JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2, 131–145 (1989)

FORMATION OF 1:1 ADDUCTS BETWEEN BIS(1,2-DIARYL-1,2-ETHYLENEDITHIOLATO)METAL(0) (METAL = NI, PD, AND PT) AND QUADRICYCLANE AND THEIR PHOTODISSOCIATION

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ABSTRACT

Bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) complexes (**1**; metal = Ni, Pd, and Pt) react with quadricyclane (Q) to give selectively 1:1 adducts which are identical with the adducts between **1** and norbornadiene (NBD). In the adducts, two sulfur atoms of the different dithiolato ligands are added to one of the double bonds of NBD. The reactions of **1** with Q are 10^3–10^4 times faster than those with NBD. The more electropositive dithiolatometal complexes react faster with Q and NBD. The adducts are dissociated to the free dithiolatometal complexes and NBD by UV-irradiation (254–436 nm). Upon irradiation with 254 nm light, the photodissociation occurs before the decomposition of the dithiolatometal complexes.

Dithiolatometal complexes belong to the set of so-called 'non-innocent complexes', which have peculiar electronic structures. Dithiolatometal complexes interact with several unsaturated hydrocarbons, probably because of their unique electronic configurations.

Schrauzer and his coworkers have reported the formation of a dihydro-1,4-dithiin derivative and a 1:1 adduct between bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(0) and norbornadiene (NBD).[1,2,3] The X-ray diffraction study on a similar adduct (the adduct between bis(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)nickel(0) and NBD) has clarified the structure in which two sulfur atoms of the different dithiolato ligands add to one of the double bonds of NBD.[4]

Baker *et al.* found that bis(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)nickel(0) reacts with conjugated dienes such as 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene more rapidly than with norbornadiene to give 1,4-addition products. The difference in reactivities between alkene and conjugated diene has been analyzed on the basis of MO correlation.[5,6] A similar adduct between bis(1,2-diphenyl-1,2-ethylenedithiolato)palladium(0) and 1,3-cyclohexadiene has also been reported.[7]

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0894–3230/89/020131–15$07.50

Received 31 March 1988
Revised 18 May 1988

Some dithiolatometal complexes such as tris(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)molybdenum(0) catalyze the exothermic isomerization of quadricyclane to norbornadiene.[8]

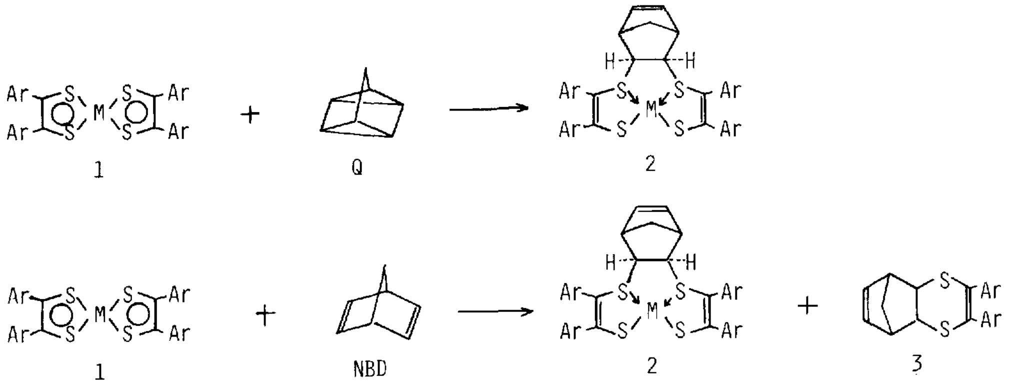
Some reports have described the photoreactivities of the adducts between the dithiolatometal complexes and norbornadiene. The 1:1 adduct between bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(0) and NBD has been reported to decompose at room temperature, when it is exposed to daylight.[1] It has also been reported that the 1:1 adduct between bis(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)nickel(0) and NBD dissociates to give an equimolar mixture of the dithiolatonickel complex and NBD, when it is irradiated by visible light.[5] The measurement of the quantum yields for the photodissociation of the adduct has revealed that the process is quite efficient and solvent-independent.

We found that bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) complexes react with quadricyclane much more rapidly ($\approx 10^4$ faster) than with norbornadiene to give selectively 1:1 adducts without forming dihydro-1,4-dithiin derivatives.[9] In this paper, we describe also a more detailed study of the effects of central metal and the substituents in the dithiolene ring on the rates of the formation of 1:1 adducts and the quantum yields for the photodissociation of the adducts.

RESULTS AND DISCUSSION

Formation of adducts between bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) and quadricyclane or norbornadiene

Bis(1,2-diaryl-1,2-ethylenedithiolato)nickel(0), -palladium(0), and -platinum(0) (**1a–1e**) react with quadicyclane to give 1:1 adducts which are identical to those of the adducts between the bisdithiolatometal complexes and norbornadiene.



1a: M = Ni, Ar = C_6H_5-
1b: M = Ni, Ar = p-F-C_6H_4-
1c: M = Ni, Ar = p-CH_3O-C_6H_4-
1d: M = Pd, Ar = C_6H_5-
1e: M = Pt, Ar = C_6H_5-

2a: M = Ni, Ar = C_6H_5-
2b: M = Ni, Ar = p-F-C_6H_4-
2c: M = Ni, Ar = p-CH_3O-C_6H_4-
2d: M = Pd, Ar = C_6H_5-
2e: M = Pt, Ar = C_6H_5-

3a: Ar = C_6H_5-
3b: Ar = p-F-C_6H_4-
3c: Ar = p-CH_3O-C_6H_4-

Bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) complexes (metal = Ni, Pd, and Pt) react with quadricyclane more selectively and more rapidly than with norbornadiene.

The reactions between **1** and NBD give 1:1 adducts (**2**) and dihydro-1,4-dithiin derivatives (**3**), while the reactions between **1** and Q give only 1:1 adducts and no dihydro-1,4-dithiin.

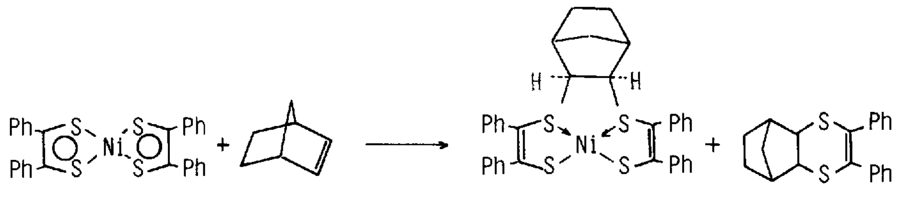
Table 1. Yields of products in reactions of bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) with quadricyclane (Q), norbornadiene (NBD), or norbornene (NB)

Dithiolatometal			Reaction with Q		Reaction with NBD		Reaction with NB	
	Metal	Aryl	Yield of product/%		Yield of product/%		Yield of product	
			2	**3**	**2**	**3**	**4**	**5**
1a	Ni	Phenyl	86	0	25	39	23	62
1b	Ni	*p*-Fluorophenyl	95	0	30	49		
1c	Ni	*p*-Methoxyphenyl	77	0	14	56		
1d	Pd	Phenyl	59	0	43	39		
1e	Pt	Phenyl	61	0	9	6		

The reactions were carried out under the reflux in benzene solutions for 2·5 h.

These facts clearly indicate that the adducts are formed directly from the dithiolatometal complexes and quadricyclane without the intermediacy of norbornadiene.

The yields of the products in the reactions of **1** with Q or NBD are summarized in Table 1. Norbornene (NB) reacts with **1a** to give a 1:1 adduct and a dihydro-1,4-dithiin derivative. The reaction of NB with **1a** is similar to that of NBD.



1a 4 5

The reactions of the dithiolatometal complexes with Q and NBD are pseudo-first-order with respect to the metal complexes under the condition of an excess of the hydrocarbons (Figures 1 and 2). The reaction of **1a** with Q has been found to be first order with respect to Q by the measurement of the reaction rate by varying the concentration of Q.

The pseudo-first-order rates of the reaction of the dithiolatometal complexes with Q and NBD are summarized in Table 2, together with the half-wave potentials of the dithiolatometal complexes.

The rates of the reactions between **1** and Q are 10^3–10^4 times faster than those of the reaction between **1** and NBD.

The reactivities of the dithiolatometal complexes toward quadricyclane as well as toward norbornadiene are dependent on the central metal and the substituents in the aryl moiety. The order of the reactivity is Pd complex > Ni complex > Pt complex. This order does not agree with the order of the elements in the periodic table. However, the order of the reactivity is well correlated to the half-wave potentials of the dithiolatometal complexes: the more

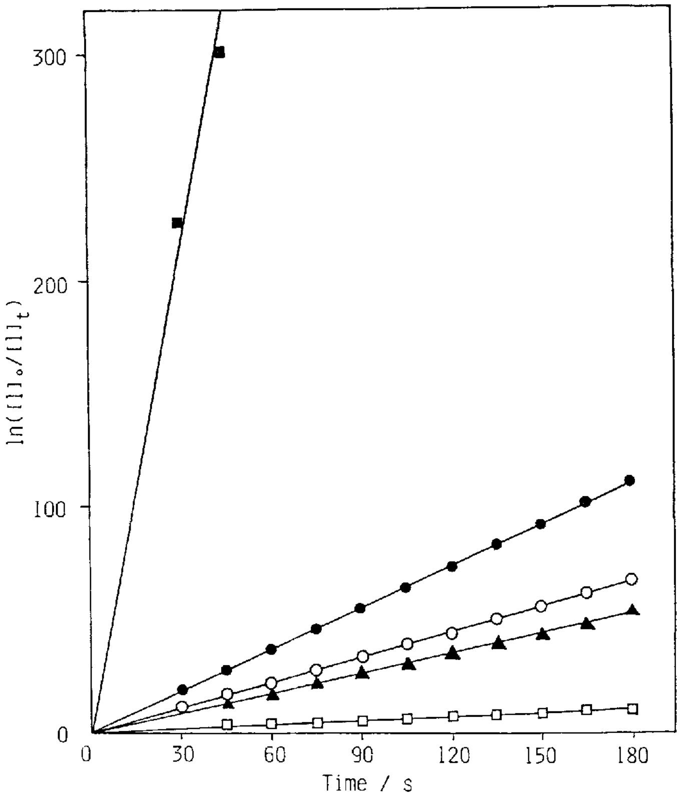


Figure 1. Plots in pseudo-first order kinetics for the reaction of bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) (**1**) with quadricyclane (Q) at 30 °C in benzene solutions $[\mathbf{1}]_0 = 2 \times 10^{-5}$ mol dm^{-3}, [Q] = 1·93 × 10^{-1} mol dm^{-3}
—○—○—, **1a** —●—●—, **1b** —□—□—, **1c** —■—■—, **1d** —▲—▲—, **1e**

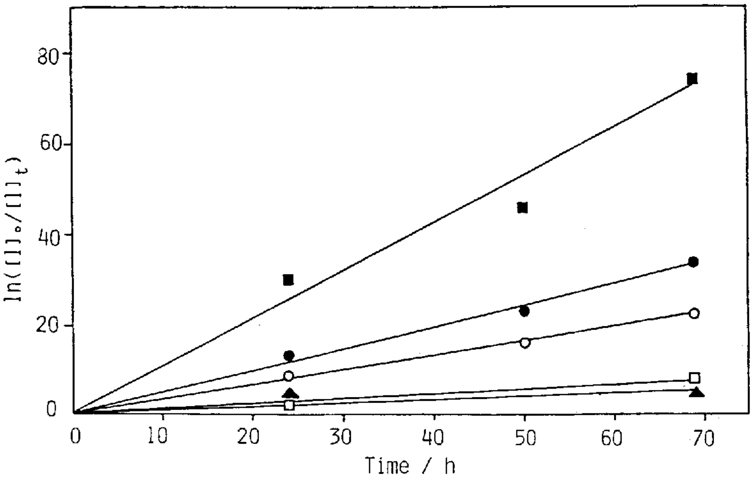


Figure 2. Plots in pseudo-first order kinetics for the reaction of bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) (**1**) with norbornadiene (NBD) at 30 °C in benzene solutions $[\mathbf{1}]_0 = 2 \times 10^{-5}$ mol dm^{-3}, [NBD] = 1·89 × 10^{-1} mol dm^{-3}
—○—○—, **1a** —●—●—, **1b** —□—□—, **1c** —■—■—, **1d** —▲—▲—, **1e**

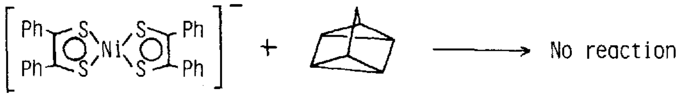
Table 2. Pseudo-first-order rate constants in reactions between bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) and quadricyclane or norbornadiene and half-wave potentials of dithiolatometal complexes

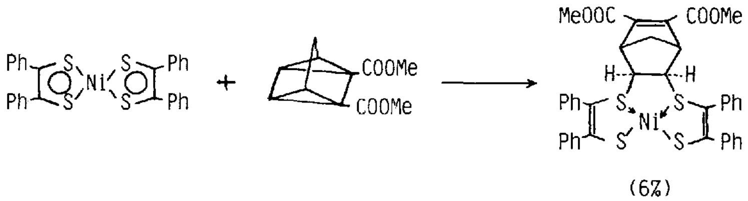
	Dithiolatometal		Half-wave Potential of Complex*	Reaction with Q	Reaction with NBD
	Metal	Aryl	$E_{1/2}$/V	k/s^{-1}†	k/s^{-1}†
1a	Ni	Phenyl	−0·35	3·6 × 10^{-3}	8·7 × 10^{-7}
1b	Ni	*p*-Fluorophenyl	−0·31	6·1 × 10^{-3}	1·3 × 10^{-6}
1c	Ni	*p*-Methoxyphenyl	−0·46	5·2 × 10^{-4}	3·2 × 10^{-7}
1d	Pd	Phenyl	−0·32	5·2 × 10^{-2}	2·8 × 10^{-6}
1e	Pt	Phenyl	−0·41	2·8 × 10^{-3}	1·5 × 10^{-7}

*vs. Ag|0·1 mol dm^{-3} $AgClO_4$-dimethylformamide.
†Pseudo-first order rate constant at the concentrations of [Q] = [NBD] = 1·9 × 10^{-1} mol dm^{-3} and [**1**] = 2 × 10^{-5} mol dm^{-3} at 30 °C in benzene solutions.

electropositive complex reacts faster. The substituent effect in the dithiolatonickel complexes gives a similar result: the electron accepting group, F, accelerates the reaction, while the electron donating group, OCH_3, retards the reaction. In the reaction of dithiolatonickel(0) complexes and Q or NBD, the reactivities of the complexes are correlated to their half-wave potentials.

The anionic bis(1,2-diphenyl-1,2-ethylenedithiolato)niccolate(-1) (as tetraethylammonium salt) does not react with Q. The quadricyclane derivative with electron attracting methoxycarbonyl group gives the 1:1 adduct with **1a** only in 6% yield. These facts indicate the importance of the donor–acceptor interaction between Q (donor) and the dithiolato complex (acceptor).





Baker, Hermann, and Wing have explained the reactions of the bisdithiolatometal complex with ene and conjugated diene in terms of the interaction between the LUMO of the dithiolatometal complex and the HOMO of the hydrocarbons.[5,6]

This mechanism can explain not only the differences in reactivities of Q and NBD toward bisdithiolatometal complexes but also the effects of substituents in the aryl moiety of the

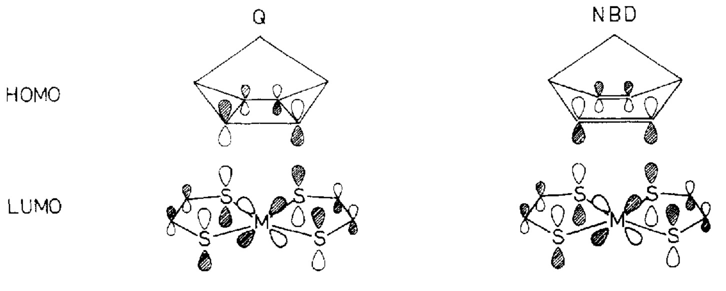


Figure 3. Molecular orbitals of bis(1,2-ethylenedithiolato)metal, quadricyclane, and norbornadiene

complex **1**. In Figure 3 are shown the reported HOMO's of quadricyclane and norbornadiene[10] and the LUMO of bis(1,2-ethylenedithiolato)metal.[11] The phase of LUMO at the two sulfur atoms of the dithiolatometal complex does not fit to the phase of the HOMO at the carbon atoms of NBD, while the former fits to the phase of the HOMO at the 2-, and 3-positions of Q. This explains the fact that Q reacts with bis(1,2-ethylenedithiolato)metal(0) much more readily than with NBD. The electron accepting group lowers the LUMO of the dithiolato complex. This would facilitate the interaction of the LUMO of the dithiolato complex with the HOMO's of the hydrocarbons.

Photodissociation of the adducts

Some adducts between bisdithiolatonickel complexes and norbornadiene have been reported to be photoreactive.[1,5] We studied the photochemical behavior of the adducts in more detail on the basis of the wavelength dependences of the photoreaction. When the adducts were irradiated in benzene or cyclohexane solutions with UV-light, some remarkable color changes

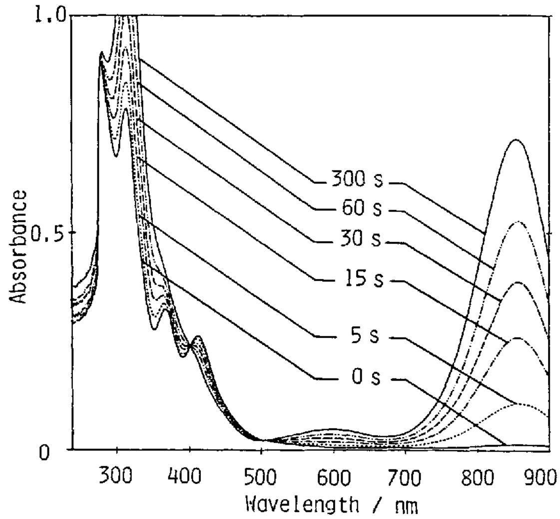


Figure 4. UV–vis spectral change of the adduct **2a** during irradiation with 365 nm light in a benzene solution $[\mathbf{2a}]_0 = 2{\cdot}98 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$

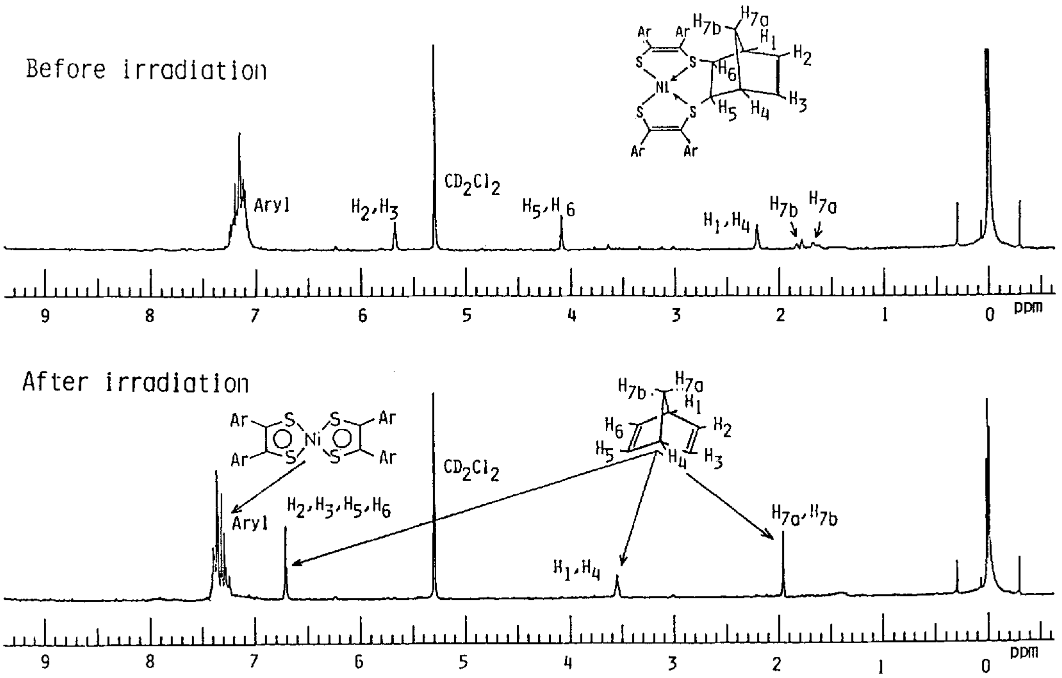


Figure 5. ^{1}H-NMR spectral change of the adduct **2a** during irradiation with a xenon lamp in CD_2Cl_2

were observed: for the adducts **2a**–**2c**, the color changes from yellow to green; for **2d**, from orange to red; and for **2e**, from yellow to purple. An example of the UV–vis spectral changes is shown in Figure 4. The UV–vis spectral changes indicate that the adducts are dissociated to the bis(1,2-ethylenedithiolato)metal complexes and the hydrocarbon. The change of ^{1}H-NMR spectra due to the irradiation of **2a** with a Xe lamp in a glass tube is shown in Figure 5. The spectra show that the adduct is dissociated to the dithiolato complex (**1a**) and NBD. Upon irradiation with light longer than 300 nm the adducts are dissociated quantitatively to the dithiolatometal complexes and norbornadiene.

During irradiation with light of 254 nm, the absorption around 855 nm due to the free dithiolato complexes increases at the first stage and then decreases, as exemplified by the photoreaction of the adduct **2a** in Figure 6. The plots of the concentration changes of **2a** and **1a** during the irradiation by 254 nm (Figure 7) show that the photoreaction occurs in two steps: first the dissociation to the free dithiolatometal complexes and second the decomposition of the dithiolatometal complexes. In the irradiation of the adduct **2a** ($1{\cdot}5 \times 10^{-5}$ mol dm^{-3}) in a cyclohexane solution for 60 s, $0{\cdot}84 \times 10^{-5}$ mol dm^{-3} of the adduct was reacted and $0{\cdot}75 \times 10^{-5}$ mol dm^{-3} of **1a** was formed. This shows that dissociation is the main reaction of the adduct during the irradiation with 254 nm light.

The quantum yields of the photodissociation of the adducts are shown in Table 3. The UV–vis spectra of the adducts are shown in Figure 8.

Only small wavelength dependencies are observed in the quantum yields of the photodissociation in the wavelength region where the adducts absorb the light. The adducts are dissociated efficiently (in fairly high quantum yields).

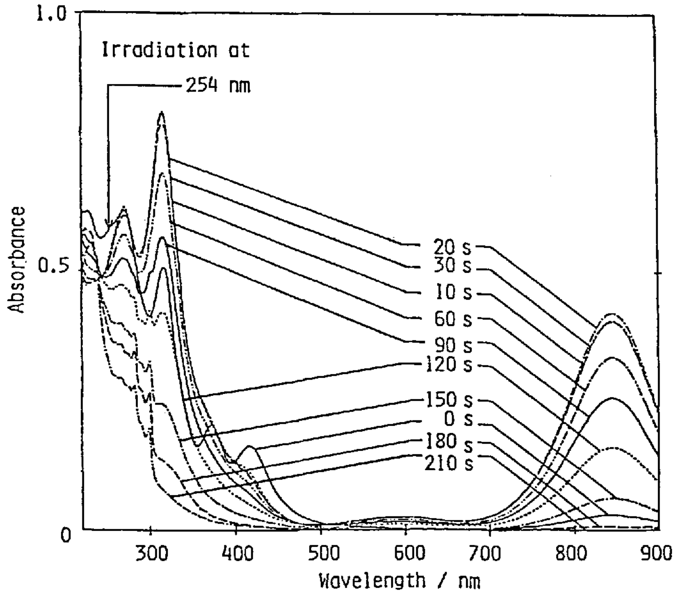


Figure 6. UV–vis spectral change of the adduct **2a** during irradiation with 254 nm light in a cyclohexane solution $[\mathbf{2a}]_0 = 1{\cdot}5 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$

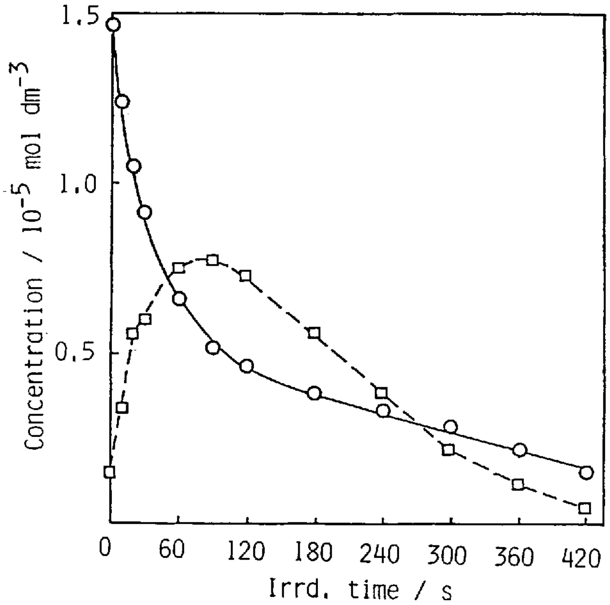


Figure 7. Change of concentrations of **2a** and **1a** during irradiation of the adduct **2a** with 254 nm light $[\mathbf{2a}]_0 = 1{\cdot}5 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$

Table 3. Quantum yields of photodissociation of adducts

	Adduct		Quantum Yield of Photodissociation			
	Metal	Aryl	254 nm	313 nm	365 nm	436 nm
2a	Ni	Phenyl	0·083	0·068	0·140	0·130
2b	Ni	*p*-Fluorophenyl	0·110	0·076	0·120	0·097
2c	Ni	*p*-Methoxyphenyl	0·084	0·071	0·110	0·130
2d	Pd	Phenyl	0·110	0·077	0·130	0·035
2e	Pt	Phenyl	0·150	0·210	0·230	—*

*Not determined because of the absence of absorption.

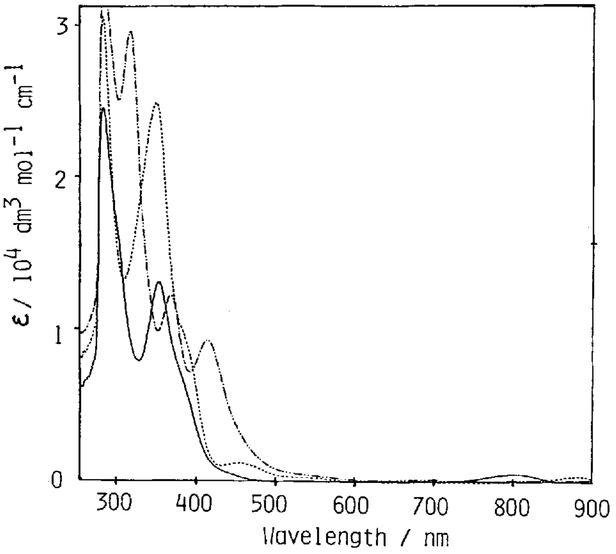
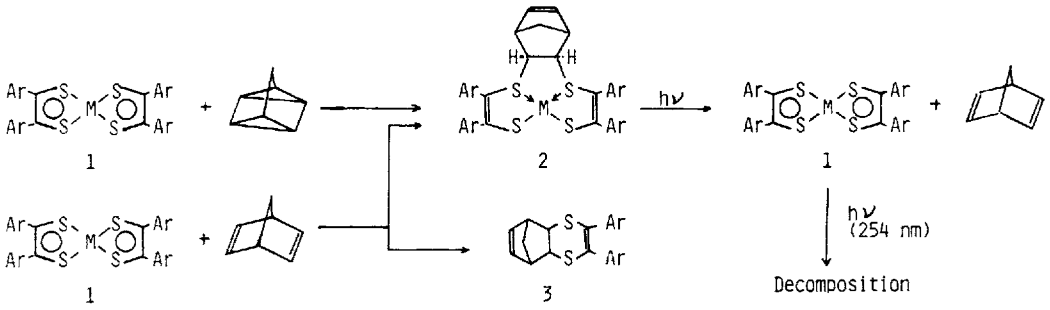


Figure 8. UV–vis spectra of adducts **2a**, **2d**, and **2e** in benzene solutions – – – – –, **2a** ············, **2d** ————, **2e**

In contrast to the large effects of the central metal and the substituents on the reactivities of the dithiolatometal complexes toward Q and NBD, the central metal and the substituents affect the photoreactivities only to a small extent. The substituents in the benzene ring in the nickel complexes have no effect either on the efficiencies for photodissociation or on the absorption spectra. The adduct of the platinum complex is more photoreactive than other adducts, but the differences in the photoreactivities is small.

The spectral change due to the irradiation of the benzene solution of the adduct between **2a** with Co-60 γ-rays does not show any increase in the absorption around 855 nm ascribable to the dissociation of the adduct, but does show a monotonous decrease of the absorption of the adducts due to the decomposition of the adduct. It has been reported that the γ-irradiation of benzene produces the excited triplet benzene efficiently.[12] In the γ-irradiation of the adduct in benzene, the formation of the excited triplet state of the adduct (via the triplet energy transfer) is expected. The above fact indicates that the excited triplet state of the adduct does not undergo dissociation but rather decomposition.

The reactions of the bis(1,2-diaryl-1,2-ethylenedithiolato)metal(0) and quadricyclane or norbornadiene and the photoreactions of the adducts are summarized in Scheme 1.



Scheme 1

EXPERIMENTAL SECTION

Benzoin (Yoneyama Chemical Industry), 4,4′-difluorobenzoin (Midori Kagaku Co.), nickel chloride hexahydrate (extra pure reagent of Junsei Kagaku Co.), potassium tetrachloropalladate(II) (Aldrich), potassium tetrachloroplatinate(II) (Aldrich), quadricyclane (Aldrich), norbornadiene (extra pure reagent of Wako Junyaku Co.), and norbornene (G. R. reagent of Wako Junyaku Co.) were used as purchased.

NMR, IR, and UV–vis spectra were recorded on a JEOL NMR spectrometer Model GX-270, on an IR spectrometer Model 260-50 of Hitachi Co., and on a UV–vis spectrometer Model 228 of Hitachi Co., respectively. MS were measured with a JEOL mass spectrometer Model JMS-D 300. For elemental analysis we used an apparatus Model 240C made by Perkin-Elmer Co.

Synthesis of bis(1,2-diaryl-1,2-ethylenedithiolatolato)metal complexes (1a–1e)

The dithiolatometal complexes were prepared by the reaction of $NiCl_2$ $2H_2O$, K_2PdCl_4, or K_2PtCl_4 with thiophosphoric esters of dithiobenzoins which were synthesized from benzoin (or substituted benzoin) and P_4S_{10}.[1] The complex **1c** was kindly provided by Midori Kagaku Co.

Bis(1,2-bis(*p*-fluorophenyl)-1,2-ethylenedithiolato)nickel(0) (**1b**) is a new complex. It was identified by its spectra and elemental analysis. Dark green crystals; mp >300 °C (decomposition); UV (benzene) 319 (ε 45000), 607 (2230), and 857 nm (31100); IR (KBr disk) 1600, 1510, 1368, 1235, 1140, 890, 855, 840, 830, 810, 558, 540, and 520 cm^{-1}; ^1H-NMR (CD_2Cl_2) δ = 7·37 (8H, m) and 7·03 (8H, m); ^{13}C-NMR (CD_2Cl_2) δ = 116·04 (d), 131·29 (d), 137·63, 163·64 (d), and 181·00; MS (70 eV) *m/z* (rel. intensity) 614 (18, M^+), 278 (43), 214 (100), and 139 (80). Found: C, 54·63; H, 2·52%. Calculated for $C_{28}H_{16}F_4NiS_4$: C, 54·65; H, 2·62%.

The other dithiolato complexes were identified by the elemental analyses and their ^{1}H-NMR, IR and MS.

1a: dark green crystals. Found: C, 61·77; H, 3·67%.
1c: dark green crystals. Found: C, 57·33; H, 4·36%.
1d: purple crystals. Found: C, 56·82; H, 3·36%.
1e: purple crystals. Found: C, 49·07; H, 2·71%.

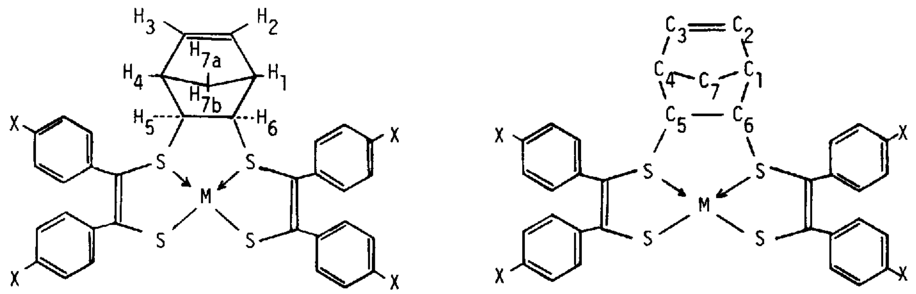
Reaction of dithiolatometal complex with quadricyclane, norbornadiene, or norbornene (for the identification of products and for the determination of the yields of products)

The solutions containing the dithiolatometal complex (*ca.* 0·1 mmol) and quadricyclane (50–60 mmol), norbornadiene (50–60 mmol), or norbornene (50 mmol) in benzene (10 cm^3) were refluxed under Ar for 2·5 h.

After the reaction, the solvent and Q or NBD were evaporated under reduced pressure. The residue was submitted to flash column chromatography with a column of silica gel (Wako gel C-300). The pure adducts were isolated and their yields were determined gravimetrically.

Identification of adducts

The adducts of the dithiolatometal complexes with Q were identical with the adducts of the dithiolatometal complexes with NBD, some of which (adducts **2a** and **2d**) have been described in the literature.[1,3] The adducts **2b**, **2c**, and **2e** are new compounds. The structure of a similar adduct between bis(1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato)nickel(0) and NBD was determined by X-ray diffraction and the stereochemistry at the 5- and 6-position has been clarified.[4] The fact that 2·13–2·57 Hz of the hyperfine coupling between H_1 and H_6 supports the conformation of H_6 (as well as H_5) at the endo position.



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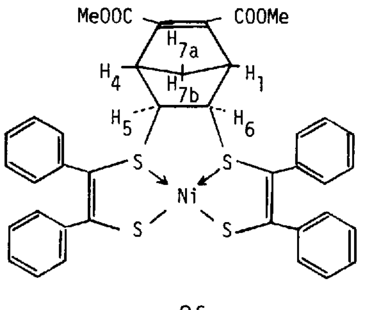
Adduct **2b**: brown solid, mp 228 °C (decomposition); UV (benzene) 316 (ε 24900), 365 (10100), and 410 nm (8200); IR (KBr disk) 2900, 1590, 1530, 1490, 1235, 860, 840, 830, 810, 560, and 540 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 1·66 (1H, dt, J = 10·27 and 2·13 Hz, H_{7a}), 1·80 (1H, d, J = 10·27 Hz, H_{7b}), 2·22 (2H, m, H_1 and H_4), 4·09 (2H, d, J = 2·13 Hz, H_5 and H_6), 5·74 (2H, m, H_2 and H_3), 6·86 (8H, m, Ar), 7·08 (4H, m, Ar), and 7·22 (4H, m, Ar); ^{13}C-NMR (CD_2Cl_2) δ = 44·85 (C_7), 47·47 (C_1 and C_4), 65·86 (C_5 and C_6), 115·28 (Ar), 115·99 (Ar), 117·91 (dithiolato ring), 131·05 (Ar), 132·06 (Ar), 133·62 (Ar), 136·67 (Ar), 136·75 (C_2 and C_3), 160·37 (dithiolato ring), 160·99 (Ar), and 164·27 (Ar); MS (70 eV) *m/z* (rel. intensity)

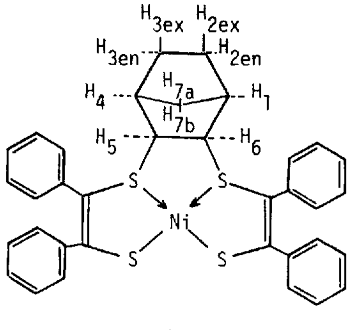
614 (12, $(M—C_7H_8)^+$), 370 (6), 304 (16), 278 (22), 214 (45), 139 (41), 92 (50), and 91 (100). Found: C, 59·08; H, 3·40%. Calculated for $C_{35}H_{24}F_4NiS_4$: C, 59·42; H, 3·42%.

Adduct **2c**: brown solid, mp 210–211 °C (decomposition); UV (benzene) 316 (ε 30900), 364 (12700), and 414 nm (8420); IR (KBr disk) 2950, 1610, 1540, 1510, 1300, 1260, 1180, 1040, 870, 840, 810, 590, 570, and 545 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 1·61 (1H, dt, *J* = 9·89 and 2·20 Hz, H_{7a}), 1·80 (1H, d, *J* = 9·89 Hz, H_{7b}), 2·22 (2H, m, H_1 and H_4), 3·72 (6H, s, OCH_3), 3·73 (6H, s, OCH_3), 4·04 (2H, d, *J* = 2·20 Hz, H_5 and H_6), 5·71 (2H, m, H_2 and H_3) 6·67 (4H, d, *J* = 9·16 Hz, Ar), 6·72 (4H, d, *J* = 9·16 Hz, Ar), 7·04 (4H, d, *J* = 9·16 Hz, Ar), and 7·20 (4H, d, *J* = 9·16 Hz, Ar); ^{13}C-NMR (CD_2Cl_2) δ = 44·73 (C_7), 47·42 (C_1 and C_4), 55·54 (OCH_3), 65·53 (C_5 and C_6), 113·51 (Ar), 114·21 (Ar), 117·75 (dithiolato ring), 128·70 (Ar), 130·44 (Ar), 130·60 (Ar), 131·64 (Ar), 133·37 (Ar), 136·76 (C_2 and C_3), 159·14 (Ar), and 159·67 (dithiolato ring); MS (70 eV) *m/z* (rel. intensity) 662 (trace, $(M—C_7H_8)^+$), 394 (7), 328 (15), 302 (66), 238 (100), 223 (41), 151 (73), and 91 (7). Found: C, 61·90; H, 4·87%. Calculated for $C_{39}H_{36}O_4NiS_4$: C, 61·99; H, 4·80%.

Adduct **2e**: pale yellow solid; mp 216 °C (decomposition); UV (benzene) 354 nm (ε 12700); IR (KBr disk) 3070, 1540, 1445, 770, 745, 730, and 700 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 1·70 (1H, dt, *J* = 9·89 and 2·57 Hz, H_{7a}), 1·93 (1H, d, *J* = 9·89 Hz, H_{7b}), 2·15 (2H, m, H_1 and H_4), 4·01 (2H, d, *J* = 2·54 Hz, H_5 and H_6), 5·58 (2H, m, H_2 and H_3), and 7·11–7·32 (20H, m, Ph); ^{13}C-NMR (CD_2Cl_2) δ = 45·62 (C_7), 47·76 (C_1 and C_4), 71·45 (C_5 and C_6), 118·97 (dithiolato ring), 128·34 (Ph), 128·84 (Ph), 129·34 (Ph), 130·31 (Ph), 133·53 (Ph), 136·49 (C_2 and C_3), 137·93 (Ph), 138·36 (Ph), 141·35 (Ph), and 161·11 (dithiolato ring); MS (70 eV) *m/z* (rel. intensity) 679 (66, $(M—C_7H_8)^+$), 242 (9), 210 (74) 178 (100), 121 (55), 92 (9), and 91 (20). Found: C; 54·51; H, 3·70%. Calculated for $C_{35}H_{28}PtS_4$: C, 55·46; H, 3·66%.



2f



4

Adduct between **1a** and dimethyl quadricyclane-1,5-dicarboxylate (**2f**): brown solid; IR (KBr disk) 2950, 1730, 1550, 1450, 1440, 1280, 1255, 745, and 700 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 1·91 (1H, d), 1·92 (1H, d), 2·62 (2H, t, H_1 and H_4), 3·44 (6H, s, $COOCH_3$), 4·09 (2H, d, H_5 and H_6), and 7·09–7·35 (20H, m, Ph); MS (70 eV) *m/z* (rel. intensity) 542 (5, $(M—C_7H_6(COOCH_3)_2)^+$), 242 (57), 210 (63), 208 (62), 178 (71), and 121 (71).

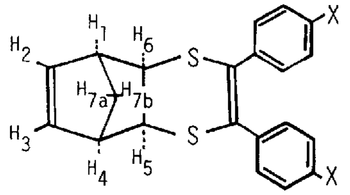
Adduct between **1a** and norbornene (**4**): brown solid; mp 200 °C (decomposition); UV (benzene) 310 (ε 34700), 368 (8450), and 416 nm (6100); IR (KBr disk) 3060, 2950, 2880, 1540, 1448, 770, 740, and 700 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 0·66 (2H, m), 0·83 (2H, m), 1·01 (1H, m, H_{7a}), 1·63 (1H, m, H_{7b}), 1·67 (2H, m, H_1 and H_4), 4·13 (2H, d, *J* = 2·16 Hz, H_5 and H_6), and 7·04–7·23 (20H, m, Ph); ^{13}C-NMR (CD_2Cl_2) δ = 26·60, 30·07, 43·04, 71·31, 119·03 (dithiolato ring), 127·65 (Ph), 128·24 (Ph), 128·33 (Ph), 128·75 (Ph), 129·13 (Ph), 130·32 (Ph), 137·85 (Ph), 140·95 (Ph), and 161·32 (dithiolato ring); MS (70 eV) *m/z* (rel. intensity) 542 (23, (M—$C_7H_{10})^+$), 242 (66), 178 (100), 121 (76), and 94 (9). Found: C, 65·47; H, 4·60%. Calculated for $C_{35}H_{30}NiS_4$: C, 65·94; H, 4·74%.

Adduct **2a**: brown solid; mp 165 °C (decomposition) (lit.[1] 165 °C (decomposition)) ^{1}H-NMR (CD_2Cl_2) δ = 1·63 (1H, dt, J = 10·25 and 2·57 Hz, H_{7a}), 1·80 (1H, d, J = 10·25 Hz, H_{7b}), 2·20 (2H, m, H_1 and H_4), 4·09 (2H, d, J = 2·57 Hz, H_5 and H_6), 5·68 (2H, m, H_2 and H_3) and 7·09–7·27 (20H, m, Ph). Found: C, 66·07; H, 4·32%.

Adduct **2d**: red–brown solid; mp 246 °C (decomposition) (lit.[1] mp 252 °C (decomposition)); ^{1}H-NMR (CD_2Cl_2) δ = 1·64 (1H, dt, J = 9·53 and 2·20 Hz, H_{7a}), 1·86 (1H, d, J = 9·53 Hz, H_{7b}), 2·13 (2H, m, H_1 and H_4), 3·96 (2H, d, J = 2·20 Hz, H_5 and H_6), 5·63 (2H, m, H_2 and H_3), and 7·10–7·32 (20H, m, Ph). Found: C, 61·16; H, 4·26%.

Identification of dihydro-1,4-dithiin

Among the dihydro-1,4-dithiins, **3a** has been described in the literature.[2] However, the reported melting point (147 °C) is different from that which we observed (mp 159–160 °C). Therefore, we identified it from its spectra and by elemental analysis.



3

3a: colorless solid; mp 159–160 °C; IR (KBr disk) 3090, 2980, 2950, 1600, 1580, 1540, 1490, 1445, 1330, 750, 740, and 700 cm^{-1}; ^{1}H-NMR (CD_2Cl_2) δ = 1·62 (1H, dm, J = 8·79 Hz, H_{7a}), 2·80 (1H, dm, J = 8·79 Hz, H_{7b}), 2·94 (2H, m, H_1 and H_4), 3·59 (2H, d, J = 1·83 Hz, H_5 and H_6), 6·17 (2H, t, J = 1·83 Hz, H_2 and H_3), and 7·05 (10H, s, Ph); MS (70 eV) m/z (rel. intensity) 334 (25, M$^+$), 268 (100). Found: C, 74·93; H, 5·39%. Calculated for $C_{21}H_{18}S_2$: C, 75·41; H, 5·42%.

3b: colorless solid; mp 209–210 °C; ^{1}H-NMR (CD_2Cl_2) δ = 1·70 (1H, dm, J = 8·79 Hz, H_{7a}), 2·85 (1H, dm, J = 8·79 Hz, H_{7b}) 3·01 (2H, m, H_1 and H_4), 3·66 (2H, s, H_5 and H_6), 6·25 (2H, m, H_2 and H_3), 6·85 (4H, m, Ar), and 7·09 (4H, m, Ar); MS (70 eV) m/z (rel. intensity) 370 (28, M$^+$), 304 (100). Found: C, 67·02; 4·42%. Calculated for $C_{21}H_{16}F_2S_2$: C, 68·08; H, 4·35%.

3c: colorless solid; mp 126 °C; ^{1}H-NMR (CCl_4) δ = 1·67 (1H, dm, J = 8·80 Hz, H_{7a}), 2·86 (1H, dm, J = 8·80 Hz, H_{7b}), 2·99 (2H, m, H_1 and H_4), 3·62 (2H, d, J = 1·84 Hz, H_5 and H_6), 3·73 (6H, s, OCH_3), 6·24 (2H, t, J = 1·84 Hz, H_2 and H_3), 6·68 (4H, d, J = 8·79 Hz, Ar), and 7·06 (4H, d, J = 8·79 Hz, Ar); MS (70 eV) m/z (rel. intensity) 349 (4, M$^+$), 328 (100). Found: C, 70·11; 5·87%. Calculated for $C_{23}H_{22}O_2S_2$: C, 70·02; H, 5·62%.

5 (the dihydro-1,4-dithiin derivative from **1a** and norbornene): colorless solid; mp 175 °C; IR (KBr disk) 3060, 2950, 2880, 1600, 1580, 1540, 1483, 1448, 1315, 770, 740, and 700 cm^{-1}; ^{1}H-NMR (CCl_4) δ = 1·31 (1H, dm, J = 10·07 Hz, H_{7a}), 1·33 (2H, dm), 1·68 (2H, dm), 2·45 (2H, m, H_1 and H_4), 2·53 (1H, dm, J = 10·07 Hz, H_{7b}), 3·54 (2H, d, J = 1·22 Hz, H_5 and H_6), and 7·11 (10H, s, Ph); MS (70 eV) m/z (rel. intensity) 336 (100, M$^+$) and 242 (92). Found: C, 74·24; H, 5·81%. Calculated for $C_{21}H_{20}S_2$: C, 74·96; H, 5·99%.

Determination of rate constants

The reaction rates between the dithiolato complexes and Q or NBD were determined by following the decrease of the absorption of the dithiolato complexes around 850 nm in a quartz cell (1 cm of width). The reaction was started by mixing 1 cm^3 of the benzene solution of the dithiolato complex ($4–9 \times 10^{-5}$ mol dm^{-3}) and 2 cm^3 of the benzene solution of Q or NBD ($2{\cdot}8–2{\cdot}9 \times 10^{-1}$ mol dm^{-3}). The temperature of the solution was kept at 30 °C.

Photoreaction of adducts (for identification of products)

The CD_2Cl_2 solution of the adducts (**2a**, **2d**, and **2e**) in a glass tube for the measurement of NMR spectra was irradiated with a Xe lamp (500 W).

Determination of quantum yields for photodissociation of adducts

The monochromatic light of 313, 365, and 436 nm was obtained by a Shimadzu-Bausch and Lomb grating monochromator (dispersion, 7·4 nm mm^{-1}; slit width, 1·5 mm) equipped with a super high pressure mercury lamp (Osram HBO 200 W). For the irradiation at 254 nm a low pressure mercury lamp was used. For the irradiations at 313, 365, and 436 nm light, benzene was used as the solvent, and for the irradiation at 254 nm, cyclohexane was used as the solvent. Each sample solution was prepared in such a concentration that its absorbance at the wavelength for irradiation is in the range of 0·8–0·9. The solution was deaerated by bubbling Ar for 15 min prior to irradiation. Then, the solution was irradiated in a quartz cell (1 cm wide) for the measurement of UV–vis spectra. The reaction was followed by measuring the UV–vis spectra.

Actinometry was carried out by using potassium trioxalatoferrate(III) according to the method in the literature.[13]

The quantities of photons absorbed by the solutions were determined on the basis of the intensities of the insident light and the absorbance of the solutions.

Gamma-irradiation

Benzene solutions of the adduct between **1a** and Q ($2{\cdot}8 \times 10^{-4}$ mol dm^{-3}) were irradiated by Co-60 γ-rays at the irradiation facility of Japan Atomic Energy Research Institute in Takasaki at the dose rates of 2, 4, 6, 8, and 10×10^5 rad h^{-1} for 1 h. The benzene solutions were deaerated by bubbling Ar before irradiation.

Determination of half-wave potentials of the dithiolatometal complexes

The half-wave potentials ($E^r_{1/2}$) of the dithiolatometal complexes were determined by cyclic voltanmetry with a Yanagimoto Polarographic Analyzer, Model P1100 at 25 °C. Dimethylformamide was used as the solvent, 0·1 mol dm^{-3} of tetraethylammonium perchlorate as the supporting electrolyte, an Ag|0·1 mol dm^{-3} $AgClO_4$–dimethylformamide electrode as the reference electrode, and a stationary disk platinum working electrode (2 mm of diameter). Two reversible one-electron reduction processes were observed for all the complexes.

ACKNOWLEDGEMENT

The authors thank Midori Kagaku Co. for giving us 4,4'-difluorobenzoin and bis(1,2-bis(*p*-methoxyphenyl)-1,2-ethylenedithiolato)nickel(0). This study was partially supported by Grant-in-Aid for Special Project Research No 61123003 from the Ministry of Education, Science and Culture.

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