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Photosensitive 1:1 Adduct between Bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(0) and Quadricyclane

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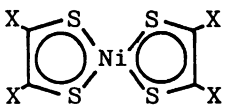
Bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(0) (1a) reacts with quadricyclane (Q) to give a 1:1 adduct which has the same structure as that of the adduct between 1a and norbornadiene (NBD). Q reacts with 1a much faster than NBD. The adduct is thermally stable but photosensitive to dissociate into 1a and NBD.

Dithiolatometal complexes belong to the set of so-called "non-innocent complexes," which have unique electronic structures.1) Several interesting reports have appeared on the interactions between dithiolatometal complexes and alkenes or strained hydrocarbons. Some dithiolatometal complexes catalyze the exothermic isomerization of quadricyclane (Q) to norbornadiene (NBD).2) Schrauzer et al.3,4) found that the reaction of 1a with NBD gives a 1:1 adduct between 1a and NBD and a dihydro-1,4-dithiin derivative (4,5-diphenyl-3,6-dithiatricyclo-[6.2.1.$0^{2,7}$]-undeca-4,9-diene (5). They gave the structure of 3a to the adduct, which they considered to be an intermediate for 5. However, Wing et al. assigned the structure of 2b (X =CF_3) to the adduct on the basis of X-ray analysis.5) Schrauzer et al. confirmed this type of structure for the adduct of X = Ph by the reaction with iodomethane.6) The process to give the dihydro-1,4-dithiin has not yet been definitely clarified.



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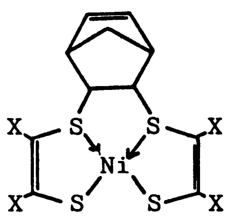

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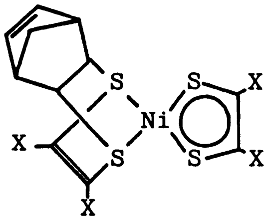

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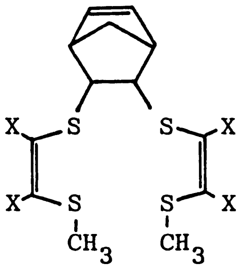

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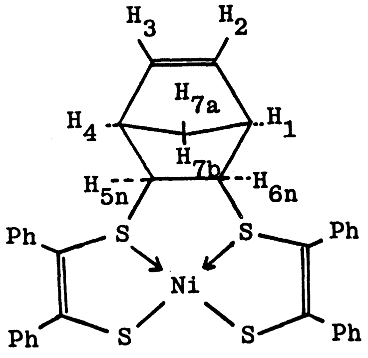
a; X = Ph, b: X = CF_3

We studied the reaction of 1a with Q. This paper describes the following points: 1) 1a reacts with Q quantitatively to give a 1:1 adduct which is identical with that between 1a and NBD, 2) Q reacts with 1a much faster than NBD, and 3) the adduct is thermally stable but photosensitive enough to undergo the dissociation to 1a and NBD.

The dithiolatonickel complex 1a$^{3)}$ (55 mg, 0.10 mmol) and quadricyclane (5.5 g, 60 mmol) were dissolved in 10 cm^3 of benzene and the mixture was refluxed under Ar for 2.5 h. After the removal of Q under reduced pressure, the products were submitted to column chromatography (column, silica gel (C-300 made by Wako Junyaku Co.); eluent, mixture of n-hexane and dichloromethane) and thin layer chromatography (plate, Kieselgel 60 GF$_{254}$ made by E. Merck Co.; developing solvent, n-hexane-dichloromethane 1:1 v/v). The product (yellow crystals) was identified as a 1:1 adduct between 1a and Q. The yield of the adduct was 100% (64.3 mg) with respect to 1a. The same compound was obtained in the reaction of 1a with NBD under the similar conditions in the yield of 25%, accompanied by the dihydro-1,4-dithiin 5 (yield, 39%).



The elemental analysis of the adduct (Found: C, 66.49; H, 4.84%) indicates that the adduct consists of one 1a and one Q (Calcd for $C_{35}H_{28}NiS_4$: C, 66.15; H, 4.44%). The reaction of the adduct with iodomethane gave 4a$^{7)}$ which is identical to the compound reported by Schrauzer et al.$^{6)}$ It indicates that the adduct has the structure of 2a. ^{1}H NMR, MS, and IR spectra are consistent with the structure 2a : ^{1}H NMR (CD_2Cl_2) $\delta = 1.63$ (1H, dt, J = 10.3 and 2.2 Hz, H$_{7a}$), 1.80 (1H, d, J = 10.3 Hz, H$_{7b}$), 2.20 (2H, t, J = 1.8 Hz, H$_1$ and H$_4$), 4.09 (2H, d, J = 2.2 Hz, H$_{5n}$ and H$_{6n}$) 5.68 (2H, t, J = 1.8 Hz, H$_2$ and H$_3$) and 7.16 (20H, m, phenyl); MS (70 eV) m/z (rel intensity) 542 (6; 1a$^+$), 242 (50), 178 (82, diphenylacetylene$^+$), 121 (75), 92 (49, (Q or NBD)$^+$), 91 (100), and 66 (42, Cp$^+$); IR (KBr disk) 3060, 1600, 1579, 1540, 1445, 860, 742, and 700 cm^{-1}.

The important differences between the reaction of 1a with Q and the reaction of 1a with NBD are the absence of dihydro-1,4-dithiin 5 in the reaction of 1a with Q and the reaction rates. Compound 5 was not obtained in the reaction of 1a and Q either at room temperature or at 80 °C at which the reaction of 1a and NBD gave 5. The second difference is the reaction rates. Figure 1 shows the decay of the concentration of 1a (measured by stopped-flow method) in the reaction with Q and NBD. The reaction of 1a with Q in acetonitrile is pseudo-first order with respect to 1a in the large excess of Q (initial concentration: [1a] = 9.9×10^{-6} mol dm^{-3}; [Q] = 0.11 mol dm^{-3}) and the rate constant is 4×10^{-2} s^{-1} at 25 °C. In contrast, the reaction of 1a with NBD is slow ($k \approx 4 \times 10^{-4}$ s^{-1}).

The adduct is photosensitive but comparatively thermally stable. When the adduct was heated in benzene at 80 °C for 110 min, the decomposition of the

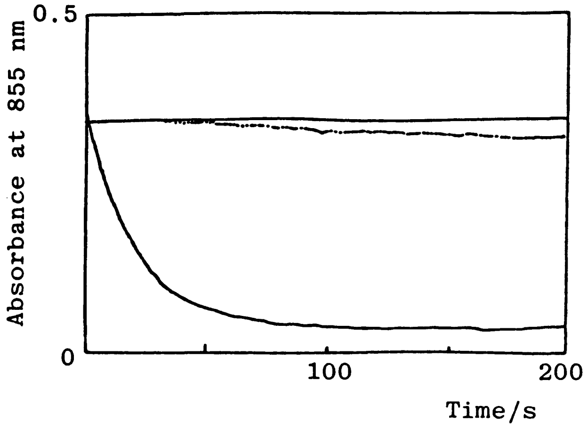


Fig. 1. Decay of [1a] in reaction with Q (——) and with NBD (·······) at 25 °C in acetonitrile measured by stopped-flow method.
[Q] = [NBD] = 0.11 mol dm^{-3}
[1a] = 9.9 x 10^{-6} mol dm^{-3}

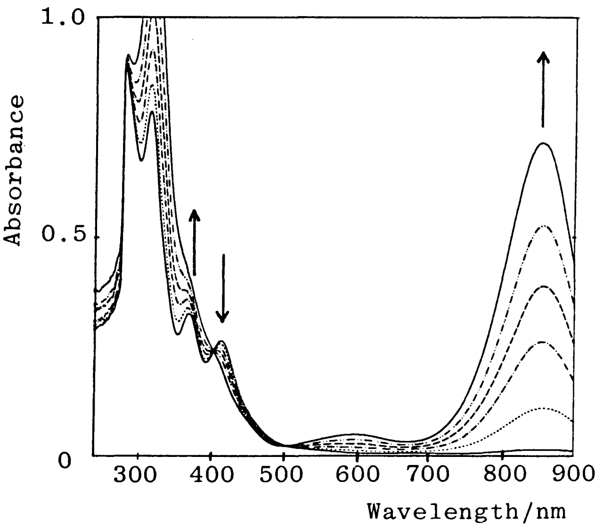
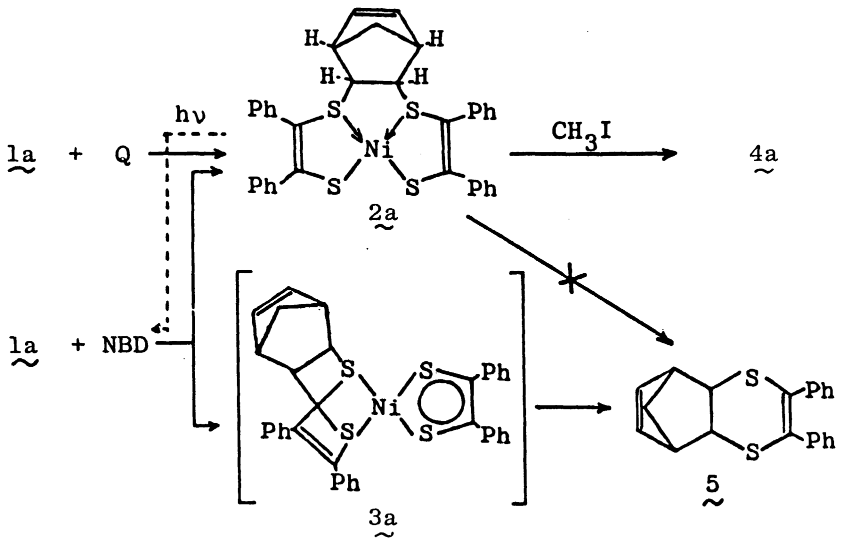


Fig. 2. Spectral change caused by irradiation at 313 nm. [2a]= 2.1 x 10^{-5} mol dm^{-3} in C_6H_6.
——, Irr. time, 0 s; ·······, Irr. time, 5 s;
—·—·—, Irr. time, 15 s; -----, Irr. time 30 s;
—··—··—, Irr. time, 60 s; ——, Irr. time, 300 s

adduct is negligible and gave no dihydrodithiin 5. This finding leads to the conclusion that the adduct 2a can not be an intermediate for the formation of the dihydro-1,4-dithiin (5), because 5 was formed in the reaction of 1a and NBD at 80 °C.

The adduct is photosensitive. When the adduct is irradiated with UV-light, it dissociates to 1a and NBD.[8] This indicates that Q is isomerized to NBD photochemically under the catalysis of 1a. The photo-dissociation is selective showing isosbestic points in the spectral changes (as exemplified in Fig. 2 in the irradiation with 313 nm). A remarkable spectral change during UV-irradiation is the appearance of a very intense absorption at 855 nm (green color). The quantum yields for the photo-dissociation at 313, 365, and 440 nm are 0.21, 0.41, and 0.39, respectively. The quantum yields for photo-dissociation in longer wavelength region (at 365 and 440 nm) are higher than the quantum yield in shorter wavelength (at 313 nm). The photo-dissociation of the adduct occurs effectively in the irradiation of the bands at 367 and 415 nm which appear in the adduct formation in place of the band at 855 nm of 1a. The bands of the adduct at 367 and 415 nm should be due to the electronic system created by the adduct formation. The excitation of such an electronic system would bring about the weakening of the bonds introduced by the adduct formation and result in the dissociation.

The reactions of 1a and the adduct 2a are summarized in Scheme 1.



Scheme 1.

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7) Compound 4a was identified by ^{1}H NMR and MS. ^{1}H NMR ($CDCl_3$) δ = 1.53 (1H, d, J = 8.9 Hz), 1.94 (6H, s, S-CH_3), 2.26 (1H, d, J = 8.9 Hz), 2.33 (2H, d, J = 1.4 Hz), 2.77 (2H, m), 5.67 (2H, s), and 7.00-7.06 (20H, m); MS (70 eV) m/z (rel intensity) 608 (10, $(M+2)^+$), 607 (15, $(M+1)^+$), 606 (34, M^+), 540 (30), 349 (23), 283 (52), 257 (20), 251 (19), 236 (25), 225 (22), 211 (20), 210 (100), 179 (20), 178 (43), 121 (19), and 91 (19).

8) Norbornadiene formed in the photolysis of the adduct was identified by ^{1}H NMR.

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