 11) is also conceivable. In the processes shown by Eqs. 9 and 11, cod and bpy may interact with Ni(cod)$_2$ (A in Eq. 9) to afford a 20 e species such as Ni(η^4-cod)$_2$(η^2-cod) and Ni(η^4-cod)$_2$(η^1-bpy). Although Ni usually does not form such a 20 e species, several examples of the 20 e species are known.[19] The intermediacy of the 20 e species also seems important in the ligand exchange reaction in DMF described later.



Scheme 1. Proposed mechanism for the ligand exchange in THF.

By assuming steady-state conditions for the intermediates B and C, k_{obs} is given by the following equation:

$$k_{obs}=\frac{k_4(k_{-1}k_3+k_1k_2[\mathrm{cod}]+k_2k_3[\mathrm{bpy}])[\mathrm{bpy}]}{k_{-1}(k_{-3}+k_4)+k_{-1}k_{-2}[\mathrm{cod}]+k_2(k_{-3}+k_4)[\mathrm{bpy}]}. \tag{13}$$

At relatively low [bpy] and constant [cod], which corresponds to an assumption that the formation of the intermediate C proceeds mainly through Eqs. 9 and 10, $1/k_{obs}$ is approximated as

$$\frac{1}{k_{obs}}=\frac{1}{k_4}\left\{\frac{k_2(k_{-3}+k_4)}{k_{-1}k_3+k_1k_2[\mathrm{cod}]}+\frac{k_{-1}(k_{-3}+k_4)+k_{-1}k_{-2}[\mathrm{cod}]}{(k_{-1}k_3+k_1k_2[\mathrm{cod}])[\mathrm{bpy}]}\right\} \tag{14}$$

and the equation gives a linear relationship between $1/k_{obs}$ and 1/[bpy] agreeing with the data shown in Fig. 4. At high [cod], Eq. 14 is expressed by

$$\frac{1}{k_{obs}}=\frac{1}{k_4}\left\{\frac{k_2(k_{-3}+k_4)}{k_1k_2[\mathrm{cod}]}+\frac{k_{-1}k_{-2}}{k_1k_2[\mathrm{bpy}]}\right\} \tag{15}$$

and this equation is consistent with the data exhibited in Fig. 5.

The reaction mechanism and the rate equation indicate that the reaction proceeds at a higher velocity under the NMR and preparative conditions of Ni(cod)(bpy), which usually contain cod and bpy in higher concentrations. For example, following the ligand exchange reaction by the NMR spectroscopy reveals that the ligand exchange reaction proceeds to about 80% extent after 30 min, although the ligand exchange reaction proceeds only to about 12% extent after 30 min under the UV-vis conditions (e.g., the conditions given in Fig. 1).

Since the k_{obs} value is considered to be influenced by many factors, as expressed by Eq. 13, meaningful discussion about the effect of temperature on k_{obs} is difficult. An apparent Arrhenius activation energy of 52 kJ mol^{-1} is estimated from the temperature dependence of the k_{obs} value at [bpy] of 5.0×10^{-3} M, where the k_{obs} is approaching the limiting value.

Exchange with DMbpy and TMbpy. Addition of DMbpy or TMbpy also causes rises of three absorption bands assigned to the MLCT bands of the Ni(cod)(bpy) type complex in the UV-vis spectrum, similar to the case of bpy shown in Fig. 1. The positions of the emerging absorption bands of Ni(cod)(DMbpy)[16] and Ni(cod)(TMbpy) are listed in Table 1. The MLCT bands of the three kinds of complexes appear at almost the same respective positions.

The rates of the reaction also follow the first order kinetics with respect to [Ni(cod)$_2$] (Eq. 8), both for DMbpy and TMbpy, and k_{obs} values obtained at various concentrations

Table 1. Data of Electronic Absorption Spectra of the Ni(cod)(bpy) Type Complexes in THF and DMF

Compound	λ_{max}/nm (in THF)	λ_{max}/nm (in DMF)
Ni(cod)(bpy)	370 sh	365 sh
	565	563
	825 b	819 b
Ni(cod)(DMbpy)	380 sh	373 sh
	581	563
	860 b	850 b
Ni(cod)(TMbpy)	362 sh	362 sh
	566	560
	804 b	797 b

sh: shoulder peaks; b: broadened.

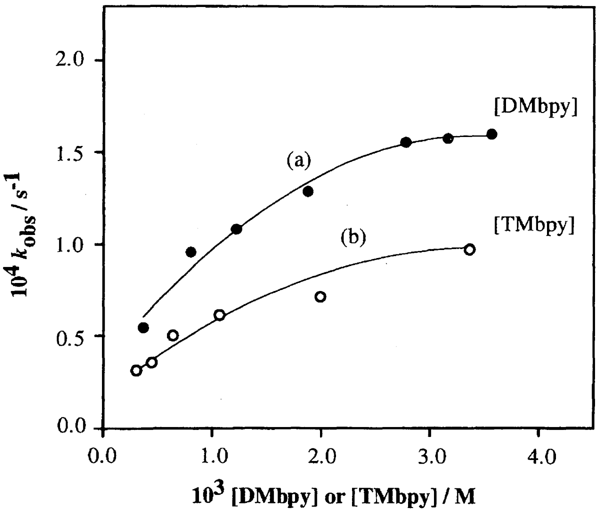


Fig. 6. Plots of k_{obs} vs. concentration of the exchanging ligand. (a): for DMbpy; [cod] = 0.07 M at 24.3 °C. (b): for TMbpy; [cod] = 0.044 M at 25 °C.

of the exchanging ligand are shown in Fig. 6. As shown in Figs. 4 and 6, bpy, DMbpy, and TMbpy have comparable reactivity toward the ligand exchange reaction.

3. Ligand Exchange in DMF. The C–C coupling reaction promoted by mixtures of Ni(cod)$_2$ and added neutral ligands proceeds well in DMF,[5—9] and the kinetic study of the ligand exchange reaction in DMF gives results different from those obtained in THF.

^{1}H NMR and UV-vis Data. The temperature dependent ^{1}H NMR spectrum of Ni(cod)$_2$ in DMF-d_7 in the absence or presence of added cod is essentially identical to that observed in THF-d_8. Following the reaction of Ni(cod)$_2$ with bpy in DMF-d_7 by NMR spectroscopy gave results analogous to those obtained in THF-d_8,[20] revealing that Ni(cod)(bpy) is the sole nickel complex formed by the ligand exchange and that the equilibrium is shifted to the direction of Ni(cod)(bpy) in DMF-d_7. UV-vis data also indicated that the equilibrium was shifted to the direction of Ni(cod)(bpy) in the final DMF solution obtained in the kinetic study (cf. Table 1).

4. Kinetic Study in DMF. Bpy. The ligand exchange reaction of Ni(cod)$_2$ with bpy in DMF gives rise to almost the same changes of the UV-vis spectrum as that in THF, and the positions of three new absorption peaks of Ni(cod)(bpy) essentially agree with those observed in THF.[21] The equilibrium (Eq. 5) is also shifted to the direction of Ni(cod)(bpy).

The first-order kinetic plot of the data obtained from the change of UV-vis spectrum during the ligand exchange reaction gives a straight line.

The pseudo first-order rate constant, k_{obs}, is comparable to k_{obs} obtained in THF at low [bpy], however, in the case of the reaction in DMF, the k_{obs} values increases proportionally with [bpy] even at high [bpy] as depicted in Fig. 7. Therefore, in a high [bpy] region, a much larger k_{obs} value is obtained in DMF than in THF.

$$\text{Rate of the reaction} = k[\text{Ni(cod)}_2][\text{bpy}]. \tag{16}$$

In addition, the rate of the reaction is independent of [cod] as shown in Fig. 7.

From these data, the following reaction mechanism, which includes the ligand exchange through an attack of DMF to Ni(cod)$_2$ (Eq. 17), is proposed. Cod and bpy may also directly attack Ni(cod)$_2$ as assumed in the reaction in THF (Eqs. 9 and 11), however, the attack (or interaction) of DMF seems predominant in DMF due to the fairly high coordinating ability of aldehyde to Ni[10] (Scheme 2).

Assumption of steady states for the intermediates B′ and C′ gives the following equation for k_{obs}:

$$k_{obs} = \frac{k'_1 k'_2 k'_3[\text{bpy}][\text{DMF}]}{k'_{-1}k'_3 + k'_{-1}k'_{-2}[\text{DMF}] + k'_2 k'_3[\text{bpy}]}. \tag{20}$$

At relatively low [bpy], Eq. 20 becomes

$$k_{obs} = \frac{k'_1 k'_2 k'_3[\text{DMF}]}{k'_{-1}k'_3 + k'_{-1}k'_{-2}[\text{DMF}]}[\text{bpy}], \tag{21}$$

which agree the results expressed by Eq. 16.

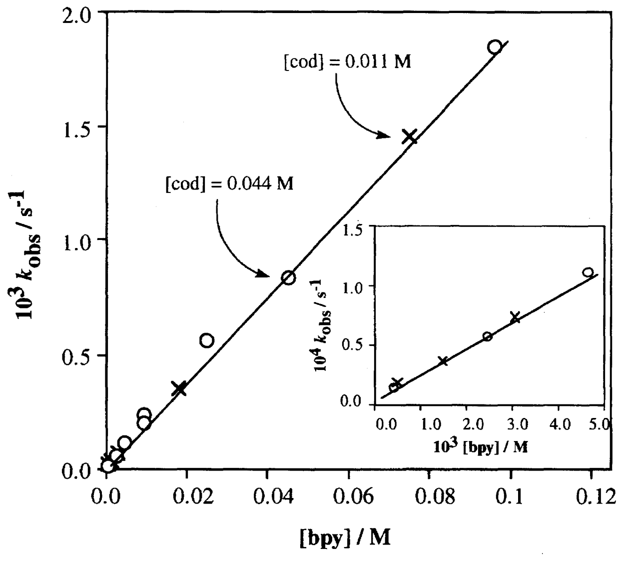
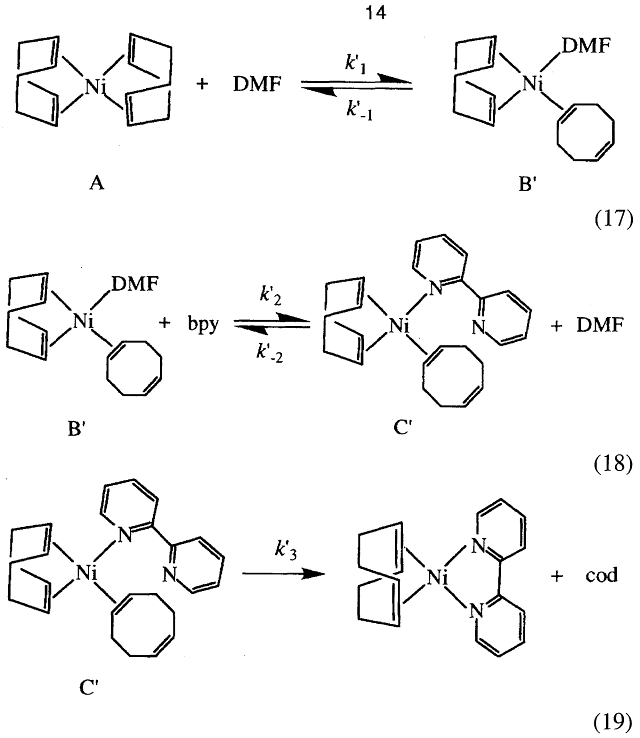


Fig. 7. Pseudo first-order rate constant k_{obs} vs. [bpy] at 25 °C. Solvent = DMF. [cod] = (○) 0.044 M or (×) 0.011 M. The inset shows the data for a low [bpy] region.

Table 2. Temperature Dependence of the Second-Order Rate Constant, *k*, and Kinetic Parameters for the Ligand Exchange Reactions of Ni(cod)$_2$ with bpy, DMbpy, and TMbpy in DMF [cod] = 0.044 M.

T/°C	bpy k/M^{-1} s^{-1}	DMbpy k/M^{-1} s^{-1}	TMbpy k/M^{-1} s^{-1}
25.0	2.41×10^{-2}	3.56×10^{-2}	8.73×10^{-2}
30.0	3.28×10^{-2}	6.20×10^{-2}	1.37×10^{-1}
35.0	4.68×10^{-2}	9.62×10^{-2}	2.27×10^{-1}
40.0	6.01×10^{-2}	1.48×10^{-1}	3.90×10^{-1}
E_a (kJ mol^{-1})	48.0	75.0	79.4
$\Delta H^\ddagger$ (kJ mol^{-1})	45.6	72.8	76.9
$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	-122.8	-28.5	-7.6
$\Delta G^\ddagger_{298}$ (kJ mol^{-1})	82.2	81.2	79.2



Scheme 2. Proposed mechanism for the ligand exchange in DMF.

According to Eq. 20, k_{obs} is to deviate from the linear dependence on [bpy] at high [bpy]. However, due to a limit of the solubility of bpy in DMF, such deviation was not observed under the experimental conditions.

DMbpy and TMbpy. The ligand exchange reactions of DMbpy and TMbpy in DMF, also obey the second order rate law expressed by Eq. 16. Table 2 summarizes the temperature dependence of the *k* value and kinetic parameters estimated from Arrhenius and Eyring plots.

As shown in Table 2, the *k* value increases in the order of bpy < DMbpy < TMbpy at 25 °C. However, the $\Delta H^\ddagger$ values suggest that bpy has the highest coordinating ability to form the intermediate C′ (Eq. 18) reflecting the strongest electron-accepting ability to stabilize the zerovalent nickel species. On the other hand, a negatively large activation entropy (cf. Table 2)[22] observed with bpy is considered to suppress the ligand exchange reaction.

Conclusion

The titled reactions have been studied kinetically by NMR and UV-vis spectroscopy. In the reactions of Ni(cod)$_2$ with bpy, DMbpy, and TMbpy, the Ni(cod)(bpy) type complexes are selectively formed under the reaction conditions. It was found that the equilibrium constants for the reaction of Ni(cod)$_2$ with bpy in both THF and DMF are large. In THF, added cod has an enhancement effect for the ligand exchange reaction, and the rate of the reaction levels off at high concentrations of cod and bpy. In DMF, the ligand exchange reaction obeys the second-order rate law and is independent of added cod. Based on these results, a mechanism involving attack of bpy, cod, and DMF to Ni(cod)$_2$ has been proposed. The ligand exchange reaction of Ni(cod)$_2$ with bpy gives a negatively large $\Delta S^\ddagger$ value in DMF. The obtained results are expected to contribute to better understanding of the organometallic and synthetic reactions using Ni(cod)$_2$.

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14) The solvent was not described.

15) a) Signals of H^b and H^c protons of cod coordinated to transition metals (e.g., MCl(cod)(PPh_3) (M = Rh, Ir)15b) and Ni(cod)(bpy)) often give their signals at considerably different positions from each other, however, H^b and H^c in $Ni(cod)_2$ seem to give their signals at close positions to show the overlapped multiplet at $\delta = 2.1$. In toluene-d_8, $Ni(cod)_2$ gives rise to essentially the same ^1H NMR data at various temperatures with and without added cod, although the H^b+H^c signal appears as a sharp singlet in toluene-d_8 presumably due to coincidence of the chemical shifts for the two protons; b) K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organomet. Chem.*, **14**, 185 (1968).

16) E. Dinjus and D. Walther, *Z. Chem.*, **21**, 270 (1981); data in benzene for Ni(cod)(bpy) (17240 cm^{-1} or 580 nm) and Ni(cod)(DMbpy) (17320 cm^{-1} or 577 nm) were reported in the literature.

17) a) For a simple equilibrium system,

$$A \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} B,$$

the k_{obs} is given by the sum of k_1 and k_{-1}: $k_{obs} = k_1 + k_{-1}$ (k_1/k_{-1} = equilibrium constant).10) For example, if k_1 and k_{-1} increase proportionally with [bpy] and [cod] for the present system, a simple relation like $k_{obs} = k_1[\mathrm{bpy}] + k_{-1}[\mathrm{cod}]$ may be derived. In this case, k_{obs} increases with increase in [cod]. However, when the equilibrium is shifted to the right (e.g., $k_{-1} \ll k_1$ or $k_{-1}[\mathrm{cod}] \ll k_1[\mathrm{bpy}]$ in the above shown equilibrium), the contribution ($k_{-1}[\mathrm{cod}]$) from the reverse reaction can be ignored; b)The reverse reaction, Ni(cod)(bpy)+cod → $Ni(cod)_2$+bpy, was actually very slow as monitored by the UV-visible spectroscopy.

18) Satisfactory kinetic analysis in the absence of excess cod was not feasible due to a change of [cod] during the reaction and instability of the nickel complexes in the absence of cod.

19) E.g., a) J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J.Chem. Soc. A*, **1971**, 448; b) T. Yamamoto and Y. Sekine, *Inorg. Chim. Acta*, **83**, 47 (1984); c) K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka, and Y. Sasada, *Acta Crystallogr., Sect. C*, **C40**, 85 (1984); d) T. L. James, D. M. Smith, and R. H. Holm, *Inorg. Chem.*, **33**, 4869 (1994).

20) Broadening of the signal of H at 6-position of free bpy in the mixture in DMF-d_7 was observed.

21) A small additional peak at 440 nm, which may be assigned to partly formed $Ni(bpy)_2$, is observed at the high concentration of bpy ([bpy] > 0.02 M).

22) The negatively large activation entropy ($\Delta S^{\ddagger}$) observed with bpy may originate from strong coordination of bpy to Ni in the intermediate C′ (so-called "compensation effect") and changes in the solvation state of bpy and $Ni(cod)_2$ with DMF.