Preliminary communication

Reductive elimination of Et–Et from NiEt₂(bpy) promoted by electron-accepting aromatic compounds

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Abstract

Reductive elimination of Et–Et (butane) from NiEt₂(bpy) (1) is enhanced by interaction with electron-accepting aromatic compounds, and the rate of the reaction (R) obeys the second-order rate law, $R = k[1][\text{aromatic compound}]$. A plot of k against Hammett's σ value gives a linear line with a ρ value of 1.4. ^{1}H NMR data support the coordination of $C_6F_5CF_3$ with 1, and reaction of C_6F_6 with 1 gives the first example of cis-type biarylnickel(II) complex Ni(C₆F₅)₂(bpy). © 1997 Elsevier Science S.A.

Keywords: Nickel; Reductive elimination; Aromatic compound; Biarylnickel(II) complex; Bipyridine; Crystal structure

1. Introduction

Nickel promoted C–C coupling reactions are now widely used as synthetic tools [1–7]. The reactions are considered to involve reductive elimination of R–R' from a diorganonickel complex Ni(R)(R')L$_n$ [8–11] as a crucial step, and it has been reported that interaction of NiR₂(bpy) (bpy = 2,2'-bipyridine) with electron-accepting olefins causes rapid reductive elimination of R–R from the nickel complex [8,10,11].

However, a similar enhancement effect of electron-accepting aromatic compounds on the reductive elimination of R–R from the diorganonickel complex has received much less attention [12]. Since synthetic reactions utilizing the C–C coupling reaction preferentially proceed with vinylic and aromatic halides which are regarded as electron-accepting olefins and aromatic compounds respectively, revealing of the enhancement effect of aromatic halide on the reductive elimination is expected to give bases for better understanding of the synthetic reactions. Here we report that interaction of NiEt₂(bpy) with electron-accepting aromatic compounds actually accelerates the reductive elimination of Et–Et from NiEt₂(bpy).

2. Results and discussion

NiEt₂(bpy) is stable in various non-aromatic solvents (e.g. acetone, THF, DMF, CH₃CN, and n-C₆F₁₄) and aromatic solvents without an electron-withdrawing group (e.g. benzene and toluene) at room temperature under N₂. On the other hand, addition of an aromatic compound with the electron-withdrawing group (e.g. C₆H₅CN and C₆F₅CF₃) into a solution (e.g. THF solution) of NiEt₂(bpy) leads to the reductive elimination of Et–Et, butane (0.71–0.96 mol/mol NiEt₂(bpy) as determined by gas chromatography). These results suggest that the coordination of the electron-accepting aromatic compounds with NiEt₂(bpy) enhances the reductive elimination, similar to the case of the interaction (or coordination) of electron-accepting olefins with NiEt₂(bpy) [8,10,11]. Several nickel complexes with π-aromatic ligands have been reported [13].

$$\text{(1)}$$
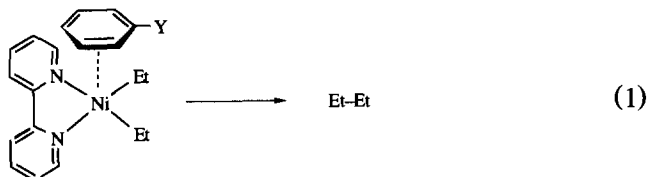
^{1}H NMR data at low temperature support the interaction of the aromatic compound with NiEt₂(bpy) through the aromatic ring. As depicted in Fig. 1, the CH₃ signal
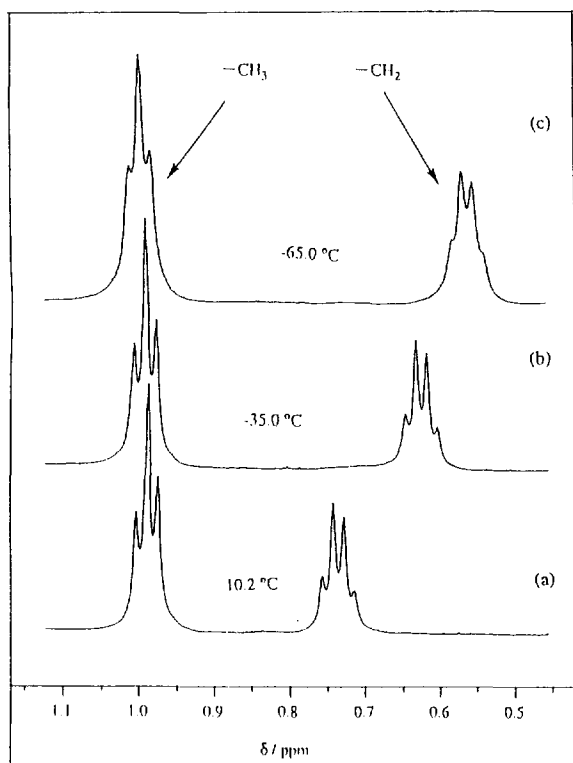
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Fig. 1. Temperature dependence of the ^{1}H NMR (400 MHz) spectrum of $NiEt_2(bpy)$ (0.14 M) in THF-d_8 containing $C_6F_5CF_3$ (1.7 M) at (a) 10.2 °C, (b) −35.0 °C and (c) −65.0 °C. The Et region is shown. At −65.0 °C, the peaks are somewhat broadened due to an increase in the viscosity of the solution.

of the Et group observed with the $NiEt_2(bpy)$-$C_6F_5CF_3$ system remains at the same position at various temperatures, whereas the CH_2 signal shifts to a higher magnetic field on cooling. At −65 °C, the CH_2 signal shifts to δ 0.56 ppm at $[C_6F_5CF_3]$ = 1.7 M. On decreasing $[C_6F_5CF_3]$ to 1.2 M, the degree of up-field shift becomes smaller, and the CH_2 signal appears at δ 0.62 ppm at −65 °C.

These results are reasonably explained by the π-coordination of the aromatic ligand with nickel, which will bring about an anisotropic up-field magnetic effect on the CH_2 group. On the other hand, the CH_3 group will receive less magnetic effect from the coordinated aromatic compound, since it locates apart from the magnetically anisotropic region of the aromatic compound. [The ring current of the coordinated aromatic compound may lead to a small down-field shift of the CH_3 in view of its position outside the aromatic ring. The effect of the ring current at the CH_3 group, if it exists, may be compensated by an electron-withdrawing effect of the aromatic compound.]

The ring current of the coordinated aromatic compound is considered to bring about the up-field shift of the CH_2 signal which is located near or inside the benzene ring, and the shift of the CH_2 signal to the higher magnetic field on cooling is reasonably ex-

plained by an increase in the fraction of $NiEt_2(bpy)$ coordinated with the aromatic ligand.

$$NiEt_2(bpy) \; + \; \langle\bigcirc\rangle\text{-}Y \; \rightleftharpoons \; NiEt_2(bpy)(\langle\bigcirc\rangle\text{-}Y) \qquad (2)$$
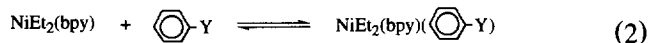
^{1}H NMR peak positions of bpy protons also show temperature dependence, which is accounted for by the magnetically anisotropic effect of the coordinated aromatic compound. Thus, the ^{1}H NMR signal of 6-H (or α-H) of bpy near the Ni center shifts to a higher magnetic field on cooling (the degree of shift Δδ = 0.13 ppm between 10 and −65 °C at $[C_6F_5CF_3]$ = 1.7 M), whereas signals of other bpy hydrogens shift to a lower magnetic field (Δδ = −0.09 to −0.13 ppm) on cooling.

According to the occurrence of the reductive elimination (Eq. (1)), the UV–visible spectrum of a THF solution of $NiEt_2(bpy)$ changes with time as depicted in Fig. 2. The change of the absorbance at 685 nm with time t obeys the following first-order rate law:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{obs}t \qquad (3)$$

where A_t, A_∞, and A_0 stand for absorbances at time t, infinite time, and time 0 respectively. The pseudo-first-order rate constant k_{obs} increases proportionally with the concentration of the electron-accepting aromatic compound, indicating that the rate of the reductive elimination can be expressed by the following second-order rate law:

$$\text{Rate} = k[NiEt_2(bpy)][\text{aromatic compound}] \qquad (4)$$

The temperature dependence of the k value for the reaction with octafluorotoluene gives an Arrhenius activation energy of 112 kJ mol^{-1}. Use of other electron-accepting aromatic compounds also gives the second-order rate equation.
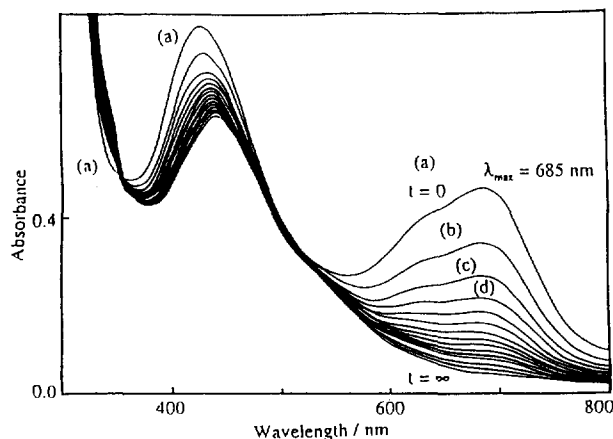

Fig. 2. Change in UV–visible spectrum during the reaction of $NiEt_2(bpy)$ with octafluorotoluene in THF at 33.3 °C. Time: (a) 0 s, (b) 600 s, (c) 1200 s, and (d) 1800 s. $[C_6F_5CF_3]$ = 0.104 M.

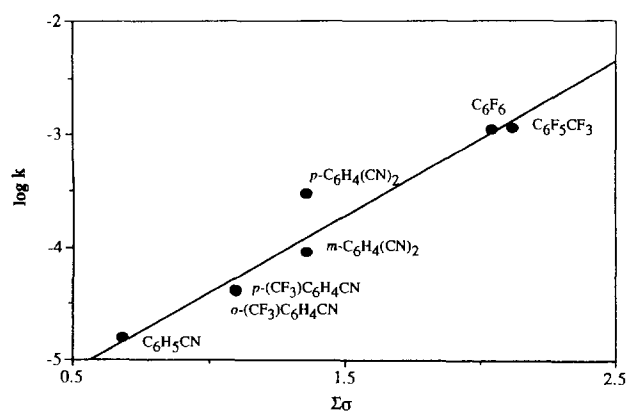Fig. 3. Plot of log k (k in $M^{-1}s^{-1}$) against $\Sigma\sigma$ at 25°C; σ = Hammett's σ. p-(CF$_3$)C$_6$H$_4$CN and o-(CF$_3$)C$_6$H$_4$CN give almost the same k value.

The second-order rate constant k has been measured with various electron-accepting aromatic compounds, and a plot of a log k value against a $\Sigma\sigma$ value (σ = Hammett's σ value of the substituent) affords a linear line as depicted in Fig. 3. The slope of the line gives a Hammett's ρ value of 1.4 for the present reaction. The ρ value is about half of the ρ value observed for a similar acceleration effect of the electron-accepting olefins [8], indicating that the electron-withdrawing effect of the substituent in the olefin gives a more direct effect on the reductive elimination.

As described above, the reductive elimination of Et–Et from NiEt$_2$(bpy) is enhanced by interaction with the electron-accepting aromatic compounds (presumably by coordination through the aromatic ring). The present basic results will contribute to understanding of the nickel promoted C–C coupling reactions.

When C$_6$F$_6$ is used as the reactant, the reaction leads to the formation of Ni(C$_6$F$_5$)$_2$(bpy) [12] with evolution of butane (0.84 mol/mol NiEt$_2$(bpy)). Ni(C$_6$F$_5$)$_2$(bpy) is considered to be formed by oxidative addition of C$_6$F$_6$ to the resulting Ni(0) complex followed by disproportionation of NiF(C$_6$F$_5$)(bpy) [12], and its square planar structure has been confirmed by X-ray crystallography, which will be reported elsewhere. [Monoclinic, a = 7.420(10) Å, b = 23.79(3) Å, c = 13.64(1) Å, β = 93.67(10)°, R = 4.7%, R_w = 4.7%.] Although there are several examples [13] of biarylnickel(II) complexes with *trans* configuration, the *cis*-type biarylnickel(II) complex has, to our knowledge, no precedent. The highly electron-accepting properties of the C$_6$F$_5$ group seem to stabilize the biarylnickel complex.

3. Experimental section

All reactions and manipulations were carried out under an inert gas using standard Schlenk techniques.

All solvents were dried and distilled prior to use. NMR spectra were recorded on a JEOL-GX 400. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder. Aromatic compounds were purified by distillation and transferred to a Schlenk-type optical cell by trap-to-trap distillation.

3.1. Preparation of Ni(C$_6$F$_5$)$_2$(bpy)

C$_6$F$_6$ (0.4 ml, 2.1 mmol) was added to a solution of NiEt$_2$(bpy) (95.4 mg, 0.35 mmol) in THF (7 ml). The solution was stirred for 12 h at 45°C to obtain a yellow solution and a yellow precipitate. After addition of hexane (20 ml), the precipitate was collected by filtration, washed with diethyl ether (5 ml, 3 times), and dried under vacuum. Recrystallization from acetone at -20°C afforded yellow crystals of 67.0 mg of Ni(C$_6$F$_5$)$_2$(bpy). Anal. Found: C, 48.05; H, 1.56; N, 5.10. Ni(C$_6$F$_5$)$_2$(bpy) Calc.: C, 48.13; H, 1.47; N, 5.10%. ^{1}H NMR (298 K, 400 MHz, DMSO-d_6): δ = 8.54 (d, 2H), 8.26 (t, 2H), 7.53 (t, 2H), 7.47 (d, 2H).

Acknowledgements

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