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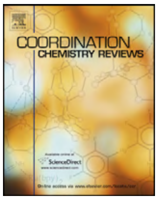

Review

Photochromism of organometallic compounds with structural rearrangement

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Contents

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ABSTRACT

This article introduces photochromic properties together with structures of organometallic compounds that undergo photo-induced structural rearrangement. The aim of this review is to survey the research on photochromism by using organometallics which possess by their own nature the properties responsible for the photochromism such as bonding and structural fluxionality, electronic state fluctuation, and photochemically active characteristic in both solution and the solid state. Therefore, the organometallics which include the well-characterized organic photochromic moieties, considered to be derivatives of such kinds of organic photochromic compounds, are excluded in this article. Mono-, di-, and poly-nuclear organometallic compounds are presented based on the reaction types such as linkage isomerization, haptotropic rearrangement, and reorganization of metal–ligand and/or metal–metal bonds. Very recently, the crystalline-state photochromism is becoming an attractive field of photochromic chemistry. As a demonstrative example, the photochromism of organometallic rhodium dinuclear complexes having a dithionite ligand (μ-O_2SSO_2), which shows 100% reversible interconversion in the crystalline-state and have been developed in the authors' laboratory, will be discussed.

1. Introduction

Photochromism is defined as "reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra" (Fig. 1) [1]. When form A is more thermodynamically stable than form B, form A is transformed by irradiation into form B. If the back reaction occurs thermally or photochemically, it is called photochromism of *type T* or *P*. *Positive* photochromism means that form A absorbs at shorter wavelengths than form B ($\lambda_{max}(A) < \lambda_{max}(B)$). When $\lambda_{max}(A) > \lambda_{max}(B)$, photochromism is called *negative* or *inverse*. Photochromism is also categorized into *unimolecular* and *bimolecular* reactions. Most of the compounds dealt with in

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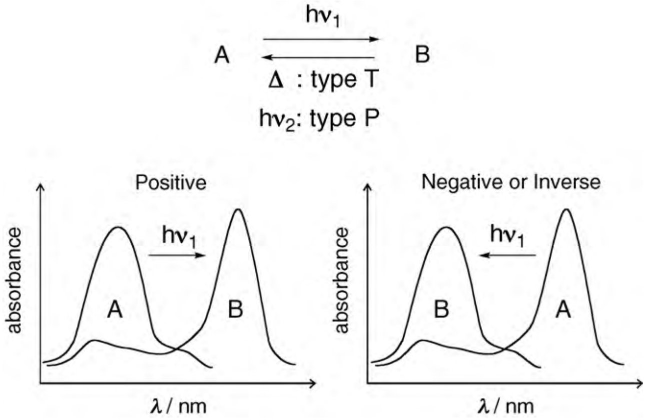


Fig. 1. Definition of photochromism between A and B.

this article belong to the *unimolecular type-T* photochromism category.

Very recently, photochromic compounds, especially organic compounds, have become appealing for their potential advantages in the construction of novel photo-switching devices and supramolecular architectures [2]. Organic compounds have dominated the development of photochromic chemistry since the discovery of tetracene in 1867 by Fritsche [3]. Various organic compounds show photochromism based on established processes such as cis/trans isomerization, pericyclic reactions, H atom transfer reactions, and dissociation processes [4]. In contrast, the photochromic chemistry of inorganic compounds including organometallic compounds is still in its infancy.

Photochromic inorganic compounds are roughly classified into two types. One type involves both inorganic units and well-characterized organic photochromic moieties such as diarylethenes, azobenzenes, and spiropyrans. These compounds are considered to be derivatives of the respective organic photochromic compounds. The second type has a photochromic property due to their intrinsic photo-induced dynamic behavior in both an electronic and structural fashion (vide infra). For the former type of inorganic compound, excellent reviews are available [5] and will not be discussed here. The latter type of inorganic compound involves photo-induced “linkage isomerization” [6], “valence tautomerization” [7], and “spin crossover phenomena” [8]. This review article only deals with “organometallic compounds” that undergo photo-induced reversible structural rearrangement, which comprise one class within the second type of photochromic inorganic compounds. In spite of the promising and useful properties for photochromism such as photochemically active character, bonding and structural fluxionality, electronic state fluctuation in both solution and the solid state, these photochromic organometallic compounds have received slight attention to date. The aim of this review is a survey of selected photochromic studies in the organometallic fields (*photochromic organometallics with structural rearrangement*) and, hopefully, this review serves as a guide for the systematic development of new photochromic research using organometallics.

This article also includes the crystalline-state photochromism that is becoming an attractive field of photochromic chemistry. The compounds that undergo photochromic reactions in the crystalline-state are limited [9]. The reason is that the crystalline-state photochromism appears only after the photochromic compounds overcome many difficult factors. For instance, keeping single-crystal integrity during the reaction and stability of the photo-generated products are very important factors. In order to find the crystalline-state photochromic compounds rationally, it is essential to understand the mechanisms of crystalline-state reversible reactions in detail. As a demonstrative example for the crystalline-state photochromism of organometallic compounds, the photochromism of rhodium dinuclear complexes having a dithionite ligand (μ-O_2SSO_2) will be discussed with a view to (i) selectivity of the reaction and (ii) crystal stabilization factors.

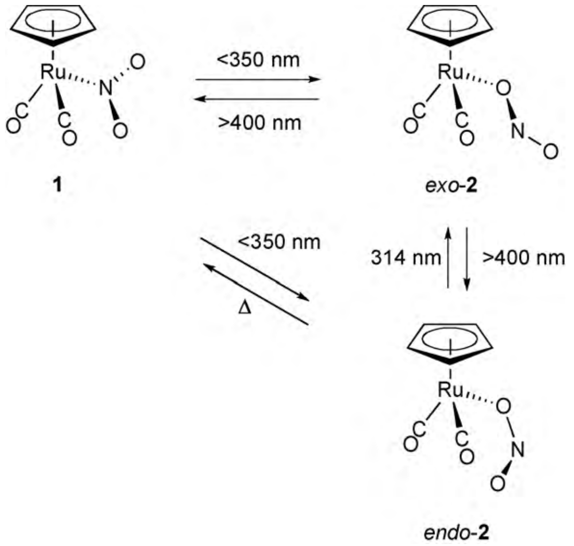


Fig. 2. Proposed matrix photochemistry of a nitro complex **1** [10].

2. Photochromism of organometallic compounds

2.1. Mononuclear system

2.1.1. Linkage isomerization

The photo-induced linkage isomerization of small ambidentate ligands, such as nitro, nitrosyl, and sulfoxide, has been used to construct photochromic metal complexes [6]. However, there are only a few examples of organometallic compounds [10–12]. In 1991, Turner et al. proposed the photochromism of an organometallic “nitro” complex $[CpRu(CO)_2NO_2]$ (**1**) [10]. Matrix isolation at 20 K combined with FT-IR spectroscopy was used to study the photochemical reaction of **1**. The proposed matrix photochemistry includes the linkage isomerization from η^1-*N*-bound nitro to η^1-O-bound *exo*- and *endo*-nitrito complexes (*exo*- and *endo*-**2**) (Fig. 2). In 1977, Crichton and Rest explored the photochemistry of an organometallic “nitrosyl” complex [CpNi(NO)] (Cp = η^5-C_5H_5) in inert matrixes (Ar, CH_4, and N_2) at 20 K [11a]. At that time, the photo-generated species was considered as an ion pair $[CpNi]^+[NO]^-$ or an intra-molecular electron transfer product. Twenty years later, by using a Cp* (η^5-C_5Me_5) ligand instead of Cp, the crystal structures of a nitrosyl complex [Cp*Ni(η^1-NO)] (**3**) and its linkage isomer [Cp*Ni(η^2-NO)] (**4**) were X-ray analyzed at 25 K by Coppens and co-workers (Fig. 3) [12]. Thus, it is proven

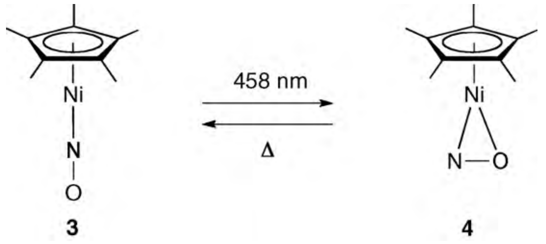


Fig. 3. Photochromism of **3** based on linkage isomerization of a nitrosyl ligand [12].

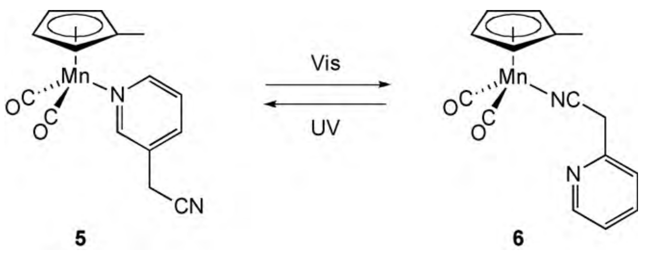


Fig. 4. *Type-P* photochromism of **5** based on linkage isomerization of a bifunctional ligand [13a].

that the nitrosyl ligand undergoes the photo-induced linkage isomerization from almost linear *N*-bound to η^2-*N*, *O*-side-bound configuration on an organometallic nickel center in the crystalline-state. As described in this paragraph, the linkage isomerization of small ambidentate ligands is a useful reaction to construct a photochromic system. However, the photo-generated isomers are usually isolated only at extremely low temperature while, at room temperature, they immediately go back to the initial complex. Therefore, an improvement of the stability of photo-generated isomers is needed.

Very recently, the linkage isomerization of bifunctional ligands having both σ-donor (pyridine) and π-accepter groups (nitrile, vinyl, or carbonyl) has been extensively investigated by Burkey and co-workers [13]. The first generation of this series of photochromic organometallics consists of several manganese complexes, [(η^5-$C_5H_4CH_3$)Mn(CO)$_2$L], where L is a bifunctional ligand (L = RC_5H_4N, R = 3-CH_2CN, 4-CN, 2-CH_2CN, 4-CHCHPh, 4-$CHCH_2$) [13a]. The photochromic reaction involves the ligand substitution of pyridine by nitrile or vinyl groups on an organometallic manganese center. For instance, visible irradiation of a red solution of a pyridine coordinated [(η^5-$C_5H_4CH_3$)Mn(CO)$_2${η^1-(3-CH_2CN)C_5H_4*N*}] (**5**) bleaches it to a yellow solution of a nitrile coordinated **6** and UV irradiation of a yellow solution changes it to red (Fig. 4). Thus, *type-P* photochromism is observed in this system. The following studies include the photochromism of cyclopentadienyl-manganese and arene–chromium complexes with tethered bifunctional ligands [13b,c] (Fig. 5). Irradiation of a pyridine-chelated manganese complex [{η^5-$C_5H_4CH_2C(O)$(2-Py-κ*N*)}Mn(CO)$_2$] (**7**, Py = pyridine) results in the linkage isomerization to a carbonyl-chelated **8**, which isomerized thermally to **7** (*type-T* photochromism). Irradiation at 335 nm of a vinyl-chelated chromium complex [{η^6-C_6H_5CH(2-Py)CH_2-η^2-$CH{=}CH_2$}Cr(CO)$_2$] (**9**) results in the isomerization to a pyridine-chelated **10** and irradiation at 532 nm isomerizes **10** to **9** (*type-P* photochromism). These complexes have been used to construct an efficient and ultrafast photochromic response. Indeed, a fast response of 50 ns has been observed in the photochromism between **9** and **10**.

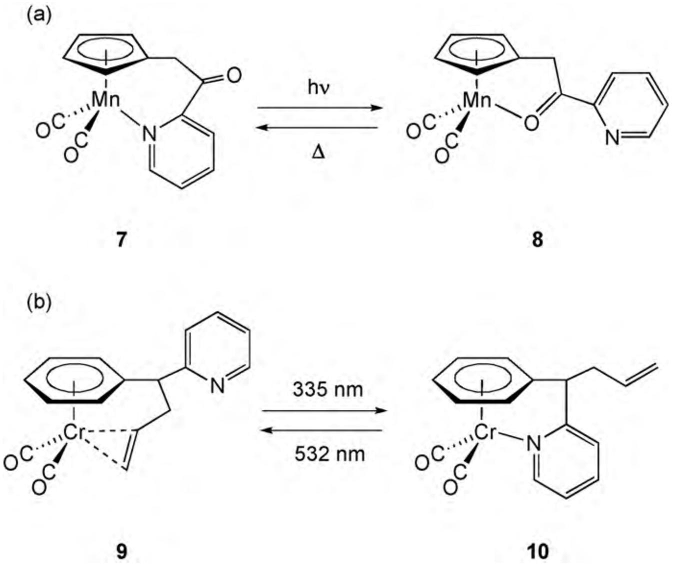


Fig. 5. Photochromism of (a) **7** and (b) **9** based on linkage isomerization of tethered bifunctional ligands [13b,c].

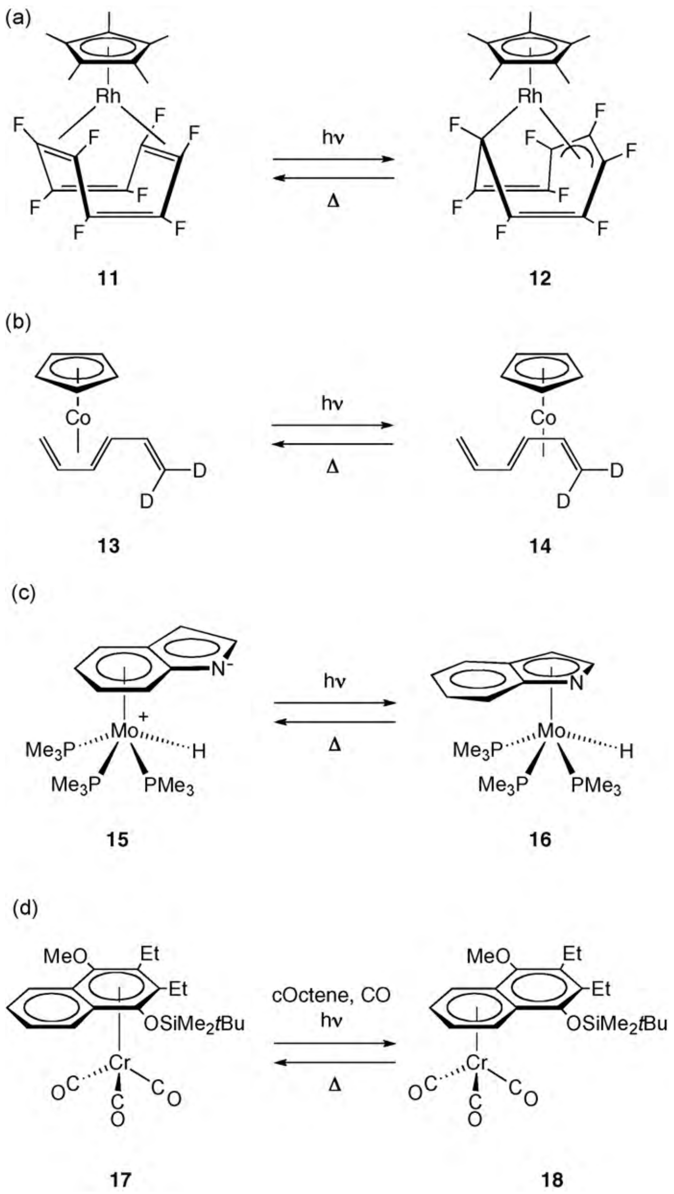


Fig. 6. *Type-T* photochromism of (a) **11**, (b) **13**, (c) **15**, and (d) **18** based on haptotropic rearrangement [15–18].

2.1.2. Haptotropic rearrangement

Haptotropic rearrangement is a migration of a transition metal fragment from one coordination site to the other on a π-conjugated polyene or polyaromatic ligand [14]. This rearrangement can be involved in a photochromic reactions. In 1986, Hughes et al. reported that the photolysis of a mononuclear [Cp*Rh(1,2,5,6-η^2:η^2-C_8F_8)] (**11**) results in isomerization to form a mixture of **11** and a formal oxidative addition product **12** in which the C_8F_8 ligand is coordinated in a 1,2,3,6-η^3:η^1-fashion: the formal oxidation states of rhodium atoms in **11** and **12** are +1 and

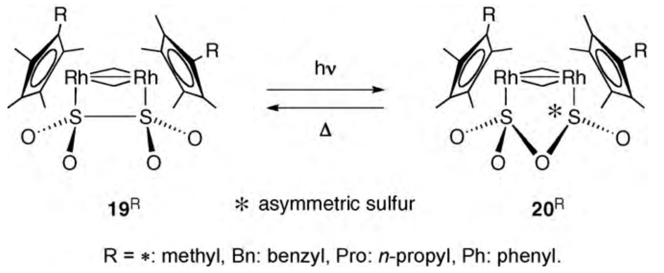


Fig. 7. Photochromism of $\mathbf{19}^{\mathrm{R}}$ based on linkage isomerization of a dithionite ligand [19].

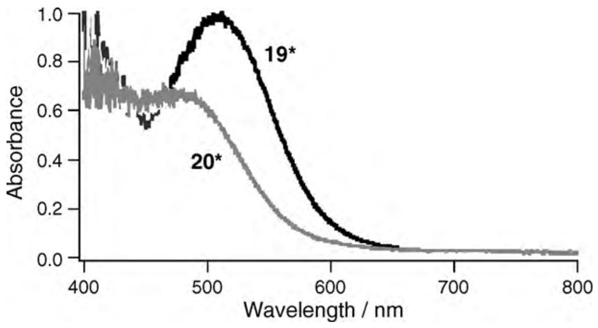


Fig. 8. UV–vis spectra of **19*** and **20*** in a microcrystalline powder film [19a].

+3, respectively (Fig. 6a) [15]. The photo-induced haptotropic "walk" of an organometallic cobalt complex [CpCo(η^4-hexatriene-d_2)] (**13**) with its regioisomer **14** was observed in 1989 by King and Vollhardt (Fig. 6b) [16]. More recently, in 2002, the photo-induced haptotropic rearrangement of a η^6-indolyl complex [(η^6-indolyl)Mo(PMe_3)$_3$H] (**15**) to a η^5-indolyl complex **16** was reported by Parkin and co-workers (Fig. 6c) [17]. It is regrettable that a detailed investigation of the above-mentioned three examples from the viewpoint of the photochromism was not done.

A unique stereospecific rearrangement based on a reversible photo- or thermo-induced haptotropic shift of a $Cr(CO)_3$ fragment along a naphthohydroquinone skeleton was reported by Dötz and co-workers (Fig. 6d) [18]. The photoreaction of an arene tricarbonyl chromium complex [1,2,3,4,5,10-η^6-{2,3-diethyl-1-metoxy-4-($OSiMe_2$*t*Bu)naphthalene}$Cr(CO)_3$] (**17**) in cyclooctene followed by CO addition gives its regioisomer **18**. In order to stabilize potential dicarbonyl intermediates and generate the tricarbonyl chromium complex **18**, both the presence of cyclooctene and the addition of CO are crucial in this photo-induced rearrangement. Warming a solution of **18** above 50 °C generates its thermodynamically more stable regioisomer **17**. Although the photochemical conversion of **17** to **18** is not quantitative (59%), the *type-T* photochromism is observed in this system. Importantly, the arene chromium complexes **17** and **18** bear a plane of chirality originating from the unsymmetric substitution of the hydroquinoid ring. The isomerization between **17** and **18** is characterized by an intermolecular shift of the $Cr(CO)_3$ moiety along the same face of the naphthalene skeleton. Through the photochromic process, the enantiopure complex (*S*)-**17** is converted to (*R*)-**18**, which is reconverted to (*S*)-**17**. Thus, the system represents a stereospecific molecular switch based on chiral arene chromium complexes.

2.2. Dinuclear system

2.2.1. Linkage isomerization

We have recently found a novel photochromic system between a rhodium dithionite complex [$(\mathrm{Cp^RRh})_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)$] ($\mathbf{19}^{\mathrm{R}}$, $\mathrm{Cp^R} = \eta^5\text{-}C_5Me_4R$, R = *: methyl, Bn: benzyl, Pro: *n*-propyl, Ph: phenyl) and its structural isomer [$(\mathrm{Cp^RRh})_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SOSO)$] ($\mathbf{20}^{\mathrm{R}}$) (Fig. 7) [19]. The *type-T* photochromic reaction involves the isomerization of the dithionite ligand ($\mu\text{-}O_2SSO_2$) in $\mathbf{19}^{\mathrm{R}}$ and forms an asymmetric sulfur atom in $\mathbf{20}^{\mathrm{R}}$. Although the linkage isomerization usually involves metal–ligand bond formation and cleavage (see: Sections 2.1.1 and 2.3.1), this isomerization proceeds *without* metal–ligand bond formation and cleavage. Thus, strictly speaking, this is a ligand isomerization not a linkage isomerization.

A notable feature of this photochromic system is that the reaction proceeds with an essentially 100% interconversion ratio in both direction in the crystalline-state. Fig. 8 shows the UV–vis absorption spectra of **19*** and **20*** in a microcrystalline powder film. A hypsochromic (blue) shift of $\lambda_{\max}$ from 510 to 475 nm is observed as a characteristic of *inverse* photochromism. In addition, the absorption coefficient of $\lambda_{\max}$ for **20*** is smaller than that for **19*** by about one-third. These are the typical UV–vis spectral features in the rhodium dithionite photochromism of $\mathbf{19}^{\mathrm{R}}$. Thus, in the photoreaction of $\mathbf{19}^{\mathrm{R}}$, the light is able to pass more easily through the crystal as the photoreaction further progresses. These photochemical properties of **19*** and **20*** contribute to the crystalline-state photoreaction showing an essentially 100% interconversion ratio (vide infra). This means that the reaction process in crystalline-state can be observed by using solid-state analytical methods such as X-ray diffraction and solid-state NMR analyses. The crystalline-state photochromism of $\mathbf{19}^{\mathrm{R}}$ will be discussed in depth in Section 3.

2.2.2. Haptotropic rearrangement

In contrast to the sparse investigation of the mononuclear system, the photochromism of dinuclear complexes based on the photo-induced haptotropic rearrangement has been systematically investigated [20]. Nagashima et al. observed the photo-induced reversible haptotropic rearrangement between two isomers of a dinuclear iron complex [(μ^2, η^3:η^5-acenaphthylene)$Fe_2(CO)_5$] (**21**) (Fig. 9) [20a]. The photoisomerization of a symmetrical isomer of **21** produces an unsymmetrical haptotropic isomer **22**, which undergoes thermal reverse isomerization in the dark to generate **21** (*type-T* photochromism). Extensive studies of the systems analogous to **21** include the substitutions of metal atoms (Ru instead of Fe), bridging ligands (guaiazulene, aceanthrylene, trimethylazulene instead of acenaphthylene), and terminal ligands (phosphorus, isocyanides instead of carbonyl) [20b–f]. Intriguingly, the detailed studies showed that the photochemical haptotropic rearrangement between **21** and **22** occurs in both solution and the solid state [20e]. Although the photochemical rearrangement from **21** to **22** does not proceed in "a single-crystal", the reversible photochromic reaction between **21** and **22** is accomplished in a solid sample dispersed in a KBr pellet.

2.2.3. Reorganization of metal–ligand and/or metal–metal bonds

The reorganization of metal–ligand and/or metal–metal bonds can be involved in the photochromic reactions. Tyler and Bruce reported in 1984 the photochemical isomerization of [Cp*Mo(μ-S)]$_2$ (**23**) to [$\mathrm{Cp^*}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$] (**24**) and [$(\mathrm{Cp^*MoS})_2(\mu\text{-}S_2)$]

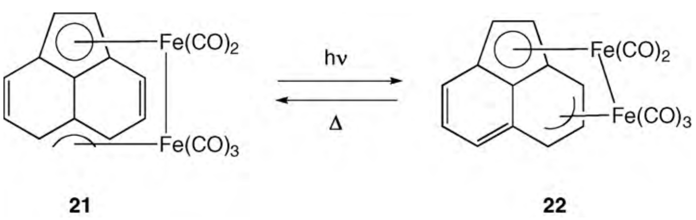


Fig. 9. Photochromism of **21** based on haptotropic rearrangement [20a].

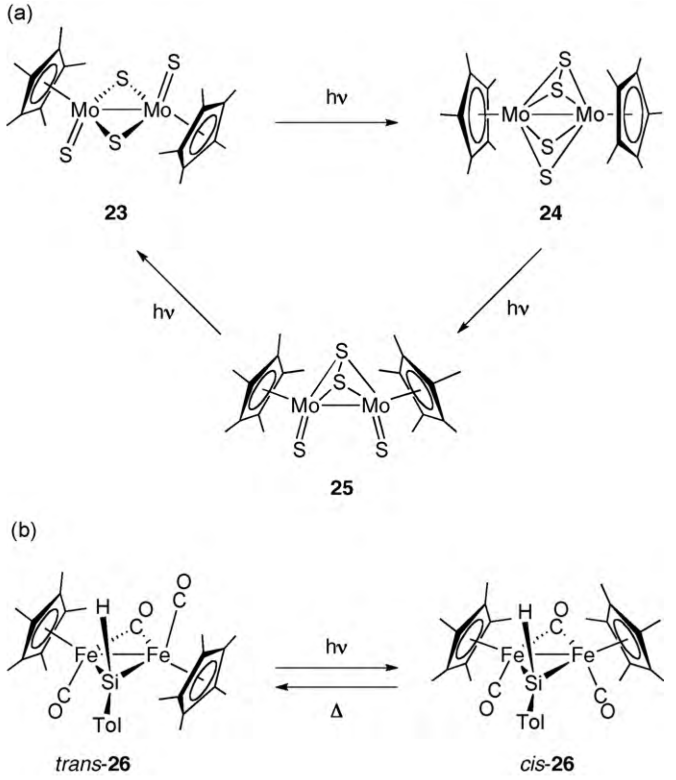


Fig. 10. Photochromism of (a) **23** and (b) **26** based on reorganization of metal–ligand bonds [21,22].

(**25**) (Fig. 10a) [21]. In order to clarify the photoreaction processes, the photoreactions of **24** and **25** has been studied independently. When **24** is irradiated (λ > 450 nm) in chloroform, the photoreaction initially forms **25** and eventually yields small amounts of **23**. Isomer **25** initially yields **23** on irradiation (λ > 450 nm). Prolonged irradiation of the reaction solution eventually yields some of isomer **24**. Thus, the irradiation of any isomer eventually yields the other two isomers. Although it is difficult to control the reactions efficiently, the reactions include the unique *type-P* photochromic process.

In 1992, Ogino et al. observed the photochemical and thermal isomerization between a silylene-bridged diiron complex *cis*-[$Cp^*_2Fe_2(CO)_3(\mu$-SiHTol)] (*cis*-**26**, Tol = *p*-$CH_3C_6H_4$) and its trans isomer (*trans*-**26**) (Fig. 10b) [22]. In this system, remarkably different cis–trans ratios have been observed between the thermal equilibrium (*cis*-**26**:*trans*-**26** = 2:98 in cyclohexane-d_{12} at 40 °C) and the photostationary state (*cis*-**26**:*trans*-**26** = 70:30). Thus, the *trans* isomer is thermodynamically more stable than the *cis* isomer due to the large steric repulsion between the two Cp* rings in the latter. The introduction of the bridging silylene and the Cp* ligands is responsible for the unique *type-T* photochromic behavior.

The photo-induced reversible metal–metal bond formation and cleavage has been found in bridged cyclopentadienyl dinuclear complexes of molybdenum, ruthenium, or tungsten. In the early 1980's, Green et al. separately found the photoreaction of [Fv(CpMoH)$_2$] (**27**, Fv = μ_2-η^5:η^5-bicyclopentadienyl) to *cis*- and *trans*-[(μ_2-η^1:η^5-cyclopentadienyl)$_2$Cp$_2$Mo$_2$H$_2$] (*cis*- and *trans*-**28**) [23a] and thermal reverse reaction of *cis*- and *trans*-**28** to **27** [23b]. Thus, the hydridomolybdenocene dimer **27** shows *type-T* photochromism based on the reversible C–C, Mo–Mo, and Mo–C bonds formation and cleavage (Fig. 11a), though the reversible conversion between **27** and **28** did not attract attention as a photochromic reaction at that time.

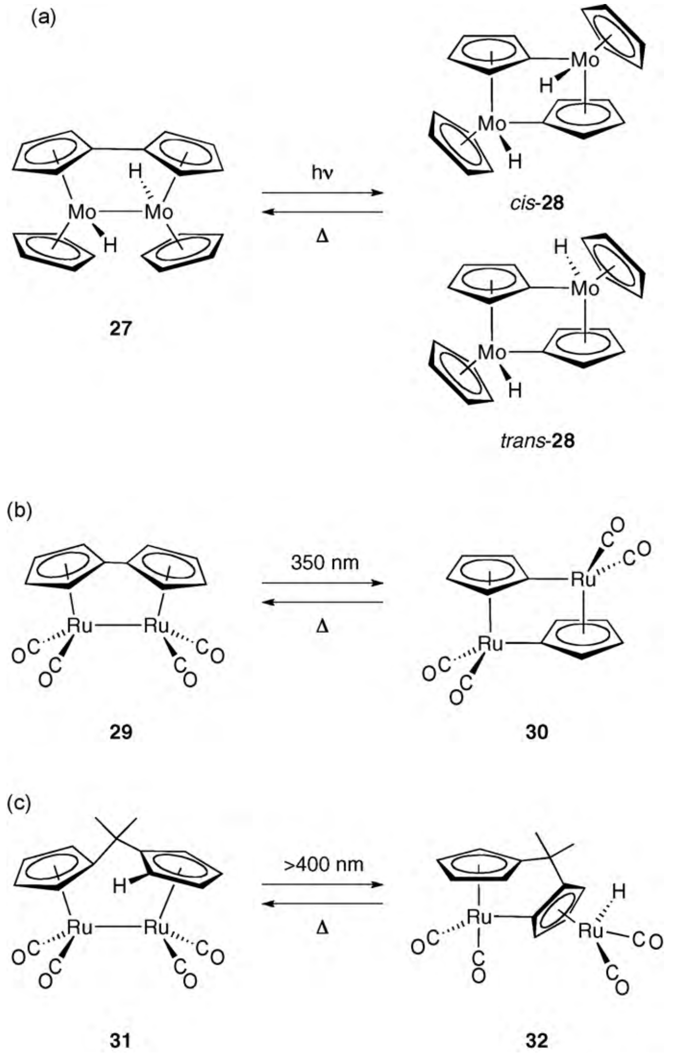
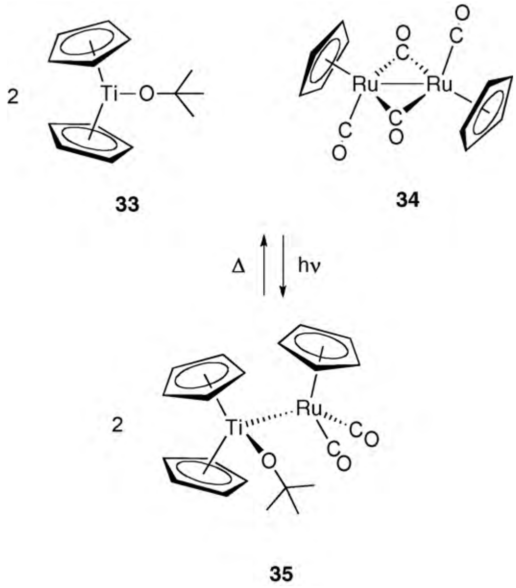


Fig. 11. Photochromism of (a) **27**, (b) **29**, and (b) **31** based on reorganization of metal–ligand and metal–metal bonds [23,24,26].

Fifteen years later, Vollhardt et al. extensively investigated the *type-T* photochromic behavior of a similar system from the viewpoint of efficient light energy storage devices (Fig. 11b) [24]. The system includes reversible formation of C–C, Ru–Ru, and Ru–C bonds and cleavage of ruthenium dinuclear compounds. Irradiation of a bright yellow solution of [FvRu$_2$(CO)$_4$] (**29**) with 350 nm light results in the formation of a colorless photoproduct [(μ_2-η^1:η^5-cyclopentadienyl)$_2$Ru$_2$(CO)$_4$] (**30**). This process contains a novel oxidative addition of the bridging C–C bond: the formal oxidation states of ruthenium atoms in **29** and **30** are +1 and +2, respectively. The thermal back reaction from **30** to **29** occurs in both solution (>65 °C) and the crystalline-state (at 208 °C). The crystals of **30** jump several centimeters high when the crystals are heated on a hot plate at 208 °C. The apparent topological changes of **30** in the crystalline-state are associated with this intriguing phenomenon. Thus, the phenomenon known as "jumping crystal" or "thermosalient" is observed in this system [25].

In 2001, Burger reported a CMe$_2$ bridged dicyclopentadienyl diruthenium complex [Me$_2$C(η^5-C$_5$H$_4$)$_2$Ru$_2$(CO)$_4$] (**31**) that shows *type-T* photochromism based on reversible Ru–Ru bond formation and cleavage (Fig. 11c) [26]. The photochromic reaction also contains the reversible C–H bond formation and cleavage of the cyclopentadienyl C–H group *ortho* to the bridgehead carbon atom. When a yellow-orange solution of **31** is irradiated with a Hg



33 **34** **35**

Fig. 12. *Bimolecular* photochromism between **33**, **34**, and **35** based on reorganization of metal–ligand and metal–metal bonds [27].

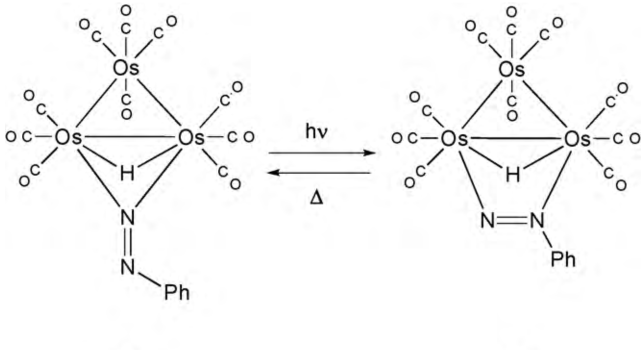
medium-pressure lamp using a UV cutoff filter with λ > 400 nm, a dramatic rearrangement to colorless complex [{μ-η^5,η^5:η^1-C_5H_4–$C(CH_3)_2$–C_5H_3}{$Ru(CO)_2$}{$Ru(CO)_2H$}] (**32**) is observed. The use of the UV cutoff filter in this photoreaction is crucial for a complete and quantitative photochemical conversion from **31** to **32**. If the photoreaction of **31** proceeds without the UV cutoff filter, the reaction is not clean and secondary photochemical processes are observed. The thermal back reaction from **32** to **31** occurs within one day when complex **32** is heated to 140 °C in a toluene solution. Analogous rearrangement processes for the tricarbonyl molybdenum and tungsten systems, [$Me_2C(\eta^5$-$C_5H_4)_2M_2(CO)_6$] (M = Mo, W), are also observed [26]. The reversed thermal reactions of the molybdenum and tungsten complexes are faster than that of the ruthenium complex **32**.

The *bimolecular T-type* photochromic reaction based on the reversible Ti–Ru bond formation and cleavage was developed in 2003 by Nagashima and co-workers (Fig. 12) [27]. The photochemical reaction (irradiation wavelength: λ > 500 nm) of [$Cp_2Ti(O^tBu)$] (**33**) and [$CpRu(CO)_2]_2$ (**34**) gives a Ti–Ru compound [$Cp_2(O^tBu)Ti$–$Ru(CO)_2Cp$] (**35**), in which the titanium and ruthenium moieties are linked by a direct Ti–Ru bond. The formation of **35** is based on the metal–metal bond cleavage of metal carbonyl dimers by the Ti(III) reducing reagent **33**. The photochemically generated **35** undergoes fragmentation to regenerate **33** and **34** when the solution stands in the dark for a while. Photochemical conversion from **33** and **34** to **35** and its thermal reaction result in a change of color of the solution (**33** + **34**: orange, **35**: dark red). To our knowledge, this is the only example of *bimolecular* photochromism of an organometallic compound.

2.3. Poly-nuclear system

2.3.1. Linkage isomerization

The linkage isomerization of aryldiazo ligands (N = NAr, Ar = Ph, p-C_6H_4F, p-$C_6H_4CH_3$) on an organometallic triosmium cluster was observed in 1984 by Churchill and co-workers (Fig. 13) [28]. Irradiation of a yellow n-heptane solution of a triosmium cluster [$Os_3(\mu$-H)$(CO)_{10}(\mu$-η^1-N=NPh)] (**36**) causes the formation of an orange solution of a cluster [$Os_3(\mu$-H)$(CO)_{10}(\mu$-η^2-N=NPh)] (**37**). The reverse isomerization takes place thermally: an n-heptane solution of **37** changes its color from orange to yellow under solvent reflux. Thus, the *type-T* photochromism is constructed on the linkage isomerization between η^1- and η^2-bridging modes of aryldiazo ligands on the trinuclear osmium cluster.

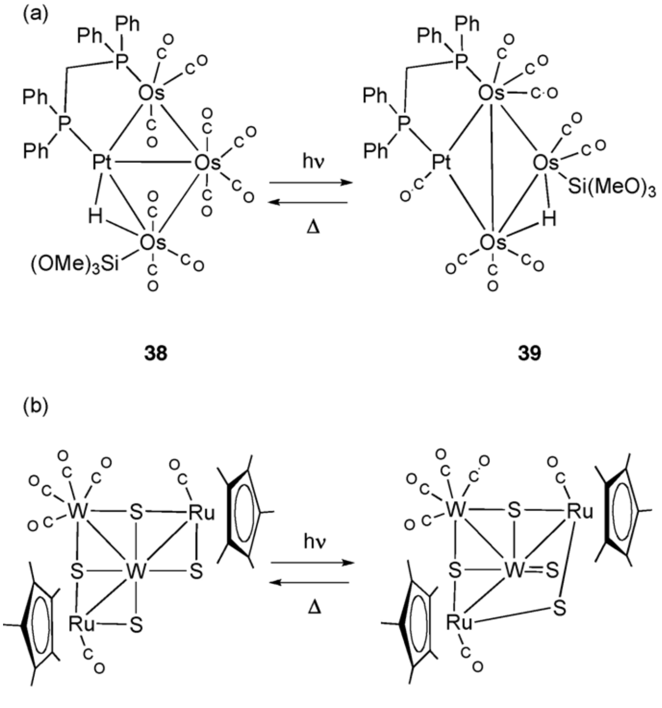


36 **37**

Fig. 13. Photochromism of **36** based on linkage isomerization of a phenyldiazo ligand [28].

2.3.2. Reorganization of metal–ligand and/or metal–metal bonds

The *type-T* photochromism based on the reorganization of Pt–Os and Os–Os bonds in a tetranuclear metal cluster complex was observed in 1993 by Adams et al. (Fig. 14a) [29]. The complex [$PtOs_3(CO)_{10}(\mu$-η^2-dppm){$Si(OMe)_3$}(μ-H)] (**38**, dppm = bis(diphenylphosphino)methane) consists of a planar butterfly cluster of one platinum and three osmium metal atoms, in which the platinum atom is located in one of the “hinge” sites and is bonded to the osmium atom containing the $Si(OMe)_3$ ligand. When compound **38** was irradiated with UV light for 6 h, it is converted to an isomer **39**, in which the platinum atom lies on the “wingtip” site and is not bonded to the osmium atom containing the $Si(OMe)_3$



38 **39**

40 **41**

Fig. 14. Photochromism of (a) **38** and (b) **40** based on reorganization of metal–ligand and/or metal–metal bonds [29,30].

ligand. Compound **39** slowly converts back to **38** under thermal conditions: its half-life is 4.6 h at 47 °C.

In 1998, Ogino et al. found the photo-induced isomerization based on the reorganization of W–S and Ru–S bonds in a tetranuclear metal cluster complex (Fig. 14b) [30]. Cluster $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2\}W(CO)_4]$ (**40**) has a WS_4 fragment as a building block. The WS_4 fragment is bound to one W atom by two S atoms and to two Ru atoms by "four" S atoms. Unlike **40**, cluster $[\{Cp^*Ru(CO)\}_2\{W(\mu_3\text{-}S)_3(=S)_2\}W(CO)_4]$ (**41**) has a terminal S ligand. The WS_4 fragment is bound to one W atom by two S atoms and to two Ru atoms by "three" S atoms. When a solution of **40** in benzene is irradiated, cluster **41** is formed in approximately 50% yield with the decomposition of an unidentified brown precipitate. The thermal back reaction from **41** to **40** occurs in approximately 90% yield when a toluene solution of complex **41** is heated for 2 h at 80 °C. Although it is necessary to improve the efficiency of the photoreaction from **40** to **41**, *type-T* photochromism between the organometallic clusters **40** and **41** is observed.

3. Crystalline-state photochromism of rhodium dithionite complexes

In the crystalline-state, the change of the molecular configuration is significantly affected by the crystal lattice (vice versa). Thus, it is expected that the crystalline-state photochromic compounds offer new insight into the application of photochromic materials [2a,c,d,g,9a].

Thanks to the full reversibility of the photochromic rhodium dithionite complexes $\mathbf{19}^{R}$ in the crystalline-state (see: Section 2.2.1), we have found that complexes $\mathbf{19}^{R}$ show the following intriguing phenomena: (i) stereoselective oxygen-atom rearrangements including an absolute asymmetric photoisomerization and (ii) release of local stress in the crystal lattice by Cp^R ligands [19]. These results provide us with an opportunity to discuss the selectivity of the reaction and crystal stabilization factors of the crystalline-state photochromism. In this section, we introduce the crystalline-state photochromism of the rhodium dithionite complexes $\mathbf{19}^{R}$, together with important work related to the selectivity of the reaction and crystal stabilization factors in the crystalline-state.

3.1. Selectivity of the reaction

One of the unique applications of crystalline-state photochromism is the construction of photo-switchable non-linear optical devices based on the topochemically regulated regio-, stereo-, and enantio-specific reactions in the crystal lattice [31]. The crystalline-state photochromism of $\mathbf{19}^*$, $\mathbf{19}^{Bn}$, and $\mathbf{19}^{Pro}$ show (i) "stereospecific" oxygen-atom rearrangement including kinetically and thermodynamically controlled processes, (ii) stereoselective photoisomerization with a certain ratio of isomers, and (iii) absolute asymmetric photoisomerization, respectively [19].

In the crystalline-state, the four oxygen atoms of the dithionite ligand ($\mu\text{-}O_2SSO_2$) are stereochemically non-equivalent: this is the origin of the stereoselective reactions seen in the crystal of $\mathbf{19}^{R}$ (Fig. 15a). The photochemical linkage isomerization of $\mathbf{19}^{R}$ in the crystalline-state produces isomers $\mathbf{20a}^{R}$–$\mathbf{20d}^{R}$. As shown in Fig. 15b, with regard to the dithionite ligand, isomers $\mathbf{20a}^{R}$ (*R*-form) and $\mathbf{20c}^{R}$ (*S*-form) are a pair of enantiomers, $\mathbf{20a}^{R}$ (*R*) and $\mathbf{20b}^{R}$ (*R*) are identical species but differ orientationally in the cavity, and $\mathbf{20c}^{R}$ (*S*) and $\mathbf{20d}^{R}$ (*S*) are also identical but differ in orientation, the absolute configurations of the sulfur atom of each being shown in parentheses. The stereoselective photoreactions of $\mathbf{19}^{R}$ have been observed in each system as described in the following paragraphs.

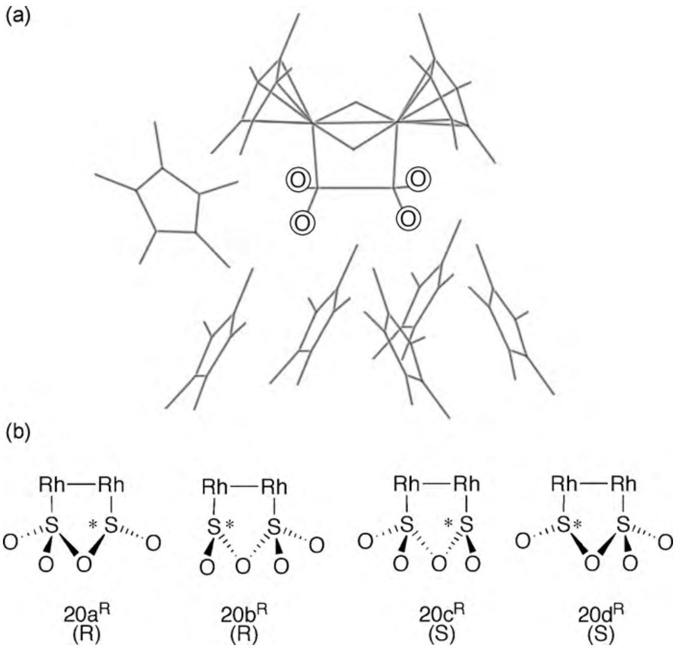


Fig. 15. (a) Reaction cavity around the $\mu\text{-}O_2SSO_2$ unit in the crystal of 19*. (b) Isomers, $\mathbf{20a}^{R}$–$\mathbf{20d}^{R}$, concerned with the dithionite ligand ($\mu\text{-}O_2SSO_2$). The Cp^R and $\mu\text{-}CH_2$ ligands are omitted for clarity.

Dynamics of the "stereospecific" oxygen-atom rearrangement, including kinetically and thermodynamically controlled processes, have been observed in the crystalline-state photoreaction of $\mathbf{19}^*$ (Fig. 16) [19a,d]. We have unequivocally followed the photoreaction of $\mathbf{19}^*$ by using conventional single-crystal X-ray diffraction. The crystalline-state photoreaction of $\mathbf{19}^*$ includes two important processes: kinetically controlled oxygen-atom transfer to produce isomers $\mathbf{20a}^*$–$\mathbf{20d}^*$ and thermodynamically controlled isomerization between the isomers $\mathbf{20a}^*$–$\mathbf{20d}^*$ to afford the most stable isomer $\mathbf{20a}^*$. Although the formation rate of $\mathbf{20a}^*$–$\mathbf{20d}^*$ is controlled kinetically and the population of $\mathbf{20a}^*$–$\mathbf{20d}^*$ in the crystal is controlled thermodynamically, both processes are regulated by the steric hindrance between $\mu\text{-}O_2SSO_2$ or $\mu\text{-}O_2SOSO$ ligand and the reaction cavity formed by the Cp* ligands. The cooperation of both processes achieves an intriguing "stereospecific" oxygen-atom rearrangement to produce only one stereoisomer of $\mathbf{20a}^*$ at the final stage of the photoreaction at room temperature (Fig. 16b). Since the photoisomerization of $\mathbf{19}^*$ in an achiral crystal affords both enantiomers of $\mathbf{20a}^*$–$\mathbf{20d}^*$ in equal amounts within a single-crystal because of its centrosymmetric space group ($P2_1/n$), this is not asymmetric photoisomerization but "stereospecific" photoisomerization.

In contrast to the "stereospecific" reaction of $\mathbf{19}^*$, which affords only one stereoisomer, stereoselective photoisomerization is observed in the photoreaction of $\mathbf{19}^{Bn}$ with a certain ratio of isomers (Fig. 17) [19c]. The crystalline-state photochromism of $\mathbf{19}^{Bn}$, in which the Cp* rings have a bulky phenyl substituent, is observed with essentially 100% interconversion ratio. When several photoreactions for separate crystals are performed under similar reaction conditions with respect to temperature, size and shape of the crystals, and the intensity of irradiation light, the resulting crystals of $\mathbf{20}^{Bn}$ in each photoreaction always contains four isomers in a ratio of nearly 3:24:60:13 for $\mathbf{20a}^{Bn}$:$\mathbf{20b}^{Bn}$:$\mathbf{20c}^{Bn}$:$\mathbf{20d}^{Bn}$. This isomer ratio does not change even if the irradiation time is prolonged. Thus, the crystal packing with this isomer ratio is the most stable packing of the photo-irradiated crystals. Similar to the photoreaction of $\mathbf{19}^*$, the photoreaction of $\mathbf{19}^{Bn}$ in an achiral crystal ($P2_1/c$) is

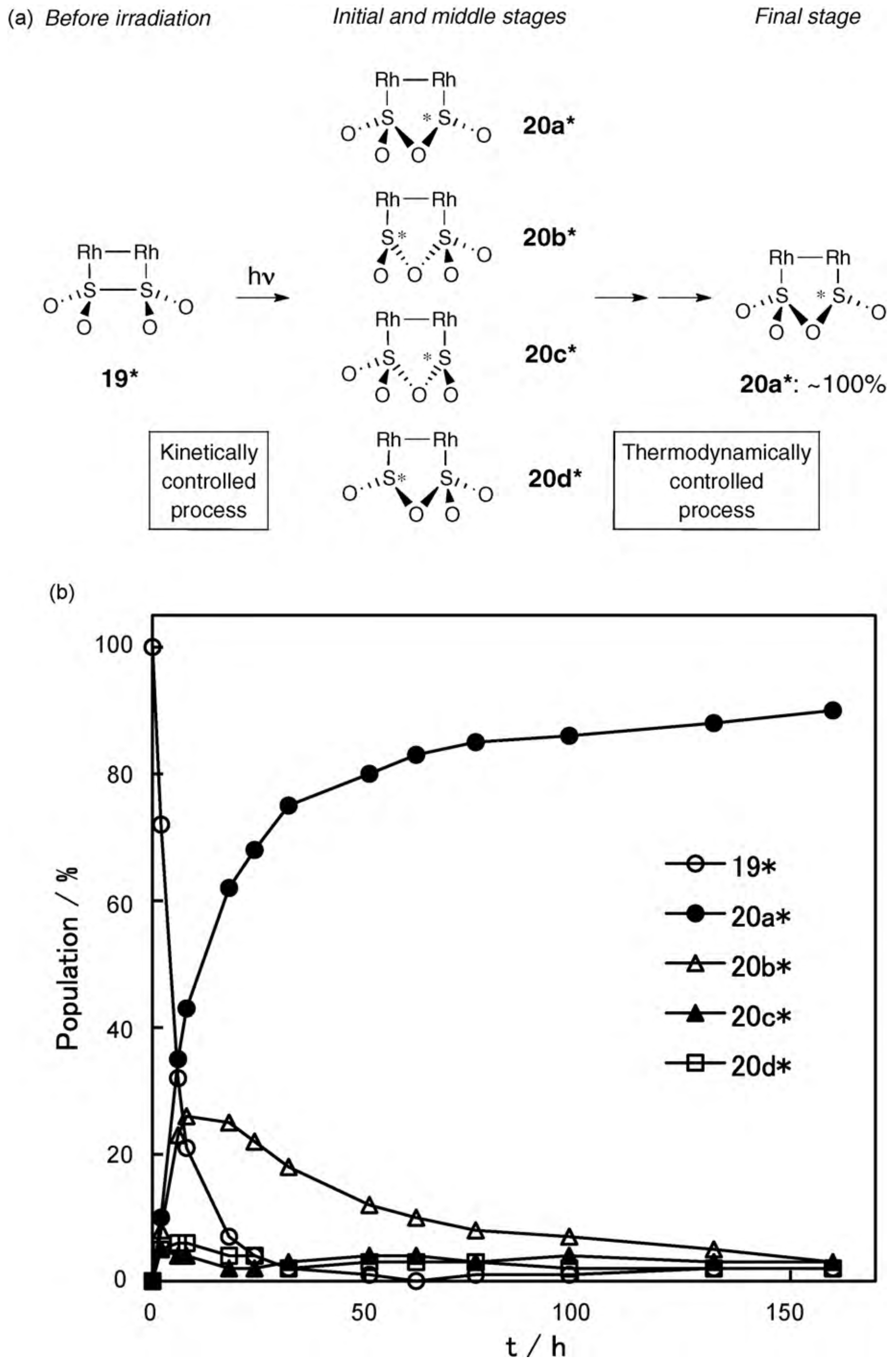


Fig. 16. (a) Stereospecific oxygen-atom rearrangement of **19***, including kinetically and thermodynamically controlled processes. (b) Change in the population of the photochemically generated isomers with irradiation time at 20 °C [19d].

not asymmetric photoisomerization but stereoselective photoisomerization.

Absolute asymmetric photoisomerization with essentially 100% interconversion ratio and ee >90% was achieved by using chiral crystals formed from achiral dithionite complex $\mathbf{19}^{\mathrm{Pro}}$ with *n*-propyl moieties (Fig. 18) [19e]. Two different kinds of crystals, consisting of (P)-$\mathbf{19}^{\mathrm{Pro}}$ and (M)-$\mathbf{19}^{\mathrm{Pro}}$, grow in the same sample tube. Arbitrary labels, P and M, indicated the chirality of the crystals as follows. These crystals belong to an orthorhombic crystal system with the non-centrosymmetric space group $P2_12_12_1$. In the crystal of (P)-$\mathbf{19}^{\mathrm{Pro}}$, two-fold helical arrangements are formed in a clockwise direction between the molecules along the *b*-axis (Fig. 19). One of the requirements for the generation of chirality from achiral molecules is the fixing of the conformation of the molecules in the crystal lattice [32]: in the case of $\mathbf{19}^{\mathrm{Pro}}$, the fixing of the conformation of two $\mathrm{Cp}^{\mathrm{Pro}}$ ligands appears in the crystals of $\mathbf{19}^{\mathrm{Pro}}$. The topochemically controlled diastereoisomeric photoreaction of $\mathbf{19}^{\mathrm{Pro}}$ in chiral crystals affords a certain enantiomer with ee >90%. For instance, the photoreaction of (P)-$\mathbf{19}^{\mathrm{Pro}}$ produces $\mathbf{20a}^{\mathrm{Pro}}$–$\mathbf{20d}^{\mathrm{Pro}}$ in 23, 71, 1 and 2% yields, respectively. Thus, in the case of (P)-$\mathbf{19}^{\mathrm{Pro}}$, the ee for the *R*-configuration of the sulfur atom is 94% and the interconversion ratio is 97%. Although a considerable number of absolute asymmetric reactions in the chiral crystalline-state have been reported in the field of organic solid-state chemistry [33], the absolute asymmetric reaction of the photochromic compounds that have reversible switching functions in the crystalline-state are scarcely known [19e,31b,c].

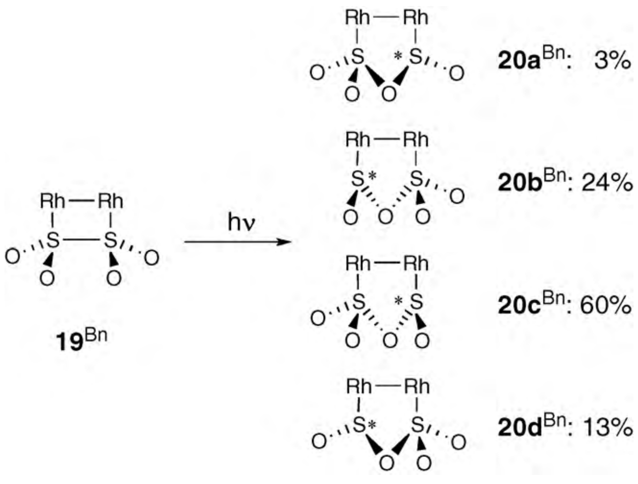


Fig. 17. Stereoselective photoisomerization of **19**^{Bn}, with a certain ratio of isomers.

3.2. Crystal stabilization factors

To date, chemists have shown that most photoreactive crystals tend to collapse and degrade as the reaction proceeds. Although the crystal packing is an important factor to stabilize the whole crystal, we have found that, during the photochromic reactions of **19***, **19**^{Bn}, and **19**^{Pro}, the crystals are also stabilized by (i) rotational motions of Cp* ligand, (ii) static disorder of the Cp^{Bn} ligand, and (iii) flipping motion of the Cp^{Pro} ligand, respectively (Fig. 20).

It is well known that flat disklike ligands, such as Cp and Cp*, can undergo $2\pi/5$ jumping motions, i.e., 'rotational motion', around the ligand-metal coordination C_5 axis in the crystal [34]. We have found that the rotational motion of the Cp* ligands in the crystal is coupled with the photochromism (Fig. 20a) [19d]. In the crystals of **19***, the stereospecific oxygen-atom rearrangement proceeds in the reaction cavities formed by the six Cp* ligands of the neighboring molecules. We have determined the effect of the oxygen-atom rearrangement on the rotational motion of the two crystallographically independent Cp* ligands (parallel and perpendicular arrangement). Using variable-temperature ^{13}C CP/MAS NMR and quadrupolar echo solid-state ^{2}H NMR spectroscopies, before photoirradiation, the activation energies for the rotation of the parallel and perpen-

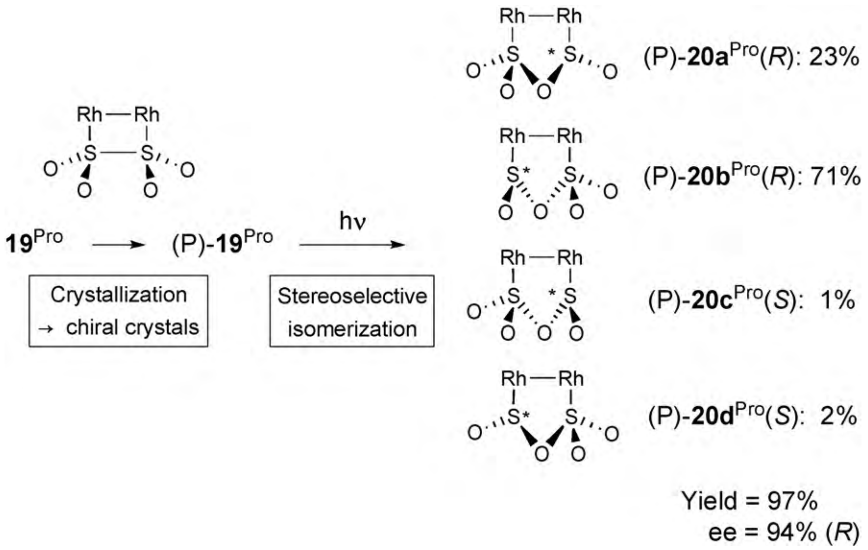


Fig. 18. Absolute asymmetric photoisomerization of **19**^{Pro}.

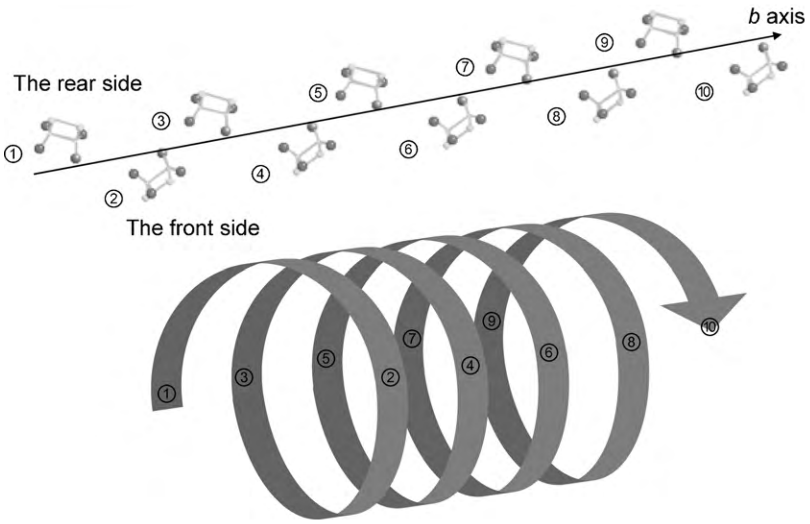


Fig. 19. Two-fold helical arrangements formed in a clockwise direction between the molecules along the *b*-axis in the crystal of (P)-**19**^{Pro}.

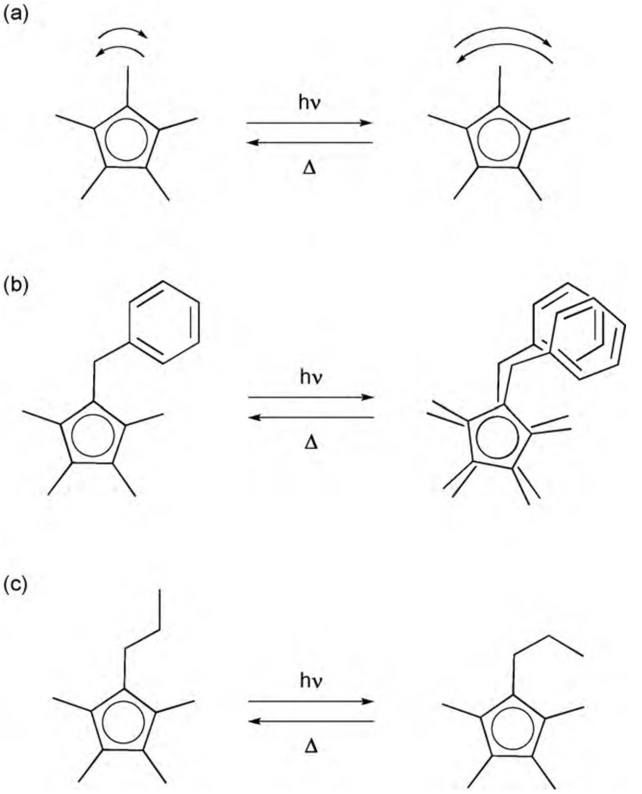


Fig. 20. (a) Rotational motions of Cp* ligand, (b) static disorder of the $\mathrm{Cp^{Bn}}$ ligand, and (c) flipping motion of the $\mathrm{Cp^{Pro}}$ ligand [19c–e].

dicular Cp* ligands in **19*** are 30 ± 3 and 10 ± 1 kJ/mol, respectively, and after photoirradiation, in **20***, they are much lower than those in **19*** (20 ± 2 and 8 ± 1 kJ/mol, respectively). Thus, the large decrease in the activation energy for the parallel Cp* in **20*** is attributed to the relaxation of molecular stress in the crystalline-state.

The static disorder of $\mathrm{Cp^{Bn}}$ ligands coupled with the photochromism of $\mathbf{19^{Bn}}$ can contribute to the crystal stabilization (Fig. 20b) [19c]. The photoisomerization of $\mathbf{19^{Bn}}$ to $\mathbf{20^{Bn}}$ proceeds without degradation of the single-crystal form, though complex $\mathbf{19^{Bn}}$ has a considerable bulky ligand of $\mathrm{Cp^{Bn}}$ ring. Unlike **19***, the $\mathrm{Cp^{Bn}}$ ligands cannot rotate in the crystal, as indicated from the crystal packing and the variable-temperature solid-state ^{13}C CP/MAS NMR spectra. In order to find the crystal stabilization factors in this system, we have carefully inspected the thermal parameter change of the carbon atoms in the $\mathrm{Cp^{Bn}}$ rings with temperature, before and after irradiation in the X-ray analysis. Static disorder of the $\mathrm{Cp^{Bn}}$ ligand that is closely located on the dithionite ligand is observed after irradiation. Thus, the generated stress is compensated by the disordering of the $\mathrm{Cp^{Bn}}$ ring to stabilize the whole crystal.

We have found the flipping motion of an ethyl moiety of the *n*-propyl group in the crystalline-state photoisomerization of $\mathbf{19^{Pro}}$ to $\mathbf{20^{Pro}}$ (Fig. 20c) [19e]. The back reaction of $\mathbf{20^{Pro}}$ to $\mathbf{19^{Pro}}$ takes place, leading to the complete regeneration of $\mathbf{19^{Pro}}$. Thus, the flipping motion, as well as the photochromic reaction, is reversibly observed in the crystals. A comparison of the crystal structure of $\mathbf{19^{Pro}}$ with $\mathbf{20^{Pro}}$ tells us that this flipping motion occurs to fill the space generated by oxygen-atom transfer. This indicates that the flipping motion considerably assists the crystalline-state reaction to maintain single-crystal integrity. Further studies are under way to clarify the dynamics between the photoisomerization and the flipping motion seen in the crystals.

Our observations demonstrate that the dynamic motions of the $\mathrm{Cp^{R}}$ ligands coupled with the stereoselective oxygen-atom rearrangement govern the factors allowing the photochromic reaction to proceed in the crystalline-state. Thus, the "flexibility" of the ligands plays an important role for stabilization of the whole crystal. Furthermore, the dynamic motions of the $\mathrm{Cp^{R}}$ ligands influence the stereoselectivity described in Section 3.1, though the selectivity of the reaction in the crystalline-state is strongly affected by the "topochemical principles" [35] and "reaction cavity" [36] enunciated by Schmidt and Ohashi, respectively. Indeed, the dynamic motions of the $\mathrm{Cp^{R}}$ ligands are closely connected to the oxygen atom that moves selectively.

4. Conclusions

We have briefly reviewed the over 20 organometallic systems that show photochromism with structural rearrangement. The basic processes comprise linkage isomerization, haptotropic rearrangement, and reorganization of M–ligand and/or M–M bonds. The organometallic compounds have unique character that are appropriate for the photochromism and are different from photochromic organic compounds. Although photochromism has been widely recognized as the light induced reversible change of "*color*", one of the principal features of photochromic reactions is the reversible change of the "*molecular configuration*". It would be useful to construct a photo-switchable catalyst, sensor, actuator, and so on.

In the crystalline-state, the change of the "*molecular configuration*" is significantly affected by the crystal lattice (vice versa). The rhodium dithionite complexes have been introduced as one of the rare examples that show the photochromic reaction and novel dynamic behavior in the crystalline-state. Since the crystalline-state photochromism has been accidentally found so far, a rational strategy to make a crystalline-state photochromic compounds is needed. Our observations strongly suggest that the key features are flexibility of the crystal. Thus, introduction of flexible unit such as alkyl-chains by chemical modification would be a valuable strategy to try.

We are expecting that a new photochromic research field will develop based on the characteristic reaction and structural diversity of organometallic compounds in both solution and the solid state.

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References

[1] H. Bouas-Laurent, H. Dürr, Pure Appl. Chem. 73 (2001) 639.
[2] (a) M. Irie, S. Kobatake, M. Horichi, Science 291 (2001) 1769;
(b) J.J.D. de Jong, L.N. Lucas, R.M. Kellogg, J.H. van Esch, B.L. Feringa, Science 304 (2004) 278;
(c) R.O. Al-kaysi, C.J. Bardeen, Adv. Mater. 19 (2007) 1276;
(d) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, Nature 446 (2007) 778;
(e) M. Yamada, M. Kondo, J.-i. Mamiya, Y. Yu, M. Kinoshita, C.J. Barrett, T. Ikeda, Angew. Chem. Int. Ed. 47 (2008) 4986;
(f) K. Fujita, S. Hatano, D. Kato, J. Abe, Org. Lett. 10 (2008) 3105;
(g) H. Koshima, N. Ojima, H. Uchimoto, J. Am. Chem. Soc. 131 (2009) 6890;
(h) T.L. Andrew, H.-y. Tsai, R. Menon, Science 324 (2009) 917.
[3] M. Fritsche, Comp. Rend. 69 (1867) 1035.
[4] (a) G.H. Brown (Ed.), Photochromism, Wiley Interscience, New York, 1971;
(b) M. Irie (Ed.), Photochromism, Memories and Switches, Chem. Rev. 100 (2000) 1683;
(c) H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 2003.
[5] (a) S. Kume, H. Nishihara, Struct. Bond. 123 (2007) 79;
(b) S. Kume, H. Nishihara, Dalton Trans. (2008) 3260.

[6] (a) E.V. Boldyreva, Mol. Cryst. Liq. Cryst. 242 (1994) 17;
(b) J.J. Rack, J.R. Winkler, H.B. Gray, J. Am. Chem. Soc. 123 (2001) 2432;
(c) P. Coppens, I. Novozhilova, A. Kovalevsky, Chem. Rev. 102 (2002) 861;
(d) A.Y. Kovalevsky, K.A. Bagley, J.M. Cole, P. Coppens, Inorg. Chem. 42 (2003) 140;
(e) T.E. Bitterwolf, Coord. Chem. Rev. 250 (2006) 1196.

[7] (a) C.W. Lange, M. Földeàki, V.I. Nevodchikov, V.K. Cherkasov, G.A. Abakumov, C.G. Pierpont, J. Am. Chem. Soc. 114 (1992) 4220;
(b) O. Sato, A. Cui, R. Matsuda, J. Tao, S. Hayami, Acc. Chem. Res. 40 (2007) 361.

[8] (a) S. Decurtins, P. Gütlich, C.P. Köhler, H. Spiering, A. Hauser, Chem. Phys. Lett. 105 (1984) 1;
(b) P. Gütlich, A. Hauser, H. Spiering, Angew. Chem. Int. Ed. Engl. 33 (1994) 2024.

[9] (a) M. Morimoto, M. Irie, Chem. Commun. (2005) 3895;
(b) K. Amimoto, T. Kawato, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 207.

[10] C.M. Gordon, R.D. Feltham, J.J. Turner, J. Phys. Chem. 95 (1991) 2889.

[11] (a) O. Crichton, A.J. Rest, J. Chem. Soc. Dalton Trans. (1977) 986;
(b) M. Herberhold, W. Kremnitz, H. Trampisch, R.B. Hitam, A.J. Rest, D.J. Taylor, J. Chem. Soc. Dalton Trans. (1982) 1261.

[12] D.V. Fomitchev, T.R. Furlani, P. Coppens, Inorg. Chem. 37 (1998) 1519.

[13] (a) T.T. To, C.E. Barnes, T.J. Burkey, Organometallics 23 (2004) 2708;
(b) T.T. To, C.B. Duke III, C.S. Junker, C.M. O'Brien, C.R. Ross II, C.E. Barnes, C.E. Webster, T.J. Burkey, Organometallics 27 (2008) 289;
(c) T.T. To, E.J. Heilweil, C.B. Duke III, K.R. Ruddick, C.E. Webster, T.J. Burkey, J. Phys. Chem. A 113 (2009) 2666.

[14] B.E. Mann, Chem. Soc. Rev. 15 (1986) 167.

[15] R.P. Hughes, R.T. Carl, R.C. Hemond, D.E. Samkoff, A.L. Rheingold, J. Chem. Soc. Chem. Commun. (1986) 306.

[16] J.A. King Jr., K.P.C. Vollhardt, J. Organomet. Chem. 369 (1989) 245.

[17] G. Zhu, J.M. Tanski, D.G. Churchill, K.E. Janak, G. Parkin, J. Am. Chem. Soc. 124 (2002) 13658.

[18] H.C. Jahr, M. Nieger, K.H. Dötz, Chem. Commun. (2003) 2866.

[19] (a) H. Nakai, M. Mizuno, T. Nishioka, N. Koga, K. Shiomi, Y. Miyano, M. Irie, B.K. Breedlove, I. Kinosita, Y. Hayashi, Y. Ozawa, T. Yonezawa, K. Toriumi, K. Isobe, Angew. Chem. Int. Ed. 45 (2006) 6473;
(b) Y. Miyano, H. Nakai, Y. Hayashi, K. Isobe, J. Organomet. Chem. 692 (2007) 122;
(c) Y. Miyano, H. Nakai, M. Mizuno, K. Isobe, Chem. Lett. 37 (2008) 826;
(d) H. Nakai, T. Nonaka, Y. Miyano, M. Mizuno, Y. Ozawa, K. Toriumi, N. Koga, T. Nishioka, M. Irie, K. Isobe, J. Am. Chem. Soc. 130 (2008) 17836;
(e) H. Nakai, M. Hatake, Y. Miyano, K. Isobe, Chem. Commun. (2009) 2685.

[20] (a) H. Nagashima, T. Fukahori, K. Itoh, J. Chem. Soc. Chem. Commun. (1991) 786;
(b) H. Nagashima, T. Fukahori, M. Nobata, A. Suzuki, M. Nakazawa, K. Itoh, Organometallics 13 (1994) 3427;
(c) K. Matsubara, T. Oda, H. Nagashima, Organometallics 20 (2001) 881;
(d) K. Matsubara, S. Mima, T. Oda, H. Nagashima, J. Organomet. Chem. 650 (2002) 96;
(e) S. Niibayashi, K. Matsubara, M.-a. Haga, H. Nagashima, Organometallics 23 (2004) 635;
(f) K. Tsuchiya, K. Ideta, K. Mogi, Y. Sunada, H. Nagashima, Dalton Trans. (2008) 2708.

[21] A.E. Bruce, D.R. Tyler, Inorg. Chem. 23 (1984) 3433.

[22] Y. Kawano, H. Tobita, H. Ogino, Organometallics 11 (1992) 499.

[23] (a) M. Berry, N.J. Cooper, M.L.H. Green, S.J. Simpson, J. Chem. Soc. Dalton Trans. (1980) 29;
(b) M. del Carmen Barral, M.L.H. Green, R. Jimenez, J. Chem. Soc. Dalton Trans. (1982) 2495.

[24] R. Boese, J.K. Cammack, A.J. Matzger, K. Pflug, W.B. Tolman, K.P.C. Vollhardt, T.W. Weidman, J. Am. Chem. Soc. 119 (1997) 6757.

[25] (a) J. Gigg, R. Gigg, S. Payne, R. Conant, J. Chem. Soc. Perkin Trans. I (1987) 2411;
(b) O. Crottaz, F. Kubel, H. Schmid, J. Mater. Chem. 7 (1997) 143.

[26] P. Burger, Angew. Chem. Int. Ed. 40 (2001) 1917.

[27] K. Matsubara, S. Niibayashi, H. Nagashima, Organometallics 22 (2003) 1376.

[28] D.E. Samkoff, J.R. Shapley, M.R. Churchill, H.J. Wasserman, Inorg. Chem. 23 (1984) 397.

[29] R.D. Adams, J.E. Cortopassi, J. Aust, M. Myrick, J. Am. Chem. Soc. 115 (1993) 8877.

[30] M. Yuki, M. Okazaki, S. Inomata, H. Ogino, Angew. Chem. Int. Ed. 37 (1998) 2126.

[31] (a) T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, M. Irie, J. Am. Chem. Soc. 122 (2000) 9631;
(b) S. Yamamoto, K. Matsuda, M. Irie, Angew. Chem. Int. Ed. 42 (2003) 1636;
(c) M. Morimoto, S. Kobatake, M. Irie, Chem. Commun. (2008) 335.

[32] T. Matsuura, H. Koshima, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 7.

[33] (a) K. Penzien, G.M.J. Schmidt, Angew. Chem. Int. Ed. Engl. 8 (1969) 608;
(b) B.S. Green, M. Lahav, D. Rabinovich, Acc. Chem. Res. 12 (1979) 191;
(c) S.V. Evans, M. Garcia-Garibay, N. Omkaram, J.R. Scheffer, J. Trotter, F. Wireko, J. Am. Chem. Soc. 108 (1986) 5648;
(d) V. Ramamurthy, K. Venkatesan, Chem. Rev. 87 (1987) 433;
(e) A. Sekine, K. Hori, Y. Ohashi, M. Yagi, F. Toda, J. Am. Chem. Soc. 111 (1989) 697;
(f) B.L. Feringa, R.A. van Delden, Angew. Chem. Int. Ed. 38 (1999) 3418;
(g) M. Sakamoto, J. Photochem. Photobiol. C: Photochem. Rev. 7 (2006) 183.

[34] (a) R.F. Bryan, P.T. Greene, M.J. Newlands, D.S. Field, J. Chem. Soc. A (1970) 3068;
(b) D. Braga, Chem. Rev. 92 (1992) 633.

[35] (a) M.D. Cohen, G.M.J. Schmidt, J. Chem. Soc. (1964) 1996;
(b) G.M.J. Schmidt, Pure Appl. Chem. 27 (1971) 647.

[36] (a) Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, Y. Ohgo, J. Am. Chem. Soc. 103 (1981) 5805;
(b) Y. Ohashi, A. Uchida, Y. Sasada, Y. Ohgo, Acta Crystallogr. Sect. B 39 (1983) 54;
(c) Y. Ohashi, Acc. Chem. Res. 21 (1988) 268.