through which the sample could be introduced. Finally, two external flats were ground and polished parallel to internal surfaces. After filling, the cell could be sealed very simply at a point well removed from the sample. The ability of the capillary section to withstand internal pressure could be made to exceed that of the main section of the cell. The cell after filling and sealing is illustrated in Figure 9a.

The cells were calibrated by comparing the optical density of a suitable solution in the cell with that of the same solution in a standard 1-cm cell. Within the calibration error, the path length corresponded to the mandrel dimension (0.25-in.).

Barring explosions from excessive pressure buildup, the cells can be reused many times, as no etching by the high-pressure liquids has been evident.

Diethyldipyridylnickel. Preparation, Characterization, and Reactions

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Abstract: Diethyldipyridylnickel, $Et_2Ni(dipy)$, was synthesized by the reaction of $Ni(acac)_2$, α,α'-dipyridyl, and Et_2AlOEt in ether. The dark green, air-sensitive, crystalline complex was characterized by means of elemental analysis, thermal decomposition, alcoholysis, hydrolysis, visible light absorption spectra, infrared spectra, and nmr spectra. The nmr spectra of the complex show a quartet and a triplet near τ 9 which are assigned to the ethyl protons σ-bonded to nickel, and a quartet and two doublets in the region τ 0.9–2.6 of the coordinated dipyridyl ligand. These data are interpreted in connection with the structure of the complex. The complex has the catalytic activity for the cyclooligomerization of butadiene to cyclododecatriene as the main product.

Wilke and his co-workers have prepared a variety of zero-valent nickel complexes relevant to the catalytic oligomerization of butadiene.[2] The main synthetic method to prepare these complexes is the reaction of nickel compounds with organoaluminum compounds in the presence of electron donors. In the preparation, organonickel complexes have been postulated as unstable intermediates which are then reduced to zero-valent nickel complexes by homolytic fission of nickel–carbon bonds. However, no such complexes have been isolated from the mixed catalyst system. In one case the formation of an ethylene–nickel π complex *via* the postulated ethyl–nickel intermediates has been described in a system of nickel acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine.[3]

The thermal instability of the nickel–ethyl σ bond makes the isolation of ethyl–nickel complexes considerably difficult.[4] It is known that the coordination of an appropriate ligand to a transition metal stabilizes the metal–alkyl bond. With a cyclopentadienyl group and triphenylphosphine as the stabilizing ligands such an ethyl–nickel complex was prepared as the first example.[5] We found that α,α'-dipyridyl is an excellent stabilizer and isolated by the reaction of metal acetylacetonates, α,α'-dipyridyl, and diethylaluminum monoethoxide, the crystalline nickel, iron,[6] and cobalt[7] complexes which have σ-ethyl groups and dipyridyl ligands.

In the present paper, we wish to report the preparation, characterization, and reactions of the nickel complex in detail.[7a]

Experimental Section

Reagents. Nickel acetylacetonate[8] and α,α'-dipyridyl were prepared with the methods in the literature.[9] Diethylaluminum monoethoxide was prepared by the reaction of triethylaluminum with ethyl alcohol in hexane followed by vacuum distillation. Solvents were purified by usual methods and distilled under purified nitrogen.

Syntheses. Every operation was carried out under vacuum or in an atmosphere of nitrogen or argon purified by an activated copper column. The reactor was a two-necked round-bottom flask with a tail stopcock as a nitrogen inlet. As a typical example, 4 g of nickel acetylacetonate and 6 g of dipyridyl were suspended in 50 ml of ether, and 7 ml of diethylaluminum monoethoxide was added to this mixture by use of a pipet at −20°. The mixture was agitated with a magnetic stirrer at −20 to ∼−10° until the reagents were completely dissolved in ether, and then it was kept standing at room temperature. Dark green crystals which precipitated were separated by filtration and washed repeatedly with ether and hexane. The yield of the crystals was 80% based on the nickel acetylacetonate.

$$Ni(acac)_2 + \alpha,\alpha'\text{-dipyridyl} \xrightarrow{Et_2AlOEt} Et_2Ni(dipy)$$

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(1) (a) University of Tokyo; (b) Tokyo Institute of Technology.

(2) G. Wilke, *et al.*, *Angew. Chem.*, **75**, 10 (1963).

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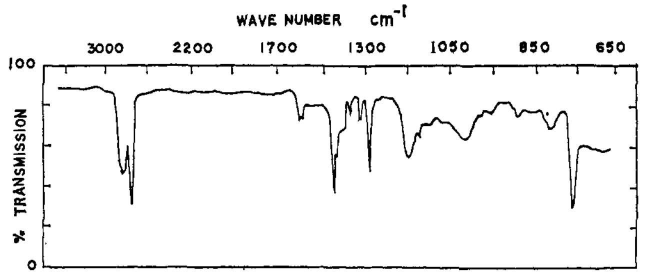

Figure 1. Infrared spectrum of $Et_2Ni(dipy)$ in benzene solution (less than 1 wt %).

The complex is slightly soluble in such organic solvents as ether, benzene, toluene, and acetone, and can be recrystallized from these solvents. The complex is very sensitive to oxygen, especially in solution, and great care must be taken to avoid the contact with air.

Anal. Calcd for $C_{14}H_{18}N_2Ni$: C, 61.61; H, 6.62; N, 10.26; Ni, 21.51. Found: C, 61.3; H, 6.28; N, 10.1; Ni, 21.4.

The emission spectroscopy of the complex indicated that the inclusion of aluminum was negligible.

Measurements of Spectra. Solutions of known concentrations of the complex for infrared, visible light absorption, nmr, and esr spectra measurements were prepared in Schlenk-type flasks. Benzene was used as the solvent for the infrared, visible light absorption, and esr spectra, and dimethylformamide or dimethoxyethane was used for the nmr spectra. A Nihon-bunko Model 201 spectrometer and 0.5-mm path length sodium chloride matched cells were used for infrared spectra measurements. Visible light absorption spectra were taken by use of a Hitachi Model EPS-2 spectrometer with quartz matched cells of 0.1-mm path length. Nmr spectra were recorded by a Nihon-denshi JEOR 3H-60 spectrometer at 60 Mc and a Varian HA-100 spectrometer at 100 Mc. Since no tetramethylsilane was added to the solution, the chemical shifts were measured from the methyl signals of the solvents and then converted to the τ scale.

Gas Chromatography. Ethane and ethylene were analyzed by use of a 2.5-m activated alumina column, and the C_4 hydrocarbons were analyzed by use of a column packed with 2 m of dimethylsulforane and 2 m of dioctyl sebacate on C-22. Butadiene oligomers were identified and quantitatively analyzed by use of a 2.5-m tricresyl phosphate (on Shimalite) column and a 3-m diethylene glycol succinate (on Diasolid) column.

Reactions. Thermal decomposition, alcoholysis, and hydrolysis of the complex were carried out under vacuum. Glass ampoules were employed for polymerization experiments, and butadiene and solvents were charged in them by means of trap-to-trap distillation in a vacuum system.

Results and Discussion

Thermal Decomposition. The complex began to decompose at 110° under vacuum. Ethane, ethylene, and *n*-butane were formed as the gaseous products. It is considered that ethane and ethylene were formed by a disproportionation reaction and *n*-butane was formed by a coupling reaction of the ethyl radicals. The number of the ethyl radicals calculated from the amount of the evolved gas was 1.6 per one molecule of the complex. The lower yield of the gas than expected from the formula $Et_2Ni(dipy)$ may be partly explained by considering that the polymerization of the evolved ethylene occurred.

Alcoholysis and Hydrolysis. The decomposition of the complex by ethyl alcohol proceeded fairly rapidly at room temperature. The only gaseous product found was ethane, and no ethylene was detected. The complex was decomposed by water to yield only ethane, although the decomposition rate was not so high as in the case of the alcoholysis. These results support the presence of σ-bonded ethyl groups.

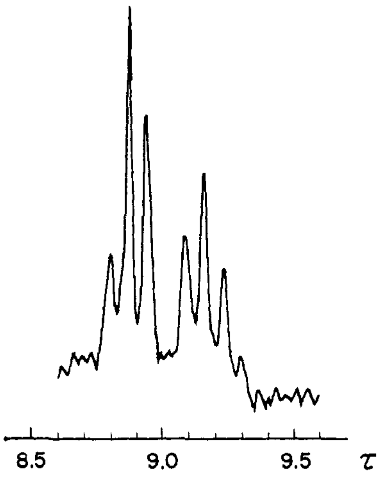

Figure 2. Nmr spectrum (100 Mc) of ethyl protons of $Et_2Ni(dipy)$ in dimethylformamide solution (less than 3 wt %).

Visible Light Absorption Spectra. The benzene solution of the complex has an intense green color which may probably be due to the charge transfer between nickel and dipyridyl ligand. The visible light absorption spectrum has absorption maxima at 430 mμ (ϵ 4500) and at 720 mμ (ϵ 4900). The green color turns to brown instantaneously on contact with air.

Infrared Spectra. The infrared spectrum of the benzene solution is shown in Figure 1. The spectrum shows the symmetric and asymmetric C–H stretching vibrations of methyl and methylene groups at 2930–2830 cm^{-1}, the band at 1311 cm^{-1} which may be characteristic of the coordinated dipyridyl,[10] the band at 755 cm^{-1} of C–H out-of-plane bending vibration of dipyridyl ring, and other bands. Thus, the infrared spectrum indicates that the complex has at least an ethyl group and a dipyridyl ligand.

Nmr Spectra. In Figures 2 and 3, the nmr spectra of the complex in dimethylformamide (ethyl proton signals at 100 Mc) and dimethoxyethane (dipyridyl proton signals at 60 Mc) are shown. The intensity ratio of the signals due to the ethyl protons and dipyridyl protons is 10:8.

Ethyl Protons. The signals of the ethyl protons of the complex show multiplets near τ 9. The comparison of the spectra observed at 60 and 100 Mc showed that the multiplets consisted of a triplet and a quartet of an area ratio of 3:2, which were assigned to methyl and methylene protons of the ethyl groups, respectively. The chemical shifts derived from the positions of the centers of these multiplets are given in Table I.

Table I. The Chemical Shifts of Ethyl Protons

Solvent	Chemical shift (τ) CH$_3$	CH$_2$	δ^c
DMF^a	8.85	9.18	−0.33
DME^b	8.95	9.20	−0.25

^{a} Dimethylformamide. ^{b} Dimethoxyethane. ^{c} $\delta = \tau_{CH_3} - \tau_{CH_2}$.

Dailey and Shoolery[11] found a straight-line correlation between the chemical shift difference of the methyl and methylene protons of ethyl halides and the Pauling electronegativities of the halogens. Narasim-

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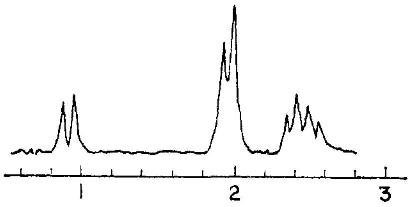

Figure 3. Nmr spectrum of (60 Mc) of dipyridyl protons of $Et_2Ni(dipy)$ in dimethoxyethane solution (less than 3 wt %).

han and Rogers[12] proposed eq 1 for a number of ethyl derivatives of metals and metalloids. In the equation,

$$X = 0.62\delta + 2.07$$
$$\delta = \tau_{CH_3} - \tau_{CH_2} \qquad (1)$$

X is the electronegativity of a metal or a metalloid, and δ is the chemical shift difference of the methyl and methylene protons of the ethyl groups. Applicability of such a straight-line correlation to the ethyl complexes of the transition metals was indicated,[13] but no well-resolved spectrum has been reported.[14]

When eq 1 is applied to the present nickel complex by use of δ values listed in Table I, the electronegativities of the nickel and dipyridyl as a whole are 1.88 in the case of the dimethylformamide solution and 1.91 of the dimethoxyethane solution. These values are close to the electronegativity value of nickel, 1.8,[15] and this result suggests that the relation holds for the nickel compound. The larger electronegativity value calculated from the δ in dimethoxyethane solution may reflect the poorer coordinating ability of the solvent than that of dimethylformamide, because the effective coordination of the solvent may probably increase the electron density on the metal, and the decrease of the electronegativity would result.

Dipyridyl Protons. The spectra of $Et_2Ni(dipy)$ in dimethoxyethane show a quartet (τ 2.45), a doublet (τ 1.95), and a doublet (τ 0.93) with the area ratio of 1:2:1. The constancy of the splittings (in cps) at 60 and 100 Mc indicates that the splittings within these multiplets are based on spin–spin couplings and not on chemical shifts. Figure 3 is the spectrum recorded at 60 Mc. The spectrum is very different from that of free dipyridyl. Recently Kramer and West[16] reported the detailed analysis of the spectrum of dipyridyl, and Castellano, Günther, and Ebersole reported the analysis of the spectra of dipyridyl and its iron complex ($Fe(dipy)_3Cl_2$).[17] According to the latter report, the spectrum of dipyridyl *cis*-coordinated to iron consists of a doublet (τ 1.15, H_3), a quintet (τ 1.74, H_4), and a doublet (τ 2.41, H_5 and H_6) of the intensity ratio of 1:1:2. The spectrum of the dipyridyl protion of $Et_2Ni(dipy)$ (Figure 3) has the pattern similar to the spectrum of the dipyridyl–iron complex, although the positions of the signals are interchanged. By the examination of these two spectra, the following assignments are made: τ 0.93, H_3; τ 1.95, H_5 and H_6; τ 2.45, H_4. These assignments are consistent with dipyridyl *cis*-coordinated to nickel. The difference of the positions of signals between the spectra of the iron and nickel complexes is considered to be mainly due to the number of dipyridyl ligands coordinated to the central metal. Castellano, *et al.*,[17] ascribed the large shift of proton 6 in $Fe(dipy)_3Cl_2$ to the shielding effect of the second dipyridyl ligand. However, $Et_2Ni(dipy)$ has only one dipyridyl ligand, and hence the shift of proton 6 (+0.51) cannot be ascribed to the effect of the second dipyridyl ligand. The upfield shift of proton 6 seems to be best explained by supposing that the central nickel atom is predominantly responsible for the large shielding of proton 6. Such shielding effect was suggested by Miller and Prince[18] in the analysis of a $Fe(phen)_3Cl_2$ spectrum.

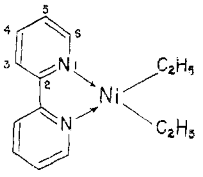

Figure 4. Structure of $Et_2Ni(dipy)$.

Esr Spectra. The spectrum of the complex showed the absence of paramagnetic species.

The Structure of the Complex. The investigation by means of thermal decompositon, alcoholysis, and hydrolysis of the complex demonstrated almost unequivocally the existence of the σ-bonded ethyl groups. Additional evidence was obtained from the infrared and nmr spectra. The intensity ratio of the ethyl and dipyridyl proton signals of 10:8 indicates that this complex has two ethyl groups and one dipyridyl ligand. The elemental analysis fits well with the empirical formula $C_{14}H_{18}N_2Ni$.

The oxidation state of the central nickel may be regarded as divalent,[19] and the complex is probably square planar because it is diamagnetic. The structure of the complex is illustrated in Figure 4. Although bonds between transition metals and alkyl groups are usually very weak, this crystalline complex survives even at considerably high temperature under vacuum. This fact indicates the great contribution of dipyridyl ligand to the stabilization.

Polymerization. It has been established by the investigations of Wilke and his co-workers[2] and others that some low-valent transition metal complexes are the active catalysts for the oligomerization of butadiene. It is of great interest that the rate and selectivity of the reaction are determined by the nature of the electron-donating ligands.

Butadiene was polymerized in the presence of 5 mmoles of $Et_2Ni(dipy)$ per mole of butadiene in benzene at 50° for 80 hr. The conversion of butadiene was 30% and the products were cyclododeca-1,5,9-triene, 63%; 4-vinylcyclohex-1-ene, 8.3%; and cycloocta-1,5-diene, 5.7%. Ethane and ethylene were found as the gaseous products after the completion of the reaction. It is probable that the complex loses

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the ethyl groups rather readily at the reaction temperature through the coordination of butadiene, and the ethyl groups play little role in the cyclotrimerization.

Cyclododecatriene is the main product when butadiene is oligomerized in the presence of the nickel catalyst without dipyridyl ligand, *e.g.*, nickel(0) cyclododecatriene complex.[2] This fact, together with the very slow rate observed in the present reaction, suggest that dipyridyl also plays little role in the selectivity of the reaction and exerts an inhibiting influence on the formation of the active catalyst species.

Acknowledgment. We are greatly indebted to Dr. Y. Fujiwara for the measurements of the nmr spectra and for the very helpful discussions.

Complete Electron-Transfer Series of the $[M-N_4]$ Type

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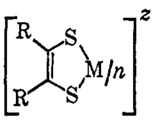
Received June 20, 1966

Abstract: The existence of the electron-transfer series of the general type $[M-N_4]^z$ has been thoroughly investigated using the dianion of *o*-phenylenediamine as the basic ligand system and M = Co, Ni, Pd, and Pt. A five-membered series of bis chelate complexes is proposed in which the members have the net charges $z = -2, -1, 0, +1, +2$. The central ($z = 0$) member of the nickel series has been definitely established as the deep blue complex $Ni[C_6H_4(NH)_2]_2^0$, which was originally prepared by Feigl and Fürth from the oxidation of *o*-phenylenediamine in aqueous ammoniacal solution in the presence of nickel ion and air. By a similar route the complexes $M[C_6H_4(NH)_2]_2^0$, M = Co, Pd, Pt, have been synthesized and their structures established. Polarography in nonaqueous solvents has established the existence of the complete five-membered series for Ni, Pd, Pt, and the existence of the $z = -2, -1, 0, +1$ members for Co. Complexes with $z = -2, -1$ were not chemically prepared due to their oxidative instability. Epr studies of the $[M-N_4]^-$ species produced by controlled potential electrolysis reveal in glasses highly anisotropic g tensors (as observed in $[M-S_4]^-$ complexes), which serve to identify these species. In addition to the $[M-N_4]^0$ complexes, $[M-N_4]I$ salts were chemically prepared for M = Co, Ni, Pd, Pt. The paramagnetic cations of the Pd and Pt salts were shown to be the same as those generated electrochemically. The members with $z = +2$ have not as yet been synthesized. The previously prepared cation $Ni[(CH_3CNC_6H_5)_2]_2^{+2}$ has been shown to be the terminal oxidized member of an electron-transfer series with four detectable members, $z = +2, 0, -1, -2$. The $z = 0$ member has been prepared chemically. A qualitative explanation of the oxidative stability trend of $Ni[C_6H_4XY]_2^z$, in which X and Y represent various donor atom sets, is presented.

In a preceding paper[2] we have briefly summarized the current body of evidence which shows that the sulfur-bonded complexes **1** and **2** are members of a series of complexes which are interrelated by one-electron transfer reactions. It is now well recognized that members of a given series may usually be detected by polarographic measurements and frequently isolated, provided half-wave potentials lie in a range which makes isolation practicable. Limiting consideration to bis complexes ($n = 2$), electron-transfer series of the $[M-S_4]^z$ type have been restricted to the $z = -2, -1, 0$ members, which are the only ones thus far isolated for any given series.[3]



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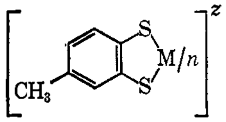

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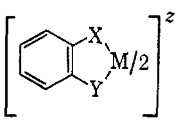
We have previously raised the question concerning the scope of such electron-transfer series in our studies of the four-coordinate complexes of general type **3**.[2,4] This question of scope actually consists of two parts: (i) what structural feature or features are necessary such that complexes exhibit oxidation–reduction propensity?; (ii) once an oxidation–reduction relationship between two complexes has been established, thereby defining a "series" of at least two members, what is the total number of members of that series which can be reasonably anticipated? We have attempted to effect a partial clarification of i by showing that with a given metal, usually nickel, at least two- or three-membered series exist with X = Y = O; X = Y = NH; X = NH, Y = S; X = O, Y = S.[4] The $z = -2$ and -1 members of X = Y = S series (specifically **2**) have now been firmly established[5] and the $z = 0$ member with M = Ni claimed.[6] In addition, a relevant suggestion concerning an electronic struc-



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(1) (a) National Science Foundation Predoctoral Fellow 1963–1966; (b) Alfred P. Sloan Foundation Fellow 1964–1967.

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