

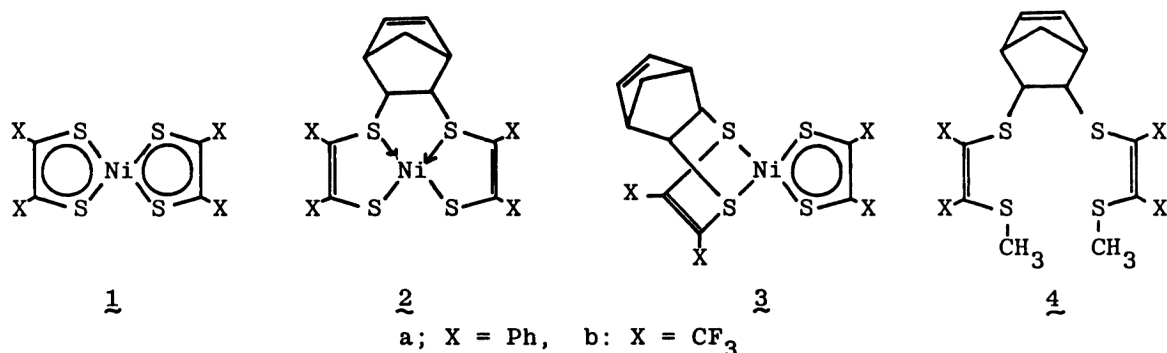
Photosensitive 1:1 Adduct between Bis(1,2-diphenyl-1,2-ethylene-
dithiolato)nickel(0) and Quadricyclane

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Bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(0) (1a) re-
acts 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-
dithiatriacyclo-[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 = CF₃) 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.



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

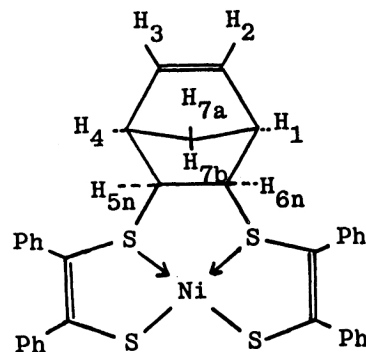
The dithiolatonickel complex $\underline{1a}^3)$ (55 mg, 0.10 mmol) and quadricyclane (5.5 g, 60 mmol) were dissolved in 10 cm³ of benzene and the mixture was refluxed under Ar for 2.5 h. After the removal of Q under reduced pressure, the products were submitted to column chromatography (column, silica gel (C-300 made by Wako Junyaku Co.); eluent, mixture of n-hexane and dichloromethane) and thin layer chromatography (plate, Kieselgel 60 GF₂₅₄ 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 $\underline{1a}$ and Q. The yield of the adduct was 100% (64.3 mg) with respect to $\underline{1a}$. The same compound was obtained in the reaction of $\underline{1a}$ with NBD under the similar conditions in the yield of 25%, accompanied by the dihydro-1,4-dithiin $\underline{5}$ (yield, 39%).

The elemental analysis of the adduct (Found: C, 66.49; H, 4.84%) indicates that the adduct consists of one $\underline{1a}$ and one Q (Calcd for C₃₅H₂₈NiS₄: C, 66.15; H, 4.44%). The reaction of the adduct with iodomethane gave $\underline{4a}^7)$ which is identical to the compound reported by Schrauzer et al.⁶⁾ It indicates that the adduct has the structure of $\underline{2a}$.

¹H NMR, MS, and IR spectra are consistent with the structure $\underline{2a}$: ¹H NMR (CD₂Cl₂) δ = 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, H₁ and H₄), 4.09 (2H, d, J = 2.2 Hz, H_{5n} and H_{6n}) 5.68 (2H, t, J = 1.8 Hz, H₂ and H₃) and 7.16 (20H, m, phenyl); MS (70 eV) m/z (rel intensity) 542 (6; $\underline{1a}^+$), 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 $\underline{1a}$ with Q and the reaction of $\underline{1a}$ with NBD are the absence of dihydro-1,4-dithiin $\underline{5}$ in the reaction of $\underline{1a}$ with Q and the reaction rates. Compound $\underline{5}$ was not obtained in the reaction of $\underline{1a}$ and Q either at room temperature or at 80 °C at which the reaction of $\underline{1a}$ and NBD gave $\underline{5}$. The second difference is the reaction rates. Figure 1 shows the decay of the concentration of $\underline{1a}$ (measured by stopped-flow method) in the reaction with Q and NBD. The reaction of $\underline{1a}$ with Q in acetonitrile is pseudo-first order with respect to $\underline{1a}$ in the large excess of Q (initial concentration: [$\underline{1a}$] = 9.9 x 10⁻⁶ mol dm⁻³; [Q] = 0.11 mol dm⁻³) and the rate constant is 4 x 10⁻² s⁻¹ at 25 °C. In contrast, the reaction of $\underline{1a}$ 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



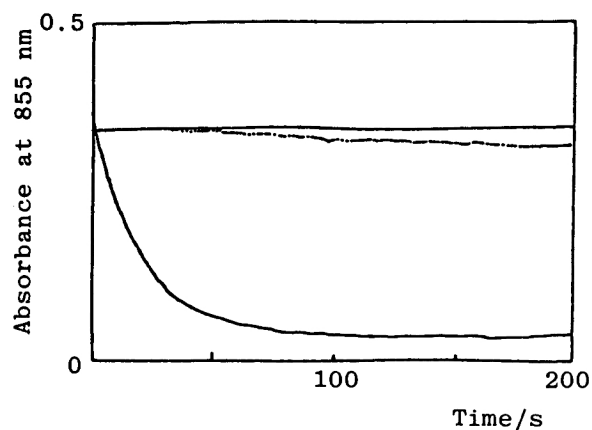


Fig. 1. Decay of [$1a$] in reaction with Q (—) and with NBD (-----) at 25 °C in acetonitrile measured by stopped-flow method.
 $[Q] = [NBD] = 0.11 \text{ mol dm}^{-3}$
 $[1a] = 9.9 \times 10^{-6} \text{ mol dm}^{-3}$

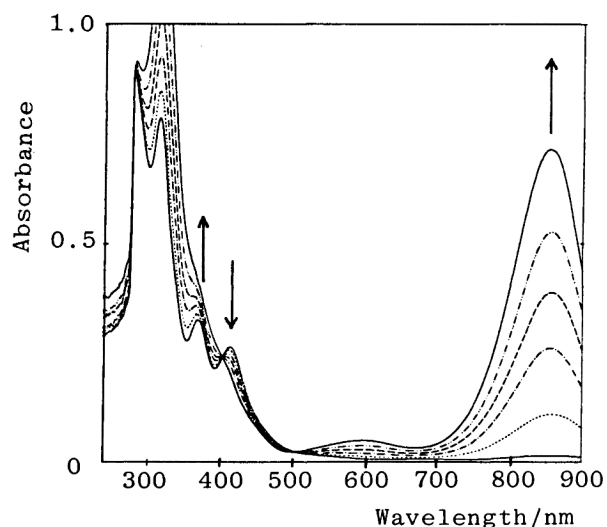
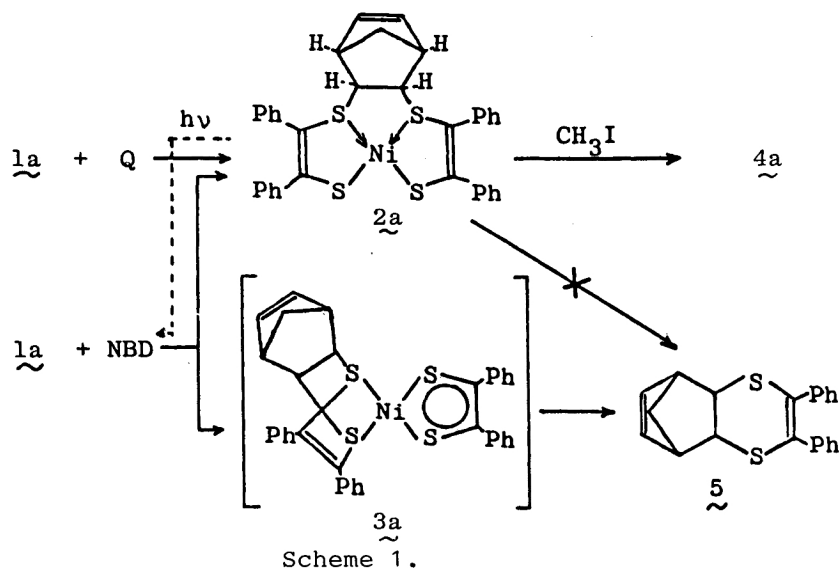


Fig. 2. Spectral change caused by irradiation at 313 nm. $[2a] = 2.1 \times 10^{-5} \text{ mol dm}^{-3}$ in C_6H_6 .
 —, Irr. time, 0 s; -----, Irr. time, 5 s;
 -----, Irr. time, 15 s; - · - · -, Irr. time, 30 s;
 - - - - -, Irr. time, 60 s; — · — · —, Irr. time, 300 s

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.



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- 7) Compound 4a was identified by ^1H NMR and MS. ^1H 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, $(\text{M}+2)^+$), 607 (15, $(\text{M}+1)^+$), 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 ^1H NMR.

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