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Photoswitchable Organoplatinum(IV) Complexes

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Supporting Information

ABSTRACT: Organoplatinum(IV) complexes, [PtBrMe₂(CH₂-4-C₆H₄-N=N-Ph)(NN)], containing *trans*-azobenzene functional groups, have been prepared by *trans* oxidative addition of BrCH₂-4-C₆H₄-N=N-Ph to the corresponding platinum(II) complexes [PtMe₂(NN)], with NN = 2,2'-bipyridine, 1,10-phenanthroline, 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine, 1,4-di-2-pyridyl-5,6,7,8,9,10-hexahydrocycloocta[*d*]pyridazine. The complexes undergo efficient and almost quantitative *trans*-*cis* isomerization on irradiation of dilute solutions at 365 nm, as monitored by UV-visible spectroscopy, and somewhat less complete photolysis in concentrated solution, as monitored by ¹H NMR spectroscopy. The



cis isomers undergo slow thermal isomerization back to the *trans* isomers, thus proving the photoswitching property of the complexes.

INTRODUCTION

The synthesis of photoresponsive materials has attracted much interest for potential applications in optical switching and optoelectronics.^{1,2} The incorporation of a transition metal into such materials can provide a photoswitching property to complement the magnetic, electrochemical, catalytic, or biological properties of the metal center.³ Among the well-known photoswitchable groups, azobenzene has been the most widely used. The popularity of the azobenzene group is due to the high efficiency of its reversible light-induced trans-cis isomerization, the significant structural change which occurs on isomerization with consequent changes in chemical and physical properties, and the high thermal and photochemical stability which allows many switching cycles to occur without any decomposition.⁴ A typical case for switching in azobenzene derivatives is illustrated, in simplified form, in Figure 1. The *trans-cis* photoisomerization begins by excitation to the S_1^{t} level, and the efficiency of the reaction depends initially on the relative ease of nonradiative decay back to the ground state S_0^{t}



Figure 1. Excitation and relaxation routes of *trans* and *cis* azobenzene isomers. Φ_{tc} and Φ_{ct} are the quantum yields of photoisomerization for *trans* to *cis* and *cis* to *trans*, respectively, and γ_0 is the thermal relaxation rate.

versus rearrangement to the *cis* isomer. As the concentration of *cis* isomer builds up, the reverse photoisomerization may occur, and this will often lead to a wavelength-dependent photo-chemical steady state between the isomers. The thermal conversion of *cis* isomer back to the more stable *trans* isomer typically takes several hours at room temperature.^{5,6}

Photoswitchable organometallic complexes are rare,^{7,8} and the first organoplatinum derivatives were reported only recently.9 The complexes contained an azobenzene substituent in a bipyridine ligand, and both platinum(II) and platinum(IV) complexes were studied (Scheme 1). By using UV light at 365 nm, the trans to cis isomerization reached a steady state containing 20-40% of the cis isomer. These relatively low conversions were attributed to conjugation of the diimine and azobenzene groups and overlap and mixing of the $n-\pi^*$ transitions associated primarily with the azobenzene groups with Pt 5d- π^* or halogen n- π^* transitions associated mainly with the diimine ligand, which gave additional routes from the cis isomer back to the more stable trans isomer.⁹ The present paper describes photoswitchable organoplatinum(IV) complexes in which the azobenzene is a substituent of an alkylplatinum group and which give higher conversion to the cis isomer.

RESULTS AND DISCUSSION

Synthesis and Characterization of $[PtMe_2(LL)]$ (2a–d). The new complexes are shown in Scheme 2. The *trans* oxidative addition of organic compounds with bromomethyl substituents has given a wide range of functional organoplatinum complexes,¹⁰ and it is now shown that the reaction of 4-bromomethylazobenzene to complexes $[PtMe_2(NN)]^{11}$ (1, NN = bipy; 2, NN = phen; 3, NN = bebipy; 4, NN = 6-dppd) gave the corresponding organoplatinum(IV) complexes

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Scheme 1. Photoswitchable Organoplatinum Complexes



Scheme 2. Synthesis of the Complexes 5-8



[PtBrMe₂(CH₂-4-C₆H₄N=NPh)(NN)] (5–8) (Scheme 2). The selective formation of the products of *trans* oxidative addition was shown initially by the ¹H NMR spectra and confirmed in each case by a structure determination. For example, the ¹H NMR spectrum of 5 showed a single methylplatinum resonance at δ 1.52, with coupling constant ²J_{PtH} = 70 Hz, and a single resonance for the PtCH₂ protons at δ 2.93 (²J_{PtH} = 97 Hz). The product of *cis* oxidative addition would have only C₁ symmetry and so would give a more complex spectrum.

The structures of the complexes 5-8 were confirmed crystallographically and are shown in Figures 2-5. A summary



Figure 2. Structure of complex 5.



Figure 3. Structures of the nonequivalent molecules in 6.0.5CH₂Cl₂.



Figure 4. Structure of complex 7.

and comparison of selected bond parameters is given in Table 1. Each complex has octahedral stereochemistry at platinum-(IV), with the expected stereochemistry formed by *trans* oxidative addition. In all cases, the Pt–CH₂ bond is slightly longer than the Pt–CH₃ bonds. The *trans*-azobenzene groups are distorted to a minor extent from planarity, as measured by the maximum values of the torsion angles CCNN = -17° , measuring the twist of the C₆H₄ group from the CNN plane for one of the molecules of **8**, and NNCC = 16° , measuring the



Figure 5. View of one of the two independent molecules in the complex $8.0.5CH_2Cl_2$. There is some disorder of the cyclooctene group, which is not shown for clarity.

twist of the C_6H_5 group from the NNC plane for one of the molecules of **6**. The maximum twist of the CNNC atoms was only 5° (Table 1). For all of the molecules except 7 the azobenzene group lay roughly above one of the pyridyl groups, with the corresponding torsion angle N-Pt-C-C in the range -7 to +15° (a positive value indicates a twist from the eclipsed conformation away from the adjacent Pt-Me group and toward the other nitrogen donor). However, the torsion angle N-Pt-C-C = -29° for complex 7 (Table 1, Figure 4). In all cases, the angle Pt-C-C was slightly higher than the ideal tetrahedral angle, suggesting that π stacking of the azobenzene and pyridyl groups is not strong, and the conformation of the benzylic group in the solid state is likely to be determined by intermolecular packing forces.

Photoisomerization Studies. The photoswitching of the azobenzene group in the complexes (Scheme 3) was monitored by both ¹H NMR and UV–visible spectroscopy.¹² Figure 6 shows changes in the ¹H NMR spectra when a solution of complex 6 in CD₂Cl₂ was irradiated with monochromic light at 365 nm in methylene chloride- d_6 at room temperature. The aromatic resonances for the azobenzene protons show the characteristic shift to lower δ for the *cis* isomer $6^{* 12b}$ and grow with irradiation time. After photolysis for 1 h, the solution contained the *trans* and *cis* isomers in the ratio $6:6^* = 40:60$. The thermal back-reaction was complete in about 2 days at 20





Figure 6. ¹H NMR spectra in the aromatic region of complex 6: (a) before irradiation (*trans* form 6 only); (b) after irradiation with monochromatic light at 365 nm for 60 min (both *trans* 6 and *cis* 6^* isomers present).

°C, as monitored by ¹H NMR spectroscopy. Similar results were obtained for the other complexes, though the ratio of isomers at the stationary state varied. For example, the ratio $7:7^* = 25:75$ after irradiation for 1 h.

The UV-visible absorption spectra of the complexes **5** and **6** in dichloromethane, and the changes on photolysis, are shown in Figure 7. Complex **5** exhibits major absorption bands at λ_{max} 363 nm, ascribed to the strong $\pi - \pi^*$ transition of the azobenzene moiety, and at λ_{max} 443 nm, attributed to the weak $n-\pi^*$ transition. As shown in Figure 7a, upon irradiation with UV light at 365 nm, a decrease in the $\pi - \pi^*$ band was observed, with the appearance of a new band at 285 nm due to formation of the *cis* isomer. There was an isosbestic point at 310 nm during this step, which was complete in about 13 min of irradiation at 365 nm. A slow further reaction then occurred with growth of a band at 393 nm, attributed to a MLCT band, 5d-*, of [PtBrMe(bipy)].¹³ The initial conversion of **5** to **5***

		5	$6(1)^{a}$	$6(2)^{b}$	7	$8(1)^{a}$	$8(2)^{b}$
	Pt–Me/Å	2.049(5)	2.085(8)	2.063(8)	2.045(6)	2.043(6)	2.062(6)
		2.050(5)	2.053(8)	2.075(8)	2.051(6)	2.071(6)	2.060(5)
	Pt-CH ₂ /Å	2.086(5)	2.121(8)	2.108(9)	2.105(6)	2.092(6)	2.100(6)
	Pt-N/Å	2.156(4)	2.161(6)	2.169(6)	2.160(5)	2.150(4)	2.144(4)
		2.165(4)	2.175(6)	2.173(7)	2.169(4)	2.151(4)	2.150(4)
	Pt-Br/Å	2.5959(6)	2.577(1)	2.598(1)	2.5870(6)	2.5749(6)	2.5735(7)
	N=N/Å	1.264(6)	1.243(9)	1.14(1)	1.271(7)	1.249(7)	1.239(7)
	Pt-C-C/deg	112.8(3)	114.4(6)	114.7(6)	113.9(4)	116.3(4)	114.3(4)
	C-N=N-C/deg	176.0(4)	178.0(5)	179.0(7)	175.6(5)	179.7(5)	178.2(6)
	C-C-N=N/deg	13.1(4)	12.6(7)	4.5(6)	-6.6(5)	2.7(6)	-17.1(7)
	N=N-C-C/deg	15.5(4)	9.3(6)	16.4(8)	-5.6(6)	-1.7(5)	5.9(6)
	N-Pt-C-C/deg	6.0(3)	10.2(5)	14.7(5)	-28.6(4)	2.1(5)	-6.8(5)

^aParameters for the Pt(1) molecule. ^bParameters for the Pt(2) molecule.



Figure 7. Changes in UV-visible spectra on photolysis at 365 nm: (a) complex 5; (b) complex 6.

was essentially quantitative under these conditions, and the reaction could be reversed thermally, as monitored by the complete recovery of the absorption band of 5 at 363 nm. The complexes 6-8 behaved in a similar way, giving rapid conversion to the *cis* isomers followed, on extended photolysis, by slow photodecomposition of the *cis* isomer. Spectral changes for complex 6 are shown in Figure 7b.

The quantum yields for the trans to photoisomerization of the ligand and complexes were determined in toluene solution, with irradiation at 365 nm (excitation into the $\pi - \pi^*$ absorption band), by comparison to azobenzene standard ($\Phi = 0.11$).¹⁴ The data are given in Table 2. It can be seen that the quantum

 Table 2. Quantum Yields for *trans-cis* Isomerization of the

 Compounds in Comparison to That of Azobenzene¹⁴

compd	$\varepsilon/\mathrm{M}^{-1}~\mathrm{m}^{-1}$	$\lambda_{ m max}/ m nm$	$\Phi_{ ext{trans-cis}}$
aobenzene	22300	319	0.11
BrCH ₂ -4-C ₆ H ₄ N=NPh	24218	328	0.10
5, NN = bipy	25022	365	0.12
6 , NN = phen	27866	368	0.11
7, NN = bebipy	23450	368	0.13
8, NN = 6-dppd	29639	369	0.09

yields fall in the narrow range 0.09–0.13, all being close to the value of 0.11 for azobenzene itself. This supports the hypothesis that the azobenzene unit is insulated from platinum by the saturated CH_2 bridge and that the isomerization occurs in the same way for all the compounds in Table 2.¹⁴ Deactivation of the excited state by coupling to the platinum–iimine transitions does not occur to a significant extent.⁹

Figure 8 shows the recovery of intensity of the visible absorption at 360 nm as a function of time during the thermal



Figure 8. Absorbance (*A*) at 360 nm versus time for the reaction of 6^* to give 6 in toluene at 55 °C.

isomerization of complex **6*** back to the more stable isomer **6** when carried out in toluene at 55 °C. The reaction followed first-order kinetics. Rate constants were obtained by simulation of the intensity—ime curves and gave $k_1 = [4.51(8)] \times 10^{-5} \text{ s}^{-1}$ at 55 °C, $[6.0(1)] \times 10^{-5} \text{ s}^{-1}$ at 60 °C, $[1.05(5)] \times 10^{-4} \text{ s}^{-1}$ at 70 °C, and $[1.92(6)] \times 10^{-4} \text{ s}^{-1}$ at 80 °C, from which the activation parameters $\Delta H^{\ddagger} = 53(2)$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -168(5)$ J K⁻¹ mol⁻¹ were determined. These rates are similar to those found for *cis* to *trans* isomerization of several organic azobenzene derivatives, which may occur by rotation or inversion mechanisms.¹⁵

CONCLUSIONS

In the first photoswitchable organoplatinum complexes A and B(Scheme 1) the azobenzene unit was conjugated to the diimine ligand, and so there was mixing of the corresponding π and π^* molecular orbitals.9 In turn, this led to overlap and mixing of the absorption bands primarily due to $n-\pi^*$ or $\pi-\pi^*$ transitions of the azobenzene group with $d-\pi^*$ or $\pi-\pi^*$ transitions of the platinum-diimine groups, and so there was easy reversible interconversion of trans and cis isomers. Thus, high conversion of trans to cis isomers was not possible. In the new compounds 5-8, the single methylene bridge between the azobenzene group and the platinum atom appears to be sufficient to prevent significant communication between the azobenzene and diimine groups. Figure 9 shows the DFT calculated structures for the complexes 5 and 5* and the first π^* level of the azobenzene group in each case. The first π^* level of the bipy ligand is slightly lower in energy, but there is no appreciable mixing of the orbitals of the azobenzene and bipy groups. This lack of orbital overlap of the azobenzene and diimine groups also leads to a shift in the absorption maximum for the $\pi - \pi^*$ transition of the *trans* isomer from about 340 nm in A and B to about 360 nm in 5-8, much closer to the wavelength of the irradiation light at 365 nm.⁹ The result is that the photoswitching is very efficient in the new complexes and the reverse cis to trans photoisomerisation is not competitive. The *cis* isomer 5^* is calculated to be 50 kJ mol⁻¹ less stable than 5, and thermal isomerization of 5* back to 5 does occur slowly, following first-order kinetics. We have attempted to grow single crystals of the cis isomers, but without success. Although the photoswitching is very efficient, the organoplatinum complexes do undergo slow photodecomposition, and this will limit the usefulness of these and similar compounds because the number of photoswitching/thermal reversion cycles will be limited.



Figure 9. Calculated structures for (a) complex 5 and (b) complex 5* and lowest energy π^* MO of the azobenzene group for (c) complex 5 and (d) complex 5*.

EXPERIMENTAL SECTION

All reactions were performed under a nitrogen atmosphere. ¹H NMR spectra were recorded by using a Varian Mercury 400 and Inova 400 spectrometer, and data are reported with respect to the labeling system of Chart 1. UV–vis spectra were measured using a Varian Cary 300

Chart 1. NMR Labeling



Bio spectrophotometer. Mass spectra were recorded using an electrospray PE-Sciex mass spectrometer (ESI-MS). 4-Bromomethylazobenzene was prepared by reaction of 4-methylazobenzene with *N*-bromosuccinimide.¹⁶ The dimethylplatinum(II) complexes 1–4 were prepared by the literature methods.^{11,17}

[PtBrMe₂(CH₂-4-C₆H₄N=NPh)(bipy)] (5). To a stirred solution of [PtMe₂(bipy)] (2; 0.09 mmol) in dry acetone (15 mL) was added bromomethylazobenzene (0.025 g, 0.09 mmol). After 1 h, the yellow solid which precipitated was separated by filtration, washed with pentane (3 × 2 mL), and dried under high vacuum. Yield: 85%. ¹H NMR in dichloromethane- d_2 : δ 1.52 (s, 6H, ²J_{PtH} = 70 Hz, PtMe), 2.93 (s, 2H, ²J_{PtH} = 97 Hz, PtCH₂), 6.45 (d, 2H, ³J_{HH} = 8 Hz, ⁴J_{PtH} = 19 Hz, H°), 7.20 (d, 2H, ³J_{HH} = 8 Hz, H^m), 7.42–7.53 (m, 5H, H°^{,m,p'}), 7.81 (d, 2H, ³J_{HH} = 7 Hz, H³), 7.96 (m, 2H, ³J_{HH} = 6, 7 Hz, H⁵), 8.06 (t, 2H, ³J_{HH} = 7 Hz, H⁴), 8.72 (d, 2H, ³J_{HH} = 6 Hz, ³J_{PtH} = 19 Hz, H⁶). HRMS (ESI): *m*/*z* 576.1290 [M⁺ − Br]. Anal. Calcd for C₂₅H₂₅BrN₄Pt: C, 45.74; H, 3.84; N, 8.53. Found: C, 45.97; N, 8.15; H, 3.81.

[PtBrMe₂(CH₂-4-C₆H₄N=NPh)(phen)] (6). This was prepared in a way similar to that for 5 and isolated as a yellow solid. Yield: 84%. ¹H

NMR in dichloromethane- d_2 : δ 1.67 (s, 6H, ${}^2J_{PtH} = 70$ Hz, PtMe), 2.97 (s, 2H, ${}^2J_{PtH} = 97$ Hz, PtCH₂), 6.13 (d, 2H, ${}^3J_{HH} = 8$ Hz, ${}^3J_{PtH} = 19$ Hz, H°), 6.86 (d, 2H, ${}^3J_{HH} = 8$ Hz, H^m), 7.49–7.55 (m, 3H, H^m·,^p), 7.77 (d, 2H, ${}^3J_{HH} = 9$ Hz, H°), 7.80 (m, 2H, ${}^3J_{HH} = 6,9$ Hz, H³), 7.90 (s, 2H, H⁵), 8.44 (d, 2H, ${}^3J_{HH} = 9$ Hz, H⁴), 9.04 (d, 2H, ${}^3J_{HH} = 6$ Hz, ${}^3J_{PtH} = 18$ Hz, H²). HRMS (ESI): m/z 600.1729 [M⁺ – Br]. Anal. Calcd for C₂₇H₂₅BrN₄Pt: C, 47.65; H, 3.70; N, 8.22. Found: C, 47.65; H, 3.69; N, 8.19.

[PtBrMe₂(CH₂-4-C₆H₄N=NPh)(bebipy)] (7). This was prepared in a way similar to that for **5** and isolated as a yellow solid. Yield: 88%. ¹H NMR in acetone- d_6 : δ = 1.34 (t, 6H, ${}^{3}J_{\text{HH}}$ = 7 Hz, CH_3CH_2), 1.57 (s, 6H, ${}^{2}J_{\text{PtH}}$ = 71 Hz, PtMe), 2.93 (s, 2H, ${}^{2}J_{\text{PtH}}$ = 97 Hz, PtCH₂), 4.39 (q, 4H, ${}^{3}J_{\text{HH}}$ = 7 Hz, CH_3CH_2), 6.57 (d, 2H, ${}^{3}J_{\text{HH}}$ = 8 Hz, ${}^{3}J_{\text{PtH}}$ = 19 Hz, H°), 7.20 (d, 2H, ${}^{3}J_{\text{HH}}$ = 8 Hz, H^m), 7.52–7.55 (m, 3H, H^{m',p'}), 7.80 (d, 2H, ${}^{3}J_{\text{HH}}$ = 9 Hz, H°'), 8.16 (d, 2H, ${}^{3}J_{\text{HH}}$ = 6 Hz, H⁵), 8.95 (s, 2H, H³), 9.02 (d, 2H, ${}^{3}J_{\text{HH}}$ = 6 Hz, ${}^{3}J_{\text{PtH}}$ = 19 Hz, H6). HRMS (ESI): m/z 720.2152 [M⁺ − Br]. Anal. Calcd for C₃₁H₃₃BrN₄O₄Pt: C, 46.51; H, 4.15; N, 7.00. Found: C, 45.51; H, 4.10; N, 6.70.

[PtBrMe₂(CH₂-4-C₆H₄N=NPh)(6-dppd)] (8). This was prepared in a way similar to that for **5** and isolated as a yellow solid. Yield: 77%. ¹H NMR in dichloromethane- d_2 : δ 1.43 (s, 3H, ²J_{PtH} = 70 Hz, PtMe), 1.78 (s, 3H, ²J_{PtH} = 71 Hz, PtMe), 1.58 (m, 2H, CH₂), 1.67 (m, 2H, CH₂), 2.09 (s, 2H, ³J_{PtH} = 92 Hz, PtCH₂), 2.89 (m, 2H, CH₂), 2.96 (m, 2H, CH₂), 3.10 (m, 2H, CH₂), 3.21 (m, 2H, CH₂), 6.53 (d, 2H, ³J_{HH} = 8 Hz, ³J_{PtH} = 19 Hz, H°), 7.22 (d, 2H, ³J_{HH} = 8 Hz, H^m), 7.54 (m, 3H, H^m,^p), 7.60 (m, 1H, H⁴), 7.78 (d, 2H, ³J_{HH} = 7 Hz, H°'), 7.90 (m, 1H, H⁴), 8.16 (m, 2H, H^{3,3}), 8.36 (m, 2H, H^{5,5}), 8.75 (d, 1H, ³J_{HH} = 7 Hz, H^{6'}), 9.13 (d, 1H, ³J_{HH} = 7 Hz, ³J_{PtH} = 22 Hz, H⁶). Anal. Calcd for C₃₅H₃₇BrN₆Pt: C, 51.47; H, 4.57; N, 10.29. Found: C, 51.70; H, 4.76; N, 9.81.

Photoswitching Studies. For UV–visible monitoring, a sample of the complex was dissolved in CH_2Cl_2 or toluene and irradiated in a quartz cuvette at room temperature with UV light at 365 nm, followed immediately by recording the absorption spectrum. For ¹H NMR monitoring, a sample in CD_2Cl_2 or $(CD_3)_2CO$ in an NMR tube was irradiated at room temperature at 365 nm, followed by recording the spectrum.

NMR in CD₂Cl₂ for cis lsomer **6***. $\delta({}^{1}H)$: 1.65 (s, 6H, ${}^{2}J_{PtH} = 70$ Hz, PtMe), 2.76 (s, 2H, ${}^{2}J_{PtH} = 96$ Hz, PtCH₂), 5.80 (d, 2H, ${}^{3}J_{HH} = 8$ Hz, H^m), 5.91 (d, 2H, ${}^{3}J_{HH} = 8$ Hz, ${}^{3}J_{PtH} = 19$ Hz, H°), 6.60 (d, 2H, ${}^{3}J_{HH} = 8$ Hz, H°'), 7.06 (t, 1H, ${}^{3}J_{HH} = 8$ Hz, HP'), 7.20 (t, 1H, ${}^{3}J_{HH} = 8$ Hz, H^m'), 7.78 (m, 2H, H³), 7.95 (s, 2H, H⁵), 8.48 (m, 2H, ${}^{3}J_{HH} = 6,8$ Hz, H⁴), 8.95 (d, 2H, ${}^{3}J_{HH} = 6$ Hz, ${}^{3}J_{PtH} = 18$ Hz, H²). NMR in CD₂Cl₂ for cis lsomer **7***. $\delta({}^{1}H)$: 1.30 (t, 6H, ${}^{3}J_{HH} = 7$ Hz,

*NMR in CD*₂*Cl*₂ *for cis lsomer* **7***. $\delta(^{1}\text{H})$: 1.30 (t, 6H, $^{3}J_{\text{HH}} = 7 \text{ Hz}$, *CH*₃*CH*₂), 1.52 (s, 6H, $^{2}J_{\text{PtH}} = 71 \text{ Hz}$, PtMe), 2.73 (s, 2H, $^{2}J_{\text{PtH}} = 97 \text{ Hz}$, PtCH₂), 4.36 (q, 4H, $^{3}J_{\text{HH}} = 7 \text{ Hz}$, CH₃*CH*₂), 6.17 (d, 2H, $^{3}J_{\text{HH}} = 6 \text{ Hz}$, $^{3}J_{\text{PtH}} = 19 \text{ Hz}$, H°), 6.25 (d, 2H, $^{3}J_{\text{HH}} = 8 \text{ Hz}$, H^m), 6.55 (d, 2H, $^{3}J_{\text{HH}} = 8 \text{ Hz}$, H°), 6.55 (t, 1H, $^{3}J_{\text{HH}} = 8 \text{ Hz}$, H°), 7.31 (t, 2H, $^{3}J_{\text{HH}} = 8 \text{ Hz}$, H^m), 8.18 (d, 2H, $^{3}J_{\text{HH}} = 7 \text{ Hz}$, H⁵), 8.92 (s, 2H, H³), 8.97 (d, 2H, $^{3}J_{\text{HH}} = 6 \text{ Hz}$, $^{3}J_{\text{PtH}} = 19 \text{ Hz}$, H⁶).

Quantum Yield Determinations. A solution of the *trans* isomer of each compound in toluene was irradiated with 365 nm light, and the absorbance at the π - π * band maximum was recorded every 20 s. The trans to cis photoisomerization rate ν was obtained from the slope of the graph of concentration of *trans* isomer against irradiation time. Azobenzene was used as a standard.¹⁴

Kinetic Studies. A sample of the complex in toluene solution in a quartz cuvet was irradiated with UV light at 365 nm until the photostationary state was reached. Then the sample was placed in the thermostated cell block of the UV–visible spectrometer and the absorbance at the maximum absorption wavelength of the *trans* isomer at 360–366 nm was recorded at intervals of 3 s until no further change in absorbance was observed (typically for 90 min). First-order rate constants were obtained by simulation of the absorbance–time data using Dynafit software.

X-ray Structure Determinations. Single crystals were grown from acetone/*n*-pentane at ambient temperature. A suitable crystal of each compound was coated in Paratone oil and mounted on a glass fiber loop. X-ray data were collected at 150 K with ω and φ scans using

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a Bruker Smart Apex II diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and Bruker SMART software.^{18a} Unit cell parameters were calculated and refined from the full data set. Cell refinement and data reduction were performed using the Bruker APEX2 and SAINT programs, respectively.^{18b} Reflections were scaled and corrected for absorption effects using SADABS.^{18c} All structures were solved by either Patterson or direct methods with SHELXS and refined by full-matrix least-squares techniques against F^2 using SHELXL.^{18d} All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined using the riding model. The data are given as Supporting Information in Table S1 and in the CID files.

DFT Calculations. DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with first-order scalar relativistic corrections and double- ζ basis set.¹⁹ All ground state structures were confirmed to be energy minima by analysis of force constants for normal vibrations.¹⁹

ASSOCIATED CONTENT

Supporting Information

Table S1, giving crystal and refinement data for the complexes and CIF files giving X-ray data for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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