urea[14] on compounds with hydrocarbon groups is also most easily interpreted as a nonspecific solvent effect.

The effectiveness of urea derivatives as denaturants is enhanced with increasing substitution of alkyl groups on the nitrogen.[15] Interestingly, the presence of a butyl group on the urea molecule also greatly improves its ability to "denature" the *p*-nitrophenyl laurate aggregates (Table I).

Hydrophobic bonding is of paramount importance in the stabilization of the structure of proteins,[16] enzyme-substrate complexes,[17] biological membranes,[18] and molecular aggregates.[18] A useful feature of this paper is the presentation of a new method for studying the nature of hydrophobic bonding. Clearly, interesting generalizations concerning hydrocarbon-solute interaction could emerge from a thorough structure-activity analysis with a large variety of additives. Our kinetic method is sensitive, fast, and simple to carry out. The solubility method[2] yields data which are somewhat easier to interpret quantitatively, but the method is slow (as much as 7 days may be required to attain equilibrium), and the changes brought about by the additives are generally quite small.[19]

Acknowledgment. We greatly appreciate assistance from the McCandless Fund of Emory University and from the Petroleum Research Foundation (Type G Grant). National Defense Education Act predoctoral support for C. E. Portnoy is also gratefully acknowledged.

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(19) Two relevant papers have appeared recently: (a) M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **71**, 3320 (1967), studied the effects of additives on the stability of micelles; (b) T. E. Wagner, C. Hsu, and C. S. Pratt, *J. Am. Chem. Soc.*, **89**, 6366 (1967), found that 5 *M* urea reduces the rate of reaction between a long-chain imidazole and a long-chain carbonate by a factor of about 10.

Diethylbis(dipyridyl)iron. A Butadiene Cyclodimerizaton Catalyst

Akio Yamamoto,[1a] Kazuhiko Morifuji,[1a] Sakuji Ikeda,[1a]
Taro Saito,[1b] Yasuzo Uchida,[1b] and Akira Misono[1b]

Contribution from the Tokyo Institute of Technology, Research Laboratory of Resources Utilization, Meguro, Tokyo, Japan, and The University of Tokyo, Department of Industrial Chemistry, Faculty of Engineering, Hongo, Tokyo, Japan. *Received August 14, 1967*

Abstract: Diethylbis(dipyridyl)iron (**1**) was isolated from a mixed catalyst system containing iron acetylacetonate, diethylaluminum monoethoxide, and dipyridyl. The structure of the ethyl-iron complex was established from elementary analysis, infrared spectroscopy, and chemical properties of the complex. Zero-valent iron-dipyridyl complexes, bis(dipyridyl)iron (**2**) and tris(dipyridyl)iron (**3**), were prepared by thermal decomposition of **1** at 50° in benzene, both in the absence and presence of excess dipyridyl. The isolated iron-dipyridyl complexes **1**-**3** showed the same catalytic behavior as the mixed catalyst system for butadiene oligomerization. The mechanism of butadiene cyclodimerization to cyclooctadiene and vinylcyclohexene by these iron-dipyridyl complexes was studied by using a deuterated monomer. Diethylbis(dipyridyl)iron was also active as a catalyst of acetylene and acrylonitrile polymerizations.

In mixed catalyst systems composed of transition metal compounds and organoaluminum compounds, the formation of organo-transition metal complexes is often suggested, but in very few cases have these complexes been isolated from the catalyst systems, because of the instability of the transition metal-carbon bond.[2] We found that α,α'-dipyridyl is an excellent stabilizer of the alkyl-transition metal bond and we have isolated from the mixed catalyst systems ethyl-iron,[3a]-cobalt,[3b] and -nickel[3a,4] complexes which catalyze oligomerization of butadiene. In this paper we wish to report the synthesis and properties of the iron complex in detail, and to discuss the mechanism of butadiene oligomerization.

Results and Discussion

The ethyl-iron complex **1** was prepared from iron(III) acetylacetonate, diethylaluminum monoethoxide, and dipyridyl in ether in a yield of 70%. The structure of the complex was established on the basis of elementary analysis, infrared and visible spectra, and chemical properties of the complex.

The infrared spectrum of the complex in benzene shows bands due to ethyl groups and coordinated

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(1) (a) Tokyo Institute of Technology, Meguro, Tokyo, Japan. (b) The University of Tokyo, Hongo, Tokyo, Japan.

(2) (a) C. Beermann and H. Bestian, *Angew. Chem.*, **71**, 618 (1959); (b) H. J. Berthold and G. Groh, *Z. Anorg. Allgem. Chem.*, **319**, 230 (1963); (c) V. N. Latjaeva, G. A. Razuvaev, A. V. Malisheva, and G. A. Kiljakova, *J. Organometal. Chem.* (Amsterdam), **2**, 388 (1964); (d) K. H. Thiele and J. Müller, *Z. Chem.*, **4**, 273 (1964).

(3) (a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, **87**, 4652 (1965); (b) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuj, and S. Ikeda, *J. Organometal. Chem.* (Amsterdam), **6**, 572 (1966).

(4) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Am. Chem. Soc.*, **88**, 5198 (1966).

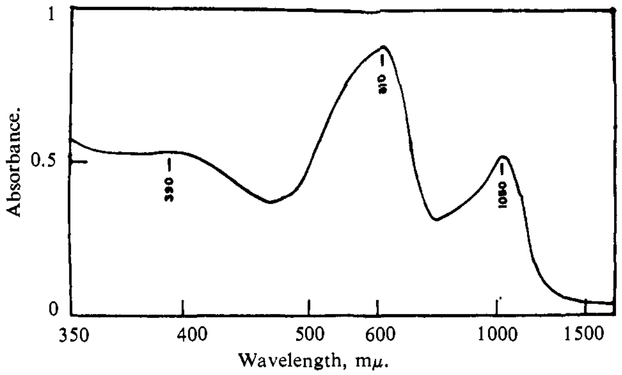


Figure 1. Visible spectrum of $FeEt_2(dipy)_2$ in benzene.

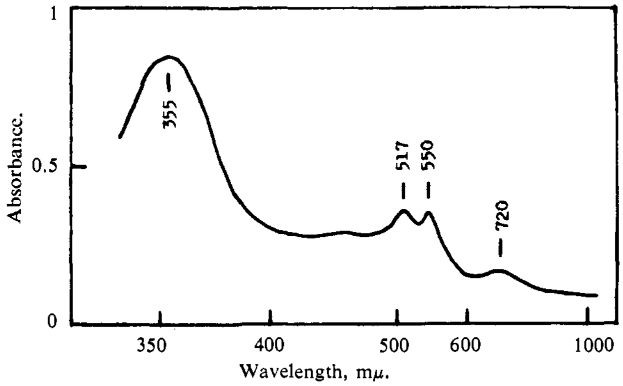
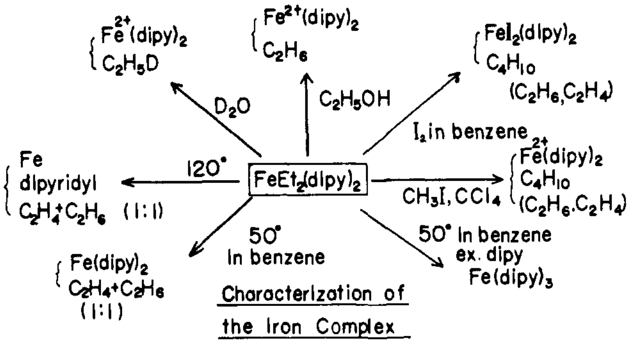


Figure 2. Visible spectrum of $Fe(dipy)_3$ in benzene.

dipyridyl ligands. The bands at 1575 and 1433 cm^{-1} may be ascribed to skeletal vibrations of the aromatic rings and at 759 cm^{-1} to C–H out-of-plane bending.[5] Besides these bands due to dipyridyl ligands, bands ascribable to aliphatic C–H stretching are clearly observed in the region between 3000 and 2800 cm^{-1}. These bands disappear with the introduction of air, and the spectrum becomes essentially identical with that of free dipyridyl.

Chemical properties of the complex are summarized in Scheme I. The reactions were carried out in the absence of air.

Scheme I



The reaction of the complex with ethanol or decanol gave ethane as the only gaseous product and a ferrous–dipyridyl complex. The reaction with water was slower than alcoholysis, and 20% of the complex was decomposed in 2 weeks at room temperature, ethane being released. Mass spectrometric analysis of the gaseous deuteriolysis product of the complex indicated the formation of C_2H_5D as the sole product and the absence of $C_2H_4D_2$. The reaction of the complex with sulfuric acid was smoother, and ethane and butane were formed in a ratio of 2:1. The amount of the gases evolved was 93% of the calculated value.

The visible spectra of the products remaining after the reactions with alcohol, water, and acid in the absence of air were identical with the spectrum of a ferrous–dipyridyl complex.

The complex **1** reacted with iodine in benzene releasing butane and a small amount of ethane and ethylene. The red reaction product was proved to be $FeI_2(dipy)_2$ by elementary analysis. The diethyl–iron complex reacted similarly with methyl iodide giving the gaseous product of a similar composition and a red ferrous–dipyridyl complex. The reaction of complex **1** with hydrogen was slow and ethane was formed. **1** reacted with pyridine, forming ethane and ethylene. A ligand-exchange reaction of dipyridyl with pyridine may probably have occurred with the resulting destabilization of the ethyl–iron bonds. **1** also reacted with carbon monoxide, forming ethane and ethylene.

When the iron complex **1** was heated at 120° in the absence of air, ethylene and ethane were evolved in a ratio of *ca.* 1:1, and a black pyrophoric ferromagnetic residue and crystals of dipyridyl were obtained as the decomposition products. The volume of the gaseous products amounted to 1.75 mol/mol of the compound.

Complex **1** is slowly decomposed in benzene at 50° releasing 1.8 mol of ethane and ethylene in equimolar quantities. The composition of the dark violet reaction product obtained agreed with the structure $Fe(dipy)_2$. On the other hand, thermal decomposition of **1** in benzene at 50°, in the presence of excess dipyridyl, gave black needles of tris(dipyridyl)iron(0) which was prepared by different methods.[6] The volume of ethane and ethylene evolved was about 1.8 mol/mol of the compound. The visible spectra of the dipyridyl complexes are shown in Figures 1 and 2.

All these chemical properties of complex **1** support the structure having two ethyl groups and two dipyridyl ligands, and the possibility of an ethylene-coordinated structure which was at first suspected was excluded.

Catalytic Reactions. In Table I are summarized typical results of butadiene oligomerization with $FeEt_2(dipy)_2$, $Fe(dipy)_2$, and $Fe(dipy)_3$, and the effect of the addition of electron donors on the conversion of butadiene to its dimers. $FeEt_2(dipy)_2$ isolated from the mixed catalyst system containing iron acetylacetonate, organoaluminum compound, and dipyridyl shows essentially the same catalytic behavior for butadiene oligomerization as the mixed catalyst system converting butadiene to its cyclodimers, cyclooctadiene and vinylcyclohexene, in a ratio of 3:1. Ethyl groups are displaced by butadiene in the oligomerization and ethane and ethylene are formed. The ratio of ethane to ethylene varied depending on the reaction conditions employed. Formation of the C_6 hydrocarbon was observed by gas chromatography, indicating the addition of butadiene to the ethylene or ethyl groups. Apparently, the presence of ethyl–iron bonds is not

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(5) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

(6) (a) S. Herzog and H. Präkel; *Proc. Intern. Conf. Coordination Chem., 8th Vienna 1964*, 214 (1964); (b) F. S. Hall and W. L. Reynolds, *Inorg. Chem.*, **5**, 931 (1966).

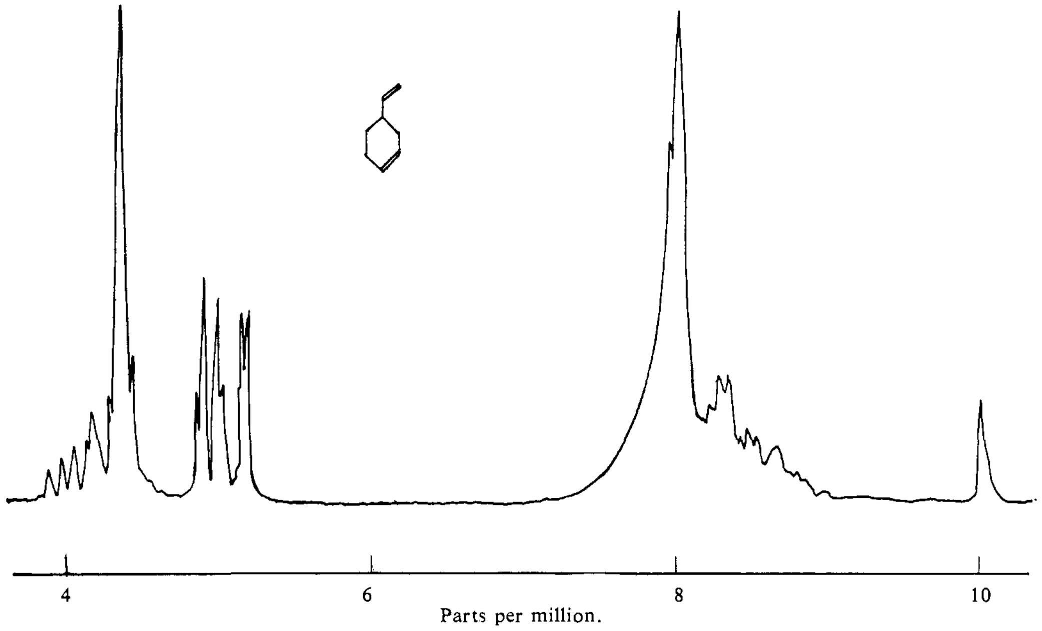


Figure 3. Nmr spectrum of vinylcyclohexene.

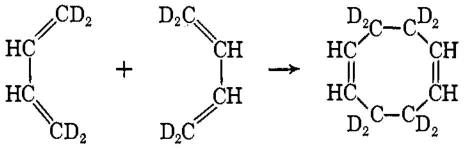
essential for the butadiene oligomerization, since Fe(dipy)$_2$ and Fe(dipy)$_3$ derived by the fission of ethyl–iron bonds of FeEt$_2$(dipy)$_2$ show catalytic activities similar to the ethyl complex.

Table I. Butadiene Dimerization with Iron–Dipyridyl Complexes[a]

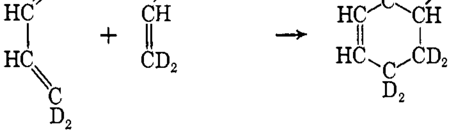
Catalyst	Amount of catalyst, mmol	Butadiene, mmol	React. time, hr	Conversion, %	COD/VCH[d]
FeEt$_2$(dipy)$_2$	0.05	37	15	90	2.7
Fe(dipy)$_2$	0.04	57	28	21	3.8
Fe(dipy)$_2$ + dipy[b]	0.06	72	27	21	2.9
Fe(dipy)$_2$ + PPh$_3$[c]	0.03	56	42	0	. . .
Fe(dipy)$_3$	0.02	67	43	63	2.4

[a] Polymerization was carried out at 50° in 10 ml of benzene. [b] α,α'-Dipyridyl (1.2 mmol) was added in 20 molar excess. [c] Triphenylphosphine (1.2 mmol) was added in 40 molar excess. [d] COD = cycloocta-1,5-diene; VCH = 4-vinylcyclohexene.

To study further the mechanism of butadiene cyclodimerization with the iron catalyst, dimerization products of butadiene-1,1,4,4-d_4 were examined by nmr and infrared spectroscopy. The dimerization products were separated by gas chromatography and compared with corresponding undeuterated samples. The nmr spectrum of the deuterated sample shows only a sharp singlet at τ 4.57 and is free from CH$_2$ protons observed in the undeuterated sample at τ 7.70. We can conclude that dimerization of butadiene-1,1,4,4-d_4 gave almost pure cyclooctadiene-3,3,4,4,7,7,8,8-d_8.



In Figures 3 and 4 the nmr spectrum of 4-vinylcyclohexene is compared with that of the same compound prepared from the deuterated butadiene. The peaks due to the ring CH$_2$ and CH protons around τ 8 in the undeuterated sample are replaced by a simple doublet (τ 7.75 and 7.86) which can be assigned to the ring CH proton at the 4 position in the deuterated sample. Bands due to the =CH$_2$ protons of the vinyl group around τ 4.8$\sim$5.2 are completely absent in the spectrum of the deuterated sample and only the peaks of —CH= protons of the vinyl group and —CH=CH— protons in the cyclohexene ring are observed at τ 4.2 $\sim$ 4.4. The result supports the formation of almost pure 4-vinyl-β,β-d_2-cyclohexene-3,3,5,5,6,6-d_6 from the end-deuterated butadiene.



Unreacted butadiene recovered from the reaction mixture was confirmed by infrared spectroscopy to be the starting butadiene-1,1,4,4-d_4. Hence the possibility of a hydrogen-exchange reaction between the end and internal positions of butadiene during the polymerization was excluded. Ethane and ethylene formed during the polymerization were not labeled with deuterium.

These results suggest that the dimerization reactions proceed through a simple coupling of butadiene coordinated with the iron catalyst.

Inhibition of the butadiene dimerization is caused by the addition of triphenylphosphine but not by excess dipyridyl (Table I). Triphenylphosphine may be strongly coordinated with the iron complex, thus blocking the site of butadiene coordination. On the other hand, it is clear that dipyridyl is participating in the regulation of the course of butadiene oligomerization with the iron complex, since a linear trimer, dodeca-1,3,6,10-tetraene, is the major product of butadiene oligomerization with a catalyst system which is composed of iron acetylacetonate and triethylaluminum

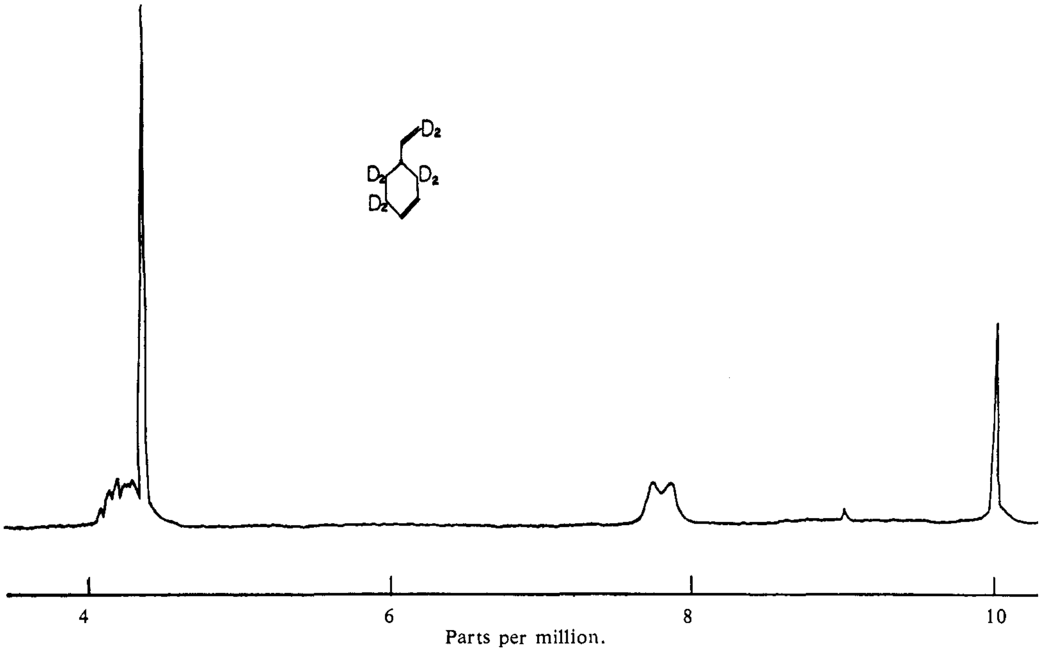


Figure 4. Nmr spectrum of a deuterated vinylcyclohexene dimerization product.

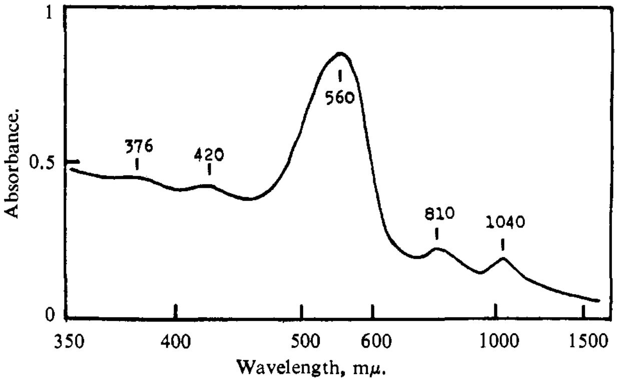


Figure 5. Visible spectrum of butadiene dimerization solution with $FeEt_2(dipy)_2$ in toluene.

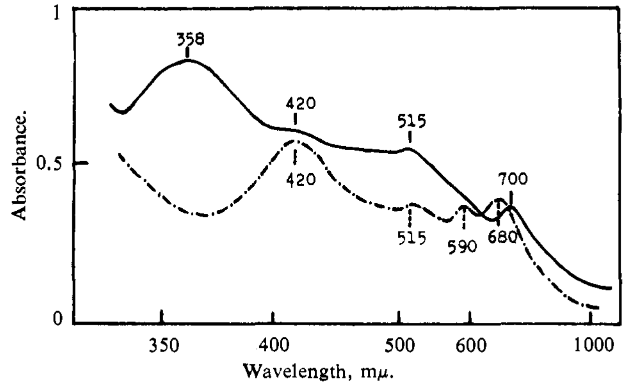
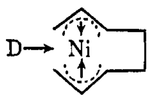
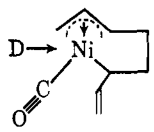


Figure 6. Visible spectrum of Fe(dipy)(butadiene) in benzene solution, ———; air was introduced to the benzene solution, —·—·—.

and contains no dipyridyl.[7] Probably one molecule of dipyridyl is coordinating with the iron complex in the catalyst system since the presence of free dipyridyl was detected after the polymerization in the catalyst solution which contained $FeEt_2(dipy)_2$. In order to get an insight into the dimerization mechanism, the isolation of a reaction intermediate was attempted, and the spectral change of the reaction solution during polymerization was followed. The original blue color of the $FeEt_2(dipy)_2$ turned to violet as the reaction proceeded and the spectrum changed from Figure 1 to Figure 5 which is different from the spectrum of $Fe(dipy)_3$ (Figure 2). From the solutions containing $FeEt_2(dipy)_2$ and butadiene under various conditions, precipitates having the catalytic activity of butadiene dimerization were separated, but the composition of the precipitates varied. However, the composition of the precipitate which was obtained from the solution when all the monomer was consumed was close to Fe(dipy)(butadiene). The spectrum of this precipitate in benzene shown in Figure 6 is different from that of the polymerization solution, but the composition of the precipitate suggests that a catalyst species with one dipyridyl ligand and coordinated butadiene molecule(s) may be present in the solution during polymerization.





Wilke and his coworkers obtained nickel complexes coordinated with electron donors and butadiene dimers having π-allyl groups as the reaction intermediates of butadiene cyclodimerization.[8] In the case of butadiene dimerization with the iron complexes containing the dipyridyl ligand, the active catalyst species may be similar to the nickel complexes prepared by Wilke and his coworkers. The following dimerization mechanism seems to be reasonable (Scheme II). It involves: (1) the displacement of dipyridyl ligand(s) by the coordinating molecules of butadiene; (2) coupling of the coordinated butadiene molecules with the formation

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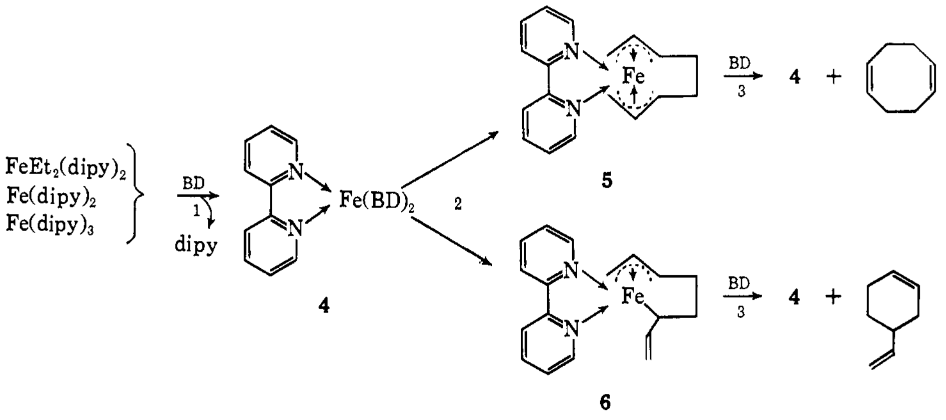
(7) M. Hidai, Y. Uchida, and A. Misono, *Bull. Chem. Soc. Japan*, **38**, 1243 (1965).

(8) G. Wilke, *Angew. Chem.*, **75**, 10 (1963); **78**, 157 (1966).

Scheme II. Proposed Mechanism of Butadiene Cyclodimerization



BD = butadiene, dipy = dipyridyl ligand

of π-allyl iron–dipyridyl complexes with structures such as **5** and **6**, (3) displacement reactions which regenerate the active species **4** with the concomitant formation of cyclooctadiene and vinylcyclohexene.

Isoprene was dimerized with the ethyl–iron complex to a mixture of cyclodimers, dimethylcyclooctadiene, isopropenylmethylcyclohexene, and dimethylvinylcyclohexene.

The diethylbis(dipyridyl)iron is also active in the polymerization of acetylene and acrylonitrile. Acetylene was converted to benzene and a black polymer with conjugated double bonds in a low yield accompanied by the formation of ethane and ethylene in a ratio of 4:1.

Acrylonitrile was polymerized with a catalytic amount of the ethyl–iron complex to a polymer having a molecular weight of the order of 10^5. The infrared spectrum of the polymer was similar to that of polyacrylonitrile obtained by radical initiators. In contrast to the butadiene oligomerization, the ethyl groups play a predominant role in the polymerization of acrylonitrile. Whereas the polymerization of acrylonitrile proceeds very rapidly with $FeEt_2(dipy)_2$, only a trace of the polymer was obtained with $Fe(dipy)_3$. The acrylonitrile polymerization with ethyl–transition metal complexes will be reported separately.[9]

Experimental Section

Reagents. Iron(III) acetylacetonate was prepared from ferric ammonium sulfate and acetylacetone.[10] Diethylaluminum monoethoxide was obtained by the reaction of triethylaluminum with ethyl alcohol and was purified by distillation under reduced pressure. α,α′-Dipyridyl was used as purchased, mp 69.5–70.0°.

Butadiene was used after drying the gas with calcium chloride and then drying the condensed liquid over calcium hydride. Butadiene-1,1,4,4-d_4 was prepared by an exchange reaction of butadiene sulfone with deuterium oxide followed by thermal decomposition of the deuterated sulfone. The exchange reaction was repeated four times at 42–48° in the dark for 3 hr, using alkaline deuterium oxide, and the sulfone was recrystallized from methanol five times.

Analysis by nmr spectroscopy indicated that the deuterated butadiene sulfone has 97–98% isotopic purity. The deuterated butadiene sulfone was then decomposed at 120° to SO_2 and butadiene-1,1,4,4-d_4, which was purified by passing through alkaline washing towers and calcium chloride. Acrylonitrile was purified by fractional distillation and the fraction of bp 77.5–78° was used for polymerization. Solvents were dried and distilled under nitrogen.

Preparation. Every operation was carried out in an atmosphere of nitrogen purified by passing through an activated copper column and a phosphorus pentoxide column, or under argon, or under vacuum. In a typical experiment of the preparation of diethylbis(dipyridyl)iron, 9.0 g of dipyridyl and 9.0 g of iron acetylacetonate were suspended in 50 ml of ether, and 9.0 ml of diethylaluminum monoethoxide was added to the suspension cooled at −20°. The mixture was stirred at 0–10° until the reagents were completely dissolved in the ether. Ethane with a small amount of ethylene was evolved. After the mixture was kept standing for a day at room temperature, dark crystals precipitated which were filtered and washed repeatedly with ether and *n*-hexane. The yield of $FeEt_2(dipy)_2$ was 70% based on the charged iron acetylacetonate. The compound is slightly soluble in inert organic solvents such as ether, benzene, and acetone and can be recrystallized from these solvents at low temperature.

Anal. Calcd for $C_{24}H_{26}N_4Fe$: C, 67.61; H, 6.15; N, 13.15; Fe, 13.1. Found: C, 67.93; H, 6.17; N, 12.6; Fe, 13.2.

The visible spectrum of the blue benzene solution shows absorption bands at 395 (ε 1.03 × 10^3), 610 (4.58 × 10^3), and 1050 mμ (2.76 × 10^3). The blue color changes rapidly on contact with air to green and then brown, and a brown precipitate is formed.

Chemical Reactions of Diethylbis(dipyridyl)iron. Alcoholysis and Hydrolysis. The complex weighed in a Schlenk-type flask (0.4∼0.6 g) was connected to a vacuum line, and alcohol or water was distilled into the Schlenk flask under a high vacuum. The gas evolved was collected, measured by a mercury manometer, and analyzed by gas chromatography. Only ethane was found as the alcoholysis and hydrolysis product. A gaseous deuteriolysis product was separated by gas chromatography, and the collected ethane was identified by mass and infrared spectrometry as C_2H_5D. The reaction with sulfuric acid was carried out by addition of sulfuric acid to the weighed sample in a Schlenk flask cooled by liquid nitrogen. The flask containing the sample and frozen acid on its wall was connected to the vacuum line and evacuated. When the acid melted, the reaction started, and the evolved gas was measured and analyzed.

Reaction with Iodine and Methyl Iodide. To the weighed sample of the complex (1.10 mmol) a benzene solution of iodine (5.93 mmol in 50 ml of benzene) was added as in the reaction with sulfuric acid. The gaseous product evolved was analyzed and found to be mainly butane containing a small amount of ethane and ethylene. The red precipitate formed by the reaction was washed with benzene and dried under vacuum.

Anal. Calcd for $C_{20}H_{16}N_2I_2Fe$: N, 9.01; I, 40.80; Fe, 8.98. Found: N, 8.73; I, 40.90; Fe, 9.02.

The visible spectrum in benzene observed in the absence of air was identical with that of the ferrous–dipyridyl complex and did not change on contact with air.

The reaction of the diethylbis(dipyridyl)iron with methyl iodide was carried out by distilling a benzene solution of methyl iodide into a flask containing the complex under vacuum. Evolved gas contained butane with a small amount of ethane and ethylene.

Thermal Reactions. a. A solid sample of $FeEt_2(dipy)_2$ was decomposed under vacuum at 120°. The volume of the gas evolved amounted to 1.75 mol/mol of the complex, and the gas contained ethane and ethylene in a ratio of *ca.* 1:1. After the thermal de-

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[9] A preliminary report was made by A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 5989 (1967)

[10] J. F. Steinbach and J. H. Burns, *ibid.*, **80**, 1839 (1958).

composition, white crystals of dipyridyl and a black pyrophoric solid which appears to be elementary iron remained.

b. $\mathrm{FeEt_2(dipy)_2}$ (0.55 g) was slowly decomposed in benzene at 50°. A dark violet precipitate was formed accompanied by the gas evolution of 1.8 mol/mol of the complex. Analysis of the gas by gas chromatography showed that it is an equimolar mixture of ethane and ethylene. The dark violet precipitate was washed with benzene and hexane and dried under vacuum.

Anal. Calcd for $\mathrm{C_{20}H_{16}N_4Fe}$: C, 65.24; H, 4.38; N, 15.22; Fe, 15.17. Found: C, 63.38; H, 4.51; N, 15.15; Fe, 15.0.

c. $\mathrm{FeEt_2(dipy)_2}$ (0.40 g, 0.93 mmol) was heated at 50° for 20 hr in 60 g of benzene containing 1.0 g (5.8 mmol) of dipyridyl. Equimolar quantities of ethane and ethylene were evolved (1.8 mol/mol of $\mathrm{FeEt_2(dipy)_2}$). Fine black needles precipitated; these were washed with benzene and dried under vacuum.

Anal. Calcd for $\mathrm{C_{30}H_{24}N_6Fe}$: C, 68.72 H, 4.61; N, 16.03; Fe, 10.65. Found: C, 68.46; H, 4.73; N, 15.63; Fe, 11.2.

Polymerization. 1. Butadiene and Isoprene. Polymerization of butadiene was carried out at 50° in as ealed tube containing $2\sim4$ g of butadiene and the catalytic amount of the iron complexes ($10\sim50$ mg) in 10 ml of benzene. The original dark blue color of the ethyl–iron complex turned to violet as the reaction proceeded. The oligomerization products, the extent of conversion of butadiene to its oligomers, and the gases evolved during polymerization were analyzed by gas chromatography. The oligomerization products of the deuterated butadiene were separated by preparative gas chromatography and analyzed by nmr and infrared spectroscopy.

Attempted Isolation of a "Polymerization Intermediate." Butadiene (1.1 g) was polymerized with 0.23 g of $\mathrm{FeEt_2(dipy)_2}$ in 20 ml of benzene for 50 hr at 50°. Under these conditions almost all the butadiene was converted to cyclodimers. A dark precipitate which formed was separated from the red-violet solution, and was washed repeatedly with hexane and dried under vacuum. The dark powder obtained (0.15 g) catalyzed butadiene oligomerization.

Anal. Calcd for $\mathrm{C_{14}H_{14}N_2Fe}$ (Fe(dipy)(butadiene)): C, 63.22; H, 4.54; N, 10.53; Fe, 20.99. Found: C, 62.52; H, 4.51; N, 11.74; Fe, 19.09.

The polymerization of isoprene was carried out similarly.

2. Acetylene. Polymerization of acetylene was carried out under a vacuum system. Acetylene (32 mmol) was introduced into a flask containing 0.10 mmol of $\mathrm{FeEt_2(dipy)_2}$ in 50 ml of toluene which was free from benzene. As polymerization proceeded, a black polymer precipitated. The formation of benzene was detected by gas chromatography.

3. Acrylonitrile. Polymerization of acrylonitrile was carried out in bulk and in benzene or pyridine solution. It did not polymerize below 0° but polymerized very rapidly at room temperature. Acrylonitrile (5.0 ml) was distilled under vacuum into a flask containing about 8 mg of $\mathrm{FeEt_2(dipy)_2}$ by using liquid nitrogen. When the solution reached room temperature, very rapid polymerization took place. The polymer was washed with methanol and then purified by reprecipitating the dimethylformamide solution of the polymer in methanol. The yield of white polymer thus obtained was about 50% for the charged acrylonitrile. The molecular weight was determined by measuring the viscosities of dimethylformamide solutions of the polymer. The infrared spectrum of the polymer was taken as a KBr disk.

Analysis. a. Gas Chromatography. Gases were analyzed by a Kotaki-Super Fractioner. The $\mathrm{C_2}$ fraction was analyzed with a silica gel column and the $\mathrm{C_4}$ fraction by a column packed with alumina containing dimethylformamide. Butadiene oligomers were analyzed with a column of tricresyl phosphate on Diasolid.

b. Infrared spectra were usually measured by a Shimadzu IR 27-C and the spectrum in the 3-μ region was measured by a Perkin-Elmer 125 spectrometer. Benzene solutions were prepared and transferred to the cell in the absence of air.

c. Electronic spectra were measured by Hitachi EPS-2 and Shimadzu SV-50A spectrometers.

d. Nmr spectra were measured by a JEOR 3H-60 spectrometer with tetramethylsilane as the internal standard.

e. Microanalysis was performed by Mr. T. Saito of Tokyo Institute of Technology, to whom the authors are very grateful.

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