ELSEVIER

Coordination Chemistry Reviews
159 (1997) 397–406

COORDINATION CHEMISTRY REVIEWS

Long-lived metal-complex-radicals in photoreactions of S,S′-dialkyl and S,S′-alkanediyl derivatives of bis(1,2-ethenedithiolato)metal complexes

Akira Sugimori

Department of Chemistry, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102, Japan

Received 22 December 1995

Contents

Abstract

The photodissociations of *S,S′*-dialkyl and *S,S′*-alkanediyl derivatives of bis(1,2-ethenedithiolato)metal complexes to give unusually long-lived metal-complex-radicals are discussed. In the photoreaction of *S,S′*-dibenzyl derivative of bis(1,2-diphenyl-1,2-ethenedithiolato)nickel, an excited triplet state of the adduct eliminates one benzyl radical and a pair, of a metal-complex-radical and a benzyl radical, is formed. The nickel-complex-radical has a lifetime of 1500 s and decomposes thermally to the free nickeladithiolene and a benzyl radical. In the photodissociation of *S,S′*-butane-1,4-diyl derivative of bis(1,2-diphenyl-1,2-ethenedithiolato)nickel, two kinds of long-lived nickel-complex-radicals participate. Radical I (presumably a biradical) undergoes three types of reaction: radical recombination to regenerate the butanediyl derivative, dissociation to give the free dithiolato complex, and transformation to another radical species, Radical II. Radical II dissociates more slowly to give the free dithiolato complex. © 1997 Elsevier Science S.A.

Keywords: Metal complex radicals; Photoreactions; Dithiolato complexes

---

PII S0010-8545(96)01313-6

1. Introduction

A metalladithiolene ring consisting of one metal atom, two coordinated sulfur atoms, and two unsaturated carbon atoms is a very interesting ring system [1]. A variety of addition and elimination (especially photochemically induced) reactions have been found to occur on the metalladithiolene rings. Such reactions have been found in metalladithiolene rings in (η^5-cyclopentadienyl)(1,2-ethenedithiolato)metal(III) complexes (metal = Co and Rh). Dimethyl acetylenedicarboxylate inserts between metal and sulfur [2]. Diazo compounds add between metal and sulfur accompanying the elimination of dinitrogen to form a three-membered metallathiirane ring [3]. Quadricyclane also adds to metalladithiolenes accompanying ring opening and rearrangement [4]. Some of these addition products undergo elimination reactions, when they are irradiated with UV-visible light. In the previous report, we reviewed several photochemical elimination reactions which occur in metalladithiolene rings in (η^5-cyclopentadienyl)(1,2-ethenedithiolato)cobalt complexes [5]. Another type of metalladithiolene complex, which contains only dithiolato as ligand, also shows addition and elimination reactions. The sulfur atoms are the reactive site of this type of metalladithiolene ring. The chemistry of this type of metalladithiolene has been developed by the group of Schrauzer in the 1960s. Schrauzer et al. reported the formation of a 1:1 adduct between bis(1,2-diphenyl-1,2-ethenedithiolato)nickel and norbornadiene [6]. In the adduct, a norbornene-5,6-diyl group bridges between two sulfur atoms. They also mentioned that the adduct decomposes at room temperature, when it is exposed to daylight. We found that quadricyclane reacts much more rapidly with bis(1,2-diphenyl-1,2-ethenedithiolato)metal (metal = Ni, Pd, and Pt) than norbornadiene and studied the photochemical behavior of the adducts in more detail [7]. Upon irradiation with light of 254–436 nm, these adducts dissociate selectively to the free bis(1,2-diphenyl-1,2-ethenedithiolato)metal and norbornadiene. The quantum yields of the photodissociation are wavelength-dependent. The order of the photoreactivity is platinum complex > palladium complex > nickel complex. Schrauzer et al. reported *S,S'*-dialkyl derivatives of bis(1,2-diphenyl-1,2-ethenedithiolato)metal (metal = Ni, Pd, and Pt) [8]. Schrauzer et al. found recently that the dialkyl derivative consists of some stereo isomers and the interconversion occurs easily at room temperature [9]. The predominant isomers are *trans-anti* and *trans-syn* isomers [10].

Their photodissociation has been described by Schrauzer et al. But the mechanism of the photodissociation has not been presented, although the possible existence of radical species was suggested [9]. We found that the mechanism of the photodissociation is a very interesting one in which some extraordinarily long-lived radical species participate. In this paper we discuss the photodissociation of the *S,S'*-dialkyl and *S,S'*-alkanediyl derivatives of bis(1,2-diphenyl-1,2-ethenedithiolato)metal complexes.

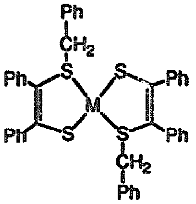
2. Photodissociation of *S,S'*-dialkyl derivatives of bis(1,2-diphenyl-1,2-ethenedithiolato)metal complexes [11,12]

The formation of *S,S'*-dibenzyl derivatives and their photochemical dissociation was reported by Schrauzer et al. as early as 1968 [9]. However, its mechanism has not yet been studied. With respect to the mechanism, the following questions should be answered. (1) Are the alkyl radicals formed photochemically? (2) Does the elimination of two alkyl groups proceed in one step or stepwise? (3) Is the excited state responsible for the dissociation singlet or triplet?

When a benzene solution of *S,S'*-dialkyl derivative of bis(1,2-diphenyl-1,2-ethenedithiolato)nickel was irradiated with a medium pressure mercury lamp, the appearance of a deep blue color was observed. The absorption around 850 nm clearly indicates the formation of the free bis(1,2-diphenyl-1,2-ethenedithiolato)nickel.

The formation of the benzyl radical was confirmed by trapping with TEMPO (2,2,6.6-tetramethylpiperidine-*N*-oxyl). The formation of a radical pair was demonstrated very clearly by time-resolved ESR. The ESR spectra taken at 1 μs after the laser flash (308 nm) show two kinds of signal: one is the signal due to the benzyl radical and the other is the signal due to the metal-complex-radical. The conventional ESR spectrum obtained at 77 K is assigned to a nickel-complex-radical (analyzed as an $S=1/2$ system with $g_1=1.997$, $g_2=2.035$, and $g_3=2.088$). The spectra are similar to those of the $[Ni(S_2C_2Ph_2)_2]^-$, monoanion of the bis(1,2-ethenedithiolato)nickel complex. This suggests that the electronic spin is delocalized in the nickeladithiolene ring.

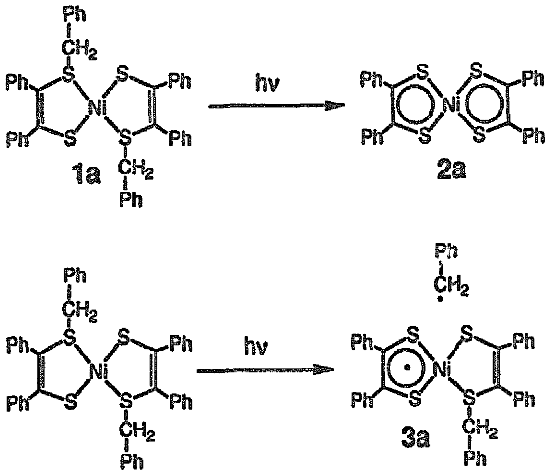
The most interesting observation was that the metal-complex-radical is long-lived in a benzene solution at room temperature and decays very slowly with an order of 1000 s. The extraordinary long lifetime is due to the delocalization of the spin in the pseudoaromatic metalladithiolene ring.



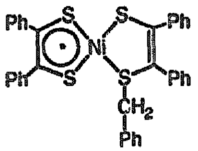
1a: M = Ni
1b: M = Pd
1c: M = Pt

(1)

The long lifetime of the metal-complex-radical enables the simultaneous measurements of ESR and UV-visible spectra. By using an ESR apparatus equipped with a rapid scan UV-visible spectrometer as shown in Fig. 1, we can follow the ESR and UV-visible spectra simultaneously.The decay of ESR (due to the nickel-complex-radical) correlates well with the formation of the free dithiolene. This shows that the dissociation proceeds stepwise. The initial photoreaction gives rise a pair, a benzyl radical and a metal-complex-radical. The metal-complex-radical decomposes thermally to a benzyl radical and the free dithiolatometal complex. The process is very slow. A kinetic analysis of the formation of the free nickelladithiolene complex using first-order kinetics gives a lifetime of about 1000 s.The existence of a back reaction of a radical pair to regenerate the *S,S'*-dibenzyl derivative (**1a**) is demonstrated from the following experimental result. The photodissociation of **1a** is promoted by TEMPO. The trapping of the benzyl radical by TEMPO inhibits the recombination of the paired benzyl and the metal-complex radical **3a**, resulting in the promotion of



(2)



(3)

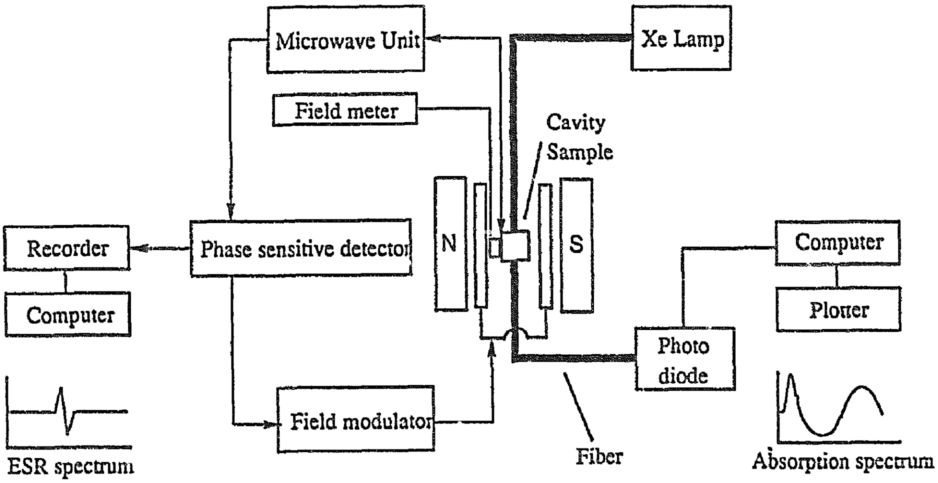


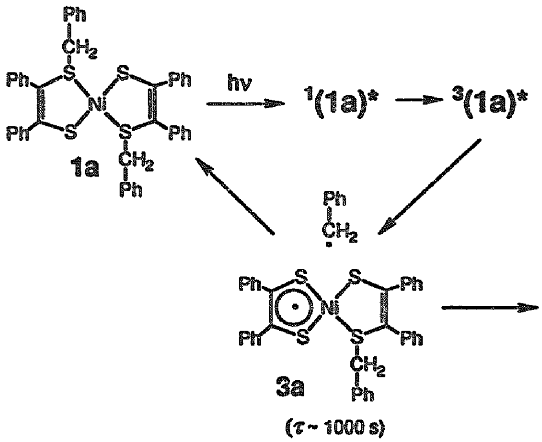
Fig. 1. Block diagram for simultaneous measurement of ESR and UV-visible spectra.

the dissociation of **3a** to **2a**. The polarization of the ESR spectrum provides information on the excited state responsible for the dissociation. The polarization of the two ESR signals are both absorptive. This shows that the excited state responsible for dissociation is a triplet state. On the basis of the above results we propose a mechanism.

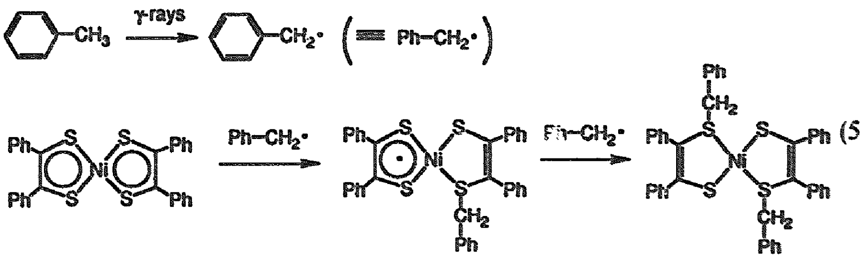
An excited triplet state of the adduct eliminates one benzyl radical and a pair, a metal-complex-radical and a benzyl radical, is formed. The metal-complex-radical decomposes thermally to the free dithiolene and a benzyl radical.

The back reaction was confirmed by the radiation-induced reaction of the free nickeladithiolene complex in toluene. In this system we have observed the formation of the dibenzyl derivative (**1a**), although the G-value (radiation chemical yield, G= number of product molecules formed/100 eV of radiation energy absorbed) is low (0.03). The radiolysis of toluene gives a benzyl radical. The benzyl radical attacks the dithiolene to give a long-lived metal-complex-radical. Its long lifetime enables the attack of the second benzyl radical, and finally the dibenzyl derivative is formed.

The photodissociation is affected by the central metal atom and the groups attached to sulfur. The palladium complex dissociates less efficiently than the nickel complex, while the platinum complex dissociates ten times more efficiently than the nickel complex. *S,S'*-Dimethyl and diethyl derivatives dissociate 10 times less efficiently than the dibenzyl derivative. *p*-Nitrobenzyl and *p*-methoxybenzyl derivatives dissociate more efficiently than the unsubstituted benzyl derivative. The reactivity is dependent on the stability of the organic radicals. The complexes which give more stable organic radicals dissociate more efficiently.



(4)



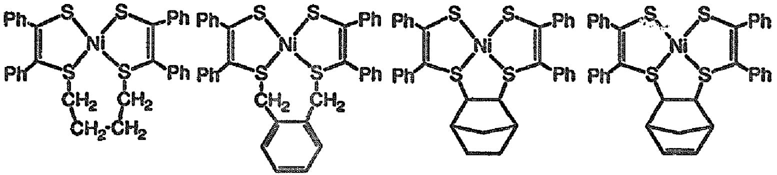
(5)

The metal-complex-radicals were detected by ESR and their fundamental properties and lifetimes were measured. The nickel-complex-radical (**3a**) has $g=2.042$ and its lifetime is 1500 s. The palladium-complex-radical (**3b**) has $g=2.014$ and $A=3.8\times10^{-4}\,\mathrm{cm}^{-1}$ and its lifetime is 5000 s. The platinum-complex-radical (**3c**) has $g=2.026$ and $A=-48\times10^{-4}\,\mathrm{cm}^{-1}$ and its lifetime is 1200 s.

3. Photodissociation of *S,S'*-alkanediyl derivatives of bis(1,2-diphenyl-1,2-ethenedithiolato)metal complexes [13]

As an extension of this study, we discuss here the photoreactions of *S,S'*-bridged adducts.

The aim of the study is to clarify how the stability of the elimination products affect the photochemical efficiencies of the dissociation and the behavior of the metal-complex-radicals. *S,S'*-Butanediyl and *o*-xylyl derivatives should give an unstable 1,4-biradical and *o*-quinonedimethane, respectively, while in the photodissociation of the norbornane-2,3-diyl derivative, we can expect the stable product, norbornene.



4a **4b** **4c** **4d** (6)

Butanediyl and *o*-xylyl derivatives dissociate 50 times less efficiently than *S,S'*-dibenzyl derivatives. In contrast, the norbornanediyl and norbornenediyl derivatives dissociate 10–100 times more efficiently than the dibenzyl derivative. With respect to the metal-complex-radicals, we also observed a remarkable effects of the bridging groups. In the photolysis of the butanediyl derivative, two kinds of metal-complex-radicals were observed: one is short-lived and the other is long-lived. In the photolysis of norbornanediyl and norbornenediyl derivatives, only very weak ESR signals were observed. Here the photoreaction of the butane-1,4-diyl derivative will be discussed in more detail. The ESR signals obtained in the photoreaction of butanediyl derivative is very similar to those observed in the case of the dibenzyl derivative. The ESR spectra taken at 77 K were analyzed as an $S=1/2$ system with $g_1=1.997$, $g_2=2.034$, and $g_3=2.088$. As in the case of dibenzyl derivatives, we could follow the reaction of the radical by simultaneous measurements of ESR and rapid scan UV-visible spectra. The most important result in the photolysis of the butanediyl derivative is the participation of two kinds of long-lived metal-complex-radicals. A logarithmic plot of the formation of the free nickeladithiolene complex after shutting off the UV-irradiation obeys double exponential kinetics (Fig. 2). This clearly indicates that the free nickeladithiolene complex **2a** is formed from two kinds of long-

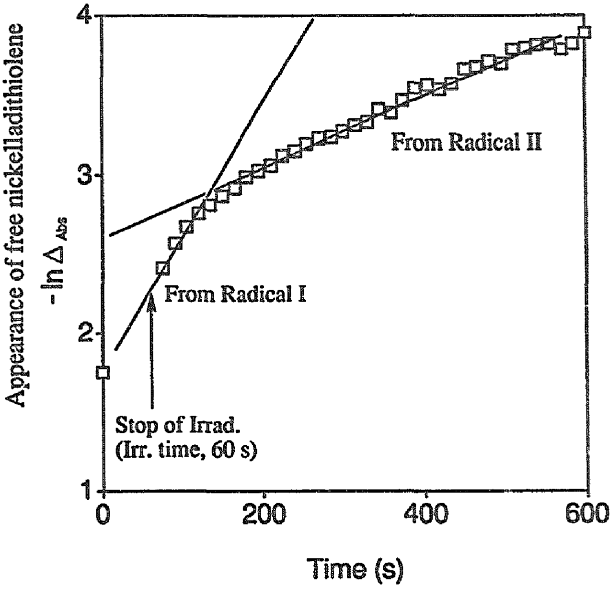
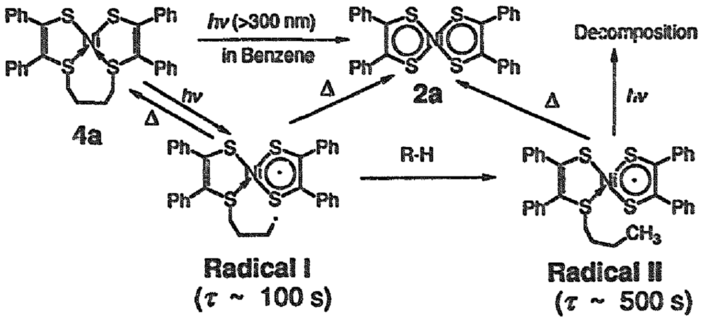


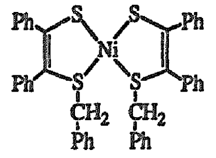
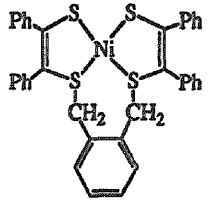
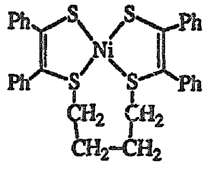
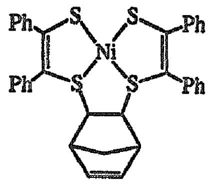
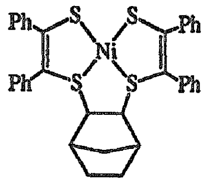
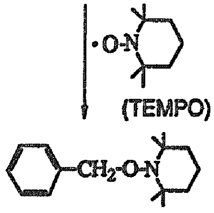
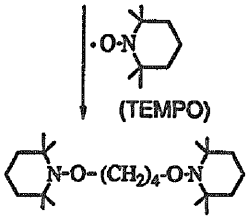
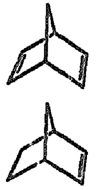
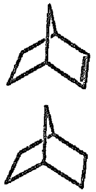
Fig. 2. Logarithmic plot of appearance of free nickeladithiolene from the intermediates in the photolysis of *S,S′*-butane-1,4-diyl derivatives of bis(1,-2-diphenyl-1,2-ethenedithiolato)nickel.

lived metal-complex-radical. The rapid process occurs on a time scale of 100 s, and the slower process occurs on a time scale of several hundred seconds. As such intermediates, we postulate a biradical for the shorter-lived intermediate, and for the longer-lived intermediate a metal-complex-radical which is formed by the hydrogen abstraction of the biradical.Thus, we propose a mechanism for the photodissociation of the bridged butanediyl derivative. UV-irradiation brings about the formation of a biradical, Radical I. Radical I undergoes three types of reactions: radical recombination to regenerate the butanediyl derivative, dissociation to give the free dithiolato complex, and transformation to another radical species, Radical II. Radical II dissociates more slowly to give the free dithiolato complex.



(7)

Table 1
Summary of photodissociation of *S,S'*-dibenzyl and *S,S'*-bridged derivatives of nickelladithiolene

				
Trap of radical 		Trap of radical 	Product (trace)	Product (trace)
Relative quantum yield 1.00 Two step reaction	Relative quantum yield ~0.02 Two step reaction?	Relative quantum yield ~0.02 Two metal-complex-radicals Short-lived radical (τ), 100 s) Dissociation and recombination	Relative quantum yield ~10 Concerted or fast two-step reaction	Relative quantum yield ~100 Concerted or fast two-step reaction
ESR signal of $\tau \sim 1500$ s	Very weak ESR signal	Longer-lived radical (τ, 500 s) Dissociation	Very weak ESR signal in a solution	Very weak ESR signal in a solution ESR signal in the solid state

The norbornanediyl and norbornenediyl adducts photodissociate much more efficiently, about 10–100 times more efficiently than the dibenzyl adduct. No ESR signals were observed for the norbornanediyl adduct during irradiation in a benzene solution. However, irradiation in the crystalline state led to signals due to a metal-complex-radical. This may suggest that the dissociation of norbornene proceeds not in the concerted process but in a fast stepwise process.

The photoreactions of the adducts and the properties of the metal-complex-radicals are summarized in Table 1.

Acknowledgements

The present study has been accomplished through collaboration between our laboratory and the ESR group of the Institute of Chemical Reaction Science of Tohoku University. I wish to thank to Dr Shin-ichi Ohkoshi, Professor Seigo Yamauchi, Professor Masamoto Iwaizumi, Dr Yasunori Ohba of Tohoku University and Mrs Miharu Ohkoshi-Ohtani, Dr Masatsugu Kajitani, Professor Takeo Akiyama of Sophia University. The study was supported by Grant-in-Aid on Priority Area-Researches on "Molecular Magnetism" No. 06218228, on "Reactive Organometallics" No. 06227260 and 07216265, and on "Photoreaction Dynamics" No. 07228259 from the Ministry of Education, Science and Culture, Japan.

References

[1] Reviews: (a) G.N. Schrauzer, Acc. Chem. Res., 2, (1969) 72; (b) J.A. McCleverty, Prog. Inorg. Chem., 10 (1969) 49; (c) R.P. Burns and C.A. McAuliffe, Adv. Inorg. Chem. Radiochem., 22 (1979) 303; (d) U.T. Mueller-Westerhoff and B. Vance, in G. Wilkinson, R. Gillard, J.A. McCleverty (eds.), Dithiolene and Related Species, in Comprehensive Coordination Chemistry, Pergamon Press, Oxford, NY, 1987, Vol. 2, p. 545; (e) A. Sugimori, Yuki Gosei Kagaku Kyokai Shi, 48 (1990) 788.

[2] (a) M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama and A. Sugimori, J. Organomet. Chem., 293 (1985) C15; (b) M. Kajitani, T. Suetsugu, T. Takagi, T. Akiyama, A. Sugimori, K. Aoki and H. Yamazaki, J. Organomet. Chem., 487 (1995) C8.

[3] M. Sakurada, M. Kajitani, K. Dohki, T. Akiyama and A. Sugimori, J. Organomet. Chem., 423 (1992) 141.

[4] M. Kajitani, H. Hatano, T. Fujita, T. Okumachi, H. Nagao, T. Akiyama and A. Sugimori, J. Organomet. Chem., 430 (1992) C64.

[5] M. Kajitani, T. Fujita, H. Hatano, T. Akiyama and A. Sugimori, Coord. Chem. Rev., 132 (1994) 175.

[6] (a) G.N. Schrauzer and V.P. Mayweg, J. Am. Chem. Soc., 87 (1965) 1483; (b) G.N. Schrauzer and H.N. Rabinowitz, J. Am. Chem. Soc., 90 (1968) 4297; (c) G.N. Schrauzer, R.K.Y. Hoo and R.P. Murillo, J. Am. Chem. Soc., 902 (1970) 3508.

[7] M. Kajitani, M. Kohara, T. Kitayama, T. Akiyama and A. Sugimori, J. Phys. Org. Chem., 2 (1989) 131.

[8] G.N. Schrauzer and H.N. Rabinowitz, J. Am. Chem. Soc., 90 (1968) 4297.

[9] C. Zhang, H.K. Reddy, E.O. Schlemper and G.N. Schrauzer, Inorg. Chem., 29 (1990) 4100.

[10] In this case, the photochemical behavior of each stereo isomer cannot be studied separately. The photoreactions discussed here are those of a mixture of the stereo isomers.

[11] M. Ohtani, S. Ohkoshi, M. Kajitani, T. Akiyama, A. Sugimori, S. Yamauchi, S. Ohba and M. Iwaizumi, Inorg. Chem., 31 (1992) 3873.

[12] S. Ohkoshi, Y. Ohba, M. Iwaizumi, S. Yamauchi, M. Ohkoshi-Ohtani, K. Tokutisa, M. Kajitani, T. Akiyama and A. Sugimori, Inorg. Chem., 35 (1996) 4569.
[13] A. Yamamoto, N. Tachiya, H. Ishikawa, T. Yamazaki, M. Ohkoshi-Ohtani, M. Kajitani, T. Akiyama and A. Sugimori, to be published.