

Photochemical or Thermal Chelate Exchange in the Ruthenium Coordination Sphere of Complexes of the Ru(phen)₂L Family (L = Diimine or Dinitrile Ligands)

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Received September 28, 2001

Complexes of the type Ru(phen)₂L²⁺, where L is a substituted bipyridine family member, have been prepared, and their photochemical substitution reactions have been investigated. In the presence of a bis-benzonitrile derivative, acting as a bidentate chelate, photoexpulsion of L is performed under the action of visible light, with quantitative formation of new complexes of the type Ru(phen)₂L'²⁺ (L' = bis-nitrile ligand). Several complexes have been characterized by X-ray crystallography. In particular, the bis-benzonitrile complexes could be crystallized, and the structure of these compounds, containing a 13-, 14-, or 15-membered metal incorporating ring, was obtained. By heating Ru(phen)₂L²⁺ with a bipy derivative in refluxing ethylene glycol, quantitative formation of the starting complex [Ru(phen)₂L²⁺] was carried out. The present series of compounds presents properties that could be profitably used in the design and construction of multicomponent systems acting as photochemically driven molecular machines.

Introduction

The control of molecular motions within synthetic compounds is an important task in relation to the new field referred to as “molecular machines”.^{1–5} Multicomponent systems can be set in motion by sending a signal to the system, with one of the components changing its position in space while the other ones are considered motionless. In biology, molecular machines and motors play an essential role. The rotary motor ATP synthase is certainly one of the most important biological motors.^{6,7} Linear motors such as myosin-actin⁸ (muscles) or kinesin-microtubules^{9,10} (transport

of organelles in the cell) are also essential. Most of the artificial systems proposed until now as models of biological motors or simply as mimics of everyday life machines can be set in motion under the action of an electrochemical signal. In this case, an electroactive component is reduced or oxidized to lead to a new and unstable species whose relaxation process to a thermodynamically more stable situation implies a motion.^{11–13} A few molecular machines have also been described which operate under the action of a chemical signal (pH change,¹⁴ metal exchange,¹⁵ or series of organic reactions¹⁶). Light irradiation has also been reported to originate in molecular motions, either in conjunction with a redox chemical reaction^{17,18} or without. In this

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respect, the rotary motor proposed by Feringa and Harada is a remarkable example because the rotation motion is realized via a sequence of photochemical or thermal steps, without consuming any chemical reagent.^{19,20} Transition metal based light-driven machines are particularly promising. For example, ruthenium(II) complexes of the Ru(bipy)₃²⁺ family (bipy = 2,2'-bipyridine) seem to be especially interesting, because, by introducing appropriate modifications in the bipy backbone, photochemical expulsion of a given ligand can be carried out specifically and quantitatively.^{21,22} We have recently taken advantage of this property to design and elaborate new ruthenium(II) complexes for which chelate exchange (expulsion or recoordination) can be performed under light irradiation or thermally.²² For instance, a Ru(phen)₂ fragment hosted in a macrocyclic receptor can be photochemically expelled,²³ with recoordination being induced by a thermal process. In the present paper, we would like to report that ligand exchange takes place between bidentate chelates. The photolabile ligand is a bipy derivative. It is substituted by a bis-nitrile ligand which, in turn, is substituted by the bipy-type compound in a thermal reaction. Remarkably, the ligand exchange is accompanied by significant photochromism.²⁴

Experimental Section

¹H NMR spectra were acquired on either a Bruker WP200 SY (200 MHz) or a Bruker AM 400 (400 MHz) spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference. Mass spectra were obtained by using a VG ZAB-HF spectrometer or a Fisons VG Trio 2000 (EI) spectrometer. Photoirradiation was performed in a quartz UV cell (*l* = 1.0 cm) or in a NMR tube (*φ* = 5.0 mm) using a Hanimex side projector (250 W halogen lamp). Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat with a standard three-electrode configuration as previously described.^{18b} Cyclic voltammetry was carried out in MeCN solution, using Bu₄NPF₆ as supporting electrolyte, a Pt working electrode, a Pt counter electrode, and SCE as reference. The typical sweep rate was 100 mV/s, and the window used was from -2.0 to +1.7 V. Absorption

spectra were recorded with a Kontron Uvikon 860 or an Uvikon XL spectrophotometer.

Synthesis. The commercial starting materials were obtained from Acros, Aldrich, Fluka, Lancaster, or Merck. Some ligands and complexes were prepared following literature procedures: dCN₂,²⁵ 6,6'-dmbp,²⁶ 3,3'-dmbp,²⁷ dClbp,²⁸ biiq (1,1'-biisoquinoline),²⁹ Ru(phen)₂(CH₃CN)₂(PF₆)₂,³⁰ Ru(phen)₂(6,6'-dmbp)(PF₆)₂,²² and Ru(phen)₂(3,3'-dmbp)(PF₆)₂.²⁷ All charged species were isolated as PF₆ salts. The solvents were distilled over the appropriate drying agents.

dCN₃. Sodium hydride (0.33 g, 8.4 mmol) was added to a stirred solution of 2-cyanophenol (1.0 g, 8.4 mmol) in dry DMF (10 mL) under argon. The mixture was heated to 80 °C until all the NaH had reacted. 1,3-Dibromopropane (0.84 g, 4.2 mmol) was then added, and the mixture was heated to reflux for 3 h. The cooled reaction mixture was poured into 30 mL of water. The precipitate obtained was separated by filtration and then washed with water (2 × 20 mL). Recrystallization from EtOH gave 0.39 g of white needles (1.4 mmol, 34%). ¹H NMR (200 MHz, CDCl₃): *δ* (ppm) 7.56 (dd, 2 H), 7.07 (dd, 2 H, *J* = 9.1, 1.0 Hz), 7.04 (dt, 2 H, *J* = 8, 1 Hz), 4.38 (t, 4 H, *J* = 5.6 Hz), 2.43 (q, 2 H, *J* = 5.6 Hz).

dCN₄. The same procedure was used as for dCN₃. Recrystallization from toluene gave 2.59 g of brown crystals (8.86 mmol, 53%). ¹H NMR (200 MHz, CDCl₃): *δ* (ppm) 7.58 (m, 4 H), 7.08 (dd, 2 H, *J* = 8, 1 Hz), 7.04 (dt, 2 H, *J* = 8, 1 Hz), 4.25 (m, 4 H), 2.18 (m, 4 H).

Ru(phen)₂(dCN₂)(PF₆)₂ (1). A mixture of dCN₂ (79 mg, 0.3 mmol), *cis*-Ru(phen)₂Cl₂ (145 mg, 0.27 mmol), EtOH (10 mL), and H₂O (10 mL) was heated to reflux for 2 h under argon. An aqueous KPF₆ solution was added to the mixture to form a yellow-orange solid, which was filtered and washed with water. Chromatography (SiO₂, acetone/H₂O/KNO₃ aq, eluent 100/10/1) followed by anion exchange gave **1** as a yellow solid in 53% yield. ¹H NMR (400 MHz, CD₂Cl₂): *δ* (ppm) 9.93 (dd, 2 H, *J* = 5.21, 1.26 Hz), 8.82 (dd, 2 H, *J* = 8.12, 1.22 Hz), 8.46 (dd, 2 H, *J* = 8.26, 1.22 Hz), 8.33 (dd, 2 H, *J* = 8.29, 5.22 Hz), 8.30 (d, 2 H, *J* = 8.88 Hz), 8.17 (d, 2 H, *J* = 8.88 Hz), 7.89 (dd, 2 H, *J* = 5.30, 1.24 Hz), 7.65 (ddd, 2 H, *J* = 8.92, 7.60, 1.72 Hz), 7.59 (dd, 2 H, *J* = 8.24, 5.30 Hz), 7.46 (dd, 2 H, *J* = 7.79, 1.69 Hz), 7.18 (d, 2 H, *J* = 8.61 Hz), 7.06 (dt, 2 H, *J* = 7.64, 0.52 Hz), 4.61 (s, 4 H). FAB-MS: *m/z* = 871.0 [M - PF₆], calcd 871. UV-vis (1,2-DCE): *λ*_{max}, nm (*ε*, L·mol⁻¹·cm⁻¹) = 382 (14100). CV (CH₃CN), *E* (V vs SCE): 1.45 (I^{3+/2+}), -1.40 irreversible (irr) (I^{2+/+}), -1.53 irr (I^{1+/0}).

Ru(phen)₂(dCN₃)(PF₆)₂ (2). The same method employed for **1** afforded **2** in 62% yield as a yellow solid. ¹H NMR (200 MHz, acetone-*d*₆): *δ* (ppm) 10.27 (dd, 2 H, *J* = 5.2, 1.2 Hz), 9.11 (dd, 2 H, *J* = 8.4, 1.1 Hz), 8.69 (dd, 2 H, *J* = 8.4, 1.2 Hz), 8.59 (dd, 2 H, *J* = 8.4, 5.2 Hz), 8.48 (d, 2 H, *J* = 8.8 Hz), 8.35 (d, 2 H, *J* = 8.8 Hz), 8.20 (dd, 2 H, *J* = 5.4, 1.2 Hz), 7.68 (ddd, 2 H, *J* = 8.6, 7.6, 1.7 Hz), 7.65 (dd, 2 H, *J* = 8.4, 5.2 Hz), 7.45 (dd, 2 H, *J* = 7.6, 1.7 Hz), 7.28 (dt, 2 H, *J* = 7.6, 0.6 Hz), 4.47 (m, 4 H), 3.63 (q, 2 H, *J* = 4.7 Hz). FAB-MS: *m/z* = 885.11 [M - PF₆], calcd 885. CV (CH₃CN), *E* (V vs SCE): 1.45 (I^{3+/2+}), -1.40 irr (I^{2+/+}), -1.54 irr (I^{1+/0}).

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Table 1. Crystallographic Data of 2–4 and 6

	2	3	4	6
formula	C ₄₉ H ₄₀ F ₁₂ N ₆ O ₂ P ₂ Ru	C ₅₀ H ₄₂ F ₁₂ N ₆ O ₂ P ₂ Ru	C ₃₆ H ₂₈ F ₁₂ N ₆ P ₂ Ru	C ₅₀ H ₃₈ F ₁₂ N ₆ P ₂ Ru
MW	1135.90	1149.93	935.66	1113.90
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 1 ₂ / <i>n</i> 1	<i>P</i> 2 ₁ 2 ₁
<i>a</i> (Å)	11.7423(2)	11.7128(2)	12.2556(3)	14.5015(5)
<i>b</i> (Å)	12.9485(4)	12.8727(3)	22.7566(6)	17.5833(4)
<i>c</i> (Å)	17.5210(5)	17.9605(4)	13.9607(2)	18.1465(5)
α (deg)	78.356(5)	81.777(5)	90	90
β (deg)	73.659(5)	73.525(5)	109.938(8)	90
γ (deg)	76.790(5)	75.868(5)	90	90
<i>V</i> (Å ³)	2461.61(6)	2510.29(3)	3660.2(4)	4627.1(4)
<i>Z</i>	2	2	4	4
color	yellow	orange	orange	dark red
<i>D</i> _{calcd} (g cm ⁻³)	1.53	1.52	1.70	1.60
μ (mm ⁻¹)	0.475	0.467	0.615	0.501
temp (K)	173	173	294	173
λ (Å)	0.71073	0.71073	0.71073	0.71073
<i>R</i> ^a	0.055	0.050	0.033	0.037
<i>R</i> _w ^b	0.084	0.075	0.045	0.046

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2)]^{1/2}.$$

Ru(phen)₂(dCN₄)(PF₆)₂ (3). The same method employed for **1** afforded **3** in 65% yield as a yellow solid. ¹H NMR (200 MHz, acetone-*d*₆): δ (ppm) 10.21 (dd, 2 H, *J* = 5.2, 1.2 Hz), 9.08 (dd, 2 H, *J* = 8.2, 1.2 Hz), 8.70 (dd, 2 H, *J* = 8.2, 1.2 Hz), 8.45 (dd, 2 H, *J* = 8.2, 5.2 Hz), 8.47 (d, 2 H, *J* = 8.8 Hz), 8.35 (d, 2 H, *J* = 8.8 Hz), 8.23 (dd, 2 H, *J* = 5.2, 1.2 Hz), 7.68 (dd, 2 H, 8.2, 5.2 Hz), 7.64 (ddd, 2 H, *J* = 8.5, 7.2, 1.7 Hz), 7.26 (d, 2 H, *J* = 7.4 Hz), 7.23 (dd, 2 H, *J* = 7.4, 1.7 Hz), 6.93 (dt, 2 H, *J* = 7.4, 0.7 Hz), 4.35 (m, 4 H), 2.14 (m, 4 H, *J* = 4.7 Hz). FAB-MS: *m/z* = 889.3 [M - PF₆], calcd 889. CV (CH₃CN), *E* (V vs SCE): 1.46 (1^{3+/2+}), -1.40 irr (1^{2+/+}), -1.54 irr (1⁺⁰).

Ru(phen)₂(dClbp)(PF₆)₂ (5). A mixture of *cis*-Ru(phen)₂Cl₂ (203 mg, 0.38 mmol) and dClbp (86 mg, 0.38 mmol) was heated at reflux in degassed ethylene glycol (5 mL) for 4 h. After the mixture had cooled to room temperature, water (10 mL) and a saturated solution of aqueous KPF₆ (30 mL) were added. The orange-brown precipitate was collected by filtration and washed with water and diethyl ether. After column chromatography on silica (eluent: CH₃CN/H₂O/KNO₃ 100/70.7) and anionic exchange using aqueous KPF₆, a bright red powder was obtained (91 mg, 0.13 mmol) with a yield of 35%. ¹H NMR (CD₃CN, 400 MHz): δ (ppm) 8.74 (dd, 2 H, *J* = 8.32, 1.20 Hz), 8.52 (dd, 2 H, *J* = 5.24, 1.20 Hz), 8.47 (dd, 2 H, *J* = 8.08, 1.20 Hz), 8.42 (dd, 2 H, *J* = 8.32, 1.20 Hz), 8.26 (d, 2 H, *J* = 9.04 Hz), 8.16 (d, 2 H, *J* = 8.80 Hz), 8.02 (t, 2 H, *J* = 8.08 Hz), 7.91 (dd, 2 H, *J* = 5.24, 8.32 Hz), 7.59 (dd, 2 H, *J* = 5.34, 1.06 Hz), 7.43 (dd, 2 H, *J* = 8.08, 1.16 Hz), 7.31 (dd, 2 H, *J* = 5.36, 8.20 Hz). FAB-MS: *m/z* = 831.0 [M - PF₆]⁺, calcd 831.00, 66%; 686.0 [M - 2 PF₆ + e⁻]⁺, calcd 686.03, 56%; 462.1 [M - 2 PF₆ - dClbp + e⁻]⁺, calcd 462.04, 100%; 343.2 [M - 2 PF₆]^{2+/2}, calcd 343.02, 62%. UV-vis (CH₃CN): λ_{max} , nm (ϵ , L·mol⁻¹·cm⁻¹) = 381 (9100), 429 (11500). CV (CH₃CN), *E* (V vs SCE): 1.43 (5^{3+/2+}), -1.12 irr (5^{2+/+}).

Ru(phen)₂(biq)(PF₆)₂ (6). In a two-neck flask, *cis*-Ru(phen)₂(CH₃CN)₂(PF₆)₂ (110 mg, 0.13 mmol) and biq (34 mg, 0.13 mmol) were heated at reflux under argon in degassed ethylene glycol (5 mL) for 1 h. The addition of a saturated solution of aqueous KPF₆ caused the precipitation of a red compound, which was collected by filtration, washed with water and diethyl ether, and then air-dried. The complex **6** was isolated (126 mg, 0.12 mmol) with a yield of 94% as a dark red solid. ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂): δ (ppm) 8.68 (d, 2 H, *J* = 8.84 Hz), 8.65 (dd, 2 H, *J* = 8.20, 1.00 Hz), 8.61 (d, 2 H, *J* = 8.60 Hz), 8.46 (dd,

2 H, *J* = 8.20, 0.88 Hz), 8.22 (d, 2 H, *J* = 8.84 Hz), 8.18 (dd, 2 H, *J* = 5.40, 1.08 Hz), 8.14 (d, 2 H, *J* = 8.84 Hz), 7.95 (d, 2 H, *J* = 7.36 Hz), 7.90 (dd, 2 H, *J* = 5.40, 8.20 Hz), 7.74 (dd, 2 H, *J* = 5.40, 1.08 Hz), 7.64 (dd, 2 H, *J* = 5.36, 8.16 Hz), 7.53 (t, 2 H, *J* = 7.20 Hz), 7.09 (dt, 2 H, *J* = 8.84, 1.28 Hz), 6.98 (d, 2 H, *J* = 9.08 Hz). UV-vis (CH₃CN): λ_{max} , nm (ϵ , L·mol⁻¹·cm⁻¹) = 377 (22300), 439 (11200), 525 (11000). CV (CH₃CN), *E* (V vs SCE): 1.38 (6^{3+/2+}), -0.90 (6^{2+/+}), -1.38 (6⁺⁰), -1.65 (6^{0/-1}).

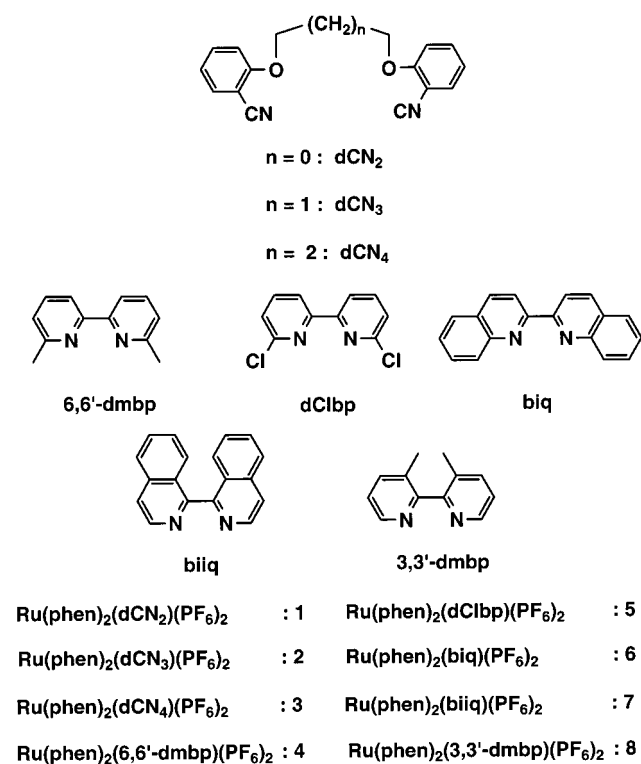
Ru(phen)₂(biq)(PF₆)₂ (7). The presence of two diastereoisomers in a 2:1 ratio²⁹ precludes the complete attribution of the ¹H NMR (400 MHz) spectrum. FAB-MS: *m/z* = 863.0 [M - PF₆]⁺, calcd 863.0, 80%; 718.1 [M - 2 PF₆ + e⁻]⁺, calcd 718.0, 100%. CV (CH₃CN), *E* (V vs SCE): 1.26 (7^{3+/2+}), -0.96 (7^{2+/+}), -1.45 (7⁺⁰), -1.67 (7^{0/-1}).

Ru(phen)₂(3,3'-dmbp)(PF₆)₂ (8). A mixture of *cis*-Ru(phen)₂Cl₂ (145 mg, 0.272 mmol), 3,3'-dmbp (55 mg, 0.300 mmol), water (10 mL), and ethanol (10 mL) was refluxed for 2 h under Ar. The black turbid mixture became a deep-red, clear solution in 1 h. After cooling the mixture down to room temperature, aq KPF₆ was added to form an orange precipitate, which was filtered off and washed with water to give a red solid. The solid was chromatographed over SiO₂ (acetone/H₂O/KNO₃ = 100/10/1) to give **8** which still contained impurity. Recrystallization from dichloromethane/methanol gave **8** in a pure form in 54% yield as an orange solid. ¹H NMR (acetone-*d*₆, 200 MHz): δ (ppm) 8.84 (dd, 2 H, *J* = 8.3, 1.2 Hz), 8.70 (dd, 2 H, *J* = 8.3, 1.2 Hz), 8.42 (d, 2 H, *J* = 8.9 Hz), 8.36 (d, 2 H, *J* = 8.9 Hz), 8.16 (dd, 2 H, *J* = 5.2, 1.2 Hz), 8.02–7.92 (m, 4 H), 7.86 (d, 2 H, *J* = 5.2 Hz), 7.68 (dd, 2 H, *J* = 9.2, 5.2 Hz), 7.33 (m, 2 H), 2.49 (s, 6 H, CH₃). UV-vis (CH₃CN): λ_{max} , nm (ϵ , L·mol⁻¹·cm⁻¹) = 423 (13360), 453 (14000). CV (CH₃CN), *E* (V vs SCE): 1.27 (8^{3+/2+}), -1.33 (8^{2+/+}), -1.48 (8⁺⁰).

X-ray Structural Studies. Single crystals suitable for X-ray analysis were obtained for complexes **2–4** and **6** by slow diffusion of *p*-xylene (99%) into a methanolic solution of the complex. For all computations, the MolEN package was used.³¹ Crystal data and details of data collection for complexes **2–4** and **6** are provided in Table 1.

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Scheme 1



Results and Discussion

Synthesis of Ligands and Complexes. The ligands and complexes synthesized or involved in this study are depicted in Scheme 1.

The dicyano ligands dCN₂, dCN₃, and dCN₄ are prepared in good yields by heating 2-cyanophenoxide with the corresponding dichloroalkane in refluxing DMF following the procedure described by Angelici et al.²⁵ The sterically hindering diimine chelates are prepared as already reported^{26–29} or are commercially available (biq). The ruthenium complexes **1–3** are obtained under relatively mild conditions by reacting the precursor Ru(phen)₂Cl₂ with the appropriate dicyano ligands in a refluxing EtOH–H₂O mixture for 2 h. By contrast, the preparation of complexes **4–7** requires harsh conditions because it is necessary to use ethylene glycol at reflux for several hours to coordinate the hindering chelate. All the complexes have been characterized by ¹H NMR and FAB-MS spectroscopy and by X-ray crystallographic study in the cases of **2–4** and **6**.

Structural Studies. The ORTEP diagrams of compounds **2** and **3** with partial atomic numbering schemes are shown in Figure 1. Selected bond lengths and bond angles are given in Table 2.

For complexes **2** and **3**, the ruthenium–nitrogen bond lengths range from 2.022 to 2.076 Å and are very similar to those observed in **1**²⁴ and in other ruthenium phenanthroline type complexes.^{32–34} The N–Ru–N bond angles indicate that

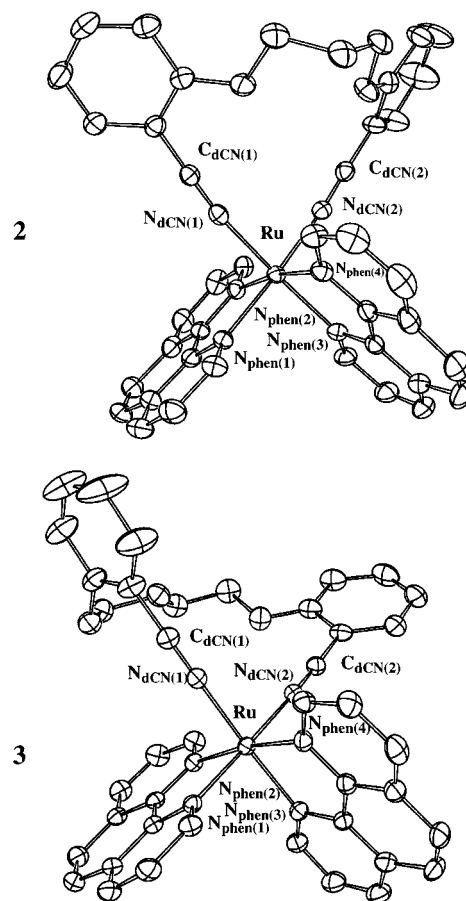


Figure 1. ORTEP view of the cationic part of **2** and **3**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**,²⁴ **2**, and **3**

	1	2	3
Ru–NdCN(1)	2.040	2.030	2.022
Ru–NdCN(2)	2.047	2.029	2.046
Ru–Nphen(1)	2.062	2.056	2.059
Ru–Nphen(2)	2.086	2.065	2.076
Ru–Nphen(3)	2.059	2.071	2.072
Ru–Nphen(4)	2.054	2.055	2.057
NdCN(1)–CdCN(1)	1.149	1.148	1.149
NdCN(2)–CdCN(2)	1.121	1.175	1.151
NdCN(1)–Ru–NdCN(2)	85.0	85.3	88.4
Nphen(1)–Ru–Nphen(2)	80.3	80.3	80.0
Nphen(3)–Ru–Nphen(4)	78.4	80.3	80.2
NdCN(1)–Ru–Nphen(4)	174.6	175.7	176.7
NdCN(2)–Ru–Nphen(1)	172.8	174.5	174.6
Nphen(2)–Ru–Nphen(3)	173.0	171.5	171.9
Ru–NdCN(1)–CdCN(1)	167.0	172.3	175.7
Ru–NdCN(2)–CdCN(2)	168.2	172.4	175.4

the geometry about the ruthenium atom is distorted from octahedral. Comparison of the NdCN(1)–Ru–NdCN(2) angles for **1–3** suggests that the degree of distortion decreases on going from **1** to **3** as a result of the greater length of the chain connecting the two benzonitrile nuclei of dCN₄ compared to dCN₂. The more open nature of the dCN ligand is clearly shown by the increasing Ru–NdCN(1)–CdCN(1) and Ru–NdCN(2)–CdCN(2) angles, average values for which are 167°, 173°, and 175° in **1**, **2**, and **3**, respectively. In addition, the dihedral angle between the two mean planes of the phenyl

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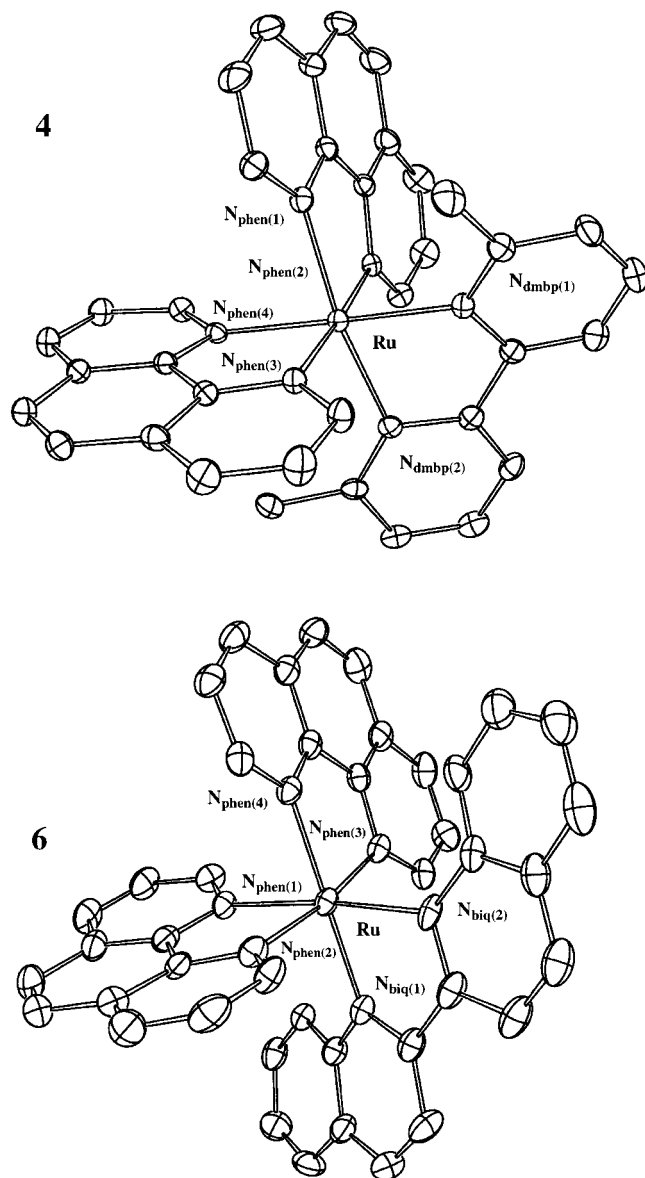


Figure 2. ORTEP view of the cationic part of **4** and **6**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted for clarity.

groups tends to increase going from **1** to **3**. In the latter, one phenyl ring is coplanar with the *trans* phenanthroline ligand. This feature was previously observed in Ru(bipy)₂(NCC₆H₅)₂²⁺ in which the phenyl rings of the benzonitrile are in the same mean plane as the corresponding *trans*-2,2'-bipyridine.³⁵

The ORTEP structures of **4** and **6** are shown in Figure 2, and selected bond lengths and bond angles are summarized in Table 3.

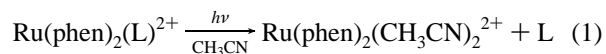
The ruthenium–nitrogen bond lengths in **4** and **6** are significantly longer than those observed in **2** and **3** or in the X-ray structures of previously reported ruthenium polypyridine complexes,^{33,34} indicating a more distorted octahedral environment about the Ru atom. As a result of steric interaction between the hindering chelate (6,6'-dmbp or biq)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **4** and **6**

Ru–N _{dmdbp} (1)	2.113	4	N _{dmdbp} (1)–Ru–N _{dmdbp} (2)	78.6
Ru–N _{dmdbp} (2)	2.100		N _{phen} (1)–Ru–N _{phen} (2)	79.5
Ru–N _{phen} (1)	2.083		N _{phen} (3)–Ru–N _{phen} (4)	79.0
Ru–N _{phen} (2)	2.077		N _{dmdbp} (1)–Ru–N _{phen} (4)	167.4
Ru–N _{phen} (3)	2.094		N _{dmdbp} (2)–Ru–N _{phen} (1)	175.2
Ru–N _{phen} (4)	2.084		N _{phen} (2)–Ru–N _{phen} (3)	177.0
			dihedral angle of dmbp	1.6
		6		
Ru–N _{biq} (1)	2.113		N _{biq} (1)–Ru–N _{biq} (2)	77.6
Ru–N _{biq} (2)	2.086		N _{phen} (1)–Ru–N _{phen} (2)	79.2
Ru–N _{phen} (1)	2.091		N _{phen} (3)–Ru–N _{phen} (4)	80.4
Ru–N _{phen} (2)	2.097		N _{biq} (1)–Ru–N _{phen} (4)	170.7
Ru–N _{phen} (3)	2.073		N _{biq} (2)–Ru–N _{phen} (1)	178.4
Ru–N _{phen} (4)	2.060		N _{phen} (2)–Ru–N _{phen} (3)	172.0
			dihedral angle of dmbp	–1.3

and the neighboring phenanthrolines, different types of distortion are induced. First, the Ru–N bonds are elongated (2.11 and 2.10 Å for 6,6'-dmbp and 2.11 and 2.086 Å for biq), and second, the hindering chelate adopts a twisted conformation, resulting in a dihedral angle between the two aromatic subunits of the bipyridine or the biquinoline of, respectively, 1.6° and 1.3°. In each complex, the bite angle of the third ligand is slightly smaller than those of the phenanthroline units. Interestingly, it should be noted that spontaneous resolution occurs during crystallization in the case of complex **6**, (noncentrosymmetric space group, orthorhombic, *P*2₁2₁2₁).

Photochemical Substitution Reactions. On irradiation with visible light in acetonitrile, solutions of all the ruthenium complexes (**4**–**8**) undergo photochemical reactions at rates varying from fast to relatively slow. The fact that the UV–visible and ¹H NMR spectra of the complexes do not change in the dark over a large range of temperatures indicates that these complexes have good thermal stability. As previously demonstrated for other ruthenium complexes in which the ruthenium coordination sphere is crowded,^{21,22} photochemical substitution of the hindering ligand by the nitrile solvent takes place efficiently and selectively (reaction 1).



On the other hand, photochemical experiments performed with a cooling system and monochromator demonstrate that thermal energy does not interfere with the photochemical process. While the photochemical reactions of **4**–**6** are fast (*t*_{1/2} ranges from seconds to minutes under the present experimental conditions), for **7** and **8** the reactions are complete only after several minutes (**8**) or hours (**7**). Using cyclic voltammetry to investigate **8**, these relatively slow processes have allowed the detection of an intermediate species. Indeed, careful examination of the anodic peak potentials reveals three distinct redox couples perfectly constant during the photolysis. Although the reversibility of the redox couple appearing as intermediate is not obvious, the value of 1.36 V (vs SCE) could be estimated. This value lies between those of starting compound **8** (1.27 V) and the final reaction product Ru(phen)₂(CH₃CN)₂²⁺ (1.45 V). In

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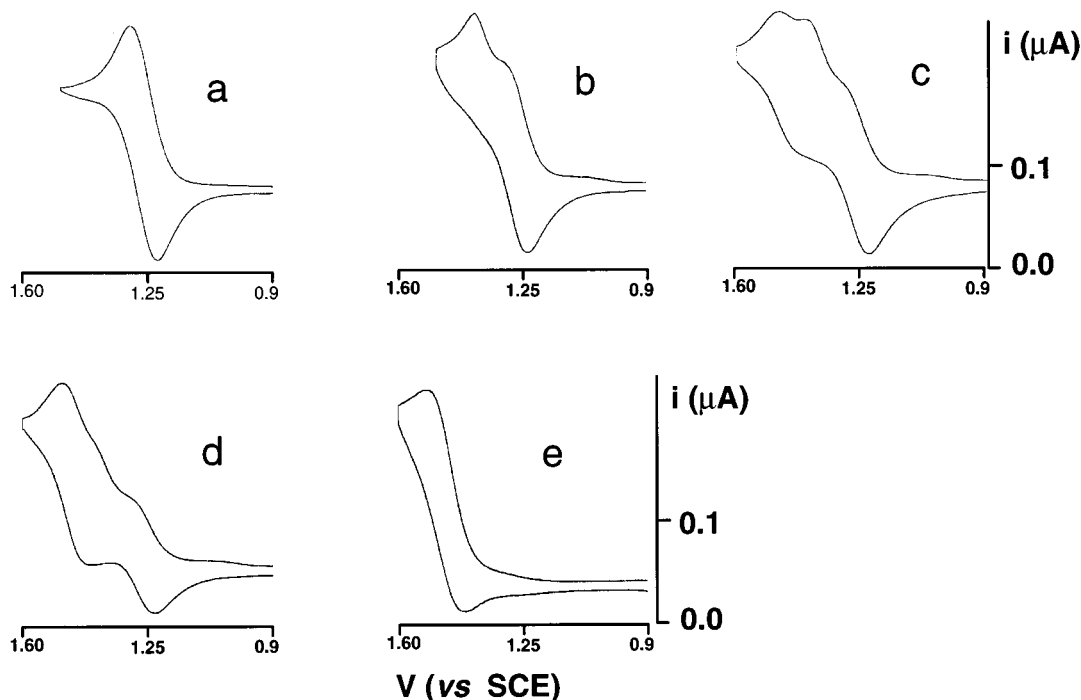


Figure 3. (a) Cyclic voltammograms of **8** before irradiation. (b)–(e) Evolution of **8** solution with irradiation time: (b) 1, (c) 5, (d) 8, and (e) 17 min. Conditions: CH_3CN , $(\text{tBu}_4\text{NPF}_6, 0.1 \text{ M})$, Pt electrode, $v = 100 \text{ mV s}^{-1}$, 25°C .

Scheme 2

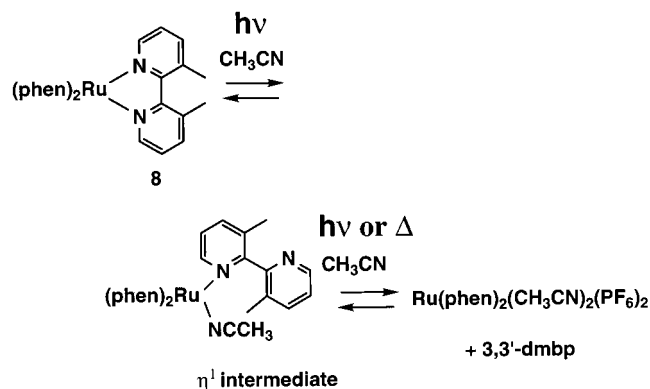
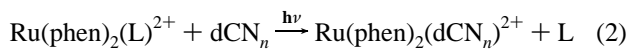


Figure 3, voltammograms of an acetonitrile solution of **8** show the changes in the three redox couples on irradiation.

As previously demonstrated by ^1H NMR and HPLC analysis of $\text{Ru}(\text{bipy})_2(3,3'\text{-dmbp})^{2+}$,³⁶ this intermediate could be postulated as a ruthenium complex incorporating both a CH_3CN molecule and an η^1 -bipyridine ligand as depicted in Scheme 2.

Photochemical Chelate to Chelate Exchange. Photochemical reactions (reaction 2) in which a hindering chelate is substituted by a dinitrile chelate have been carried out for different complexes under varying experimental conditions.



By using UV–visible and ^1H NMR techniques, it has been demonstrated that reaction 2 takes place quantitatively and selectively. Figure 4 shows the ^1H NMR spectra in CD_2Cl_2

of the starting compounds, complex **4** (a), ligand dCN_2 (b), and an equimolar mixture of **4** and dCN_2 (c).

After irradiating an NMR tube containing the mixture (c) for a few minutes, the spectrum obtained (d) corresponds to a mixture of $\text{Ru}(\text{phen})_2(\text{dCN}_2)^{2+}$ and 6,6'-dmbp (spectra e and f, respectively). The selectivity of the photoreaction can also be proven by following the evolution of the electronic spectrum of the starting mixture, because strongly marked isosbestic points appear during the irradiation process. More generally, the presence of such isosbestic points has been used in order to select the best experimental conditions for the photoreaction. Solvents such as acetone, 1,2-dichloroethane, and CH_2Cl_2 (stabilized with amylene) facilitate clean reactions leading to the expected products, whereas the presence of alcohols generates small amounts of unidentified byproducts. The concentration of the dCN_2 ligand with respect to complex concentration turns out to be critical. Not surprisingly, a large excess of the dicyano ligand speeds up the reaction rate and suppresses parasitic reactions. The efficiency of the photochemical exchange reaction is also very dependent on the nature of the leaving chelate. Although no quantum yields have been determined, the following efficiency order, $6,6'\text{-dmbp} = \text{dClbp} > \text{biq} > 3,3'\text{-dmbp} > \text{biq}$, is suggested by monitoring UV–visible spectra as a function of time during the irradiation experiments. Figure 5 shows some examples of photosubstitution reactions for different complexes under varying experimental conditions.

By using dCN_3 or dCN_4 as the bis-nitrile chelate, photochemical substitution occurs with the same efficiency and selectivity. Plot b in Figure 5 shows the spectra obtained during the irradiation of complex **4** in the presence of dCN_3 . Interestingly, as is shown in plot c in Figure 5, the photoexchange is accompanied by a significant degree of

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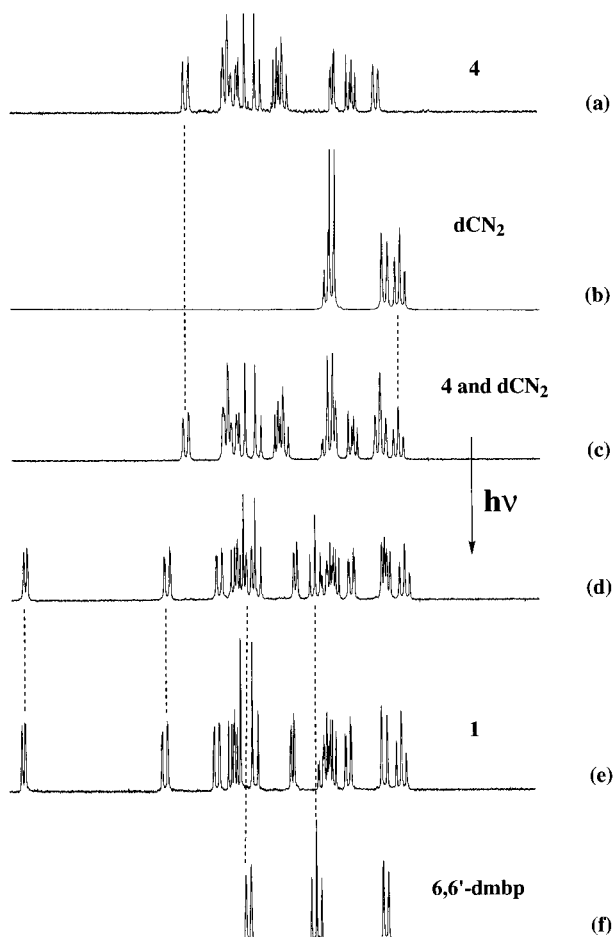


Figure 4. ¹H NMR spectra (200 MHz, aromatic region) in CD₂Cl₂ of **4** (a), dCN₂ (b), equimolecular mixture of **4** and dCN₂ (c), this same mixture after light irradiation during 10 min (d), and the expected reaction products **1** (e) and 6,6'-dmbp (f). Dotted lines indicate some typical signals of the starting complex **4**, the complex **1** and the 6,6'-dmbp ligand in the mixture before (c) and after irradiation (d).

photochromism. The deep red color of Ru(phen)₂(biq)²⁺ ($\lambda_{\text{max}} = 525$ nm in 1,2-DCE) changes in a few seconds of irradiation to orange-yellow, the characteristic color of Ru(phen)₂(dCN₂)²⁺ ($\lambda_{\text{max}} = 382$ nm in 1,2-DCE). The differences in the absorption spectra of **1** and **6** originate from the different nature of the third ligand coordinated to the common Ru(phen)₂ core. The dicyano ligand, which is a poor σ -donor and good π -acceptor, stabilizes the d _{π} (t_{2g}) orbitals of Ru which results in a high energy MLCT excited state. The bis-quinoline ligand, on the other hand, is a better π -acceptor than phenanthroline, which lowers the energy of the MLCT excited state. To obtain reversible systems, that is, to reverse reactions 1 or 2, photochemical experiments were performed starting from Ru(phen)₂(dCN₂)²⁺ with an excess of the hindering chelate. The photoexpulsion of the bis-nitrile ligand occurs cleanly with 2,2'-bipyridine and to some extent with 3,3'-dmbp. Because it is known that nitrile ligands are photochemically labile,³⁷ these results can be attributed to strong steric congestion inhibiting the coordination reaction when the entering ligand is a bipy-type chelate bearing bulky substituents ortho to the nitrogen atoms.

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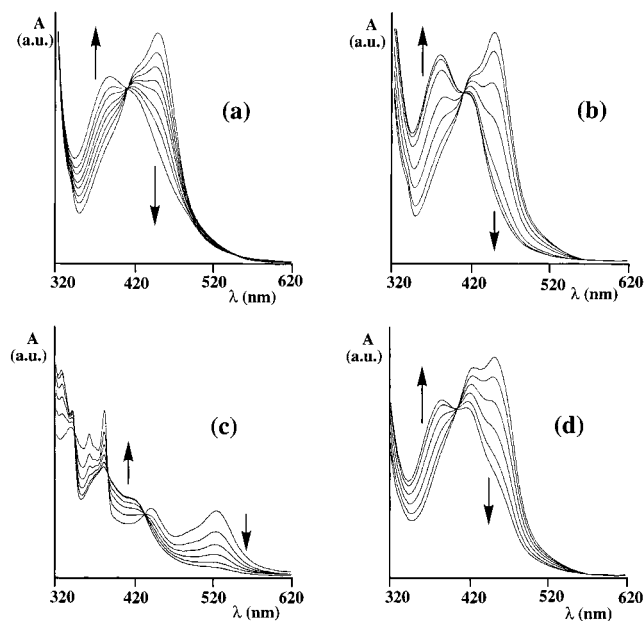
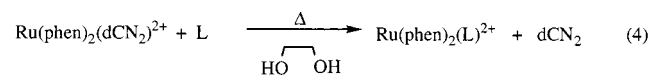
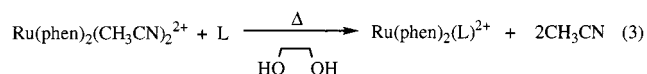


Figure 5. Electronic absorption spectra of **4**, **6**, and **8** before and after different irradiation times. Experimental conditions: (a) **4** in acetone in the presence of 10 equiv of dCN₂, (b) **4** in 1,2-DCE in the presence of 10 equiv of dCN₂, (c) and (d) **6** and **8**, respectively, in 1,2-DCE in the presence of 10 equiv of dCN₂.

Thermal Back Reaction. It was possible to regenerate the starting complexes (**4–8**) almost quantitatively from either Ru(phen)₂(CH₃CN)₂²⁺ or **1** following reactions 3 or 4 by refluxing the reagents in ethylene glycol for 4 h. These high yields strongly contrast with those obtained in the initial preparation of complexes **4–8** in which the starting compound is Ru(phen)₂Cl₂.



L = 6,6'-dmbp, dClbp, biq, 3,3'-dmbp, and biiq.

Importantly, it was possible to carry out the photochemical forward reaction (hindering chelate release) and the thermal back reaction (dCN₂ release with recoordination of 6,6'-dmbp or biq) in the same reaction mixture containing an excess of both ligands, dCN₂, the aromatic diimine, and the starting ruthenium(II) complex. The solvent, EtOCH₂CH₂OCH₂CH₂-OH, in which all the components (ligands and complexes) are soluble, proved to be compatible with both the photochemical and thermal processes.

It is now recognized that the initial step of photochemical substitution reactions in the ruthenium polypyridine complexes occurs following a dissociative mechanism.^{37,38} Excitation of the MLCT bands leads to the charge-transfer excited state, allowing the thermal population of dissociative d–d states.^{37–39} These states lie only slightly above the

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³MLCT state, especially when the ligand field is diminished by distortions due to the sterically hindering ligands used in the present study. In the particular case of photosubstitution of bidentate chelate exchange, numerous steps could be invoked. In addition, the complexity of the processes is possibly increased by the photoreactivity of intermediates and products. To dissect such processes, complete photochemical and photophysical studies will be undertaken. In addition, the synthesis of multicomponent systems incorporating both bis-nitrile and bipy chelates seems promising in regards to the realization of artificial light-driven molecular machines.

Acknowledgment. We would like to thank the CNRS for financial support and the European Commission COST Program D11/0004/98. We thank André De Cian and Jean Fischer for the X-ray structures. A.-C.L. acknowledges support from the French Ministry of Education, and Y.F. thanks Osaka Prefecture (Japan) for a fellowship.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **2–4** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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