A reversibly photoswitchable mononuclear palladium(II) complex with *ortho*-diethylated azobenzene ligands†

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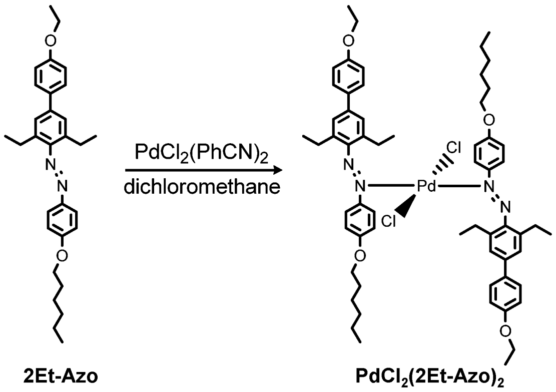
A mononuclear palladium(II) complex ($PdCl_2(2Et\text{-}Azo)_2$), with sterically bulky *ortho*-diethylated azobenzenes (2Et-Azo) in the long-lived *cis* form, was designed to achieve reversible photoswitching originating from a reversible change in its molecular structure. An X-ray crystallographic study indicated that the metal center in the complex has a *trans* square-planar structure, with two 2Et-Azo ligands coordinated to a palladium ion in a monodentate manner. Alternating UV and visible light irradiation of $PdCl_2(2Et\text{-}Azo)_2$ gave rise to reversible changes in the molecular structure between the *trans* and *cis* forms, confirmed by UV-vis absorption and NMR spectroscopic measurements. Neither significant decomposition nor fast dissociation of $PdCl_2(2Et\text{-}Azo)_2$ was observed by UV and visible light irradiation. Furthermore, slow thermal back-isomerization occurred over the course of 2 days at ambient temperature, which may be closely related to the stability of the *cis* form of the *ortho*-alkylated azobenzene ligand.

Introduction

The design of photochromic materials and their photoisomerization reactions have attracted considerable attention because of their potential applicability in optical data storage,[1,2] nonlinear optoelectronics,[3] and photoswitching devices.[4] Among various photochromic organic molecules, such as spiropyrans, fulgides, diarylethenes and azobenzenes, extensive interest on azobenzenes have concentrated on their interaction with light, in order to elucidate the relationship between their molecular structure and the control of the *trans*↔*cis* photoisomerization.[1–6] An appropriate combination of photoisomerizable azobenzene molecules with transition metal complexes would make it possible to elicit their intrinsic photochemical, electrochemical, and magnetic properties, originating from the d-electrons.[7]

Numerous reports are available on dinuclear orthometalated complexes which involve the azobenzene ligand coordinated in a bidentate manner to a transition metal such as palladium(II),[8] platinum(II),[7c,9] or nickel(II),[10] whereas limited investigations have been made in connection with the azobenzene ligand coordinated in a monodentate manner to a palladium(II) through an N:→Pd σ-bond (mononuclear palladium complexes).[11] Moreover, there are only a few reports on photoswitching arising from a reversible change in the molecular structure of the above-mentioned palladium(II) complexes in solution.[11c,d] The possible reasons for this include (1) the suppression of the *trans*↔*cis* photoisomerization of the *trans*-blocked azobenzene ligand[8e,12] in orthometalated complexes, (2) the facile dissociation of azobenzene ligands from mononuclear palladium complexes[11c] in solution, (3) the low solubility of palladium complexes in organic solvents, and (4) the thermodynamic instability of the *cis* form.

To improve the stability of the *trans* and *cis* forms as well as their solubility in common organic solvents, we first designed an *ortho*-diethylated azobenzene ligand (2Et-Azo, see Scheme 1), which is expected to give long-lived *cis*-azobenzene.[13] Mononuclear palladium(II) complex ($PdCl_2(2Et\text{-}Azo)_2$) was successfully synthesized by a ligand-exchange reaction between the corresponding azobenzene and dichlorobis(benzonitrile)palladium(II) in dichloromethane at room temperature (Scheme 1). By comparison, a model palladium complex with azobenzenes lacking the *ortho* substituents could not be isolated pure because of the very low solubility of both the free ligand and the palladium complex in organic solvents. $PdCl_2(2Et\text{-}Azo)_2$ showed good solubility in organic solvents as well as reversible photoisomerization by UV and visible light irradiation. We also examined thermal back-isomerization together with stability against dissociation of the complex in solution.



Scheme 1 Synthesis of $PdCl_2(2Et\text{-}Azo)_2$.

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Results and discussion

An X-ray crystallographic study revealed that the metal center in the complex adopts a square-planar geometry, with two azobenzene ligands coordinated in a monodentate manner to a palladium ion through an N:→Pd σ-bond, as shown in Fig. 1. The two nitrogen atoms of the azo groups are equidistant from the Pd atom, at a distance of 2.053(2) Å, longer by 0.01–0.03 Å than the corresponding distances in related compounds.[11b,c]

The nitrogen–nitrogen bond length (1.251(3) Å) in the coordinated azobenzene was within the range of 1.24–1.26 Å found in free azobenzenes,[14] indicative of significant double-bond character. Although the azobenzene ligand maintained a *trans* configuration with respect to the azo group, the planes (1 and 2, see Fig. 1) of the two phenyl rings in the azobenzene unit were almost perpendicular to each other (dihedral angle 88.90°). Such considerable distortion from a conventional planar *trans*-azobenzene structure[5,15] is mainly caused by steric hindrance resulting both from the formation of the N:→Pd σ-coordinated metal complex[11,16] and from the introduction of bulky ethyl groups into the *ortho* positions with respect to the azo group.[13,17]

The *ortho*-diethylated azobenzene ligand (2Et-Azo) exhibited a typical azobenzene monomer-like absorption spectrum[5,18] with a strong π–π* transition at 353 nm and a weak n–π* transition at 452 nm in solution (Fig. 2 and Table 1). Upon UV light irradiation at 365 nm, a prominent decrease in the absorbance at 353 nm was observed as a consequence of a typical *trans*-to-*cis* photoisomerization of the azobenzene unit. More than 95% of the *cis* form was generated in a photostationary state, confirmed by ^{1}H NMR spectral data. Subsequent irradiation with visible light at 436 nm to induce *cis*-to-*trans* isomerization reversed the absorption spectral change, keeping an isosbestic point at 316 nm.[19] With respect to thermal *cis*-to-*trans* isomerization, the half-life of the *cis* form of 2Et-Azo was found to be approximately 13 days. Such a long lifetime can be interpreted in terms of steric hindrance arising from the bulky ethyl groups at the *ortho* positions, which restrict large-scale distortion (such as rotation and/or inversion) of the azo group during isomerization.[13,20,21]

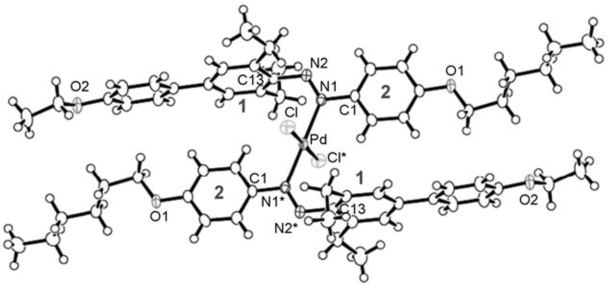


Fig. 1 ORTEP drawing of $PdCl_2(2Et\text{-}Azo)_2$ with thermal ellipsoids at 50% probability. The complex has an inversion center at the Pd atom. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected bond lengths (Å) and bond angles (°): Pd–Cl 2.2942(8), Pd–N1 2.053(2), N1–N2 1.251(3), N1–C1 1.444(3), N2–C13 1.442(3), Cl–Pd–N1* 90.86(7), Cl*–Pd–N1* 89.14(7), Pd–N1–N2 127.68(17), N2–N1–C1 115.1(2).

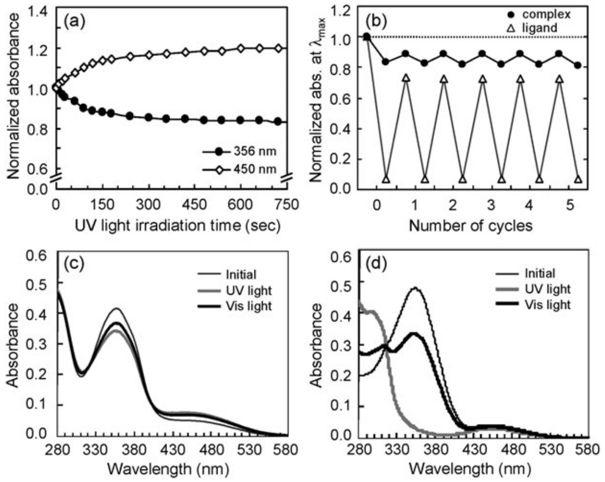


Fig. 2 (a) Changes in normalized absorbance of $PdCl_2(2Et\text{-}Azo)_2$ in dichloromethane as a function of irradiation time of UV light at 365 nm. (b) Reversible changes in normalized absorbances at 353 nm for 2Et-Azo (ligand) and at 356 nm for $PdCl_2(2Et\text{-}Azo)_2$ (complex) by alternating UV (365 nm) and visible (436 nm) light irradiation. (c) Changes in UV-vis absorption spectra of $PdCl_2(2Et\text{-}Azo)_2$ (1×10^{-5} M) in dichloromethane. (d) Changes in UV-vis absorption spectra of 2Et-Azo (2×10^{-5} M) in cyclohexane.

Table 1 UV-vis absorption spectral data of 2Et-Azo and $PdCl_2(2Et\text{-}Azo)_2$

Compound	λ/nm (ε/L mol^{-1} cm^{-1})	Half-life (*cis* form)[c]
2Et-Azo[a]	353 (23 900), 452 (2100)	13 days
$PdCl_2(2Et\text{-}Azo)_2$[b]	356 (46 300), 450 (7500)	—

[a] In cyclohexane. [b] In dichloromethane. [c] Determined by NMR.

$PdCl_2(2Et\text{-}Azo)_2$ containing the *ortho*-diethylated azobenzene ligands showed good solubility in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran (THF), and dimethylformamide (DMF), giving transparent solutions, whereas a mononuclear palladium(II) complex ($PdCl_2(MeOazbH)_2$)[11c] containing photochromic 4-methoxyazobenzenes (MeOazbH) was practically insoluble in organic solvents. The UV-vis absorption spectrum of the as-prepared solution indicated characteristic absorption bands at 356 nm and near 450 nm (Fig. 2 and Table 1). On the basis of both the molar extinction coefficient (ε) and the similarity with the π–π* absorption band of 2Et-Azo, the strong band at 356 nm can be ascribed to a π–π* azobenzene-based transition. A relatively strong band near 450 nm is tentatively attributable to an n–π* transition involving the azobenzene ligand and charge-transfer (CT) transitions involving metal–ligand (ML) interactions.[8e,22]

Reversible changes in the geometric structure of $PdCl_2(2Et\text{-}Azo)_2$ were monitored by UV-vis absorption and ^{1}H NMR spectroscopies (Fig. 2 and 3). To estimate the respective ratios of the *cis* to *trans* forms on the basis of the proton signals of the azobenzene unit, both the *trans* and *cis* forms produced by UV light irradiation were purified by silica gel chromatography to give a major component (Fig. 3b). Irradiation of $PdCl_2(2Et\text{-}Azo)_2$ solution with UV light led to a gradual decrease in the absorbance at 356 nm and an increase

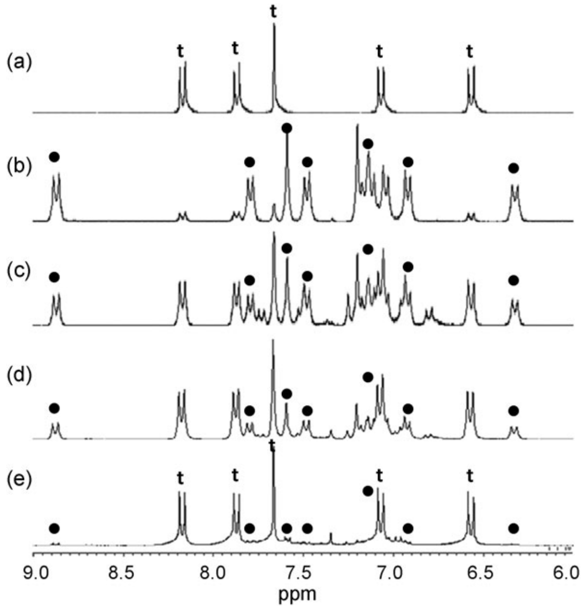
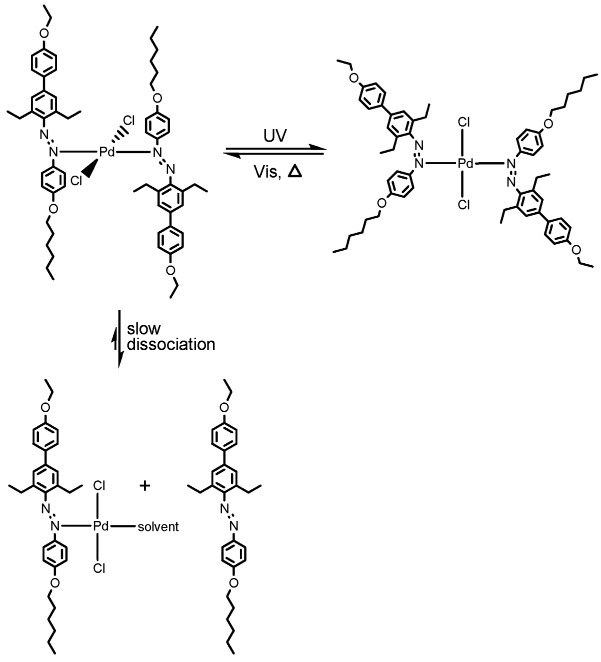


Fig. 3 ^{1}H NMR spectral changes of $PdCl_2(2Et\text{-}Azo)_2$ in CD_2Cl_2. (a) Initial (all-*trans* state). (b) Purified after UV light irradiation (*cis*-rich state: *cis*/*trans* = 92/8). (c) After UV light irradiation for 2–5 h (*cis*/*trans* = 60/40). (d) After visible light irradiation for 3.5 h (*cis*/*trans* = 40/60). (e) After 2 days' thermal back-isomerization. The filled circles correspond to the newly emerged proton signals after UV light irradiation.

in the absorbance near 450 nm, and a photostationary state was reached within approximately 660 s in dilute solution (1×10^{-5} M, see Fig. 2a and c). The ^{1}H NMR spectral data indicated that *ca.* 60% of the *cis* form existed at the photostationary state of UV light (Fig. 3c). Upon subsequent irradiation with 436-nm light to induce the reverse *cis*-to-*trans* isomerization, an increase in the absorbance at 356 nm and a slight decrease in the absorbance near 450 nm were recorded in the absorption spectrum. The ratio of the *cis* to *trans* forms was then estimated to be 40/60 at the photostationary state (Fig. 3d).

As clearly displayed in Fig. 2b, $PdCl_2(2Et\text{-}Azo)_2$ exhibited distinguishable, reversible photoswitching accompanied by molecular structural changes between the *trans* and *cis* states upon alternating UV and visible light irradiation (Scheme 2). In sharp contrast to a previous report which described very fast dissociation of 4-methoxyazobenzene ligands from mononuclear palladium complex upon UV light irradiation,[11c] neither undesirable decomposition nor fast dissociation of $PdCl_2(2Et\text{-}Azo)_2$ was apparently facilitated by exposure to UV or visible light for 2–5 h, as clearly seen in Fig. 3. These results suggest that both the *trans* and *cis* forms of the palladium complex with *ortho*-diethylated azobenzenes show high stability even under UV and visible light irradiation.

In contrast, thermal *cis*-to-*trans* isomerization of the UV-exposed $PdCl_2(2Et\text{-}Azo)_2$ solution proceeded over the course of 2 days in the dark at ambient temperature, confirmed by the reversion of the NMR signals to the spectrum of the original *trans* form (Fig. 3e). Considering that thermal *cis*-to-*trans* isomerization of palladium(II) complexes with dendritic azobenzenes can be complete within 2–3 h,[11d] $PdCl_2(2Et\text{-}Azo)_2$ underwent very slow thermal back-isomerization, which is most likely due to the *ortho*-diethylated azobenzene ligand possessing the long lifetime of the *cis* form.[13,20,21]



Scheme 2

Furthermore, NMR spectroscopy was used to investigate the stability of the N:→Pd σ-bond in $PdCl_2(2Et\text{-}Azo)_2$ in solution. Changes in the content of free 2Et-Azo released from $PdCl_2(2Et\text{-}Azo)_2$ as a function of incubation time in the dark were determined by the integral intensities of the proton signals from phenyl rings at around 6.5–8.5 ppm (Fig. 4). No appreciable dissociation of the free azobenzene ligand was found over a 1-day period. However, the content of 2Et-Azo gradually increased as incubation time increased, and *ca.* 16% and 67% of 2Et-Azo were detected after 7 and 32 days, respectively. That is, the N:→Pd σ-bond was weakened and the complex then slowly dissociated to release the azobenzene ligand back to the surrounding solvent (Scheme 2).

Conclusions

We have demonstrated that a palladium(II) complex ($PdCl_2(2Et\text{-}Azo)_2$) which involves two *ortho*-diethylated azobenzene ligands coordinated to a palladium ion through the N:→Pd σ-bond exhibits (1) good solubility in common organic solvents, and (2) improved stability of the *trans* and *cis* forms in solution. $PdCl_2(2Et\text{-}Azo)_2$ underwent reversible photoswitching between the two states upon alternating UV and visible light irradiation and slow thermal back-isomerization in solution at ambient temperature. Furthermore, irrespective of the irradiation conditions, keeping the complex solution for more than 1 day resulted in a slow release of the azobenzene ligand into the surrounding medium. Our current investigation suggests that understanding the relationship between the molecular structure and photoisomerization characteristics of the metal complex provides insight into the molecular

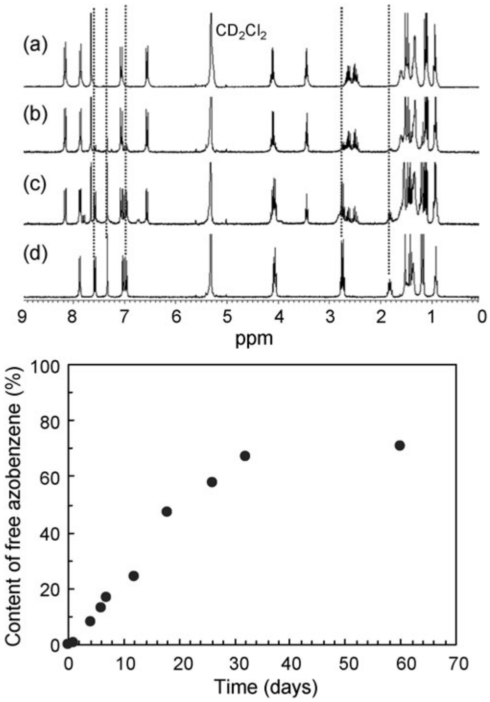


Fig. 4 Top: ^{1}H NMR spectral changes of $PdCl_2(2Et\text{-}Azo)_2$ in CD_2Cl_2: (a) Initial; (b) After 7 days in the dark; (c) After 32 days in the dark; (d) ^{1}H NMR spectrum of 2Et-Azo ligand in CD_2Cl_2. Bottom: Changes in the content of free 2Et-Azo as a function of incubation time in the dark of $PdCl_2(2Et\text{-}Azo)_2$ in CD_2Cl_2.

design strategy for developing photochromic metal complexes in combination with suitable molecular release systems.

Experimental

Dichloromethane and cyclohexane of spectroscopic grade were used to dissolve 2Et-Azo and $PdCl_2(2Et\text{-}Azo)_2$. After a 30-s nitrogen purge, a screw-cap quartz cuvette containing azobenzene solution was sealed with Parafilm®. Azobenzene solutions were exposed to UV light (365 nm, Mineralight® lamp, Model UVGL-25) or visible light (436 nm, a high-pressure UV lamp, Ushio Inc., combination of Toshiba color filters, Y-43 + V-44). Absorption spectra were recorded on a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer. NMR spectra were obtained using a JEOL JNM-ECP300 (300 MHz) spectrometer.

Synthesis

2Et-Azo. 2Et-Azo was prepared by reacting the precursor ((*E*)-4-((4′-ethoxy-3,5-diethylbiphenyl-4-yl)diazenyl)phenol, 0.93 g, 2.48 mmol) with 1-bromohexane (1.23 g, 7.44 mmol) in acetone (15 mL) in the presence of K_2CO_3 (1.03 g, 7.44 mmol) and a catalytic amount of tetrabutylammonium bromide. The reaction mixture was stirred at 60 °C for 7 h and then cooled to room temperature, followed by the addition of water and ethyl acetate. The organic layer was collected and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane–dichloromethane, v/v = 1/3). (0.89 g, yield: 79%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H, CH_3), 1.18 (t, 6H, CH_3), 1.33–1.46 (m, 9H, CH_2 and CH_3), 1.77–1.86 (m, 2H, $ArOCH_2CH_2(CH_2)_3CH_3$), 2.74 (q, 4H, $ArCH_2CH_3$), 4.05 (m, 4H, $ArOCH_2(CH_2)_4CH_3$ and $ArOCH_2CH_3$), 6.96 (d, 2H, Ar-*H*), 7.10 (d, 2H, Ar-*H*), 7.31 (s, 2H, Ar-*H*), 7.55 (d, 2H, Ar-*H*), 7.88 (d, 2H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 14.9, 15.6, 22.6, 25.5, 25.7, 29.2, 31.6, 63.5, 68.4, 114.7, 114.8, 124.3, 125.9, 128.1, 133.4, 137.1, 140.3, 147.2, 149.9, 158.6, 161.7. Anal. Calcd: C, 78.56%; H, 8.35%; N, 6.11%. Found: C, 78.58%; H, 8.52%; N, 5.94%. FAB-MS (*m*/*z*): $[M + Na]^+$, found 481.2849 (M + Na), calcd for $C_{30}H_{38}N_2O_2Na$ 481.2831.

$PdCl_2(2Et\text{-}Azo)_2$. A mixture of 2Et-Azo (0.45 g, 0.98 mmol), $PdCl_2(PhCN)_2$ (0.19 g, 0.49 mmol), and dichloromethane (10 mL) was vigorously stirred at room temperature for 24 h. The mixture was purified by silica gel column chromatography (*n*-hexane–ethyl acetate, v/v = 1/20) to afford the product as an orange solid (0.12 g, yield: 11%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 6H, CH_3), 1.11 (t, 12H CH_3), 1.33–1.59 (m, 22H, CH_2 and CH_3), 2.44–2.75 (m, 8H, CH_2), 3.38, (t, 4H, CH_2), 4.10 (q, 4H, CH_2), 6.51 (d, J = 9.3 Hz, 4H, Ar-*H*), 7.03 (d, J = 8.7 Hz, 4H, Ar-*H*), 7.62 (s, 4H, Ar-*H*), 7.82 (d, J = 8.7 Hz, 4H, Ar-*H*), 8.15 (d, J = 9.3 Hz, 4H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 14.2, 14.8, 22.5, 25.5, 26.1, 28.9, 31.5, 63.4, 68.1, 114.5, 114.9, 124.1, 127.6, 127.9, 132.7, 135.7, 134.0, 146.6, 150.6, 158.8, 163.3. Anal. Calcd: C, 65.84%; H, 7.00%; N, 5.12%. Found: C, 65.58%; H, 6.87%; N, 5.13%. FAB-MS (*m*/*z*): $[M + Na]^+$, found 1115.4146 (M + Na), calcd for $C_{60}H_{76}Cl_2N_4O_4PdNa$ 1115.4176.

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