Photochemical Behavior of Aluminum-Ethyl Complex with Tetraaza Macrocyclic Ligand, $Al(C_{22}H_{22}N_4)(C_2H_5)$

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Synopsis. Homolytic photocleavage of an aluminum carbon bond in ethyl(1,8-dehydro-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)aluminum was confirmed by using EPR technique. The photochemistry of this aluminum carbon bond was also studied by NMR and emission spectroscopic experiments.

Photoreactivity of metal-alkyl bonds has been an increasing interest.1—5) In this note, we report some photochemical behaviors of $Al(C_{22}H_{22}N_4)(C_2H_5)$ (**1**) which has known to be remarkably stable to Al-ethyl dissociation in the dark and resistant to demetallation.6)

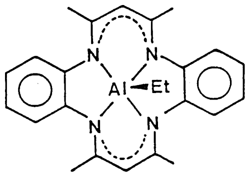

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Figure 1 shows the electronic spectrum of compound **1**. This compound has a strong absorption band at 358 nm (ε=7.0×10^4) and a shoulder at about 410 nm ($\varepsilon\simeq$10^4). This spectrum is similar to that of $Ni(C_{22}H_{22}N_4)$,7) though the bands of **1** lie at shorter wavelengths than those of the Ni complex. Structual study of **1** showed that the in-plane ligand is not planar but take the suddle shape structure.6) Previous semi-empirical Pariser-Par-Pople MO calculation8) implied that the visible absorption bands of **1** are predominantly due to the $\pi\pi^*$ transition of deformed macrocyclic ligand.

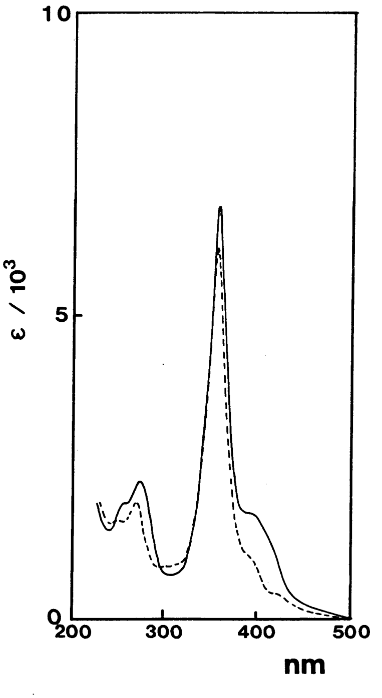


Fig. 1. Electronic spectra of compound **1** (——) and $Al(C_{22}H_{22}N_4)Cl$ (----) in methanol.

Figure 2(A) shows a ^1H NMR spectrum of **1** in $CDCl_3$ at 20 °C. When the solution was irradiated with visible light (λ>450 nm), the spectrum changed with irradiation time (Fig. 2(B—D)). The signal intensities due to the ethyl group at δ 0.18 (t, CH_3) and −0.92 (q, $-CH_2-$) decreased as a new peak of ethane appeared at δ 0.85. Simple spectral change was also observed at lower magnetic field region. Three hours irradiation brought the reaction to completion under the experimental conditions. The main product was identified as $Al(C_{22}H_{22}N_4)Cl$ by means of mass spectrometry of the product (m/z=404). The absorption spectrum of

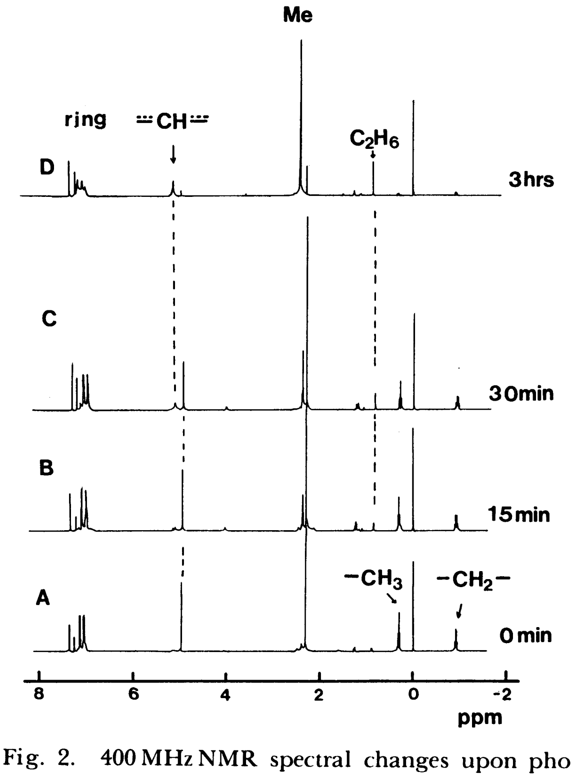
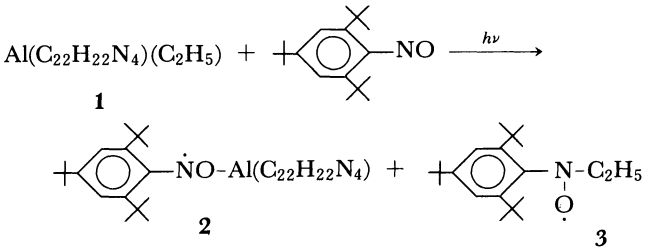


Fig. 2. 400 MHz NMR spectral changes upon photolysis of $CDCl_3$ solution of $Al(C_{22}H_{22}N_4)(C_2H_5)\cdot 1/2C_6H_6$ at 20°C. A: Before irradiation, B, C, and D: after 15, 30 minutes, and 3 hours irradiations, respectively.

the chloro complex isolated by passing through Al_2O_3 column is also depicted in Fig.1. The simple spectral change in Fig. 2 indicates that the reaction proceeds rather simply and smoothly at 20 °C. However, prolonged irradiation at room temperature caused the solution dark and turbid, possibly due to the simultaneous side reactions of the radicals arising from the solvent. An attempt to determine the quantum yield of the photo-induced chlorination by the spectrophotometric method[4] was unsuccessful because of the small spectral change during the reaction (see Fig. 1). However, it was roughly estimated to be in the order of 10^{-3} from the initial absorbance change of the reaction at 400 nm. The value was in the same order of magnitude as reported for photolysis of [Al(tpp)Et] in $CHCl_3$.[4]

Figure 3(A) shows an EPR spectrum obtained upon irradiation of a degassed benzene solution of **1** with visible light ($\lambda > 450$ nm) in the presence of ten-fold excess of spin trapping agent, 2,4,6-tri-*t*-butylnitrosobenzene (TBN). Though the spectral pattern is rather complicated, the spectrum can be unequivocally assigned as an overlap of signals due to two spin adducts, **2** and **3** in Eq. 1.



(1)

Figures 3(B) and 3(C) show the simulation spectra of **3** and **2**. EPR parameters obtained were: for **2**, $a^N=1.06$, $a^{Al}=0.14$, $a^H_m=0.17$[9] mT, and g=2.0048; for **3**, $a^N=1.34$, $a^H=1.78$, and $a^H_m=0.08$[9] mT, and g=2.0061. These values are almost identical with those previously reported for TBN spin adducts obtained upon photolysis of [Al(tpp)(Et)].[4] Spin adduct **2** is the anilino radical bonded through O to Al, while **3** is the nitroxyl radical bonded through N to Et. The EPR intensity ratio for spin adducts **3** and **2** was found to be approximately 1 : 1.5. This ratio is likely to depend on trapping rate. In the absence of TBN, no EPR signal was observed under the same conditions. The recombination of radicals may be too fast to detect the EPR signals.

Emission behavior from photoexcited state of **1** and its free ligand $H_2(C_{22}H_{22}N_4)$ has been also studied in 2-methyltetrahydrofuran (MTHF).[10] Complex **1** showed emission with a maximum peak at 580 nm and the lifetime was found to be 50 ms at 77 K. Excitation spectrum was in accord with its absorption. These results indicate that the emitting state is attributable to the excited triplet state of the ligand π-conjugated system. Recently we observed the triplet signal for compound **1** using time resolved EPR technique.[8] It should be noted that the phosphoresence was not observed at 290 K when the oxygenated solution was used, while it was observed at both 77 and 290 K when the solution was degassed. That is, the triplet state was quenched by oxygen at room temperature.

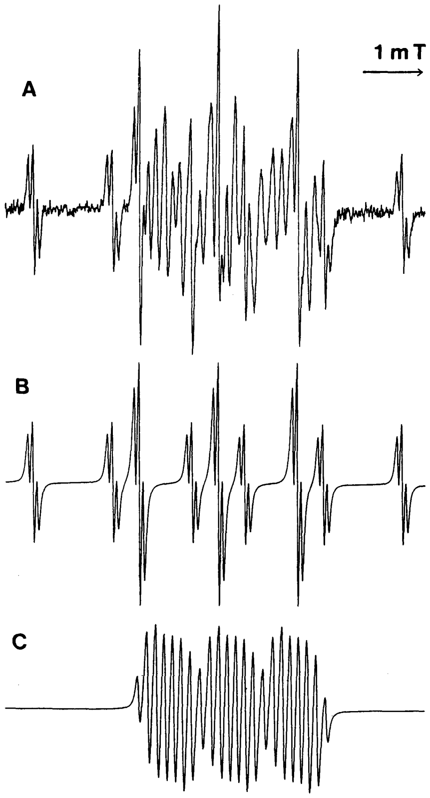


Fig. 3. A: EPR spectrum of a benzene solution of $Al(C_{22}H_{22}N_4)(C_2H_5)$ with TBN upon light irradiation ($\lambda > 450$ nm). B and C: EPR simulation spectra of TBN–C_2H_5 and TBN–$Al(C_{22}H_{22}N_4)$, respectively.

This work clearly indicates that the homolytic cleavage of Al–C bond of the present complex is induced by visible light, that is mainly by the in-plane ligand absorption. However, when the reaction was carried out in non-reactive solvent such as benzene or in the absence of spin traps, neither EPR signal nor NMR spectral change was observed under the irradiation. In order to clarify whether the photochemically reacting species is singlet or triplet, further detailed studies are necessary.

Experimental

Sample Preparation. $Al(C_{22}H_{22}N_4)(C_2H_5)$ was prepared by the method reported in the literature.[6]

NMR Measurement and Visible-Light Irradiation. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer. An Ushio ultra-high pressure 500 W mercury lamp and Toshiba glass filter ($\lambda > 450$ nm) were used for irradiation of visible light at 20 °C.

EPR Measurement. EPR spectra were recorded on a JEOL FE2XG spectrometer (100 kHz modulation) at room temperature. Visible light irradiation was carried out with the use of the same mercury lamp and glass filter as those in the NMR measurements.

Emission Experiment. Fluoresence and phosphoresence spectra were recorded on a Spex Fluorolog 2 fluorimeter quipped with a Xenon lamp.

References

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9) a_m^H denotes hyperfine coupling constants with benzene ring proton at meta position.

10) The emission from the free ligand was disclosed to be fluoresence. The free ligand showed an emission spectrum with maximum at 560 nm, but its excited state decayed very rapidly after the pulsed excitation. It is suggested that the presence of Al makes the intersystem crossing from S_1 or S_2 to T_1 easier.