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Activation of Iron-Alkyl Bonds in Dialkylbis(dipyridyl)iron(II) by Interaction with Olefins

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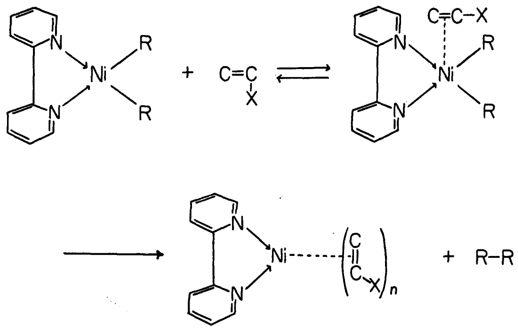
The reactions of dialkylbis(dipyridyl)iron(II) **1** with various substituted olefins were studied. Tetracyanoethylene, maleic anhydride, and acrylamide gave olefin-coordinated π-complexes on reactions with **1**, whereas other vinyl monomers with relatively large e-values were polymerized by the alkyl-iron complex. Kinetic study of the reactions of **1** with olefins by a spectroscopic method revealed that the reaction rate can be expressed by

$$-\frac{\mathrm{d}[\mathrm{FeR_2(dipy)_2}]}{\mathrm{d}t}=\frac{[\mathrm{olefin}][\mathrm{FeR_2(dipy)_2}]}{A+B[\mathrm{olefin}]+C[\mathrm{dipy}]}.$$

On the basis of kinetic results and from comparison with the reactions of dialkyl(dipyridyl)nickel with olefins, a mechanism involving partial dissociation of the dipyridyl ligand from **1**, followed by a coordination of the olefin and activation of a Fe-alkyl bond was proposed.

Transition metal-alkyl complexes are generally considered to be the active species in various catalytic reactions involving olefins such as polymerization with Ziegler type catalysts, hydroformylation, hydrogenation, isomerization, and oligomerization[1]. Instability of the transition metal-alkyl bond usually makes isolation of the alkyl complexes difficult, thus hindering a detailed study of the interaction of olefins with the alkyl complexes, a crucial step in catalyses. From Ziegler type catalyst systems we have isolated transition metal-alkyl complexes, the metal alkyl bonds of which are stabilized by the presence of a ligand dipyridyl[2]. These alkyl complexes are very stable and prove to be particularly suitable for studying the mechanism of activation of the metal-carbon bond by coordination of olefins[3],[4]. In some cases the reactions of some olefins with the alkyl complexes lead to polymerization[5] while in other cases a scission of the metal-alkyl bonds yielding metal-olefin π-complexes resulted[3]. We previously studied the reactions of dialkyldipyridylnickel with various olefins in detail[3] and found that the essential feature of the reactions of the nickel complex can be expressed by the following scheme.



(1)

The rate of the reaction is given by the equation

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[1] a) M. L. H. Green, "Organometallic Compounds, Vol. 2, The Transition Elements," Methuen and Co. Ltd., London (1968); b) P. Cossee, *J. Catal.*, **3**, 80 (1964).

[2] a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965); b) *ibid.*, **90**, 1878, (1968); c) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Organometal. Chem.*, **6**, 572 (1966); d) *J. Amer. Chem. Soc.*, **88**, 5198 (1966).

[3] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3350, 3360 (1971).

[4] A general term "olefin" is used throughout this series of papers including a substituted olefin.

[5] A. Yamamoto, T. Shimizu, and S. Ikeda, *Makromol. Chem.*, **136**, 297 (1970).

Table 1. Reaction of $\mathrm{FeEt_2(dipy)_2}$ with olefins

Olefin	*e*-value[7]	Results	Shifts of IR bands
Tetracyanoethlene (TCNE)		Dark brown solid $(\mathrm{Fe(dipy)_2(TCNE)_2})$	$\nu_{\mathrm{C\equiv N}}$ 2220 → 2110 cm^{-1}
Maleic anhydride (MAH)	2.25	Red solid $(\mathrm{Fe(dipy)(MAH)_4})$	$\nu_{\mathrm{C=O}}$ 1780 → 1780∼1730 cm^{-1}
Acrylamide (AcAm)	1.30	Reddish brown solid $(\mathrm{Fe(AcAm)_2}$?)	$\nu_{\mathrm{N-H}}$ 3370 → 3280 cm^{-1} $\nu_{\mathrm{C=O}}$ 1670 → 1660 cm^{-1}
Acrylonitrile (AN)	1.20	Polymerization took place.	
Methacrylonitrile (MAN)	0.81	Polymerization took place.	
Acrolein (AC)	0.73	Polymerization took place.	
Methyl vinyl ketone (MVK)	0.69	Polymerization took place.	
Methyl acrylate (MA)	0.60	Polymerization took place.	
Methyl methacrylate (MMA)	0.40	Polymerization took place.	
Vinyl chloride (VCl)	0.20	Dark red solid	
Vinyl acetate (VAc)	−0.22	Reddish purple solid $(\mathrm{Fe(dipy)(Vac)_2})$	$\nu_{\mathrm{C=O}}$ 1800∼1730 → 1600∼1560
2-Vinylpyridine (2-Vi-Py)	−0.50	Polymerization took place.	
Styrene (St)	−0.80	No apparent change was observed.	
Isobutyl vinyl ether (IBVE)	−1.77	No apparent change was observed.	
Ethylene (E)		No apparent change was observed.	

$$r = -\frac{d[\mathrm{NiR_2(dipy)}]}{dt} = k_{\mathrm{Ni}}[\mathrm{NiR_2(dipy)}][\mathrm{olefin}] \qquad (2)$$

In contrast to the alkyl-nickel complex which does not initiate vinyl polymerization in the absence of oxygen, dialkylbis(dipyridyl)iron(II) (**1**) initiates the polymerization of some vinyl compounds and gives iron-olefin π-complexes. In this paper we report the results of preparative and spectroscopic studies of the reactions of $\mathrm{FeR_2(dipy)_2}$ **1** with various olefins. The propagation mechanism in the polymerization of methyl methacrylate was discussed in a previous paper.[6]

Results and Discussion

Alkyl-iron complex **1** is fairly stable in the solid state but decomposes slowly in solution at room temperature. The methyl and ethyl complexes begin to decompose at about 95°C and the propyl complex at about 80°C when heated in the absence of solvent. Pyrolysis of the methyl complex released mainly methane, the ethyl complex ethane (65%) and ethylene (35%) and the propyl complex propane (60%) and propylene (40%). The compositions of the evolved gases differ from those of the pyrolysis products of $\mathrm{NiR_2(dipy)}$ which gave ethane from the methyl complex, butane from the ethyl complex and propane and propylene from the propyl complex. The rates of pyrolysis of the solid alkyl-iron complexes[3] are proportional to the amounts of remaining **1**. The activation energy for the pyrolysis of $\mathrm{Fe(CH_3)_2(dipy)_2}$ was estimated to be 23 kcal/mol, $\mathrm{Fe(C_2H_5)_2(dipy)_2}$ 47—54 kcal/mol and $\mathrm{Fe(\mathit{n}\text{-}C_3H_7)_2(dipy)_2}$ 16 kcal/mol. The variation of gaseous decopmosition products and of activation energies of the pyrolysis of the three alkyl-iron complexes suggest that the mechanism of pyrolysis in solid state is not simple.

The results of the reactions of **1** with various olefins are summarized in Table 1. Olefins are arranged in the decreasing order of Alfrey-Price's *e*-value which is considered to reflect the electronegativity of the olefin.[7] Except for the top three olefins, the olefins with large *e*-values were polymerized by **1**. The α,β-disubstituted olefins such as tetracyanoethylene (TCNE) and maleic anhydride (MAH) gave complexes containing a part of the dipyridyl ligands. The ethyl groups were absent in these complexes as proved by IR spectroscopy and methanolysis. Acrylamide has exceptionally high reactivity toward the iron complex and displaces both of the dipyridyl ligands. A similar behavior was observed in other cobalt-dipyridyl[8a] or phosphine complexes[8b]. In the case of vinyl chloride, C–Cl bond was cleaved and a complex of an approximate composition $\mathrm{Fe(dipy)_2Cl_2}$ was obtained. With vinyl acetate (VAc) the iron complex gave a reddish purple solid with composition $\mathrm{Fe(dipy)(VAc)_2}$ with extraordinarily low $\nu_{\mathrm{C=O}}$ bands as compared with those of the free vinyl acetate. The vinyl acetate may be coordinated with iron through both double bond and the carbonyl group as in the case of nickel-vinyl acetate complex[3]. In most cases where olefin-coordinated iron complexes were obtained, purification of the complexes was difficult and the solid complexes appear to be mixtures of $\mathrm{Fe(dipy)}_x\mathrm{(olefin)}_y$ with different x and y values depending on the relative coordinating abilities of the dipyridyl and the olefin.

With olefins of large negative *e*-values no apparent reaction was observed, although spectral study revealed slow decomposition of **1** in some cases. Among olefins 2-vinylpyridine is exceptional in yielding a high polymer initiated by the alkyl-iron complex. As

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[6] A. Yamamoto, T. Shimizu, and S. Ikeda, *Polymer Journal* (Japan.), **1**, 171 (1970).

[7] J. Brandrup and E. H. Immergut, "Polymer Handbook," II-341, Interscience Publishers, New York, London, Sydney (1966).

[8] a) A. Yamamoto, T. Yamamoto, and S. Ikeda, unpublished result; b) A. Yamamoto, Y. Kubo, and S. Ikeda, unpublished result.

in the case of vinyl acetate 2-vinylpyridine may coordinate to iron through both the double dond and the nitrogen of the pyridine ring, thus causing greater enhancement of the reactivity of the alkyl-iron bond.

Kinetics of Decomposition of $FeR_2(dipy)_2$ *in Solution.* On reactions of $FeR_2(dipy)_2$ with olefins, the deep blue color of the initial solutions turns brown or reddish brown both in polymerization and dealkylation reactions. The color change is considered to reflect the decomposition of the original complex, and the decomposition reaction was followed spectroscopically. As an example of the spectral study, the change of the electronic spectrum of $Fe(C_2H_5)_2(dipy)_2$ in solvents on addition of acrylonitrile is given in Fig. 1. The iron complex **1** decomposes very slowly in tetrahydrofuran even in the absence of olefin (*vide infra*), but the rate of decomposition is strikingly accelerated by the addition of olefins and the decomposition rate in the absence of olefins can be regarded negligible as compared with that in the presence of olefins.

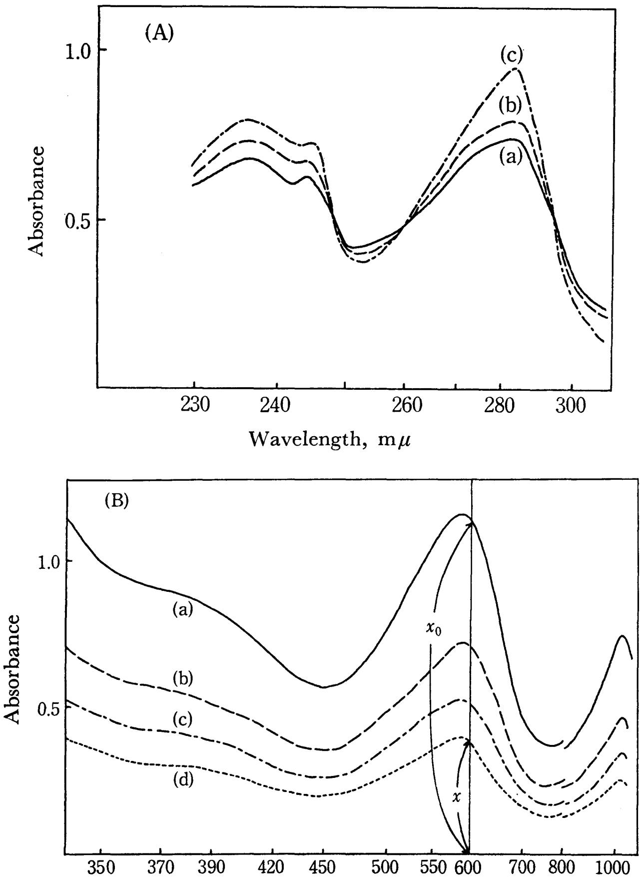


Fig. 1. Change of the ultraviolet (A) and visible spectra (B) of $Fe(C_2H_5)_2(dipy)_2$ by addition of acrylonitrile; (A) in diethyl ether at 24.3°C, [acrylonitrile]$=1.5\times10^{-3}$ M, (a) 0 min, (b) 2.5 min, (c) 18 min,; (B) in tetrahydrofuran at 23.4°C, [acrylonitrile]$=1.0\times10^{-3}$ M, (a) 0 min, (b) 3 min, (c) 6 min, (d) 9 min.

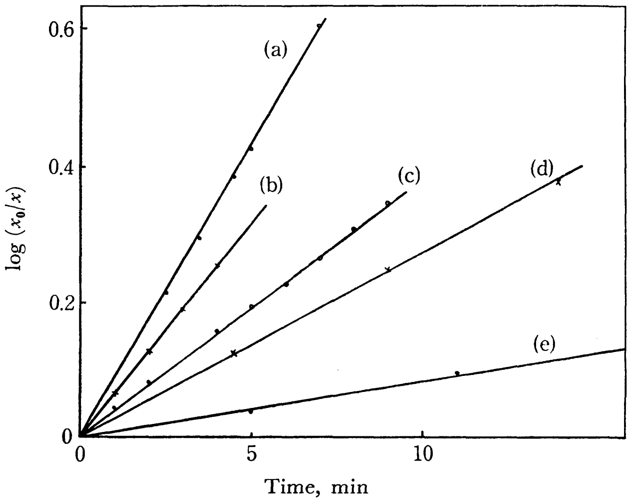


Fig. 2. Plots of log (x_0/x) (*cf.* Fig. 1) against time. (a): methyl acrylate (MA), 0.43 M, 22°C; (b): acrylonitrile (AN), 1.7×10^{-3}M, 22°C; (c): methyl vinyl ketone (MVK), 4.6×10^{-3}M, 23°C; (d): methacrylonitrile (MAN), 5.0×10^{-3}M, 23°C; (e): methyl methacrylate (MMA), 0.21 M. 24°C. solvent=tetrahydrofuran.

We assigned the two couples of absorption band of $Fe(C_2H_5)_2(dipy)_2$ **1** in UV (237, 282 mμ) and visible rgeions (590, 1010 mμ) to $\pi\rightarrow\pi^*$ excitation bands ($\varepsilon=2\times10^4$) and $d\rightarrow\pi^*$ charge-transfer bands ($\varepsilon=3\times10^3$)[3]. Since the final solution does not absorb at 600 mμ after the reaction, we measured the rate of decomposition of **1** by observing the decrease of the absorbance at 600 mμ. The plots of log (x_0/x) values in Fig. 1 against time give linear relationships for various olefins (Fig. 2). The pseudo-first-order rate constants k were calculated from the slopes of the lines.

Rate of decomposition =

$$-\frac{d[Fe(C_2H_5)_2(dipy)_2]}{dt}=k[Fe(C_2H_5)_2(dipy)_2] \qquad (3)$$

Figure 3 indicates the variation of k with the concentrations of olefins. The k values change with the olefin concentration at low concentrations of olefin but level off at higher concentrations and approach a limiting value independent of the olefins. In the case of isobutyl vinyl ether (IBVE) k does not reach the limiting value even in bulk because of a very weak interaction of isobutyl vinyl ether with the iron com-

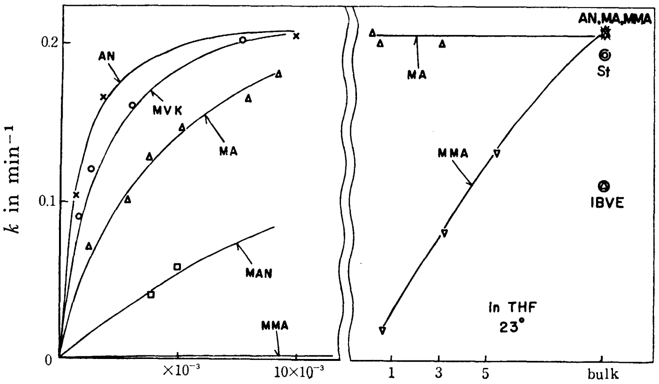


Fig. 3. Pseudo-first-order rate constant k *versus* concentration of olefin at 23°C; solvent=tetrahydrofuran. AN=acrylonitrile, MVK=methyl vinyl ketone, MA=methyl acrylate, MAN=methacrylonitrile, MMA=methyl methacrylate, St=styrene, and IBVE=isobutyl vinyl ether.

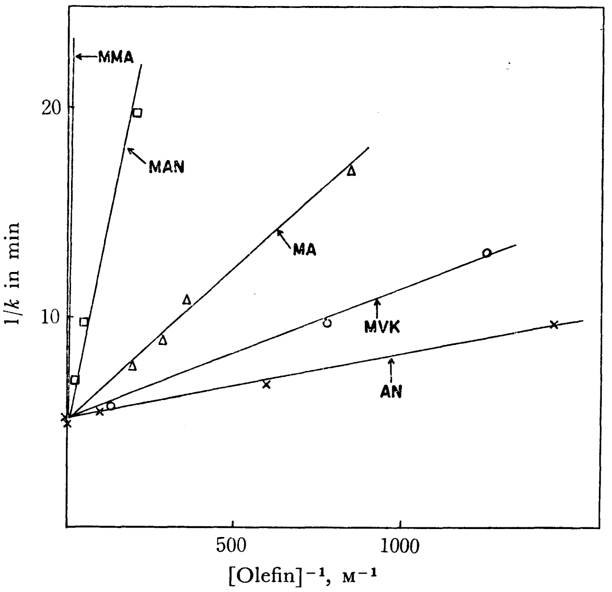


Fig. 4. The reciprocal plot for the data shown in Fig. 3.

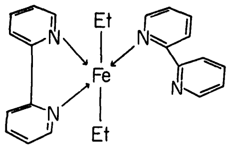
plex. The pattern as shown in Fig. 3 suggests an S_N1 mechanism. A similar pattern has been observed in the reaction of methyl manganese pentacarbonyl with nucleophiles.[9] The reciprocal plots of k against olefin concentrations give linear relationships as shown in Fig. 4. The results can be explained by assuming the following three-stage mechanism.

$$\underset{\mathbf{1}}{\mathrm{Fe(C_2H_5)_2(dipy)_2}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{2}}{\mathrm{Fe(C_2H_5)_2(dipy)(dipy)^*}} \tag{4}$$

$$\mathbf{2} + \text{olefin} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\mathbf{3}}{\mathrm{Fe(C_2H_5)_2(olefin)(dipy)(dipy)^*}} \tag{5}$$

$$\mathbf{3} \xrightarrow{k_3} \text{decomposition products} \tag{6}$$

Since the initial complex $\mathrm{Fe(C_2H_5)_2(dipy)_2}$ is coordinatively saturated and the kinetic results suggest an S_N1 mechanism, it is reasonable to assume a partial dissociation of dipyridyl ligands from **1** to make a coordination site available for the incoming olefin molecule. $\mathrm{Fe(C_2H_5)_2(dipy)(dipy)^*}$ represents a partially dissociated species which may have a structure as shown below[10,11].



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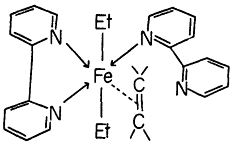

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The complex may be either five-coordinated or have a solvent molecule in the sixth coordination position.

For complex **3** we assume an iron complex with an olefin coordinated through the double bond in analogy with that we observed in $\mathrm{Ni(C_2H_5)_2(dipy)(olefin)}$.[3] The steady state approximation for the concentrations of **2** and **3** yields the rate equation:

$$\text{Rate} = -\frac{d[\mathrm{Fe(C_2H_5)_2(dipy)_2}]}{dt} = k_3[\mathbf{3}]$$

$$= \frac{k_1k_2k_3[\text{olefin}][\mathrm{Fe(C_2H_5)_2(dipy)_2}]}{k_{-1}(k_{-2}+k_3)+k_2k_3[\text{olefin}]} \tag{7}$$

The observed pseudo-first-order rate constant k is given by

$$k = \frac{k_1k_2k_3[\text{olefin}]}{k_{-1}(k_{-2}+k_3)+k_2k_3[\text{olefin}]} \tag{8}$$

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}(k_{-2}+k_3)}{k_1k_2k_3[\text{olefin}]} \tag{9}$$

The linear relationships between $1/k$ and $1/[\text{olefin}]$ and convergence of plots for different olefins into a single intercept as shown in Fig. 4 are in line with Eq. (9). Intercept $1/k_1$ is a function only of **1** and not of olefin. If we assume the partial dissociation of complex **1** into **2**, the frequency of dissociation can be estimated to be about 0.2/min. If we assume $k_{-2} \gg k_3$, as we observed in the decomposition of the olefin coordinated $\mathrm{Ni(C_2H_5)_2(dipy)}$,[3] the reciprocal of the slope becomes $(k_1k_2k_3/k_{-1}k_{-2})$. Since the values k_1 and k_{-1} are functions only of the iron complexes **1** and **2** and not of olefin, the value $k_1k_2k_3/k_{-1}k_{-2}$ is proportional to the relative reactivity of olefin.

Concerning activation of Ni–R bonds by coordination of olefins we observed that electronegative olefins activate the Ni–R bonds more strongly than less electronegative olefins and that the rate constants (k_{Ni}) for decomposition of $\mathrm{NiR_2(dipy)}$ are larger in reactions of $\mathrm{NiR_2(dipy)}$ with more electronegative olefins. If we assume a similar mechanism of activation for the Fe–Et bond as in Eqs. (5) and (6), we can expect a parallel relation between the k_{Ni} value for the ethyl-nickel complex and the $k_1k_2k_3/k_{-1}k_{-2}$

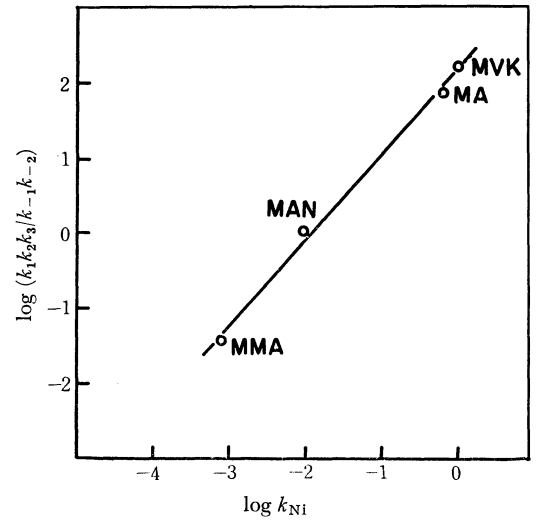

Fig. 5. Plot of log $(k_1k_2k_3/k_{-1}k_{-2})$ obtained from the reciprocal slopes of the lines in Fig. 4 against $\log k_{\mathrm{Ni}}$ where k_{Ni} is a rate constant for the decomposition of $\mathrm{NiEt_2(dipy)}$.[3]

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[9] B. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 3994 (1964).

[10] A similar species was assumed in an acid-catalyzed replacement of a dipyridyl ligand from $\mathrm{Fe(dipy)_3^{2+}}$, F. Basolo, J. C. Hayes, and H. M. Neuman, *J. Amer. Chem. Soc.*, **75**, 5102 (1953).

[11] This is a partial revision of our mechanism[5,6] in which complete dissociation of one dipyridyl ligand was postulated.

value for the ethyl-iron complex. Figure 5 clearly demonstrates that a similar factor operates both in the activation of the nickel–ethyl and iron–ethyl bonds.

1 is stable in the solid state, but slowly decomposes in solution with evolution of ethane and ethylene even in the absence of olefins. The composition of the dark violet decomposition product obtained approximately agreed with the structure Fe(dipy)$_2$.[2b] The ethyl-iron bonds and hydrogen-iron bond, which might be formed through a hydrogen extraction from the ethyl group by iron, were not detected in the decomposition product. The decomposition rate depends on the nature of the solvent as shown in Fig. 6. The decomposition rate was higher in a solvent of greater coordinating ability. Decomposition was not detectable in diethyl ether and *n*-hexane.

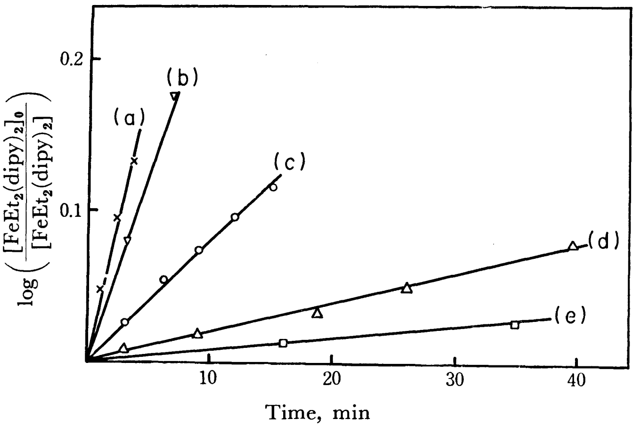


Fig. 6. Decomposition of Fe(C$_2$H$_5$)$_2$(dipy)$_2$ in solvents. (a): acetonitrile, 24.6°C; (b): dimethylformamide (DMF), 24.6°C; (c): Acetone, 23.5°C; (d): DMF, 22.4°C, containing dipyridyl (0.0137 M); (e): tetrahydrofuran, 25.6°C.

We observed a blue shift of the charge-transfer bands of Ni(C$_2$H$_5$)$_2$(dipy) in solvents of strong coordinating ability, and explained this shift as the lowering of the energy of the *d*-orbitals of nickel through the coordination of solvent[3]. We have further postulated that an electron excitation from a σ_{Ni-C} orbital to a vacant *d*-orbital of nickel is a necessary step for the activation of the Ni–C bond. In the case of Ni(C$_2$H$_5$)$_2$(dipy), however, the lowering of the *d*-level by coordination of the solvent was not sufficient to induce scission of the very stable Ni–C bond, whereas olefins with electronegative substituents caused the scission. If we assume that a similar factor operates in determining the activation of the iron-carbon as in nickel-carbon bond and take a smaller activation energy for the pyrolysis of Fe(C$_2$H$_5$)$_2$(dipy)$_2$ (about 50 kcal/mol) compared with the one for the corresponding ethyl-nickel complex (68 kcal/mol) into account, the easier scission of the Fe–Et bond in strongly coordinating solvents can be explained by the lowering of the energy of the vacant *d*-orbital of the iron complex. The decomposition rates of **1** in solvents are proportional to the concentration of **1** (Fig. 6). The decreasing order of the first-order rate constants was in line with that of the magnitude of the blue shifts of Ni(C$_2$H$_5$)$_2$(dipy) caused by coordination of solvents: acetonitrile>dimethylformamide>acetone>tetrahydrofuran>ether, *n*-hexane.

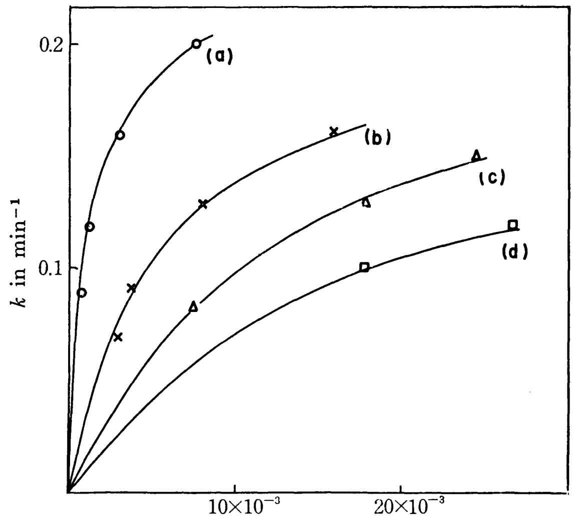


Fig. 7. Effect of the concentration of dipyridyl added on the pseudo-first-order rate constant k for the decomposition of FeEt$_2$(dipy)$_2$ in tetrahydrofuran at 23°C. (a): [dipy] = 0 mol/l, (b): 1.4×10^{-3} mol/l, (c): 2.31×10^{-3} mol/l, (d): 3.88×10^{-3} mol/l.

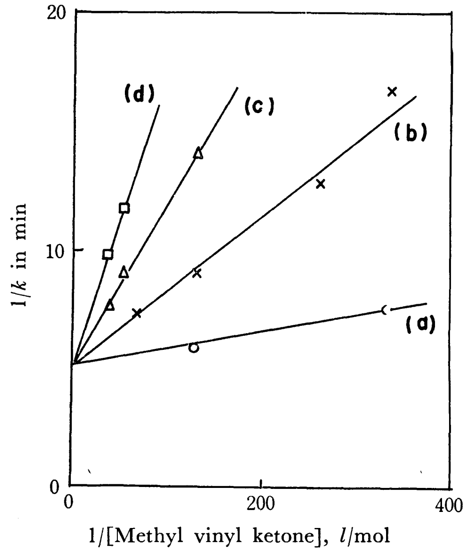
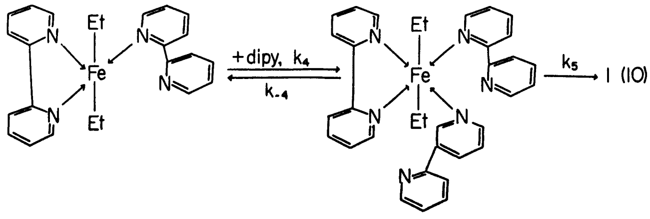


Fig. 8. The reciprocal plot for the data shown in Fig. 7.

Addition of dipyridyl to the reaction systems hinders the decomposition of Fe(C$_2$H$_5$)$_2$(dipy)$_2$ in the absence of olefin (Fig. 6, curve (d)) as well as in the presence of olefins (Fig. 7). The decomposition rates are still proportional to concentrations of Fe(C$_2$H$_5$)$_2$(dipy)$_2$. Figure 8 shows $1/k$ *versus* 1/[olefin] plots for the data shown in Fig. 7. Since the intercept is common to all lines in Fig. 8, the effect of dipyridyl can be explained in terms of a competitive coordination of dipyridyl with olefin and solvent to **2** to form a complex **4** which may be in equilibrium with **2**. Complex **4** may be converted directly into **1** through the process given below:



2 **4**

Using the steady-state approximation for concentrations of the intermediate complexes **2**, **3** and **4**, we get the rate equation:

$$\text{Rate} = -\frac{d[\text{FeEt}_2(\text{dipy})_2]}{dt} = k_3[\mathbf{3}]$$

$$= \frac{k_1k_2k_3[\text{olefin}][\text{FeEt}_2(\text{dipy})_2]}{k_{-1}(k_{-2}+k_3)+k_2k_3[\text{olefin}]+\dfrac{k_4k_5(k_{-2}+k_3)[\text{dipy}]}{k_{-4}+k_5}} \tag{11}$$

When k_{-2} is much greater than k_3, the observed pseudo-first-order rate constant k is given by:

$$k = \frac{k_1k_2k_3[\text{olefin}]}{k_{-1}k_{-2}+k_2k_3[\text{olefin}]+\underline{k}[\text{dipy}]} \tag{12}$$

where $\underline{k}=k_{-2}k_4k_5/(k_{-4}+k_5)$. The plots of $1/k$ against $1/[\text{olefin}]$ with varying concentrations of dipyridyl added (Fig. 8) substantiate the validity of Eq. (12). The intercept of the lines is $1/k_1$ and the slopes are $(k_{-1}k_2+\underline{k}[\text{dipy}])/k_1k_2k_3$. The effect of variation of the added dipyridyl concentration on the slopes in Fig. 8 is shown in Fig. 9. The linear relationship confirms Eq. (12).

The intercepts of the lines in Fig. 9 represent $k_{-1}k_{-2}/k_1k_2k_3$ values in the absence of added dipyridyl and the slopes $\underline{k}/k_1k_2k_3$. The results are in line with the postulated mechanism expressed by Eqs. (4), (5), (6), and (10), where spontaneous partial dissociation of dipyridyl forming **2** and the succeeding competitive coordination of olefin, solvent, and dipyridyl to **2** are assumed.

When a very polar solvent was employed in place of tetrahydrofuran and extra dipyridyl was not added to the solution, $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{dipy})_2$ decomposed at an appreciable rate even in the absence of olefin. Accordingly we could not obtain the k *versus* [olefin] relationship as shown in Fig. 3 in the polar solvent with no dipyridyl in the solution. When extra dipyridyl was added to the solution, the decomposition of $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{dipy})_2$ caused by the interaction of the polar solvent was hindered and the normal k *versus* [olefin] pattern was obtained.

With $\text{Fe}(\text{CH}_3)_2(\text{dipy})_2$ and $\text{Fe}(n\text{-C}_3\text{H}_7)_2(\text{dipy})_2$, similar kinetic patterns as in Fig. 3 have been obtained. The liniting k_1 values with the series of $\text{FeR}_2(\text{dipy})_2$ were 0.27 min^{-1} for the propyl, 0.21 for the ethyl, and 0.013 for the methyl complexes. We previously found a linear relation between the inductive effect of the alkyl groups and the highest occupied energy level of $\text{NiR}_2(\text{dipy})_2$, and discussed the influence of the alkyl groups on the reactivity of the complexes.3) We see a similar linear relation between the rate constant k_1 and σ^* value proposed by Taft12) in Fig. 10. The decrease in the partial dissociation rate of one dipyridyl ligand influenced by the decrease of the inductive effects of the alkyl groups is understandable if the decreasing stability of amine complexes with decreasing electronegativity of a transition metal13) is taken into account.

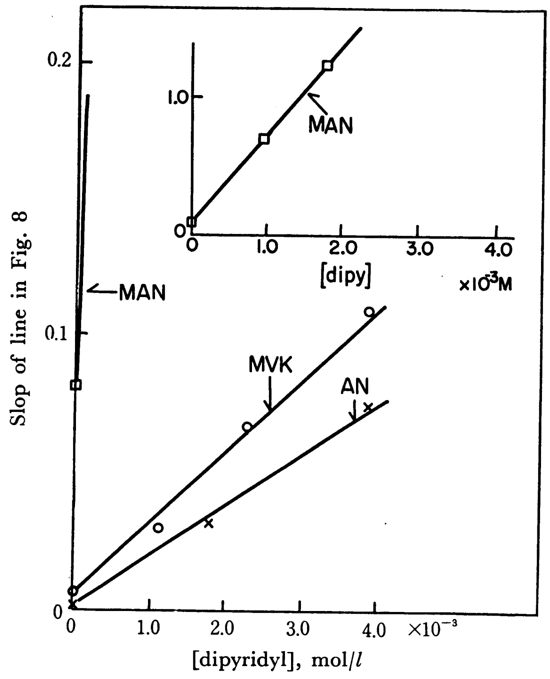


Fig. 9. Plot of the slopes of lines in Fig. 8 against the dipyridyl concentration, (○) for methyl vinyl ketone; analogous plots for methacrylonitrile (□) and acrylonitrile (×).

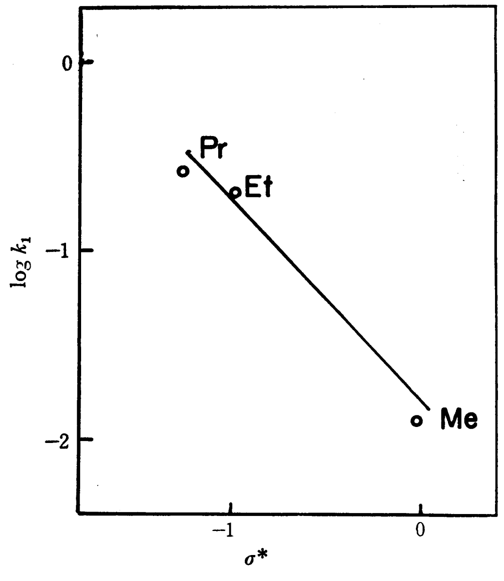


Fig. 10. Relation between the rate constant k_1 and σ^*.

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13) a) D. P. Graddon, "An Introduction to Co-ordination Chemistry," Pergamon Press Ltd. Oxford, London, (1961); b) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reaction, Second Edition," John Wiley and Sons, Inc., New York, London, Sydney (1968).

Experimental

I. Materials and General Procedures. $Fe(C_2H_5)_2(dipy)_2$ was prepared by the method reported previously.[2] $Fe(CH_3)_2(dipy)_2$ and $Fe(C_3H_7)_2(dipy)_2$ were prepared in an analogous way. Found: C, 65.8; H, 5.73; N, 13.8%. Calcd for $C_{22}H_{22}N_4Fe$: C, 66.3; H, 5.57; N, 14.1%. Found: C, 67.8; H, 6.65; N, 12.2%. Calcd for $C_{26}H_{30}N_4Fe$: C, 68.8; H, 6.61; N, 12.3%. Olefins and solvents were purified and stored, and general procedures and techniques were almost the same as previously reported.[3] Because of the lack of suitable procedures for purification, some complexes can not be claimed very pure. However, structures which are consistent with the analytical data are given.

II. Reactions of $Fe(C_2H_5)_2(dipy)_2$ with Olefin and Isolations of Olefin-Coordinated Iron Complexes. *1. Tetracyanoethylene (TCNE)*: Ether (10 m*l*) was distilled in a vacuum into a reaction vessel containing 1.58 g of $Fe(C_2H_5)_2(dipy)_2$ (3.7 mmol) and 1.52 g of tetracyanoethylene (12 mmol). The mixture was allowed to react at room temperature for a day. The composition of the gas evolved was ethane, ethylene, and butane in a molar ratio of 1 : 1 : 0.1. The dark brown precipitate was filtered, washed many times with ether, and dired in a vacuum. The dark brown solid was insoluble in almost all organic solvents. The yield of the solid was almost quantitative. Found: C, 59.3; H, 2.16; N, 25.4%. Calcd for $Fe(dipy)_2(TCNE)_2$: C, 61.4; H, 2.56; N, 26.9%.

2. Maleic anhydride (MAH): A mixture of 0.60 g (1.4 mmol) of $Fe(C_2H_5)_2(dipy)_2$ and 4.2 g (43 mmol) of maleic anhydride in 10 m*l* of ether was allowed to react at room temperature for 20 hr. The gas evolved consisted of ethane, ethylene, and butane in a molar ratio of 0.1 : 1 : 1. The red solid was filtered, washed many times with ether and dried in a vacuum. The yield was almost quantitative. Found: C, 51.1; H, 2.52; N, 3.97%. Calcd for $Fe(dipy)(MAH)_4$: C, 51.5; H, 2.64; N, 4.61%.

3. Acrylamide (AcAm): A mixture of 0.38 g (0.89 mmol) of $Fe(C_2H_5)_2(dipy)_2$ and 2.0 g (28 mmol) of acrylamide in 40 m*l* of ether was allowed to react at room temperature for a day. The deep blue color of $Fe(C_2H_5)_2(dipy)_2$ turned reddish brown in 2 or 3 hr. The gas evolved consisted of ethane and ethylene in a molar ratio of 1 : 1. The reddish brown precipitate was filtered, washed, and dried under vacuum. The IR spectrum of the complex gave no peak characteristic of dipyridyl complexes. Found: C, 37.0; H, 4.12; N, 12.8%. Calcd for $Fe(AcAm)_2$: C, 36.4; H, 5.05; N, 14.1%.

4. Polymerization of Acrylonitrile (AN), Methacrylonitrile (MAN), Acrolein (AC), Methyl Vinyl Ketone (MVK), Methyl Acrylate (MA), Methyl Methacrylate (MMA), and 2-Vinylpridine (2-Vi-Py): These olefins were polymerized with $Fe(C_2H_5)_2(dipy)_2$. Temperatures when polymerization started were −30°C for acrylonitrile, −20°C to −10°C for methacrylonitrile, acrolein, 2-vinylpyridine and methyl vinyl ketone, 20°C for methyl acrylate and methyl methacrylate. The compositions of the gases evolved were ethane and ethylene in ratios of 1 : 1∼2.5.

5. Vinyl Chloride (VCl): Dry vinyl chloride was introduced into tetrahydrofuran solution (30 m*l*) containing 0.50 g (1.2 mmol) of $Fe(C_2H_5)_2(dipy)_2$. The deep blue color of $Fe(C_2H_5)_2(dipy)_2$ turned dark red in a day at room temperature. The dark red precipitate was filtered, washed with benzene, and dried in a vacuum. Found: C, 50.5; H, 3.63; N, 10.9; Cl, 21.7%. Calcd for $Fe(dipy)_2Cl_2$: C, 55.5; H, 3.66; N, 12.8; Cl, 16.7%. Calcd for $Fe(dipy)Cl_3$: C, 37.4; H, 2.49; N, 8.72; Cl, 33.2%. As judged from analytical data, the solid is considered to be a mixture of $Fe(dipy)_2Cl_2$ and $Fe(dipy)Cl_3$ in a molar ratio of about 3 : 1.

6. Vinyl acetate (VAc): Vinyl acetate (5.5 m*l*, 59 mmol) was distilled *in vacuo* into a flask containing 0.91 g (2.1 mmol) of $Fe(C_2H_5)_2(dipy)_2$. The mixture was allowed to react for 3 days at room temperature. The reddish purple solid was filtered and recrystallized from acetone. The gas evolved consisted of ethane and ethylene in a molar ratio of 1 : 3. Found: C, 58.5; H, 5.04; N, 8.23%. Calcd for $Fe(dipy)(VAc)_2$: C, 56.2; H, 5.21; N, 7.31%.

7. Styrene (St), Isobutyl vinyl ether (IBVE), and Ethylene (E): No apparent change took place. Polymer was not obtained when $Fe(C_2H_5)_2(dipy)_2$ was treated with St, IBVE, or E for a few days at room temperature.

III. Spectral Measurements. The infrared spectra were obtained with a Shimadzu model IR 27C or Hitachi Model EPI-G3. Visible and ultraviolet spectra were recorded on a Shimadzu SV-50A spectrometer. When necessary, the temperature was controlled within 0.5°C by circulating water of a constant temperature around the cuvette.

IV. Analysis. The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. Considerable difficulties were encountered in the microanalysis of unstable complexes.