Study of Organo(dipyridyl)nickel Complexes. I. Stability and Activation of the Alkyl–Nickel Bonds of Dialkyl(dipyridyl)nickel by Coordination with Various Substituted Olefins

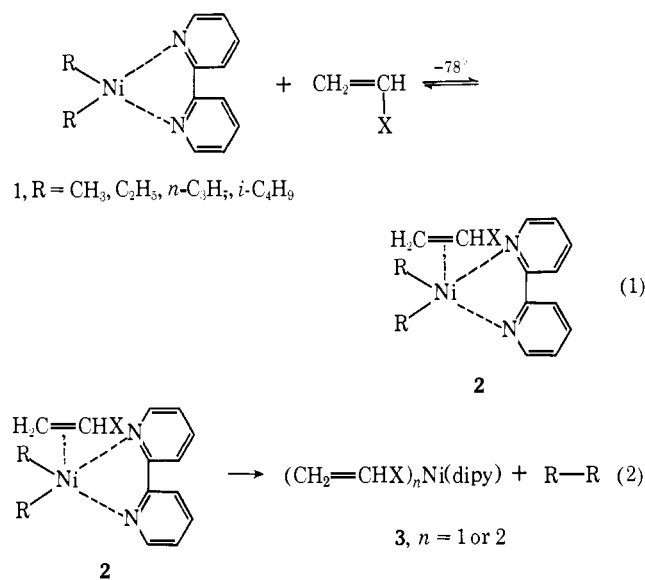Takakazu Yamamoto, Akio Yamamoto,* and Sakuji Ikeda

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Abstract: A series of dialkyl(dipyridyl)nickel complexes $R_2Ni(dipy)$ (1, R = CH_3, C_2H_5, n-C_3H_5, or i-C_4H_9) was prepared. The thermal stability of 1 decreases in the order $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$. Thermal decomposition of 1 is first order with respect to 1, and the activation energy for pyrolysis of $(C_2H_5)_2Ni(dipy)$ is 68 kcal/mol. Reactions of 1 with olefins (tetracyanoethylene, maleic anhydride, acrylamide, acrylonitrile, methacrylonitrile, acrolein, methyl vinyl ketone, methyl acrylate, methyl methacrylate, vinyl chloride, vinyl acetate, 2-vinylpyridine, styrene, isobutyl vinyl ether, ethylene, norbornene, and cyclooctadiene) at room temperature led in most cases to cleavage of the R–Ni bond and to formation of olefin-coordinated complexes of the type Ni(dipy)(olefin)$_n$ (3, n = 1 or 2). The R–Ni bonds are activated through coordination of the olefins to 1; with acrylonitrile and acrolein the complexes $R_2Ni(dipy)(olefin)$ (2) were isolated as unstable intermediates. From infrared and electronic spectroscopy, the coordinated olefins in 2 and 3 appear to be π bonded. Based on a kinetic study of the reactions of 1 with olefins at room temperature a mechanism involving the formation of 2 as an intermediate is proposed. Olefins with electronegative substituents form stronger π complexes with 1 and activate the Ni–R bonds more strongly than those with less electronegative substituents. The observation of charge-transfer bands in the complexes allows estimation of the energy levels of the highest occupied d orbitals and a study of the effect of solvent and olefin coordination to the metal. A mechanism for the activation of Ni–R bonds by interaction of 1 with olefins is proposed.

The coordination of olefins with alkyl–transition metal compounds and the resulting activation of the alkyl–metal bonds constitute the crucial steps in various catalytic reactions, particularly in polymerization with Ziegler-type catalysts. However, because of the instability of the alkyl–transition metal bonds, examples of the isolation of such alkyl–transition metal complexes are limited, and very few systematic studies concerning the reaction of alkyl–transition metal compounds with olefins[1] have been made.[2]

We previously found that α,α'-dipyridyl is an excellent stabilizer of the alkyl–transition metal bond, and we were able to isolate ethyliron,[3] -cobalt,[4a] and -nickel[3,4b,5] complexes which catalyze the oligomerization of butadiene and polymerization of vinyl monomers.[3,4] Later we reported[6] briefly the isolation of a coordination compound (2, X = CN) of acrylonitrile with diethyl(dipyridyl)nickel (1).

Complexes of type 2 are among the few examples of isolated complexes with σ-bonded alkyl groups and a π-bonded olefin moiety.[7] The acrylonitrile-coordinated diethyl complex 2 is stable only at low temperature, whereas the original diethyl(dipyridyl)nickel 1 is quite stable at room temperature. The C_2H_5–Ni bonds are considered to be activated by coordination of acry-

1, R = CH_3, C_2H_5, n-C_3H_7, i-C_4H_9

$$ \text{(1)} $$

2

$$ \longrightarrow (CH_2=CHX)_n Ni(dipy) + R\!-\!R \quad (2) $$

3, n = 1 or 2

2

lonitrile and are readily cleaved at room temperature with the formation of acrylonitrile-coordinated zerovalent nickel complexes 3 (n = 1 or 2) and butane plus small amounts of ethane and ethylene. In the cases of ethyliron and -cobalt complexes the activation of the alkyl–transition metal bonds leads to the initiation of polymerization of vinyl monomers,[3b,8] but with the ethylnickel complex no polymerization takes place.[9] We prepared a series of dialkyl(dipyridyl)nickel compounds with R = CH_3, C_2H_5, n-C_3H_7, and i-C_4H_9 and studied their thermal stabilities. The reactions of R_2Ni(dipy) with a variety of substituted olefins were carried out and various olefin-coordinated transition metal

(1) The term olefin used in this and the succeeding papers includes a substituted olefin.

(2) C. Beermann and H. Bestian, *Angew. Chem.*, 71, 618 (1959); H. Bestian, K. Clauss, H. Jensen, and E. Prinz, *ibid.*, 74, 955 (1962).

(3) (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).

(4) (a) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Organometal. Chem.*, 6, 572 (1966); (b) *J. Amer. Chem. Soc.*, 88, 5198 (1966).

(5) Dimethyl(dipyridyl)nickel was prepared independently by G. Wilke and J. Herrman, *Angew. Chem.*, 78, 591 (1966).

(6) A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, 89, 5989 (1967).

(7) Recently another example of a complex with σ-cyanoethyl and π-acrylonitrile ligands was reported: W. H. Baddley and M. S. Fraser, *ibid.*, 91, 3661 (1969).

(8) A. Yamamoto, T. Shimizu, and S. Ikeda, *Polym. J.*, 1, 171 (1970); *Makromol. Chem.*, 136, 297 (1970).

(9) Previously we reported that $(C_2H_5)_2Ni(dipy)$ also initiates the polymerization of acrylonitrile,[6] but we confirmed later that the initiation requires the presence of a trace of oxygen, whereas this is not the case for ethyliron and -cobalt complexes.

complexes of types 2 and 3 were isolated. In this paper we report the results of our study on the mechanism of the reactions of 1 with olefins, and present a hypothesis based on energetic considerations to explain the activation of the metal–alkyl bonds by coordination of olefins.

Results and Discussion

Thermal Stability of Dialkyl(dipyridyl)nickel. The pyrolysis of $R_2Ni(dipy)$, in the absence of solvent, was followed by measuring the gas evolved at a fixed temperature as a function of time. A plot showing the $[(C_2H_5)_2Ni(dipy)]$ remaining at any time t as a function of t is shown in Figure 1. While the entire curve shows marked curvature, it can be resolved into two straight-line segments. The straight line appropriate to the latter stages of the process is considered here. The rate constants in the first-order expression

$$-d[R_2Ni(dipy)]/dt = k[R_2Ni(dipy)] \qquad (3)$$

are shown in Table I for various temperatures and for the two cases where $R = C_2H_5$ or $n\text{-}C_3H_7$.

Table I. Specific Rate Constants of Pyrolysis of $(C_2H_5)_2Ni(dipy)$ and $(C_3H_7)_2Ni(dipy)$

Temp, °C	$(C_2H_5)_2Ni\text{-}$ (dipy) $k \times 10^4$, sec^{-1}	Temp, °C	$(C_3H_7)_2Ni\text{-}$ (dipy) $k \times 10^4$, sec^{-1}
97.3	1.93	94.4	6.80
103.8	9.09	106.0	9.92
107.2	16.4	115.1	24.5
112.8	73.0	127.6	~50

A plot similar to Figure 1 for the methyl complex shows even more marked deviation from linearity. The methyl complex decomposes at a higher temperature (over 160°). Since dipyridyl, which is released by decomposition of the complex, melts at this temperature, it may alter the mechanism of decomposition of the methyl complex and explain the deviation from a straight line. The pyrolysis of di-n-propyl(dipyridyl)-nickel gives propane and propylene as products in approximately equal amounts. Diisobutyl(dipyridyl)-nickel is much less stable and decomposes even at $-15°$. The stabilities of the alkylnickel complexes indicated by the decomposition temperatures of complexes are $CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_4H_9$.

From the Arrhenius plot of log k $vs.$ $1/T$ the activation energy for the splitting of the C_2H_5–Ni bonds was estimated as 68 kcal/mol. The activation energy for the pyrolysis of $(C_3H_7)_2Ni(dipy)$ was estimated as 16 kcal/mol; the activation energies for the methyl and isobutyl complexes were not determined. Because the activation energy for the pyrolysis of $(C_3H_7)_2Ni(dipy)$ is fairly small, $(C_3H_7)_2Ni(dipy)$ gradually decomposes at room temperature with evolution of propane and propylene. The value of 68 kcal/mol for $(C_2H_5)_2Ni(dipy)$ is considerably higher than the activation energies for pyrolysis of $(C_2H_5)_2Fe(dipy)_2$ (47–54 kcal/mol) and $(CH_3)_2Fe(dipy)_2$ (23 kcal/mol[10]), and indicates the re-

(10) T. Yamamoto, A. Yamamoto, and S. Ikeda, presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969.
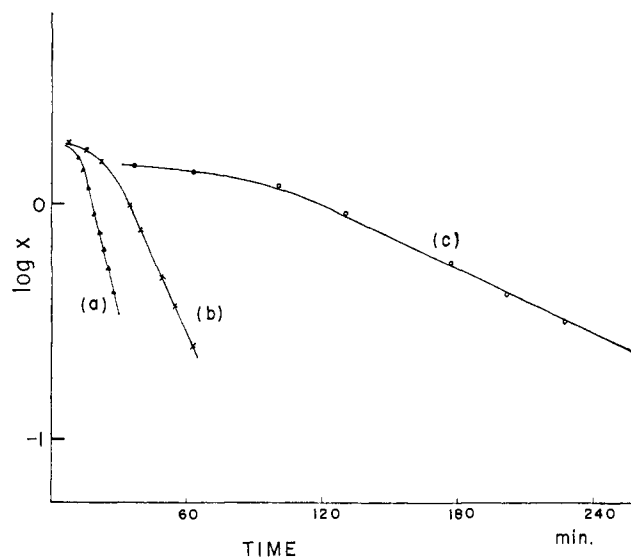
Figure 1. Thermal decomposition of $(C_2H_5)_2Ni(dipy)$: (a) 460 mg at 107.2°, (b) 449 mg at 103.8°, (c) 400 mg at 97.3°. The value x corresponds to the remaining amount of $(C_2H_5)_2Ni(dipy)$ determined volumetrically.

markable thermal stability of the C_2H_5–Ni bonds in the nickel complex.

π-Complex Formation between Nickel and Olefins. The C_2H_5–Ni bonds of $(C_2H_5)_2Ni(dipy)$ are easily cleaved during reactions with substituted olefins to give olefin-coordinated zerovalent complexes. If the olefins are arranged in decreasing order of the Alfrey-Price e values,[11] which are considered to reflect the polarity of the vinyl group, striking correlations are noted. Reactions of $(C_2H_5)_2Ni(dipy)$ with electron-withdrawing olefins of higher e values (maleic anhydride, acrylonitrile) took place at lower temperatures and higher rates. Reactions with olefins of medium e values (methacrylonitrile, methyl acrylate, methyl methacrylate, 2-vinylpyridine) took place slowly, while reactions with olefins with low or negative e values (vinyl acetate, styrene, isobutyl vinyl ether, ethylene, norbornene, and 1,5-cyclooctadiene) either proceeded slowly or did not take place. With olefins of relatively high e values (acrylonitrile and acrolein) unstable five-coordinate adducts, $R_2Ni(dipy)(olefin)$, of type 2 were isolated in addition to dealkylated complexes, Ni-(dipy)(olefin)$_n$, of type 3. Formation of five-coordinate type-2 complexes was also indicated by color change with maleic anhydride, methyl acrylate, methyl vinyl ketone, cyclooctadiene, and norbornene, but the complexes were not isolable in these cases. The reaction with styrene gave butane and a greenish yellow zerovalent complex with an approximate composition of Ni(dipy)(styrene)$_n$ ($n = 0.6$–0.7). Probably a complex Ni(dipy)(styrene) dissociates in solution and consequently the pure complex is not isolable. Acrylonitrile, methyacrylonitrile, and methyl acrylate yield complexes of type 3 with $n =$ both 1 and 2, depending on the preparative conditions (see Experimental Section). The variation of products with different olefins can be explained by differences in stabilities of the π complexes.[10,12] The reaction of 1 with vinyl chloride

(11) J. Brandrup and E. H. Immergut, "Polymer Handbook," Vol. II, Interscience, New York, N. Y., 1966, p 341.

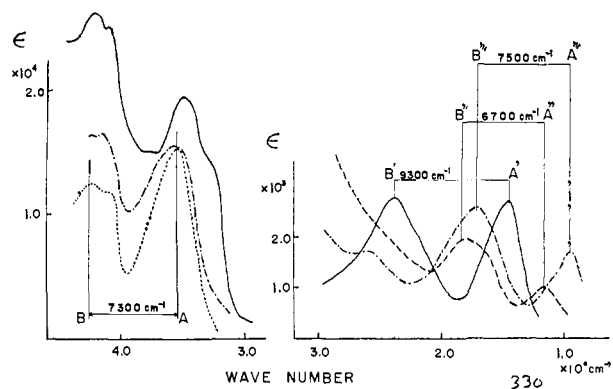(12) Stability constants of Ni(dipy)(olefin) were measured spectro-

Figure 2. Ultraviolet and visible spectra of $(C_2H_5)_2Ni(dipy)$ (———), $(C_2H_5)_2Fe(dipy)_2$ (–·–·–·), $C_2H_5Co(dipy)_2$ (— — —), and dipyridyl (·····) in tetrahydrofuran.

Figure 3. Energy level diagram of the alkyl(dipyridyl)(transition metal) complexes. As to the signs, A-B''' refer to Figure 2.

caused the splitting of the C–Cl bond and resulted in the formation of $Ni(dipy)Cl_2$. No reaction of 1 with isobutyl vinyl ether and ethylene was observed at room temperature or at 60°.

Dimethyl(dipyridyl)nickel resembles its ethyl homolog and gives ethane and various olefin-coordinated zerovalent complexes of the type $Ni(dipy)(olefin)_n$ on reaction with olefins. Reaction rates are considerably lower.

Infrared Spectra. Infrared bands related to double bonds of free olefins are not observed in the olefin-coordinated complexes of type 3, since a profound change in the nature of the double bond occurs on coordination. The change of the double bond in the olefin can be observed indirectly by shifts of the $\nu_{C\equiv N}$ and $\nu_{C=O}$ bands of the substituents. In adducts of acrylonitrile and methacrylonitrile, the $\nu_{C\equiv N}$ bands are lowered by 30–40 cm^{-1} with respect to the free nitriles. It is known that the coordination of saturated nitriles with metals through nitrogen causes the shift of $\nu_{C\equiv N}$ bands to higher frequencies,[13] whereas a shift in the opposite direction in the adducts of unsaturated nitriles has been interpreted as an indication of bonding through the double bond.[13,14] The shifts of the $\nu_{C\equiv N}$ bands to lower frequencies in our olefin–nickel complexes suggest the coordination of olefins with nickel through double bonds.

The carbonyl stretching frequencies of olefins having carbonyl substituents are also lowered on formation of π complexes with nickel. Similar shifts have been reported on various iron–carbonyl complexes coordinated with α,β-unsaturated carbonyl compounds[15] and on a nickel complex of maleic anhydride.[16] It is noted that the $\nu_{C=O}$ of vinyl acetate are shifted to extraordinarily low frequencies on coordination with nickel when compared with other α,β-unsaturated carbonyl compounds. The color of the vinyl acetate complex (light green) is also quite different from those of other nickel complexes

of olefins having conjugated carbonyl substituents (red or reddish brown). These facts, together with the isolation of only the 1:1 adduct of vinyl acetate with nickel, suggest that vinyl acetate is coordinated with nickel through both the vinyl and carbonyl groups. The presence of oxygen between the vinyl and carbonyl groups might give a favorable arrangement for the formation of a chelate as depicted in I.

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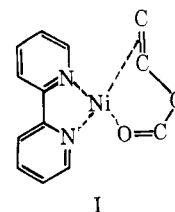
In contrast to the reactions of $(C_2H_5)_2Ni(dipy)$ with unsaturated nitriles and carbonyl compounds, saturated nitriles and carbonyl compounds do not give rise to the splitting of ethyl–nickel bonds at room temperature and no adduct was isolable even at $-78°$. These facts indicate a weak interaction between nickel and nitrile or carbonyl groups and support the assumption of strong π-bond formation between nickel and the double bond.

Electronic Spectra. Ultraviolet and visible spectra of $(C_2H_5)_2Ni(dipy)$ in tetrahydrofuran are shown in Figure 2 together with those of dipyridyl, $(C_2H_5)_2Fe$-$(dipy)_2$, and $(C_2H_5)Co(dipy)_2$. Each alkyl(dipyridyl) complex of Ni, Fe, and Co has two absorption bands in the visible region with an energy difference of 6700–9300 cm^{-1}, corresponding to an energy difference of 7300 cm^{-1} between the two absorption bands of free dipyridyl in the uv region. This fact strongly supports our previous assignment[4a] of the visible absorptions of the nickel complex to charge-transfer bands on the basis of a large molar extinction coefficient (approximately 3×10^3). Furthermore, it is seen in Figure 2 that the maxima of the absorption bands (ν_{max} values) shift to higher frequencies in the order of atomic number: $\nu_{max}(Fe) < \nu_{max}(Co) < \nu_{max}(Ni)$. This further supports the assignment of the visible absorptions to charge-transfer bands, because the ionization potential, IP, of outer-shell electrons (3d, 4s, etc.) is considered to increase in order of atomic number in the first transition series,[17] and the energy of the charge-transfer band ex-

scopically and are reported in the succeeding paper: T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3360 (1971).

(13) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963); M. F. Farona and G. R. Tompkin, *Spectrochim. Acta, Part A*, **24**, 788 (1968).

(14) G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961).

(15) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963); G. O. Schenck, E. K. von Gustorf, and M. J. Jun, *Tetrahedron Lett.*, 1059 (1962); E. K. von Gustorf, M. J. Jun, and G. O. Schenck, *Z. Naturforsch. B*, **18**, 503 767 (1963).

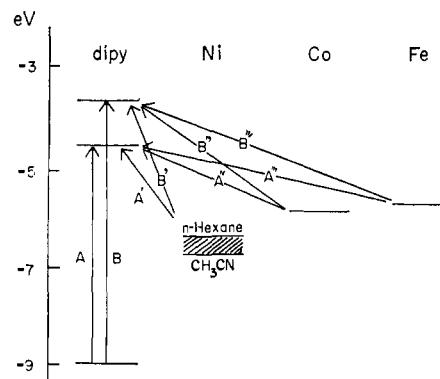(16) E. Weiss and K. Stark, *ibid.*, B, **20**, 490 (1965).

(17) H. B. Gray and C. J. Ballhausen, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964.
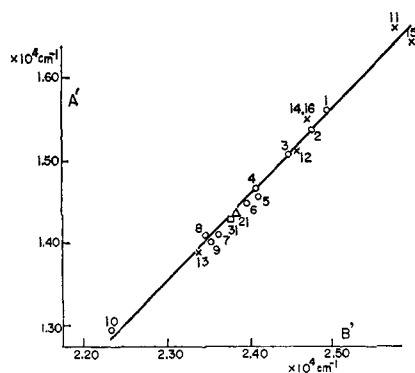
Figure 4. Relation between the two charge-transfer bands of R_2Ni-(dipy): (A') lower frequency band, (B') higher frequency band. For R $= C_2H_5$ (○): (1) acetonitrile, (2) dimethylformamide, (3) acetone, (4) methyl methacrylate, (5) ethyl acetate, (6) tetrahydrofuran, (7) styrene, (8) toluene, (9) benzene, (10) n-hexane. For R $=$ CH$_3$ (✕): (11) acetonitrile, (12) tetrahydrofuran, (13) n-hexane, (14) ethyl acetate, (15) acrylonitrile, (16) methyl acrylate. For R $=$ n-C$_3$H$_7$ (△): (21) tetrahydrofuran. For R $=$ i-C$_4$H$_9$ (□): (31) tetrahydrofuran.

Figure 5. Relation between ν_{max} of the lower charge-transfer band of R_2Ni(dipy) and the σ^* value of R.[24]

pressed by the equation[18] $h\nu_{CT} \cong IP - EA$ is expected to increase in the order Fe $<$ Co $<$ Ni, where EA is the electron affinity of the acceptor, dipyridyl.

Figure 3 is an energy level diagram based on these facts. The ionization potential of dipyridyl was estimated as 9.0 eV from a comparison of the IP's of benzene[19] (9.46 eV), biphenyl[20] (8.79 eV), and pyridine[19] (9.70 eV), and assuming IP(pyridine) − IP(dipyridyl) = IP(benzene) − IP(biphenyl).[21] The lowest vacant energy levels of dipyridyl were evaluated from the absorption maxima of dipyridyl (A and B in Figure 2), and the highest occupied energy levels of Ni, Co, and Fe were estimated from the charge-transfer bands of the corresponding complexes in Figure 2. It is seen from Figure 3 that the IP's of Ni, Co, and Fe are close to the first ionization potentials (about 7.5 eV) and are much smaller than the second ionization potentials of these metal ions (about 17 eV).[22] Therefore, the formally divalent alkyldipyridyl complexes may be regarded as in essentially zerovalent states. The visible bands of R_2-Ni(dipy) shift only slightly to lower frequency with variation of alkyl groups from methyl to isobutyl, whereas the stabilities of R–Ni bonds change drastically from methyl to isobutyl. Therefore, the highest filled orbital of R_2Ni(dipy) is considered to be a d orbital and not the σ_{R-Ni} orbital. The assignment of the visible absorption bands of R_2Ni(dipy) to the charge transfer between the highest filled energy level of the transition metal and the vacant antibonding energy levels of dipyridyl proves reasonable and very useful in the following discussions.

In contrast to the octahedral iron complex R_2Fe-(dipy)$_2$, the nickel complex of type 1 has a planar configuration as can be judged from its diamagnetism,[4b] and hence has one or two sites open for coordination of other ligands. This is reflected in the shift of absorption bands of the complexes in various solvents. Whereas $(C_2H_5)_2$Fe(dipy)$_2$ shows only minor changes of spectrum in different solvents, the spectrum of $(C_2H_5)_2$-Ni(dipy) is affected markedly by the solvent. The relation between the two absorption maxima of $(C_2H_5)_2$Ni-(dipy) and the solvent is shown in Figure 4. The methyl, propyl, and isobutyl complexes also show similar spectral changes (see Figure 4). Figure 4 indicates that the energy difference between the higher frequency band B′ and the lower band A′ remains constant despite the change of the absolute values of the energy levels in different solvents. This result agrees with our previous conclusion as shown in Figure 3 and renders additional support to the energy level diagram.

If we compare the absorption maxima of the methyl, ethyl, propyl, and isobutyl complexes in the same solvent (tetrahydrofuran), we note that the absorption maxima shift to higher frequency in the order of i-C$_4$H$_7 <$ n-C$_3$H$_7 <$ C$_2$H$_5 <$ CH$_3$. This shift may indicate the lowering of the energy of the highest occupied level in the order of i-C$_4$H$_9 >$ n-C$_3$H$_7 >$ C$_2$H$_5 >$ CH$_3$, reflecting the inductive effect of the alkyl groups attached to nickel.[12] The magnitude of the energy change is approximately parallel to the σ^* values proposed by Taft[23] (Figure 5).

In Figure 4 we also note that solvents which are empirically regarded as having higher coordinating ability cause larger blue shifts.[24] Polar solvents cause blue shifts in the following order: acetonitrile $\approx$ acrylonitrile $>$ dimethylformamide $>$ acetone $>$ ethyl acetate $\approx$ methyl methacrylate $\approx$ methyl acrylate $>$ tetrahydrofuran $>$ benzene $\approx$ toluene $\approx$ styrene $>$ diethyl ether $\approx$ isobutyl vinyl ether $\gg$ n-hexane. The blue shift is explained as the lowering of the highest occupied energy level of nickel by the coordination of solvent as illustrated in Figure 3.

That the solvents causing larger blue shifts have in fact higher coordinating ability toward nickel was shown as follows. The spectra of $(C_2H_5)_2$Ni(dipy) in different mixtures of CH$_3$CN and diethyl ether were observed. The concentrations of the nickel complexes

(18) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(19) I. Omura, H. Baba, and K. Higasi, J. Phys. Soc. Jap., 10, 317 (1955).

(20) A. Streitwieser, Jr., J. Amer. Chem. Soc., 82, 4123 (1960).

(21) This equation is based on the assumption that the decrease in IP caused by enlarging the π system of aromatic hydrocarbons is also the same in aromatic heterocyclic compounds.

(22) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards (U. S.) Circular No. 467, Vol. II, U. S. Government Printing Office, Washington, D. C., 1952, pp 49, 78, 97; "American Institute of Physics Handbook," McGraw-Hill, New York, N. Y., 1957, pp 7–14.
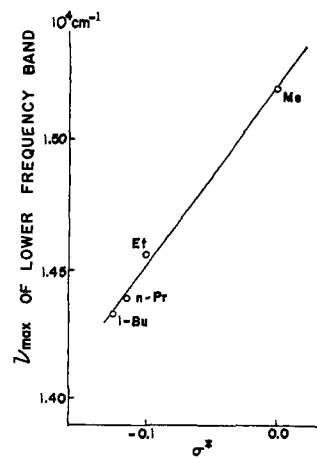
(23) R. W. Taft, Jr., J. Amer. Chem. Soc., 75, 4231 (1953).

(24) A. Burawoy, Chem. Ber., 63, 3155 (1930); J. Chem. Soc., 1177 (1939); 20 (1941); G. J. Brealey and M. Kasha, J. Amer. Chem. Soc., 77, 4462 (1955); H. McConnell, J. Chem. Phys., 20, 700 (1952); V. G. Krishna and L. Goodman, J. Amer. Chem. Soc., 83, 2043 (1961).
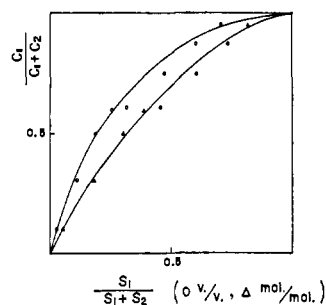
Figure 6. Solvation of $(C_2H_5)_2Ni(dipy)$ in mixed solvents; S_1 = the amount of added acetonitrile (in volume (O) and moles (△)), S_2 = the amount of diethyl ether, C_1 = the concentration of $(C_2H_5)_2$-Ni(dipy) coordinated with acetonitrile, and C_2 = the concentration of $(C_2H_5)_2Ni(dipy)$ coordinated with diethyl ether. Concentrations of the solvent-coordinated $(C_2H_5)_2Ni(dipy)$ were determined spectroscopically.
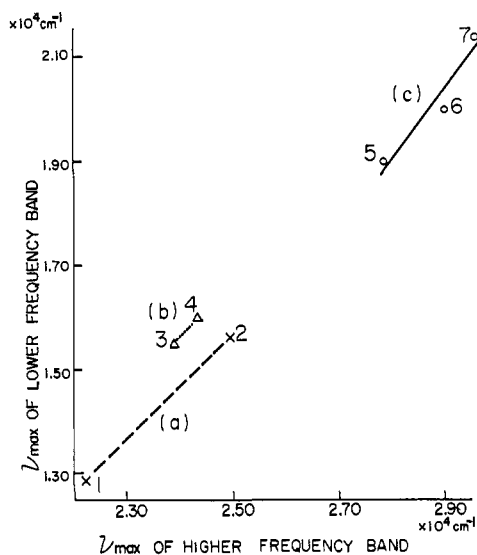

Figure 7. Relations between two ν_{max} values: (a) $(C_2H_5)_2Ni(dipy)$ in various solvents, cf. Figure 4; (b) green solutions of Ni(dipy)-(methyl acrylate)$_2$ in (3) tetrahydrofuran (THF) and (4) acetone; (c) red solutions of (5) Ni(dipy)(methyl methacrylate) in THF, (6) Ni(dipy)(methyl acrylate) in THF, and (7) Ni(dipy)(methacrylonitrile) in THF.

Figure 8. Change of the spectrum in the reaction of $(C_2H_5)_2Ni$-(dipy) with methyl methacrylate at 14°.

coordinated respectively with acetonitrile and ether could be estimated from the absorbances characteristic of the two species. The concentration of the acetonitrile-coordinated species is plotted against the molar concentration of acetonitrile in the acetonitrile–ether mixtures in Figure 6. Similar results can be obtained with other couples of solvents. The result is consistent with our assumption that a solvent causing a larger blue shift has a higher coordinating ability.

Another remarkable observation is that the spectra of $(C_2H_5)_2Ni(dipy)$ in methyl methacrylate and styrene, taken shortly after the dissolution of $(C_2H_5)_2Ni(dipy)$, are substantially the same as those in ethyl acetate and benzene, respectively. This implies that methyl methacrylate and styrene may first coordinate with nickel through the carbonyl and phenyl groups. Since $(CH_3)_2$-Ni(dipy) reacts with olefins much more slowly than $(C_2H_5)_2Ni(dipy)$, the spectral change can be followed in the absence of solvent even in reactions of olefins with strongly electron-withdrawing substituents (e.g., acrylonitrile and methyl acrylate).
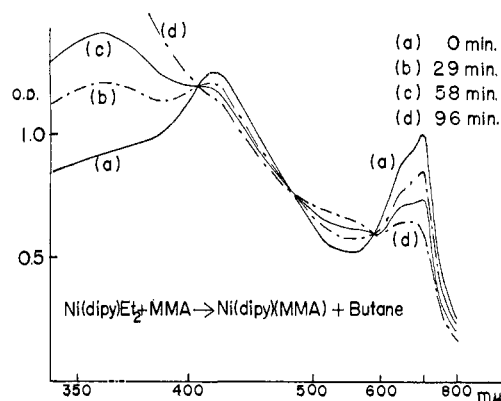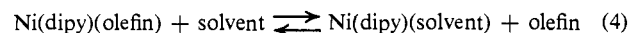
The visible spectra of the olefin-coordinated nickel complexes are of interest. The isolated zerovalent π complexes are usually red or reddish brown but dissolve in excess solvent to give green solutions which turn red upon addition of olefins to the solutions. We assume the following equilibrium in solution[12]

$$Ni(dipy)(olefin) + solvent \rightleftharpoons Ni(dipy)(solvent) + olefin \quad (4)$$

The green species is considered to be Ni(dipy)(solvent) and the red one Ni(dipy)(olefin). The green solutions and the red solutions show two absorption bands in the visible region, although part of the band of some of the red solution is obscured by the slope of the strong ultraviolet band. The relations of the ν_{max} values of these two absorption bands are presented in Figure 7 together with the previously described relation in Figure 4. Figure 7 indicates strong blue shifts of the charge-transfer bands in the olefin-coordinated complexes when compared with the uncoordinated species. Spectra similar to that in Figure 7c were also observed at low temperatures in the unstable five-coordinate olefin-coordinated dialkyl complexes of the type $R_2Ni(dipy)$-(olefin). The visible spectrum of orange $(C_2H_5)_2Ni$-(dipy)(acrylonitrile) at $-78°$ shows an absorption maximum at 480 mμ and resembles that of Ni(dipy)-(acrylonitrile) at 430 mμ. These bands are considered to be the lower charge-transfer bands of the nickel-dipyridyl complexes. The strong blue shifts of the charge-transfer bands compared with those of $(C_2H_5)_2$-Ni(dipy) can be interpreted as the lowering of the highest occupied energy level of nickel by coordination of olefins, and the similarity of the spectra of $(C_2H_5)_2Ni$-(dipy)(olefin) 2 and Ni(dipy)(olefin) 3 suggests the similarity of the interactions of the olefin with nickel in 2 and 3.[12]

Reaction Mechanism of $(C_2H_5)_2Ni(dipy)$ with Olefins. The reactions of $(C_2H_5)_2Ni(dipy)$ with various olefins were studied spectroscopically, usually in tetrahydrofuran, but for methyl methacrylate and styrene pure olefins were used to obtain reasonably fast reaction rates. As reaction proceeds, $(C_2H_5)_2Ni(dipy)$ turns from green to red. The spectral change of $(C_2H_5)_2Ni$-(dipy) in the reaction with methyl methacrylate is shown in Figure 8. Except for acrylonitrile, clear isosbestic points were observed, suggesting the essentially exclusive occurrence of $R_2Ni(dipy)$ and Ni(dipy)(olefin) as shown in Figure 8. Since the products do not absorb at 700 mμ, reaction can be followed by the decrease

of the optical density at 700 mμ. For methyl methacrylate and styrene, the optical density at the lower ν_{max} of $(C_2H_5)_2Ni(dipy)$ was employed.

Figure 9 indicates that the reaction rates are first order with respect to the concentrations of $(C_2H_5)_2Ni(dipy)$ and olefins.

$$R = -d[(C_2H_5)_2Ni(dipy)]/dt =$$
$$k[(C_2H_5)_2Ni(dipy)][olefin] \quad (5)$$

This rate equation holds for methacrylonitrile, acrolein, methyl vinyl ketone, acrylamide, methyl acrylate, methyl methacrylate, and styrene.

In Table II the temperature dependences of the rate constants for different olefins are shown. Rate constants at 27°, activation energies, and activation parameters derived from plots of log k vs. $1/T$ are summarized in Table III.

Table II. Specific Rate Constants of Reactions of $(C_2H_5)_2Ni(dipy)$ with Olefins

Olefin	Temp, °C	k, 1. mol⁻¹ min⁻¹
Acrolein	22.6	1.66
	28.4	2.24
	34.7	4.59
Methyl vinyl ketone	23.5	0.87
	28.9	1.59
	34.0	2.48
Acrylamide	23.2	0.176
	28.7	0.342
	30.2	0.359
Methyl acrylate	21.1	0.045
	29.1	0.096
	30.5	0.103
	34.7	0.148
Methacrylonitrile	21.8	0.0076
	28.7	0.0190
	34.3	0.0429
Styrene	19.6	0.00207
	30.3	0.00502
	34.7	0.00630
Methyl methacrylate	17.2	0.00058
	30.0	0.00113
	35.3	0.00139

Table III. Rate Constants and Activation Parameters of the Reactions of $(C_2H_5)_2Ni(dipy)$ with Various Olefins at 300°K

Olefin	$k,^a$ 1. mol⁻¹ min⁻¹	E_a, kcal/ mol	$\Delta H^{\ddagger}$, kcal/ mol	$\Delta S^{\ddagger}$, eu
Acrolein	2.5	16.2	15.6	−12.8
Methyl vinyl ketone	1.3	18.1	17.5	−7.8
Acrylamide	0.27	19.9	19.3	−5.1
Methyl acrylate	0.074	16.0	15.4	−20.4
Methacrylonitrile	0.015	25.4	24.8	+7.7
Styrene^a	0.0038	13.6	13.0	−33.6
Methyl methacrylate^a	0.0011	9.0	8.4	−52.2

^{a} Since the reactions of $(C_2H_5)_2Ni(dipy)$ with styrene and methyl methacrylate in dilute solutions are too slow, approximate rate constants were evaluated from the reaction in bulk using the rate equation $r = k[(C_2H_5)_2Ni(dipy)][olefin]$ and the concentrations of undiluted olefins.

From the above experimental results we assume that the reaction proceeds through the following steps: (a) coordination of the olefin with nickel through the substituent, (b) rearrangement to a π complex of a type-2 complex and activation of the alkyl–nickel bonds, and
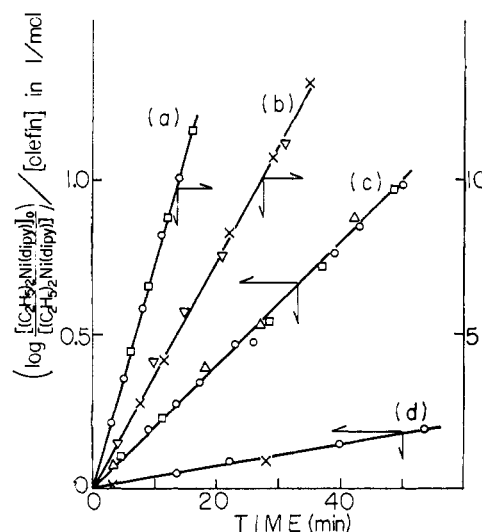

Figure 9. Reaction of $(C_2H_5)_2Ni(dipy)$ with various substituted olefins in tetrahydrofuran. The concentrations of $(C_2H_5)_2Ni(dipy)$ were evaluated from the optical densities at fixed λ_{max}: (a) acrolein, 22.6°, (O) 0.115 and (□) 0.0344 mol/l.; (b) methyl vinyl ketone, 23.5°, (∇) 0.0507 and (×) 0.0172 mol/l.; (c) methyl acrylate, 21.1°, (□) 0.918, (O) 0.597, and (△) 0.128 mol/l.; (d) methacrylonitrile, 21.8°, (O) 0.867 and (×) 0.263 mol/l.

(c) splitting of the alkyl–nickel bonds with the resultant formation of an olefin-coordinated zerovalent complex of type 3 and coupling or disproportionation of the two alkyl groups. These steps may be expressed as follows for the reaction of $(C_2H_5)_2Ni(dipy)$ with a substituted olefin.
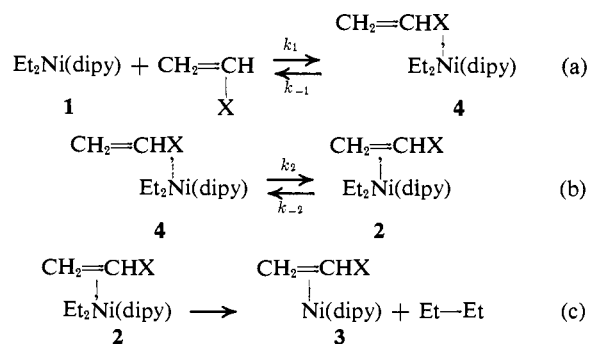
Initial coordination of the olefin through the substituent was observed spectroscopically with methyl methyacrylate and styrene. The coordination through the nitrile group with nickel was observed in the reaction of acrylonitrile with $(C_2H_5)_2Ni(dipy)$, where a transient absorption band was observed at the same frequency as one of two bands of complex 1 in CH_3CN (this explains the failure to observe isosbestic points in the case of acrylonitrile). Since $(C_2H_5)_2Ni(dipy)$ is quite stable in ethyl acetate, benzene, or acetonitrile in the absence of air, the carbonyl, phenyl, or nitrile group of the substituted olefin apparently does not cause enough activation of the alkyl–nickel bonds to lead to splitting, and the interaction of the double bond with nickel is necessary for the required activation of the alkyl–nickel bonds.

For most reactions involving complex 1 in tetrahydrofuran, clear isosbestic points were observed until the reactions were 70–80% completed. This indicates that only the starting species 1 and the end product 3 are present in solution. Since the interaction of the double
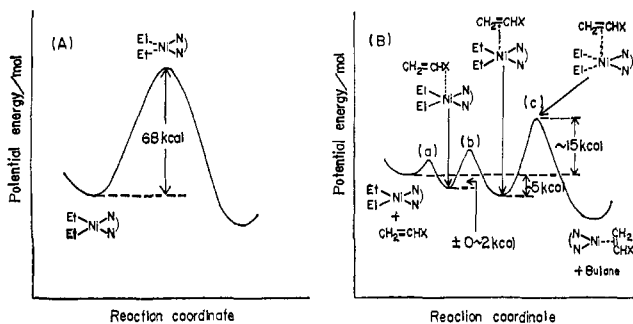
Figure 10. Potential energy curves for the splitting reaction of R–Ni bonds (A) in the absence and (B) in the presence of olefin.

bond of the olefin with nickel is necessary for activation of alkyl–nickel bonds, the rate-determining step should occur after (b). Since we can sometimes isolate complexes of type 2 at low temperatures and since such complexes can be converted to the original complex 1 by raising the temperature and removing the coordinated olefins, complexes of types 1, 2, and 4 are regarded to be in equilibrium. Therefore the rate-determining step should be (c) and the equilibria a and b should be shifted to the left in reactions at room temperature. The rate equation derived from the above assumptions can be expressed as follows.

$$ r = k_3 \left[\frac{CH_2{=}CHX}{(C_2H_5)_2Ni(dipy)} \right] = $$

$$ k_3 \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}} [(C_2H_5)_2Ni(dipy)][CH_2{=}CHX] $$

This equation is in agreement with the experimental reults.

The reaction profile is schematically represented by Figure 10. Thermolysis of $(C_2H_5)_2Ni(dipy)$ in the absence of an olefin requires a large activation energy (68 kcal/mol) to break Ni–Et bonds (Figure 10A). In the presence of an olefin the activation energy for the scission of Ni–Et bonds is about 15 kcal/mol. We assume that this decrease in the activation energy is caused by π-complex formation between $Et_2Ni(dipy)$ and the olefin (Figure 10 B). The enthalpy difference between the reactants and the adduct 2 as revealed from the measurement of the equilibrium constants[12] was evaluated to be of the order of 5 kcal/mol. As described earlier, the presence of $(C_2H_5)_2Ni(dipy)$ coordinated with the olefin through the substituent has been proved spectroscopically. Judging from coordination ability, represented in Figures 4 and 6, we estimate that the enthalpy of the nitrile-coordinated species will be 2 kcal/mol less than that of an ether-coordinated species, but in some cases the substituent-coordinated species may have larger enthalpy than the original $(C_2H_5)_2Ni(dipy)$ coordinated by the solvent employed.

In the cases of reactions of $(C_2H_5)_2Ni(dipy)$ (1) with undiluted methyl methacrylate and styrene, equilibrium a is toward the right, favoring formation of the substituent-coordinated species 4, and the reactions we observe spectroscopically start from the substituent-coordinated species 4. The reaction rate is thus first order in the concentration of $(C_2H_5)_2Ni(dipy)(olefin)$ 4.

As shown in Table III, the activation enthalpies are smaller and the activation entropies more negative in

reactions of $(C_2H_5)_2Ni(dipy)$ with neat styrene and methyl methacrylate compared with the values for other substituted olefins in tetrahydrofuran. This fact might be explained by assuming the coordination of two olefin molecules with the nickel in the transition states in the absence of solvent. Such a double coordination of olefins to complex 1 might enhance the activation of Ni–C bonds.

The complexes $Ni(dipy)(acrylonitrile)_2$, $Ni(dipy)(maleic\ anhydride)_2$, and $Ni(dipy)(methyl\ vinyl\ ketone)_2$ were prepared in a similar manner from $(CH_3)_2Ni(dipy)$ and identified. In efforts to isolate unstable adducts of type 2 in the reactions of $(CH_3)_2Ni(dipy)$ with acrylonitrile and acrolein, we observed a color change from green to red, indicating complex formation. However, attempts to isolate the orange adducts failed. Removal of olefins by evaporation at 10^{-3} mm and at $-78°$ gave only the green starting material, $(CH_3)_2Ni(dipy)$. The affinity of the methyl–nickel complex for olefins was found to be smaller than that of ethyl–nickel complex.[12]

The reactions of $(n\text{-}C_3H_7)_2Ni(dipy)$ with acrylonitrile and methyl acrylate were also studied. These reactions were faster than those of $(C_2H_5)_2Ni(dipy)$ (Table IV). In Table IV the σ^* values[23] are also given.

Table IV. Rate Constants of the Reactions of $R_2Ni(dipy)$ with Methyl Acrylate at 23.3°

$R_2Ni(dipy)$	σ^* of R	k, l. mol^{-1} sec^{-1}
$(CH_3)_2Ni(dipy)$	0.00	5.8×10^{-6}
$(C_2H_5)_2Ni(dipy)$	-1.00	9.2×10^{-4}
$(n\text{-}C_3H_7)_2Ni(dipy)$	-1.15	4.3×10^{-3}

A plot of σ^* vs. log k indicates a linear relationship. Besides the zerovalent π complex of type 3, the unstable adduct of type 2 involving $(n\text{-}C_3H_7)_2Ni(dipy)$ with acrylonitrile was isolated at $-78°$. But only 86% of acrylonitrile could be recovered from the supposed adduct of type 2 when it was warmed to room temperature in vacuo. Partial reaction according to eq 2 is suggested.

An Energetic Consideration of the Stability and Activation of the Alkyl–Nickel Bonds. Chatt and Shaw have used ligand-field theory to account for the stability of alkyl–metal complexes.[25] They considered two possibilities for the splitting of the carbon–metal bond: (a) an electron promotion from the relatively high-energy filled d orbital to the antibonding σ orbital of the metal-to-carbon bond and (b) electron promotion from a bonding σ_{R-M} orbital to a vacant d orbital. They explained the stability of the alkyl–metal complex by considering the energy gaps between the two orbitals in case a and case b. For case a, which is applicable to square-planar and octahedral complexes of d^6–d^8 systems, the stability is considered to increase if the energy difference is large, which is accomplished by choosing ligands capable of forming strong π bonds with the metal. This explanation is now widely accepted. For metal complexes with fewer d electrons (e.g., Ti and V), case b has been considered, and the requirement of having an electronegative ligand with a small ligand-field strength was postulated to achieve the stabilization. An increase in the energy difference

(25) J. Chatt and B. L. Shaw, J. Chem. Soc., 705 (1959).

between the empty non-σ-bonding d orbitals and low-lying σ-bonding orbitals provides the extra stability. This view was further advanced by Cossee to explain the activation of the metal–alkyl bond by coordination of an olefin.[26] In Cossee's model, the lowering of a vacant or partly vacant d orbital of the central metal atom by coordination of an olefin through π bonding was assumed. This lowering will make the energy gap between the d orbital and a low-lying σ_{R-M} orbital smaller and make the promotion of an electron from the σ_{R-M} orbital to the d orbital easier. Thus the R–M bond becomes more susceptible to breakage. We believe that a similar explanation accounts for the stability and activation of the alkyl–metal bond in d^6–d^8 systems. In discussing the alkyl–metal bond, electron promotion from the bonding alkyl–metal orbital to a vacant d orbital appears to be a more direct and logical explanation of the bond splitting. There may be another path for electron promotion from the low-lying σ_{R-M} orbital to the vacant d orbital; i.e., an electron may be promoted to a lowest vacant energy level from a highest occupied energy level, to which, in turn, an electron may be promoted from the σ_{R-M} orbital. Both types of direct and indirect promotions will lead to the same conclusion as far as the stability of the R–M bond is concerned. In the case of the alkyl(dipyridyl)metal complexes stabilization of the alkyl–metal bonds may be ascribed to any or all of the following reasons. (1) The small values of the ionization potentials of the complexes (Figure 3) suggest that the energy levels of the occupied d orbitals of the metals are higher compared with those of the metal complexes in their higher oxidation states and the energy gaps between the bonding σ_{R-M} orbitals and the vacant d orbitals are larger. (2) Dipyridyl, a strong-field ligand, increases the energy gap Δ between the highest occupied level and the lowest vacant level, and also the energy difference between the σ_{R-M} orbital and the lowest vacant orbital. Both factors may be operative to enhance the stability of the alkyl(dipyridyl) complexes.

As we see from the shift of the charge-transfer bands of $(C_2H_5)_2Ni(dipy)$, coordination of solvents to the vacant site(s) of the square-planar complex depresses the energy levels of the d orbitals; polar solvents such as CH_3CN are more effective than nonpolar solvents such as hexane. This effect is not enough for excitation of the bonding C–Ni orbital, whereas in the alkyl–iron complexes with weaker R–M bonds, strongly coordinating solvents cause the cleavage of the C–Fe bonds.[27] Coordination of olefins having electron-withdrawing substituents to the nickel complex causes marked lowering of the energy levels of the d orbitals, as demonstrated by blue shifts of the charge-transfer bands. If we assume that the magnitude of ligand-field splitting is chiefly determined by a strong-field ligand, dipyridyl, the values of Δ_1, Δ_2, and Δ_3 in Figure 11 may not be so different, and the lowering of the spectrally observed highest occupied energy level may be accompanied by lowering of the lowest vacant orbital. If the energy level of the Ni–C bond is seriously affected by coordination of the olefin to the empty site(s) of the square-planar nickel complex, the lowering of the vacant orbital would make excitation from the C–Ni

(26) P. Cossee, *J. Catal.*, 3, 80 (1964).
(27) T. Yamamoto, A. Yamamoto, and S. Ikeda, presented at the 24th Annual Meeting of the Chemical Society of Japan, Apr 1970, Tokyo.
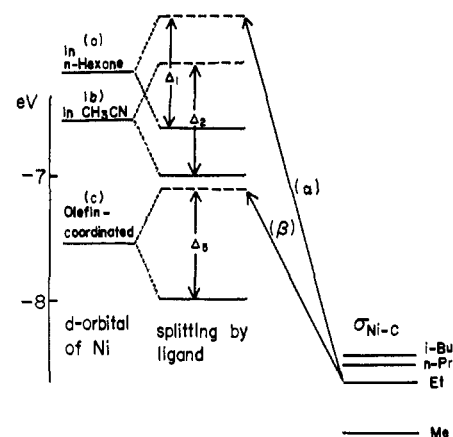
Figure 11. Tentative energy level relation diagram in activation of Ni–C bonds: (a) energy levels of d orbitals in *n*-hexane or without solvent, (b) coordinated with acetonitrile, (c) coordinated with an olefin. Δ_1, Δ_2, and Δ_3 represent energy level differences between the highest occupied energy levels and the lowest vacant energy levels. (α) and (β) represent the activations of an electron from the bonding orbital of Ni–C bond to the lowest vacant d orbitals.

orbital[28] much easier (the excitation energy required will decrease from α to β in Figure 11), and thus splitting of the C–Ni bonds would result.

In order to avoid ambiguity regarding the assignment of each orbital, we discuss the problem in terms of a simple ligand-field theory, but similar arguments may be made in terms of molecular orbital theory.

As is seen in Figure 7c, electron-withdrawing olefins give complexes with correspondingly higher frequencies of the charge-transfer bands, and hence the lowering of the d-orbital energy levels is indicated. This migration of electrons from nickel to olefins may be interpreted as back-donation from a d orbital of nickel to the antibonding π^* orbital of the olefin. In an extreme case, as in the tetracyanoethylene complex of nickel, back-donation causes complete charge transfer accompanied by oxidation of nickel, and the resultant complex becomes paramagnetic.

In other words, it may be simply stated that the withdrawing of electrons from nickel by π-bond formation with an olefin weakens the C–Ni bonds. The interaction between nickel and various substituted olefins will be discussed in detail in the succeeding paper.

The relative stabilities of the methyl, ethyl, propyl, and isobutyl complexes may be also discussed in terms of the energy level diagram shown in Figure 11. The specific alkyl group attached to nickel affects the energy levels of σ_{Ni-C} bonds and the d orbitals to different extents. The energy levels of the d orbitals are influenced indirectly by the kinds of alkyl groups present. The energy levels of the highest occupied d orbitals as estimated from the charge-transfer bands of R_2Ni-(dipy) in tetrahydrofuran (Figure 5) are on the order of -6.46 eV for the methyl complex, -6.37 eV for the ethyl complex, -6.32 eV for the propyl complex, and -6.31 eV for the isobutyl complex. On the other hand, the energy levels of the σ_{Ni-C} bonds are considered to be mainly determined by the energy levels of the alkyl radicals, and the energy level of the orbital as estimated from the ionization potential of the alkyl radical falls from -8.35 eV[29a] for the isobutyl group, to

(28) The Et–Ni orbital may lie in the vicinity of -8.5 eV as estimated from the IP value of the ethyl radical.

-8.67 eV[20] for the ethyl group, and to -9.90 eV[29b] for the methyl groups. Thus the stabilities of alkyl–nickel complexes are influenced to a greater extent by the energy levels of the σ_{Ni-C} orbitals than by those of the metal orbitals. The order of the thermal stabilities of $R_2Ni(dipy)$ as judged from the decomposition temperatures of the complexes is in agreement without our expectation from the energetic considerations. In the case of the isobutyl group, some steric factor may be also involved to destabilize the complex.

Experimental Section

I. Materials. Solvents and liquid olefins were dehydrated, distilled, and stored under nitrogen before use. Tetracyanoethylene was recrystallized from chlorobenzene, mp 195°. Maleic anhydride was purified by sublimation. $(C_2H_5)_2Ni(dipy)$, $(C_2H_5)_2Fe$-$(dipy)_2$, and $C_2H_5Co(dipy)_2$ were prepared using the methods described in our previous papers.[3,4] $(CH_3)_2Ni(dipy)$, $(n-C_3H_7)_2Ni$-$(dipy)$, and $(i-C_4H_9)_2Ni(dipy)$ were prepared in analogous manners using corresponding dialkylaluminum monoethoxide.

Anal. Calcd for $(CH_3)_2Ni(dipy)$: C, 58.9; H, 5.75; N, 11.4. Found: C, 58.7; H, 5.55; N, 11.2. Calcd for $(C_3H_7)_2Ni(dipy)$: C, 63.8; H, 7.31; N, 9.30. Found: C, 61.7; H, 7.00; N, 9.19. $(C_3H_7)_2Ni(dipy)$ gradually decomposed at room temperature and after 10 days the analytical values were changed. Found: C, 62.3; H, 6.59; N, 9.69. The isolation of $(i-C_4H_9)_2Ni(dipy)$ was difficult owing to the low thermal stability of the complex and the lack of a suitable solvent from which the crystals can be obtained, and the analytical data always showed the product to be a mixture of $(i-C_4H_9)_2Ni(dipy)$ and dipyridyl.

II. General Preparative Procedures. All procedures were carried out under deoxygenated nitrogen, argon, or *in vacuo*. Liquid olefin and solvent were introduced by condensation *in vacuo* into a reaction vessel at $-196°$ containing the dialkyl(dipyridyl)-nickel. The reaction system was allowed to warm slowly to room temperature. With solid olefins such as tetracyanoethylene, maleic anhydride, and acrylamide, the solvent was introduced to a mixture of dialkyl(dipyridyl)nickel and olefin in a vacuum system by a trap-to-trap distillation. Gas in the reaction vessel was occasionally taken out for analysis by gas chromatography. The temperature at which evolution of gas begins was regarded as the decomposition temperature of the alkyl complex. In most cases yields of type **3** complexes were almost quantitative, and after recrystallization from appropriate solvents, usually over 65% of the crystals were recovered.

III. Reactions of Dialkyl(dipyridyl)nickel with Olefins and Isolation of the Olefin Adducts. 1. (Tetracyanoethylene)(dipyridyl)nickel, (TCNE)Ni(dipy). A mixture of 0.67 g (5.2 mmol) of tetracyanoethylene and 0.83 g (3.0 mmol) of dark green crystals of $(C_2H_5)_2Ni(dipy)$ in 20 ml of THF was allowed to react for 48 hr at 60°. The evolved gas consisted of almost pure n-butane. The dark brown precipitate was filtered and washed many times with diethyl ether and tetrahydrofuran and dried under vacuum. The dark brown solid was insoluble in almost all organic solvents. Esr spectrum of the complex (solid) showed a broad signal at $g = 2$; mp 116°, ir (KBr) 2190 cm⁻¹ (C≡N, shifted 40 cm⁻¹ to lower frequency). *Anal.* Calcd for $C_{16}H_8N_6Ni$: C, 56.0; H, 2.33; N, 24.6. Found: C, 53.8; H, 2.07; N, 26.6.

2. Bis(maleic anhydride)(dipyridyl)nickel, (MAH)₂Ni(dipy). A mixture of 5.00 g (5 mmol) of maleic anhydride (*e* value = 2.25) and 1.27 g (4.7 mmol) of $(C_2H_5)_2Ni(dipy)$ in 6 ml of acetone became immediately red on mixing at $-78°$ and evolved ethane and butane in a molar ratio of 1:12. The red complex was separated from the reaction mixture, crystallized from acetone, and dried *in vacuo;* mp 220°; ir (KBr) 1815–1730 cm⁻¹ (C=O, shifted about 50 cm⁻¹ to lower frequency). *Anal.* Calcd for $C_{18}H_{12}N_2O_2Ni$: C, 52.5; H, 2.92; N, 6.81; dipy, 40.0. Found: C, 53.1; H, 2.88; N, 6.74; dipy, 38.0.

A mixture of 1.10 g of maleic anhydride and 0.35 g of $(CH_3)_2$-$Ni(dipy)$ in 10 ml of ether did not show any change below $-15°$. At room temperature the mixture gradually became red and evolved a gas (methane:ethane = 1:8). The infrared spectrum of the red complex isolated from the reaction mixture was indentical with

that of the red complex obtained from the mixture of maleic anhydride and $(C_2H_5)_2Ni(dipy)$.

3. Reaction of Acrylonitrile with R₂Ni(dipy). (a) Low-Temperature Reaction and Isolation of R₂Ni(dipy)(AN). Acrylonitrile (*e* value = 1.20) was distilled *in vacuo* into a flask containing $(C_2H_5)_2$-$Ni(dipy)$ (0.972 g, 3.56 mmol) at $-78°$. The mixture was stirred for several hours until the solid became orange. Excess acrylonitrile was removed by evaporation at $-78°$ (10^{-4} mm) for 40 hr. The orange adduct is stable only at low temperature. Its acrylonitrile content was determined by warming it slowly to room temperature; the released acrylonitrile was condensed into a liquid nitrogen trap. The amount of acrylonitrile condensed was 0.180 g (3.39 mmol). The dark green residue (0.980 g, 101% of the original weight) was crystallized from acetone. The starting material, $(C_2H_5)_2Ni(dipy)$, was identified by infrared comparison and analytical data.

A similar orange 1:1 acrylonitrile adduct of $(n-C_3H_7)_2Ni(dipy)$ was prepared at $-78°$ in an analogous way, but only 86% of the coordinated acrylonitrile was recovered by warming the complex slowly to room temperature. In the case of $(CH_3)_2Ni(dipy)$ the similar orange adduct was formed in the presence of excess acrylonitrile, but when the excess acrylonitrile was removed by evaporation at $-78°$ (10^{-4} mm), the color of the solid changed to green and $(CH_3)_2Ni(dipy)$ was recovered.

(b) Room-Temperature Reaction. Reaction of $(C_2H_5)_2Ni(dipy)$ (0.80 g, 2.9 mmol) with acrylonitrile (1.0 ml, 15 mmol) in ether or tetrahydrofuran at room temperature and crystallization from a cold mixture of tetrahydrofuran and n-hexane containing excess acrylonitrile gave relatively stable red crystals of composition $Ni(dipy)(AN)_2$: mp 155.5° dec; ir (KBr) 2180 cm⁻¹ (C≡N, shifted 40 cm⁻¹ to lower frequency). *Anal.* Calcd for $C_{16}H_{14}N_4Ni$: C, 59.9; H, 4.40; N, 17.5. Found: C, 59.8; H, 4.51; N, 17.5.

On the other hand, crystallization from solvents without excess acrylonitrile yielded mixtures of $Ni(dipy)(AN)_2$ and $Ni(dipy)(AN)$, as judged from the elemental analysis, but no difference was observed between the infrared spectrum of the mixture and that of $Ni(dipy)(AN)_2$.

A mixture of 5.0 ml (76 mmol) of acrylonitrile and 0.42 g (1.7 mmol) of $(CH_3)_2Ni(dipy)$ slowly became red at room temperature, releasing ethane. The reaction was very slow compared with the reaction of $(C_2H_5)_2Ni(dipy)$. The infrared spectrum of the red solid obtained was almost the same as that of $Ni(dipy)(AN)_2$.

4. Reactions of Acrolein with $(C_2H_5)_2Ni(dipy)$. (a) Diethyl-(dipyridyl)(acrolein)nickel, $(C_2H_5)_2Ni(dipy)(AC)$. Acrolein (*e* value = 0.73) was distilled *in vacuo* into a reaction vessel containing $(C_2H_5)_2Ni(dipy)$ (0.87 g, 3.2 mmol) at $-78°$. The mixture was kept at this temperature overnight until all the solid became orange. Excess acrolein was removed by evaporation at $-78°$ (10^{-3} mm) for 60 hr. The orange solid which remained was then warmed to room temperature *in vacuo*. The volatile matter was condensed with liquid nitrogen and shown to be acrolein (0.20 g, 3.5 mmol) by infrared spectroscopy. The infrared spectrum of the green residue was identical with that of $(C_2H_5)_2Ni(dipy)$. This process was reproducible.

(b) Bis(acrolein)(dipyridyl)nickel, $(AC)_2Ni(dipy)$. A mixture of 4.0 ml (60 mmol) of acrolein and 0.95 g (3.5 mmol) of $(C_2H_5)_2$-$Ni(dipy)$ in 23 ml of tetrahydrofuran turned orange at $-78°$ as described above. The reaction mixture was gradually warmed to room temperature and the original dark green color of $(C_2H_5)_2$-$Ni(dipy)$ reappeared at about $-50°$. The mixture became red again at about $-5°$, where evolution of gas (mainly butane) was observed. After reaction for 48 hr at room temperature, the reddish brown solid was separated from the solution and crystallized from acetone and n-hexane: mp 266° dec; ir (KBr) 1595 cm⁻¹ (C=O, shifted 95 cm⁻¹ to lower frequency). *Anal.* Calcd for $C_{16}H_{18}N_2O_2Ni$: C, 58.8; H, 4.92; N, 8.53. Found: C, 60.8; H, 5.05; N, 8.08.

5. Bis(methacrylonitrile)(dipyridyl)nickel, (MAN)₂Ni(dipy), and (Methacrylonitrile)(dipyridyl)nickel, (MAN)Ni(dipy). A mixture of 5.0 ml (60 mmol) of methyacrylonitrile (*e* value = 0.81) and 1.38 g (4.9 mmol) of $(C_2H_5)_2Ni(dipy)$ was dark green below 0° and slowly became red at 0°, releasing ethane, ethylene, and butane in a ratio of 1:0.1:1.5. The mixture was allowed to react for 9 hr at room temperature. The dark red solid was crystallized from acetone: mp 240° dec; ir (KBr) 2160 cm⁻¹ (C≡N, shifted 30 cm⁻¹ to lower frequency). *Anal.* Calcd for $C_{14}H_{13}N_3Ni$: C, 59.6; H, 4.55; N, 14.9. Found: C, 57.9; H, 4.59; N, 14.2. The dark red solid was recrystallized from a mixture of n-hexane and acetone containing excess methacrylonitrile, and red crystals were obtained, ir (KBr) 2165 cm⁻¹ (C≡N). *Anal.* Calcd for

(29) (a) F. P. Lossing and J. B. deSousa, *J. Amer. Chem. Soc.*, **81**, 281 (1959); (b) F. P. Lossing, K. U. Ingold, and I. H. S. Henderwon, *J. Chem. Phys.*, **22**, 621 (1954).

$C_{18}H_{18}N_4Ni$: C, 61.9; H, 5.16; N, 16.1. Found: C, 61.2; H, 5.05; N, 16.0.

6. Bis(methyl vinyl ketone)(dipyridyl)nickel, (MVK)₂Ni(dipy). A mixture of 4.0 ml (49 mmol) of methyl vinyl ketone (e value = 0.69) and 1.11 g (4.1 mmol) of $(C_2H_5)_2Ni(dipy)$ was faintly reddish at −196°, green at −78°, and became red at about 0°, releasing butane. The red solid was washed with acetone several times: mp 125° dec; ir (KBr) 1595 cm⁻¹ (C=O, shifted 80 cm⁻¹ to lower frequency). Anal. Calcd for $C_{16}H_{20}N_2O_2Ni$: C, 60.9; H, 5.64; N, 7.86. Found: C, 59.4; H, 5.61; N, 7.34.

7. Bis(methyl acrylate)(dipyridyl)nickel and (Methyl acrylate)-(dipyridyl)nickel, Ni(dipy)(MA)₂ and Ni(dipy)(MA). A mixture of 5.0 ml (55 mmol) of methyl acrylate (e value = 0.60) and 1.34 g (4.9 mmol) of $(C_2H_5)_2Ni(dipy)$ became red at −196°, turned to dark green at −78°, and became red again at 0-20°. At 0-20° butane was evolved. The reddish brown solid was crystallized from acetone: mp 133-139° (melting is accompanied by a color change from red to green); ir (KBr) 1670 cm⁻¹ (C=O, shifted 68 cm⁻¹ to lower frequency). Anal. Calcd for $C_{14}H_{14}N_2O_2Ni$: C, 55.8; H, 4.65; N, 9.30; dipy, 51.9. Calcd for $C_{18}H_{20}N_2O_4Ni$: C, 55.8; H, 5.16; N, 7.24; dipy, 40.3. Found: C, 56.1; H, 5.12; N, 8.35; dipy, 45.0.

From the analytical data, the complex is considered to be a mixture of (MA)₂Ni(dipy) and (MA)Ni(dipy). Recrystallization of the red solid from a mixture of n-hexane and acetone gives red crystals of a composition (MA)₂Ni(dipy). Anal. Found: C, 56.9; H, 5.18, N, 7.31. The infrared spectra of the complexes were almost identical. A mixture of methyl acrylate (6.0 ml) and $(CH_3)_2Ni(dipy)$ (0.45 g) showed no change below 0°. At about 20° the mixture gradually became red and released a gas (methane: ethane = 1:6). The infrared spectrum of the red solid was almost the same as those of the complexes obtained from $(C_2H_5)_2Ni(dipy)$.

8. (Methyl methacrylate)(dipyridyl)nickel, Ni(dipy)(MMA). A mixture of 5.0 ml (47 mmol) of methyl methacrylate (e value = 0.40) and 0.70 g (2.6 mmol) of $(C_2H_5)_2Ni(dipy)$ remained dark green below room temperature, but gradually became red at room temperature, releasing a gas (mainly n-butane). The mixture was allowed to react for 24 hr at room temperature. The red solid which separated was crystallized from acetone containing methyl methacrylate: mp 65° dec; ir (KBr) 1660 cm⁻¹ (C=O, shifted 50 cm⁻¹ to lower frequency). Anal. Calcd for $C_{15}H_{16}N_2O_2Ni$: C, 57.1; H, 5.01; N, 8.91. Found: C, 56.8; H, 5.10; N, 8.67.

9. (Vinyl acetate)(dipyridyl)nickel, Ni(dipy)(VAc). A mixture of 5.0 ml (54 mmol) of vinyl acetate (e value = −0.22) and 0.89 g (3.3 mmol) of $(C_2H_5)_2Ni(dipy)$ remained dark green below room temperature and became light green at room temperature; ethane, ethylene, and butane were released in a ratio of 2:2:3. The light green solid was washed many times with acetone: mp 318-328° dec; ir (KBr) 1600-1510 cm⁻¹ (shifted about 220 cm⁻¹ to lower frequency). Anal. Calcd for $C_{14}H_{14}N_2O_2Ni$: C, 55.8; H, 4.65; N, 9.30; dipy, 51.8. Found: C, 54.2; H, 4.50; N, 9.01; dipy, 49.2.

10. Bis(acrylamide)(dipyridyl)nickel, Ni(dipy)(AcAm)₂. Ether was distilled in vacuo into a reaction vessel containing 2.0 g (28 mmol) of acrylamide (e value = 1.30) and 0.79 g (2.9 mmol) of $(C_2H_5)_2Ni(dipy)$ at −196°. Below room temperature no change was observed. This might be due to insolubility of acrylamide

in ether below room temperature. At room temperature the system gradually became red and was allowed to react for a day. The released gas was mainly n-butane. The red solid was washed many times with ether: mp 191° dec; ir (KBr) 1580 cm⁻¹ (C=O, shifted 82 cm⁻¹ to lower frequency). Anal. Calcd for $C_{16}H_{18}N_4O_2Ni$: C, 53.7; H, 5.04; N, 15.7. Found: C, 53.2; H, 5.24; N, 15.6.

11. (2-Vinylpyridine)(dipyridyl)nickel, (2-ViPy)Ni(dipy). A mixture of 4.0 ml (38 mmol) of 2-vinylpyridine (e value = −0.50) and 0.78 g (2.9 mmol) of $(C_2H_5)_2Ni(dipy)$ became dark brown in several hours at −30°. The mixture was allowed to react for 2 days at room temperature. The released gas was mainly n-butane. The dark brown solid was crystallized from benzene-n-hexane, mp 140-144° dec. Anal. Calcd for $C_{17}H_{15}N_3Ni$: C, 63.7; H, 4.70; N, 13.1. Found: C, 63.2; H, 4.78; N, 12.6.

12. Reaction of $(C_2H_5)_2Ni(dipy)$ with Styrene. Gradual evolution of a gas (mainly n-butane) was observed when $(C_2H_5)_2Ni(dipy)$ and styrene (e value = −0.80) reacted at room temperature. The greenish yellow precipitate was filtered in a nitrogen atmosphere. The analytical data indicated that the precipitate contained nickel, dipyridyl, and styrene in a ratio 1:1:ca. 0.5.

13. Reaction of $(C_2H_5)_2Ni(dipy)$ with Ethylene and Isobutyl Vinyl Ether. Ethylene (1 atm) was treated with $(C_2H_5)_2Ni(dipy)$ in various solvents such as benzene and tetrahydrofuran. No pressure change was observed in a day. A mixture of $(C_2H_5)_2Ni(dipy)$ and isobutyl vinyl ether (e value = −1.77) was kept at room temperature for a few days, but no reaction took place (no gas was evolved).

14. Reaction of $(C_2H_5)_2Ni(dipy)$ and 1,5-Cyclooctadiene. A mixture of $(C_2H_5)_2Ni(dipy)$, 1,5-cyclooctadiene, and a solvent (benzene or toluene) became dark blue at about 0° and dark blue needles deposited. The mixture became dark green at about 20°. Evaporation of the mixture in vacuo at −78° gave the starting material, $(C_2H_5)_2Ni(dipy)$, and no adduct of 1,5-cyclooctadiene was obtained.

15. Reaction of $(C_2H_5)_2Ni(dipy)$ with Norbornene. A mixture of $(C_2H_5)_2Ni(dipy)$ and norbornene in acetone gave a small amount of a gas containing ethane and ethylene in a 1:1 ratio after 15 hr at 50°. However, a pure product could not be isolated; the analytical data varied.

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

The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito of our laboratory by using a Yanagimoto CHN Autocorder, Type MT-2. Considerable difficulty was encountered in the microanalysis of unstable complexes. The content of dipyridyl in the complexes was determined spectrophotometrically by observation of the absorbance of dipyridyl after decomposing the complex with diluted sulfuric acid.